Magnetoimage effects in the van der Waals interaction of an atom and a bounded, dynamic, nonlocal plasmalike medium

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We present a theory of van der Waals (vdW) atom-surface attraction in which the second order vdW energy is explicitly exhibited as a correlation–self-energy of atomic electrons generated by a dynamic, nonlocal image potential due to polarization of the electrons of the bounded metal-semiconductor surface system in the electrostatic limit. This formulation is applied to a metal-semiconductor plasma in a magnetic field perpendicular to its bounding surface. The dependence of the atom-surface vdW energy on magnetic field strength provides an adjustable parametrization of the underlying zero-point photon energy (represented in terms of the nonretarded longitudinal plasmon-photons of the Coulomb interaction), opening the possibility of analyzing the concomitant fundamental quantum phenomenology in detail with material parameters that can be examined experimentally. The determination of the image potential, including its nonlocal and dynamic magnetic field effects, involves the construction of a ''surface dielectric function,'' which is carried out using a Green's function joining procedure for nonlocal dynamic electrostatics. In this aspect of our second-order vdW energy calculation, we take account of the role of the magnetic field by means of a hydrodynamic model of magnetoplasma nonlocality in dynamic longitudinal dielectric response. Both local and nonlocal magnetic field effects in vdW energy are analyzed within the framework of a multipole expansion, and are also discussed, respectively, in expansions in powers of ω_c^2 (ω_c is the cyclotron frequency). Furthermore, we determine the role of Landau quantization magnetic field effects in the skewing of the surface electron charge distribution from its uniform positive background, exhibiting de Haas–van Alphen oscillatory (and ''staircase'') behavior.

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I. INTRODUCTION

The phenomenon of van der Waals (vdW)–Casimir interaction between neutral systems has attracted surges of intense scientific interest over many decades because of its fundamental nature. It is of profound importance as an observable manifestation [1] of the uniquely quantum mechanical feature of zero-point photon energy, including Coulomb interactions representative of longitudinal plasmon-photons in the nonretarded limit [2–19]. To the many fine and insightful existing theories focused on the zero-point energy basis, we introduce here yet another theoretical point of view, which we hope provides some calculational advantage in addressing the parametrization of atom-surface vdW energy in terms of the strength of a magnetic field (relative to matter parameters) applied normal to the surface. Starting from the Gell-Mann–Low theorem for interaction energy of the systems, we show that, to second order in the atom-surface Coulomb interaction, the vdW energy can be understood as a correlation effect manifested as a self-energy of the first system due to interaction among the particles of the first system arising from an effective potential associated with polarization of the second system, including the role of nonlocality. While our focus here involves the electrons bound to an atom as the first system with the second system as a semi-infinite magnetized plasma behind the nearby surface of a semiconductor or metal, the roles of first and second can be reversed (in principle, but with resulting calculational difficulty); this point of view is readily extended to the vdW interaction between two surfaces, and even between two atoms. Considering the atom and surface to be sufficiently close so that we can neglect retardation, the effective potential between atomic electrons due to polarization of the semi-infinite plasma is just the dynamic, nonlocal, and inhomogeneous image potential formed behind the surface of the bounded plasma. Taking the magnetic field normal to the plasma surface (and neglecting its effect on the tightly bound atomic electrons), we determine the appropriate image potential that provides the vdW correlation–self-energy interaction among the electrons of the atom. To accomplish this, we employ a ''hydrodynamic'' model of magnetoplasma nonlocality and use it in the construction of the effective image potential for the semi-infinite magnetoplasma. On this basis, we analyze the multipole expansion of the vdW interaction, identifying the roles of both local and nonlocal magnetic field effects in the vdW energy within the framework of the (magneto)hydrodynamic model. Finally, we briefly examine the expansion of vdW energy to second order in the cyclotron frequency. Our results provide the parametrization of the vdW energy discussed above in terms of the magnetic field as the ratio of the cyclotron frequency ω_c to plasma frequency ω_p, as well as nonlocal (material) parameters involving the magnetic field. This opens the possibility of analyzing experimental data on vdW energy reflecting the underlying quantum mechanical zero-point photon energy in its detailed dependence on magnetic field. Moreover, in our examination of first-order energy, we determine the skewing of the surface electron charge distribution from its semi-infinite uniform positive background, with its full complement of Landau quantization effects due to the magnetic field, for both nondegenerate and degenerate plasma statistical re-

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gimes. Since the skewing distance alters the effective atom-surface separation, this introduces purely quantum magnetic field parameters (such as $\hbar\omega_c/E_F$, with E_F as the Fermi energy) which will further affect the vdW energy, adding yet more material parametrization of the underlying quantum mechanical zero-point photon energy that can be examined experimentally.

II. FORMULATION OF ATOM-SURFACE INTERACTION ENERGY

A. Quantum mechanical perturbation theory for nonretarded interaction energy between an atom and a semiconductor or metal surface

Our formulation of perturbation theory for nonretarded van der Waals atom-surface interaction energy will be focused on the effective potential concept for a bounded dynamic nonlocal medium and its concomitant image potential, with sufficient generality to incorporate both classical and quantum magnetic field effects and the role of optical phonons as well as stratification of the medium. To this end, we reexamine atom-surface interaction energy making the usual implicit assumptions (1) that the adatom electrons do not penetrate the surface (thus excluding chemisorption and tunneling phenomenology), and (2) that the adatom is far enough from the surface that the repulsive exchange effects between its electrons and those of the surface medium are small (such that the quantitative measure of the corresponding loss of indistinguishability of the two sets of electrons is negligible). On this basis, we take the nonretarded vdW energy to be due solely to Coulombic interaction of the two sets of electrons and, considering their substantial spatial separation, we treat this particular electron-electron (e-e) interaction perturbatively in a power series while retaining the full e-e interaction and concomitant correlation effects among the atomic electrons and, separately, among the surface medium electrons to include collective modes and nonlocal screening effects with the various features indicated above.

The interaction energy, E_{int}, between two systems, say a neutral helium atom and a bounded semiconductor or metal, can be written using a theorem of Gell-Mann and Low as [20]

$$E_{int}=\lim_{\epsilon\to 0}\frac{\langle\Phi_0|H_I U_\epsilon(0,-\infty)|\Phi_0\rangle}{\langle\Phi_0|U_\epsilon(0,-\infty)|\Phi_0\rangle}. \tag{2.1}$$

Here, $|\Phi_0\rangle$ is the ground state of the noninteracting system and is to be understood as a product state, i.e.,

$$|\Phi_0\rangle=|\Phi_0\rangle^a|\Phi_0\rangle^s, \tag{2.2}$$

with $|\Phi_0\rangle^a$ as the state of the atomic electrons and $|\Phi_0\rangle^s$ as the state of the electrons of the surface medium (in the absence of the mutual interaction H_I). Also, all operators that appear in Eq. (2.1), as well as states, are in the second-quantized interaction picture, referred to the atom-surface Coulomb interaction Hamiltonian H_I given as

$$H_I=\frac{1}{2}\int d\mathbf{r}_1\int d\mathbf{r}_2[\hat{\rho}^a(\mathbf{r}_1,0)V(\mathbf{r}_1-\mathbf{r}_2)\hat{\rho}^s(\mathbf{r}_2,0) + \hat{\rho}^s(\mathbf{r}_1,0)V(\mathbf{r}_1-\mathbf{r}_2)\hat{\rho}^a(\mathbf{r}_2,0)], \tag{2.3}$$

with $V(\mathbf{r}_1-\mathbf{r}_2)$ being the Coulomb interaction. The $\hat{\rho}(\mathbf{r},0)$ operators are second-quantized fermion field operators for electron density given by $\hat{\rho}(\mathbf{r},0)=\psi^\dagger(\mathbf{r},0)\psi(\mathbf{r},0)$. The time evolution operator U_ϵ, which has the property $|\Phi_0(t)\rangle=U_\epsilon(t,t_0)|\Phi_0(t_0)\rangle$, is given by the time-ordered exponential ($\epsilon\to 0$)

$$U_\epsilon(0,-\infty)=\left(\exp\left[-\frac{i}{\hbar}\int_{-\infty}^{0}dt'e^{-\epsilon|t'|}H_I(t')\right]\right)_+. \tag{2.4}$$

As indicated above, we perform a perturbative power expansion for U_ϵ in powers of H_I, the Coulomb interaction between atomic electrons and bound surface electrons, with the result to first order in H_I as

$$U_\epsilon(0,-\infty)=1-\frac{i}{\hbar}\int_{-\infty}^{0}dt'e^{-\epsilon|t'|}H_I(t'), \tag{2.5}$$

or, with Eq. (2.3), we have (suppress the "convergence factor" $e^{-\epsilon|t|}$)

$$U_\epsilon(0,-\infty) =1-\frac{i}{\hbar}\int_{-\infty}^{0}dt\int d\mathbf{r}_1\int d\mathbf{r}_2\psi^{a\dagger}(\mathbf{r}_1,t)\psi^a(\mathbf{r}_1,t) \times V(\mathbf{r}_1-\mathbf{r}_2)\psi^{s\dagger}(\mathbf{r}_2,t)\psi^s(\mathbf{r}_2,t). \tag{2.6}$$

Within the framework of this perturbation theory, the atomic electrons and bounded surface system electrons do not interact with one another, but each is subject to heavy correlations from its own electron-electron interactions. Correspondingly, the field operators of the atomic electrons and those of the surface electrons act in different subspaces of the product space of Eq. (2.2).

Considering the matrix elements of Eq. (2.1), we have from Eq. (2.6) the result

$$\langle\Phi_0|U_\epsilon(0,-\infty)|\Phi_0\rangle =\langle\Phi_0|\Phi_0\rangle-\frac{i}{\hbar}\int_{-\infty}^{0}dt\int d\mathbf{r}_1\int d\mathbf{r}_2V(\mathbf{r}_1-\mathbf{r}_2) \times\langle\Phi_0|\psi^{a\dagger}(\mathbf{r}_1,t)\psi^a(\mathbf{r}_1,t)\psi^{s\dagger}(\mathbf{r}_2,t)\psi^s(\mathbf{r}_2,t)|\Phi_0\rangle. \tag{2.7}$$

Taking $|\Phi_0\rangle^a$ as the ground state of the atom, we average over the degenerate states $|\Phi_0\rangle^s$ for a given macroscopic number and energy of the electrons of the surface system. This microcanonical ensemble average is asymptotically equivalent to the grand canonical ensemble average for the

surface electrons for large number and energy, and the associated n-particle thermodynamic Green's function definition is given by [21]

$$G_n^{i\lambda,i\tau}(\mathbf{r}_1,t_1,\ldots,\mathbf{r}_n,t_n;\mathbf{r}_1',t_1',\ldots,\mathbf{r}_n't_n') = (-i)^n\tilde{\epsilon}\langle(\psi(\mathbf{r}_1t_1)\cdots\psi(\mathbf{r}_nt_n)\psi^\dagger(\mathbf{r}_n't_n')\cdots\psi^\dagger(\mathbf{r}_1't_1'))_+\rangle, \tag{2.8}$$

where $(\cdots)_+$ denotes time ordering, $\tilde{\epsilon}$ is identically $+1$ for bosons while for fermions it is the antisymmetrical function of the time coordinates ($+1$ for an even permutation of the coordinates as shown; -1 for an odd permutation), and

$$\langle X\rangle^{i\lambda,i\tau}=\frac{\mathrm{Tr}(e^{-iN\lambda-iH\tau}X)}{\mathrm{Tr}(e^{-iN\lambda-iH\tau})}, \tag{2.9}$$

with $i\tau=\beta=1/k_BT$, $i\lambda=-\mu/k_BT$ (T is the temperature, k_B is the Boltzmann constant, and μ is the chemical potential). Tr denotes the trace whose diagonal sum extends over all states of the system with all possible numbers of particles for surface electrons (whose total number operator is N).

