

# Self-consistent inhomogeneous dielectric response profiles from a nonlocal continuous Lifshitz formulation of van der Waals interactions

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**Abstract.** We show that a nonlocal formulation of the Lifshitz theory of van der Waals interactions valid for continuous dielectric profiles can be used as a starting point to *calculate* self-consistent dielectric profiles. The general approach advocated here is very close to the formulation of electrostatic self-consistent charge density profiles obtained from the Poisson - Boltzmann theory. The calculated dielectric profiles obtained from minimization of the free energy containing a lattice gas entropy contribution on top of the Lifshitz interaction energy give quite surprising and interesting results. The ramifications of these results for the distribution of polarizable matter between two homogeneous dielectric slabs will be discussed in detail.

## 1. Introduction

A growing number of polycrystalline ceramic systems has been found in the past decade that form partially ordered, disordered, or even amorphous equilibrium intergranular films at grain boundaries as well as at interfaces between dissimilar ceramic crystals [1]. In many cases this glassy film has an equilibrium thickness of the order of 1 nm, that depends strongly on the composition and type of ions in the glass phase and only weakly on the total amount of additives in the bulk [2]. The equilibrium thickness of an intergranular film can be understood from a colloid-like approach pioneered by Clarke and coworkers [3, 4] as a result of various attractive and repulsive contributions to the total free energy of the system. In a symmetric intergranular film the attractive contribution to the free energy is identified as the long-range van der Waals interaction, apart from which one should also include various specific interactions such as the effects of steric, disjoining, electrical double layer, solute adsorption, hydrogen bonding, capillary and applied external forces [5].

Van der Waals (vdW) interactions are ubiquitous and their effects are fundamental for understanding various properties of physical, chemical and biological systems [6]. In particular their effect has been recently considered in inorganic systems such as the intergranular films in silicon nitride structural ceramics [7] or interfaces and grain boundaries in perovskite based

electronic ceramics [8]. By far the most drastic effect of vdW interactions is observed in the surface water films on ice [9].

A decent estimate of the magnitude of the vdW interactions, usually codified in terms of the Hamaker coefficients [7], is always a demanding task that entails a detailed model for the frequency as well as spatial dependence of the dielectric spectra of substances involved [10]. The difficulties in the estimation of the magnitude of vdW interactions is translated into quite opposite conclusions as to whether they should be important [5] or negligible [11] in determining the equilibrium intergranular film thickness. In the first work [5] they appear to be the sole mechanism leading to attractive interactions that are counteracted by the steric repulsion due to ordering induced in the amorphous film, whereas in the second [11] they seem to be overshadowed by the image interactions in cases where at least one of the interfaces is metallic (a metalalumina interface).

In the Lifshitz theory of vdW interactions, which is a standard approach used in calculations of vdW interactions, one usually starts with a given frequency and spatial dependence of the dielectric response functions [6, 12]. The latter is usually assumed to be piecewise constant, exhibiting sharp Heaviside-like boundaries between different dielectric media [14]. It is now understood that this is an approximation [10] that can be circumvented [15, 13] and that the Lifshitz theory of vdW interactions can be formulated even for continuous boundaries. Equivalent results for a consistent extension of the Lifshitz theory have been obtained by the seamless extension of the DFT energy functionals (see [16, 17, 18, 19] and references therein) as well as the field approach based on the original Lifshitz formulation of the theory of vdW interactions [15, 13].

In this contribution we shall go one step further and investigate to what extent and at what conditions can the vdW interactions themselves self-consistently determine the spatial profile of the dielectric response. We will thus relax the constraint of a fixed, either piecewise constant or continuously varying, dielectric profile and will try to derive this profile by a self-consistent minimization of the complete (free) energy of the system. The *ansatz* for the free energy will contain only the soft contributions, *i.e.* the entropy and the vdW interaction energy, and will thus not contain any short-range, specific terms that are usually included into the DFT formulation [20]. In setting up the appropriate (free) energy functional we will conceptually follow the case of electrostatic interactions in intergranular films [11] substituting the non-local vdW (free) energy functional in place of the Coulomb interaction while keeping the lattice gas entropy the same. We then proceed just as in the Poisson-Boltzmann theory of electrostatic interactions except that in our case the minimization of the free energy functional can only be accomplished numerically. A somewhat related approach that, however, does not take into account the ion-ion dispersion interactions but only the wall-ion ones has been introduced recently by Edwards and Williams [21].

