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Dielectric continuum theory of the Van der Waals interaction

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We extend our local dielectric model of surface properties to encompass the calculation of the (nonretarded) Van der Waals interaction between two dissimilar media separated by a third. As established earlier, the computation of this energy reduces to the evaluation of the classical electrostatic fields associated with a point charge in the three-medium geometry. Explicit results are given for three media separated by parallel planar boundaries, in which case the requisite electrostatic fields may be evaluated simply by the method of images. These results reduce to those obtained earlier for two identical media separated by a vacuum.

The Van der Waals force between two identical half-spaces separated by a vacuum gap initially was calculated by Lifshitz¹ using a phenomenological treatment of the electromagnetic field fluctuations. Assuming sharp boundaries and a local behavior of the dielectric function within the half-spaces, Lifshitz obtained the Van der Waals force as a functional of the frequency-dependent dielectric function of the (identical) media. Later, under the same assumptions, Dzyaloshinskii, Lifshitz, and Pitaevski² elaborated a microscopic quantum-field theory of the Van der Waals interaction between two planar interfaces with three adjoining media. For the case of two identical media separated by vacuum their results coincide with those of Lifshitz. Since the microscopic approach is rather complicated, however, there has been a continuing interest in simpler formulations³⁻¹⁴ which in turn have enabled the extension of results obtained for a planar geometry to other fields of physics¹⁴⁻³⁵ and biology.³⁶⁻³⁸ There also have been efforts³⁹⁻⁴⁴ to include spatial dispersion into the Van der Waals problem of planar interfaces through the use of nonlocal dielectric functions. Barash and Ginzburg¹⁰ have considered the case of absorptive media as well.

In this paper we report an extension of our previous work⁴⁵ on the electronic structure of solid

interfaces to the calculation of the nonretarded Van der Waals interaction between local dielectric media. Specifically we show that the evaluation of the Van der Waals force can be reduced to an electrostatic calculation of the surface charge density induced at the boundaries by a point charge. As an illustration of the method we calculate the Van der Waals interaction energy of two planar interfaces with three adjoining media through the method of images. In addition to illustrating the simplicity and power of our model, these results extend earlier ones¹⁻¹⁴ by virtue of describing three media with completely arbitrary local dielectric functions.

The Van der Waals interaction energy between macroscopic bodies is derived from a general expression for the correlation energy of an inhomogeneous electron gas.⁴⁶⁻⁴⁸ For bodies with sharp boundaries the bulk contribution to the interaction energy is, to a good approximation,^{6,7,45,49} independent of the separation and therefore does not contribute to the Van der Waals interaction. Thus, the Van der Waals interaction energy is defined as

$$E_{\text{vw}}(l) = \gamma(l) - \gamma(l \rightarrow \infty), \quad (1)$$

the change in the surface energy $\gamma(l)$ of the system when the bodies are a distance l apart with

respect to the surface energy of the system at infinite separation.

Now we write the surface energy of the system as⁴⁵⁻⁴⁸

$$\gamma = \hbar \int_0^1 \frac{dg}{g} \int_0^\infty \frac{d\omega}{2\pi} \int d^3r \operatorname{Im} \alpha_s(\vec{r}, \vec{r}; \omega), \quad (2)$$

where the integration over $g = e^2$ (e is the electronic charge) is the coupling constant integral, and α_s is the surface density-density response function defined by

$$\delta\rho_s(\vec{r}, \omega) = \int \alpha_s(\vec{r}, \vec{r}'; \omega) \delta\rho_{\text{ext}}(\vec{r}', \omega) d^3r'. \quad (3)$$

Here $\delta\rho_s$ is the induced surface electron density at \vec{r} due to the presence of external electron-density at \vec{r}' oscillating with frequency ω . Setting $\delta\rho_{\text{ext}}(\vec{r}, \omega) = \delta(\vec{r} - \vec{r}_0)$ in Eq. (3) one sees immediately that $\alpha_s(\vec{r}, \vec{r}_0; \omega)$ is simply the surface electron density induced by an external point charge at \vec{r}_0 oscillating with frequency ω . If we further assume a local response of the system, the calculation of α_s becomes a well-defined electrostatic problem. Taking then α_s in the limit $\vec{r}_0 \rightarrow \vec{r}$ and integrating Eq. (2) one obtains the Van der Waals interaction energy. The calculation is valid even in the case when dissipative media are present.⁴⁵ As an example of this approach we calculate the Van der Waals interaction energy for a system with planar interfaces by computing α_s through the method of

images.

