JOURNAL OF CHEMICAL PHYSICS VOLUME 121, NUMBER 15 15 OCTOBER 2004

Van der Waals interactions in a dielectric with continuously varying dielectric function

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(Received 11 May 2004; accepted 29 July 2004)

We formulate and evaluate the van der Waals part of the free energy due to a dielectric profile that varies continuously throughout the space between two interacting bodies. Not considering the work needed to create the inhomogeneous dielectric profile, focusing only on that part of the free energy affected by the inhomogeneity, we compare the ensuing interaction free energy with that of the original Lifshitz formulation with its step function changes at material boundaries and uniform dielectric medium. Rather than the monotonically varying attraction between like bodies given by the original formulation, the inhomogeneous continuous dielectric function leads to attractions as well as repulsions. The Lifshitz result emerges naturally in the limit of separations much larger than the thickness of the interfaces. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1796234]

I. INTRODUCTION

Fifty years after its formulation,[1] the Lifshitz theory of van der Waals interactions thrives,[2] its results essential in condensed matter physics, high-energy physics, colloid science, and cosmology.[3] The approximations on which it is based are usually realistic and lead to results that can be reliably compared with measurement. One restrictive condition built into the theory is the assumed steplike change in the dielectric permeability at the interfaces of bodies that interact across spatially homogeneous media. Several extensions of the theory have relaxed the condition of steplike interfaces but none has suggested a way to relax the condition of a uniform dielectric medium. What happens if one assumes a medium whose local dielectric response varies continuously across the entire space between bodies? So as to keep within the conditions of a macroscopic-continuum theory, we evaluate only that part of the van der Waals interaction free energy that is due to the inhomogeneity of the dielectric profile that varies slowly compared to the interatomic spacing.

We build on a recent reformulation of the Lifshitz theory[4] for media whose dielectric response varies stepwise in the z direction perpendicular to the planar interacting surfaces. We smooth that discrete result to the limit of a continuous dielectric profile $\epsilon(z)$. The new result is that at small spacings, where the diffuse interface profiles overlap, there is apparent repulsion; the removal of regions of inhomogeneity increases the interaction free energy leading finally to a vanishing interaction free energy upon the disappearance of inhomogeneities. At spacings that are large compared to the width of the inhomogeneous material interfaces, the Lifshitz form emerges naturally.

For illustration, we examine the consequences of the formulation for a representative form of the dielectric profile. We derive the interaction free energy as a function of the separation between diffuse interfaces. The properties revealed here should be relevant to interactions between the interfaces that exhibit a continuously varying dielectric profile whose form changes with separation.

II. THE DISCRETE LIMIT

We have recently reformulated the Lifshitz theory of macroscopic van der Waals interactions across a region composed of piecewise continuous dielectric response, by mapping it onto an algebra of 2×2 matrices that allows for a straightforward computation of the secular determinant of the electromagnetic (EM) field modes. Here we schematize the problem as shown in Fig. 1 to apply the reformulated Lifshitz theory as in Ref. 4.

We build on two fundamental matrices: the first is due to dielectric discontinuity

$$\mathbb{D}^{(i)} = \begin{bmatrix} 1 & -\overline{\Delta}_i \\ -\overline{\Delta}_i & 1 \end{bmatrix}, \tag{1}$$

where

$$\overline{\Delta}_i = \left(\frac{\rho_{i-1}\epsilon_i - \rho_i \epsilon_{i-1}}{\rho_{i-1}\epsilon_i + \rho_i \epsilon_{i-1}} \right). \tag{2}$$

Here, $\epsilon_i(\omega)$ is the (constant) dielectric function in the region

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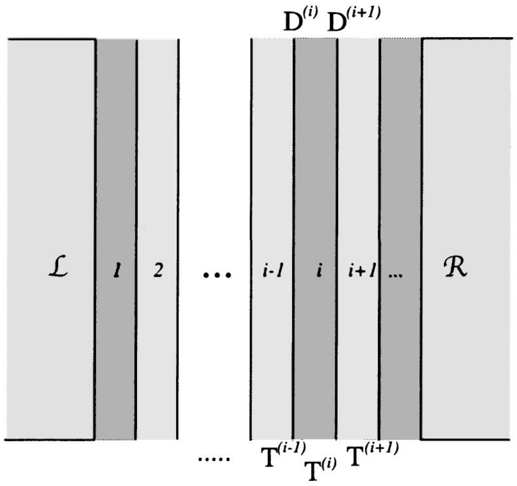

FIG. 1. Schematic representation of geometry in the discrete limit. The region between $\mathcal{L}$ and $\mathcal{R}$ of thickness ℓ is divided into N layers of thickness a, leading to the 11th element of the transfer matrix Eq. (9). In the continuous limit this leads to Eq. (13). Then we extend the region by moving the $\mathcal{L}$ boundary to $z\to-\infty$ and $\mathcal{R}$ to $z\to\infty$, as well as by assuming that there are no remainig dielectric discontinuities at these boundaries. This leads to Eq. (14) in the continuous limit.

