PHYSICAL REVIEW A VOLUME 25, NUMBER 2 FEBRUARY 1982

van der Waals interaction between a point particle and a metallic surface. I. Theory

A. M. Marvin
Istituto di Fisica Teorica, Università di Trieste, Miramare-Grignano, 34014 Trieste, Italy

F. Toigo
Istituto di Fisica dell'Università e Unità Gruppo Nazionale della Struttura della Materia-Consiglio Nazionale delle Ricerche Via Marzolo n.8 35100 Padova, Italy

(Received 2 June 1980; revised manuscript received 3 June 1981)

The van der Waals potential between a neutral atom (no permanent dipole) and a metallic surface is presented. The treatment, based on the normal modes of the system, allows a deeper understanding of the nature of van der Waals forces and makes it practically possible to calculate for complex geometries. To show this we derive theoretical expressions for the interactions of atoms with cylinders and spheres, besides the well-known plane-geometry formula. These formulas are new in some aspects and constitute the theoretical counterpart of many experimental situations. In the same vein we allow a stochastic surface roughness to be present in the plane geometry and show how the problem can be solved analytically in the electrostatic approximation. Numerical calculations and comparison with experiments are presented in paper II.

I. INTRODUCTION

The problem of the van der Waals attraction between atoms is as old as quantum mechanics itself since it is directly connected with the uncertainty principle. Solving for the interaction between two isolated atoms in the electrostatic (es) approximation, London[1] was able to explain in the early 1930's the cohesion in metals. The inclusion of retardation was due to Casimir and Polder[2] who used a second quantization approach and applied perturbation theory up to fourth order. In the same scheme they were also able to calculate the interaction between an external atom and a semi-infinite perfect conductor.[2] But the van der Waals problem between macroscopic bodies had to wait till 1956 when Lifshitz[3] calculated the force exerted between two solid surfaces in terms of fluctuating electromagnetic (em) fields as a problem of statistical physics.[4] The Lifshitz problem was studied again in the last decade by van Kampen *et al.*[5] and successively by Gerlach[6] who showed how the force between the two bodies may be explained in terms of the surface-plasmon energy. The double advantage of the "normal modes" Gerlach's method over the "fluctuation method" due to Lifshitz is manifestly understood by its mathematical simplicity and by a deeper physical meaning as well. Langbein[7] took advantage of the first point to calculate the van der Waals attraction between more complex macroscopic particles like spheres and cylinders where, due to mathematical complexities, the fluctuation method becomes questionable.

The second point allows an intimate connection between the response of a bounded metal to external charges and the surface-plasmon field at its surface and shows by itself the theoretical progress in this area of physics. We refer to Langbein's work[7] for a complete review until 1974.

The high degree of efficiency achieved nowadays in the experimental apparatus, allows a direct measurement of van der Waals forces between solids with good accuracy. Fairly good agreement was obtained in measuring the Lifshitz force[3] between two metallic surfaces.[8,9]

Recently in a series of papers[10–13] Shih *et al.* tried to detect direct evidence of the interaction between a neutral atom (no permanent dipole) and a metallic surface, from scattering experiments, but no agreement with the theory has been obtained. In order to explain this disagreement, a hypothetical surface roughness has been introduced on the metal,[14] but with "apparently" no positive answer. On the other hand, a full quantum treatment of

the scattering problem in the cylindrical geometry of the experiments[10–13] is shown to lead to the same expression as a classical calculation.[15]

In the authors' opinion the problem of atom-surface interaction requires more attention than it has received till now. In particular, the roughness effect, even if already considered,[14] needs a deeper and more careful theoretical analysis. We note also the strong disparity in theoretical formulations between the Lifshitz problem between macroscopic bodies[3,5–7] and its single-atom bounded-metal counterpart. The more reliable expression for atom-surface van der Waals interaction is given by Parsegian[16] who starts from the Lifshitz formula and allows one of the two bodies to become a vapor. It is this formula that has been used in Refs. 12–15 in trying to explain the experimental results. We are reminded, however, that the Parsegian expression[16] is suited for a plane geometry, while in the experiments cited above the particles are deflected by metallic cylinders and a cylindrical solution would be more appropriate. It is certainly true that the radius of the cylinder is enormously large compared to the distance of closest approach to the surface. This fact and the "short"-ranged van der Waals attraction makes sense of the assumption of the metallic surface as a plane. On the other hand, the radius dependence found experimentally in the coupling constant of the atom-surface interaction,[11] suggests that we be extremely careful in making any *a priori* conclusion.

Also the possibility of exchanging the two limits in the Parsegian[16] paper is not well understood. In fact, the Lifshitz[3] formulas were derived under the assumption that the distance between bodies is large when compared to the atomic distances between atoms in the two media, while the Parsegian[16] limit is a first-order expansion in density in one of the two media; which is inconsistent with the above hypothesis.

To overcome this difficulty we prefer to give a complete treatment of the problem and do not restrict ourselves to surface roughness correction only. The plan of the paper is as follows.

In Sec. II we derive an expression for the potential between an atom and a plane surface to be compared with Parsegian's[16] form. The result is extremely suggestive since Parsegian's formula is nothing but a linear expansion of our expression in terms of the atomic polarizability.

In Sec. III we still study a plane geometry but include dynamical effects on the potential as felt by a moving projectile near the surface. This is the situation in the scattering problems we are interested in[10–13] and has been recently treated by Ferrell and Ritchie.[17] A considerable effort is required in evaluating the surface curvature correction to the plane-geometry formulas of Sec. II. This is undertaken in Sec. IV where the problem is solved in a cylindrical geometry. Particular care is taken in expanding the potential in the large radius limit (Appendix A). Still retaining the linear terms in the atomic polarizability only, we recover from our formulas of Secs. III and IV the Ferrell and Ritchie[17] dynamical potential and the Nabutovskii *et al.*[18] cylindrical solution, respectively.

In Sec. V we report the full retarded result for a sphere geometry. This has no immediate experimental interest but has been included since perhaps in its small radius limit[19] it is appropriate in treating colloidal suspensions on the surface. In Sec. VI we include a surface roughness on the semi-infinite bounded metal and show how the problem can be solved analytically in the es approximation.

The method we employ throughout the paper is the normal modes Gerlach's method we present in Sec. II below. Finally, in Sec. VII we summarize the results and get a deeper insight into the origin of the logarithmic expression in the general atom-surface potential relation. To this end a brief calculation with the fluctuation method is sketched in the es limit within a plane geometry.

II. GENERAL FORMULATION AND PLANE-GEOMETRY RESULT

The system of an isolated atom and a metallic body can be regarded as a system of coupled harmonic oscillators. It has been shown[20] that the interaction energy for such a system is given by

$$U=\frac{k_BT}{2}\sum_{n=-\infty}^{n=+\infty}\ln F(iu_n)\;;\quad u_n=\frac{2\pi k_BTn}{\hbar}\;, \tag{2.1}$$

where $F(\omega)$ is such that its zeros characterize the frequency spectrum ω_{oi} of the coupled system of oscillators and its poles give the eigenvalues ω_{pi} in the absence of coupling:

$$F(\omega)=0 \text{ if } \omega=\omega_{oi}\;, \tag{2.2}$$

$$1/F(\omega)=0 \text{ if } \omega=\omega_{pi}\;. \tag{2.2'}$$

If no damping is present in the system, the general relation is valid:

$$F(iu)=F(-iu)\ , \tag{2.3}$$

and (2.1) becomes

$$U=\frac{k_BT}{2}\sum_{n=0}^{n=\infty}\epsilon_n \ln F(iu_n)\ , \tag{2.4}$$

where ϵ_n is the Neuman factor, $\epsilon_n=1$ for $n=0$, and $\epsilon_n=2$ otherwise. In the zero temperature limit we replace the sum in (2.4) by an integration and have

$$U=\frac{\hbar}{2\pi}\int_0^\infty du\ \ln F(iu)\ . \tag{2.5}$$

Equation (2.5) has been successfully used in Refs. 5 and 6 to calculate the Lifshitz force exerted between two solid surfaces and we shall use it as a starting formula for our calculations. Let us begin with the system of an atom and a semi-infinite medium which is the simplest situation. We fix the axis such that the solid occupies the region $z<0$, while the atom is placed in a vacuum along the z axis at a distance l from the surface. The secular equation (2.2) for the atom-surface coupled system can be found from the macroscopic Maxwell's equation,

$$\begin{aligned}\vec{\nabla}\times\vec{E}(\vec{r},\omega)&=i\frac{\omega}{c}\vec{B}(\vec{r},\omega)\ ,\\ \vec{\nabla}\times\vec{B}(\vec{r},\omega)&=-i\frac{\omega}{c}[\epsilon_\omega(\vec{r})\vec{E}(\vec{r},\omega)\\ &\qquad +4\pi\vec{P}_\omega\delta(\vec{r}-\vec{r}_A)]\ ,\end{aligned} \tag{2.6}$$

where

$$\epsilon_\omega(\vec{r})=\epsilon(\omega)\theta(-z)+\theta(z)\ , \tag{2.7}$$

with $\theta(z)$ the Heaviside step function; $\epsilon(\omega)$ is the dielectric function of the medium, $\vec{P}_\omega$ is the induced dipole of the atom, and $\vec{r}_A\equiv(\vec{R}_A=0,\ z_A=l)$ is its position in the vacuum. The solution of (2.6) and (2.7) is the sum of an inhomogeneous solution which in a vacuum is of the dipole type, i.e.,

$$\vec{E}^{\rm inh}(\vec{r},\omega)=\frac{i}{2\pi}\int\frac{d\vec{K}}{p}\left[\left[\frac{\omega}{c}\right]^2\vec{P}_\omega-\vec{k}'(\vec{k}'\cdot\vec{P}_\omega)\right]\times e^{ip|z-l|}e^{i\vec{K}\cdot\vec{R}}\ , \tag{2.8}$$

where

$$\vec{r}\equiv(\vec{R},z)\ ,\quad \vec{k}'\equiv[\vec{K},p\,\mathrm{sgn}(z-l)]\ ,$$

and

$$p=[(\omega/c)^2-K^2]^{1/2}\ ,\quad \mathrm{Im}p\geq 0 \tag{2.9}$$

and of a homogeneous solution of the form

$$\vec{E}^h(\vec{r},\omega)=\int d\vec{K}\,\vec{E}^h_{\vec{K},\omega}(z)e^{i\vec{K}\cdot\vec{R}}\ , \tag{2.10}$$

with

$$\vec{E}^h_{\vec{K},\omega}(z)=[A_{||}(\vec{K}/K-K\hat{z}/p)+A_\perp\hat{z}\times\vec{K}/K]e^{ipz} \tag{2.11a}$$

in vacuum ($z>0$) and

$$\vec{E}^h_{\vec{K},\omega}(z)=[C_{||}(\vec{K}/K+K\hat{z}/W)+C_\perp\hat{z}\times\vec{K}/K]e^{-iWz} \tag{2.11b}$$

in the medium ($z<0$).

