Polarization Energy in the Atom-Surface Interaction for an Anisotropic Substrate with Non-Local Effects

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§ 1. Introduction.

We study the generalization of the Lifshitz formula[1] for the nonretarded van der Waals interaction between two semi-infinite media including non-local dielectric effects and anisotropy. In 1955 Lifshitz[1] presented a formula to calculate the van der Waals forces between two metal half-spaces. From his formula the net interaction energy between one adatom and a semi-infinite solid can be expressed at a moderate distance z from the planar surface as

$$V(z) = -C_3/z^3, \qquad (1)$$

where

$$C_3 = \frac{1}{4\pi} \int_0^\infty d\omega \, \{[\varepsilon(i\omega)-1]/[\varepsilon(i\omega)+1]\} \, \alpha(i\omega), \qquad (2)$$

$\varepsilon(i\omega)$ is the dielectric constant of the solid and $\alpha(i\omega)$ is the electric polarizability of the adatom, both evaluated at pure imaginary frequency. With the same approach Kihara and Honda[2] generalized this formula to the interaction of two anisotropic bodies. For a solid surface such as basal plane graphite with dielectric functions $\varepsilon_\perp$ and $\varepsilon_{//}$ for electric fields parallel and perpendicular to the basal plane, the prescription is to replace ε in Eq. (2) by $\bar\varepsilon$, where $\bar\varepsilon$ is defined by

$$\bar\varepsilon = \{\varepsilon_{//}(i\omega)\varepsilon_\perp(i\omega)\}^{1/2}. \qquad (3)$$

Recently many authors have studied this problem of van der waals interaction with many different methods[3]-[5]. Nevertheless all these studies include only the local effects of dielectric constant. J. Heinrichs[6] and D.

Chang et al[7] tried to expand the formula of Lifshitz to have the effects of spacial dispersion and showed non-local dispersion is very important. Their calculations are done, however, in the case of hydrodynamical treatment of electron gas. Here we evaluate the van der Waals interaction energy between two semi-infinite media using the expression for the energy in terms of the shift of the zero-point energy of their surface modes[8]. We also present the results of numerical calculations for C_3 for some adatoms on graphite basal plane with the values derived from recent experiments[9]. To our regret we can not estimate the effect of the non-local effect of dielectric media for there is still no experimental data of dielectric

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constant of graphite with wave vector dependence..

§ 2. Polarization forces between two semi-infinite dielectric media with non-local effects.

We first treat the case of isotropic media with planar surfaces at $z=\pm l/2$ and a vacuum gap between them ; the modification of the result for anisotropic media is stated at the end. We neglect retardation effects.

For a medium of wave-vector (k) and frequency (ω) dependent dielectric function $\varepsilon(k, \omega)$, we obtain the electric potential from the Poisson equation :

$$\phi(r, \tau)=(2\pi)^{-4}\int dk \int d\omega \exp[i(k\cdot r-\omega\tau)]$$
$$4\pi\rho(k, \omega)/[k^2\varepsilon(k, \omega)].$$

The fourier component of the space and time varying charge density $\rho(r, \tau)$ is

$$\rho(k, \omega)=\int dr \int dt \rho(r, t) \exp[i(k\cdot r-\omega t)].$$

Let medium I lie to the left of the plane $z=-l/2$ and let II lie to the right of the plane $z=+l/2$. Then, following Ritchie and Marusak,[10] the potential in I for a surface charge density ρ_I^S,

$$\rho_I(r, t)=\rho_I^S(x, y, t)\delta(z+[l/2]), \qquad (4)$$

has a (partial) Fourier transform

$$\phi_I(\kappa, z, \omega)=\int dx\ dy \int dt\ \phi_I(r, t) \exp[i(\kappa_x x+\kappa_y y-\omega t)]$$
$$=2\int_{-\infty}^{\infty} dk_z \exp[ik_z(z+[l/2])]\rho_I^S(\kappa, \omega)/[k^2\varepsilon_I(k)]. \qquad (5)$$

The 3-vector k has (x, y, z) components $(\kappa_x, \kappa_y, \kappa_z)$. There is a similar expression for the electric potential ϕ_{II} in region II.