$z_{i-1}<z<z_i$ and $\rho_i(\omega)^2=Q^2-\{[\epsilon_i(\omega)\mu_i(\omega)\omega^2]/c^2\}$, where $\mu_i(\omega)$ is the magnetic permeability, $\mathbf{Q}$ is the wave vector perpendicular to the transverse direction, ω is the frequency, and c is the velocity of light in vacuum. The second matrix is due to the propagation

$$\mathbb{T}^{(i)}=\begin{bmatrix}1 & 0\\ 0 & e^{-2\rho_i(z_i-z_{i-1})}\end{bmatrix}=\begin{bmatrix}1 & 0\\ 0 & c_i\end{bmatrix}. \tag{3}$$

$\mathbb{D}^{(i)}$ describes the effect of the boundary conditions on the EM modes at the dielectric boundary and $\mathbb{T}^{(i)}$ their propagation across a dielectrically homogeneous region. The above definitions are for the TM field modes. TE field modes are described analogously via a formal substitution

$$\overline{\Delta}_i=\left(\frac{\rho_{i-1}\epsilon_i-\rho_i\epsilon_{i-1}}{\rho_{i-1}\epsilon_i+\rho_i\epsilon_{i-1}}\right)\to\Delta_i=\left(\frac{\rho_{i-1}\mu_i-\rho_i\mu_{i-1}}{\rho_{i-1}\mu_i+\rho_i\mu_{i-1}}\right). \tag{4}$$

The region between $\mathcal{L}$ and $\mathcal{R}$ in Fig. 1, with its dielectric function continuously varying in the transverse z coordinate, is now discretized into N layers, where each of the layers of thickness $a_i=a=z_i-z_{i-1}$ is characterized by a constant dielectric function. In the limit of $N\to\infty$ and/or $a_i=a\to 0$ the discretized scheme smoothly approaches the continuum limit. More on this will be discussed later.

We introduce the transfer matrix $\mathbb{M}$,

$$\begin{aligned}\mathbb{M}&=\mathbb{D}^{(\mathcal{L})}\times\mathbb{T}\times\mathbb{D}^{(\mathcal{R})}\\ &=\begin{bmatrix}1 & -\overline{\Delta}_{\mathcal{L}}\\ -\overline{\Delta}_{\mathcal{L}} & 1\end{bmatrix}\times\mathbb{T}\times\begin{bmatrix}1 & -\overline{\Delta}_{\mathcal{R}}\\ -\overline{\Delta}_{\mathcal{R}} & 1\end{bmatrix},\end{aligned} \tag{5}$$

where

$$\mathbb{T}=\lim_{N\to\infty}\mathbb{T}^{(1)}\times\mathbb{D}^{(1)}\times\mathbb{T}^{(2)}\times\mathbb{D}^{(2)}\ldots\mathbb{T}^{(N-1)}\times\mathbb{D}^{(N-1)}\times\mathbb{T}^{(N)}. \tag{6}$$

Van der Waals interactions are then evaluated via an equation connecting the secular determinant (determinant of the coefficients of the EM modes in the prescribed geometry) with the fluctuation free energy of the form[4]

$$\mathcal{F}=kT\sum_{Q}\sum_{n=0'}^{\infty}\ln m_{11}(i\xi_n,Q), \tag{7}$$

where m_{11} is the 11th element of the transfer matrix $\mathbb{M}$, with an analogous form for the TE modes. The n sum goes over all the Matsubara frequencies, $\xi_n=2\pi(kT/\hbar)n$. The prime in the summation means that the $n=0$ term is given weight 1/2.

The matrix $\mathbb{M}$ can be evaluated explicitly to all orders in the discontinuity matrices $\mathbb{D}^{(i)}$ only for very simple dielectric profiles, most notably for profiles with a periodic motif as in Ref. 4. In the present case there is no periodicity in the profile. The methods of explicit evaluation of $\mathbb{M}_{11}$ to all orders do not apply. Nevertheless, if we limit ourselves to the lowest order limit (pairwise approximation) in the powers of the discontinuity matrices, we can still obtain an *approximate* form of the transfer matrix.

Consider the case of $N=2$, then $N=3$ and so on, to determine by induction the general form of $\mathbb{T}$ to the lowest order in $\overline{\Delta}_i$. To terms up to second order in $\overline{\Delta}_i$, we derive

$$\mathbb{T}=\begin{bmatrix}1+\sum_{i=1}^{N}\sum_{k=i+1}^{N-1}\overline{\Delta}_i\Delta_k\prod_{j=i+1}^{k}c_j+\cdots & -\sum_{k=1}^{N-1}\overline{\Delta}_k\prod_{j=k+1}^{N}c_j+\cdots\\ -\sum_{k=1}^{N-1}\overline{\Delta}_k\prod_{j=k+1}^{k}c_j+\cdots & \prod_{i=1}^{N}c_i+\sum_{i=1}^{N-1}\sum_{k=i+1}^{N-1}\overline{\Delta}_i\overline{\Delta}_k\prod_{j=1}^{i}\prod_{m=k+1}^{N}c_jc_m+\cdots\end{bmatrix}. \tag{8}$$