In this notation [Eq. (2.8)] with the further simplification for surface electrons, $G_n^{i\lambda,i\tau}\rightarrow G_n^s$, and with a similar definition for Green's functions of the atomic electrons G_n^a (averaged in the atom ground state), we have the denominator of Eq. (2.1) as

$$\langle\Phi_0|U_\epsilon(0,-\infty)|\Phi_0\rangle = 1+\frac{i}{\hbar}\int_{-\infty}^0 dt\int d\mathbf{r}_1\int d\mathbf{r}_2V(\mathbf{r}_1-\mathbf{r}_2) \times G_1^a(\mathbf{r}_1t;\mathbf{r}_1t^+)G_1^s(\mathbf{r}_2t;\mathbf{r}_2t^+). \tag{2.10}$$

The numerator of Eq. (2.1) may be described in a similar fashion except for the appearance of the two-particle Green's function G_2 as well as the G_1 function, with the result

$$\langle\Phi_0|H_IU_\epsilon(0,-\infty)|\Phi_0\rangle=-\int d\mathbf{r}_1\int d\mathbf{r}_2V(\mathbf{r}_1-\mathbf{r}_2)G_1^a(\mathbf{r}_10;\mathbf{r}_10^+)G_1^s(\mathbf{r}_20;\mathbf{r}_20^+)-\frac{i}{\hbar}\int_{-\infty}^0 dt\int d\mathbf{r}_1\int d\mathbf{r}_2\int d\mathbf{r}_3\int d\mathbf{r}_4 \times V(\mathbf{r}_1-\mathbf{r}_2)V(\mathbf{r}_3-\mathbf{r}_4)G_2^a(\mathbf{r}_10,\mathbf{r}_3t;\mathbf{r}_10^+,\mathbf{r}_3t^+)G_2^s(\mathbf{r}_20,\mathbf{r}_4t;\mathbf{r}_20^+,\mathbf{r}_4t^+). \tag{2.11}$$

To second order in the atom-surface interaction V, it is sufficient in forming $[\langle\Phi_0|U_\epsilon(0,-\infty)|\Phi_0\rangle]^{-1}$ to keep only terms linear in the Coulomb potential, which, considered jointly with Eq.(2.11), yield the result

$$E_{int}=-\int d\mathbf{r}_1\int d\mathbf{r}_2V(\mathbf{r}_1-\mathbf{r}_2)G_1^a(\mathbf{r}_10;\mathbf{r}_10^+)G_1^s(\mathbf{r}_20;\mathbf{r}_20^+)-\frac{i}{\hbar}\int_{-\infty}^0 dt\int d\mathbf{r}_1\int d\mathbf{r}_2\int d\mathbf{r}_3\int d\mathbf{r}_4V(\mathbf{r}_1-\mathbf{r}_2)V(\mathbf{r}_3-\mathbf{r}_4) \times G_2^a(\mathbf{r}_10,\mathbf{r}_3t;\mathbf{r}_10^+,\mathbf{r}_3t^+)G_2^s(\mathbf{r}_20,\mathbf{r}_4t;\mathbf{r}_20^+,\mathbf{r}_4t^+)+\frac{i}{\hbar}\int_{-\infty}^0 dt\int d\mathbf{r}_1\int d\mathbf{r}_2\int d\mathbf{r}_3\int d\mathbf{r}_4V(\mathbf{r}_1-\mathbf{r}_2)V(\mathbf{r}_3-\mathbf{r}_4) \times G_1^a(\mathbf{r}_10,\mathbf{r}_10^+)G_1^s(\mathbf{r}_20,\mathbf{r}_20^+)G_1^a(\mathbf{r}_3t,\mathbf{r}_3t^+)G_1^s(\mathbf{r}_4t,\mathbf{r}_4t^+). \tag{2.12}$$

B. First-order energy and skewing of the surface electron charge distribution from its uniform positive background

Considering the first-order energy term,

$$E_{int}^{(1)}=-\int d\mathbf{r}_1 \times\int d\mathbf{r}_2V(\mathbf{r}_1-\mathbf{r}_2)G_1^a(\mathbf{r}_10;\mathbf{r}_10^+)G_1^s(\mathbf{r}_20;\mathbf{r}_20^+), \tag{2.13}$$

we note that the Green's functions G_1^a and G_1^s involve equal space-time arguments and are thus simply related to their corresponding densities, $G_1(\mathbf{r}0,\mathbf{r}0^+)=-i\langle\hat{\rho}(\mathbf{r})\rangle\equiv-i\rho(\mathbf{r})$. Moreover, in this level of approximation they do not depend on their mutual interaction, V, so the planar geometry of the surface system dictates that $G_1^s(\mathbf{r}0,\mathbf{r}0^+)=G_1^s(z,0^+)$ and the surface electron density in the semi-infinite limit depends only on the "z" coordinate perpendicular to the surface, $\rho(z)$ (see Fig. 1).

Since the surface electrons occupy only the region $z>0$, and the atomic electrons occupy only the region $z<0$, we have (set $x-x'=X$, $y-y'=Y$ and introduce polar coordinates $dXdY=rdrd\theta$, $r=\sqrt{X^2+Y^2}$),

$$E_{int}^{(1)}=2\pi\int_{-\infty}^{+\infty}dx'\int_{-\infty}^{+\infty}dy'\int_{-\infty}^{0}dz'\int_0^{+\infty}dz \times\int_0^{+\infty}dr\,r\frac{\rho^s(z)\rho^a(\mathbf{r}')}{\sqrt{r^2+(z-z')^2}}. \tag{2.14}$$

Replacing the upper limit of r integration by R, a large constant, a straighforward integration yields

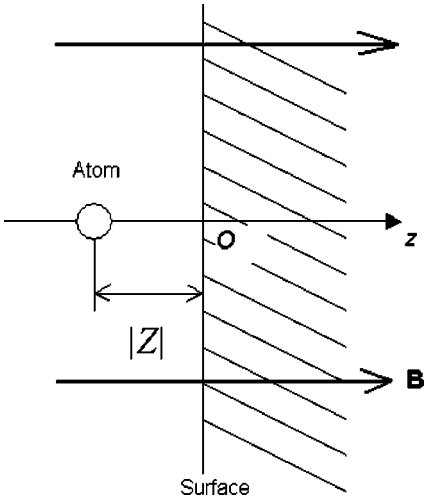

FIG. 1. Atom in the vdW interaction with semi-infinite medium at a distance $|Z|$ from its surface, with a magnetic field **B** normal to the surface.

$$\int_0^R dr\, r \frac{\rho^s(z)\rho^a(\mathbf{r}')}{\sqrt{r^2+(z-z')^2}} = \rho^s(z)\rho^a(\mathbf{r}')[\sqrt{R^2+(z-z')^2}-|z-z'|] \simeq \rho^s(z)\rho^a(\mathbf{r}')R, \tag{2.15}$$

and in the planar limit ($R\to\infty$) we have

$$E_{int}^{(1)} = 2\pi R \int_{-\infty}^{+\infty} dx' \int_{-\infty}^{+\infty} dy' \int_{-\infty}^{0} dz' \rho^a(\mathbf{r}') \times \int_0^{+\infty} dz \rho^s(z) = \frac{2}{R} Q^a Q^s = 0, \tag{2.16}$$

where Q^s is the total charge of the surface system, which vanishes by its neutrality, and Q^a is the total charge of the atom, which also vanishes by neutrality. Moreover, even if Q^s and Q^a represented systems having a net charge, $E_{int}^{(1)}$ would still vanish in the planar limit $R\to\infty$ because of the prefactor $2/R$. This result is to be expected by Gauss's law for the planar surface system, which precludes the existence of a nonzero electric field in the vicinity of the atom, $z'<0$, so no work can be done and no electrostatic energy can be formed (in first order).

Notwithstanding the null result, $E_{int}^{(1)}=0$, we can learn more about the system by analyzing the density integrals. The requisite thermodynamic Green's function for the surface electron system can be constructed in the case of a magnetic field normal to the interface, using a thermodynamic Schrödinger image Green's function to simulate a boundary condition of specular reflection with $G_1(\cdots)$ vanishing at $z=0$, such that for $z>0$ $[\mathbf{r}=(\overline{\mathbf{r}},z)=(x,y,z)]$

$$G_1(\mathbf{r},\mathbf{r}';T) = G_1^{\infty}(\overline{\mathbf{r}},z;\overline{\mathbf{r}}',z',T) - G_1^{\infty}(\overline{\mathbf{r}},z;\overline{\mathbf{r}}',-z',T), \tag{2.17}$$

wherein we take the surface barrier potential to be infinitely high. Here, $G_1^{\infty}(\mathbf{r},\mathbf{r}';T)$ is the infinite-space one-electron thermodynamic Schrödinger Green's function in the presence of a magnetic field in the z direction, which has been determined as [22] ($T=t-t'$; **B** is the magnetic field; ω_c is the cyclotron frequency; μ_0 is the Bohr magneton; σ_3 is the Pauli spin matrix no. 3; $\mathbf{R}=\mathbf{r}-\mathbf{r}'$; $f_0(\omega)$ is the Fermi function; μ is the chemical potential; β is inverse thermal energy; m is the mass)

$$\begin{pmatrix} G_{1>}^{\infty}(\mathbf{r},\mathbf{r}',T) \\ G_{1<}^{\infty}(\mathbf{r},\mathbf{r}',T) \end{pmatrix} = e^{i\mu T} C(\mathbf{r},\mathbf{r}') \int \frac{d\omega}{2\pi} e^{-i\omega T} \begin{pmatrix} -i[1-f_0(\omega)] \\ i f_0(\omega) \end{pmatrix} \int_{-\infty}^{\infty} dT' e^{i\omega T'} \int \frac{d\mathbf{p}}{(2\pi)^3} e^{i\mathbf{p}\cdot\mathbf{R}} \exp\left[-i\left(\mu_0 B\sigma_3 + \frac{p_z^2}{2m}\right)T'\right] \times \sec\left(\frac{\omega_c T'}{2}\right) \exp\left[-i\frac{p_x^2+p_y^2}{m\omega_c}\tan\left(\frac{\omega_c T'}{2}\right)\right], \tag{2.18}$$

where $C(\mathbf{r},\mathbf{r}')=\exp\{i[e\mathbf{r}\cdot\mathbf{B}\times\mathbf{r}'/2-\phi(\mathbf{r})+\phi(\mathbf{r}')]\}$ with $\phi(\mathbf{r})$ as an arbitrary gauge function, and we take the Landau level separation and spin splitting to be the same. Carrying out the **p** integrations of Eq. (2.18), taking the spin-space trace and setting $\mathbf{r}=\mathbf{r}'$, $t-t'=T=0$ in $G_{1<}^{\infty}$ to construct the electron contribution to $\rho^s(z)$, the uniform background density $\rho_{Back}(z>0)$ is added to ensure charge neutrality, with the result

$$\rho^s(z) = \rho_{back} + \left(\frac{m}{2\pi}\right)^{3/2} \hbar\omega_c \int_0^{\infty} \frac{d\omega}{\hbar^3} f_0(\omega) \times \int_{-i\infty+\delta}^{i\infty+\delta} \frac{ds}{2\pi i} \frac{e^{s\omega}}{s^{1/2}} \coth\left(\frac{\hbar\omega_c s}{2}\right) \times [1-e^{-2mz^2/\hbar^2 s}] \quad (z>0). \tag{2.19}$$