## 2. Formulation

Let us assume that we have a dielectric slab of dielectric permittivity  $\epsilon_m$  sandwiched between two semi-infinite regions of  $\epsilon_{\mathcal{R}}$  and  $\epsilon_{\mathcal{L}}$ . In the Lifshitz theory the fundamental quantity that determines the strength of vdW interactions are the dielectric permittivities evaluated at imaginary frequencies  $\xi$ , thus  $\epsilon_m(i\xi)$ ,  $\epsilon_{\mathcal{R}}(i\xi)$  and  $\epsilon_{\mathcal{L}}(i\xi)$  that can be obtained *via* the Kramers-Kronig transform from the real frequency response. The slab  $m$  between  $\mathcal{L}$  and  $\mathcal{R}$  is assumed to be composed of polarizable continuous matter of density  $\rho(z)$ , modelling the disordered core of an intergranular film. The spatial density profile thus leads to a spatial dielectric profile  $\epsilon(i\xi; z) = \epsilon(i\xi; \rho(z))$ . To the lowest order one can assume a linear relationship between the density and the dielectric permittivity mediated by the frequency dependent polarizability  $\alpha(i\xi)$  thus giving

$$\epsilon(i\xi; z) = \epsilon(i\xi; \rho(z)) \cong 1 + \alpha(i\xi)\rho(z) + \mathcal{O}(\rho^2(z)). \quad (1)$$

We start with the boundary integral representation of the nonretarded dispersion interaction [22], which allows us to express the vdW free energy functional in terms of operators whose domain is limited only to the boundaries between the domains of different constant permittivity

$$\mathcal{F}_{\text{vdW}} = k_B T \sum_{n=0}'^{\infty} \text{Tr}_S \ln (1 + 2\Delta_{\mathbf{r}}(i\xi_n) \mathbf{n}_{\mathbf{r}} \cdot \nabla G_{\mathbf{r},\mathbf{r}'}) \quad (2)$$

where  $\text{Tr}_S$  denotes the surface integral over all the boundaries in the system,  $\Delta_{\mathbf{r}} = \frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1}$ , where  $\epsilon_2$  is the dielectric constant of the material on the side of the boundary to which the normal  $\mathbf{n}_{\mathbf{r}}$  is pointing,  $G_{\mathbf{r},\mathbf{r}'} = 1/|\mathbf{r} - \mathbf{r}'|$  and where  $\xi_n = \frac{2\pi n k_B T}{\hbar}$  are the imaginary Matsubara frequencies. The prime in the above summation over  $n$  denotes that the zero term should be taken with the weight of one half. The distance variation of the vdW interaction enters via the Green's function  $G$ , whose contributions decrease as the boundaries between different regions are separated.

In [22], we also treated the Lifshitz case [6] of a planar slab of a dielectric that is surrounded by two other semi-infinite dielectrics to either side using the above formulation. In this case, due to the translational symmetry, the eigenvalues of the above operator are separated with respect to the perpendicular wavevector  $Q$ , which allows the free energy to be written alternatively as

$$\mathcal{F}_{\text{vdW}} = k_B T \sum_{n=0}'^{\infty} \int \frac{d^2 \mathbf{Q}}{(2\pi)^2} \ln \det(1 + K(Q, i\xi_n)), \quad (3)$$

where

$$K(Q, i\xi_n) = \begin{bmatrix} 0 & -\Delta_1 \exp(-Qd) \\ \Delta_2 \exp(-Qd) & 0 \end{bmatrix} \quad (4)$$

if the  $\Delta_i$  are defined as if all the normals point in the same chosen direction and where  $d$  is the distance between the two boundaries. The dependence on  $\xi_n$  enters via the frequency dependence of  $\epsilon$  in the definition of  $\Delta_i$ . The  $\Delta_{1,2}$  are defined for each of the boundaries as in the equation (2).

