Long-range correlations in a liquid filling a thin slit or pore

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In a thin slit filled with a dielectric liquid, the long-range correlations in density fluctuations fall off much more slowly with distance if the slit walls are made of a metal than if they are made of a dielectric. A power-law dependence of the correlation function on the distance is found in the corresponding distance intervals. Results of the same type are found for thin slits and pores with dielectric walls filled with a conducting liquid. Two interrelated factors which are specific to this problem are pointed out: the modification of the Coulomb interaction in thin films and filaments and the specific dispersion of 2D and 1D plasma excitations. The van der Waals interaction of atoms in thin slits and pores is described.

1. INTRODUCTION

Under certain conditions, long-range correlations in a liquid filling a thin slit or pore may be quite different from the corresponding correlations in the interior of a large volume of liquid, as we will show below. We say that a plane slit or cylindrical pore is "thin" if the distance R over which the correlations are considered are significantly greater than the slit width l or the pore radius a:

$$R \gg l,\ a. \tag{1}$$

Under this condition, the parameters l and a can lie in a fairly wide interval, say, from ten to several hundred (or even thousand) angstroms. The only reason for the upper limit here is the question of whether it is possible to observe a contribution from the long-range (and therefore quite weak) correlations under consideration here in (for example) experiments on scattering in a slit. The reasons for the lower limit on l and a, on the other hand, are not simply the matter of experimental feasibility but also the assumptions used in the theory. For example, in the discussion below we will ignore the spatial dispersion of the dielectric constant of the liquid and of the surrounding media.

The asymptotic behavior of the correlation function of classical density fluctuations in a liquid is known to be governed by the van der Waals interaction.[1,2] The variation of the van der Waals interaction with distance is usually quite universal. If retardation can be ignored, for example, the energy of the van der Waals interaction of atoms is proportional to R^{-6}. The specific properties of the particular atoms and of the surrounding medium (if we are thinking of impurity atoms in a bulk liquid volume) affect only the proportionality factor in the interaction power law; the exponent does not depend on these properties.

We show below that in a thin slit or pore the interaction of the atoms and the asymptotic behavior of the correlation function of the liquid can be of a specific nature. The corresponding exponents in the power-law functions of the distance are quite different for metals and dielectrics. This difference is a direct consequence of collective many-particle effects in condensed media; it is present even in the simplest case, when two atoms interact in an empty thin slit with metal or dielectric walls. Two interrelated factors play an important role in determining the distance dependence of the interaction here: the modification of the Coulomb interaction in thin slits and films (or in thin filaments) and the specific nature of the dispersion of plasmons and other electromagnetic excitations in 2D (or 1D) systems. Excitations with wavelengths $\lambda \gtrsim R$ are important for the van der Waals interaction. We then find $\lambda = 2\pi/k \gg l, a.$ from condition (1). It follows that 2D or 1D virtual electromagnetic excitations propagating along the slit or film (or filament) with a 2D or 1D wave vector $k \ll l^{-1}, a^{-1}$ which may be damped, may be important in problems of this type.

2. VAN DER WAALS INTERACTION IN A THIN SLIT

The correlation function of density fluctuations, $\gamma(\mathbf{r},\mathbf{r}')$, in an isotropic liquid at large distances $R = |\mathbf{r}-\mathbf{r}'| \gg a_0, \hbar u/T$ (a_0 is a distance at the atomic scale, and u is the sound velocity), is given by[1,2]

$$\gamma(\mathbf{r},\mathbf{r}') = -\frac{T}{nb^2}U(\mathbf{r},\mathbf{r}'), \tag{2}$$

$$U(\mathbf{r},\mathbf{r}') = -T\sum_{s=0}^{\infty}{}' \alpha_{eff,1}(i\omega_s)\alpha_{eff,2}(i\omega_s) \times \left(\frac{\omega_s^2}{\hbar c^2}\right)^2 D_{ik}^2(\omega_s;\mathbf{r},\mathbf{r}'). \tag{3}$$

Here n is the average density of the liquid, the coefficient b is determined by short-range forces, and

$$\alpha_{eff}(\omega) = \frac{1}{4\pi}\frac{\partial\varepsilon(\omega)}{\partial n},$$

where $\varepsilon(\omega)$ is the dielectric constant of the liquid. The temperature Green's function of a photon in the medium which appears in (3) satisfies the equation

$$\left[\frac{\partial^2}{\partial r_i\,\partial r_j} - \delta_{ij}\Delta + \frac{\omega^2}{c^2}\varepsilon(i\omega,\mathbf{r})\delta_{ij}\right]D_{jk}(\omega;\mathbf{r},\mathbf{r}') = -4\pi\hbar\delta_{ik}\delta(\mathbf{r}-\mathbf{r}'). \tag{4}$$

Expression (3) also describes the free energy of the van der Waals interaction of impurity particles in a liquid. In this case we should set

$$\alpha_{eff}(\omega) = \frac{1}{4\pi}\frac{\partial\varepsilon_u(\omega)}{\partial N}\bigg|_{N\to 0},$$

where N is the concentration of impurity particles, and $\varepsilon_u(\omega)$ is the dielectric constant of the solution. If we are instead dealing with the interaction of atoms in a bounded empty volume, we should replace $\alpha_{eff}(\omega)$ in (3) by the dynamic atomic polarizabilities $\alpha(\omega)$.

We first consider a liquid-filled plane slit of width l (whose boundaries run perpendicular to the x axis). For this system, we will find the Green's function $D_{ik}(\omega;\mathbf{r},\mathbf{r}')$ in the region $0<x, x'<l$ and $R=|\mathbf{r}-\mathbf{r}'|\gg l$. The coordinates x and x' are assumed to be far enough from the walls of the slit that we can ignore the short-range forces exerted by the walls and induced by the walls in the atoms of the liquid by van der Waals dipole moments. At the middle of the slit the dipole polarization is obviously zero, because the effects of the opposite walls cancel out.