Deep in the medium, $z\to\infty$, the bulk electron density ρ_{bulk} is properly identified as

$$\rho_{bulk}(z)=\left(\frac{m}{2\pi}\right)^{3/2}\hbar\omega_c\int_0^\infty\frac{d\omega}{\hbar^3}f_0(\omega)\times\int_{-i\infty+\delta}^{i\infty+\delta}\frac{ds}{2\pi i}\frac{e^{s\omega}}{s^{1/2}}\coth\left(\frac{\hbar\omega_c s}{2}\right). \quad (2.20)$$

As a result of forcing the electron Green's function and charge density to vanish at $z=0$ [Eq. (2.19)], it is clear that the electron and background charge distributions are skewed, with an offset in their z termination points required to assure overall charge neutrality. This is readily seen by integrating Eq. (2.19) with respect to volume (half-space $z>0$). The result, setting the total charge to zero for neutrality, is given by ($\mathcal{A}$ is area)

$$\rho_{Back}V_0+\rho_{bulk}V+\mathcal{A}\left(\frac{m}{2\pi}\right)^{3/2}\hbar\omega_c\left(\frac{\hbar^2\pi}{8m}\right)^{1/2}\int_0^\infty\frac{d\omega}{\hbar^3}f_0(\omega)\times\int_{-i\infty+\delta}^{i\infty+\delta}\frac{ds}{2\pi i}e^{s\omega}\coth\left(\frac{\hbar\omega_c s}{2}\right)=0. \quad (2.21)$$

The z integral is a Gaussian. This facilitates identification of the offset, $z_0\equiv|V_0-V|/\mathcal{A}$, as

$$z_0=\frac{1}{\rho_{bulk}}\left(\frac{m}{2\pi}\right)^{3/2}\hbar\omega_c\left(\frac{\hbar^2\pi}{8m}\right)^{1/2}\int_0^\infty\frac{d\omega}{\hbar^3}f_0(\omega)\times\int_{-i\infty+\delta}^{i\infty+\delta}\frac{ds}{2\pi i}e^{s\omega}\coth\left(\frac{\hbar\omega_c s}{2}\right). \quad (2.22)$$

It should be noted that an effective area density of electrons, ρ_{area}, can be defined as the coefficient of the term proportional to $\mathcal{A}$ on the left hand side of Eq. (2.21), such that

$$\rho_{area}=z_0\rho_{bulk}=\left(\frac{m}{2\pi}\right)^{3/2}\hbar\omega_c\left(\frac{\hbar^2\pi}{8m}\right)^{1/2}\times\int_0^\infty\frac{d\omega}{\hbar^3}f_0(\omega)\int_{-i\infty+\delta}^{i\infty+\delta}\frac{ds}{2\pi i}e^{s\omega}\coth\left(\frac{\hbar\omega_c s}{2}\right). \quad (2.23)$$

In the nondegenerate limit $f_0(\omega)=e^{\mu\beta-\omega\beta}$, the ω and s integrations are Laplace transform and inverse. One then immediately obtains

$$z_0=\left(\frac{\hbar^2\pi\beta}{8m}\right)^{1/2}, \quad (2.24)$$

where

$$\rho_{bulk}=\frac{e^{\mu\beta}}{\hbar^3}\left(\frac{m}{2\pi}\right)^{3/2}\frac{\hbar\omega_c}{\beta^{1/2}\tanh(\beta\hbar\omega_c/2)} \quad (2.25)$$

has been used. Note that the corresponding ρ_{area} for the nondegenerate case is given by

$$\rho_{area}=\frac{e^{\mu\beta}\hbar\omega_c m}{8\pi\hbar^2\tanh(\beta\hbar\omega_c/2)}. \quad (2.26)$$

A general evaluation of z_0 [Eq. (2.22)] and ρ_{area} [Eq. (2.23)] for arbitrary statistical regime can be carried out using the expansion

$$\coth\left(\frac{\hbar\omega_c s}{2}\right)=\sum_{\pm}\sum_{r=0}^{\infty}\exp([\pm1-1-2r]\hbar\omega_c s/2), \quad (2.27)$$

which yields

$$\int_{-i\infty+\delta}^{i\infty+\delta}\frac{ds}{2\pi i}e^{s\omega}\coth(\hbar\omega_c s/2)=\sum_{\pm}\sum_{r=0}^{\infty}\delta(\omega+[\pm1-1-2r]\hbar\omega_c/2), \quad (2.28)$$

and, consequently,

$$z_0=\frac{1}{\rho_{bulk}}\left(\frac{m}{2\pi}\right)^{3/2}\left(\frac{\hbar^2\pi}{8m}\right)^{1/2}\frac{\hbar\omega_c}{\hbar^3}\times\sum_{\pm}\sum_{r=0}^{\infty}f_0([\mp1+1+2r]\hbar\omega_c/2), \quad (2.29)$$

with

$$\rho_{area}=\left(\frac{m}{2\pi}\right)^{3/2}\left(\frac{\hbar^2\pi}{8m}\right)^{1/2}\frac{\hbar\omega_c}{\hbar^3}\times\sum_{\pm}\sum_{r=0}^{\infty}f_0([\mp1+1+2r]\hbar\omega_c/2). \quad (2.30)$$

In the degenerate zero-temperature limit [$\eta_+(x)$ is the Heaviside unit step function],

$$\sum_{\pm}\sum_{r=0}^{\infty}f_0([\mp1+1+2r]\hbar\omega_c/2)=\sum_{\pm}\sum_{r=0}^{\infty}\eta_+(\mu-[\mp1+1+2r]\hbar\omega_c/2)=1+2\left[\frac{\mu}{\hbar\omega_c}\right]_{maxI}, \quad (2.31)$$

where $[x]_{maxI}$ is the maximum integer less than or equal to x. This ''staircase'' function is depicted in Fig. 2. Using the identity

$$[x]_{maxI}=x-1/2+[1/2-x]_{per}, \quad (2.32)$$

it can be reexpressed in terms of the periodic linear sawtooth function $[1/2-x]_{per}$, shown in Fig. 3, with a semiclassical average of $(x-1/2)$. The function $[1/2-\mu/\hbar\omega_c]_{per}$ is periodic in the de Haas–van Alphen sense and can be written in terms of oscillatory exponentials as

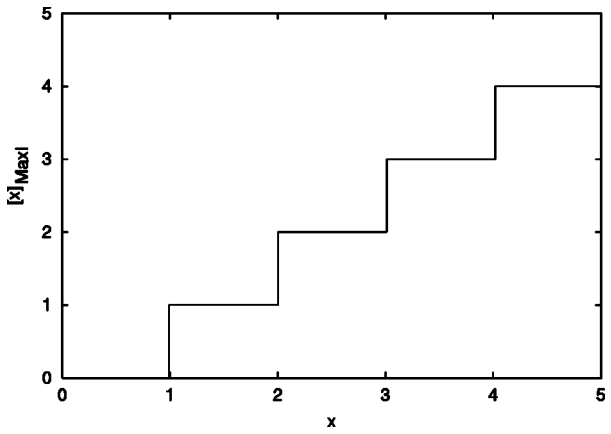

FIG. 2. The ''staircase'' maximum integer function.

$$\left[\frac{1}{2}-\frac{\mu}{\hbar\omega_c}\right]_{per}=\frac{1}{\hbar\omega_c}\sum_{n\neq 0}^{\infty}\frac{e^{i2\pi n\mu/\hbar\omega_c}}{i2\pi n/\hbar\omega_c} \tag{2.33}$$

to exhibit its spectral constitution. These results, Eqs. (2.31)–(2.33), provide explicit quantum magnetic field oscillations in the structure of z_0 and ρ_{area} [Eqs. (2.29),(2.30)]. The zero-field limit, given by (p_F is the Fermi wave number)

$$z_0=\frac{1}{\rho_{bulk}}\frac{\mu}{\hbar^3}\frac{\hbar m}{8\pi}=\frac{3\pi\hbar}{8p_F}, \tag{2.34}$$

is in agreement with earlier results of Huntington [23] in the absence of a magnetic field. Finally, the quantum strong field limit, in which $\hbar\omega_c\sim\mu$, may be obtained for z_0 and ρ_{area} by neglecting all terms on the right hand sides of Eqs. (2.29) and (2.30) except for the leading terms, since the remaining terms represent relatively very lightly populated contributions.

III. THE ROLE OF SURFACE PLASMA DIELECTRIC RESPONSE PROPERTIES IN SECOND-ORDER van der WAALS ENERGY

A. The effective potential in second-order perturbation theory and dynamic, nonlocal imaging for a planar surface

We now consider the second-order terms $E_{int}^{(2)}$ in the van der Waals energy expression (2.12) and examine their interpretation in terms of the dynamic, nonlocal, and inhomogeneous inverse dielectric function $K(1,2)$ of the bounded solid-state plasma. The defining equation for $K(1,2)$ is given as ($1=\mathbf{r}_1,t_1$, etc.)

