Long-range correlations and anisotropy in simple liquids and gases near the surfaces of solids

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A nonpolar dielectric medium (gas or liquid) on the surface of a solid is considered. It is shown that the inhomogeneity of the fluctuating substrate field and the weak spatial dispersion of the medium produce near the surface a quasi-two-dimensional layer that is dipole-ordered in a direction perpendicular to the substrate. The interaction between the atoms and the correlations in the layer are long-range and decrease like $1/r^3$ with increasing distance. The dipole moment and the interaction between the atom decrease with increasing distance from the surface like $1/x^4$ and $1/x^8$, respectively, and their values are determined by two macroscopic parameters, the dielectric constant of the substrate and the quadrupole susceptibility of the medium. Numerical estimates demonstrate the existence of a temperature region in which these phenomena are effective and can have observable aftereffects.

1. INTRODUCTION

Many phenomena in liquids and gases interfacing with solids are determined by the interaction of the atoms with the substrate and by their interaction with one another through the substrates. Forces of varying origin contribute to these interactions for different adatoms and substrates. There are grounds for assuming that a noticeable contribution to the interaction between noble-gas atoms on metal, quartz, or graphite surfaces is made by inhomogenous long-wave electromagnetic fluctuations.

The present paper deals with thin layers of simple gases and liquids on solid surfaces. The contributions of the inhomogeneous parts of long-wave electromagnetic fluctuations to the interaction between the atoms in a gas and to the correlation function in a liquid are calculated.

These contributions have already been discussed in the literature (see, e.g., Refs. 1 and 2), with the following results. If two atoms are located at distances x_1 and x_2 from a plane substrate and r is the distance between them, then at $r > x_1$, x_2 and at $a < r$, x_1, $x_2 < \lambda_0$ (a is the atom size and λ_0 is the characteristic wavelength in the absorption spectrum of the solid), the interatomic interaction V_2 is always an attraction with a $1/r^6$ law and can be represented in the form $-A(x)/r^6$. The interaction with the substrate alters the coefficient A compared with the case of two atoms in vacuum, decreasing or increasing it in accord with the placement of the atoms relative to the substrate. The situation is similar for the correlation function g of a liquid at points x_1 and x_2 of the substrate. The correlation is positive and proportional to $1/r^6$ for all liquids and substrates and at all x_1, $x_2 < r$. The contribution of the inhomogeneity to V_2 and g is quite noticeable here and has some physical applications, but does not lead to any qualitatively new properties of the gas or liquid at the substrate.

A recalculation of V_2 and g may be prompted by the following considerations. The interaction between two atoms is via exchange of two virtual photons,[3] i.e., V_2 is proportional to the square of the photon propagator, which depends on the interatomic distance like $1/r^3$. In the presence of an inhomogeneity, the propagator is replaced by the photon Green's function in the inhomogeneous medium and V_2 acquires contributions that depend on x_1 and x_2. As $r \to \infty$, however, V_2 remains proportional to $1/r^6$ as before, but in the presence of an inhomogeneity the following three-photon process can contribute to the interaction: The atoms exchange one photon directly (and the corresponding Green's function is proportional to $1/r^3$), and the other is reradiated by the substrate. For the last process the Green's functions depend only on x_1 and x_2, and the interatomic interaction turns out to decrease like $1/r^3$. Such a result can be expected in approximation VI of invariant perturbation theory. It is easily noted, however, that if only the dipole moments of the atoms are included in the electromagnetic-interaction operator, this process makes a zero contribution to the scattering amplitude. Actually, the third power of the dipole-moment operator will be averaged out in this case for each atom over its ground state. It is therefore necessary to retain in the electromagnetic-interaction operator also the quadrupole-moment operators of the atoms, and accordingly the gradients of the electric-field operators, i.e., the effect of the $1/r^3$ interaction can appear only when account is taken of the inhomogeneity of the fluctuating electromagnetic field of the substrate or, equivalently, when account is taken of the dipole-quadrupole interaction in nonrelativistic quantum mechanics. The product of the squared dipole-moment and the quadrupole-moment operators is then averaged out over the ground state of the atom. Such "triangles" differ from zero.

One more peculiarity in the behavior of atoms near a surface is noted if it is recognized that the inhomogeneity plays the role of a random electric field $\mathscr{E}$ and polarizes the atoms. In the expansion of their average dipole moment in powers of the field there are no odd or even powers, since these powers are multiplied by zero mean values of an odd power of the atom's dipole-moment operator. When account is taken of the dipole-quadrupole interaction, the nonzero terms of the average dipole moment are those proportional

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to the mean value of $\mathscr{E}_i \nabla \mathscr{E}_k$, which is the gradient of the inhomogeneous part of the Green's function of the photon in the medium. Its coefficients are equal to the "triangle." For a surface that coincides with the $x = 0$ plane, only the x-component of the Green's-function gradient differs from zero, so that the substrate-induced dipole moment is perpendicular to the substrate and decreases with increasing distance from it like $1/x^4$. The described three-photon interatomic interaction is therefore connected with the dipole-dipole interaction of the dipoles induced by the substrate.