We denote by $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ the dielectric constants of the walls of the slit for $x<0$ and $x>l$, respectively, while $\varepsilon_3(\omega)$ is the dielectric constant of the liquid filling the slit. We find solutions of Eqs. (4) after Fourier-transforming in the coordinates y and z,

$$D_{ik}(\omega;\mathbf{r},\mathbf{r}')=\int\frac{d\mathbf{q}}{(2\pi)^2}\exp[i\mathbf{q}(\mathbf{r}-\mathbf{r}')]D_{ik}(\omega;\mathbf{q},x,x') \qquad (5)$$

and using the conditions that the quantities $\varepsilon D_{xk}, D_{yk}, D_{zk}$ and $\mathrm{curl}_{yj}D_{jk}$ and $\mathrm{curl}_{zj}D_{jk}$ are continuous at the boundaries $x=0,l$. We write the solutions for the region of ω and q values of interest here, which are related by the inequality

$$l\left[\frac{\omega^2}{c^2}\varepsilon_j(i\omega)+q^2\right]^{1/2}\ll 1,\quad j=1,2,3, \qquad (6)$$

under which the components of the Green's function are actually independent of the coordinates x and x'. Here we have

$$D_{xx}(\omega;\mathbf{q})=\frac{4\pi\hbar\varepsilon_1\varepsilon_2q^2}{\varkappa_3^2}[\varepsilon_3(\varepsilon_1\rho_2+\varepsilon_2\rho_1)$$
$$+l(\varepsilon_1\rho_3+\varepsilon_3\rho_1)(\varepsilon_2\rho_3+\varepsilon_3\rho_2)]^{-1}, \qquad (7)$$

$$D_{yy}(\omega,\mathbf{q})=-4\pi\hbar\frac{q_z^2}{q^2}[(\rho_1+\rho_2)+l(\rho_1+\rho_3)(\rho_2+\rho_3)]^{-1}$$
$$-4\pi\hbar\frac{q_y^2\rho_1\rho_2\varepsilon_3^2}{q^2\varkappa_3^2}[\varepsilon_3(\varepsilon_1\rho_2+\varepsilon_2\rho_1)$$
$$+l(\varepsilon_1\rho_3+\varepsilon_3\rho_1)(\varepsilon_2\rho_3+\varepsilon_3\rho_2)]^{-1}, \qquad (8)$$

$$D_{xy}(\omega,\mathbf{q})=i\frac{4\pi\hbar q_y\varepsilon_3[\varepsilon_1\rho_2\theta(x'-x)-\varepsilon_2\rho_1\theta(x-x')]}{\varkappa_3^2[\varepsilon_3(\varepsilon_1\rho_2+\varepsilon_2\rho_1)+l(\varepsilon_1\rho_3+\varepsilon_3\rho_1)(\varepsilon_2\rho_3+\varepsilon_3\rho_2)]} \qquad (9)$$

All the dielectric constants depend on the imaginary frequency $i\omega$ here. In (7)–(9) we have introduced

$$\rho_j=\left[\frac{\omega^2}{c^2}\varepsilon_j(i\omega)+q^2\right]^{1/2};\quad \varkappa_j=\frac{\omega}{c}\varepsilon_j^{1/2}(i\omega),$$
$$\theta(x)=\begin{cases}1, & x>0\\ 0, & x<0\end{cases}. \qquad (10)$$

Expressions for D_{zz} and $D_{xy}=D_{yz}$ are found from (8) by replacing the factor q_z^2 in the first term by q_y^2 and $-q_yq_z$, respectively, and by replacing the factor q_y^2 in the second by q_z^2 and q_yq_z, respectively. The expression for D_{xz} follows from (9) after we replace the factor q_y by q_z. In addition, the following relations hold:

$$D_{yx}(\mathbf{q},x,x')=D_{xy}(-\mathbf{q},x',x),$$
$$D_{xz}(\mathbf{q},x,x')=-D_{zx}(-\mathbf{q},x',x).$$

It can be seen from (9) that at the distances under consideration here, $R\gg l$, in coordinate space we have

$$D_{xy}(\mathbf{r},\mathbf{r}')=D_{yx}(\mathbf{r},\mathbf{r}')=D_{xz}(\mathbf{r},\mathbf{r}')=D_{zx}(\mathbf{r},\mathbf{r}')=0.$$

If the relations $\varepsilon_1(i\omega)\sim\varepsilon_2(i\omega)\sim\varepsilon_3(i\omega)$ hold in the frequency region of interest, by making use of relation (6) we can ignore the second terms, containing the factor l, in square brackets in (7)–(9). These terms, however, may be important, in the case $\varepsilon_1(i\omega)\sim\varepsilon_2(i\omega)\gg\varepsilon_3(i\omega)$ for example. In such a case the first and second terms in square brackets in (7) are comparable in magnitude under the condition $\varepsilon_1\rho_3^2l\sim\varepsilon_3\rho_1$, which is compatible with (6). We will be discussing these cases separately below. For simplicity we set

$$\varepsilon_1(\omega)=\varepsilon_2(\omega)\equiv\varepsilon(\omega),\qquad \alpha_{eff,1}(\omega)=\alpha_{eff,2}(\omega)\equiv\alpha_{eff}(\omega).$$

Interaction potential (3) and correlation (2) behave in the usual way if the terms containing the factor l, which we just mentioned, can be ignored in the calculation of the Green's function in (5). In this case the characteristic frequency of the problem, ω_0, is independent of R, being determined exclusively by the absorption spectra of the given condensed media.