We consider an inhomogeneous system with planar interfaces perpendicular to the z axis characterized by the sequence of local dielectric functions:

$$\begin{aligned} \epsilon_1(\omega); & \quad z < -a, \\ \epsilon_2(\omega); & \quad -a < z < a, \\ \epsilon_3(\omega); & \quad z > a. \end{aligned} \quad (4)$$

With this geometry it is convenient to take a two-dimensional Fourier transform parallel to the various surfaces so that Eq. (2) becomes

$$\gamma = \hbar \int_0^1 \frac{dg}{g} \int \frac{d^2q}{(2\pi)^2} \int_0^\infty \frac{d\omega}{2\pi} \int_{-\infty}^\infty dz \operatorname{Im} \alpha_s(z, z; \vec{q}, \omega), \quad (5)$$

where \vec{q} is a two-dimensional vector parallel to the surface.

Using the method of images we calculate the surface electron density $\alpha_s(z, z'; \vec{q}, \omega)$ induced by a unit point charge at z' oscillating with frequency ω . The resulting surface contribution to $\alpha(z, z'; \vec{q}, \omega)$ is given by

$$\begin{aligned} \alpha_s(z, z'; \vec{q}, \omega) = & \alpha_s(z, z'; \vec{q}, \omega; 123, a) \\ & + \alpha_s(-z, -z'; \vec{q}, \omega; 321, a), \end{aligned} \quad (6a)$$

where

$$\begin{aligned} \alpha_s(z, z'; \vec{q}, \omega; 123, a) = & -\delta(z - a) \left\{ \frac{\epsilon_3 - \epsilon_2}{\epsilon_3(\epsilon_3 + \epsilon_2)} + \left(\frac{2}{\epsilon_3 + \epsilon_2} \right) \Delta e^{-a|z' - a|} \Theta(-a + z') \right. \\ & + \frac{1}{\epsilon_2} \left[\left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) (1 + \Delta) e^{-a|z' - a|} + \Delta e^{2qa} e^{-a|z' + a|} \right] [\Theta(a - z') + \Theta(a + z') - 1] \\ & \left. + \left(\frac{2}{\epsilon_1 + \epsilon_2} \right) \Delta e^{4qa} e^{-a(|z'| + a)} \Theta(-a - z') \right\} \end{aligned} \quad (6b)$$

is the surface electron density induced at $z = a$ and the second term in Eq. (6a) is the surface electron density induced at $z = -a$. Here

$$\Delta \equiv \left[\left(\frac{\epsilon_2 + \epsilon_1}{\epsilon_2 - \epsilon_1} \right) \left(\frac{\epsilon_2 + \epsilon_3}{\epsilon_2 - \epsilon_3} \right) e^{4qa} - 1 \right]^{-1} \quad (6c)$$

and

$$\Theta(x) = \begin{cases} 1; & x > 0, \\ \frac{1}{2}; & x = 0, \\ 0; & x < 0 \end{cases} \quad (6d)$$

is the step function.

Inserting the limit $z' \rightarrow z$ of Eq. (6) into Eq. (5) yields

$$\begin{aligned} \gamma = \hbar \int_0^1 \frac{dg}{g} \int \frac{d^2q}{(2\pi)^2} \int_0^\infty \frac{d\omega}{2\pi} \operatorname{Im} \left[\frac{(\epsilon_2 - \epsilon_3)^2}{2\epsilon_2\epsilon_3(\epsilon_2 + \epsilon_3)} \right. \\ \left. + \frac{(\epsilon_2 - \epsilon_1)^2}{2\epsilon_2\epsilon_1(\epsilon_1 + \epsilon_2)} \right. \\ \left. - \left(\frac{2}{\epsilon_2 + \epsilon_3} + \frac{2}{\epsilon_2 + \epsilon_1} \right) \Delta \right]. \end{aligned} \quad (7)$$

The first two terms in the right-hand side of Eq. (7) do not depend on the separation between the two interfaces: they are simply the surface energies of the two isolated interfaces.⁴⁵ Thus, the Van der Waals interaction energy as defined in Eq. (1) becomes

$$E_{\text{vw}}(l) = \hbar \int_0^1 \frac{dg}{g} \int \frac{d^2q}{(2\pi)^2} \times \int_0^\infty \frac{d\omega}{2\pi} \text{Im} \left[\left(\frac{2}{\epsilon_2 + \epsilon_3} + \frac{2}{\epsilon_2 + \epsilon_1} \right) \Delta \right], \quad (8)$$

where $l = 2a$ is the separation between the two half-spaces.