All this means that a thin "quasi-two-dimensional" dipole-ordered layer in which long-range $1/r^3$ repulsion takes place can be produced in the gas near the substrate. Such systems are of considerable interest and are extensively discussed in the literature.

On the surface of a liquid, paired interatomic interaction can be introduced only in a certain effective sense. A more suitable characteristic is the correlation function g, from which the aforementioned effective interaction can be deduced. It follows from the consideration of V_2 above, that to extract g from the general theory of Van der Waals forces[4] it is necessary to take into account in this theory spatial dispersion, i.e., go outside the framework of the loop approximation in the free-energy expansion. It suffices for this purpose to take into account the appearance of the new topological element, the "triangle" and then turn attention to three-photon processes in the calculation of g. Just as in the case of V_2, this leads to the appearance of long-range correlations and of an effective long-range repulsion in the dipole-ordered surface layer of the liquid.

In §2 are calculated the interaction of two atoms on the surface and their dipole moments, the correlation function of the liquid near the surface is found in §3, while §4 contains a discussion of the results and numerical estimates.

§2. INTERACTION AND DIPOLE MOMENTS OF ATOMS AT A SURFACE

Consider a medium at temperature $T = 0$, constituting a solid occupying the half-space $x < 0$ with its surface at $x = 0$, and a vacuum at $x > 0$. We denote the Hamiltonian of the medium by H and the Green's function of a photon in the medium by $D_{ik}(\mathbf{r}_i, \mathbf{r}_2, \omega)$. We place atoms 1 and 2 at distances $x_1, x_2 > a$ from the surface. The distance r between the atoms exceeds x_1 and x_2. Under these conditions only long-range forces contribute to the interaction between the atoms. The potential energy V_2 of the interaction is the electronic term of the two-atom system in the substrate field. A formalism for the calculation of V_2 can be easily developed on the basis of Dzyaloshinskiĭ's method[3] for atoms in a vacuum and by applying the Dzyaloshinskiĭ-Pitaevskiĭ diagram technique to the long-wave field in a condensed medium[4] at $T = 0$. We represent the Hamiltonian of the atoms and of the medium as a sum of H, of the Hamiltonians H_1 and H_2 of the immobile isolated atoms, and of the operator V of the potential energy of the atoms in the field produced by them and by the medium. In accordance with the premises set forth in §1, we take into account in V, besides the atom dipole-moment operators $\mathbf{d}^{(n)}$ $(n = 1, 2)$ also the quadrupole-moment operators $Q(n)$:

$$V=-\sum_{n=1}^{2}\left\{\mathbf{d}^{(n)}\mathbf{E}(\mathbf{r}_n)+\frac{1}{6}\tilde{Q}^{(n)}:[\nabla\times\mathbf{E}]_{\mathbf{r}_n}\right\}. \tag{1}$$

Here $\mathbf{r}_n$ are the coordinates of the nuclei, while $E(\mathbf{r}_n)$ and $[\nabla_i E_k]\mathbf{r}_n$ are the operators of the long-wave electric field and of its gradient at the point $\mathbf{r}_n$. We neglect the influence of the atoms on the medium.

The potential energy V_2, which depends on the interatomic distance r, is connected with the value of the S operator of the considered problem for the ground state of the system with Hamiltonian $H_1 + H_2 + H$, by a relation known from the problem of the interaction of two atoms in a vacuum[2] For the three-photon process of interest to us we then obtain in approximation VI of perturbation theory

$$V_2(r, x_1, x_2) = -\frac{1}{it}\frac{(-i)^6}{6!}\int dt_1\ldots\int dt_6\langle T\{V(t_1)\ldots V(t_6)\}\rangle_{H_1+H_2+H}. \tag{2}$$

The dipole and quadrupole moment operators are averaged in (2) over the state of the noninteracting atoms. The electric-field operators, on the other hand, are averaged over the ground state of the condensed medium with Hamiltonian H, and Wick's theorem does not hold for them.

After substitution of (1) in (2), averaging of the operators lead to functions of the type

$$\Phi_{iklm}^{(n)}(t_1, t_2, t_3) = -{}^1/_6\langle T d_i^{(n)}(t_1)\, d_k^{(n)}(t_2)\, Q_{lm}^{(n)}(t_3)\rangle_{H_n},\quad n=1, 2. \tag{3}$$

Their Fourier transforms $\beta_{iklm}^{(n)}(\omega_1,\omega_2)$ are the frequency-dependent quadrupole polarizabilities of the atoms.[5] The function remaining in the integral of (2) is

$$\langle TE_i(\mathbf{r}_1, t_1)E_k(\mathbf{r}_1, t_2)E_l(\mathbf{r}_1, t_3)E_j(\mathbf{r}_2, t_4)E_p(\mathbf{r}_2, t_5)E_q(\mathbf{r}_2, t_6)\rangle_H. \tag{4}$$

