

## Wetting and thick-thin film transitions in a model of argon at a solid CO<sub>2</sub> substrate

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(Received 30 September 1982)

Using a simple free-energy functional, we have determined the location of the transition from partial to complete wetting and the thick-thin-film transition line for a model of gaseous argon at a solid carbon dioxide substrate. The wetting transition temperature is significantly higher than that calculated by Ebner and Saam for the same model and the thick-thin transition line lies much closer to the bulk gas-liquid coexistence curve. Our results suggest that thick-film formation will only occur for high temperatures and this is why such films have not been observed in computer simulations and in other recent studies of this model. We show that long-ranged transverse (parallel to the surface) pairwise correlations occur at the edge of the thick and thin films which coexist on the transition line. The range of these correlations becomes infinite at the surface critical temperature and, for the thick film, at the wetting transition temperature.

It is the purpose of this Comment to reexamine the problem of thick-film formation and wetting transitions in models of adsorption. This subject has been somewhat controversial since 1977 when Ebner and Saam<sup>1</sup> reported the calculation of a new surface phase transition for a gas adsorbed at a model substrate. By minimizing an approximate free-energy functional they calculated the equilibrium density profiles and the free energy for a Lennard-Jones 12-6 model of gaseous argon at a Lennard-Jones 9-3 model of a solid carbon dioxide substrate. They found that for temperatures  $T < T_w$ , the wetting temperature, the coverage remained finite in the limit where the bulk gas pressure  $p \rightarrow p_0(T)$ , the saturated vapor pressure, from below. In this temperature range very thick, unsaturated films never appeared. For  $T_w \leq T < T_{sc}$  a thick film of liquidlike density develops at the substrate when the gas is slightly undersaturated and the thickness of the film becomes infinite at saturation,  $p = p_0(T)$ . This latter situation corresponds to complete wetting<sup>2</sup> of the solid-gas interface by liquid. When the undersaturation is larger (smaller pressure) the thick film becomes unstable with respect to the formation of a thin film and the equilibrium structure of the interface changes discontinuously; this is referred to as the thick-thin-film transition or the first-order surface transition<sup>2</sup> or, more recently, prewetting.<sup>3</sup> The relevant order parameter is the coverage or the film thickness which changes discontinuously at the transition. On the transition line the two different films coexist. As  $T \rightarrow T_{sc}$ , the surface critical temperature, from below, the distinction between the coexisting thick and thin films disappears and at  $T = T_{sc}$  there is only one density profile and a single finite coverage. For  $T_{sc} < T < T_c$ , where  $T_c$  is the bulk liquid-gas critical

temperature, the coverage grows continuously and becomes infinite as  $p \rightarrow p_0(T)$ .

Ebner and Saam's work is important since it appears to provide the first explicit calculation of the wetting transition, i.e., the transition from partial wetting ( $T < T_w$ ) to complete wetting ( $T > T_w$ ), and of the thick-thin-film transition. Both were predicted from general arguments by Cahn<sup>2</sup> in a seminal paper also published in 1977. Cahn's paper has stimulated much recent experimental<sup>4</sup> and theoretical<sup>5</sup> work on wetting transitions. Subsequently several authors<sup>6-9</sup> have cast doubts on the validity of Ebner and Saam's results.

Monte Carlo simulations<sup>6</sup> of the same model failed to find the thick-thin-film transition and did not find *any* thick, liquidlike films at the temperatures and bulk gas densities for which they performed the simulations. Calculations based on a linearized Percus-Yevick<sup>6,10</sup> and a modified hypernetted chain<sup>8</sup> closure approximation of exact equations for the density profile of the inhomogeneous fluid yield results which are close to those obtained in the simulations; these theories do not predict thick-film formation at the temperatures and densities for which Ebner and Saam found such films. Recent calculations<sup>9</sup> based on a square-gradient approximation to the free-energy functional also contradict Ebner and Saam's results. On the other hand, Monte Carlo simulations<sup>11</sup> and mean-field treatments<sup>12</sup> of *lattice-gas* models of adsorption have demonstrated the existence of both the wetting transition and the thick-thin-film transition. Moreover, the calculated (temperature-thickness) coexistence curve for the latter is similar to that found by Ebner and Saam<sup>1</sup> in their density functional calculations for continuum fluids.