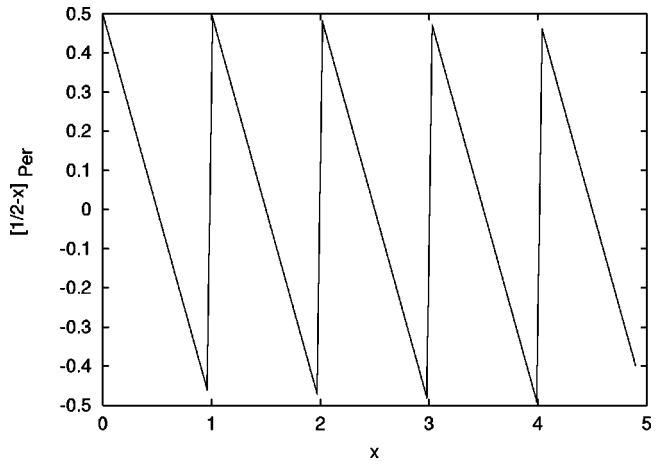

FIG. 3. The periodic linear sawtooth function.

$$K(1,2)=\frac{\delta V_{eff}(1)}{\delta U(2)},$$

$$V_{eff}(1)=\int d^{(4)}2K(1,2)U(2), \tag{3.1}$$

which states that $K(1,2)$ linearly relates the effective potential $V_{eff}(1)$ with an impressed potential $U(2)$. This linear response function for the surface medium and its equilibrium two-particle Green's function G_2^s are related as

$$K(1,2)=\delta^{(4)}(1-2)+i\int V(1-3)[G_2^s(2,3;2^+,3^+)-G_1^s(2,2^+)G_1^s(3,3^+)]d^{(4)}3. \tag{3.2}$$

Employing this equation to replace $\int VG_2^s$ in terms of $K(1,2)$ in Eq. (2.12), we obtain,

$$E_{int}^{(2)}=-\frac{1}{\hbar}\int_{-\infty}^{0}dt\int d\mathbf{r}_1\int d\mathbf{r}_2\int d\mathbf{r}_3V(\mathbf{r}_1-\mathbf{r}_2)G_2^a(\mathbf{r}_1 0,\mathbf{r}_3 t;\mathbf{r}_1 0^+,\mathbf{r}_3 t^+)K(\mathbf{r}_3 t,\mathbf{r}_2 0)+\frac{1}{\hbar}\int_{-\infty}^{0}dt\int d\mathbf{r}_1\int d\mathbf{r}_2\int d\mathbf{r}_3$$
$$\times V(\mathbf{r}_1-\mathbf{r}_2)\delta(\mathbf{r}_3-\mathbf{r}_2)\delta(t)G_2^a(\mathbf{r}_1 0,\mathbf{r}_3 t;\mathbf{r}_1 0^+,\mathbf{r}_3 t^+)-\frac{i}{\hbar}\int_{-\infty}^{0}dt\int d\mathbf{r}_1\int d\mathbf{r}_2\int d\mathbf{r}_3\int d\mathbf{r}_4V(\mathbf{r}_1-\mathbf{r}_2)V(\mathbf{r}_3-\mathbf{r}_4)$$
$$\times G_2^a(\mathbf{r}_1 0,\mathbf{r}_3 t;\mathbf{r}_1 0^+,\mathbf{r}_3 t^+)G_1^s(\mathbf{r}_2 0,\mathbf{r}_2 0^+)G_1^s(\mathbf{r}_4 t,\mathbf{r}_4 t^+)+\frac{i}{\hbar}\int_{-\infty}^{0}dt\int d\mathbf{r}_1\int d\mathbf{r}_2\int d\mathbf{r}_3\int d\mathbf{r}_4V(\mathbf{r}_1-\mathbf{r}_2)V(\mathbf{r}_3-\mathbf{r}_4)$$
$$\times G_1^a(\mathbf{r}_1 0,\mathbf{r}_1 0^+)G_1^s(\mathbf{r}_2 0,\mathbf{r}_2 0^+)G_1^a(\mathbf{r}_3 t,\mathbf{r}_3 t^+)G_1^s(\mathbf{r}_4 t,\mathbf{r}_4 t^+). \tag{3.3}$$

Recalling the first-order energy $E^{(1)}$ as given by Eq. (2.13), we note that the last term of Eq. (3.3) involving "$G_1^a G_1^a G_1^s G_1^s$" vanishes by Eq. (2.16), since

$$\frac{i}{\hbar}\int_{-\infty}^{0} dt \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 \int d\mathbf{r}_4 V(\mathbf{r}_1-\mathbf{r}_2)V(\mathbf{r}_3-\mathbf{r}_4)G_1^a(\mathbf{r}_1 0,\mathbf{r}_1 0^+)G_1^a(\mathbf{r}_3 t,\mathbf{r}_3 t^+)G_1^s(\mathbf{r}_2 0,\mathbf{r}_2 0^+)G_1^s(\mathbf{r}_4 t,\mathbf{r}_4 t^+)$$

$$= \frac{i}{\hbar}\int_{-\infty}^{0} dt E^{(1)}E^{(1)} = 0, \tag{3.4}$$

where we have used the fact that $G_1^{a,s}(\mathbf{r}_1,t;\mathbf{r},t^+)=G_1^{a,s}(\mathbf{r}_1,0;\mathbf{r},0^+)$. Finally, considering the third term of Eq. (3.3) involving "$G_2^a G_1^s G_1^s$," we observe that

$$G_1^s(\mathbf{r},t;\mathbf{r},t^+)=G_1^s(\mathbf{r},0;\mathbf{r},0^+)=-i\rho^s(z), \tag{3.5}$$

since the density for the surface electrons depends only on the z coordinate perpendicular to the surface. Therefore, the "$G_2^a G_1^s G_1^s$" term takes the form

$$-\frac{i}{\hbar}\int_{-\infty}^{0} dt \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 \int d\mathbf{r}_4 V(\mathbf{r}_1-\mathbf{r}_2)V(\mathbf{r}_3-\mathbf{r}_4)G_2^a(\mathbf{r}_1 0,\mathbf{r}_3 t;\mathbf{r}_1 0^+,\mathbf{r}_3 t^+)G_1^s(\mathbf{r}_2 0,\mathbf{r}_2 0^+)G_1^s(\mathbf{r}_4 t,\mathbf{r}_4 t^+)$$

$$= \frac{i}{\hbar}\int_{-\infty}^{0} dt \int dz_1 \int dz_2 \int dz_3 \int dz_4 \rho^s(z_2)\rho^s(z_4) \int d\bar{\mathbf{r}}_1 \int d\bar{\mathbf{r}}_2 \int d\bar{\mathbf{r}}_3 \int d\bar{\mathbf{r}}_4 V(|\bar{\mathbf{r}}_1-\bar{\mathbf{r}}_2|,z_1-z_2)$$

$$\times V(|\bar{\mathbf{r}}_3-\bar{\mathbf{r}}_4|,z_3-z_4)G_2^a(\mathbf{r}_1 0,\mathbf{r}_3 t;\mathbf{r}_1 0^+,\mathbf{r}_3 t^+). \tag{3.6}$$

Changing variable in the translationally invariant $\bar{\mathbf{r}}=(x,y)$ plane of the surface,

$$\bar{\mathbf{R}}_2=\bar{\mathbf{r}}_2-\bar{\mathbf{r}}_1, \quad \bar{\mathbf{R}}_4=\bar{\mathbf{r}}_4-\bar{\mathbf{r}}_3, \tag{3.7}$$

we note that as a consequence of the fact that $\rho^s(z)$ has no dependence on $\bar{\mathbf{r}}$, we have

$$\int d\bar{\mathbf{r}}_1 \int d\bar{\mathbf{r}}_2 \int d\bar{\mathbf{r}}_3 \int d\bar{\mathbf{r}}_4 \times V(|\bar{\mathbf{r}}_1-\bar{\mathbf{r}}_2|,z_1-z_2)V(|\bar{\mathbf{r}}_3-\bar{\mathbf{r}}_4|,z_3-z_4) \times G_2^a(\mathbf{r}_1 0,\mathbf{r}_3 t;\mathbf{r}_1 0^+,\mathbf{r}_3 t^+)$$

$$= \int d\bar{\mathbf{r}}_1 \int d\bar{\mathbf{r}}_3 \int d\bar{\mathbf{R}}_2 \int d\bar{\mathbf{R}}_4 \times V(|\bar{\mathbf{R}}_2|,z_1-z_2)V(|\bar{\mathbf{R}}_4|,z_3-z_4) \times G_2^a(\mathbf{r}_1 0,\mathbf{r}_3 t;\mathbf{r}_1 0^+,\mathbf{r}_3 t^+). \tag{3.8}$$

The $\bar{\mathbf{R}}$ integrals involved here may be viewed as the limit of the two-dimensional space Fourier transform of the Coulomb potential, so that

$$\int \frac{d^2\bar{\mathbf{R}}}{(2\pi)^2} V(|\bar{\mathbf{R}}|,z_1-z_2)$$

$$= \lim_{\bar{\mathbf{q}}\to 0}\int \frac{d^2\bar{\mathbf{R}}}{(2\pi)^2} e^{i\bar{\mathbf{q}}\cdot\bar{\mathbf{R}}}V(|\bar{\mathbf{R}}|,z_1-z_2)$$

$$= \lim_{\bar{\mathbf{q}}\to 0}\frac{2\pi}{\bar{q}} e^{-\bar{q}|z_1-z_2|} = C, \tag{3.9}$$

where C is a large constant independent of z_1,z_2 (apparently infinite, but limited by the cross-sectional area). Therefore,

$$\int d\bar{\mathbf{r}}_1 \int d\bar{\mathbf{r}}_2 \int d\bar{\mathbf{r}}_3 \int d\bar{\mathbf{r}}_4 VVG_2^a = (2\pi)^4 C^2 \int d\bar{\mathbf{r}}_1 \int d\bar{\mathbf{r}}_3 G_2^a(\mathbf{r}_1 0,\mathbf{r}_3 t;\mathbf{r}_1 0^+,\mathbf{r}_3 t^+), \tag{3.10}$$

and we obtain

$$-\frac{i}{\hbar}\int_{-\infty}^{0} dt \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 \int d\mathbf{r}_4 VVG_2^a G_1^s G_1^s$$

$$= \frac{i}{\hbar}(2\pi)^4 C^2 \int_{-\infty}^{0} dt \int dz_2 \int dz_4 \rho^s(z_2)\rho^s(z_4) \times \int d\bar{\mathbf{r}}_1 \int d\bar{\mathbf{r}}_3 G_2^a(\mathbf{r}_1 0,\mathbf{r}_3 t;\mathbf{r}_1 0^+,\mathbf{r}_3 t^+)$$

$$= \frac{i}{\hbar}(2\pi)^4 \frac{(CQ^s)^2}{A^2}\langle \hat{Q}^a(0)\hat{Q}^a(t)\rangle = 0, \tag{3.11}$$

where we again note that $\int dz \rho^s(z) = Q^s/A = 0$ is the total charge (per unit area) of the surface medium, and we have introduced the total atomic charge operator $\hat{Q}^a$ in the ground-state average of the atom defining G_2^a, which also vanishes for a neutral atom.