The averaging is carried out here over the ground state of the medium, and the time-dependent technique of field theory can be used. We separate in H terms H_0 and the interaction

$$V_{\mathrm{lr}} = -\int \mathbf{d}(\mathbf{r})\mathbf{E}(\mathbf{r})\,d\mathbf{r} \tag{5}$$

of the particles with the long-wave electromagnetic field. In Eq. (5), $\mathbf{d}(\mathbf{r})$ is the dipole-moment density operator. We carry out next in (5) calculations in accordance with the rules and approximation of Ref. 4, but for the case of a time-dependent diagram technique. In the zeroth approximation this leads to a product of three photon propagators. Allowance of the next approximations, neglecting the irreducible polygons, transforms the propagators into the Green's functions of a photon in the medium

$$D_{ik}^{E}(\mathbf{r}_1, \mathbf{r}_2, t_1-t_2) = \langle TE_i(\mathbf{r}_1, t_1)E_k(\mathbf{r}_2, t_2)\rangle_H. \tag{6}$$

Returning to (2), we obtain from (3), (4), and (5)

$$V_2(r, x_1, x_2)$$
$$= \frac{1}{it} \int dt_1 \ldots \int dt_6 \Phi^{(1)}_{iklm}(t_1, t_2, t_3) \left\{ \frac{\partial}{\partial X_{1m}} D_{kl}{}^E(\mathbf{r}_1, \mathbf{r}_1, t_2, t_3) \right\}$$
$$\times D_{ij}{}^E(\mathbf{r}_1, \mathbf{r}_2, t_1, t_4) \Phi^{(2)}_{jpqs}(t_4, t_5, t_6) \left\{ \frac{\partial}{\partial X_{2s}} D_{pq}{}^E(\mathbf{r}_2, \mathbf{r}_2, t_5, t_6) \right\}. \quad (7)$$

We introduce the Fourier transforms of the functions $\Phi^{(n)}_{iklm}$ and D^E_{ik} and obtain for V_2

$$V_2(r, x_1, x_2)$$
$$= \frac{1}{(2\pi)^2} \left\{ \int_{-\infty}^{\infty} d\omega\, \omega^2 \beta^{(1)}_{iklm}(0, \omega) \frac{\partial}{\partial X_{1m}} D_{kl}(\mathbf{r}_1, \mathbf{r}_1, \omega) \right\}$$
$$\times \{D_{ij}(\mathbf{r}_1, \mathbf{r}_2, \omega_1)\, \omega_1{}^2\}_{\omega_1=0}$$
$$\times \left\{ \int_{-\infty}^{\infty} d\omega_2\, \omega_2{}^2 \beta^{(2)}_{jpqs}(0, \omega_2) \frac{\partial}{\partial X_{2s}} D_{pq}(\mathbf{r}_2, \mathbf{r}_2, \omega_2) \right\}. \quad (8)$$

In this form, the result is applicable to a surface of any shape. The functions $\beta^{(n)}_{iklm}$ are averages over the ground state of the atoms and reduce to the scalars

$$\beta^{(n)}_{iklm} = \beta^{(n)} [{}^3/_4 (\delta_{il}\delta_{km} + \delta_{im}\delta_{kl}) - {}^1/_2 \delta_{ik}\delta_{lm}]. \quad (9)$$

We recognize that the inhomogeneous parts of the Green's functions of like argument depend in the chosen geometry only on the distance x to the substrate, $\beta^{(n)}$ are even functions of ω, and at $T = 0$ we have

$$D_{ik}(\mathbf{r}_1, \mathbf{r}_2, \omega) = D_{ik}{}^R(r_1, r_2, |\omega|), \quad (10)$$

where D^R_{ik} is a retarded Green's function. This leads to

$$V_2(r, x_1, x_2) = \frac{1}{4(2\pi)^2} \left\{ \int_0^{\infty} d\omega\, \omega^2 \beta^{(1)}(0, \omega) \frac{\partial}{\partial x_1} [D_{xx}{}^R(r_1, r_1, \omega) \right.$$
$$\left. + 3D_{kk}{}^R(r_1, r_1, \omega)] \right\} [D_{xx}{}^R(r_1, r_2, \omega_1)\, \omega_1{}^2]_{\omega_1=0}$$
$$\times \left\{ \int_0^{\infty} d\omega_2\, \omega_2{}^2 \beta^{(2)}(0, \omega_2) \right.$$
$$\left. \times \frac{\partial}{\partial x_2} [D_{xx}{}^R(r_2, r_2, \omega_2) + 3D_{pp}{}^R(r_2, r_2, \omega_2)] \right\} \quad (11)$$