At distances $l\ll R\ll c/\omega_0\varepsilon^{1/2}(i\omega_0)$ (and $T\ll\hbar\omega_0$) we find

$$U(R)=-\frac{\hbar}{2\pi R^6}\int_0^{+\infty}d\omega\,\frac{\alpha_{eff}^2(i\omega)}{\varepsilon^2(i\omega)}\left[5+\frac{\varepsilon^4(i\omega)}{\varepsilon_3^4(i\omega)}\right]. \qquad (11)$$

In the opposite limit $R\gg l$, $c/\omega_0\varepsilon^{1/2}(i\omega_0)$ and $T\ll\hbar c/R\varepsilon_0^{1/2}$), we find

$$U(R)=-\frac{\hbar c\alpha_{eff,0}^2}{8\pi\varepsilon_0^{5/2}R^7}\left(33+13\frac{\varepsilon_0^4}{\varepsilon_{30}^4}\right). \qquad (12)$$

Here we write the temperature-dependent component of the interaction potential, which is described by the $s=0$ term in (3):

$$U_{s=0}(R)=-\frac{T\alpha_{eff,0}^2}{2\varepsilon_0^2R^6}\left(5+\frac{\varepsilon_0^4}{\varepsilon_{30}^4}\right). \qquad (13)$$

According to (11)–(13), the specific properties of the walls of the slit and those of the liquid filling the slit affect only the proportionality factors (which contain the dielectric constants of the media) in the power-law functions of the distance. The exponents in these functions are universal. As we have already mentioned, the approximations used in deriving (11)–(13) are generally not valid in the case $\varepsilon(i\bar{\omega})\gg\varepsilon_3(i\bar{\omega})$, where $\bar{\omega}$ is a characteristic frequency. It follows from the general properties of dielectric constants that the strong inequality $\varepsilon(i\omega)\gg R\varepsilon_3(i\omega)$ can hold on the upper imaginary frequency semiaxis only if ω is not too large. For a modification of expression (13) which describes the contribution of classical fluctuations to the interaction, it is sufficient to impose the condition $l\varepsilon_0\gtrsim R\varepsilon_{30}$, which pertains to static values of the dielectric constants. The inequality $l\varepsilon(i\omega) \gtrsim R\varepsilon_3(i\omega)$ can lead to changes in expressions (11) and (12), on the other hand, only if this inequality pertains to characteristic frequencies $\omega \sim \overline{\omega}$. The contribution from the component D_{xx} of the Green's function turns out to be the most important one in (3).

If a nonpolar dielectric liquid fills a slit with walls made of a polar dielectric, then we have $\varepsilon(i\omega) \gg \varepsilon_3(i\omega)$ for $\omega < 10^{12}$ s^{-1} and $\varepsilon(i\omega) \sim \varepsilon_3(i\omega)$ for higher frequencies. Expressions (11) and (12) then remain essentially unchanged over a wide temperature range (which includes, in particular, temperatures on the order of room temperature), except that the static values of the dielectric constants in (12) should be replaced by their values for frequencies $\sim c/R \gg 10^{12}$ s^{-1}. In (13), the static values of the dielectric constants still appear, and the quantity $U_{s=0}(R)$, increases significantly in absolute value as the ratio $\varepsilon_0/\varepsilon_{30}$ increases, according to (13). On the other hand, expression (13) is valid only in the distance region $R \gg l\varepsilon_0/\varepsilon_{30}$, which becomes progressively more remote with increasing ε_0. In the opposite limit $R \ll l\varepsilon_0/\varepsilon_{30}$ we find

$$U_{s=0}(R) = -\frac{8T\alpha^2_{eff,0}}{\varepsilon_0{}^2 l^4 R^2}. \tag{14}$$

The large factor ε_0^2 here, in contrast with the situation in (13), appears only in the denominator. It makes the quantity $U_{s=0}(R)$ small.

The most interesting case is that in which a dielectric liquid (or gas) is in a thin slit with metal walls. Because of the divergence of $\varepsilon_M(i\omega)$ as $\omega \to 0$ for a metal, the formal use of Eqs. (11)–(13) leads to infinite values of the interaction. Actually, the approximations made in the derivation of (11)–(13) are not justified here under any conditions. The calculations must be revised.

It follows from (14) that in the limit $\varepsilon_0 \to \infty$ the quantity $U_{s=0}(R)$ is zero. For a dielectric gap with metal walls the thermal component of $U(R)$ is thus extremely small in general. It is described for the most part by the term $U_{s=1}(R)$; at large distances it usually falls off exponentially. That component will be ignored below.

The behavior of the dielectric constant of the metal on the upper imaginary frequency semiaxis can be approximated over a fairly broad part of the spectrum of interest here by the simple expression

$$\varepsilon_M(i\omega) = 1 + \frac{\omega_p{}^2}{\omega(\omega+\nu)}. \tag{15}$$

Below we assume $\nu \ll \omega_p$.

We first assume that the width of the thin slit satisfies $l \ll c/\omega_p$. A calculation from (7), (15), (5), and (3) then leads to the following results.

In the distance interval $l \ll R \ll c/\omega_p$, $l\omega_p^2/2\nu^2\varepsilon_{30}$ the basic component of the interaction is found to be

$$U(R) = -A\,\frac{\hbar\omega_p\alpha^2_{eff,0}}{\varepsilon_{30}^{5/2} l^{3/2} R^{9/2}}, \tag{16}$$

where the numerical factor A is given by

$$A = \frac{\sqrt{2}}{\pi}\int_0^\infty dt\, t^4 F^2(t^2), \qquad F(z) = \frac{\pi}{2}z[H_0(z) - N_0(z)] - 1, \tag{17}$$

and $H_0(z)$ and $N_0(z)$ are respectively the Struve function and the Bessel function of the second kind. A numerical calculation yields $A \approx 0.05$. The characteristic frequency here depends on the distance R and is given by $\overline{\omega} = \omega_p(l/2\varepsilon_{30}R)^{1/2}$. Using (1) we find $\overline{\omega}^2 \ll \omega_p^2/\varepsilon_{30}$. Assuming $\omega_p \sim \omega_0$ and $\nu \ll \overline{\omega}$, we find the relations $\varepsilon_3(i\overline{\omega}) \approx \varepsilon_{30}$, $\alpha_{eff}(i\overline{\omega}) \approx \alpha_{eff,0}$, and $l\varepsilon(i\overline{\omega}) \sim R\varepsilon_3(i\overline{\omega})$.