We are thus left with only the first terms of Eq. (3.3) as contributors to the vdW energy. They may be written together as

$$E_{int}^{(2)} = -\frac{1}{\hbar}\int_{-\infty}^{0} dt \int d\mathbf{r}_1 \int d\mathbf{r}_2 \int d\mathbf{r}_3 \times G_2^a(\mathbf{r}_1 0, \mathbf{r}_3 t; \mathbf{r}_1 0^+, \mathbf{r}_3 t^+) \times [K(\mathbf{r}_3 t, \mathbf{r}_2 0) - \delta(\mathbf{r}_3 - \mathbf{r}_2)\delta(t)] V(\mathbf{r}_2 - \mathbf{r}_1). \tag{3.12}$$

Bearing in mind Eq. (3.1), we can relate the inverse dielectric function $K(\mathbf{r}_3 t; \mathbf{r}_2 0)$ to the effective potential due to a Coulumb center at $\mathbf{r}_1$. Replacing the impressed potential $U(2)$ by the Coulumb potential $V(2-1)$, the effective potential $V_{eff}(3) \to V_{eff}(3,1)$ is given by

$$V_{eff}(3,1) = \int d(2) K(3,2) V(2-1) = \int d\mathbf{r}_2 K(\mathbf{r}_3 t_3; \mathbf{r}_2 t_1) V(\mathbf{r}_2 - \mathbf{r}_1) \tag{3.13}$$

with

$$U(2) = V(2-1) = V(\mathbf{r}_2 - \mathbf{r}_1)\delta(t_2 - t_1). \tag{3.14}$$

Hence, we may rewrite Eq. (3.3) as

$$E_{int}^{(2)} = -\frac{1}{\hbar}\int_{-\infty}^{0} dt \int d\mathbf{r}_1 \int d\mathbf{r}_3 G_2^a(\mathbf{r}_1 0, \mathbf{r}_3 t; \mathbf{r}_1 0^+, \mathbf{r}_3 t^+) \times [V_{eff}(\mathbf{r}_3 t, \mathbf{r}_1 0) - V(\mathbf{r}_3 - \mathbf{r}_1)\delta(t)]. \tag{3.15}$$

In Eq. (3.15), the last term in the square brackets on the right represents the role of direct Coulomb interaction between two atomic electrons. While this is an important part of the electronic energy of the atom, including correlations, it is not involved in atom-surface interaction. It is therefore quite appropriate that this term appears as a subtraction from the total effective interaction V_{eff} between atomic electrons. The remainder (the whole bracket) is that part of the interaction between two atomic electrons that is generated by polarization of the electrons of the surface system; that is, in fact, the image contribution (which carries information about correlation among the surface electrons) to be denoted by V_{img}, so $E_{int}^{(2)}$ may be written as

$$\begin{aligned} E_{int}^{(2)} &= -\frac{1}{\hbar}\int_{-\infty}^{0} dt \int d\mathbf{r}_1 \int d\mathbf{r}_3 G_2^a(\mathbf{r}_1 0, \mathbf{r}_3 t; \mathbf{r}_1 0^+, \mathbf{r}_3 t^+) \times V_{img}(\mathbf{r}_3 t, \mathbf{r}_1 0) \\ &= -\frac{1}{\hbar}\int_{-\infty}^{0} dt \int d\mathbf{r}_1 \int d\mathbf{r}_3 G_2^a(\mathbf{r}_1 0, \mathbf{r}_3 t; \mathbf{r}_1 0^+, \mathbf{r}_3 t^+) \times \int \frac{d\omega}{2\pi} e^{-i\omega t} \int \frac{d\overline{\mathbf{p}}}{(2\pi)^2} e^{i\overline{\mathbf{p}}\cdot(\overline{\mathbf{r}_3} - \overline{\mathbf{r}_1})} V_{img}(z_3, z_1; \overline{\mathbf{p}}, \omega), \end{aligned} \tag{3.16}$$

where, in the last line of Eq. (3.16), we have Fourier transformed V_{img} using space-translational invariance in the lateral plane of the surface, as well as time-translational invariance. In Eq. (3.16), we have a general interpretation of $E_{int}^{(2)}$ as given by the image part of the interaction of two electrons of the atom; thus it is a correlation or self-energy of the atomic electrons mediated by the image potential arising from the surface system polarization (without the direct Coulomb interaction of the atomic electrons). Of course, this image potential of the surface system is dynamic, nonlocal, and inhomogeneous.

The determination of the effective potential (and hence the image potential) attracted much attention in connection with the theory of surface collective modes [24]. Even the case of a sharp surface with an infinite potential barrier introduced quantum phenomenology into electrostatics, such as the vanishing of wave function and density at an infinite barrier boundary with a spatial Friedel oscillation increasing to the bulk value in the interior (with associated Landau quantization effects in the presence of a magnetic field). A detailed analysis of the deviation of dielectric response properties from their bulk values near the surface due to such quantum effects and its impact on V_{eff} and V_{img} was carried out in the absence of a magnetic field by Newns [25] and it was later done in the presence of a magnetic field by Horing and Yildiz [26]. However, the deviation from bulk dielectric properties occurs only over a small region near the surface, of the order of an inverse Fermi wave number, and we can therefore neglect much of the associated detail and gain considerable insight by assuming that the bulk dielectric properties extend up to the bounding surface (including their bulk quantum and magnetic field effects). In this connection, we employ a Green's function joining method of Inglesfield [27] and Garcia Moliner *et al.* [28] applied to $V_{eff}(z_1, z_2) \equiv \mathcal{G}(z_1, z_2)$ (suppressing $\overline{\mathbf{p}}, \omega$) as the Green's function of the Poisson equation in the presence of the semi-infinite surface electron system, $z_1, z_2 > 0$ [with its nonlocal, dynamic bulk dielectric function $\varepsilon(\mathbf{p}, \omega)$ extended up to the surface from within the metal/semiconductor] and the atom outside, $z_1, z_2 < 0$ (with its unit vacuum dielectric constant extended up to the surface from the outside). Denoting the surface electron region by B ($z > 0$), and the vacuum region of the atom outside by A ($z < 0$), the effective potential $V_{eff}(z', z'')$ experienced by atom electrons in A is determined by this method in terms of $\mathcal{G}_A(z', z'')$ and $\mathcal{G}_B(z', z'')$, the dynamically, nonlocally screened Coulomb interaction potentials of

regions A and B alone, respectively (with unit point charges at z'' and field points at z'). The corresponding components of the electric displacement field are given by $D_{\{A,B\}}(z',z'')=-\int dz'''\varepsilon_{\{A,B\}}(z',z''')\partial\mathcal{G}_{\{A,B\}}(z''',z'')/\partial z'''$.

Requiring continuity of $\mathcal{G}(z',z'')$ and of $D(z',z'')$ at the interface of regions A and B $(z=0)$, the result for $V_{eff}(z',z'')$ (suppressing the lateral wave vector $\overline{\mathbf{p}}$ and ω) is given by (region A)

$$V_{eff}(z',z'')=\mathcal{G}_A(z',z'')+\frac{1}{4\pi}[\mathcal{G}(0,z'')D_A(0,z') - \mathcal{G}_A(z',0)D(0,z'')], \tag{3.17}$$

where the factors on the right of Eq. (3.17) are given by

$$\mathcal{G}(0,z'')=\frac{\mathcal{G}_B(0,0)\mathcal{G}_A(0,z'')}{\mathcal{G}_A(0,0)+\mathcal{G}_B(0,0)} \tag{3.18}$$

and (further details may be found in Ref. [29])

$$D(0,z'')=\frac{4\pi\mathcal{G}_A(0,z'')}{\mathcal{G}_A(0,0)+\mathcal{G}_B(0,0)}. \tag{3.19}$$

We distinguish the infinite space Green's function for region A, $\mathcal{G}_A^\infty$, from $\mathcal{G}_A$, as they can differ by a boundary condition. In particular, for convenience, we employ a subsidiary image in this respect to force vanishing of $D_A(0,z'')$ at the interface. Correspondingly,

$$\mathcal{G}_A(z',z'')=\mathcal{G}_A^\infty(z'-z'')+\mathcal{G}_A^\infty(z'+z''),$$

$$\mathcal{G}_A^\infty(z'-z'')=\frac{2\pi}{\overline{p}}e^{-\overline{p}|z'-z''|}, \tag{3.20}$$

with $D_A(z',z'')=-\partial\mathcal{G}_A(z',z'')/\partial z'$ since region A is local (vacuum). Furthermore, for the surface electron dielectric region B, we have similar relations for $\mathcal{G}_B(z',z'')$ and $D_B(z',z'')$ involving denominator factors of $\varepsilon_B(\overline{\mathbf{p}},\omega)$ with a similar subsidiary image. In particular,

$$\mathcal{G}_A(0,0)=\frac{4\pi}{\overline{p}}$$

and

$$\mathcal{G}_B(0,0)=4\int_{-\infty}^{\infty}dp_z\frac{1}{(p_z^2+\overline{p}^2)\varepsilon_B(\mathbf{p},\omega)}=\frac{4\pi}{\overline{p}}\varepsilon_{\overline{p}}^{-1}(\omega), \tag{3.21}$$

since our choice of subsidiary image doubles $\mathcal{G}_{\{A,B\}}(0,z'')$ at the interface $z'=0$. The last part of Eq. (3.21) on the right defines the "surface dielectric function" $\varepsilon_{\overline{p}}(\omega)$ for the semi-infinite region B. Finally, noting that the image potential is given by $V_{img}(z',z'')=V_{eff}(z',z'')-\mathcal{G}_A^\infty(z',z'')$, we have

$$V_{img}(z',z'';\overline{\mathbf{p}},\omega) = -\frac{2\pi}{\overline{p}}\exp[-\overline{p}(|z'|+|z''|)]\frac{\varepsilon_{\overline{p}}(\omega)-1}{\varepsilon_{\overline{p}}(\omega)+1}, \tag{3.22}$$

which is well known in the local limit.

B. Multipole expansion and nonlocality

Considering G_2^a of Eq. (3.16) written in terms of the atomic electron density operator $\hat{\rho}^a$ and its matrix elements between the atom's electronic energy eigenstates, $H_a|\Phi_n^a\rangle=E_n^a|\Phi_n^a\rangle$, which include internal correlations due to intra-atomic-electron interactions, we have

$$G_2^a(\mathbf{r}''t'',\mathbf{r}'t';\mathbf{r}''t''^+,\mathbf{r}'t'^+) = {\sum_n}' \langle\hat{\rho}^a(\mathbf{r}'')\rangle_{0n}\langle\hat{\rho}^a(\mathbf{r}')\rangle_{n0}e^{i\omega_{n0}^a(t'-t'')}, \tag{3.23}$$

where $\langle\Phi_0^a|\hat{\rho}^a(\mathbf{r}'',t'')|\Phi_n^a\rangle=\langle\hat{\rho}^a(\mathbf{r}'')\rangle_{0n}$ and $\omega_{n0}^a=E_n^a-E_0^a$. (The prime on Σ' indicates that the $n=0$ term is excluded since it has no time dependence and yields a constant, static contribution, which is irrelevant to the van der Waals interaction.) Substitution of this into Eq. (3.16) (first equality) yields $E_{int}^{(2)}$ in terms of the Fourier time transform of $V_{img}(t'-t'')\to V_{img}(\omega)$ as

$$E_{int}^{(2)}=\frac{1}{\hbar}\int d\mathbf{r}'\int d\mathbf{r}''\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}V_{img}(\mathbf{r}',\mathbf{r}'';\omega) \times{\sum_n}'\frac{\langle\hat{\rho}^a(\mathbf{r}'')\rangle_{0n}\langle\hat{\rho}^a(\mathbf{r}')\rangle_{n0}}{\omega-\omega_{n0}^a}, \tag{3.24}$$

where we have recalled the "convergence factor" $e^{-\epsilon|t|}$ of Eq. (2.4) in performing the time integration. Considering spatial translational invariance [Eq.(3.16)] in the $\overline{\mathbf{r}}=(x,y)\to\overline{\mathbf{p}}$ (lateral) plane and using Eq. (3.22) for $V_{img}(z',z'';\overline{\mathbf{p}},\omega)$, we obtain

$$E_{int}^{(2)}=\frac{1}{\hbar}\int\frac{d\overline{\mathbf{p}}}{(2\pi)^2}\int d\mathbf{r}'\int d\mathbf{r}'' \times\int_{-\infty}^{\infty}\frac{d\omega}{2\pi i}e^{i\overline{\mathbf{p}}\cdot(\overline{\mathbf{r}}'-\overline{\mathbf{r}}'')}\frac{2\pi}{\overline{p}}e^{-\overline{p}(|z'|+|z''|)} \times\frac{\varepsilon_{\overline{p}}(\omega)-1}{\varepsilon_{\overline{p}}(\omega)+1}{\sum_n}'\frac{\langle\hat{\rho}^a(\mathbf{r}'')\rangle_{0n}\langle\hat{\rho}^a(\mathbf{r}')\rangle_{n0}}{\omega-\omega_{n0}^a}. \tag{3.25}$$