(with summation over the repeated indices k and p). We transform in (11) to integration over the positive imaginary axis and note that if the photon propagator $D^0_{ik}(\mathbf{r},\omega)$ is represented in the form

$$D_{ik}{}^0(\mathbf{r}, \omega) = -\frac{1}{\omega^2} T_{ik}{}^0(\mathbf{r}, \omega), \quad (12)$$

then $T^0_{ik}(\mathbf{r},\omega)$ is the tensor of the dipole-dipole interaction in vacuum with allowance for the retardation. At $\omega = 0$ it becomes the static tensor of the dipole-dipole interaction. Similarly,

$$T_{xx}(\mathbf{r}_1, \mathbf{r}_2) = -[D_{xx}{}^R(\mathbf{r}_1, \mathbf{r}_2, \omega_1)\, \omega_1{}^2]_{\omega_1=0} \quad (13)$$

is the xx component of the static dipole-dipole interaction in an inhomogeneous medium. We introduce the following notation for the integrals in (11):

$$f^{(n)}(x_n) = \frac{1}{4\pi} \int_0^{\infty} d\omega\, \omega^2 \beta^{(n)}(0, i\omega) \frac{\partial}{\partial x}$$
$$\times [D_{xx}{}^R(\mathbf{r}_n, \mathbf{r}_n, i\omega) + 3D_{kk}{}^R(\mathbf{r}_n, \mathbf{r}_n, i\omega)] \quad (14)$$

and represent V_2 in the form

$$V_2(r, x_1, x_2) = f^{(1)}(x_1)\, T_{xx}(\mathbf{r}_1, \mathbf{r}_2)\, f^{(2)}(x_2). \quad (15)$$

The retarded Green's functions in (14) are connected simply with the known temperature Green's functions of the considered medium.[2] At the chosen r, x_1, and x_2 their inhomogeneous parts are given by

$$D_{xx}{}^R(\mathbf{r}_n, \mathbf{r}_n, i\omega) = \frac{\Delta(i\omega)}{4\omega^2 x_n{}^3},$$
$$D_{yy}{}^R(\mathbf{r}_n, \mathbf{r}_n, i\omega) = D_{zz}{}^R(\mathbf{r}_n, \mathbf{r}_n, i\omega) = \frac{1}{2} D_{xx}{}^R(\mathbf{r}_n, \mathbf{r}_n, i\omega), \quad (16)$$

where

$$\Delta(i\omega) = \frac{\varepsilon_1(i\omega) - 1}{\varepsilon_1(i\omega) + 1} \quad (17)$$

and $\varepsilon_1(i\omega)$ is the dielectric constant of the solid on the positive imaginary axis at $T = 0$. If r is considerably larger than x_1 and x_2, Eq. (13) leads to[2]

$$T_{xx}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{r^3} \left(1 + \frac{\varepsilon_1(0) - 1}{\varepsilon_1(0) + 1} \right), \quad (18)$$

where $\varepsilon_1(0)$ is the static dielectric constant of the solid. The second term of (18) is the contribution of the surface to the dipole-dipole interaction tensor. Substitution of (17) in (14) leads to

$$f^{(n)}(x_n) = -\frac{21}{16\pi} \frac{1}{x_n{}^4} \int_0^{\infty} d\omega\, \beta^{(n)}(0, i\omega)\, \Delta(i\omega). \quad (19)$$

From (15) and (18) we get for the interaction between the two atoms and the surface

$$V_2(r, x_1, x_2) = \frac{f^{(1)}(x_1) f^{(2)}(x_2)}{r^3} \left(1 + \frac{\varepsilon_1(0) - 1}{\varepsilon_1(0) + 1} \right). \quad (20)$$

The interaction between the atoms via the substrate leads thus to a long-range repulsion between them in a thin layer near the surface, where the functions $f^{(n)}(x_n)$ differ from zero.

We call attention to the connection between the expression obtained for V_2 and the substrate-induced dipole moments of the atoms. Let one atom be placed at a distance $x > a$ from the surface and let the entire (medium + atom) system be in a weak constant uniform electric field $\mathscr{E}$. The average dipole moment $\langle d \rangle$ of the atom is then connected with the mean value of the operator S of this problem over the ground state of the system with Hamiltonian $H_a + H$ (H_a is the Hamiltonian of the immobile isolated atom) by the relation[5]

$$\langle d \rangle = \frac{1}{it} \langle \{\nabla_{\mathscr{E}} S\}_{\mathscr{E}=0} \rangle_{H_a+H} \quad (21)$$

(the contribution of the external field has been added to the interaction operator). Expanding the S operator in a series and performing the operations indicated in (21), we get

$$\langle d_i\rangle = -\frac{1}{2t}\int dt_1 \int dt_2 \int dt_3 \langle T d_i(t_1)\, V(t_2)\, V(t_3)\rangle_{H_a+H}. \qquad (22)$$

Averaging the dipole- and quadrupole-moment operators leads to quadrupole polarizability of the atom, and the product of the electric-field operators is averaged over the ground state of the medium with Hamiltonian H, and leads directly to the Green's function of a photon in the medium at $T=0$. Since the inhomogeneous part of the Green's function depends at equal arguments only on x, only the x component of the substrate-induced dipole moment of the atom differs from zero. The dipole moments induced by the interatomic interaction are of the same origin.[5–7] The role of the wall is played for the atom in this case by the other nonidentical atom.