The next order term in the off-diagonal elements would be of third order in $\overline{\Delta}_i$; and in the diagonal elements, of fourth order in $\overline{\Delta}_i$. For smooth dielectric profiles the third and the fourth order terms are much smaller then the second order terms and can be omitted. To apply Eq. (7), we evaluate

$$\begin{aligned} m_{11} &= [\mathbb{D}^{(\mathcal{L})} \times \mathbb{T} \times \mathbb{D}^{(\mathcal{R})}]_{11} \\ &= 1 + \sum_{i=1}^{N} \sum_{k=i+1}^{N-1} \overline{\Delta}_i \overline{\Delta}_k \prod_{j=i+1}^{k} c_j + \overline{\Delta}_{\mathcal{R}} \\ &\quad \times \sum_{k=1}^{N-1} \overline{\Delta}_k \prod_{j=k+1}^{N} c_j + \overline{\Delta}_{\mathcal{L}} \sum_{k=1}^{N-1} \overline{\Delta}_k \\ &\quad \times \prod_{j=k+1}^{N} c_j + \overline{\Delta}_{\mathcal{L}} \overline{\Delta}_{\mathcal{R}} \\ &\quad \times \left(\prod_{i=1}^{N} c_i + \sum_{i=1}^{N-1} \sum_{k=i+1}^{N-1} \overline{\Delta}_i \overline{\Delta}_k \prod_{j=1}^{i} \prod_{m=k+1}^{N} c_j c_m \right). \end{aligned} \tag{9}$$

Again this result is exact to third order in $\overline{\Delta}_i$. The inhomogeneities in the dielectric response have to be overall small and, in the limit of $a_i = a \to 0$, the dielectric function should be continuous. Under these conditions, we now smooth the discrete jumps in the dielectric response ϵ_i, a formal consequence of the discretization procedure, into a continuous variation of $\epsilon(z)$.[5] Specifically

$$\epsilon_i \to \epsilon(z), \quad \rho_i \to \rho(z), \tag{10}$$

as well as

$$\epsilon_{i+1} - \epsilon_i \to \left(\frac{d\epsilon(z)}{dz} \right) dz, \quad \rho_{i+1} - \rho_i \to \left(\frac{d\rho(z)}{dz} \right) dz, \tag{11}$$

and with Eq. (2)

$$\overline{\Delta}_i \to \hat{\Delta}(z) dz, \quad \hat{\Delta}(z) = \frac{1}{2} \frac{d \ln \epsilon(z)/\rho(z)}{dz}. \tag{12}$$

The summation over i in Eq. (9) become integrals over z. In this way we obtain the *continuous* form of Eq. (9) as

$$\begin{aligned} \lim_{N\to\infty} m_{11} = {} & 1 + \int_0^{\ell} dz \int_z^{\ell} dz' \hat{\Delta}(z) \hat{\Delta}(z') \exp\left(-2 \int_z^{z'} \rho(z'') dz'' \right) + \Delta_{\mathcal{R}} \int_0^{\ell} dz \hat{\Delta}(z) \exp\left(-2 \int_z^{\ell} \rho(z'') dz'' \right) + \Delta_{\mathcal{L}} \int_0^{\ell} dz \hat{\Delta}(z) \\ & \times \exp\left(-2 \int_0^{z} \rho(z'') dz'' \right) + \Delta_{\mathcal{R}} \Delta_{\mathcal{L}} \exp\left(-2 \int_0^{\ell} \rho(z'') dz'' \right) \left(1 + \int_0^{\ell} dz \int_z^{\ell} dz' \hat{\Delta}(z) \hat{\Delta}(z') \exp\left(2 \int_z^{z'} \rho(z'') dz'' \right) \right). \end{aligned} \tag{13}$$

If the dielectric slab is homogeneous with small dielectric discontinuities at $\mathcal{L}$ and $\mathcal{R}$, the above result for the secular determinant obviously reverts to the standard form of the Lifshitz interaction[6] on the pairwise level in the limit of small inhomogeneities in the dielectric and magnetic permeabilities.

We now extend the region of inhomogeneity between $\mathcal{R}$ and $\mathcal{L}$ so that it comprises the whole z axis. We assume further that there are no discontinuities at the two boundaries, i.e., $\overline{\Delta}_{\mathcal{R}}$, $\overline{\Delta}_{\mathcal{L}} = 0$. Then, to lowest order, the secular determinant can be written as

$$\lim_{N\to\infty} m_{11} = 1 + \int_{-\infty}^{\infty} dz \int_z^{\infty} dz' \hat{\Delta}(z) \hat{\Delta}(z') \times \exp\left(-2 \int_z^{z'} \rho(z'') dz'' \right). \tag{14}$$

Note that the range of integration is now $-\infty$, $+\infty$ and that $\epsilon(z)$ is defined over the whole z axis. Should there be any additional discontinuities in the $\epsilon(z)$ the appropriate terms would have to be retained in Eq. (14), just as they were in Eq. (13).

From Eq. (7) we obtain the surface density of the Lifshitz free energy as a functional of the continuously graded dielectric function profile $\epsilon(z)$

$$\begin{aligned} \mathcal{F}[\epsilon(z)] &= kT \sum_{n=0}^{\infty}{}' \sum_{\mathbf{Q}} \ln m_{11} \\ &\simeq kT \sum_{n=0}^{\infty}{}' \int \frac{d^2\mathbf{Q}}{(2\pi)^2} \int_{-\infty}^{\infty} dz \int_z^{\infty} dz' \hat{\Delta}(z) \hat{\Delta}(z') \\ &\quad \times \exp\left(-2 \int_z^{z'} \rho(z'') dz'' \right), \end{aligned} \tag{15}$$

derived to the lowest order in the gradient of the dielectric function. In the nonretarded limit $c \to \infty$ only the $n=0$ term survives, leading to $\rho(z,\omega) = Q$. We can perform the Q integral explicitly, obtaining

$$\begin{aligned} \mathcal{F}[\epsilon(z)] &= \frac{kT}{16\pi} \int_{-\infty}^{\infty} dz \int_z^{\infty} dz' \frac{\hat{\Delta}(z) \hat{\Delta}(z')}{|z - z'|^2} \\ &= \frac{kT}{64\pi} \int_{-\infty}^{\infty} dz \int_z^{\infty} dz' \frac{\dfrac{d \ln \epsilon(z)}{dz} \dfrac{d \ln \epsilon(z')}{dz'}}{|z - z'|^2}. \end{aligned} \tag{16}$$