An analogous expression for the magnetic field can be found by using Eqs. (2.11) and (2.8) in the first equation (2.6). In (2.11) we have introduced

$$W=[\epsilon(\omega)(\omega/c)^2-K^2]^{1/2}\ ,\quad \mathrm{Im}W>0\ . \tag{2.12}$$

The coefficients $A_{||(\perp)}$, $C_{||(\perp)}$ have to be regarded as arbitrary $\underline{K}$, ω dependent quantities. The standard boundary conditions at the surface $z=0$ determine these constants uniquely. For the field in vacuum ($z>0$) we obtain

$$\begin{aligned}A_{||}&=\frac{i}{2\pi}\Delta_p[KP_{\omega,z}+p(\vec{K}\cdot\vec{P}_\omega)/K]e^{ipl}\ ,\\ A_\perp&=\frac{-i}{2\pi}\Delta_s\frac{(\omega/c)^2}{p}\left[\frac{\vec{K}}{K}\times\vec{P}_\omega\right]\cdot\hat{z}e^{ipl}\ ,\end{aligned} \tag{2.13}$$

where, for future use, the dimensionless quantities

$$\Delta_p=\frac{W-\epsilon(\omega)p}{W+\epsilon(\omega)p}\ ,\quad \Delta_s=\frac{W-p}{W+p} \tag{2.14}$$

have been introduced. Expressing the induced dipole $\vec{P}_\omega$ appearing in (2.13) in terms of the atomic polarizability $\alpha_A(\omega)$ as

$$\vec{P}_\omega=\alpha_A(\omega)\vec{E}^h(\vec{r}_A,\omega)\ , \tag{2.15}$$

Eq. (2.11a) offers a set of linear equations for $\vec{P}_\omega$ of the matrix type

$$[1+\overleftrightarrow{I}(\omega)]\vec{P}_\omega=0\ . \tag{2.16}$$

A short calculation gives the diagonal matrix

$$I_{i,j}(\omega)=I_i(\omega)\delta_{i,j}\quad (i,j=x,y,z) \tag{2.17}$$

where

$$I_x(\omega)=I_y(\omega)$$
$$=\frac{i}{2}\alpha_A(\omega)\int_0^\infty dK\frac{K}{p}e^{2ipl}[(\omega/c)^2\Delta_s-p^2\Delta_p]\,,$$
$$I_z(\omega)=i\alpha_A(\omega)\int_0^\infty dK\frac{K}{p}e^{2ipl}K^2\Delta_p\,. \tag{2.18}$$

The frequency spectrum ω_{oi} of the coupled atom-surface system is then determined by the implicit equation (2.2) with

$$F(\omega)=\det[1+\overleftrightarrow{I}(\omega)]$$
$$=[1+I_x(\omega)][1+I_y(\omega)][1+I_z(\omega)]\,. \tag{2.19}$$

It is easy to show that Eq. (2.19) satisfies Eq. (2.3). We also note that the expression under the integral sign in (2.18) diverges when

$$\Delta_p^{-1}=0\,, \tag{2.20}$$

which is the dispersion relation of surface plasmons (SP) in a semi-infinite geometry. Hence, Eq. (2.18), i.e., (2.19) contains all the SP frequencies as poles in its density representation and (2.2') is therefore satisfied. This is clearly seen in the es limit when the SP modes degenerate into a single level ω_{SP} given by

$$\epsilon(\omega_{SP})+1=0 \tag{2.21}$$

and Eq. (2.18) becomes

$$1+I_x(\omega)=1+I_y(\omega)=1-\frac{\alpha_A(\omega)}{8l^3}\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\,,$$
$$1+I_z(\omega)=1-\frac{\alpha_A(\omega)}{4l^3}\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\,, \tag{2.22}$$

showing poles at the SP frequencies.

To evaluate the van der Waals potential we insert Eq. (2.19) into (2.4) and make a change of variables $K\to\eta$ in the integrals (2.18) according to

$$\eta(\omega/c)=p\,, \tag{2.23}$$

where p is given in (2.9). The path of integration in the new variable is defined by $\eta=\mathrm{sgn}(u)\times(1+K^2c^2/u^2)^{1/2}$. The result we get is

$$U(l)=k_BT\sum_{n=0}^{n=\infty}{}'\epsilon_n\left\{\ln\left[1-\tfrac{1}{2}\alpha_A(iu_n)\left[\frac{u_n}{c}\right]^3\int_1^\infty d\eta(\Delta_s-\eta^2\Delta_p)e^{-2\eta(u_nl/c)}\right]\right.$$
$$\left.+\tfrac{1}{2}\ln\left[1-\alpha_A(iu_n)\left[\frac{u_n}{c}\right]^3\int_1^\infty d\eta(1-\eta^2)\Delta_pe^{-2\eta(u_nl/c)}\right]\right\}, \tag{2.24}$$

where now Δ_p and Δ_s [Eq. (2.14)] become

$$\Delta_p=\frac{\sigma-\epsilon(iu_n)\eta}{\sigma+\epsilon(iu_n)\eta}\,,\quad \Delta_s=\frac{\sigma-\eta}{\sigma+\eta}\,;\quad \sigma=[\eta^2+\epsilon(iu_n)-1]^{1/2}\,, \tag{2.25}$$

and u_n are given in (2.1). Expanding the logarithm in (2.24) and retaining only linear terms in α_A, we get Parsegian's[16] expression [his Eq. (9)],

$$U(l)=-\frac{k_BT}{2}\sum_{n=0}^{n=+\infty}{}'\epsilon_n\alpha_A(iu_n)(u_n/c)^3\int_1^\infty d\eta[\Delta_s+(1-2\eta^2)\Delta_p]e^{-2\eta(u_nl/c)}\,. \tag{2.26}$$

The result has to be expected since, starting from the Lifshitz[3] formula and letting one of the two media to become a vapor, Parsegian[16] lets the quantity

$$\alpha_A(\omega)N \tag{2.27}$$

go to zero with N being the number of atoms per unit volume. Thus only the linear term in the polarizability α_A can be retained in the potential energy u. On the opposite, as seen in (2.24), our expansion parameter is either of the dimensionless quantities

$$\alpha_A(\omega)/\lambda_a^3\,,\quad \alpha_A(\omega)/l^3\,, \tag{2.28}$$

where λ_a denotes a typical wavelength of the absorption spectra, and the second is suggested by evaluating the integral over η in (2.24) in the es limit.

For (2.26) to make sense, both of these quantities must be small. For usual values of the polarizability α_A, since λ_a lies in the infrared region, the condition $\alpha_A/\lambda_a^3<<1$ is well satisfied. For $l\gtrsim 300$ Å, which is typical of scattering problems, the condition $\alpha_A/l^3<<1$ is also met and the linearized expression (2.26) does

hold.

The origin of the logarithm in (2.24) can be attribed to a renormalization of the dipole via the neighboring surface. This effect becomes stronger as the atom approaches the surface and, while it is totally negligible in scattering experiments, it becomes crucial in physisorption problems. An expression analogous to ours is present in a paper by Mahan and Lucas[21] who treat physisorption. It is hard to justify the use of a local response function $\epsilon(\omega)$ and visualize the atom as a point dipole at such distances[22,23]; nevertheless, we note that Eq. (2.24) and not (2.26) gives the correct interaction energy for the atom-surface within the model (2.6) and (2.15). This point will be further considered in Sec. VII, where the es limit of (2.24) is found from the fluctuation approach, and the origin of the logarithm in (2.24) is better visualized.

However interested in scattering experiments, we shall consider in the following its linearized expression only.

For distance such that

$$k_B T l/\hbar c << 1 , \tag{2.29}$$

the zero temperature limit can be taken in (2.26), i.e.,

$$U(l)=-\frac{\hbar}{2\pi}\int_0^\infty du\,\alpha_A(iu)(u/c)^3\int_1^\infty d\eta[\Delta_s+(1-2\eta^2)\Delta_p]e^{-2\eta(u/c)l} . \tag{2.26'}$$

In general the above second integral can be evaluated analytically only in the perfect conductor (pc) limit where $\Delta_s=-\Delta_p=1$ and in the es limit where

$$\Delta_p=\frac{1-\epsilon(iu)}{1+\epsilon(iu)} , \quad \Delta_s=0 . \tag{2.30}$$

The potential is usually written as[14]

$$U(l)=-k_L/l^3 . \tag{2.31}$$

In the pc limit one finds for k_L the expression

$$k_L \underset{\text{pc}}{\to} \frac{\hbar}{4\pi}\int_0^\infty du\,\alpha_A(iu) \times\left[1+2\frac{u}{c}l+2\left[\frac{u}{c}\right]^2 l^2\right]e^{-2(u/c)l} , \tag{2.32a}$$

while in the es limit it becomes a bar (l independent) coupling constant

$$k_L=\frac{\hbar}{4\pi}\int_0^\infty du\,\alpha_A(iu)\frac{\epsilon(iu)-1}{\epsilon(iu)+1} . \tag{2.32b}$$

The first above is the well-known Casimir and Polder[2] result (their Eq. 27) originally obtained by a perturbative approach. The retardation can be partially introduced in the second es limit, starting from (2.26') and using the approximate relation (2.30). The result is

$$k_L=\frac{\hbar}{4\pi}\int_0^\infty du\,\alpha_A(iu)\frac{\epsilon(iu)-1}{\epsilon(iu)+1} \times\left[1+\frac{u}{c}l\right]^2 e^{-2(u/c)l} , \tag{2.33}$$

which can be generally retained valid[3] for $l/\lambda_a \lesssim 1$.

III. DYNAMICAL EFFECT

In this section we shall extend the previous results to the case in which the atom strikes the plane surface with a constant parallel velocity $\vec{v}_{||}$. Interested in scattering experiments and in particular in its small deflection limit[10–13] we allow the projectile to move along the unperturbed trajectory, i.e., following the straight line

$$\vec{r}_A(t)=(\vec{R}_A=\vec{v}_{||}t,l) . \tag{3.1}$$

Maxwell's equations (2.6) are still valid but

$$\vec{P}_\omega\delta(\vec{r}-\vec{r}_A)\to[\vec{P}(t)\delta(\vec{r}-\vec{r}_A(t))]_\omega , \tag{3.2}$$

where the last parentheses means Fourier transform (FT) in time. The inhomogeneous solution can be found as before. Equation (2.8) remains valid but, as implied by (3.2), with

$$\vec{P}_\omega\to\vec{P}_{\omega-\vec{K}\cdot\vec{v}_{||}} . \tag{3.3}$$

The same recipe applies for its homogeneous part (2.13). The constitutive equation for $P(t)$ is given by the time-convolution relation

$$\vec{P}(t)=\int\frac{dt'}{2\pi}\alpha_A(t-t')\vec{E}^h(\vec{r}_A(t'),t') , \tag{3.4}$$

or by its FT,

$$\vec{P}_\omega=\alpha_A(\omega)\int d\vec{K}\,\vec{E}^h_{\vec{K},\omega'}(l) , \quad \omega'=\omega+\vec{K}\cdot\vec{v}_{||} . \tag{3.4'}$$

Equation (3.4') replaces relation (2.15) for a moving atom.

Inserting the homogeneous field expression with

the use of (2.11a), (2.13), and (3.3), we recognize in the last expression (3.4'), a matrix equation for $\vec{P}_\omega$ again in the form

$$(1+\overleftrightarrow{I}(\omega))\vec{P}_\omega=0\ . \tag{3.5}$$

One can easily see that the matrix $\overleftrightarrow{I}(\omega)$ is no longer diagonal as in the static case and the general form for the potential $U(l)$ it originates from is a rather complicated expression we shall not write explicitly. However, in expanding the results in powers of the atomic polarizability and taking the linear term, the off-diagonal elements do not contribute and the whole expression may be considerably simplified. From the $T=0$ Eq. (2.5), which now becomes

$$U(l)=\frac{\hbar}{4\pi}\int_{-\infty}^{+\infty}du\ \ln\{\det[1+\overleftrightarrow{I}(iu)]\}$$
$$\approx\frac{\hbar}{4\pi}\int_{-\infty}^{+\infty}du\ I_{jj}(iu)\ , \tag{3.6}$$

we have, after a short calculation,

$$U(l)=i\frac{\hbar}{4\pi}\int_{-\infty}^{+\infty}du\int\frac{d\vec{K}}{2\pi p'}\alpha_A(\omega)[(\omega'/c)^2\Delta_s'-(p'^2-K^2)\Delta_p']e^{2ip'l}\ , \tag{3.7}$$

where $\omega=iu$ and p',Δ_p',Δ_s' are defined in (2.9) and (2.14) in terms of $\omega'=\omega+\vec{K}\cdot\vec{v}_{||}$ as in (3.4').

Exchanging the two integrals in (3.7) and making the change of variable

$$u=u-i\vec{K}\cdot\vec{v}_{||} \tag{3.8}$$

followed by $K\rightarrow\eta$ according to (2.23), the potential becomes

$$U(l)=-\frac{\hbar}{2\pi}\int_0^{+\infty}\left[\frac{u}{c}\right]^3du\int_1^{+\infty}\int_0^{2\pi}\frac{d\varphi}{2\pi}\alpha_A\{iu[1+i(\eta^2-1)^{1/2}\beta_{||}\cos\varphi]\}[\Delta_s+(1-2\eta^2)\Delta_p]e^{-2\eta(u/c)l}\ , \tag{3.9}$$

where $\beta_{||}=v_{||}/c$ and Δ_s,Δ_p are given through (2.25).