Ebner<sup>11,12</sup> does make the important remark that the location of the wetting transition temperature  $T_W$ , which marks the low-temperature end of the thick-thin-film transition line, is strongly dependent on the strength of the attractive part of the substrate-gas potential and is probably also strongly dependent on the type of theory used to calculate it. We have come to the same conclusion from our recent study<sup>13</sup> of wetting transitions for various models of the solid-gas interface. Using mean-field free-energy functionals of the type employed by Sullivan<sup>7</sup> we have shown that the wetting transition can be first order, as predicted by Cahn<sup>2</sup> and found by Ebner and Saam,<sup>1</sup> or second order, as found by Sullivan.<sup>7</sup> In the latter case the coverage increases continuously at the transition and there is no thick-thin-film transition for  $T > T_W$ . If the attractive solid-fluid and fluid-fluid potentials are taken to be exponentially decaying functions of distance, the transition is second order if the range of solid-fluid potential is less than or equal to that of

the fluid-fluid potential; it is possible for the transition to be of first order only if the solid-fluid potential is longer ranged. We found that the location of the thick-thin-film transition line depends sensitively on the strength and range of the attractive part of the solid-fluid potential; the stronger and longer its range, the smaller is  $T_W$ . The results<sup>13</sup> of some numerical calculations and of an approximate analytical theory indicate that the wetting transition is always first order for the Lennard-Jones 12-6 fluid at a Lennard-Jones 9-3 substrate but we again expect  $T_W$  to depend strongly on the well-depth of the solid-fluid potential.

The present work was undertaken in an attempt to determine whether the model system studied by Ebner and Saam does exhibit a wetting transition and a thick-thin-film transition and, if so, what are their locations in the temperature-density plane.

In our calculations we have used the same grand potential functional as previously<sup>13,7</sup>:

$$\Omega_V[\rho] = \int d\vec{r} f_h(\rho(\vec{r})) + \frac{1}{2} \int \int d\vec{r} d\vec{r}' w_2(|\vec{r} - \vec{r}'|) \rho(\vec{r}) \rho(\vec{r}') - \int d\vec{r} [\mu - V(\vec{r})] \rho(\vec{r}) \quad , \quad (1)$$

where  $\mu$  is the chemical potential and  $V(\vec{r})$  is an external potential. In this model the repulsive-force contribution to the free energy is treated in the local-density approximation<sup>14</sup>:  $f_h(\rho)$  is the Helmholtz free-energy density of a uniform hard-sphere fluid of density  $\rho$ ; the attractive forces are treated in mean-field fashion:  $w_2(r)$  is the attractive part of the pairwise potential characterizing fluid-fluid interactions. The equilibrium density of the inhomogeneous fluid,  $\rho(\vec{r})$ , is given by minimizing (1) and satisfies, therefore,

$$\mu_h(\rho(\vec{r})) = \mu - V(\vec{r}) - \int d\vec{r}' w_2(|\vec{r} - \vec{r}'|) \rho(\vec{r}') \quad , \quad (2)$$

where  $\mu_h(\rho) = df_h(\rho)/d\rho$  is the hard-sphere chemical potential. The minimum value of  $\Omega_V$  is the grand potential of the inhomogeneous fluid. The solid-fluid potential is that used by Ebner and Saam to model argon on carbon dioxide:

$$V(\vec{r}) \equiv V(z) = 4\pi\epsilon_0 w \rho_w \sigma_w^3 \left[ \frac{1}{45} \left( \frac{\sigma_w}{z} \right)^9 - \frac{1}{6} \left( \frac{\sigma_w}{z} \right)^3 \right] \quad , \quad (3)$$

with  $\epsilon_0 w/k_B = 153$  K,  $\sigma_w = 3.727$  Å, and  $\rho_w \sigma_w^3 = 0.988$ .  $w_2(r)$  is taken to be the attractive part of the Lennard-Jones 12-6 potential; it is zero for  $r < \sigma$  and equal to  $\phi_{LJ}(r)$  for  $r > \sigma$ .

The Lennard-Jones parameters are those for argon:  $\epsilon/k_B = 119.76$  K and  $\sigma = 3.405$  Å and the hard-sphere free energy was calculated from the Carnahan-Starling<sup>15</sup> formula using the hard-sphere diameter  $d$

obtained from the Barker-Henderson<sup>16</sup> prescription.  $d$  is weakly temperature dependent. Equation (2) was solved iteratively<sup>13</sup> to obtain the equilibrium density profiles  $\rho(\vec{r}) \equiv \rho(z)$ . The method of locating the wetting transition temperature and determining the thick-thin transition line is described fully in our earlier paper.<sup>13</sup>