For distances

$$l \ll \frac{c}{\omega_p} \ll R \ll \frac{c}{\nu}\left(\frac{l\omega_p}{2c\varepsilon_{30}}\right)^{1/2}$$

we find

$$U(R) = -\frac{27\pi}{256\sqrt{2}}\,\frac{\hbar\omega_p{}^{1/2}c^{1/2}\alpha^2_{eff,0}}{\varepsilon_{30}^{5/2} l^{3/2} R^5}. \tag{18}$$

Here the characteristic frequency also depends on R:

$$\overline{\omega} = \frac{c}{R(2\varepsilon_{30})^{1/2}}\left(\frac{\omega_p l}{c}\right)^{1/2}.$$

Under our assumptions we have $\overline{\omega} \gg \nu$ and $l\varepsilon(i\overline{\omega}) \gg R\varepsilon_{30}$. We also assume $\varepsilon_3(i\overline{\omega}) \approx \varepsilon_{30}$ and $\alpha_{eff}(i\overline{\omega}) \approx \alpha_{eff,0}$, since we have $\overline{\omega} \lesssim c/R \ll \omega_p \sim \omega_0$.

At distances $R \gg (c/\nu)(l\omega_p/2c\varepsilon_{30})^{1/2}$ we have $\omega \ll \nu$. Under the additional condition

$$R \gg \left(\frac{c\varepsilon_{30}{}^{1/2}}{2\pi\sigma l}\right)^2 \frac{l}{2}, \qquad \left(\frac{c\varepsilon_{30}{}^{1/2}}{2\pi\sigma l}\right)^{1/2} \frac{l}{2}$$

we find

$$U(R) \approx -0{,}8\,\frac{\hbar\sigma^{1/3}c^{2/3}\alpha^2_{eff,0}}{\varepsilon_{30}^{8/3} l^{4/3} R^{16/3}}. \tag{19}$$

The conductivity σ of the metal walls which appears here has been introduced by means of the relation $\omega_p^2 = 4\pi\sigma\nu$, which corresponds to the model expression (15), which we used for the dielectric constant of the metal. The characteristic frequency is given under these conditions by

$$\overline{\omega} = (\pi\sigma c^2 l^2/\varepsilon_{30}{}^2 R^4)^{1/3}.$$

It depends on the distance R and satisfies the inequalities $\overline{\omega} \ll \nu$ and $l\varepsilon(i\overline{\omega}) \gg R\varepsilon_{30}$. Here $\varepsilon_3(i\overline{\omega}) \approx \varepsilon_{30}$ and $\alpha_{eff}(i\overline{\omega}) \approx \alpha_{eff,0}$.

Above we assumed $\omega_p l/c \ll 1$. If the opposite condition holds instead ($\omega_p l/c \gg 1$), we find the following expression in the distance interval $(c/\omega_p) \ll l \ll R \ll (c/\nu\varepsilon_{30}^{1/2})$ (in which we have $\overline{\omega} = c/R\varepsilon_{30}^{1/2}$):

$$U(R) = -\frac{27\pi\hbar c\alpha^2_{eff,0}}{256\varepsilon_{30}^{5/2} l^2 R^5}. \tag{20}$$

In the particular case of an empty slit, $\varepsilon_{30} = 1$, expression (20) is the same as the result of Ref. 3. The conditions under which this result is applicable were not pointed out in Ref. 3, however. Even under the condition $\omega_p l/c \gg 1$, expression (19) again holds at sufficiently large distances.

To determine the physical meaning of these results, let us examine, for example, expression (16), which holds when the retardation is totally ignored. To estimate the energy of the van der Waals interaction of the atoms when the retardation is ignored, we should (first) work from the distance dependence of the interaction energy of electric dipoles and (second) determine the characteristic frequency of the photons or other electromagnetic excitations in the medium whose exchange constitutes the van der Waals interaction. The interaction energy of electric dipoles in a medium is usually proportional to $\varepsilon^{-1}R^{-3}$; if retardation is ignored the characteristic frequency ω_0 is independent of the distance and usually lies in the interval 10^{16}–$10^{17}\,\mathrm{s}^{-1}$. The expression for the energy of the van der Waals interaction of the atoms is then

$$-\hbar\omega_0\alpha^2(i\omega_0)/R^6\varepsilon^2(i\omega_0).$$

For a thin dielectric gap with metal walls, there are modifications of both the distance dependence of the energy of the electric dipoles and the expression for the characteristic frequency $\overline{\omega}$, which in this case also depends on the distance.

Keldysh[4] has shown that the Coulomb interaction energy of changes in thin films is modified substantially if the dielectric constant of the thin film is significantly greater than that of the surrounding media. In the distance region of importance for the problem at hand, this energy is proportional to $l^{-1}\ln R$. It can be shown that results largely analogous to those found by Keldysh[4] can be found in the opposite limit, in which the dielectric constants of the surrounding media are significantly greater than that of the film (in the case at hand, this is the dielectric constant of the liquid filling the slit). These comments apply in particular to the proportionality of the charge interaction energy to the quantity $l^{-1}\ln R$. The interaction energy of two electric dipoles oriented perpendicular to the slit is then proportional to $\varepsilon_3^{-1}l^{-1}R^{-2}$. The van der Waals interaction energy can then be estimated from the following expression in this case:

$$-\hbar\overline{\omega}(R)\alpha^2(i\overline{\omega})/\varepsilon_3^2(i\overline{\omega})l^2R^4.$$