Note that in writing (3.9) we have made use of the relation

$$\alpha_A(iz)=\alpha_A(-iz)\ , \tag{3.10}$$

with z complex.

For $v_{||}=0$ Eq. (3.9) reduces to the static potential Eq. (2.26'), while in the es limit one recovers Ferrell and Ritchie's[17] result

$$U(l)=-\frac{\hbar}{\pi}\int_0^{+\infty}du\frac{\epsilon(iu)-1}{\epsilon(iu)+1}\int_0^{\infty}dK\int_0^{2\pi}\frac{d\varphi}{2\pi}\alpha_A(iu-Kv_{||}\cos\varphi)K^2e^{-2Kl}\ . \tag{3.11}$$

The dynamical correction present in (3.9) can be better seen by expanding this result in powers of $v_{||}$. Limiting to $l/\lambda_a\lesssim 1$, one has, to a good approximation,[3]

$$U(l)=-k_L/l^3\ ,$$

$$k_L=\frac{\hbar}{4\pi}\int_0^{+\infty}du\frac{\epsilon(iu)-1}{\epsilon(iu)+1}e^{-2(u/c)l}\left\{\alpha_A(iu)\left[1+\frac{u}{c}l\right]^2+\frac{3}{4}\left[\frac{v_{||}}{l}\right]^2\frac{d^2}{d\omega^2}\alpha_A(\omega)\Big|_{\omega=iu}\right.$$
$$\left.\times\left[\left[1+\frac{u}{c}l\right]^2+\frac{1}{2}\left[\frac{u}{c}l\right]^2\left[1+\frac{2}{3}\frac{u}{c}l\right]\right]+O(v_{||}^4)\right\}\ . \tag{3.12}$$

The first term in the curly bracket is the zero-order result Eq. (2.33) while the second term is the dynamical correction. We shall return to it when discussing the applications in paper II.

IV. CYLINDRICAL GEOMETRY

The convenience of using the normal modes method in calculating the van der Waals attraction

has been illustrated in Sec. III where the dynamical effect has been considered in a plane geometry. In this section we shall analyze the surface curvature effect and study the attraction felt by an atom placed near a metallic cylinder. We neglect dynamical effects; in a cylindrical system of coordinates (R,φ,z) we fix the atom at the position $\vec{r}_A \equiv (R_A,O,O)$. The z axis is the cylinder axis and the metal occupies the region $R<R_0$. In this geometry the atom is at a distance $l=R_A-R_0$ from the cylinder surface.

Maxwell's equations are given in (2.6) but now with

$$\epsilon_\omega(\vec{r})=\epsilon(\omega)\theta(R_0-R)+\theta(R-R_0)\ . \tag{4.1}$$

A general homogeneous solution of (2.6) can be found in standard textbooks,[24,25] while the inhomogeneous solution can be gotten from the first Hertz vector potential which is essentially the 2D Green function.[26] As usual, the matching boundary condition at the cylinder surface will then uniquely determine the homogeneous part as a function of $\vec{P}_\omega$, in perfect analogy to what happens in the plane-geometry case, Eq. (2.13). The constitutive equation (2.15) will then solve the problem for the normal modes with a matrix-type equation as in (2.16),

$$[\delta_{i,j}+I_{i,j}(\omega)]P_{\omega,j}=0 \quad (i,j=R,\varphi,z)\ . \tag{4.2}$$

We shall not enter into the details of the calculation for two reasons. First, because it is a standard procedure and nothing is done which is physically new in respect to what was already done in Sec. II. Second, the mathematical complexities inherent to a cylindrical geometry which one usually encounters, would tend to obscure the meaning of this paper.

Suffice it to say that as a final result of the calculation one finds the matrix I_{ij} to be still diagonal with the diagonal elements $I_R(\omega)$, $I_\varphi(\omega)$, and $I_z(\omega)$ given by

$$\begin{aligned}
I_R(\omega)&=i\alpha_A(\omega)\sum_{m=-\infty}^{m=+\infty}\int_0^{+\infty}dp\left[m^2\frac{H_m^2(x_A)}{x_A^2}\left[\frac{\omega}{c}\right]^2\Delta_s+H_m'^2(x_A)p^2\Delta_p\right.\\
&\qquad\left.+2\frac{p^2m^2}{\Delta_m(H,H)}\left[1-\frac{K_0^2}{K^2}\right]\frac{H_m(x_A)}{x_A}H_m'(x_A)\frac{2i}{\pi x_0^2}\right],\\
I_\varphi(\omega)&=I_R\left(\omega;\left[\frac{\omega}{c}\right]^2\Delta_s\rightleftarrows p^2\Delta_p\right),\\
I_z(\omega)&=i\alpha_A(\omega)\sum_{m=-\infty}^{m=+\infty}\int_0^{\infty}dp\,H_m^2(x_A)K_0^2\Delta_p\ ,
\end{aligned} \tag{4.3}$$

where $x_A=K_0R_A$, $x_0=K_0R_0$, $K_0=[(\omega/c)^2-p^2]^{1/2}$, $K=[\epsilon(\omega)(\omega/c)^2-p^2]^{1/2}$, $\mathrm{Im}K_0\geq 0$, $\mathrm{Im}K>0$, and $H_m(x)$ are Haenkel functions of the *first* kind.

In (4.3) we have introduced the symbols Δ_s, Δ_p given by

$$\Delta_s=\frac{\Delta_m(H,J)}{\Delta_m(H,H)}\ ,\quad \Delta_p=\frac{\Delta_m(J,H)}{\Delta_m(H,H)}\ , \tag{4.4}$$

where

$$\begin{aligned}
\Delta_m(X,Y)=&\left[X_m'(x_0)-\epsilon(\omega)\frac{K_0}{K}\frac{J_m'(y_0)}{J_m(y_0)}X_m(x_0)\right]\left[Y_m'(x_0)-\frac{K_0}{K}\frac{J_m'(y_0)}{J_m(y_0)}Y_m(x_0)\right]\\
&-\frac{m^2}{x_0^2}\left[1-\frac{K_0^2}{K^2}\right]\left[1-\epsilon(\omega)\frac{K_0^2}{K^2}\right]X_m(x_0)Y_m(x_0)\ ,
\end{aligned} \tag{4.5}$$

with $y_0=KR_0$, $J_m(x)$ being the Bessel function while the prime means derivative with respect to the argument.

In analogy to (2.20) we recognize in

$$\Delta_m(H,H)=0 \tag{4.6}$$

the SP dispersion relation in cylindrical geometry.[25] Equations (4.2) and (4.6) identify the function $F(\omega)$ appearing in the potential expressions of Sec. II. Since (2.3) in this case is also satisfied, the potential for $T=0$ can be calculated through Eq. (2.5) as

$$U(R_A;R_0)=\frac{\hbar}{2\pi}\int_0^{+\infty} du\,\ln\{[1+I_R(iu)][1+I_\varphi(iu)][1+I_z(iu)]\}\ . \tag{4.7}$$

Changing variable from p to η in (4.3) according to

$$\frac{\omega}{c}\eta=K_0\ ,\quad \frac{\omega}{c}\sigma=K\ ,\quad \omega=iu\ ;\quad \sigma=[\eta^2+\epsilon(iu)-1]^{1/2}\ , \tag{4.8}$$

and introducing the hyperbolic functions K_m, I_m (Ref. 26),

$$K_m(x)=\frac{\pi}{2}i^{m+1}H_m(ix)\ ,\quad I_m(x)=i^{-m}J_m(ix)\ , \tag{4.9}$$

a short calculation gives

$$I_R(iu)=\frac{2}{\pi}\alpha_A(iu)\left[\frac{u}{c}\right]^3\sum_{m=-\infty}^{m=+\infty}\int_1^{+\infty}d\eta\frac{\eta}{(\eta^2-1)^{1/2}}\left\{m^2\frac{K_m^2(x_A)}{x_A^2}\Delta_s^h+K_m'^2(x_A)(1-\eta^2)\Delta_p^h\right.$$
$$\left.-2m^2\frac{(1-\epsilon(iu)\eta^2/\sigma^2)}{\Delta_m^h(K,K)}\frac{K_m(x_A)K_m'(x_A)}{x_A x_0^2}\right\}, \tag{4.10}$$

$$I_\varphi(iu)=I_R(iu\ ;\ \Delta_s^h\rightleftarrows(1-\eta^2)\Delta_p^h)\ ,$$
$$I_z(iu)=-\frac{2}{\pi}\alpha_A(iu)\left[\frac{u}{c}\right]^3\sum_{m=-\infty}^{m=+\infty}\int_1^{+\infty}d\eta\frac{\eta}{(\eta^2-1)^{1/2}}K_m^2(x_A)\eta^2\Delta_p^h\ ,$$

where, according to (4.9), we have redefined $x_A=(u/c)\eta R_A$, $x_0=(u/c)\eta R_0$, $y_0=(u/c)\sigma R_0$. The other quantities in (4.10) are the hyperbolic counterpart of the previous definitions and are explicitly given by

$$\Delta_s^h=\frac{\Delta_m^h(K,I)}{\Delta_m^h(K,K)}\ ,\quad \Delta_p^h=\frac{\Delta_m^h(I,K)}{\Delta_m^h(K,K)}\ ,$$

$$\Delta_m^h(X,Y)=\left[X_m'(x_0)-\epsilon(iu)\frac{\eta}{\sigma}\frac{I_m'(y_0)}{I_m(y_0)}X_m(x_0)\right]\left[Y_m'(x_0)-\frac{\eta}{\sigma}\frac{I_m'(y_0)}{I_m(y_0)}Y_m(x_0)\right]$$
$$-\frac{m^2}{x_0^2}\left[1-\frac{\eta^2}{\sigma^2}\right]\left[1-\epsilon(iu)\frac{\eta^2}{\sigma^2}\right]X_m(x_0)Y_m(x_0)\ . \tag{4.11}$$

Retaining only the terms linear in α_A in the expansion of the logarithm one gets Nabutovskii's *et al.*[18] result. This is to be expected from the discussion of Sec. II since those authors still use a density expansion as in Parsegian's paper.[16]

To complete this section we show explicitly how the present formulas reduce to those of Sec. II in the large radius limit; this procedure constitutes the most interesting result of this section. We shall restrict ourselves to the pc and es limits and take the linearized potential as the expression to be compared. This does not really constitute a restriction since, equivalently, one can start from normal modes equations and show how (4.2) reduces to (2.16).

Taking $\epsilon(\omega)\to\infty$ in (4.10), and using $I_m'\approx I_m$ and $K_m'\approx -K_m$ whenever possible, one finds

$$U_{\rm pc}(R_A;R_0)\underset{R_0>>1}{\to}-\frac{\hbar}{\pi^2}\int_0^\infty du\,\alpha_A(iu)\left[\frac{u}{c}\right]^3$$
$$\times\sum_{m=-\infty}^{m=+\infty}\int_1^{+\infty}d\eta\frac{\eta^3}{(\eta^2-1)^{1/2}}\left[\left[1+\frac{m^2}{x_A^2}\right]K_m^2(x_A)+K_m'^2(x_A)\right]\frac{I_m(x_0)}{K_m(x_0)}\ . \tag{4.12}$$

Using relations (A13), (A17), and (A20) of Appendix A we write equivalently,

$$U_{\rm pc}(l;R_0>>1)=-\frac{\hbar}{\pi^2}\int_0^\infty du\,\alpha_A(iu)\left[\frac{u}{c}\right]^3\int_1^{+\infty}\frac{dx}{(x-1)^{1/2}} \times\left[xK_0\left[2l\frac{u}{c}\sqrt{x}\right]+\sqrt{x}\frac{K_1\left[2l\frac{u}{c}\sqrt{x}\right]}{2l\frac{u}{c}}\right]+O(l/R_0)\,, \tag{4.13}$$

with $x=\eta^2$.