This limiting form of the free energy corresponds to a summation of the $(z - z')^{-2}$ interactions between thin slabs located at different z and z' and is thus intuitively very simple to understand. One could refer to it as the Hamaker limit for the continuous inhomogeneous dielectric. However at $z = z'$ this form of the free energy contains a spurious divergence, due to the continuum limit, which needs to be subtracted appropriately so as to regularize the free energy.

Note that Eq. (16) is a functional of the *gradients* of the dielectric function. The more inhomogeneous the dielectric profile the larger the integrand in the free energy Eq. (16). For vanishing inhomogeneities this free energy likewise vanishes by definition.

III. THE CONTINUUM LIMIT

Because we derived the result Eq. (13) via a continuum limit of a discretized problem, we have to be careful to exclude the self-interaction term, at $z=z'$, correctly from the expression Eq. (16). For points $z=z'$, we would obtain an infinite value of the integrand. This divergence is nevertheless spurious and is due to the following fact: in the discrete version of Eq. (15), the first term in Eq. (9), the index k starts at $k=i+1$, and is thus never equal to i. When going to a continuous limit, Eq. (15) the integral over z' should not start at z, but at a value $z'=z+a$, where at the end we should let $a\to 0$. In this way we exclude the van der Waals interaction self energy from Eq. (15).

We introduce the cutoff a into Eq. (15) that will take care of the self-interaction term. Then Eq. (15) becomes

$$\mathcal{F}[\epsilon(z)]=\frac{kT}{16\pi}\int_{-\infty}^{\infty}dz\int_{z}^{\infty}dz'\frac{\hat{\Delta}(z)\hat{\Delta}(z')}{(z'-z+a)^2}, \tag{17}$$

so that the two discrete layers in the sum, converted into an integral, cannot coincide. We now take the limit of this expression as $a\to 0$ and subtract this limit from $\mathcal{F}[\epsilon(z)]$. In this way we eliminate the infinite but artificial self-interaction term and thus regularize the interaction free energy. Regularization of the van der Waals interaction energy is well known in many different contexts.[3] First we expand

$$\hat{\Delta}(z')=\hat{\Delta}[z+(z'-z)]\sim\hat{\Delta}(z)-(z-z')\hat{\Delta}'(z)+\cdots, \tag{18}$$

where $\hat{\Delta}'(z)$ stands for the derivatives of $\hat{\Delta}(z)$ with respect to z. It will be clear that the first term gives the largest contribution in the limit $a\to 0$, and we can stop there. Inserting the above three terms into Eq. (17) and introducing new variables of integration, we obtain

$$\begin{aligned}\mathcal{F}_0[\epsilon(z)]&=\frac{kT}{16\pi}\int_{-\infty}^{\infty}dz\int_{z}^{\infty}dz'\frac{\hat{\Delta}(z)\hat{\Delta}(z')}{(z'-z+a)^2}\\&=\frac{kT}{16\pi}\int_{-\infty}^{\infty}dz\hat{\Delta}^2(z)\frac{1}{a}\int_0^{\infty}\frac{dy}{(1+y)^2}\\&\quad-\frac{kT}{16\pi}\int_{-\infty}^{\infty}dz\hat{\Delta}(z)\hat{\Delta}'(z)\int_0^{\infty}\frac{y\,dy}{(1+y)^2}+\cdots.\end{aligned} \tag{19}$$

Clearly the first term diverges in the limit $a\to 0$, and thus gives the largest contribution to the self-energy. The omitted higher order terms go to zero with different positive powers of a. Subtracting this divergent self-energy from Eq. (17) we remain with a well-defined and well-behaved regularized result

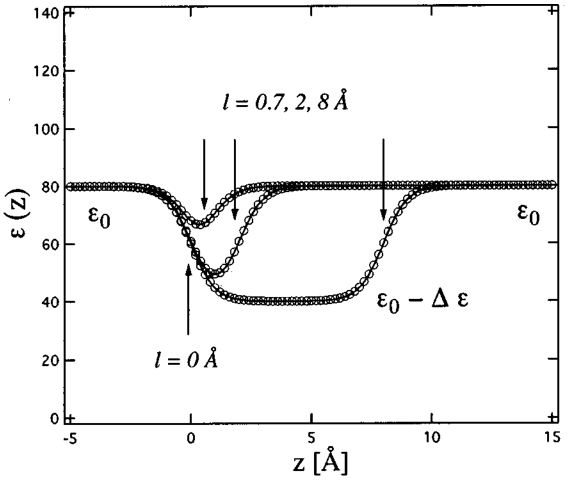

FIG. 2. The model inhomogeneous dielectric function $\epsilon(z)$ given by Eqs. (30) and (31) with $\sigma=1$ Å; $\ell=0.7$, 2, and 8 Å. For small $\ell\to 0$ the dielectric profile goes smoothly to a homogeneous dielectric response; for large ℓ it approaches a box with diffuse boundaries. Here $\epsilon_0=80$ and $\Delta\epsilon=40$. The origin of ℓ and the position of the second interface for $\ell=0.7$, 2, and 8 Å are indicated with arrows.