The allowed surface modes are determined by connecting ϕ_I and ϕ_{II} through a solution ϕ_{III} in the vacuum gap,

$$\phi_{III}(\kappa, z, \omega)=A(\kappa, \omega)e^{\kappa z}+B(\kappa, \omega)e^{-\kappa z}, \kappa=[\kappa_x^2+\kappa_y^2]^{1/2}.$$

From the electrostatic boundary conditions at the interfaces $z=\pm l/2$ we obtain

$$g(\kappa, \omega)\equiv(\varepsilon_I^S+1)(\varepsilon_{II}^S+1)-(\varepsilon_I^S-1)(\varepsilon_{II}^S-1)e^{-2\kappa d}=0, \qquad (6)$$

where the surface dielectric functions $\varepsilon_{I, II}^S(\kappa, \omega)$ are defined by

$$\varepsilon_{I, II}^S(\kappa, \omega)=\{(\kappa/\pi)\int_{-\infty}^{\infty} dk_z/[k^2\varepsilon_{I, II}(k, \omega)]\}^{-1}. \qquad (7)$$

The zero point energy of the allowed surface modes for given κ is

$$\sum_n \frac{1}{2} \hbar\omega_n=(\hbar/2)(1/2\pi i)\oint_C \omega \ln g(\kappa, \omega)d\omega,$$

where the contour integral c encloses the positive frequency roots of Eq. (6).

Then, with a sum over surface mode wave

vectors, the generalized Lifshitz formula for the interaction energy per interface area is

$$U(l)=(\hbar/8\pi^2)\int_{-\infty}^{\infty} d\xi \int_0^{\infty} \kappa d\kappa$$

$$\ln\left\{1-\left(\frac{\varepsilon_I^S-1}{\varepsilon_I^S+1}\right)\left(\frac{\varepsilon_{II}^S-1}{\varepsilon_{II}^S+1}\right)e^{-2\kappa l}\right\}. \qquad (8)$$

The surface dielectric functions in Eg. (7) are functions of argument $(\kappa, i\xi)$, $\varepsilon_{I, II}^S(\kappa, i\xi)$.

For a single adatom at distance l from the substrate I the usual limit-procedure[11] is performed on Eq. (8) : we assume medium II is dilute, of number density ρ and (local) molecular polarizability $\alpha_{II}(\omega)$. Then with the Clausius-Mossotti equation

$$\frac{\varepsilon_{II}(k,\ i\omega)-1}{\varepsilon_{II}(k,\ i\omega)+1}=(4\pi/3)\rho\alpha_{II}(i\omega), \qquad (9)$$

applied at very low number density, we expand Eq. (8) and have the generalization of Eq. (2). The energy of interaction of an adatom II with substrate I is

$$E(l)=-(\hbar/\pi)\int_0^\infty d\xi\int_0^\infty \kappa^2 d\kappa e^{-2\kappa l}\ \alpha_{II}(i\xi)[\varepsilon_I^S(\kappa,\ \omega)-1]/[\varepsilon_{II}^S(\kappa,\ \omega)+1]. \qquad (10)$$

In the case of local dispersion ; $\varepsilon(k,\omega)$ is independent of k, this reduces to the well known Lifshitz formula of Eq (1).

§ 3. Van der Waals forces between two anisotropic semi-infinite media.

Here we want to obtain a formula of van der Waals forces with the anisotropic effects.

For the generalization of the results of § 2 to anisotropic media we consider the same geometry as before and assume the axes of that coordinate system coinside with the principal axes of the dielectric tensor. The Fourier transform of the generalized Poisson equation satisfy

$$\{\varepsilon_x(k,\ \omega)k_x^2+\varepsilon_y(k,\ \omega)k_y^2+\varepsilon_z(k,\ \omega)k_z^2\}\,\phi(k,\ \omega)=4\pi\rho(k,\ \omega),$$

and the electric potential is

$$\phi(r,t)=\frac{4\pi}{(2\pi)^4}\int d^3k\int d\omega\frac{\rho(k,\ \omega)\cdot\exp\left[i(k\cdot r-\omega t)\right]}{\varepsilon_x(\kappa,\ \omega)\kappa_x^2+\varepsilon_y(\kappa,\ \omega)k_y^2+\varepsilon_z(k,\ \omega)k_z^2}.$$

For an explicit result, we consider the special case $\varepsilon_x=\varepsilon_y=\varepsilon_\perp$ and $\varepsilon_z=\varepsilon_{//}$, as for basal-plane graphite. Then the definition of the surface dielectric function is

$$\varepsilon^S(\kappa,\ \omega)=\{(\kappa/\pi)\int_{-\infty}^\infty dk_z\ [\kappa^2\varepsilon_\perp(k,\ \omega)+k_z^2\varepsilon_{//}(k,\ \omega)]^{-1}\}^{-1}. \qquad (11)$$

Using the same method as in § 2 we can obtain the following equation

$$(h_I(\kappa,\ \omega)\cdot\varepsilon_I^S(\kappa,\ \omega)+1)(h_{II}(\kappa,\ \omega)\varepsilon_{II}^S(\kappa,\ \omega)+1)$$
$$-(h_I(\kappa,\ \omega)\varepsilon_I^S(\kappa,\ \omega)-1)(h_{II}(k,\ \omega)\varepsilon_{II}^S(\kappa,\ \omega)-1)e^{-2\kappa d}=0. \qquad (12)$$