The second integral in (4.13) can be done exactly making use of the relation[27]

$$\int_1^\infty dx\,x^{\lambda/2}(x-1)^{\mu-1}K_\lambda(a\sqrt{x})=\left[\frac{2}{a}\right]^\mu\Gamma(\mu)K_{-\lambda-\mu}(a)\,. \tag{4.14}$$

This gives

$$U_{\rm pc}(l,R_0>>1)=-\frac{\hbar}{4\pi l^3}\int_0^{+\infty}du\,\alpha_A(iu)\left[1+2\frac{u}{c}l+2\left[\frac{u}{c}\right]^2l^2\right]e^{-2(u/c)l}+O(l/R_0)\,, \tag{4.15}$$

i.e., we find again the plane-geometry result (2.31) and (2.32a). In the es limit we change $\eta\to\eta(u/c)$ in (4.10) and then let $c\to\infty$. In the large radius limit the potential is

$$U_{\rm es}(R_A,R_0)\underset{R_0>>1}{\to}-\frac{\hbar}{\pi^2}\int_0^{+\infty}du\,\alpha_A(iu)\frac{\epsilon(iu)-1}{\epsilon(iu+1)} \times\sum_{m=-\infty}^{m=+\infty}\int_0^{+\infty}d\eta\,\eta^2\left[K_m^2(\eta R_A)\left[1+\frac{m^2}{\eta^2R_A^2}\right]+K_m'^2(\eta R_A)\right]\frac{I_m(\eta R_0)}{K_m(\eta R_0)}\,, \tag{4.16}$$

i.e., using the same relation (A13), (A17), and (A20) as above,

$$U_{\rm es}(l,R_0>>1)=-2\frac{\hbar}{\pi^2}\int_0^{+\infty}du\,\alpha_A(iu)\frac{\epsilon(iu)-1}{\epsilon(iu)+1}\int_0^{+\infty}d\eta\,\eta^2\left[K_0(2\eta l)+\frac{K_1(2\eta l)}{2\eta l}\right]+O(l/R_0)\,. \tag{4.17}$$

Making use of the well-known integral[27]

$$\int_0^{+\infty}dt\,t^{\mu-1}K_\nu(t)=2^{\mu-2}\Gamma\left[\frac{\mu-\nu}{2}\right]\Gamma\left[\frac{\mu+\nu}{2}\right], \tag{4.18}$$

Eq. (4.17) reduces to the plane-geometry result (2.31) and (2.32b):

$$U_{\rm es}(l;R_0>>1)=-\frac{\hbar}{4\pi l^3}\int_0^\infty du\,\alpha_A(iu)\frac{\epsilon(iu)-1}{\epsilon(iu)+1}+O(l/R_0)\,. \tag{4.19}$$

V. SPHERICAL GEOMETRY

In spherical coordinates Maxwell's equations are still separable and the solution can be obtained analytically. The diffraction from a sphere has been solved by Mie[28] at the beginning of this century and the problem is well discussed in Stratton's book.[24]

Our geometry is such that the atom is placed on the azimuthal axis at a distance r_A from the origin and r_0 is the sphere radius.

The metallic sphere occupies the region $r<r_0$ and we are looking for solutions of (2.6) subject to (2.15) and where

$$\epsilon_\omega(\vec{r})=\epsilon(\omega)\theta(r_0-r)+\theta(r-r_0)\ . \tag{5.1}$$

The homogeneous solution can be found in Ref. 24 and the inhomogeneous one is obtained through the 3D Green function.[26] The boundary conditions and the constitutive equation (2.15) will give the normal modes matrix equation (2.2) as

$$(\delta_{i,j}+I_{i,j}(\omega))P_{\omega,j}=0 \quad (i,j=r,\vartheta,\varphi)\ . \tag{5.2}$$

Again an explicit calculation shows $\overleftrightarrow{I}(\omega)$ to be diagonal. Calling $I_r(\omega)$, $I_\vartheta(\omega)$, and $I_\varphi(\omega)$ its diagonal elements, at $T=0$ the potential may be written as

$$U(r_A;r_0)=\frac{\hbar}{2\pi}\int_0^\infty du\,\ln\{[1+I_R(iu)][1+I_\vartheta(iu)][1+I_\varphi(iu)]\}\ . \tag{5.3}$$

Going from the real axis to the positive imaginary axis in the complex ω plane one finds the following expressions:

$$I_r(iu)=\frac{2}{\pi}\alpha_A(iu)\left[\frac{u}{c}\right]^3\sum_{n=0}^{n=\infty}(2n+1)n(n+1)\frac{k_n^2(x_A)}{x_A^2}\Delta_p^h\ ,$$

$$I_\theta(iu)=I_\varphi(iu)=\frac{1}{\pi}\alpha_A(iu)\left[\frac{u}{c}\right]^3\sum_{n=0}^{n=\infty}(2n+1)\left[k_n'(x_A)+\frac{k_n(x_A)}{x_A}\right]^2\Delta_p^h-k_n^2(x_A)\Delta_s^h\ ,$$

where we have introduced the symbols

$$\Delta_p^h=\frac{\epsilon^{1/2}(iu)i_n'(y_0)i_n(x_0)-\epsilon(iu)i_n(y_0)i_n'(x_0)+[1-\epsilon(iu)]i_n(y_0)i_n(x_0)/x_0}{\epsilon^{1/2}(iu)i_n'(y_0)k_n(x_0)-\epsilon(iu)i_n(y_0)k_n'(x_0)+[1-\epsilon(iu)]i_n(y_0)k_n(x_0)/x_0}\ , \tag{5.5}$$

$$\Delta_s^h=\frac{\epsilon^{1/2}(iu)i_n'(y_0)i_n(x_0)-i_n(y_0)i_n'(x_0)}{\epsilon^{1/2}(iu)i_n'(y_0)k_n(x_0)-i_n(y_0)k_n'(x_0)}\ ,$$

and $x_A=u/cr_A$, $x_0=u/cr_0$, $y_0=\epsilon^{1/2}(iu)u/cr_0$.

Still i_n, k_n are hyperbolic spherical Bessel functions[26]

$$i_n(n)=\left[\frac{\pi}{2x}\right]^{1/2}I_{n+(1/2)}(x)\ ,\quad k_n(x)=\left[\frac{\pi}{2x}\right]^{1/2}K_{n+(1/2)}(x)\ , \tag{5.6}$$

and the prime means derivative with respect to the argument. The relation (2.2′) is again satisfied since

$$(\Delta_p^h)^{-1}=0 \tag{5.7}$$

has solutions on the real axis in the complex ω plane and gives the SP dispersion relation in spherical geometry[29] [using $i_n(x)=i^{-n}j_n(ix)$, $k_n(x)=-(\pi/2)i^n h_n(ix)$].

Expanding the logarithm in (5.3) and retaining linear terms in α_A the potential becomes

$$U(r_A;r_0)\approx\frac{\hbar}{2\pi}\int_0^\infty du[I_r(iu)+I_\vartheta(iu)+I_\varphi(iu)]\ , \tag{5.8}$$

and one recovers Nabutovskii's *et al.*[18] result. The above formula simplifies in the es limit. Expanding i_n, k_n as

$$i_n(x)=\frac{x^n}{(2n+1)!!}\ ,\quad k_n(x)=\frac{\pi}{2}\frac{(2n-1)!!}{x^{n+1}}\ ,\quad x<<1 \tag{5.9}$$

and then letting $c\to\infty$ in (5.8), one finds

$$U_{\rm es}(r_A;r_0)=\frac{\hbar}{\pi}\frac{r_0}{r_A^4}\int_0^{+\infty}du\,\alpha_A(iu)\sum_{n=0}^{n=\infty}n(n+\tfrac{1}{2})\frac{1-\epsilon(iu)}{1+\dfrac{n}{n+1}\epsilon(iu)}\left[\frac{r_0}{r_A}\right]^{2n}\ . \tag{5.10}$$

We may now study the two opposite limits $l>>r_0$ and $l<<r_0$ of Eq. (5.10), $l=r_A-r_0$ is the distance of

the atom from the spherical surface. In the first case the series is rapidly converging and one takes the first few terms as

$$U_{es}(l;r_0)_{l>>r_0}\approx -\frac{3\hbar}{\pi}\frac{r_0^3}{l^6}\int_0^\infty du\,\alpha_A(iu)\frac{\epsilon(iu)-1}{\epsilon(iu)+2}\left[1-6\frac{r_0}{l}\right]+O\left[\frac{r_0^2}{l^2}\right]. \tag{5.11a}$$

For $r_0\to 0$ and using the Clausius-Mosotti relation,

$$4\pi\frac{\alpha_{sp}(\omega)}{v_{sp}}=\frac{\epsilon(\omega)-1}{\epsilon(\omega)+2},\quad v_{sp}=\tfrac{4}{3}\pi r_0^3, \tag{5.12}$$

where $\alpha_{sp}(\omega)$ is the sphere polarizability, we recover in (5.11a) the Casimir and Polder[2] result [their Eq. (55)] for the van der Waals attraction between two point particles.

Vice versa for $l<<r_0$, large n's dominate in the sum in (5.10) and the following expansion can be used:

$$\frac{1-\epsilon}{1+\frac{n}{n+1}\epsilon}\approx\frac{1-\epsilon}{1+\epsilon}\left[1+\frac{\epsilon}{1+\epsilon}\frac{1}{n}+O\left[\frac{1}{n^2}\right]\right]. \tag{5.13}$$

The result is

$$U_{es}(l;r_0)_{l<<r_0}\approx -\frac{\hbar}{4\pi l^3}\int_0^\infty du\,\alpha_A(iu)\frac{\epsilon(iu)-1}{\epsilon(iu)+1}\left[1-\frac{l}{r_0}\frac{\epsilon(iu)+2}{\epsilon(iu)+1}+O\left[\frac{l^2}{r_0^2}\right]\right] \tag{5.11b}$$

and thus one gets back the plane-geometry-result (2.31) and (2.32b) for $r_0\to\infty$.

VI. SURFACE ROUGHNESS IN A PLANE

In the previous sections we have considered the interaction between an external atom and a metallic surface in various geometries. The case of the cylinder was treated in detail because of its importance in experimental studies. The metallic sphere has been studied for completeness, to get a view of how, within our scheme, the calculation becomes practically possible for more complex geometries. Till now, however, the surface was assumed to be well shaped without microscopic irregularities, which is certainly not a realistic case. To get closer to the experimental situation it is thus desirable to allow a stochastic surface roughness and to evaluate its influence on the van der Waals interaction. Obviously, the roughness will affect the potential only at small distances, while it becomes completely negligible at higher distances. Without restrictions we can therefore neglect the small curvature of the cylinder or sphere, since in the region where the roughness plays a role in the scattering, the atom feels nothing but a flat surface. The formulas we shall derive in this section and those of the two previous sections are in a sense complementary. The former give the actual potential for a rough cylinder or sphere at small distances as a generalization of the plane-geometry formulas of Sec. II, while the latter have to be used at large distances, where the curvature of the surface is not negligible but the roughness is immaterial. This point will be discussed further in paper II.

In Cartesian coordinates $\vec{r}\equiv(\vec{R},z)$, $\vec{R}\equiv(x,y)$ we choose the surface to be represented by the equation

$$z=\xi(\vec{R}), \tag{6.1}$$

$$\xi(\vec{R})=\int d\vec{K}\,\xi_{\vec{K}}\,e^{i\vec{K}\cdot\vec{R}}. \tag{6.2}$$

The metal occupies the region $z<\xi$, while the atom is fixed at $\vec{r}_A\equiv(\vec{R}_A=0,\ z_A=l)$ as in Sec. II.