The frequency of 2D plasmons with wave vectors $q\sim R^{-1}$ serves as the characteristic frequency here. If a thin metal layer is surrounded by dielectric media, we have $\omega(q)\propto(ql)^{1/2}$ for the dispersion of the spectrum of the 2D plasmons, as we know. It turns out that a similar dispersion prevails for collective plasma excitations which are propagating along the slit and which are localized near it in the case of a thin dielectric-filled (or empty) slit with metal walls. For an estimate we can assume $\overline{\omega}(R)\approx(l/R\varepsilon_{30})^{1/2}\omega_0$. Since $\overline{\omega}^2\ll\omega_0^2$ follows from (1), we have $\alpha(i\overline{\omega})\approx\alpha_0$ and $\varepsilon_3(i\overline{\omega})\approx\varepsilon_{30}$, and we find the following result for the interaction energy of atoms in a slit with metal walls:

$$U(R)=-\frac{\hbar\omega_0\alpha_0^2}{\varepsilon_{30}^{5/2}l^{3/2}R^{9/2}}.$$

This result agrees with (16).

The estimate

$$-\hbar\overline{\omega}\alpha_{eff}^2(i\overline{\omega})/\varepsilon_3^2(i\overline{\omega})l^2R^4$$

follows directly from (3), (5), and (7) in the case

$$l\varepsilon(i\overline{\omega})\gtrless R\varepsilon_3(i\overline{\omega}),\qquad \overline{\omega}\varepsilon_3^{1/2}(i\overline{\omega})/c\lesssim q\sim R^{-1}.$$

This estimate agrees completely with the results in (16)–(20), when the particular characteristic frequency $\overline{\omega}$ specified for each of those results is used. For example, if we set

$$\overline{\omega}\sim c/R\varepsilon_{30}^{1/2},\qquad \alpha_{eff}(i\overline{\omega})\approx\alpha_{eff,0},\qquad \varepsilon_3(i\overline{\omega})\approx\varepsilon_{30},$$

then we find expression (20) to within a numerical factor. The appearance of an $l^{-2}R^{-5}$ dependence instead of a Casimir–Polder dependence R^{-7} in (20) is then due entirely to the modification of the Coulomb interaction in a thin slit with metal walls. The dynamic nature of the interaction is also extremely important for the validity of this estimate, and retardation is important for the results in (18)–(20). In the static limit ($\omega=0$), if we ignore the first term in square brackets in (7), we find (after a transformation to the coordinate representation) that D_{xx} is essentially zero everywhere except at small distances, $R\lesssim 1$. At large distances, D_{xx} is then dominated by the following term in the expansion in powers of the parameter $R\varepsilon_{30}/(l\varepsilon_0)$. Assuming $q\sim R^{-1}$ and $\varepsilon_0\gg\varepsilon_{30}$, we find

$$(\omega^2/\hbar c^2)D_{xx}(\omega,R)|_{\omega=0}\propto(\varepsilon_0 l^2R)^{-1},$$

in agreement with (14). In a slit with metal walls ($\varepsilon_0\to\infty$) the static Coulomb interaction is completely screened at distances $R\gtrsim 1$.

It can be seen from a comparison of (16)–(20) with (11)–(13) that the van der Waals interaction of atoms and the long-range correlations in a thin slit with metal walls, filled with a dielectric liquid, fall off much more slowly with distance than they do with dielectric walls, because of collective effects.

Let us take a brief look at the question of long-range correlations and the van der Waals interaction of impurity particles in a thin layer of a liquid metal in a slit with dielectric walls. If $l\varepsilon_3(i\overline{\omega})\gtrsim R\varepsilon(i\overline{\omega})$, then we are again obliged to consider the second terms, containing the factor l, in square brackets in expressions (7)–(9). The Green's-function components D_{yy}, D_{zz}, D_{yz}, and D_{zy} dominate in (3) in this case. Under these conditions, the long-range correlations in a liquid metal fall off with distance much more slowly than does the van der Waals interaction of electrically neutral impurity particles (atoms) in the same metal. Under the conditions

$$l\varepsilon_3(i\overline{\omega})\gtrless\varepsilon(i\overline{\omega})R,\qquad \overline{\omega}\varepsilon^{1/2}(i\overline{\omega})/c\lesssim q\sim R^{-1},$$

we find the following estimate of the interaction potential from (3), (5), and (8):

$$-\hbar\overline{\omega}\alpha_{eff}^2(i\overline{\omega})/\varepsilon_3^2(i\overline{\omega})l^2R^4.$$

For impurity particles, the metal filling the slit substantially weakens the interaction; this weakening is described by the factor $\varepsilon_3^{-2}(i\overline{\omega})=\varepsilon_M^{-2}(i\overline{\omega})$. For simplicity we consider only the case in which retardation can be ignored. For $\overline{\omega}\gg\nu$ we have

$$\overline{\omega}(R)\approx\left(\frac{l}{R\varepsilon_0}\right)^{1/2}\omega_0,\qquad \varepsilon_M(i\overline{\omega})\approx\frac{\omega_p^2}{\overline{\omega}^2(R)}\sim\frac{R\varepsilon_0}{l}\gg 1.$$

This contribution to the interaction of the impurity particles is then

$$U(R)\approx\frac{-\hbar\overline{\omega}(R)\alpha_{eff,0}^2}{l^2R^4\varepsilon_M^2(i\overline{\omega})}\approx\frac{-\hbar\omega_0\alpha_{eff,0}^2l^{1/2}}{R^{13/2}\varepsilon_0^{5/2}}.$$

This component of the energy falls off extremely rapidly with distance and is comparatively small in magnitude. In addition to this component of the interaction energy of the impurity atoms there are terms proportional to R^{-6}. The latter are the main components here; an estimate of them takes the usual form

$$-\hbar\omega_0\alpha_{eff}^2(i\omega_0)/\varepsilon_M^2(i\omega_0)R^6.$$

The quantity $\varepsilon_M(i\omega_0)$ [in contrast with $\varepsilon_M(i\bar{\omega})$] is small because of the rather large value of the frequency ω_0.