It is important to note that nonlocality of the surface plasma changes the character of a "standard" multipole expansion of $E_{int}^{(2)}$, such that it no longer has a term by term correspondence with a series in inverse powers of the separation of the center of the atom, Z, from an origin of coordi-

nates located on the surface. Denoting the lateral coordinate of the atom center by $\overline{\mathbf{R}}$, we have

$$\overline{\mathbf{r}'}=\overline{\mathbf{R}}+\Delta\overline{\mathbf{r}'},\quad \overline{\mathbf{r}''}=\overline{\mathbf{R}}+\Delta\overline{\mathbf{r}''},$$
$$z'=Z+\Delta z',\quad z''=Z+\Delta z'', \tag{3.26}$$

and

$$e^{i\overline{\mathbf{p}}\cdot(\overline{\mathbf{r}'}-\overline{\mathbf{r}''})}e^{-\overline{p}(|z'|+|z''|)}=e^{-2\overline{p}|Z|}e^{-\overline{p}(|\Delta z'|+|\Delta z''|)}e^{i\overline{\mathbf{p}}\cdot(\Delta\overline{\mathbf{r}'}-\Delta\overline{\mathbf{r}''})}, \tag{3.27}$$

from which a multipole expansion may be undertaken by expanding the exponentials in powers of $\Delta\overline{\mathbf{r}}$ and Δz. The leading term involves matrix elements of the total charge operator for the atom,

$$\hat{Q}=\int d\mathbf{r}'\,\hat{\rho}^a(\mathbf{r}')=0,\ \langle\hat{Q}\rangle_{0n}\equiv 0, \tag{3.28}$$

which vanishes identically for a neutral atom along with all its matrix elements. The dipole moment operator for the atom $\vec{\mathcal{D}}$ and its matrix elements involved in the second term are

$$\vec{\mathcal{D}}=\int d\mathbf{r}'\,\hat{\rho}^a(\mathbf{r}')\Delta\mathbf{r}',\quad \vec{\mathcal{D}}_{0n}=\langle\Phi_0^a|\vec{\mathcal{D}}|\Phi_n^a\rangle=\vec{\mathcal{D}}_{n0}^{*}. \tag{3.29}$$

Similarly, the quadrupole moment operator of the third term written in dyadic form is

$$\Theta=\int d\mathbf{r}'\,\hat{\rho}^a(\mathbf{r}')\left[\Delta\mathbf{r}'\Delta\mathbf{r}'-\frac{1}{3}\mathbf{I}|\Delta\mathbf{r}'|^2\right], \tag{3.30}$$

with matrix elements Θ_{0n}, etc. With these definitions, the position-space integrals of Eq. (3.25) yield $E_{int}^{(2)}$ to dipole-dipole terms as ($\hbar\to 1$)

$$E_{int}^{(2)}=\frac{1}{3\pi}\sum_n{}'\,|\mathcal{D}_{0n}|^2\int_{-\infty}^{\infty}d\omega\,\frac{1}{i(\omega-\omega_{n0}^a)}\times\int_0^{\infty}d\overline{pp^2}e^{-2\overline{p}|Z|}\left(\frac{1-\varepsilon_{\overline{p}}(\omega)}{1+\varepsilon_{\overline{p}}(\omega)}\right). \tag{3.31}$$

The $\overline{p}$ integral is of central importance in determining the Z dependence of $E_{int}^{(2)}$. Defining $\overline{q}=\overline{p}Z$, it takes the form

$$\int_0^{\infty}d\overline{pp^2}e^{-2\overline{p}|Z|}\left(\frac{1-\varepsilon_{\overline{p}}(\omega)}{1+\varepsilon_{\overline{p}}(\omega)}\right)=\frac{1}{Z^3}\int_0^{\infty}d\overline{qq^2}e^{-2\overline{q}}\left(\frac{1-\varepsilon_{\overline{q}/Z}(\omega)}{1+\varepsilon_{\overline{q}/Z}(\omega)}\right). \tag{3.32}$$

It is at once apparent that the inclusion of quardrupole and higher-order moments, which involve higher powers of $\Delta\overline{\mathbf{r}}$ and/or Δz, would bring additional powers of $\overline{p}$ with them into the $\overline{p}$ integrand through the expansion of the exponential discussed above. Every such additional power of $\overline{p}$ in the $\overline{p}$ integrand contributes another factor of $1/Z$ to the corresponding integral in $E_{int}^{(2)}$, as one readily sees from the substitution $\overline{q}=\overline{p}Z$ above. Thus, it is only the dipole-dipole term of $E_{int}^{(2)}$ which varies as $1/Z^3$ and any involvement of quadrupole or higher-order multipoles produces terms which vary at least like $1/Z^4$. *Even within the framework of the dipole-dipole term, however, the nonlocality of* $\varepsilon_{\overline{p}}(\omega)$ *results in terms varying at least like* $1/Z^4$ (in competition with quadrupole terms). It is only the local limit of $\varepsilon_{\overline{p}}(\omega)\to\varepsilon(\omega)$ that genuinely results in $E_{int}^{(2)}$ varying like $1/Z^3$. In this case, Eq. (3.31) readily yields the result of Mavroyannis [30],

$$E_{int}^{(2)}=\frac{1}{6\pi Z^3}\sum_n{}'\,|\mathcal{D}_{0n}|^2\times\int_0^{\infty}du\,\frac{\omega_{n0}^a}{u^2+(\omega_{n0}^a)^2}\left(\frac{1-\varepsilon(iu)}{1+\varepsilon(iu)}\right), \tag{3.33}$$

where we have set $\omega=iu$ and deformed the contour of frequency integration. Considering a perfect metal of infinite polarizability, $\varepsilon(iu)\to\infty$, the u integral is elementary, leading to

$$E_{int}^{(2)}=-\frac{1}{12Z^3}\sum_n{}'\,|\mathcal{D}_{0n}|^2=-\frac{e^2}{12Z^3}\langle|\Delta\mathbf{r}|^2\rangle_0, \tag{3.34}$$

which is the well-known Lennard-Jones result [31] for neutral atoms interacting with a perfect metal. Of course, a close approach of the atom to the metal will result in Pauli exclusion exchange effects coming into play, with a concomitant repulsive potential which dominates over the weak van der Waals attraction at very short distances.

IV. MAGNETIC FIELD EFFECTS IN VAN DER WAALS ENERGY OF INTERACTION BETWEEN A NEUTRAL ATOM AND A SEMI-INFINITE SURFACE MAGNETOPLASMA

A. Magnetoplasma models

Considering the dipole term of $E_{int}^{(2)}$ as given by Eq. (3.31), the effects of a magnetic field are fully embodied in the structure of $\varepsilon_{\overline{p}}(\omega)$, defined in Eq. (3.21) as

$$\varepsilon_{\overline{p}}^{-1}(\omega)=\frac{\overline{p}}{\pi}\int_{-\infty}^{\infty}\frac{dp_z}{(p_z^2+\overline{p^2})\varepsilon_B(\mathbf{p},\omega)}, \tag{4.1}$$

where $\varepsilon_B(\mathbf{p},\omega)$ is the *bulk* dynamic nonlocal dielectric function of the semi-infinite surface electron plasma, which we take to be in a magnetic field perpendicular to the surface. This bulk dielectric function has been determined in the random phase approximation (RPA) [22] with its full complement of quantum effects and magnetic field effects in all statistical regimes (degenerate, nondegenerate) and its application here would produce de Haas–van Alphen oscillatory effects, as well as classical magnetic field effects. However, that study involves a highly complicated analysis and it can

be deferred while a simpler hydrodynamic analysis is applied here to exhibit some of the principal features of the role of a magnetic field in van der Waals atom-surface attraction.

The hydrodynamic model [24] is based on linearized classical continuity and force balance equations (collisionless) in the form [δ designates the departure from equilibrium values, n_0 is the equilibrium number density, $\mathbf{v}(\mathbf{r},t)$ is the velocity field]

$$\frac{\partial}{\partial t}\delta n(\mathbf{r},t)+n_0\nabla\cdot\delta\mathbf{v}(\mathbf{r},t)=0, \tag{4.2}$$

$$n_0 m\frac{\partial}{\partial t}\delta\mathbf{v}(\mathbf{r},t)=n_0 e\,\delta\mathbf{E}(\mathbf{r},t)+n_0 e\,\delta\mathbf{v}\times\mathbf{B}-\boldsymbol{\nabla}_{\mathbf{r}}\cdot\Pi(\mathbf{r},t), \tag{4.3}$$

where the magnetic Lorentz force has been included. The hydrodynamic model closes this set of equations with the stress tensor $[\Pi(\mathbf{r},t)]$ ansatz,

$$\boldsymbol{\nabla}_{\mathbf{r}}\cdot\Pi(\mathbf{r},t)=m\beta^2\boldsymbol{\nabla}_{\mathbf{r}}\delta n(\mathbf{r},t), \tag{4.4}$$

with β as a constant parameter having the dimensions of speed. (The choice $\beta^2=v_F^2/3$ properly reproduces the static Thomas-Fermi shielding law, while $\beta^2=\frac{3}{5}v_F^2$ matches the leading nonlocal correction of the hydrodynamic zero-field bulk plasmon to that of the RPA.) Fourier transforming $(\mathbf{r}\to\mathbf{p},\ t\to\omega)$, these equations may be rewritten as

$$-i\omega\delta n(\mathbf{p},\omega)+in_0\mathbf{p}\cdot\delta\mathbf{v}(\mathbf{p},\omega)=0, \tag{4.5}$$

$$\delta v_x=\frac{(e/m)\omega\delta E_x+i(e\omega_c/m)\delta E_y+\omega_c\beta^2 p_y\delta n/n_0-i\beta^2\omega p_x\delta n/n_0}{i(\omega_c^2-\omega^2)}, \tag{4.6}$$

$$\delta v_y=\frac{(e/m)\omega\delta E_y-i(e\omega_c/m)\delta E_x-\omega_c\beta^2 p_x\delta n/n_0-i\beta^2\omega p_y\delta n/n_0}{i(\omega^2-\omega_c^2)}, \tag{4.7}$$

$$\delta v_z=i\frac{e\,\delta E_z}{m\omega}+\frac{\beta^2}{\omega}p_z\frac{\delta n}{n_0}. \tag{4.8}$$