Neglecting from the start dynamical effects, Maxwell's equations are written as in (2.6) with

$$\epsilon_\omega(\vec{r})=\theta(z-\xi(\vec{R}))+\theta(\xi(\vec{R})-z)\epsilon(\omega). \tag{6.3}$$

The constraint (2.15) will then give us the normal modes equation, i.e., the potential expression for an atom in the presence of a rough surface. As is well known the exact solution of (2.6) and (6.3) can only be obtained as a series in ascending powers of the roughness ξ. The problem was studied in connection with the light scattering from rough surfaces in a paper by Toigo *et al.*[30] There, it has been shown that the most convenient way to go through it is within the Rayleigh hypothesis [Eq. (2.11a) for $z>\xi$ and Eq. (2.11b) for $z<\xi$] and with the extinction theorem formalism. As a generalization of the 1D grating results one gets the 2D rough surface analogous[31]

$$\int d\vec{K}' \frac{(e^{-i(W-p')\xi})_{\vec{K}-\vec{K}'}}{(W-p')p'} \left[\left[KK' + \frac{\vec{K}\cdot\vec{K}'}{KK'} p'W \right] A'_{||} - \left[\frac{\vec{K}}{K} \times \frac{\vec{K}'}{K'} \right] \cdot \hat{z} p' W A'_{\perp} \right]$$

$$= \int d\vec{K}_0 \frac{(e^{-i(W+p_0)\xi})_{\vec{K}-\vec{K}_0}}{(W+p_0)p_0} \left[\left[KK_0 - \frac{\vec{K}\cdot\vec{K}_0}{KK_0} p_0 W \right] A^{\text{inc}}_{||,\vec{K}_0} + \left[\frac{\vec{K}}{K} \times \frac{\vec{K}_0}{K_0} \right] \cdot \hat{z} p_0 W A^{\text{inc}}_{\perp,\vec{K}_0} \right], \tag{6.4a}$$

$$\int d\vec{K}' \frac{(e^{-i(W-p')\xi})_{\vec{K}-\vec{K}'}}{W-p'} \left[\frac{\vec{K}\cdot\vec{K}'}{KK'} A'_{\perp} + \left[\frac{\vec{K}}{K} \times \frac{\vec{K}'}{K'} \right] \cdot \hat{z} A'_{||} \right]$$

$$= \int d\vec{K}_0 \frac{(e^{-i(W+p_0)\xi})_{\vec{K}-\vec{K}_0}}{W+p_0} \left[\frac{\vec{K}\cdot\vec{K}_0}{KK_0} A^{\text{inc}}_{\perp,K_0} + \left[\frac{\vec{K}}{K} \times \frac{\vec{K}_0}{K_o} \right] \cdot \hat{z} A^{\text{inc}}_{||,\vec{K}_0} \right]. \tag{6.4b}$$

The brackets with a suffix in Eqs. (6.4a) and (6.4b) indicate Fourier transforms; $A'_{||}$ and $A'_{\perp}$ are the $(\omega,\vec{K}')$ unknown amplitudes of the homogeneous field (2.11a); p, W are given in (2.9) and (2.12), and p', W' stay in the same relation with K'. We note that in the above formulas the field in the medium (2.11b) has been totally decoupled although it explicitly appears in the matching boundary conditions. This constitutes the major advantage of this procedure.

Equations (6.4a) and (6.4b) refer to an incident field of the form

$$\vec{E}_{\text{inc}}(\vec{r},\omega) = \int d\vec{K}_0 e^{i\vec{K}_0\cdot\vec{R}} e^{-ip_0 z} \times \left[\left[\frac{\vec{K}_0}{K_0} + \frac{K_0}{p_0}\hat{z} \right] A^{\text{inc}}_{||,K_0} + \hat{z} \times \frac{\vec{K}_0}{K_0} A^{\text{inc}}_{\perp,K_0} \right] \tag{6.5}$$

appearing on the rhs at $z=\xi$. Comparing (6.5) with (2.8) and after using $z=\xi<l$ in the last, one can easily see that Eqs. (6.4a) and (6.4b) are still valid for the dipole case if we identify $A^{\text{inc}}_{||,\vec{K}_0}$ and $A^{\text{inc}}_{\vec{K}_0}$ with

$$A^{\text{inc}}_{||,\vec{K}_0} = \frac{i}{2\pi} e^{ip_0 l} \left[p_0 \vec{P}_\omega \cdot \frac{\vec{K}_0}{K_0} + K_0 P_{\omega,z} \right],$$

$$A^{\text{inc}}_{\perp,\vec{K}_0} = \frac{i}{2\pi} e^{ip_0 l} \frac{(\omega/c)^2}{p_0} \left[\frac{\vec{K}_0}{K_0} \times \vec{P}_\omega \right] \cdot \hat{z}\,. \tag{6.6}$$

The unknown $A_{||}$, $A_{\perp}$ can thus be determined without difficulties in ascending power in the roughness by using the expansion

$$(e^{a\xi})_{\vec{K}} = \delta_{\vec{K},0} + a\xi_{\vec{K}} + \frac{a^2}{2!} \int d\vec{K}'\, \xi_{\vec{K}-\vec{K}'} \xi_{\vec{K}'} + \cdots \tag{6.7}$$

in (6.4). Up to record order we get

$$A_{||,\perp} = A^{(0)}_{||,\perp} + A^{(1)}_{||,\perp} + A^{(2)}_{||,\perp} + \cdots \tag{6.8}$$

with

$$A^{(0)}_{||} = \Delta_p A^{\text{inc}}_{||,\vec{K}}\ ;\ A^{(0)}_{\perp} = -\Delta_s A^{\text{inc}}_{\perp,\vec{K}}\,, \tag{6.9a}$$

as the zero-order result (2.13).

$$A^{(1)}_{||} = \frac{1}{\pi} \frac{(1-\epsilon)}{W+\epsilon p} \int d\vec{K}'\, \xi_{\vec{K}-\vec{K}'} e^{ip'l} \left[\left[\frac{\vec{K}\cdot\vec{K}'}{KK'} WW' - \epsilon KK' \right] \frac{pp'}{W'+\epsilon p'} \times \left[\frac{\vec{K}'}{K'} \cdot \vec{P}_\omega + \frac{K'}{p'} P_{\omega,z} \right] - \left[\frac{\vec{K}}{K} \times \frac{\vec{K}'}{K'} \right] \cdot \hat{z} \left[\frac{\vec{K}'}{K'} \times \vec{P}_\omega \right] \cdot \hat{z} \left[\frac{\omega}{c} \right]^2 \frac{Wp}{W'+p'} \right], \tag{6.9b}$$

$$A^{(1)}_{\perp} = \frac{1}{\pi} \frac{(1-\epsilon)}{W+p} \left[\frac{\omega}{c} \right]^2 \int d\vec{K}'\, \xi_{\vec{K}-\vec{K}'} e^{ip'l} \left[\left[\frac{\vec{K}}{K} \times \frac{\vec{K}'}{K'} \right] \cdot \hat{z} \frac{W'p'}{W'+\epsilon p'} \left[\frac{\vec{K}'}{K'} \cdot \vec{P}_\omega + \frac{K'}{p'} P_{\omega,z} \right] + \frac{\vec{K}}{K} \cdot \frac{\vec{K}'}{K'} \left[\frac{\vec{K}'}{K'} \times \vec{P}_\omega \right] \cdot \hat{z} \left[\frac{\omega}{c} \right]^2 \frac{1}{W'+p'} \right],$$

as the first-order correction and

$$A_{\parallel}^{(2)}=\frac{i}{2\pi}\frac{1-\epsilon}{W+\epsilon p}$$
$$\times\int d\vec{\mathbf{K}}'d\vec{\mathbf{K}}''e^{ip''l}\xi_{\vec{\mathbf{K}}-\vec{\mathbf{K}}'}\xi_{\vec{\mathbf{K}}'-\vec{\mathbf{K}}''}$$
$$\times\left\{\frac{pp''}{W''+\epsilon p''}\left[\frac{\vec{\mathbf{K}}''}{K''}\cdot\vec{\mathbf{P}}_{\omega}+\frac{K''}{p''}P_{\omega,z}\right]\left[KK''(\epsilon W+W'')-\frac{\vec{\mathbf{K}}}{K}\cdot\frac{\vec{\mathbf{K}}''}{K''}W(WW''+\epsilon p''^2)\right.\right.$$
$$\left.-2(1-\epsilon)\frac{K^2K'^2+\vec{\mathbf{K}}\cdot\vec{\mathbf{K}}'p'W}{KK'(W'+\epsilon p')}\left[\frac{\vec{\mathbf{K}}'}{K'}\cdot\frac{\vec{\mathbf{K}}''}{K''}W'W''-\epsilon K'K''\right]\right.$$
$$\left.+2(1-\epsilon)\left[\frac{\omega}{c}\right]^2\frac{WW''}{W'+p'}\left[\frac{\vec{\mathbf{K}}}{K}\times\frac{\vec{\mathbf{K}}'}{K'}\right]\cdot\hat{z}\left[\frac{\vec{\mathbf{K}}'}{K'}\times\frac{\vec{\mathbf{K}}''}{K''}\right]\cdot\hat{z}\right]$$
$$+\left[\frac{\omega}{c}\right]^2\frac{p}{W''+p''}\left[\frac{\vec{\mathbf{K}}''}{K''}\times\vec{\mathbf{P}}_{\omega}\right]\cdot\hat{z}\left[W(W+W'')\left[\frac{\vec{\mathbf{K}}}{K}\times\frac{\vec{\mathbf{K}}''}{K''}\right]\cdot\hat{z}\right.$$
$$\left.\left.+2(1-\epsilon)W'\frac{K^2K'^2+\vec{\mathbf{K}}\cdot\vec{\mathbf{K}}'p'W}{(W'+\epsilon p')KK'}\left[\frac{\vec{\mathbf{K}}'}{K'}\times\frac{\vec{\mathbf{K}}''}{K''}\right]\cdot\hat{z}+2(1-\epsilon)\left[\frac{\omega}{c}\right]^2\frac{W}{W'+p'}\left[\frac{\vec{\mathbf{K}}}{K}\times\frac{\vec{\mathbf{K}}'}{K'}\right]\cdot\hat{z}\frac{\vec{\mathbf{K}}'\cdot\vec{\mathbf{K}}''}{K'K''}\right]\right\},$$

(6.9c)

$$A_{\perp}^{(2)}=-\frac{i}{2\pi}\frac{1-\epsilon}{W+p}\left[\frac{\omega}{c}\right]^2$$
$$\times\int d\vec{\mathbf{K}}'d\vec{\mathbf{K}}''e^{ip''l}\xi_{\vec{\mathbf{K}}-\vec{\mathbf{K}}'}\xi_{\vec{\mathbf{K}}'-\vec{\mathbf{K}}''}$$
$$\times\left\{\frac{1}{W''+p''}\left[\frac{\omega}{c}\right]^2\left[\frac{\vec{\mathbf{K}}''}{K''}\times\vec{\mathbf{P}}_{\omega}\right]\cdot\hat{z}\left[\frac{\vec{\mathbf{K}}}{K}\cdot\frac{\vec{\mathbf{K}}''}{K''}(W+W'')+2(1-\epsilon)\left[\frac{\omega}{c}\right]^2\frac{1}{W'+p'}\left[\frac{\vec{\mathbf{K}}}{K}\cdot\frac{\vec{\mathbf{K}}'}{K'}\right]\left[\frac{\vec{\mathbf{K}}'}{K'}\cdot\frac{\vec{\mathbf{K}}''}{K''}\right]\right.\right.$$
$$\left.-2(1-\epsilon)\frac{W'p'}{W'+\epsilon p'}\left[\frac{\vec{\mathbf{K}}}{K}\times\frac{\vec{\mathbf{K}}'}{K'}\right]\cdot\hat{z}\left[\frac{\vec{\mathbf{K}}'}{K'}\times\frac{\vec{\mathbf{K}}''}{K''}\right]\cdot\hat{z}\right]$$
$$+\frac{p''}{W''+\epsilon p''}\left[\frac{\vec{\mathbf{K}}''}{K''}\cdot\vec{\mathbf{P}}_{\omega}+\frac{K''}{p''}P_{\omega,z}\right]\left[(WW''+\epsilon p''^2)\left[\frac{\vec{\mathbf{K}}}{K}\times\frac{\vec{\mathbf{K}}''}{K''}\right]\cdot\hat{z}\right.$$
$$+2(1-\epsilon)\left[\frac{\omega}{c}\right]^2\frac{W''}{W'+p'}\frac{\vec{\mathbf{K}}}{K}\cdot\frac{\vec{\mathbf{K}}'}{K'}\left[\frac{\vec{\mathbf{K}}'}{K'}\times\frac{\vec{\mathbf{K}}''}{K''}\right]\cdot\hat{z}$$
$$+2(1-\epsilon)\frac{p'}{W'+\epsilon p'}\left[\frac{\vec{\mathbf{K}}}{K}\times\frac{\vec{\mathbf{K}}'}{K'}\right]\cdot\hat{z}$$
$$\left.\left.\times\left[\frac{\vec{\mathbf{K}}'}{K'}\cdot\frac{\vec{\mathbf{K}}''}{K''}W'W''-\epsilon K'K''\right]\right]\right\},$$

as a second-order correction.