We find a completely different result when we look at the long-range correlations in a thin layer of a liquid metal. Instead of the relation $\alpha_{eff}(i\bar{\omega}) \approx \alpha_{eff,0}$ we should set

$$\alpha_{eff}(i\bar{\omega}) \approx \frac{\partial \omega_p^2}{\partial n} \frac{1}{4\pi\bar{\omega}^2}$$

in this case. We then find the following contribution to $U(R)$ from the exchange of 2D plasmons:

$$-\hbar\bar{\omega}(R)\left(\frac{\partial \omega_p^2}{\partial n}\right)^2 \frac{1}{16\pi^2\omega_p^4 l^2 R^4} \approx \frac{-\hbar\omega_0}{16\pi^2 n^2 l^{3/2} R^{9/2}\varepsilon_0^{1/2}}.$$

This is the dominant component. A systematic calculation yields

$$\gamma(R) = B\frac{T\hbar\omega_p}{n^3 b^2 \varepsilon_0^{1/2} l^{3/2} R^{9/2}}, \tag{21}$$

where the numerical factor B is given by

$$B = \frac{1}{32\sqrt{2}\pi}\int_0^\infty dx\, x^8 \Phi(x^2),$$

$$\Phi(z) = \frac{1}{z^2}\left[\frac{\partial(H_0(z) - N_0(z))}{\partial z}\right]^2 + \left[\frac{\partial^2(H_0(z) - N_0(z))}{\partial z^2}\right]^2. \tag{22}$$

A numerical calculation yields $B \approx 0.006$.

3. VAN DER WAALS INTERACTION IN A THIN CYLINDRICAL PORE

We denote the dielectric constant of a thin cylindrical pore or filament of radius a by $\varepsilon_1(\omega)$, and that of the surrounding medium by $\varepsilon_2(\omega)$. Using the cylindrical coordinate system ρ, φ, z, we first find the photon Green's function $D_{ik}(\omega; \mathbf{r}, \mathbf{r}')$ for this system in the region $0 < \rho, \rho' < a$, $R = |\mathbf{r} - \mathbf{r}'| \gg a$. As in the case of a thin slit, it is assumed that the vectors $\mathbf{r}$ and $\mathbf{r}'$ are not too close to the interface. The spatial variation of the Green's function then essentially reduces to a dependence on $z - z'$, without a dependence on ρ, ρ' or φ, φ'. For the Green's-function components $D_{\rho\varphi}$, $D_{\varphi\rho}$, $D_{z\varphi}$, and $D_{\varphi z}$ we find from (4) a homogeneous system of equations (without sources) which do not depend on the other components. These components are thus zero. Under the conditions specified above, the quantities $D_{z\rho}$ and $D_{\rho z}$ are also zero. For the components $D_{\rho\rho}(\omega; z - z')D$ and $D_{\varphi\varphi}(\omega; z - z')$ we find the expression

$$D_{\rho\rho} = D_{\varphi\varphi} = -\frac{\hbar c^2}{\omega^2\varepsilon_1(i\omega)}\left[\frac{1}{|z - z'|^3} + \frac{\omega\varepsilon_1^{1/2}(i\omega)}{c(z - z')^2} + \frac{\omega^2\varepsilon_1(i\omega)}{c^2|z - z'|}\right] \times \exp\left[-\frac{\omega}{c}\varepsilon_1^{1/2}(i\omega)|z - z'|\right]. \tag{23}$$

The expression for D_{zz} is slightly more complicated:

$$D_{zz} = \frac{2\hbar c^2}{\omega^2\varepsilon_1(i\omega)}\left[\frac{1}{|z - z'|^3} + \frac{\omega\varepsilon_1^{1/2}(i\omega)}{c(z - z')^2}\right] \times \exp\left(-\frac{\omega}{c}\varepsilon_1^{1/2}(i\omega)|z - z'|\right) + \frac{\hbar c^2}{\pi\omega^2}\int_{-\infty}^{+\infty} dk \times \exp[ik(z - z')]\frac{\dfrac{p_2^2}{\varepsilon_2(i\omega)}K_0(p_2 a) + \dfrac{p_1^2}{\varepsilon_1(i\omega)}K_0(p_1 a)}{1 + \dfrac{\varepsilon_1(i\omega)}{2\varepsilon_2(i\omega)}(p_2 a)^2 K_0(p_2 a)}, \tag{24}$$

where $p_{1,2} = [k^2 + (\omega^2/c^2)\varepsilon_{1,2}(i\omega)]^{1/2}$ and where we can set $p_{1,2}a \ll 1$ in (24) by virtue of condition (1).

If the inequality

$$\frac{\varepsilon_1(i\bar{\omega})}{2\varepsilon_2(i\bar{\omega})}\left(\frac{a}{R}\right)^2 \ln\left(\frac{R}{a}\right) \ll 1 \tag{25}$$

holds along with (1), we find from (23), (24), and (3) the expression

$$U(R) = -\frac{\hbar}{\pi R^6}\int_0^\infty d\omega\, \alpha_{eff}^2(i\omega)\left[\frac{1}{\varepsilon_1^2(i\omega)} + \frac{2}{\varepsilon_2^2(i\omega)}\right] \tag{26}$$

for distances $R \gg \lambda_0$ and $T \ll \hbar\omega_0$, while we find

$$U(R) = -\frac{\hbar c\alpha_{eff,0}^2}{4\pi R^7}\left(\frac{13}{\varepsilon_{10}^{5/2}} + \frac{10}{\varepsilon_{20}^{5/2}}\right) \tag{27}$$

for $R \gg \lambda_0$ and $T \ll \hbar c/R$.