$$\begin{aligned}\mathcal{F}(\ell)&=\lim_{a\to 0}\{\mathcal{F}[\epsilon(z)]-\mathcal{F}_0[\epsilon(z)]\}\\&=\frac{kT}{16\pi}\int_{-\infty}^{\infty}dz\int_{z}^{\infty}dz'\frac{\hat{\Delta}(z)\hat{\Delta}(z')}{(z'-z+a)^2}\\&\quad-\frac{kT}{16\pi}\int_{-\infty}^{\infty}dz\hat{\Delta}^2(z)\frac{1}{a}.\end{aligned} \tag{20}$$

This regularized form of the free energy, where we have explicitly extracted the divergent self-interaction term is our objective. We should point out that the above regularization procedure is not extraordinary in any respect, one just needs to carry through the continuum limit of Eq. (9) appropriately.

In order to become familiar with the physical meaning of this result we consider the general and plausible spatially dependent dielectric function of the form

$$\epsilon(z)=\epsilon_0-\frac{\Delta\epsilon}{2}[f(z,0,\sigma)-f(z,\ell,\sigma)], \tag{21}$$

where for small σ, $f(z,z_0,\sigma)$ is almost steplike at $z=z_0$, of width σ. $\Delta\epsilon$ is the difference between $\epsilon(|z|\to\pm\infty)=\epsilon_0$ and the dielectric function at the midpoint $z=\ell/2$, see Fig. 2.

In standard Lifshitz theory $f(z,z_0,\sigma)$ is indeed a zero width Heaviside step function. Because $f(z,z_0,\sigma)$ is steplike, its derivative with respect to z, $f'(z,z_0,\sigma)$, must be deltalike. Here we give it a Gaussian form

$$f'(z,z_0,\sigma)=\frac{e^{-(z-z_0)^2/(2\sigma^2)}}{\sqrt{2\pi}\sigma} \tag{22}$$

together with the condition of small difference in the dielectric response, $(\Delta\epsilon/4\epsilon_0)\ll 1$. Then

$$\hat{\Delta}(z)=\frac{1}{2}\frac{d\ln\epsilon(z)}{dz}\approx\frac{\Delta\epsilon}{4\epsilon_0}[f'(z,0,\sigma)-f'(z,\ell,\sigma)]. \tag{23}$$

Inserting this into the free energy Eq. (20), we obtain

$$\mathcal{F}(\ell)=\mathcal{F}_0+\mathcal{F}_1(\ell), \tag{24}$$

where the ℓ-dependent part of the free energy can be written as

$$\begin{aligned}\mathcal{F}_1(\ell)=&-\frac{kT}{8\pi}\left(\frac{\Delta\epsilon}{4\epsilon_0}\right)^2\left(\int_{-\infty}^{\infty}dz\int_{z}^{\infty}dz'\right.\\&\times\frac{f'(z,0,\sigma)f'(z',\ell,\sigma)}{(|z-z'|+a)^2}\\&\left.-\frac{1}{a}\int_{-\infty}^{\infty}dz f'(z,0,\sigma)f'(z,\ell,\sigma)\right)\\=&-\frac{kT}{8\pi}\left(\frac{\Delta\epsilon}{4\epsilon_0}\right)^2\left(\int_{-\infty}^{\infty}dz\int_{0}^{\infty}du\right.\\&\times\frac{f'(z,0,\sigma)f'(z+u,\ell,\sigma)}{(u+a)^2}\\&\left.-\frac{1}{a}\int_{-\infty}^{\infty}dz f'(z,0,\sigma)f'(z,\ell,\sigma)\right).\end{aligned} \tag{25}$$

The ℓ-independent part of the free energy $\mathcal{F}_0$ is not of concern here. In the limit of large separations ℓ, where $\sigma \ll z_0$ so that $f'(z,z_0,\sigma)$ is a deltalike function, Eq. (25) takes on the form

$$\mathcal{F}_1(\ell)=-\frac{kT}{8\pi}\left(\frac{\Delta\epsilon}{4\epsilon_0}\right)^2\frac{g(\sigma/\ell)}{\ell^2} \tag{26}$$

where $\lim_{\ell\to\infty}g(\sigma/\ell)=\text{const}$ the expected lowest order inverse-square Lifshitz form for the attraction between two like, semi-infinite media of ϵ_0 across a medium of $\epsilon_0-\Delta\epsilon$. The Hamaker coefficient is slightly modified due to the smooth, diffuse boundaries.