All the subsequent operations in (22) are similar to those performed above in the calculation of V_2. As a result we obtain for $\langle d_x\rangle$ an expression that coincides with $f(x)$ of (19):

$$\langle d_x\rangle = -\frac{21}{16\pi x^4}\int_0 d\omega\, \beta(0, i\omega)\, \Delta(i\omega). \qquad (23)$$

As follows from (23), the considered three-photon contribution to the interaction between the atoms can be represented as an interaction between two substrate-induced dipoles.

It can be concluded that dipole ordering in a direction perpendicular to the substrate and long-range repulsion in the plane of the substrate exist in a thin nonpolar-gas layer near or directly on the surface.

§3. CORRELATION FUNCTION OF A SIMPLE LIQUID AT A SURFACE

Consider, at finite temperature, a system comprising flat-surface solid at $x<0$ and a liquid at $x>0$. We are interested in the correlation function of the liquid at points for which r, x_1, and x_2 satisfy the relations indicated in §2.

The contribution of the three-photon process considered above to the correlation function $g(r,x_1,x_2)$ can be easily found if its contribution ΔF to the free energy of the system is known. ΔF can be related to $g(r,x_1,x_2)$ in the following manner. We place the system in an auxiliary scalar weakly nonuniform field $\varphi(r)$ whose contribution to the Hamiltonian of the system we represent in the form

$$H' = \int d\mathbf{r}\rho(\mathbf{r})\varphi(\mathbf{r}), \qquad (24)$$

where $\rho(\mathbf{r})$ is the particle-number density operator. This field alters the system free energy, $\Delta F \to \Delta F(\varphi)$. The latter is connected with that part of the correlation function which is of interest to us by the known relation

$$g(\mathbf{r},\mathbf{r}') = -T\left\{\frac{\delta^2 \Delta F(\varphi)}{\delta\varphi(\mathbf{r})\,\delta\varphi(\mathbf{r}')}\right\}_{\varphi(\mathbf{r})=0}. \qquad (25)$$

Under the conditions indicated above for r, x_1, and x_2 the correlation between two such points is due only to long-range forces. We shall calculate their contribution to the free energy by the method of Dzyaloshinskiĭ and Pitaevskiĭ,[4,8] generalized somewhat to take into account in the correlation function the interaction of the liquid particles through the substrate. The character of the required generalization is already clear enough from §2.

We separate in the Hamiltonian of the system in the auxiliary field the short-range part $H_0(\varphi)$, transfer also H' to it, and represent V_{lr} in the form

$$V_{\mathrm{lr}} = -\int d_i(\mathbf{r})E_i(\mathbf{r})\,d\mathbf{r} - {}^1/_6\int Q_{ik}(\mathbf{r})\,\nabla_k E_i(\mathbf{r})\,d\mathbf{r}, \qquad (26)$$

where $d_i(\mathbf{r})$ and $Q_{ik}(\mathbf{r})$ are the density operators of the dipole and quadrupole moments of the liquid. We calculate the contribution of V_{lr} to the free energy, recognizing that the second term of (26) leads to the appearance of an irreducible triangle

$$\eta_{iklm}(X_1, X_2, X_3) = -{}^1/_6\langle T_\tau d_i(X_1)\, d_k(X_2)\, Q_{lm}(X_3)\rangle_{H_0},$$
$$X = (\mathbf{r}, \tau). \qquad (27)$$

Just as in Ref. 4 the loop is the true Matsubara linear susceptibility of the medium (i.e., it determines the response to the mean field in the medium), Eq. (27), since it is averaged not over the total Hamiltonian of the system but only over its short-range part, is the true Matsubara quadrupole susceptibility of the liquid.

The perturbation-theory series contains only approximations of even order, and irreducible triangles appear first in VI approximation. In the reducible hexagon here we can separate loops, triangles, irreducible quadrangles, and an irreducible hexagon. From among the breakdowns into triangles we can select those that describe photon exchange via the substrate. The triangle (quadrupole polarizability) is considerably smaller than the loop (polarizability). The minimum number of triangles in the diagram is two. Therefore we retain in each of the reducible polygons (multiples of 6) only two triangles, and unlink all the rest into loops. Triangles are encountered in the temperature Green's functions $\mathscr{D}^E_{ik}(X_1,X_2)$ in the medium in sums with loops, and can therefore be neglected. The so selected diagram series will contain two triangles and three functions $\mathscr{D}^E_{ik}(X_1,X_2)$ in the loop approximation. The variation of this series is summable and can be represented in the form

$$\delta\Delta F(\varphi) = -2T\int dX_1 \ldots \int dX_6\, \delta\eta_{iklm}(X_1, X_2, X_3, \varphi)$$
$$\times\{\nabla_{x_{3m}}\mathscr{D}_{kl}{}^E(X_2, X_3, \varphi)\}\, D_{in}{}^E(X_1, X_6, \varphi)\, \eta_{njpq}(X_4, X_5, X_6, \varphi)$$
$$\times\{\nabla_{x_{5q}}\mathscr{D}_{jp}{}^E(X_4, X_5, \varphi)\}, \qquad \int dX = \int d\mathbf{r}\int_0^{1/T} d\tau. \qquad (28)$$