We may consider the smooth density profile in the slab  $m$  to be split into thinner slabs of constant permittivity. Proceeding in a similar way as for the Lifshitz case, this approach then gives a larger matrix  $K$  of dimension  $N \times N$ , where  $N$  is the number of boundaries between the slabs. The matrix elements corresponding to the interaction between the boundaries  $i$  and  $j$  are

$$K_{ij} = \text{sgn}(d_{ij}) \Delta_i \exp(-|Qd_{ij}|) \quad (5)$$

where  $d_{ij} = z_i - z_j$  is the difference of the  $z$  coordinates (perpendicular to the slabs) between two different slab boundaries  $i$  and  $j$ , with the  $z$  direction being perpendicular to the slabs, and

$$\Delta_i = \frac{\epsilon_{i+1} - \epsilon_i}{\epsilon_{i+1} + \epsilon_i}, \quad (6)$$

where  $\epsilon_i, \epsilon_{i+1}$  are the dielectric constants of the slabs to the either side of the boundary  $i$ . If the material in the entire slab contains no polarizable continuously distributed matter, then all the  $\Delta_i$  apart from those corresponding to the boundaries of  $m$  with  $\mathcal{R}$  and  $\mathcal{L}$  are equal to 0 and  $N = 2$ . In this case the above result obviously reduces to the standard non-retarded Lifshitz formula for the interaction between  $\mathcal{R}$  and  $\mathcal{L}$  across  $m$  [6].

Choosing the form of  $\rho(z)$ , the above vdW free energy functional gives us the corresponding vdW interaction energy in the non-retarded limit. The form of the spatial density profile here is completely arbitrary. If there are other contributions to the total free energy of the system due to the same inhomogenous density distribution, then the total free energy should be given by

$$\mathcal{F}_{\text{tot}} = \mathcal{F}_o[\rho(z)] + \mathcal{F}_{\text{vdW}}[\rho(z)] \quad (7)$$

and is of course itself a functional of the inhomogeneous density.  $\mathcal{F}_o[\rho(z)]$  is in general a complicated density functional containing the effects of steric disjoining, electrical double layer, solute adsorption, hydrogen bonding, capillary and applied external forces [5]. It contains all the short range interactions as well as the various entropy terms. We will not deal with the short range terms here. Instead we will concentrate solely on the entropy.

Assume that the thermalized polarizable particles composing  $\rho(z)$  live on a background crystalline lattice which is a reasonable assumption for intergranular films. In this case one can take the entropy to be given by its lattice gas expression [11] yielding

$$\mathcal{F}_o[\rho(z)] = -TS[\rho(z)] = k_B T \int_0^\ell dz \left[ \rho(z) \ln \frac{\rho(z)}{\rho_0} + (\rho_1 - \rho(z)) \ln \frac{\rho_1 - \rho(z)}{\rho_1 - \rho_0} \right]. \quad (8)$$

Here  $\rho_0$  can be identified either with the density in the reservoir assumed to be in thermodynamic equilibrium with the slab or simply seen as a constant determined by the chemistry of the film. This form of the entropy obviously saturates for  $\rho(z) = \rho_1$  and thus allows only finite density bounded by  $\rho_1$ . The lattice gas entropy and the vdW interaction free energy are by assumption the only terms entering the total free energy functional of the system. If we do not assume a form for the inhomogeneous density profile  $\rho(z)$ , then Eq. 7 represents a non-equilibrium free energy and its minimum value is the equilibrium free energy.

In principle this is all very similar to the case of a classical Coulomb lattice gas [11], except that the vdW interaction energy takes the role of the Coulomb interaction energy. In the case of a Coulomb lattice gas the minimization of the equivalent free energy functional leads to a Poisson-Boltzmann type mean-field theory [11]. In the present formulation it leads to equilibrium density determined not by the Coulomb interactions but by the vdW interactions. Analogous but different. We also need to point out the fundamental difference between this work and the superficially similar work of Edwards and Williams [21]. Note that in their case the vdW interaction modifies only the mean-electrostatic potential of charged particles, but does not influence in any way the density of non-charged but polarizable particles.

The total free energy functional, Eq. 7, is essentially non-linear and does not lead to any simple if even approximate expressions as in the case of the Poisson-Boltzmann theory. This means that it can and has to be minimized numerically.

### 3. Method of solution

Experience shows that using the fomulation in Eq. 5, which is the approximation of local dielectric response, the full free energy functional Eq. 7 does not lead to nonsingular solutions. This is to be expected as it has been shown [12] that it is only when properly taking into account the nonlocality of the dielectric response, which is typically related to atomic size, that the short distance singularities of the vdW theory are removed. In our example, it is not even sufficient to introduce nonlocality just in the direction of the planar symmetry [16] but a full nonlocal treatment is required in the  $z$  direction as well.