Here we introduced the limit-equations for function h_I and h_{II} (defined at $z=-l$, and $+l$, respectively).

$$h_{I/II}(\underline{\kappa},\ \omega)=(\pm)\lim_{(z\uparrow-l)/(z\downarrow l)}\ (\frac{i}{\kappa})\int_{-\infty}^\infty dk_z k_z\cdot$$

$$\cdot\ \exp\left[ik_z(z\pm l)\right]/\{k_z^2+\kappa^2(\frac{\varepsilon_\perp}{\varepsilon_{//}})(\underline{k},\ \omega)\}. \qquad (13)$$

If the ratios $\varepsilon_\perp/\varepsilon_{//}$ are finite in the limit $|k_z|\to\infty$, the functions h_I and h_{II} are equal to one and Eqs. (6), (8), and (10) hold with Eq. (11) for the surface dielectric function.

If the ratio $\varepsilon_\perp/\varepsilon_{//}$ is not finite in the limit $|k_z|\to\infty$, the function h may differ from one ; in that case the product ε^S formed from Eqs. (11) and (13) replaces ε^S in Eqs. (6), (8)

and (10).

In quite the same way we can get a result

$$U(z)=\frac{\hbar}{8\pi^2}\int_{-\infty}^{\infty}d\xi\int_0^{\infty}\kappa d\kappa\ln\left[1-\frac{(h_I\varepsilon^{S_I}-1)(h_{II}\varepsilon^{S_{II}}-1)}{(h_I\varepsilon^{S_I}+1)(h_{II}\varepsilon^{S_{II}}+1)}e^{-2\kappa z}\right].\qquad(14)$$

When we use the formula of Clausius Mossotti, we get the formula of interaction

for the interaction energy as follows for the anisotropic non-local dispersion substrates.

energy for one adatom on a substrate.

$$E(z)=\frac{\hbar}{2\pi}\frac{d}{dz}\left[\int_0^{\infty}d\xi\int_0^{\infty}\kappa d\kappa e^{-2\kappa z}\frac{h^{S_I}\varepsilon^{S_I}-1}{h^{S_I}\varepsilon^{S_I}+1}\cdot\alpha(i\xi)\right].\qquad(15)$$

It is very easy to see that this is same to the equation of Kihara in the local dispersion case.

§ 4. The calculation of interaction coefficients from optical data on basal plane graphite.

We calculated coefficients C_3 for H_e, N_e, A_r, K_r and X_e on basal plane graphite. For graphite we used $\varepsilon_\perp$ data of Taft and

Philipp[12] and $\varepsilon_{//}$ data of Tosatti and Bassani[13]. We obtained values for $\varepsilon(i\omega)$ for the absorptive part of the dielectric function with a Kramers-Krönig relation. We used polarizability function $\alpha(i\omega)$ constructed with the bounding approximation summarized by Tang et al.[14] In table we also list C_{S1} and C_{S2} which occur in the interaction between adatoms at lateral separation ρ and height L above an effective surface plane.[4]

$$\phi(\rho,L)=\left\{\left[\frac{4}{3}-(4L^2/[\rho^2+4L^2]\right]/[\rho^2+4L^2]^{3/2}\rho^3\right\}C_{S1}-(\rho^2+4L^2)^{-3}C_{S2},\qquad(16)$$

$$C_{S1}=\frac{3\hbar}{\pi}\int_0^{\infty}[\alpha(i\omega)]^2\{[\varepsilon(i\omega)-1]/[\varepsilon(i\omega)+1]\}d\omega,$$

$$C_{S2}=\frac{3\hbar}{\pi}\int_0^{\infty}[\alpha(i\omega)]^2\{[\varepsilon(i\omega)-1]/[\varepsilon(i\omega)+1]\}^2d\omega.$$

	C_3	C_{S1}	C_{S2}
H_e	0.043	0.57	0.31
N_e	0.086	2.2	1.2
A_r	0.30	30.	18.
K_r	0.43	63.	38.
X_e	0.61	142.	89.

Table. Dispersion forces on basal plane graphite. Values in atomic units.[9]

Acknowledgments

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〔**内容抄録**〕 非等方性のある固体表面に吸着した分子の分極エネルギー

渡辺歪俊

　分子が固体表面に物理吸着された時の分極エネルギーは，リフシッツの公式としてよく知られている。ここではこの公式を，非等方の固体や，非局所的な分極率を持つ固体表面での場合に拡張することを行う，また非等方的物質の場合の一例として，最近よく問題とされるグラファイトを扱い，これまでに知られた光学実験のデータを使って，この表面にいろいろな不活性ガスが吸着された時の分極エネルギーを計算する。