The van der Waals interaction potential has its usual form here. An inhomogeneity in the system (a cylindrical pore in the case at hand) affects only the proportionality factor in the corresponding power law for the potential of the interatomic interaction; there is no change in the exponent.

If no condition (1) holds, condition (25) may be violated only if $\varepsilon_1(i\bar{\omega}) \gg \varepsilon_2(i\bar{\omega})$. In particular, the inequality $\varepsilon_1(i\bar{\omega}) \gg \varepsilon_2(i\bar{\omega})$ might be applied to the case of a conducting liquid filling a thin pore with dielectric walls (if $\bar{\omega}^2 \ll \omega_0^2 \sim \omega_p^2$). Analysis shows, however, that the van der Waals interaction of impurity atoms in a thin pore has its usual form even when condition (25) is violated. The additional correction terms which arise in this case are usually small. This situation can be explained in the following way. An important distinction between the problem of a thin plane slit and that of a thin cylindrical pore is that for the pore there is a significant modification of the Coulomb interaction only in the one limiting case in which the dielectric constant of the pore, ε_1, is significantly larger than that of the surrounding medium, ε_2. A collective mode of the 1D-plasmon type also exists only in the case of a thin metal filament surrounded by a dielectric medium (it does not exist for a dielectric filamentary pore in a metal). This situation is in total agreement with the circumstance that the van der Waals interaction in a thin cylindrical pore could have specific features only for $\varepsilon_1(\bar{\omega}) \gg \varepsilon_2(i\bar{\omega})$.

Furthermore, under the condition $\varepsilon_1 \gg \varepsilon_2$ the Coulomb interaction of charges in a thin cylindrical pore can be represented in the distance interval of importance here as a series whose first three terms (the most important ones) are proportional to the quantities

$$\frac{(\ln\varepsilon_1)^{1/2}}{a\varepsilon_1^{1/2}},\qquad \frac{R}{a^2\varepsilon_1},\qquad \frac{R^2}{a^3\varepsilon_1^{1/2}(\ln\varepsilon_1)^{1/2}}$$

respectively (see Ref. 5, where the first two terms are written out explicitly). The interaction energy of electric dipoles is thus proportional to the quantity $[a^3\varepsilon_1^{1/2}(\ln\varepsilon_1)^{1/2}]^{-1}$ in a first approximation. The corresponding contribution of the van der Waals interaction potential in a thin pore filled with a liquid conductor can then be written

$$U(R)=-\hbar\overline{\omega}(R)\alpha_{eff}^2(i\overline{\omega})/\varepsilon_M^3(i\overline{\omega})a^6\ln\varepsilon_M(i\overline{\omega}).$$

If retardation is ignored, and if the condition $\overline{\omega}(R)\gg\nu$ holds, the role of the characteristic frequency is played here by the frequency of 1D plasmons with a wavelength $\lambda\sim R$:

$$\overline{\omega}(R)\approx\frac{a}{R}\omega_0\ln^{1/2}\frac{R}{a}\ll\omega_0.$$

Here

$$\varepsilon_M(i\overline{\omega})\approx\frac{\omega_p^2}{\overline{\omega}^2}\sim\left(\frac{R}{a}\right)^2\ln^{-1}\frac{R}{a}\gg 1$$

[see (1); we are assuming $\omega_p\sim\omega_0$], and we find the following expression for the interaction potential of impurity atoms:

$$U(R)=-\hbar\omega_0\alpha_{eff,0}^2\frac{a}{R^7}\ln^{5/2}\frac{R}{a}.$$

If, on the other hand, we have $\overline{\omega}(R)\ll\nu$, then

$$\overline{\omega}(R)\approx\left(\frac{a}{R}\right)^2 2\pi\sigma\ln\frac{R}{a},$$

$$\varepsilon_M(i\overline{\omega})\approx 2\left(\frac{R}{a}\right)^2\ln^{-1}\frac{R}{a}\gg 1,$$

$$U(R)\approx-\hbar\omega_0\alpha_{eff,0}^2\frac{a^2}{R^8}\ln^3\frac{R}{a}.$$

Retardation does not cause any substantial changes in these estimates. Under the condition $(a\omega_p/c)^2\ll 1$, retardation plays a minor role over the entire distance interval for this component of the interaction, due to the exchange of 1D plasmons. By virtue of (1), and according to these estimates, these contributions to the interaction potential of the impurity atoms are smaller in the region $R\ll\lambda_0$ than the terms of the usual type,

$$U=-\hbar\omega_0\alpha_{eff}^2(i\omega_0)/\varepsilon^2(i\omega_0)R^6$$

which are also present. At distances $R\gg\lambda_0$, and only in the case $\overline{\omega}(R)\gg\nu$, this contribution gives rise to an important change in the coefficient of the R^{-7} power law, but it does not cause a change in the exponent.

For long-range correlations, however, some new exponents arise. In examining long-range correlations in a liquid conductor filling a thin filamentary pore in a bulk dielectric, we should set $\alpha_{eff}(i\overline{\omega})\approx\omega_p^2/4\pi n\overline{\omega}^2$ for $\overline{\omega}(R)\gg\nu$ and $\alpha_{eff}(i\overline{\omega})\approx(\partial\sigma/\partial n)/\overline{\omega}$ for $\overline{\omega}(R)\ll\nu$ in the estimates above. As a result, we find the following estimates for $\gamma(R)$, ignoring retardation:

$$\frac{T\hbar\omega_p}{16\pi^2b^2n^3a^3R^3}\ln^{1/2}\frac{R}{a}\quad\text{for}\quad\overline{\omega}(R)\gg\nu$$

$$\frac{T\hbar}{4\pi^2b^2n\sigma a^2R^4}\left(\frac{\partial\sigma}{\partial n}\right)^2\ln\frac{R}{a}\quad\text{for}\quad\overline{\omega}(R)\ll\nu.$$