If nonlocality is omitted, then the approach based on Eq. 5 is equivalent to the nonretarded version of the free energy formulation [15] that involves a product of  $2 \times 2$  matrices, but is more expensive to compute as it involves an  $\mathcal{O}(N^3)$  diagonalization in order to compute the determinant, while the matrix product approach is of the order  $\mathcal{O}(N)$  in terms of computational complexity. To introduce nonlocality in the  $z$  direction we are, however, required to use the full matrix approach. One approximation that can, however, be made, is to take the lowest nonzero contributing term in the logarithmic expansion, such that

$$\ln \det(1 + K) = -\frac{1}{2} \text{Tr} K^2 + \mathcal{O}(K^3). \quad (9)$$

This follows from the relationship  $\ln \det A = \text{Tr} \ln A$ , the expansion of the logarithm and taking into account that the linear term is  $\text{Tr} A = 0$ . This approximation is only of the order of  $\mathcal{O}(N^2)$  in computational complexity and corresponds to a pairwise summation of vdW forces. We use this approximation in the computations that follow.

Polarizability of a medium is not local but responds also to the nearby electric fields. The typical distance for such a response is atomic in scale. As in [12], we use the Gaussian ansatz

$$\alpha(\mathbf{r}, \mathbf{r}') \propto \exp(-(\mathbf{r} - \mathbf{r}')^2 / (2\sigma^2)). \quad (10)$$

Where  $\mathbf{r}$  is the point of the electric field application and  $\mathbf{r}'$  is the point of induced polarization. This introduces nonlocality in both the planar and perpendicular directions. In the directions of the plane, this results in a  $Q$  dependent dielectric function where we may use the ansatz

$$\tilde{\epsilon} = 1 + (\epsilon - 1) \exp(-Q^2\sigma^2/2), \quad (11)$$

which is just the statement (10) in a Fourier transformed representation. The nonlocality in the  $z$  direction can be handled by smoothing out the matrix elements  $K_{ij}$  in a similar fashion to the smoothing of the Green functions in [12]. This smoothing turns the  $\text{sgn}$  function into an  $\text{erf}$ . We use a simpler *ansatz* to compute

$$\tilde{K}_{ij} = \tanh\left(\frac{d_{ij}\sqrt{2}}{\sigma\sqrt{\pi}}\right) \Delta_i \exp(-|Qd_{ij}|), \quad (12)$$

where we match the derivative of the  $\tanh$  function at the origin to that expected from the  $\text{erf}$ .

Using expression Eq. 3 for the vdW free energy, we then set on to minimize the combined free energy Eq. 7. We split the area between the outmost boundaries into  $M$  slabs of piecewise constant density  $\rho$ . Clearly the number of boundaries is then  $N = M + 1$ . We then seek to minimize the functional with respect to  $M$  density variables via the steepest descent method.

The components of the gradient of the functional are determined numerically by slightly varying each individual density variable and recalculating the free energy, then subtracting this value from the reference density. As the computation of the gradient is the most computationally expensive part, the search proceeds in (adaptable) discrete steps along this direction until an approximate minimum is found, upon which a new gradient is computed and the process is repeated until convergence. In case there is more than a single local minimum present in the density functional, the steepest descent minimization also allows us to observe hysteresis effects if we take the solution of one problem as a starting condition for a slightly different problem.