Using (6.9) it is not a difficult task to find the normal modes matrix equation

$$[\delta_{i,j}+I_{i,j}(\omega)]P_{\omega,j}=0\ , \tag{6.10}$$

i.e., the corresponding potential

$$U(l;\xi)=\frac{\hbar}{2\pi}\int_0^{+\infty} du\ \ln\{\det[\mathbf{1}+\vec{\vec{I}}(iu;\xi)]\}$$
$$+O(\xi^3)\ . \tag{6.11}$$

Equation (6.11) refers to a particular distribution ξ. In order to get the potential for a rough surface an averaging process over all possible distributions has to be performed in (6.11) to get

$$U(l;\sigma)=\langle U(l;\xi)\rangle\ . \tag{6.12}$$

This can be easily done for the linearized potential. Using

$$\langle \xi_{\vec{K}}\rangle=0\ ,\quad \langle \xi_{\vec{K}}\xi_{\vec{K}'}\rangle=\frac{1}{(2\pi)^2}\delta(\vec{K}+\vec{K}')\langle|\xi_{\vec{K}}|^2\rangle\ , \tag{6.13}$$

and introducing the Gaussian autocorrelation function (ACF)

$$A(\vec{R})=\sigma^2 e^{-R^2/a^2}\ , \tag{6.14a}$$

i.e., its FT,

$$\langle|\xi_{\vec{K}}|^2\rangle=[A(\vec{R})]_{\vec{K}}=\pi\sigma^2a^2e^{-K^2a^2/4}\ , \tag{6.14b}$$

where σ is the rms deviation and "a" the autocorrelation length (ACL), one finds for (6.12)

$$U(l;\sigma)=-\frac{\hbar}{2\pi}\int_0^{\infty} du\ \alpha_A(iu)\left\{\left[\frac{u}{c}\right]^3\int_1^{+\infty} d\eta[\Delta_s+(1-2\eta^2)\Delta_p]e^{-2\eta(u/c)/l}-R(iu;\sigma)\right\}+O(\sigma^4) \tag{6.15}$$

$$R(\omega;\sigma)=i\frac{a^2\sigma^2}{(2\pi)^2}(1-\epsilon)\int d\vec{K}\,d\vec{K}'e^{-|\vec{K}-\vec{K}'|^2a^2/4}e^{2ipl}$$
$$\times\left\{\frac{K^2-p^2}{(W+\epsilon p)^2}\left[\epsilon(1-\epsilon)\frac{K^2K'^2}{W'+\epsilon p'}+W^2(W'-p')-\epsilon\left[\frac{\omega}{c}\right]^2W+2\epsilon W\vec{K}\cdot\vec{K}'\frac{W'+p'}{W'+\epsilon p'}\right.\right.$$
$$\left.+(1-\epsilon)\frac{W^2}{K^2}\frac{(\vec{K}\cdot\vec{K}')^2}{W'+\epsilon p'}\right]$$
$$\left.-\left[\frac{\omega}{c}\right]^4\frac{1}{(W+p)^2}\left\{(1-\epsilon)\frac{K'^2}{W'+\epsilon p'}\left[1+\left[\frac{\vec{K}}{K}\cdot\frac{\vec{K}'}{K'}\right]^2\right]+W'-p'-W\right\}\right]. \tag{6.16}$$

Taking polar coordinates in the integral expression (6.16), the angular integrations can be performed in terms of Bessel functions $I_n(x)$, $n=0,1,2$ but the remaining integrals have to be done numerically. This constitutes a strong disadvantage for the applications we have in mind.

We notice, however, that for distances such that

$$l\lesssim\lambda_a\ , \tag{6.17}$$

the es limit is sensible and in this case an analytical solution is possible. Letting $c\to\infty$ in (6.16) and proceeding as above one has

$$R_{es}(\omega;\sigma)=-2\sigma^2a^2\frac{(\epsilon-1)^2}{(\epsilon+1)^2}\int_0^{\infty} dK\int_0^{\infty} dK'K^3K'^2e^{-(K^2+K'^2)a^2/4}e^{-2Kl}$$
$$\times\left[(\epsilon-\tfrac{1}{2})I_0\left[\frac{KK'a^2}{2}\right]+\frac{4\epsilon}{\epsilon-1}I_1\left[\frac{KK'a^2}{2}\right]-\frac{1}{2}I_2\left[\frac{KK'a^2}{2}\right]\right]. \tag{6.18}$$

A similar equation was treated recently by Maradudin and Rahman.[32] Using the relation[27]

$$\int_0^{\infty} dx\,e^{-\beta x^2}I_n(x)=\frac{1}{2}\left[\frac{\pi}{\beta}\right]^{1/2}e^{1/8\beta}I_{n/2}\left[\frac{1}{8\beta}\right] \tag{6.19}$$

and proceeding as in Appendix A of Ref. 32, the integration over K' can be performed and gives

$$R_{es}(\omega;\sigma)=-\pi^{1/2}\frac{\sigma^2}{a^5}\frac{(\epsilon-1)^2}{(\epsilon+1)^3}\int_0^\infty dy\, y^5 e^{-y^2/8}e^{-2yz_0}\left\{\epsilon\left[\left[1+\frac{4}{y^2}\right]I_0\left[\frac{y^2}{8}\right]+I_1\left[\frac{y^2}{8}\right]\right]\right.$$
$$+\frac{4\epsilon}{\epsilon+1}\left[I_{1/2}\left[\frac{y^2}{8}\right]+I_{-1/2}\left[\frac{y^2}{8}\right]\right]$$
$$\left.-\left[\left[1+\frac{2}{y^2}\right]I_0\left[\frac{y^2}{8}\right]+\left[1-\frac{2}{y^2}\right]I_1\left[\frac{y^2}{8}\right]\right]\right\}, \quad (6.20)$$

where $y=Ka$ and we have defined

$$z_0=l/a\ . \quad (6.21)$$

The second term in the curly bracket in (6.20) can be integrated trivially using the expression for $I_{1/2}$, $I_{-1/2}$. For the remaining two terms one starts from the identity[27]

$$\int_0^\infty dy\, e^{y^2/8}e^{-\beta y}I_0(y^2/8)=\pi^{-1/2}e^{\beta^2/2}K_0(\beta^2/2) \quad (6.22)$$

and notices that

$$\int_0^\infty dy\, e^{-y^2/8}e^{-\beta y}y^n I_0(y^2/8)=(-1)^n\pi^{-1/2}\frac{\partial^n}{\partial\beta^n}[e^{\beta^2/2}K_0(\beta^2/2)]\ , \quad (6.23a)$$

$$\int_0^\infty dy\, e^{-y^2/8}e^{-\beta y}y^n I_1(y^2/8)=(-1)^n\pi^{-1/2}\left[\frac{\partial^n}{\partial\beta^n}-4\beta\frac{\partial^{n-1}}{\partial\beta^{n-1}}-4(n-1)\frac{\partial^{n-2}}{\partial\beta^{n-2}}\right][e^{\beta^2/2}K_0(\beta^2/2)]\ . \quad (6.23b)$$

All integrals in (6.20) are thus performed analytically to get

$$R_{es}(\omega;\sigma)=-2\frac{\sigma^2}{a^5}\frac{[\epsilon(\omega)-1]^2}{[\epsilon(\omega)+1]^3}\left\{\epsilon(\omega)\left[\left[\frac{3}{z_0}-8z_0\right]K_0(2z_0^2)+\left[\frac{3}{z_0^3}-\frac{5}{z_0}+8z_0\right]K_1(2z_0^2)\right]e^{2z_0^2}+\frac{6}{z_0^5}\frac{\epsilon(\omega)}{\epsilon(\omega)-1}\right.$$
$$\left.-\left[\left[\frac{3}{z_0}-16z_0\right]K_0(2z_0^2)+\left[\frac{3}{z_0^3}-\frac{7}{z_0}+16z_0\right]K_1(2z_0^2)\right]e^{2z_0^2}\right\}. \quad (6.24)$$

To go through (6.23) and (6.24) we have used an integration by parts [in (6.23b)] and the recursive relations $(d/dx)I_0(x)=I_1(x)$, $(d/dx)K_0(x)=-K_1(x)$, and $(d/dx)K_1(x)=-K_0(x)-K_1(x)/x$. From (6.24) and (6.15) we note that the roughness will tend to increase the interaction. This is generally valid and is what one would expect since the roughness acts on the average as if the surface would be closer to the atom. In the limits $l<<a$ and $l>>a$ we have from (6.24) the expansions

$$R_{es}(\omega;\sigma)\approx-3\frac{\sigma^2}{l^5}\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\left[1+\frac{1}{3}\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\left[\frac{l}{a}\right]^2+O(z_0^4)\right],\quad l<<a \quad (6.25a)$$

$$R_{es}(\omega;\sigma)\approx-3\frac{\pi^{1/2}}{2}\frac{\sigma^2}{al^4}\frac{[\epsilon(\omega)-1]^2[\epsilon(\omega)-\frac{1}{2}]}{[\epsilon(\omega)+1]^3}\left[1+\frac{a}{l}\frac{8\epsilon(\omega)}{[\epsilon(\omega)-1][\epsilon(\omega)-\frac{1}{2}]}+\frac{5}{8}\left[\frac{a}{l}\right]^2\frac{\epsilon(\omega)-\frac{5}{4}}{\epsilon(\omega)-\frac{1}{2}}+O(z_0^{-4})\right],$$
$$l>>a\ . \quad (6.25b)$$

In the pc limit [$\epsilon(\omega)\to\infty$], Eqs. (6.25a) and (6.25b) reduce to the results given by Mehl and Schaich[33] who used the same model (6.1) for the roughness. Thus, Eqs. (6.24) are a generalization of their formulas.

Equations (6.25a) and (6.25b) can be visualized in physical terms. Taking the es limit for the zero-order term in (6.15) and using $R(\omega;\sigma)$ as from the first above, we have

$$U_{\rm es}(l;\sigma)=-\frac{k_\perp}{l^3}\left[1+6\frac{\sigma^2}{l^2}\right],\quad a\to\infty \tag{6.26}$$

with $k_\perp$ given in (2.32b).

This equation can be readily derived by taking the limit $a\to\infty$ from the start. In this limit the atom feels for every distribution nothing but a rigid shift of the whole surface.[33] Thus, in Eq. (2.31) one may use

$$l\to l-\xi\ . \tag{6.27}$$

From $(l-\xi)^{-3}\approx l^{-3}(1+6\xi^2/l^2)$, $\langle\xi^2\rangle=\sigma^2$, the result follows. The same result (but with different $k_\perp$, of course) can be obtained within the additive hypothesis starting from the r^{-6} dependence of the potential between atoms and integrating over the whole medium. In this way, we recognize in $6\sigma^2/l^2$, a surface-curvature effect. The opposite limit (6.25b) is harder to study. The result can be interpreted as due to additional dipoles located on the surface between grooves. They act on the atom with a l^{-4} dependence and their effect is favored at large distances; but the es limit would be improperly taken in this case. On the other hand, when $a\to 0$ so that Eq. (6.25b) would apply, the whole picture breaks down since expansion (6.7) cannot be used for $a\to 0$. Vice versa a large "a" is compatible with the es limit. This is clearly expressed through (6.17) where a does not appear and it can be justified by looking at Eq. (6.16) and noticing that

$$\langle\,|\xi_{\vec K-\vec K'}|^2\rangle\underset{a\to\infty}{\to}(2\pi)^2\sigma^2\delta(\vec K-\vec K') \tag{6.28}$$

for $a\to\infty$. Thus, Eq. (6.28) contributes to the integral (6.16), no matter how large K is.