A systematic calculation yields

$$\gamma(R)\approx\frac{T\hbar\omega_pK_0^{1/2}\left(\frac{a}{R}\right)}{2^{11/2}\pi^3b^2n^3\varepsilon_{20}^{1/2}a^3R^3}\times\frac{\left[1-\frac{1}{2}\left(\frac{\omega_pa}{c}\right)^2K_0\left(\frac{a}{R}\left[1+\left(\frac{\omega_pR}{c}\right)^2\right]^{1/2}\right)\right]^2}{\left[1+\frac{1}{2}\left(\frac{\omega_pa}{c}\right)^2K_0\left(\frac{a}{R}\right)\right]^{5/2}}\tag{28}$$

in the distance region $R\gg a$ and under the condition $\overline{\omega}(R)\gg\nu$. Here retardation has been taken into account, and we have

$$\overline{\omega}(R)=\frac{\omega_p}{(2\varepsilon_{20})^{1/2}}\frac{a}{R}\ln^{1/2}\frac{R}{a}\left[1+\frac{1}{2}\left(\frac{\omega_pa}{c}\right)^2\ln\frac{R}{a}\right]^{-1/2}.\tag{29}$$

For distances satisfying the conditions

$$R\gg\frac{2\pi\sigma a^2}{c\varepsilon_{20}^{1/2}}\ln\frac{R}{a},\qquad R\gg\left[\frac{2\pi\sigma}{\varepsilon_{20}\nu}\ln\frac{R}{a}\right]^{1/2}a,\qquad R\gg a,\tag{30}$$

we have

$$\gamma(R)=\frac{3T\hbar}{16\pi^2b^2n\varepsilon_{20}\sigma a^2R^4}K_0\left(\frac{a}{R}\right)\left(\frac{\partial\sigma}{\partial n}\right)^2.\tag{31}$$

The modified Bessel function $K_0(a/R)$ which appears in (28) and (31) actually reduces to $\ln(R/a)$ by virtue of (1).

The decay of the long-range correlations over distance in (28) and (31) is considerably slower than the usual expression $\propto R^{-6}$. The inapplicability of the expressions (26) and (27) in this case can be seen formally in the circumstance that these expressions become infinite because of the divergence of $\alpha_{eff}(i\omega)=\partial\varepsilon_M(i\omega)/4\pi\partial n$ as $\omega\to 0$.

The difference between the exponents in the power-law functions of the distance for long-range correlations of density fluctuations in a conducting liquid and for the van der Waals interaction potential of impurity atoms in this liquid also prevails in the spatially homogeneous case at large distances $R\gg\lambda_0$. In this case the result found in Refs. 1 and 2,

$$\gamma(R)=\frac{23T\hbar c}{4\pi b^2n\varepsilon_0^{5/2}R^7}\left(\frac{\partial\varepsilon_0}{4\pi\partial n}\right)^2,$$

vanishes, since for a metal we have $\varepsilon(i\omega)\to\infty$ as $\omega\to 0$. In this case the interaction is dominated by the low-frequency part of the spectrum, in which we can set $\varepsilon_M(i\omega)=4\pi\sigma/\omega$. For impurity particles the result is

$$U(R)=-\frac{10395\hbar c^6\alpha_{eff,0}^2}{2^{13}\pi^6\sigma^5R^{12}},\tag{32}$$

and the correlation function of the density fluctuations becomes

$$\gamma(R)=\frac{T\hbar c^2}{4\pi^4b^2n\sigma^3R^8}\left(\frac{\partial\sigma}{\partial n}\right)^2.\tag{33}$$

This result of course applies to classical density fluctuations, in the case

$$\frac{\hbar u}{R}\ll T\ll\frac{\hbar c^2}{4\pi\sigma R^2}.$$

The role of the characteristic frequency is played here by the quantity $\overline{\omega}=c^2/4\pi\sigma R^2$. In the distance region

$R\gg\lambda_0\sim c/\omega_p$ we have $\bar{\omega}\ll\nu$. An estimate of $U(R)$ for both cases yields

$$U\sim-\hbar\bar{\omega}\alpha_{eff}^2(i\bar{\omega})/\varepsilon_M^2(i\bar{\omega})R^6.$$

Measurements of the structure factor in bulk liquid and gas volumes have recently become much more accurate, particularly at small values of the wave vectors.[6,7] At the same time, progress is being made in scattering techniques and in techniques for measuring atomic properties in thin slits.[8] There is accordingly the hope that the basic results derived above will be of interest for experimental research.

[1] M. P. Kemoklidze and L. P. Pitaevskiĭ, Zh. Eksp. Teor. Fiz. **59**, 2187 (1970) [Sov. Phys. JETP **32**, 1183 (1971)].

[2] E. M. Lifshitz and L. P. Pitaevskiĭ, Statisticheskaya fizika Nauka, Moscow, 1978 (Statistical Physics. Part 2. Theory of the Condensed State, Pergamon, Oxford, 1987).

[3] H. Miyagi, Phys. Lett. A **111**, 187 (1985).

[4] L. V. Keldysh, Pis'ma Zh. Eksp. Teor. Fiz. **29**, 716 (1979) [JETP Lett. **29**, 658 (1979)].

[5] V. S. Babichenko, L. V. Keldysh, and A. P. Silin, Fiz. Tverd. Tela (Leningrad) **22**, 1238 (1980) [Sov. Phys. Solid State **22**, 723 (1980)].

[6] M. C. Bellissent-Funel, P. Chieux, D. Levesque, and J. J. Weis, Phys. Rev. A **39**, 6310 (1989).

[7] H. Fredrikze, J. B. van Tricht, A. van Well, *et al.*, Phys. Rev. Lett. **62**, 2612 (1989).

[8] S. Haroche and J. M. Raimond, Adv. At. Mol. Phys. **20**, 347 (1985).

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