Considering self-consistency with the Poisson equation in the presence of an external source $s(\mathbf{r},t)\to s(\mathbf{p},\omega)$, $\boldsymbol{\nabla}\cdot\mathbf{E}(\mathbf{r},t)\to i\mathbf{p}\cdot\mathbf{E}(\mathbf{p},\omega)$ we have

$$i\mathbf{p}\cdot\delta\mathbf{E}(\mathbf{p},\omega)=4\pi e[s(\mathbf{p},\omega)+\delta n(\mathbf{p},\omega)]. \tag{4.9}$$

Equations (4.6) to (4.8) may be used to eliminate δv_x, δv_y, δv_z from the equation of continuity [Eq. (4.5)] in favor of $\delta\mathbf{E}$ and δn, and Eq. (4.9) may then be used to eliminate $\delta\mathbf{E}$ in favor of δn or s (also using $\boldsymbol{\nabla}\times\mathbf{E}=0$ and $\boldsymbol{\nabla}\times\boldsymbol{\nabla}\delta n=0$). The resulting relation between δn and s may be expressed as

$$\left[-\omega^2+\left(\frac{\omega_p^2}{p^2}+\beta^2\right)\gamma(\omega,\omega_c)\right]\delta n(\mathbf{p},\omega)=-\frac{\omega_p^2}{p^2}\gamma(\omega,\omega_c)s(\mathbf{p},\omega), \tag{4.10}$$

where

$$\gamma(\omega,\omega_c)=p_z^2-\frac{\omega^2\overline{p^2}}{\omega_c^2-\omega^2}\quad\text{and}\quad\omega_p^2=\frac{4\pi n_0 e^2}{m}. \tag{4.11}$$

Noting that the bulk dielectric function may be written in the form

$$\varepsilon_B^{-1}(\mathbf{p},\omega)=\frac{\delta n(\mathbf{p},\omega)+s(\mathbf{p},\omega)}{s(\mathbf{p},\omega)}, \tag{4.12}$$

we obtain

$$\varepsilon_B^{-1}(\mathbf{p},\omega)=1-\frac{\omega_p^2\gamma(\omega,\omega_c)}{-\omega^2p^2+(\omega_p^2+p^2\beta^2)\gamma(\omega,\omega_c)}. \tag{4.13}$$

In the local limit $(\beta\to0)$, we have

$$\varepsilon_B(\mathbf{p},\omega)=1-\frac{\omega_p^2p_z^2}{\omega^2p^2}-\frac{\omega_p^2}{\omega^2-\omega_c^2}\frac{\overline{p^2}}{p^2}, \tag{4.14}$$

which correctly yields the local bulk anisotropic magnetoplasma spectrum. The nonlocal bulk hydrodynamic magnetoplasmon disperson relation arising from the vanishing of $\varepsilon_B(\mathbf{p},\omega)$ in Eq. (4.13) with $\beta\neq0$ is given by

$$\omega^2=\frac{1}{2}\left\{\omega_p^2+\omega_c^2+\beta^2p^2\pm\left[(\omega_p^2+\omega_c^2+\beta^2p^2)^2-4\left(\frac{\omega_p^2}{p^2}+\beta^2\right)p_z^2\omega_c^2\right]^{1/2}\right\}. \tag{4.15}$$

B. Construction of the surface dielectric function $\varepsilon_{\bar{p}}(\omega)$ in the magnetohydrodynamic model: Magnetic field effects on van der Waals interaction

We construct $\varepsilon_{\bar{p}}(\omega)$ using Eqs. (4.1) to (4.13) as

$$\varepsilon_{\bar{p}}^{-1}(\omega)=\frac{2\bar{p}}{\pi}\int_0^\infty dp_z\frac{\beta^2\gamma(\omega,\omega_c)-\omega^2}{\gamma(\omega,\omega_c)(\beta^2p^2+\omega_p^2)-\omega^2p^2}. \tag{4.16}$$

With the definition of $\gamma(\omega,\omega_c)$ [Eq. (4.11)], this can be rewritten in the form

$$\varepsilon_{\bar{p}}^{-1}(\omega)=\frac{2\bar{p}}{\pi}\int_0^\infty dp_z\frac{p_z^2-A}{(p_z^2+d_+)(p_z^2+d_-)}, \tag{4.17}$$

where

$$\begin{aligned}A&=\frac{\omega^2\overline{p^2}}{\omega_c^2-\omega^2}+\frac{\omega^2}{\beta^2},\\ B&=\overline{p^2}-\frac{\omega^2\overline{p^2}}{\omega_c^2-\omega^2}+\frac{\omega_p^2-\omega^2}{\beta^2},\\ d_\pm&=\frac{1}{2}(B\mp\sqrt{B^2-4C}),\\ C&=-\left(\frac{\omega^2}{\beta^2}+\frac{\omega^2\omega_p^2}{\beta^2(\omega_c^2-\omega^2)}+\frac{\omega^2\overline{p^2}}{\omega_c^2-\omega^2}\right)\overline{p^2}.\end{aligned} \tag{4.18}$$

The p_z integrals involved in Eq. (4.17) are carried out on the understanding that the subsequent ω integration will be performed with the substitution $\omega=iu$ and contour deformation to the real u axis (so there is no singular behavior), with the result

$$\varepsilon_{\bar{p}}^{-1}(\omega)=\frac{\bar{p}}{\sqrt{d_-}+\sqrt{d_+}}\left(1-\frac{A}{\sqrt{d_+d_-}}\right). \tag{4.19}$$

Considering a low-wave-number power expansion, we obtain

$$\varepsilon_{\bar{p}}^{-1}(\omega)=\frac{1}{\sqrt{(1-\omega_p^2/(\omega^2-\omega_c^2))(1-\omega_p^2/\omega^2)}}+\frac{\beta\bar{p}\omega_p^2}{(\omega_p^2-\omega^2)^{3/2}}. \tag{4.20}$$

These expressions describe the role of a magnetic field in the effective surface dielectric function. The associated surface plasmon dispersion relation $\varepsilon_{\bar{p}}(\omega)+1=0$ is given to order $\bar{p}$ by

$$\omega^2=\frac{\omega_p^2+\omega_c^2}{2}+\frac{\beta\bar{p}(\omega_p^2+\omega_c^2)}{\sqrt{2(\omega_p^2-\omega_c^2)}}, \tag{4.21}$$

which is in agreement with the well known nonlocal result of Ritchie [32] in the zero-field limit.

Equation (4.20) may be employed to determine the role of magnetic field effects in the van der Waals interaction energy within the framework of the hydrodynamic model. Following Eq. (3.31) and setting $\omega=iu$ with a deformation of the contour, we have

$$E_{int}^{(2)}=\frac{2}{3\pi\hbar}{\sum_n}'|\mathcal{D}_{0n}|^2\omega_{n0}^a\int_0^\infty d\bar{p}\overline{p^2}e^{-2\bar{p}|Z|}\times\int_0^\infty\frac{du}{u^2+{\omega_{n0}^a}^2}\left(\frac{\varepsilon_{\bar{p}}^{-1}(iu)-1}{\varepsilon_{\bar{p}}^{-1}(iu)+1}\right), \tag{4.22}$$

and expansion of the integrand to linear order in $\bar{p}$ yields the corresponding vdW energy as

$$E_{int}^{(2)}=\frac{1}{6\pi\hbar}{\sum_n}'|\mathcal{D}_{0n}|^2\omega_{n0}^a\times\int_0^\infty\frac{du}{u^2+(\omega_{n0}^a)^2}\left\{\frac{1-W(u)}{1+W(u)}\frac{1}{|Z|^3}+\frac{\omega_p^2\beta}{(\omega_p^2+u^2)^{3/2}}\frac{W^2(u)}{[1+W(u)]^2}\frac{3}{|Z|^4}\right\}, \tag{4.23}$$

where magnetic field dependence is embedded in both the local $(1/|Z|^3)$ and nonlocal $(1/|Z|^4)$ terms through $W(u)$ defined as

$$W(u)=\left[\left(1+\frac{\omega_p^2}{u^2+\omega_c^2}\right)\left(1+\frac{\omega_p^2}{u^2}\right)\right]^{1/2}, \tag{4.24}$$

within the framework of the hydrodynamic model of dynamic, nonlocal dielectric response of the semi-infinite surface plasma system.

One may obtain further information about magnetic field effects on the vdW energy $E_{int}^{(2)}$ in the hydrodynamic model by directly employing Eq. (4.16) in Eq. (4.22), avoiding the expansion in inverse powers of Z. While this would enrich the description of the Z dependence of $E_{int}^{(2)}$, it severely complicates the analysis of the $\bar{p}$ integral. For example, considering the magnetic field (ω_c) to be small in all senses, the expansion of $\varepsilon_{\bar{p}}^{-1}(\omega)$ [Eq. (4.16)] to order $O(\omega_c^2)$ yields

$$\varepsilon_p^{-1}(\omega)=\frac{2\overline{p}}{\pi}\int_0^\infty dp_z\left[\frac{\beta^2p^2-\omega^2}{p^2(\beta^2p^2+\omega_p^2-\omega^2)}+\frac{\omega_c^2\overline{p^2}\omega_p^2}{p^4(\beta^2p^2+\omega_p^2-\omega^2)^2}\right]. \tag{4.25}$$

The resulting p_z integral may be expressed in the form

$$\varepsilon_p^{-1}(\omega)=\varepsilon_{\omega_c^0}^{-1}(\omega)+\varepsilon_{\omega_c^2}^{-1}(\omega), \tag{4.26}$$

where the first term on the right, of order $O(\omega_c^0)$, is the null magnetic field limit given by

$$\varepsilon_{\omega_c^0}^{-1}(\omega)=\frac{\omega^2}{\omega^2-\omega_p^2}-\frac{\overline{p}\beta\omega_p^2}{(\omega^2-\omega_p^2)\sqrt{\overline{p^2}\beta^2-\omega^2+\omega_p^2}}, \tag{4.27}$$

and the second term on the right, of order $O(\omega_c^2)$, is

$$\varepsilon_{\omega_c^2}^{-1}(\omega)=\frac{\overline{p^3}\beta^3\omega_c^2\omega_p^2(4\overline{p^2}\beta^2-5\omega^2+5\omega_p^2)}{2(-\omega^2+\omega_p^2)^3(\overline{p^2}\beta^2-\omega^2+\omega_p^2)^{3/2}}+\frac{\omega_c^2\,\omega_p^2(4\overline{p^2}\beta^2+\omega^2-\omega_p^2)}{2(\omega^2-\omega_p^2)^3}. \tag{4.28}$$

Using this result for $\varepsilon_p^{-1}(\omega)$, we may express $E_{int}^{(2)}$ to order ω_c^2 as ($\omega_{n0}^a\to\omega_{n0}$ hereafter)

$$E_{int}^{(2)}=\frac{2}{3\pi}{\sum_n}'\,|\mathcal{D}_{0n}|^2\omega_{n0}\int_0^\infty d\overline{pp^2}e^{-2\overline{p}|Z|}\int_0^\infty\frac{du}{u^2+\omega_{n0}^2}\times\left\{\frac{\varepsilon_{\omega_c^0}^{-1}(iu)-1}{\varepsilon_{\omega_c^0}^{-1}(iu)+1}+\frac{2\varepsilon_{\omega_c^2}^{-1}(iu)}{(\varepsilon_{\omega_c^0}^{-1}(iu)+1)^2}\right\}. \tag{4.29}$$