Here both functions η and $\mathscr{D}^E_{ik}$ depend on φ, since the moment operators are averaged over the state of the system with Hamiltonian $H_0 + H'$. When substituting (28) in (25) we take it into account that variation of the Green's function yields a product of such functions and accelerates the decrease of the correlation function with increasing r, x_1, and x_2. To calculate the correlation function that decreases most slowly with distance we shall vary only the functions η. As a result we get

$$g(\mathbf{r},\mathbf{r}') = 2T^2\int dX_1 \ldots \int dX_6 \left\{\frac{\delta\eta_{iklm}(X_1, X_2, X_3, \varphi)}{\delta\varphi(\mathbf{r})}\right\}_{\varphi(\mathbf{r})=0}$$
$$\times\{\nabla_{x_{3m}}\mathscr{D}_{kl}{}^E(X_2, X_3)\}\,\mathscr{D}_{in}{}^E(X_1, X_6)$$

$$\times\left\{\frac{\delta\eta_{njpq}(X_4, X_5, X_6, \varphi)}{\delta\varphi(\mathbf{r}')}\right\}_{\varphi(\mathbf{r}')=0}$$

$$\times\nabla_{X_{5q}}\mathscr{D}^E(X_4, X_5, \varphi). \tag{29}$$

Let us calculate the variational derivatives contained in (29). We introduce the notation

$$\eta_{iklm}(X_1, X_2, X_3, \varphi)=\langle\hat{\Pi}_{iklm}(X_1, X_2, X_3)\rangle_{H_0+H'} \tag{30}$$

and transform to the interaction representation in terms of the auxiliary field (24). We obtain

$$\left\{\frac{\delta\eta_{iklm}(X_1, X_2, X_3, \varphi)}{\delta\varphi(\mathbf{r})}\right\}_{\varphi(\mathbf{r})=0}$$

$$=-\int_0^{1/T} d\tau\langle\hat{\Pi}_{iklm}(X_1, X_2, X_3)\,\delta\rho(\mathbf{r},\tau)\rangle_{H_0}. \tag{31}$$

Here $\delta\rho(\mathbf{r},\tau)=\rho(\mathbf{r},\tau)-\rho$, ρ is the average density, and

$$\rho(\mathbf{r},\tau)=e^{\tau H_0}\rho(\mathbf{r})\,e^{-\tau H_0}. \tag{32}$$

The auxiliary field is weakly nonuniform, i.e., the wavelengths of its constitutent spatial harmonics are much larger than a, whereas the averaging in (31) is over a state in which the correlation radius is of the order of a. At such lengths, the auxiliary field can be regarded as uniform, and we should put $k=0$ in the spatial Fourier transform of the density $\delta\rho(k,\tau)$, and then $\delta\rho(k,\tau)=\hat{N}-N$, where $\hat{N}$ is the particle-number operator and N is the total number of particles. This leads to

$$\left\{\frac{\delta\eta_{iklm}(X_1, X_2, X_3, \varphi)}{\delta\varphi(\mathbf{r})}\right\}_{\varphi(\mathbf{r})=0}$$

$$=-\frac{\partial\eta_{iklm}(X_1, X_2, X_3)}{\partial\mu}\delta(\mathbf{r}-\mathbf{r}_1). \tag{33}$$

We recognize that the points **r** and **r**′ are located in the liquid and their distances from the surface exceed the radius of the short-range forces. For mean values over the state of the system with Hamiltonian H_0 the system is therefore homogeneous and the tensor η_{iklm} reduces to a scalar in accordance with (9). Neglecting finally the spatial correlations in regions of order a (all the irreducible polygons contract into a point, i.e., are regarded as local), we rewrite (33) in the form

$$\left\{\frac{\delta\eta_{iklm}(X_1, X_2, X_3, \varphi)}{\partial\varphi(\mathbf{r})}\right\}_{\varphi(\mathbf{r})=0}$$

$$=-\frac{\partial\eta(\tau_1, \tau_2, \tau_3)}{\partial\mu}\delta(\mathbf{r}-\mathbf{r}_1)\,\delta(\mathbf{r}_1-\mathbf{r}_2)$$

$$\times\delta(\mathbf{r}_2-\mathbf{r}_3)\,[{}^3/_4(\delta_{il}\delta_{km}+\delta_{im}\delta_{kl})-{}^1/_2\delta_{ik}\delta_{km}]. \tag{34}$$