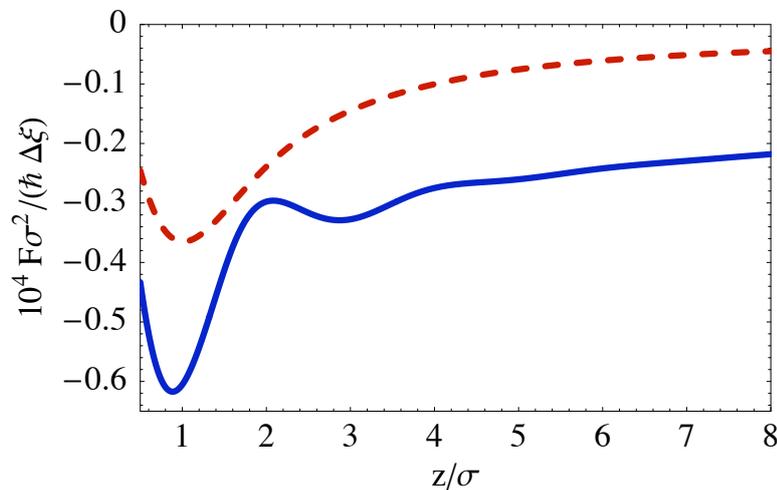
#### 4. Results

We have minimized the total free energy Eq. 7 for a system with a continuous density distribution described by a lattice gas entropy and interacting via vdW interactions, obtained the corresponding equilibrium density profiles and evaluated the equilibrium total free energy. For the model purposes we assume that the dielectric response  $\epsilon(i\xi)$  is constant on an interval from 0 to  $\Delta\xi$  and then drops to 1, as this effectively reduces the summation over  $n$  in Eq. 3 to a single term. The dielectric constant of the surrounding material was taken to be  $\epsilon_{\mathcal{L}} = \epsilon_{\mathcal{R}} = 2$ , with the dielectric constant for the gas varying linearly from  $\epsilon_0 = 1$  for zero density and  $\epsilon_1 = 2$  for maximum density  $\rho_1$ . The equilibrium density was chosen as  $\rho_0 = \rho_1/2$ . The minimization routine was run for two different values of the coupling constant defined as

$$\gamma = \frac{k_B T \rho_1 \sigma^3}{\hbar \Delta\xi} \quad (13)$$

which is obviously proportional to the temperature.

We are concerned with  $\gamma$  in the region where the self interaction of the gas via the vdW interaction starts to qualitatively alter the solution from the high temperature, almost homogeneous case. In Fig. 1, for high temperature  $\gamma = 10^{-3}$ , as shown dashed, the free energy is monotonic, behaving asymptotically as the inverse square of the interlayer separation just as in the standard Lifshitz case [6], while the equilibrium density profile as shown on the left side of the series of pictures in the Fig. 2 shows only marginal inhomogeneity. The van der Waals interactions never become infinite for small interfacial separations as is usual in the standard Lifshitz theory [6]. That divergence was shown to be an artifact due to the assumption of step-like dielectric boundaries preserved for all separations [15], while in our case the divergence is removed due to the nonlocality of the polarizability. The nonlocality is also responsible for the first minimum of the vdW interaction as a function of the separation distance  $z$  at about  $z \approx \sigma$  in Fig 1. The dispersion interactions can only become significant once the walls are separated by more than the typical atom size, but then also drop off with the distance as per the usual Lifshitz example.