The $g(=e^2)$ dependence of any model local dielectric function which obeys the f sum rule is given by⁴⁵

$$\epsilon(\omega; g) - 1 = g[\epsilon(\omega; g=1) - 1]. \quad (9)$$

Thus, the integration over g from 0 to 1 in Eq. (8) can be performed easily to give

$$E_{\text{vw}}(l) = \hbar \int \frac{d^2q}{(2\pi)^2} \int_0^\infty \frac{d\omega}{2\pi} \ln f(i\omega), \quad (10a)$$

where

$$f(\omega) = \left[1 - \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \right) \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) e^{-2ql} \right]^{-1}. \quad (10b)$$

Here $\epsilon_i(\omega) \equiv \epsilon_i(\omega; g=1)$ and the analytic properties of $f(\omega)$ in the complex ω plane were exploited in order to convert the ω integral along the real axis into an integral along the imaginary axis.⁵⁰

A change of variable $x = 2ql$ and integration by parts in the x variable in Eq. (10) yields directly

$$E_{\text{vw}}(l) = -\frac{\hbar}{32\pi^2 l^2} \times \int_0^\infty x^2 dx \int_0^\infty d\omega \left[\left(\frac{\epsilon_2 + \epsilon_1}{\epsilon_2 - \epsilon_1} \right) \left(\frac{\epsilon_2 + \epsilon_3}{\epsilon_2 - \epsilon_3} \right) e^x - 1 \right]^{-1}, \quad (11)$$

where $\epsilon_i \equiv \epsilon_i(i\omega)$. This expression coincides with the corresponding expression of Ref. 2 in the non-retarded limit.

Our approach follows the work of Craig¹⁴ with respect to the calculation of surface density-density response function. Unfortunately, however, an attempt to include spatial dispersion into the problem led him to certain inconsistencies.^{43, 45} Comparison of Eq. (11) with the results given in Refs. 1 and 2 reveals that contrary to Craig's assertion,¹⁴ the dielectric continuum approach does reproduce the Lifshitz result for local dielectric media. The

reason that this fact is not transparent from Craig's formulas [Eqs. (3.1) and (3.2) in Ref. 14] is that they are analogs of Eq. (7) above. The explicit performance of the coupling-constant integration [Eqs. (10)] and a subsequent integration by parts in the momentum transfer variable [Eq. (11)] are required to recover the functional form of the Lifshitz result. Heinrichs also has shown⁴³ that in the local limit his general expression for the Van der Waals interaction energy between two half-spaces (in which spatial dispersion was considered through a hydrodynamic model dielectric function) also reduces to Lifshitz's expression.

There are additional ways of calculating the Van der Waals interaction energy between macroscopic bodies. For example, a fruitful and relatively simple approach is the one developed by Van Kampen *et al.*⁸ They proved that for transparent bodies in the local limit, the Van der Waals interaction energy is the change in the zero-point energies of the surface collective modes originated when the bodies are displaced from infinity to their actual separation. This method has been extended to other geometries,¹⁹ to dissipative media^{9, 10} and to media with spatial dispersion.⁴¹⁻⁴³ It produces results equivalent to those derived above in the limit that damping is not included in the local dielectric function.⁴⁵ We already have shown,⁴⁵ however, that for dissipative media it is important to use a proper retarded dielectric function rather than the zero-point-energy formulas directly.

In summary, we have shown that our dielectric continuum model permits an elementary, almost trivial, derivation of Van der Waals energies in terms of textbook classical electrostatics. While prior limiting cases have been recovered, our results extend the earlier ones by virtue of being applicable for any combination of three planar media described by arbitrary local dielectric functions. Moreover, our approach is particularly useful when the method of images is applicable and in the case of the solid-molecule Van der Waals interaction as it will be shown elsewhere.

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