Trickier, the small ℓ limit leads to a more fundamental insight. In the first integral of Eq. (25), it is clear on inspection that the only nonvanishing part of the integral is due to the region close to $u=0$. Thus we expand $f'(z+u,\ell,\sigma) = f'(z,\ell,\sigma)+uf''(z,\ell,\sigma)+(1/2)u^2f'''(z+u,\ell,\sigma)+\cdots$. Inserting this expansion into Eq. (25) and rearranging terms, we are left with

$$\begin{aligned}\mathcal{F}_1(\ell)=&-\frac{kT}{8\pi}\left(\frac{\Delta\epsilon}{4\epsilon_0}\right)^2\left[f_1(\ell)-\frac{f'(0,\ell,\sigma)}{a}\right.\\&\left.+\frac{1}{2}\sigma^2\left(f_3(\ell)-\frac{f'''(0,\ell,\sigma)}{a}\right)\right],\end{aligned} \tag{27}$$

where

$$\begin{aligned}f_1(\ell)&\equiv\int_0^\infty du\,\frac{f'(u,\ell,\sigma)}{(u+a)^2}\\f_3(\ell)&\equiv\int_0^\infty du\,\frac{f'''(u,\ell,\sigma)}{(u+a)^2}.\end{aligned} \tag{28}$$

Performing these integrals and taking the $a\to0$ limit we obtain

$$\mathcal{F}_1(\ell)=-\frac{kT}{8\pi}\left(\frac{\Delta\epsilon}{4\epsilon_0}\right)^2\frac{\ell e^{-(\ell^2/2\sigma^2)}}{\sqrt{2\pi}\sigma^3}\left(1-\frac{\ell^2}{\sigma^2}\right). \tag{29}$$

This expression represents the qualitative features of the small ℓ limit of the interaction free energy. Obviously in this limit attractive van der Waals interactions give way to repulsions. These are due to the fact that because the van der Waals interaction free energy Eq. (16) is a bilinear functional of $[d\ln z(z)/dz]$, it prefers gradients in the dielectric function. With the form of the dielectric function Eq. (21) for small ℓ, the state with larger inhomogeneities corresponds to larger spacings ℓ. Thus repulsion takes place.

Because of the repulsive small ℓ and the attractive large ℓ limit, the interaction free energy must have a minimum. Numerical computation with a specific model of the inhomogeneous dielectric function confirms these general traits.

IV. MODEL CALCULATIONS

Assume that the dielectric profile can be described as a box with diffuse boundaries, i.e.,

$$\epsilon(z)=\epsilon_0-\frac{\Delta\epsilon}{2}[f(z,0,\sigma)-f(z,\ell,\sigma)], \tag{30}$$

where now we consider

$$f(z,x,\sigma)=\tanh\frac{z-x}{\sigma}, \tag{31}$$

with σ the width of the dielectric interface, a step function if $\sigma\to0$. As a convenient numerical example we take $\epsilon_0=80$ and $\epsilon_1=40$. The dielectric profile for this form of $\epsilon(z)$ is presented in Fig. 2. It clearly shows how gradients in dielectric response develop for small ℓ and then lead to a diffuse box profile for large ℓ. This form of the inhomogeneous dielectric function is consistent with recent experimental results on the refractive index profile between two closely apposed grain boundaries.[7]

What are the consequences of assuming the above form of the inhomogeneous dielectric response for the van der Waals interaction free energy Eq. (20)? Does subtraction of the self-energy part of the interaction using the correct transition to the continuum limit in Eq. (20), really lead to a regularized free energy? Figure 3 shows the dependence of the regularized free energy on the self-energy cutoff a. For $a<0.01$ Å, this free energy effectively ceases to vary as a function of a. Thus the regularized free energy is indeed a well-behaved, finite function of separation ℓ.

Next we see from Fig. 4 that for large ℓ the van der Waals interaction free energy asymptotically approaches a constant value that reflects the van der Waals part of the formation energy of the interfaces. Because one usually defines the van der Waals interaction free energy to equal zero at large ℓ, it would be instructive to subtract the value found here at infinite spacing and plot the rescaled result $\mathcal{F}_{\mathrm{RS}}(\ell) = \mathcal{F}(\ell)-\mathcal{F}(\ell\to\infty)$. Also, in order to be able to compare the interaction for different values of the width of the diffuse interfaces σ, we define an effective spacing $D=\ell-\ell_{\min}$, where the rescaled interaction free energy goes through zero at $\ell_{\min}$ (usually at about $\ell\sim1.7\sigma$). The corresponding res-

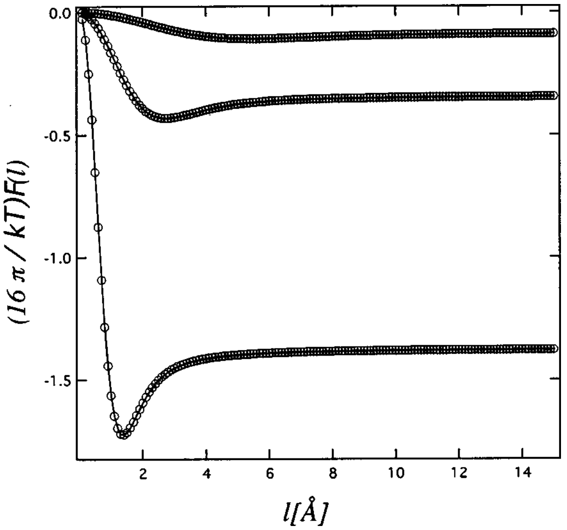

FIG. 3. The free energy vs ℓ computed using four different values of cut-off distance, $a=0.1$, 0.01, 0.001, and 0.0001 Å (curves from top to bottom). In all cases interfacial width is taken as $\sigma=1$ Å. For $a<0.01$ this regularized free energy losses its dependence on a.

caled free energy would then be $\mathcal{F}_{\mathrm{RS}}(D)=\mathcal{F}(D)-\mathcal{F}(D\rightarrow\infty)$. These rescaled plots for three values of σ, $\sigma=2$, 1, and 0.5 Å, are presented on Fig. 5.