The null magnetic field part of $E_{int}^{(2)}$, given by the first term on the right hand side of Eq. (4.29), involves both local structure leading to Mavroyannis' result and nonlocal features of the type discussed by Mahanty and Paranjape [33]. This zero-field nonlocal term is

$$E_{\omega_c^0,nonloc}^{(2)}=\frac{2}{3\pi}{\sum_n}'\,|\mathcal{D}_{0n}|^2\omega_{n0}\int_0^\infty d\overline{pp^2}e^{-2\overline{p}|Z|}\int_0^\infty\frac{du}{u^2+\omega_{n0}^2}\,\frac{2\overline{p}\beta\omega_p^2(u^2+\omega_p^2)}{(2u^2+\omega_p^2)[\overline{p}\beta\omega_p^2+(2u^2+\omega_p^2)\sqrt{\overline{p^2}\beta^2+u^2+\omega_p^2}]}, \tag{4.30}$$

and its leading term in an expansion in inverse powers of Z is given by

$$E_{\omega_c^0,nonloc}^{(2)}=\frac{1}{2\pi|Z|^4}{\sum_n}'\,|\mathcal{D}_{0n}|^2\omega_{n0}\times\int_0^\infty\frac{du}{u^2+\omega_{n0}^2}\frac{\beta\omega_p^2\sqrt{u^2+\omega_p^2}}{(2u^2+\omega_p^2)^2}. \tag{4.31}$$

Carrying out the u integral, we obtain

$$E_{\omega_c^0,nonloc}^{(2)}=\frac{\beta}{4\pi|Z|^4}{\sum_n}'\,\frac{|\mathcal{D}_{0n}|^2}{(\omega_p^2-2\omega_{n0}^2)^2}\times\left\{(2-\pi)\omega_{n0}^3+(\pi-1)\omega_{n0}\omega_p^2-2\omega_p^2\sqrt{\omega_p^2-\omega_{n0}^2}\arctan\left(\frac{\omega_{n0}}{\sqrt{\omega_p^2-\omega_{n0}^2}}\right)\right\}. \tag{4.32}$$

The leading magnetic field correction $[O(\omega_c^2)]$ also has both local and nonlocal parts: the local vdW energy correction of order ω_c^2 is (define $\omega_s=\omega_p/\sqrt{2}$)

$$E_{\omega_c^2}^{(2)}=\frac{\omega_c^2\omega_s^2}{12\pi Z^3}{\sum_n}'\,|\mathcal{D}_{0n}|^2\omega_{n0}\times\int_0^\infty\frac{du}{(u^2+\omega_{n0}^2)(u^2+\omega_s^2)^2}=\frac{\omega_c^2/\omega_s}{48Z^3}{\sum_n}'\,|\mathcal{D}_{0n}|^2\frac{\omega_{n0}+2\omega_s}{(\omega_{n0}+\omega_s)^2}, \tag{4.33}$$

and the nonlocal contribution of order ω_c^2 is given by

$$E_{\omega_c^2,nonloc}^{(2)}=\frac{2}{3\pi}{\sum_n}'\,|\mathcal{D}_{0n}|^2\omega_{n0}\int_0^\infty d\overline{pp^2}e^{-2\overline{p}|Z|}\times\int_0^\infty\frac{du}{u^2+\omega_{n0}^2}\left[\frac{M(\overline{p})}{N(\overline{p})}-\frac{\omega_c^2\omega_p^2}{(2u^2+\omega_p^2)^2}\right], \tag{4.34}$$

with the definitions

$$M(\overline{p}) = \omega_c^2 \omega_p^2 \{\overline{p^3}\beta^3(5u^2 + 4\overline{p^2}\beta^2 + 5\omega_p^2) + \sqrt{u^2 + \overline{p^2}\beta^2 + \omega_p^2}[u^4 - 3u^2\overline{p^2}\beta^2 - 4\overline{p^4}\beta^4 + (2u^2 - 3\overline{p^2}\beta^2)\omega_p^2 + \omega_p^4]\}, \quad (4.35)$$

$$N(\overline{p}) = (u^2 + \omega_p^2)\sqrt{u^2 + \overline{p^2}\beta^2 + \omega_p^2} \times [2u^2\sqrt{u^2 + \overline{p^2}\beta^2 + \omega_p^2} + \omega_p^2(\overline{p}\beta + \sqrt{u^2 + \overline{p^2}\beta^2 + \omega_p^2})]^2. \quad (4.36)$$

The leading term of $E^{(2)}_{\omega_c^2, nonloc}$ of Eq. (4.34) is of order $O(|Z|^{-4})$ due to the cancellation of the last term of its integrand with part of the ratio $M(\overline{p})/N(\overline{p})$, as one should expect. It is given by

$$E^{(2)}_{\omega_c^2, nonloc} \simeq -\frac{\omega_c^2 \beta \omega_p^4}{2\pi |Z|^4} {\sum_n}' |\mathcal{D}_{0n}|^2 \omega_{n0} \int_0^\infty \frac{du}{u^2 + \omega_{n0}^2} \frac{1}{(2u^2 + \omega_p^2)^3 \sqrt{u^2 + \omega_p^2}}$$
$$\simeq \frac{\omega_c^2 \beta}{8\pi \omega_p^2 |Z|^4} {\sum_n}' |\mathcal{D}_{0n}|^2 \left\{ \frac{(3\pi + 4)\omega_p^4 \omega_{n0} - (4\pi + 8)\omega_p^2 \omega_{n0}^3 + 4\pi \omega_{n0}^5}{[\omega_p^2 - 2\omega_{n0}^2]^3} + \frac{4\omega_p^6 \arctan(\omega_{n0}/\sqrt{\omega_p^2 - \omega_{n0}^2})}{[\omega_p^2 - 2\omega_{n0}^2]^3 \sqrt{\omega_p^2 - \omega_{n0}^2}} \right\}. \quad (4.37)$$

V. CONCLUSIONS

We have determined the role of a magnetic field in the vdW atom-surface interaction to second order in the nonretarded electrostatic Coulomb force between atomic electrons and surface electrons. In this, we have exhibited the energy of interaction in terms of an indirect correlation or self-energy of the atomic electrons mediated by the polarization of the surface-electron system described in terms of a dynamic, nonlocal image potential. A Green's function joining procedure has been applied to semi-infinite nonlocal electrostatics in the construction of a ''surface dielectric function,'' which incorporates the dynamic, nonlocal, and inhomogeneous dielectric properties of the surface medium in a normal magnetic field, using a (magneto)hydrodynamic model of plasma nonlocality. Furthermore, we have explicitly exhibited quantum magnetic field effects in the skewing of the surface electron charge distribution from its positive background, effects which play a role in altering the effective atom-surface separation. Our results, described in Eqs. (4.30)–(4.37) as well as Eqs. (2.24) and (2.29)–(2.33), provide a basis for employing magnetic field strength (taken in a dimensionless combination with material constants, such as ω_c/ω_p, $\hbar\omega_c/E_F$, etc.) as an adjustable parametrization of the vdW energy, and of the underlying fundamental quantum phenomenology of zero-point plasmon-photon energy, in experimental studies.

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[1] U. Mohideen and Anushree Roy, Phys. Rev. Lett. **81**, 4549 (1998).
[2] K.A. Milton, *The Casimir Effect* (World Scientific, Singapore, 2001).
[3] *The Casimir Effect 50 Years Later*, edited by Michael Bordag (World Scientific, Singapore, 1999).
[4] Peter W. Milonni, *The Quantum Vacuum* (Academic, New York, 1994).
[5] W. Dittrich and H. Gies, *Probing the Quantum Vacuum*, Vol. 166 of *Tracts in Modern Physics* (Springer-Verlag, Berlin, 2000).
[6] Paul R. Berman, *Cavity Quantum Electrodynamics* (Academic, New York, 1994).
[7] *Long Range Casimir Forces* edited by F.S. Levin and D.A. Micha (Plenum Press, New York, 1993).
[8] V.M. Mostrepanenko and N.N. Trunov, *The Casimir Effect and its Applications* (Clarendon Press, Oxford 1997); Sov. Phys. Usp. **31**, 965 (1988).
[9] G. Plunien, B. Müller, and W. Greiner, Phys. Rep. **134**, 87 (1986).
[10] J. Mahanty and B.W. Ninham, *Dispersion Forces* (Academic, New York, 1976).
[11] D. Langbein, *Theory of van der Waals Attraction*, Tracts in Modern Physics Vol. 72 (Springer-Verlag, Berlin, 1974).
[12] J.N. Israelachvilli and D. Tabor, Prog. Surf. Membrane Phys. **7**, 1 (1973).
[13] G. Feinberg, J. Sucher, and C.-K. Au, Phys. Rep. **180**, 83 (1989).
[14] I.E. Dzyaloshinskii, E.M. Lifshitz, and L.P. Pitaevskii, Adv. Phys. **10**, 165 (1961).

[15] E.A. Power and T. Thirunamachandran, Phys. Rev. A **50**, 3929 (1994).
[16] M. Hawton, Phys. Rev. A **46**, 6846 (1992).
[17] Yu.S. Barash and V.L. Ginzburg, Sov. Phys. Usp. **18**, 306 (1975).
[18] P.W. Milonni and M.L. Shih, Phys. Rev. A **45**, 4241 (1992).
[19] J. Bardeen, Phys. Rev. **58**, 727 (1940).
[20] A.L. Fetter and J.D. Walecka, *Quantum Theory of Many Particle Systems* (McGraw-Hill, New York, 1971).
[21] P.C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).
[22] N.J.M. Horing, Ann. Phys. (N.Y.) **31**, 1 (1965); N.J.M. Horing and M.M. Yildiz, Phys. Rev. B **33**, 3895 (1986).
[23] H.B. Huntington, Phys. Rev. **81**, 1035 (1957).
[24] A.D. Boardman, *Electromagnetic Surface Modes* (John Wiley, New York, 1982).
[25] D.M. Newns, Phys. Rev. B **1**, 3304 (1978).
[26] N.J.M. Horing and M.M. Yildiz, Phys. Rev. B **33**, 3895 (1986).
[27] J.E. Inglesfield, J. Phys. C **4**, L14 (1971).
[28] F. Garcia-Moliner and F. Flores, *Introduction to the Theory of Solid Surfaces* (Cambridge University Press, Cambridge, England, 1979); F. Garcia-Moliner and V. R. Velasco, *Theory of Singlet and Multiple Interfaces* (World Scientific, Singapore, 1992).
[29] N.J.M. Horing (unpublished).
[30] C. Mavroyannis, Mol. Phys. **6**, 593 (1963).
[31] J.E. Lennard-Jones, Trans. Faraday Soc. **28**, 333 (1932).
[32] R.H. Ritchie, Phys. Rev. **106**, 874 (1957).
[33] J. Mahanty and B.V. Paranjape, Solid State Commun. **24**, 651 (1977); G. Mukhopadhyay and J. Mahanty, *ibid.* **16**, 597 (1975); J. Mahanty and B.W. Ninham, J. Chem. Phys. **59**, 6157 (1973).