Our results for the thick-thin-film transition line are plotted in Fig. 1, where they are compared with those of Ebner and Saam.<sup>1</sup> Also plotted in this figure are the gas-liquid coexistence curves calculated from the two different theories. It is clear that our present value for the (reduced) wetting transition temperature  $T_W^* \equiv k_B T_W/\epsilon = 0.957$  is significantly higher than that found by Ebner and Saam ( $T_W^* = 0.77$ ). The difference between the results becomes more significant when these are expressed as a fraction of the bulk critical temperature. Our result is  $T_W/T_c = 0.871$ , whereas that of Ebner and Saam is  $T_W/T_c = 0.582$  (Ebner and Saam determined the bulk coexistence curve from the Percus-Yevick approximation which gives a critical temperature  $T_c^* = 1.325$ , whereas our value is  $T_c^* = 1.099$ ). The thick-thin-film transition line is very short in our case since  $T_{sc}^* = 0.988$ . Ebner and Saam calculate a much longer transition line (see Fig. 1) with  $T_{sc}^* = 0.92$ . Moreover our transition line lies extremely close to the gas-liquid coexistence curve (this is not apparent from the diagram but see the figure caption). The relative undersaturation of the bulk gas, defined by  $\delta_g \equiv 1 - \rho_b/\rho_g$ , where  $\rho_b$  is the density of the bulk gas and  $\rho_g$  is the saturated vapor density at the same temperature, is only  $\sim 0.01$  at the surface critical point. The corresponding quantity in Ebner and

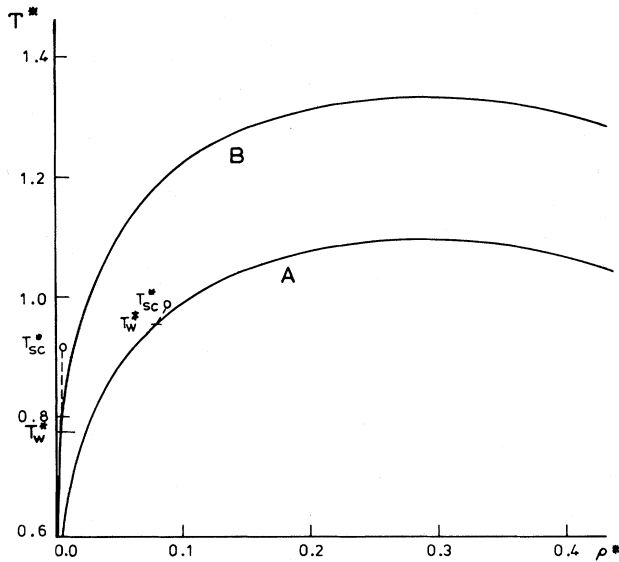


FIG. 1. Temperature-density phase diagrams for the present model of Ar adsorbed on a  $\text{CO}_2$  substrate. The solid curves are portions of the gas-liquid coexistence curves calculated by the present theory (A) and by Ebner and Saam (B). The dashed lines are the corresponding thick-thin transition lines. These terminate, in each case, at the wetting-transition temperature  $T_w^*$  and at the surface critical temperature  $T_{sc}^*$ , the latter is marked by a circle. In reality the transition lines lie almost on top of the coexistence curves but we have displaced the former to make them more distinct.  $\rho^* \equiv \rho\sigma^3$  and  $T^* \equiv k_B T/\epsilon$ .

Saam's work is  $\sim 0.07$ . In other words we find that for  $T \leq T_{sc}$  thick films are only stable if the relative undersaturation is less than 1% while for temperatures just above  $T_w$  thick films will only be stable at extremely small undersaturations. In Fig. 2 we plot the temperature-thickness phase diagram calculated for this model. For  $T < T_w$  the thickness  $t$  corre-

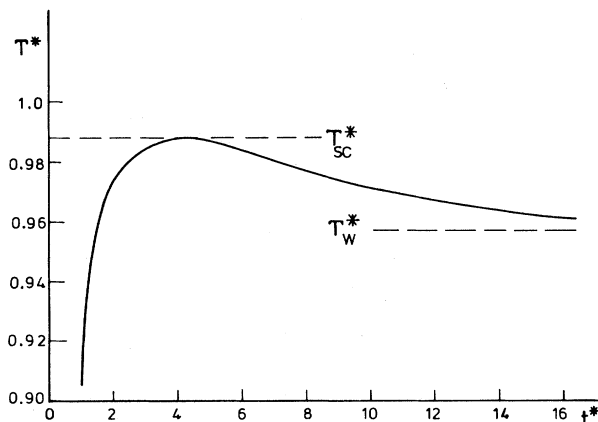


FIG. 2. Temperature-thickness diagram for the present model. The thickness  $t$  is defined by Eq. (4).  $t^* \equiv t/\sigma$  and  $T^* \equiv k_B T/\epsilon$ .

sponds to the density profile of the fluid when  $p = p_0(T)$ . For  $T_w < T < T_{sc}$  there are two branches; the branch with the smaller values of  $t$  refers to the thickness of the coexisting thin film at the thick-thin-film transition and the other to the thickness of the coexisting thick film. The thickness  $t$  is calculated for each density profile  $\rho(z)$  as

$$t = \int_0^\infty dz [\rho(z) - \rho_b] / \rho_l, \quad (4)$$

where  $\rho_l$  is the density of the coexisting liquid at the temperature in question. Although our coexistence curve is similar to that obtained by Ebner and Saam,<sup>1</sup> our present films are thicker, at temperatures just below  $T_{sc}$ , than those calculated by these authors. We estimate the thickness of the (single) film at  $T = T_{sc}$  to be  $\sim 4.1\sigma$ , while Ebner and Saam's value is  $\sim 2.5\sigma$ . Since our surface critical point occurs at a much smaller undersaturation than theirs, this difference was to be expected.