In addition, expansions (6.25) tell us that a scattering process will be more affected by a surface roughness of large ACL's (l^{-5} correction), while the roughness is completely irrelevant in the opposite case.[14] Keeping this in mind we use the recipe

$$\xi_{\vec K-\vec K'}\to\xi_0\delta(\vec K-\vec K') \tag{6.29}$$

in (6.8) and (6.9) and get

$$A_{||}\approx A^{\rm inc}_{||,\vec K}\Delta_p(1-2ip\xi_0-2p^2\xi_0^2+\cdots)$$
$$\to A^{\rm inc}_{||,\vec K}\Delta_p e^{-2ip\xi_0}\ , \tag{6.30a}$$

$$A_\perp\to -A^{\rm inc}_{\perp,\vec K}\Delta_s e^{-2ip\xi_0}\ , \tag{6.30b}$$

$$U(l;\xi)=-\frac{\hbar}{2\pi}\int_0^\infty du\,\alpha_A(iu)\left[\frac{u}{c}\right]^3$$
$$\times\int_1^{+\infty}d\eta[\Delta_s+(1-2\eta^2)\Delta_p]e^{-2\eta(u/c)(l-\xi_0)}$$
$$=U(l-\xi)\ . \tag{6.31}$$

We recognize in (6.30) and (6.31) the Kirchoff-approximation formulas which become exact for $a=\infty$ and (6.27) can be applied. With (6.30) and (6.31) we get rid of any perturbative approach and the roughness is not necessarily small. We shall devote Eqs. (6.15), (6.24), and (6.31) in paper II to applications.

VII. DISCUSSION AND COMPARISON WITH THE FLUCTUATION METHOD

In this paper we have analyzed the interaction between a nonpolarized atom and differently shaped (planes, cylinders, spheres) metallic surfaces. The plane-geometry result has been generalized in two aspects: the first by looking at dynamical effects treated in Sec. III and the second by taking care of a surface roughness which can be perhaps present on the metal. Both corrections are dictated not simply by purely theoretical motivations, but reflect actual experimental scattering situations whose results will be examined in the light of the present theory in paper II.

The roughness correction of Sec. VI [Eqs. (6.15) and (6.24)] is a new result. The main advantage of the method is that of being solvable analytically in the es limit, but in the second-order roughness. We are free of these two limitations for large ACL's when Kirchoff formulas become valid.

The interaction with spheres, cylinders, and the simplest plane surface has been treated by various authors[2,7,16–18] and in this sense, the results we got for these geometries [(2.24), (4.7), and (5.3)], are certainly not new. The reason why we present them here lies, however, in a logarithmic expres-

sion we find throughout for the atom-surface interaction whose presence has, till now, been missed in the literature. This term has a renormalization origin due to the presence of the surface acting on the atomic dipole. It can be totally neglected in scattering problems (as discussed in Sec. II) but become crucial in physisorption problems when the atom is placed just a few atomic layers away from the metallic surface. This is a noteworthy point and can be visualized not within Gerlach's framework where Eq. (2.1) is imposed *ab initio,* but by going through the fluctuation approach that we shall therefore analyze.

Following Lifshitz[3] we introduce auxiliary driving forces in the atom-surface system. Maxwell's equations are written as in the macroscopic case but without any time averaging on a microscopic scale. One then associates an instantaneous polarization $\vec{P}^{\text{inst}}_{A,\omega}$, with the external atom and a continuous distribution of dipoles $\vec{P}_m(\vec{r},\omega)$ with the medium as well.

It follows therefore that in Maxwell's equations the atom appears through the total dipole $\vec{P}^T_{A,\omega}$,

$$\vec{P}^T_{A,\omega}=\vec{P}^{\text{inst}}_{A,\omega}+\vec{P}_{A,\omega} , \tag{7.1}$$

where $\vec{P}_{A,\omega}$, as in Eq. (2.15), is the dipole induced by the homogeneous solution, i.e.,

$$\vec{P}_{A,\omega}=\alpha_A(\omega)\vec{E}^h[\vec{r}_A,\omega;\vec{P}^T_{A,\omega};\vec{P}_m(\vec{r},\omega)] . \tag{7.2}$$

In the last equation we have taken care to indicate explicitly that the homogeneous field is some functional of $\vec{P}^T_{A,\omega}$ and $\vec{P}_m(r,\omega)$; the particular functional form depending upon the geometry of the system. Equations (7.1) and (7.2) constitute a Lippman-Schwinger-type equation for $\vec{P}^T_{A,\omega}$ that can be solved exactly for a point dipole. Note that Eq. (7.2) renormalizes the induced atomic dipole and it can be shown that the logarithm in the potential expression (2.4) is originated just by this term.

To check this, we choose the simplest possible model, i.e., the es limit of a point particle and a plane geometry. We derive the homogeneous field from a scalar potential ϕ^h:

$$\phi^h(\vec{r},\omega)_{z>0}=\int d\vec{K} A_{\vec{K},\omega} e^{i\vec{K}\cdot\vec{R}} e^{-Kz} , \tag{7.3}$$

where $A_{\vec{K},\omega}$ are determined by the usual boundary conditions and are given in Eq. (B1) of Appendix B. The Lorentz force exerted on the atom is thus given in the present es limit by

$$\begin{aligned}\vec{F}&=\int_0^{+\infty} d\omega \vec{F}_\omega ,\\ \vec{F}_\omega&=-\int d\vec{K} K^2 e^{-Kl}\left[i\frac{\vec{K}}{K}+\hat{z}\right]\\ &\quad\times\left[\left[i\frac{\vec{K}}{K}+\hat{z}\right]\cdot\vec{P}^T_{A,\omega}\right]A^*_{\vec{K},\omega}+\text{c.c.} ,\end{aligned} \tag{7.4}$$

where $\vec{P}^T_{A,\omega}$, the solution of (7.1) and (7.2) is reported in Eq. (B3) of Appendix B. Using the same Eq. (B3), the fluctuation-dissipation theorem for the $P^T_{A,\omega}$ gives

$$\langle P^T_{A,\omega;i}P^{T*}_{A,\omega';j}\rangle=\frac{\hbar}{2\pi}\,\text{Im}\alpha^T_i(\omega)\coth\left[\frac{\hbar\omega}{2k_BT}\right]\times\delta(\omega-\omega')\delta_{i,j} , \tag{7.5}$$

where

$$\alpha^T_x(\omega)=\alpha^T_y(\omega)=\alpha_A(\omega)\Big/\left[1-\frac{\alpha_A(\omega)}{8l^3}\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\right] , \tag{7.6}$$

$$\alpha^T_z(\omega)=\alpha_A(\omega)\Big/\left[1-\frac{\alpha_A(\omega)}{4l^3}\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\right] .$$

From Eq. (7.5) an easy calculation gives the Lorentz force

$$\vec{F}=-\hat{z}\frac{3\hbar}{16\pi}\frac{1}{l^4}\,\text{Im}\int_0^\infty d\omega\,\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}[\alpha^T_x(\omega)+\alpha^T_y(\omega)+2\alpha^T_z(\omega)]\coth\left[\frac{\hbar\omega}{2k_BT}\right] . \tag{7.7}$$

Equivalently this force can be expressed via a logarithmic-type potential U given by

$$U=\frac{\hbar}{2\pi}\,\text{Im}\int_0^{+\infty} d\omega\left[2\ln\left[1-\frac{\alpha_A(\omega)}{8l^3}\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\right]+\ln\left[1-\frac{\alpha_A(\omega)}{4l^3}\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\right]\right]\coth\left[\frac{\hbar\omega}{2k_BT}\right] . \tag{7.8}$$

Once the path of integration in Eq. (7.8) is changed from the real to the imaginary axis in the usual way,[3,7] we get back the result (2.24) that we got in Sec. II, and when, of course, the last is evaluated in the same es limit.

To conclude, we comment on the physical meaning of Eq. (7.5). In going from the "bare" fluctuating dipole $\vec{P}^{\text{inst}}_{A,\omega}$, to the renormalized one $\vec{P}^T_{A,\omega}$,

one replaces in the fluctuation-dissipation relations the bare isotropic polarizability α_A with the expressions α_i^T of Eq. (7.6).

In any respect, α_i^T can therefore be regarded as a renormalized polarizability due to the presence of the surface; in fact, we see from Eq. (2.22) that it contains the actual modes of the atom-surface system. Still, notice that by replacing in Eq. (7.7) the renormalized polarizability $\alpha_i^T(\omega)$ with the bare atomic polarizability, one gets the Parsegian result, and the logarithm in the potential expression is lost.

ACKNOWLEDGMENT

This work was supported by the Consiglio Nazionale delle Ricerche through GNSM.

APPENDIX A

In this appendix we evaluate the series

$$\lim_{\substack{x\to\infty\\ y\to\infty}} \sum_{m=-\infty}^{m=+\infty} c_m(x,y)K_{m+n}(x)I_m(y)\ ,$$

$$x-y=z\ ,\ \text{finite} \tag{A1}$$

with

$$c_m(x,y)=\begin{cases} K_m(x)/K_m(y)\ , & n=0 \quad (A2)\\ (m^2/x^2)K_m(x)/K_m(y)\ , & n=0 \quad (A3)\\ K_{m+1}(x)/K_m(y)\ , & n=1 \quad (A4)\end{cases}$$

To solve for (A1) we use the asymptotic expansion of the modified Haenkel functions $K_m(x)$ and $K_m(y)$ appearing in the coefficients $c_m(x,y)$ in (A2)–(A4). These coefficients assume the form

$$c_m(x,y)=e^{-z}\sum_{p=0}^{p=+\infty} d_p(x,y)m^p/x^p\ . \tag{A5}$$

When (A5) is inserted in (A1), after using the addition theorem for Bessel functions[34]

$$e^{in\psi}K_n(\tilde{z})=\sum_{m=-\infty}^{m=+\infty} K_{m+n}(x)I_m(y)e^{im\varphi}\ ,$$

$$\tilde{z}=(x^2+y^2-2xy\cos\varphi)^{1/2}\ , \tag{A6}$$

$$e^{in\psi}=\left[\frac{x-ye^{-i\varphi}}{x-ye^{+i\varphi}}\right]^{n/2}\ ,$$

the series of (A1) becomes

$$\lim_{\substack{x,y\to\infty\\ x-y=z}} e^{-z}\sum_{p=0}^{p=-\infty} d_p(x,y) \times\left[\frac{1}{x^p}\lim_{\varphi\to 0}(-i)^p\frac{d^p}{d\varphi^p}[e^{in\psi}K_n(\tilde{z})]\right]\ . \tag{A7}$$

It is not difficult to show that one has

$$\frac{1}{x^{2t}}\lim_{\varphi\to 0}(-1)^t\frac{d^{2t}}{d\varphi^{2t}}K_0(\tilde{z}) =\frac{(2t-1)!!}{z^t}\,[K_t(z)+O(1/x^2)] \tag{A8}$$

and

$$\frac{1}{x^{2t}}\lim_{\varphi\to 0}(-1)^t\frac{d^{2t}}{d\varphi^{2t}}e^{i\psi}K_1(\tilde{z})=\frac{(2t-1)!!}{z^t}[K_{t+1}(z)+O(1/x^2)]\ ,$$

$$\frac{1}{x^{2t+1}}\lim_{\varphi\to 0} i(-1)^{t+1}\frac{d^{2t+1}}{d\varphi^{2t+1}}e^{i\psi}K_1(\tilde{z})=\frac{(2t+1)!!}{z^{t+1}}[K_{t+1}(z)+O(1/x^2)]\ , \tag{A8'}$$

for any $t\geq 0$ if the convention $(-1)!!=1$ is used. Equations (A8) and (A8') tell us we can retain, in (A5), only the zero-order term $d_p(x,y)$, i.e.,

$$d_p(x,y)\to\lim_{x,y\to\infty} d_p(x,y)=d_p\ , \tag{A9}$$

while higher orders may be neglected.