The rescaled interaction free energy turns repulsive in the regime of the rescaled separations where diffuse interfaces start interpenetrating. As indicated in the preceding section, reversal from attraction to repulsion is due to the suppression of inhomogeneities in the dielectric function in the regime of small separations, see Fig. 2. The same effect can also be seen if we plot the local pressure $\mathcal{P}(z,\ell)$, such that the interaction free energy is

$$\mathcal{F}(\ell)=\int_{-\infty}^{+\infty}\mathcal{P}(z,\ell)dz. \tag{32}$$

Figure 6 shows $\mathcal{P}(z,\ell)$ for three values of ℓ at a constant diffuseness of the interfaces σ. Clearly the regions of z with largest attraction correspond to regions of $\epsilon(z)$ with the steepest gradients. As these regions become smaller with di-

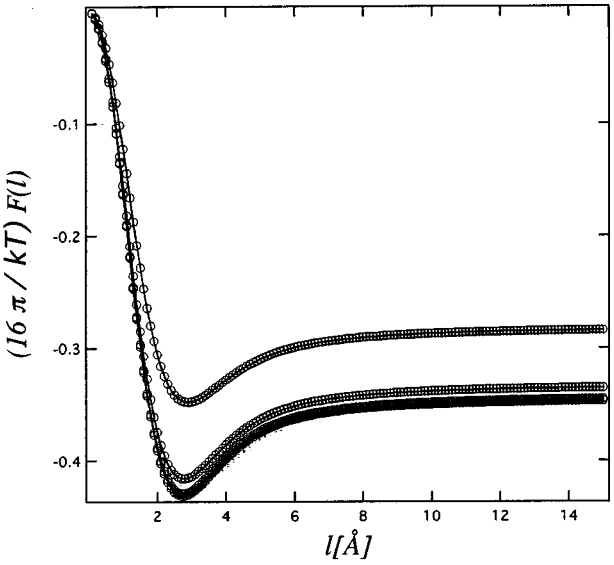

FIG. 4. Variation of the free energy Eq. (20) vs separation ℓ for three different values of the thickness of the interface σ, $\sigma=2$ (top), 1 (middle), and 0.5 Å (bottom curve) in the model inhomogeneous dielectric profile Eq. (30). In all three cases the free energy starts from zero and approaches a constant negative value for large spacings with a minimum in between.

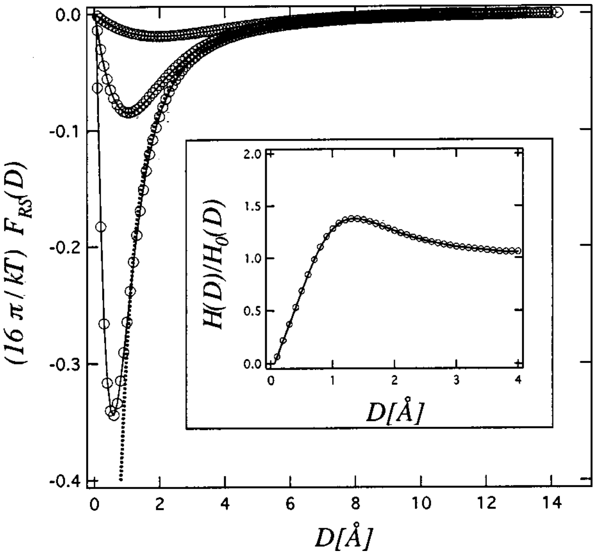

FIG. 5. Variation of the rescaled free energy Eq. (20) as a function of the interface thickness σ as well as the rescaled separation $D\equiv\ell-\ell_{\min}$, where at $\ell_{\min}$ the rescaled interaction free energy goes through zero (usually at about $\ell\sim1.7\sigma$). Top curve $\sigma=2$ Å, middle curve $\sigma=1$ Å and bottom curve $\sigma=0.5$ Å. The continuous dotted line represents the standard Lifshitz result with a sharp box profile. Clearly at large separations the inhomogeneous $\epsilon(z)$ result goes smoothly to the Lifshitz result. At small values of ℓ the interaction free energy goes continuously to zero for any finite value of the interfacial thickness σ. The inset shows the variation of the ratio between the interaction free energies (as effective Hamaker coefficients) for sharp $[H_0(D)]$ and diffuse $[H(D)]$ interfacial profiles for the case of $\sigma=1$ Å.