We substitute (34) in (29), expand $\eta(\tau_1,\tau_2,\tau_3)$ and $\mathscr{D}^E_{ik}$ in Fourier series in the temporal variable, and change from summation over discrete frequencies to integration. As a result we get

$$g(r, x_1, x_2)=-T\left(\rho\frac{\partial\rho}{\partial p}\right)^2_T\frac{1}{(4\pi)^4}\left\{\int_0^\infty d\omega\,\omega^2\frac{\partial\eta(0, i\,\omega)}{\partial\rho}\frac{\partial}{\partial x_1}\right.$$

$$\left.\times[\mathscr{D}_{xx}(\mathbf{r}, \mathbf{r}, \omega)+3\mathscr{D}_{kk}(\mathbf{r}, \mathbf{r}, \omega)]\right\}[\omega_1^2\mathscr{D}_{xx}(\mathbf{r}_1, \mathbf{r}_2, \omega_1)]_{\omega_1=0}$$

$$\times\left\{\int_0^\infty d\omega_2\,\omega_2^2\frac{\partial\eta(0, i\omega_2)}{\partial\rho}\frac{\partial}{\partial x_2}\right.$$

$$\left.\times[\mathscr{D}_{xx}(\mathbf{r}', \mathbf{r}', \omega)+3\mathscr{D}_{kk}(\mathbf{r}', \mathbf{r}', \omega)]\right\}. \tag{35}$$

The inhomogeneous parts of the temperature functions, which are contained in (39), take the form[2]

$$\mathscr{D}_{xx}(\mathbf{r}, \mathbf{r}, \omega)=\frac{\bar{\Delta}(i\omega)}{4\varepsilon_2(i\omega)\,\omega^2x^3};$$

$$\mathscr{D}_{yy}(\mathbf{r}, \mathbf{r}, \omega)=\mathscr{D}_{zz}(\mathbf{r}, \mathbf{r}, \omega)=\frac{1}{2}\mathscr{D}_{xx}(\mathbf{r}, \mathbf{r}, \omega),$$

$$\bar{\Delta}(i\omega)=\frac{\varepsilon_1(i\omega)-\varepsilon_2(i\omega)}{\varepsilon_1(i\omega)+\varepsilon_2(i\omega)}. \tag{36}$$

Here $\varepsilon_2(i\omega)$ is the dielectric constant of the liquid. Just as in the case of the interaction between atoms, we introduce for the integrals in (35) the notation:

$$\bar{f}(x)=\frac{1}{4\pi^2}\int_0^\infty d\omega\frac{\partial\eta(0, i\omega)}{\partial\rho}\frac{\partial}{\partial x}[\mathscr{D}_{xx}(\mathbf{r}, \mathbf{r}, \omega)+3\mathscr{D}_{kk}(\mathbf{r}, \mathbf{r}, \omega)]. \tag{37}$$

Substitution of (36) in (35) and (37) leads to:

$$\bar{f}(x)=-\frac{21}{64\pi^2x^4}\int_0^\infty d\omega\frac{\bar{\Delta}(i\omega)}{\varepsilon_2(i\omega)}\frac{\partial\eta(0, i\omega)}{\partial\rho}, \tag{38}$$

$$g(r, x_1, x_2)=-T\left(\rho\frac{\partial\rho}{\partial p}\right)^2_T\frac{\bar{f}(x_1)\bar{f}(x_2)}{r^3}\left(1+\frac{\varepsilon_1(0)-\varepsilon_2(0)}{\varepsilon_1(0)+\varepsilon_2(0)}\right) \tag{39}$$

($\varepsilon_2(0)$ is the static dielectric constant of the liquid). This result shows that the liquid has on its surface a thin layer in which long-range negative correlations exist. If the liquid becomes rarefied

$$\varepsilon_2(0)\to1,\quad \partial\eta(0, i\omega)/\partial\rho\to4\pi\beta(0, i\omega),\quad \bar{\Delta}(i\omega)\to\Delta(i\omega),$$

and comparison with (20) leads to the known asymptotic relation for the correlation function

$$g(r, x_1, x_2)=-T\left(\rho\frac{\partial\rho}{\partial p}\right)^2_T V_2(r, x_1, x_2). \tag{40}$$

This enables us to interpret $f(x)$ as the substrate-induced dipole-moment density in the liquid, and interpret the function by which $-T(\rho\partial\rho/\partial p)^2_T$ in (39) is multiplied as the effective dipole-dipole interaction in the liquid at the surface.

§4. DISCUSSION OF RESULTS

The basic relations (20), (23), and (39) are greatly simplified if the gas or liquid absorption region is in the ultraviolet and the solid absorbs at significantly lower frequencies. In this case the dipole moment of the atom at the surface is

$$\langle d_x\rangle=-\frac{21}{16\pi}\frac{\hbar\bar{\omega}\beta}{x^4}, \tag{41}$$

where β is the static quadrupole polarizability of the atom and

$$\hbar\bar{\omega}=\int_0^\infty d\omega\Delta(i\omega) \tag{42}$$

is the measurable characteristic energy of the solid, which was introduced in Ref. 4. From (20) we get for the interaction energy of the atoms at the metal surface ($\varepsilon_1(0)\to\infty$)

$$V_2(r,x,x)=\frac{441(\hbar\bar{\omega}\beta)^2}{8(4\pi)^2x^8}\frac{1}{r^3}. \tag{43}$$

The correlation function of the liquid at the metal surface takes the form

$$g(r,x,x)=-T\left(\rho\frac{\partial\rho}{\partial p}\right)_T^2\frac{441}{8(4\pi)^4x^8}\left(\frac{\hbar\omega}{\varepsilon_2(0)}\frac{\partial\eta(0)}{\partial\rho}\right)^2\frac{1}{r^3}. \tag{44}$$