From (A2), (A5), and (A9) one can verify, with an explicit calculation for the first few terms in the expansion (A5), that the following relation is valid:

$$e^{-z}d_{2t}=\frac{z^{2t}}{2^t t!}\left[\frac{1}{z}\frac{d}{dz}\right]^t e^{-z} =(-1)^t\frac{z^t}{2^t t!}\left[\frac{2z}{\pi}\right]^{1/2}K_{t-1/2}(z)\ , \tag{A10}$$

$$e^{-z}d_{2t+1}=0\ ,\quad t\geq 0\ .$$

Inserting (A10) in (A7) and using (A8) we find

$$\lim_{\substack{x,y\to\infty \\ x-y=z}} \sum_{m=-\infty}^{m=+\infty} \frac{K_m^2(x)}{K_m(y)} I_m(y)$$

$$= \left[\frac{2z}{\pi}\right]^{1/2} \sum_{t=0}^{t=+\infty} \begin{bmatrix} -\frac{1}{2} \\ t \end{bmatrix} K_{t-1/2}(z) K_t(z) \ . \tag{A11}$$

The term on the rhs in the relation above can be calculated through the relation[27,34]

$$K_\mu(z)K_\nu(z) = \int_{-\infty}^{+\infty} d\eta \, e^{-(\mu-\nu)\eta} K_{\mu+\nu}(2z\cosh\eta) \ . \tag{A12}$$

With $\mu=-t$, $\nu=t-\frac{1}{2}$, and $K_{-t}(x)=K_t(x)$ in (A12) and summing under the integral sign, Eq. (A11) becomes

$$\left[\frac{2z}{\pi}\right]^{1/2} \sum_{t=0}^{t=+\infty} \begin{bmatrix} -\frac{1}{2} \\ t \end{bmatrix} K_{t-1/2}(z) K_t(z)$$

$$= \int_{-\infty}^{+\infty} d\eta \frac{e^{-2z\cosh\eta}}{e^{\eta}(e^{\eta}+e^{-\eta})}$$

$$= \int_0^{\infty} d\eta e^{-2z\cosh\eta} \ .$$

The last integral is nothing else than $K_0(2z)$, therefore, the limit (A1) with coefficients given by (A2) is

$$\lim_{x,y\to\infty} \sum_{m=-\infty}^{m=+\infty} \frac{K_m^2(x)}{K_m(y)} I_m(y) = K_0[2(x-y)] \ . \tag{A13}$$

The second case for (A1), namely, with $c_m(x,y)$ given by (A3), can be found easily using the previous result. By comparing (A2) with (A3) and using (A10) one gets trivially the new relation

$$e^{-z} d_{2t} = (-1)^{t-1} \frac{z^{t-1}}{2^{t-1}(t-1)!} \left[\frac{2z}{\pi}\right]^{1/2} K_{t-3/2}(z) \ , \tag{A14}$$

$$e^{-z} d_{2t+1} = 0 \ , \quad t \geq 0 \ .$$

Inserting (A14) in (A7), using (A8) and $t \to t+1$ we have

$$\lim_{\substack{x,y\to\infty \\ x-y=z}} \sum_{m=-\infty}^{m=+\infty} \frac{m^2}{x^2} \frac{K_m^2(x)}{K_m(y)} I_m(y)$$

$$= \left[\frac{2}{\pi z}\right]^{1/2} \sum_{t=0}^{t=-\infty} \begin{bmatrix} -\frac{3}{2} \\ t \end{bmatrix} K_{t-1/2}(z) K_{t+1}(z) \ . \tag{A15}$$

From (A12) with $\mu=-(t+1)$, $\nu=t-\frac{1}{2}$, and proceeding as before, (A15) is transformed into

$$\frac{1}{(\pi z)^{1/2}} \int_0^{\infty} d\eta \frac{K_{3/2}(2z\cosh\eta)}{(\cosh\eta)^{1/2}}$$

$$= \frac{1}{(\pi z)^{1/2}} \int_0^{\infty} dt \frac{K_{3/2}[2z(t^2+1)^{1/2}]}{(t^2+1)^{3/4}} \ ,$$

where we have used the change of variable $t=\sinh\eta$ in the last expression. To evaluate the integral above we use the general relation[27]

$$\int_0^{\infty} K_\nu[z(t^2+a^2)^{1/2}](t^2+a^2)^{-\nu/2} t^{2\mu+1} dt$$

$$= 2^\mu z^{-(\mu+1)} a^{1+\mu-\nu} \Gamma(1+\mu) K_{\nu-\mu-1}(az) \ . \tag{A16}$$

The result is

$$\lim_{x,y\to\infty} \sum_{m=-\infty}^{m=+\infty} \frac{m^2}{x^2} \frac{K_m^2(x)}{K_m(y)} I_m(y) = \frac{K_1[2(x-y)]}{2(x-y)} \ . \tag{A17}$$

For the case (A4) the calculation is more difficult. With an explicit calculation for the first few terms in the expansion (A5) one can verify for (A9) that the following is valid:

$$e^{-z} d_{2t} = \frac{(-1)^t z^t}{2^t t!} \left[\frac{2z}{\pi}\right]^{1/2} \times \left[K_{t+1/2}(z) - \frac{2t}{z} K_{t-1/2}(z)\right] \ , \tag{A18}$$

$$e^{-z} d_{2t+1} = \frac{(-1)^t z^t}{2^t t!} \left[\frac{2}{\pi z}\right]^{1/2} K_{t-1/2}(z) \ .$$

Inserting (A18) in (A7) and using (A8′) we have

$$\lim_{\substack{x,y\to\infty \\ x-y=z}} \sum_{m-\infty}^{m=+\infty} \frac{K_{m+1}^2(x)}{K_m(y)} I_m(y) = \left[\frac{2z}{\pi}\right]^{1/2} \sum_{t=0}^{t=+\infty} \begin{bmatrix} -\frac{1}{2} \\ t \end{bmatrix} K_{t+1/2}(z) K_{t+1}(z) + \left[\frac{2}{\pi z}\right]^{1/2} \sum_{t=0}^{t=+\infty} \begin{bmatrix} -\frac{1}{2} \\ t \end{bmatrix} K_{t-1/2}(z) K_{t+1}(z) \ .$$

The last two terms on the left above can be calculated through (A12) and (A16) as before and we have

$$\lim_{x,y\to\infty}\sum_{m=-\infty}^{m=+\infty}\frac{K_{m+1}^2(x)}{K_m(y)}I_m(y)=K_0[2(x-y)]+2\frac{K_1[2(x-y)]}{2(x-y)}\ . \tag{A19}$$

From (A17) and (A19) and squaring the recurrence relation

$$K_{t+1}(x)=\frac{t}{x}K_t(x)-K_t'(x)\ ,$$

one can show finally,

$$\lim_{x,y\to\infty}\sum_{m=-\infty}^{m=+\infty}\frac{K_m'^2(x)}{K_m(y)}I_m(y)=K_0[2(x-y)]+\frac{K_1[2(x-y)]}{2(x-y)} \tag{A20}$$

to be valid.

APPENDIX B

We have the following:

$$A_{\vec{K},\omega}=\frac{1}{2\pi}\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}e^{-Kl}\left[i\frac{\vec{K}}{K}+\hat{z}\right]\cdot\vec{P}_{A,\omega}^{T}+\frac{4i\pi}{\epsilon(\omega)+1}\int dq_z\frac{1}{q_z-iK}\left[i\frac{\vec{K}}{K}-\hat{z}\right]\cdot\vec{P}_m(\vec{q},\omega)\ , \tag{B1}$$

where $\vec{q}\equiv(\vec{K},q)$ and $\vec{P}_m(\vec{q},\omega)$ denotes the FT of $\vec{P}_m(\vec{r},\omega)$,

$$\vec{P}_m(\vec{q},\omega)=\int d\vec{r}\,e^{-i\vec{q}\cdot\vec{r}}\vec{P}_m(\vec{r},\omega)\ . \tag{B2}$$

The solution of the Lippman-Schwinger equation [Eqs. (7.1) and (7.2)] is

$$P_{A,\omega x(y)}^{T}=\left[1-\frac{\alpha_A(\omega)}{8l^3}\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\right]^{-1}\left\{P_{A,\omega x(y)}^{\text{inst}}+\frac{4\pi\alpha_A(\omega)}{\epsilon(\omega)+1}\int d\vec{q}\,\frac{e^{-Kl}}{q_z-iK}\vec{K}\cdot\hat{x}(\hat{y})\left[i\frac{\vec{K}}{K}-\hat{z}\right]\cdot\vec{P}_m(\vec{q},\omega)\right\}\ ,$$

$$P_{A,\omega z}^{T}=\left[1-\frac{\alpha_A(\omega)}{4l^3}\frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}\right]^{-1}\left\{P_{A,\omega z}^{\text{inst}}+\frac{4\pi i\alpha_A(\omega)}{\epsilon(\omega)+1}\int d\vec{q}\,\frac{Ke^{-Kl}}{q_z-iK}\left[i\frac{\vec{K}}{K}-\hat{z}\right]\cdot\vec{P}_m(\vec{q},\omega)\right\}\ . \tag{B3}$$

[1]F. London, Z. Phys. Chem. (Leipzig) B11, 222 (1930); see also, M. Born, *Atomic Physics* (Blackie, Glasgow, 1962), 7th ed., p. 438.

[2]H. B. G. Casimir and D. Polder, Phys. Rev. 73, 360 (1948).

[3]E. M. Lifshitz, Zh. Eksp. Teor. Fiz. 29, 94 (1955) [Sov. Phys.—JETP 2, 73 (1956)].

[4]L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, New York, 1960), Chap. XIII.

[5]N. G. van Kampen, B. R. A. Nijboer, and K. Schram, Phys. Lett. 26A, 307 (1968).

[6]E. Gerlach, Phys. Rev. B 4, 393 (1971).

[7]D. Langbein, Springer Tracts Mod. Phys. 72, 1 (1974).

[8]F. R. S. D. Tabor and R. H. S. Winterton, Proc. R. Soc. London Ser. A 312, 435 (1969).

[9]W. Arnold, H. Hunklinger, and K. Dransfeld, Phys. Rev. B 19, 6049 (1979) and erratum 21, 1713 (1980).

[10]D. Raskin and P. Kusch, Phys. Rev. 179, 712 (1969).

[11]A. Shih, D. Raskin, and P. Kusch, Phys. Rev. A 9, 652 (1974).

[12]A. Shih, Phys. Rev. A 9, 1507 (1974).

[13]A. Shih and V. A. Parsegian, Phys. Rev. A 12, 835 (1975).

[14]M. J. Mehl and W. L. Schaich, Phys. Rev. A 16, 921 (1977).

[15]M. J. Mehl and W. L. Schaich, Phys. Rev. A 21, 1177 (1980).

[16]V. A. Parsegian, Mol. Phys. 27, 1503 (1974).

[17]T. L. Ferrell and R. H. Ritchie, Phys. Rev. A 21, 1305 (1980).

[18]V. M. Nabutovskii, V. R. Belosludov, and A. M. Korotkikh, Zh. Eksp. Teor. Fiz. 77, 700 (1979) [Sov. Phys.—JETP 50, 352 (1979)].

[19]R. H. Doremus, J. Chem. Phys. 68, 1344 (1978).

[20]Chapter 3 in Ref. 7.

[21]G. D. Mahan and A. A. Lucas, J. Chem. Phys. 68,

1344 (1978).
[22]T. Maniv and H. Metiu, J. Chem. Phys. 72, 1996 (1980).
[23]S. Efrima and H. Metiu, Surf. Sci. 92, 433 (1980).
[24]J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941), Chaps. 6 and 7.
[25]E. N. Economou, C. Pfeiffer, and K. L. Ngai, Phys. Rev. B 10, 3038 (1974); note an error sign in their Eq. (21).
[26]P. M. Morse and H. Feshbach, *Methods for Theoretical Physics* (McGraw-Hill, New York, 1953), Chaps. 10 and 11.
[27]I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals Series and Products* (Academic, New York, 1965).
[28]C. Mie, Ann. Phys. (Leipzig) 25, 377 (1908); see also M. Born and E. Wolf, in *Principles of Optics* (Pergamon, New York, 1975), 5th ed.,p. 633.
[29]E. N. Economou and K. L. Ngai, Adv. Chem. Phys. 27, 265 (1974).
[30]F. Toigo, A. M. Marvin, V. Celli, and N. R. Hill, Phys. Rev. B 15, 5618 (1977).
[31]V. Celli (private communication).
[32]T. S. Rahman and A. A. Maradudin, Phys. Rev. B 21, 504 (1980).
[33]M. J. Mehl and W. L. Schaich, Surf. Sci. 99, 553 (1980).
[34]G. N. Watson, *A Treatise on the Theory of Bessel Function* (Cambridge University Press, London, 1962); H. Bateman, in *Bateman Manuscript Project* (McGraw-Hill, New York, 1953).