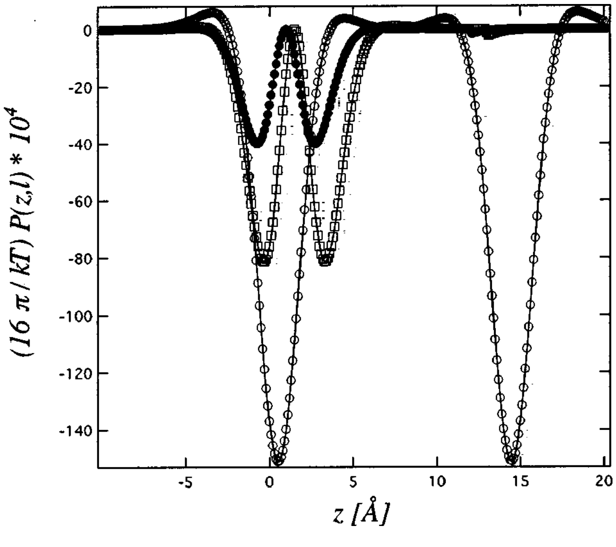

FIG. 6. Variation of the pressure $\mathcal{P}(z,\ell)$, defined in Eq. (32), as a function of the position z, for $\ell=20$ (open circles), 3 (squares), and 2 Å (filled circles); $\sigma=3$ Å in all three cases. Regions of z that make the biggest contribution to the free energy are clearly associated with most pronounced inhomogeneities in the z dependent dielectric function, i.e., the interfacial regions.

minishing ℓ, Fig. 6, the attraction itself becomes smaller and eventually vanishes. This is the reason that the inhomogeneity contribution to the interaction free energy between diffuse interfaces eventually turns repulsive at small spacings ℓ.

In the opposite limit of large ℓ the interaction free energies approach continuously the $\sigma=0$ Lifshitz limit of sharp interfaces. The smaller the diffuseness of the interfaces as quantified by σ, the faster the interaction free energy approaches the Lifshitz limiting form. Also the interaction free energies for different σ go through zero for the same values of the rescaled separation D.

The way the interaction free energy for diffuse interfaces approaches the Lifshitz result is more clearly seen if we plot the effective Hamaker coefficient, defined as $H(D) = 12\pi D^2 \mathcal{F}_{\mathrm{RS}}(D)$, as a function of the rescaled separation D. This is obtained by dividing the interaction free energy corresponding to finite σ with its Lifshitz value for infinitely sharp interfaces, everything else remaining the same. This is done in the inset of Fig. 5. We observe first of all that the effective Hamaker coefficient continuously approaches zero for small values of the rescaled spacing D. On increase of D it first overshoots the Lifshitz value and then approaches it from above. The reason for this is quite simple. Because of the diffuseness of the interfaces, parts of their dielectric profiles are at a smaller spacing than their average position. Parts of them are of course at a bigger spacing then the average position. However the van der Waals interaction decays approximately as the square of the separation and the parts of the dielectric profile, which are at smaller separations are weighted more heavily then the parts at larger separartions. This leads to an overshooting of the effective Hamaker constant that approaches its Lifshitz limit from above.

Though quantitative details will depend on the model inhomogeneous dielectric function, the qualitative features of the interaction are model independent.

V. CONCLUSIONS

Using a recent reformulation of the Lifshitz theory in terms of the transfer matrix, we have explored the effects of a continuously varying inhomogeneous dielectric response across the space between interacting planar bodies with diffuse boundaries. In particular, we have focused on that part of the van der Waals interaction free energy caused by a smoothly varying dielectric profile. At distances much larger than the width of the diffuse interfaces, the Lifshitz form of attraction between like bodies emerges naturally as expected. At small distances, comparable to the width of the interfaces, the calculated interaction free energy goes through a minimum, then increases with closer approach, as the diffuse interfaces merge and the region of inhomogeneity is suppressed.

Van der Waals forces feed off gradients, differences in dielectric response. In principle, an infinite amount of positive energy is needed to create the hypothetical step-function boundaries assumed in the original theory. The divergence of the Lifshitz energy at contact can be seen as a recovery of interface-creation energy. Conversely, gently graded interfaces enjoy gentler interactions. Here as in the original theory, we raise the question: What energy it takes to create the interface? We only assume a continuous profile of the dielectric function rather than the step between homogeneous media assumed in the original Lifshitz theory. We are able to extract that part of the interaction free energy that is due to inhomogeneities and notice its disappearance at small values of the separation when there are no more gradients. We are able to see too how this energy varies at all separations and, pleasingly, how it depends on the shape of the dielectric function profile.

Here the van der Waals interactions never become infinite for small interfacial separations as is usual in the standard Lifshitz theory. That divergence was an artifact due to the assumption of steplike dielectric boundaries preserved for all separations while in our case at small separations the interfaces smoothly merge. We can thus describe in detail how this merger is accomplished and what features of the interactions emerge at different spacings.

In doing so, we have pushed the continuum Lifshitz theory to its limit where macroscopic dielectric models must merge with microscopic considerations such as cost of creating a dielectric profile and changes in the profile themselves as functions of separation. Given a strategy to incorporate dielectric inhomogeneity, it is now possible to consider the continuously changing profile of gas or a solute molecules between confining walls even as it modifies the force between them. Van der Waals interactions between mobile molecules—with each other and with the walls—necessarily create nonuniform distribution. The resulting profile can be calculated self-consistently by invoking the Clausius-Mosotti equation, writing the free energy as a functional of solute density, then minimizing with appropriate constraints such as pressure or chemical potential. The power of this approach has already been demonstrated in the relation between ion binding to an interface, driven by van der Waals attraction, and ion specificity.[8] Extension to include forces of dielectric inhomogeneity from nonhomogeneous distribution of solute is a logical next step.[9]

ACKNOWLEDGMENT

The authors would like to thank Barry Ninham for his comments on an earlier version of the manuscript and for reassuring them that they were on the right track.

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