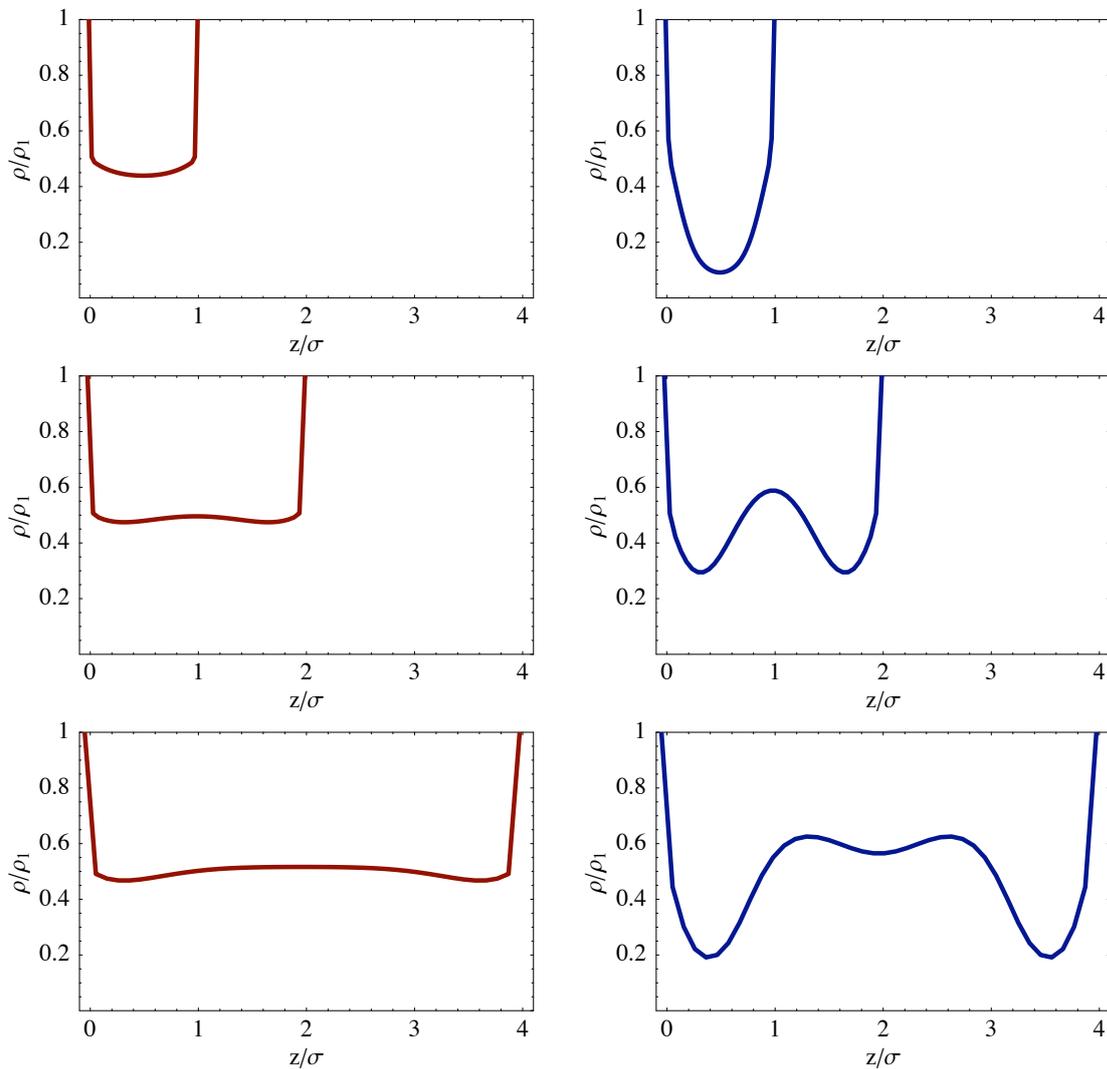


**Figure 1.** The minimum free energy as a function of the separation for the coupling constant  $\gamma = 10^{-3}$  (dashed) and  $\gamma = 2.5 \times 10^{-4}$  (full curve).

At a smaller value of the coupling constant  $\gamma = 2.5 \times 10^{-4}$ , corresponding also to a smaller temperature, the vdW interaction free energy (shown as a full curve in Fig. 1), as well as the equilibrium density profile (the right hand side series of pictures in Fig. 2), show a much richer texture. As vdW interactions, that feed off gradients in the density profile, become more dominant the equilibrium density shows incipient layering between the outer semi-infinite homogeneous dielectrics. The imprint of this layering shows as a non-monotonic dependence of the equilibrium free energy on the interlayer spacing. In this case the lattice gas entropy is simply not enough to smoothen out the tendency of the vdW functional towards layering. Further reduction of the coupling constant would make these tendencies even more pronounced leading finally to a complete layering of the density profile. In the case of these strong inhomogeneities the free energy functional would have to be augmented by appropriate (gradient) terms that would tend to counter the vdW tendency towards layering.

## 5. Conclusions

We have constructed a non-equilibrium free energy functional that contains the contribution of vdW interactions as well as a lattice-gas entropy term, capturing some degrees of freedom of the interlayer material. Numerical minimization of this functional, yielding equilibrium density



**Figure 2.** The self consistent density profiles for the separations  $1\sigma$ ,  $2\sigma$  and  $4\sigma$  from top to bottom, with the left series corresponding to  $\gamma = 10^{-3}$  and the right series to  $\gamma = 2.5 \times 10^{-4}$ .

profiles as well as the equilibrium free energy, clearly shows the tendency of vdW interactions towards layering. In the present description this tendency is opposed solely by the lattice-gas entropy terms. A more realistic description would have to acknowledge also other, short range interaction terms in the total free energy functional that would presumably lead to further smoothing out of the density profile. For small enough temperatures the vdW layering should nevertheless be the salient feature of the behavior of this system.

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