Here $\eta(0)$ is the static quadrupole polarizability of the liquid, and

$$\hbar\bar{\bar{\omega}}=\int_0^\infty d\omega\,\bar{\Delta}(i\omega). \tag{45}$$

Thus, a phenomenon of universal origin and physical properties takes place in a nonpolar medium at the surface of a solid. The nonuniform fluctuating electromagnetic field of the substrate generates in a medium having a weak spatial dispersion (in a liquid one takes into account the quadrupole susceptibility of the atoms, and in a solid their quadrupole polarizability) a layer that is quasi-two-dimensional and dipole ordered in a direction perpendicular to the substrate. The interaction and the correlation in this layer are long-range and decrease like $1/r^3$. The layer parameters (the dipole moment and the dipole-dipole interaction constant) decrease rapidly (like $1/x^4$ and $1/x^8$, respectively) with increasing distance from the surface, and it is this which makes the layer two-dimensional. The dependence of the interactions and of the correlations on the distances r and x, just as in other dispersion phenomena, has a universal character that does not depend on the substrate and on the medium. These quantities are determined by two macroscopic parameters, the dielectric constant of the substrate and the quadrupole susceptibility of the medium. At large distances compared with a this Van der Waals mechanism determines the interactions at the surface, while at shorter distances it competes with other short-range forces.

Two-dimensional dipole ordering in a liquid on a surface can manifest itself in various phenomena, such as physical adsorption, the phase state of a thin film and phase transitions on the surface, the ferroelectric and magnetic properties of thin films, the dielectric constant of the film, the addition of polarization fluctuations to the density fluctuations and the ensuing new details in the light and neutron scattering spectra, the onset of new branches in the collective-excitation spectra in liquid films in view of the appearance of a low-symmetry phase in the liquid at the surface, and others. It is also important that the dynamic properties of systems with $1/r^3$ potentials are similar in many respects to the properties of two-dimensional Coulomb systems having close values of the dimensionless ratio Γ of the average potential energy per particle to the average kinetic energy. At $\Gamma \gg 1$, furthermore, the atoms can become ordered on the surface into a two-dimensional lattice via the considered interatomic-interaction mechanism.

Naturally, implementation of these possibilities depends on the order of magnitude of the induced dipole moment and on the temperature range in which the long-range properties of V_2 and the dipole ordering are effective.

For a numerical estimate of the quantities (41) and (43) above we must know two parameters, $\hbar\bar{\omega}$ from (42) and the quadrupole polarizability β of the atoms. The first of them is known[9] well enough for metal surfaces, $\hbar\bar{\omega}\approx 10^{-11}$ (all the quantities here and below are in cgs units). Less is known concerning β. It can be determined by measuring the anisotropy of the refractive index in a nonuniform electric field and, by way of example, $\beta\approx-0.3\cdot10^{-38}$ for the nonpolar CH_4 molecules.[10] Calculations for the hydrogen atom lead to $\beta=10^{-38}$ (Ref. 10). For the He atom we have estimated $\beta\approx-10^{-39}$. Just as in the case of a related phenomenon, the dipole moment induced by interatomic interaction,[5–7] it can be assumed that for a number of atoms and molecules such as Ar, Kr, Xe, and CCl_4, whose polarizability increases and exceeds in the case of CCl_4 the polarizability of He by two orders, the value of β will also increase and reach $5\cdot10^{-38}$. These estimates of $\hbar\bar{\omega}$ and β yield for an H atom at a metallic wall ($x\sim10^{-8}$) an estimated value of the order of 1 Debye, i.e., a value typical of polar molecules. In this case the interaction between the hydrogen atoms at the wall, for distances exceeding several atomic dimensions, lies in the temperature interval 10–100 K, i.e., it reaches values typical of Coulomb systems.

We turn now to a ^4He film on a metal surface. In this case $x>1.8\cdot10^{-8}$ and $\langle d_x\rangle$, despite the small polarizability of the He atom, is quite noticeable, ≈ 0.05 D. When the distances between the atoms exceed their sizes ($2.6\cdot10^{-8}$) the dipole-dipole interaction lands in the temperature interval 0.1–1 K, i.e., the obtained long-range action will be effective enough at experimentally attainable temperatures. Wigner crystallization temperatures $\Gamma\gg1$ are also attainable here.

It is useful to compare the interatomic interaction in a surface layer with the attraction, caused by the same Van der Waals forces, of an atom to a substrate[4,8]:

$$V_1(x)=-\frac{\alpha\hbar\bar{\omega}}{4\pi}\frac{1}{x^3} \tag{46}$$

(α is the polarizability of the atom). For liquid helium on a metallic surface this attraction exceeds V_2 by two orders. For atoms with larger polarizability, V_2 can reach values exceeding V_1. In these cases the dispersion forces considered suffice to explain the atomic smoothness of the surfaces and the possibility of formation of incommensurate phases on them.

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