The density profiles of the coexisting films at the transition are shown in Figs. 3(a) and 4(a) for two different temperatures. At the lower temperature the thick film is much thicker ( $t \sim 12.2\sigma$ ) than the thin film ( $t \sim 1.8\sigma$ ), whereas at the higher temperature the thick film has reduced in thickness ( $t \sim 5.8\sigma$ ) and the thin film has grown ( $t \sim 2.8\sigma$ ). The profiles plotted in Fig. 4(a) are somewhat similar to the profiles of the coexisting films shown in Fig. 3 of Ref. 1. Our films are thicker, as explained above, and our profiles do not exhibit the very large maxima at  $z \sim \sigma$  which are associated with short-range correlations.<sup>14</sup> The sharp maxima which occur in our results are located at the minimum of  $V(z)$ , i.e., at  $z = (\frac{2}{5})^{1/6} \sigma_w \sim 0.94\sigma$ .

We have also calculated the transverse structure factor  $H(z, Q)$  for coexisting thick and thin films. This is defined<sup>17,13</sup> by

$$H(z, Q) \equiv 1 + \int dz' \rho(z') \int d\vec{R} \exp(i\vec{Q} \cdot \vec{R}) h(z, z', R), \quad (5)$$

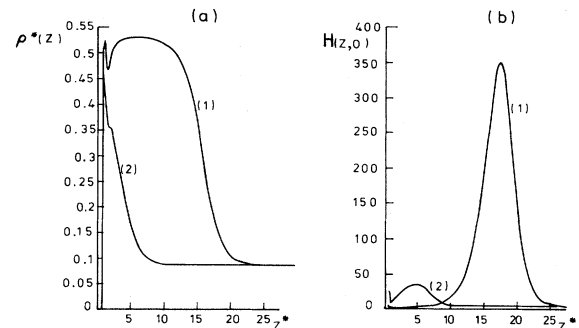


FIG. 3. (a) Density profiles  $\rho(z)$  for the solid-gas interface calculated at the thick-thin film transition for  $T^* = 0.967$ . (b) Corresponding results for the  $Q = 0$  limit of the transverse structure factor,  $H(z, 0)$ . (1) Thick film; (2) thin film.  $\rho^*(z) \equiv \rho(z)\sigma^3$  and  $z^* \equiv z/\sigma$ .

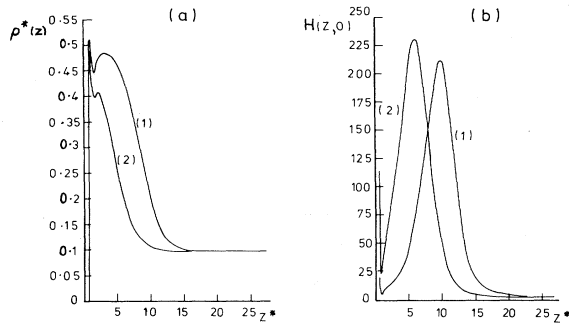


FIG. 4. (a) Density profiles  $\rho(z)$  calculated at the thick-thin-film transition for  $T^* = 0.983$ . (b) Corresponding results for  $H(z,0)$ . (1) Thick film; (2) thin film.

where  $R = [(x' - x)^2 + (y' - y)^2]^{1/2}$  is the mutual separation of particles measured parallel to the surface,  $Q$  is the corresponding (transverse) wave vector, and  $h(z, z', R) \equiv h(\bar{r}, \bar{r}')$  is the total pairwise correlation function of the inhomogeneous fluid. In the limit of complete wetting [when  $p \rightarrow p_0(T)$  for  $T > T_W$ ]  $H(z, Q)$  exhibits<sup>13,17</sup> Ornstein-Zernike behavior for small values of  $Q$  provided  $z$  is located in the edge of the thick film where the profile resembles that of a liquid-gas interface.  $H(z, 0)$  diverges as  $\delta_g^{-1}$  in the limit  $\delta_g \rightarrow 0$ . Our results for  $H(z, 0)$  at two points on the transition line are shown in Figs. 3(b) and 4(b)—alongside the corresponding density profiles.  $H(z, 0)$  for the thin film in Fig. 3(b) has a maximum at  $z \sim 5\sigma$ , which corresponds to the edge of the thin film in Fig. 3(a), while the thick film has a larger maximum at  $z \sim 17\sigma$ . These maxima are very large—approximately 10 and 100 times the bulk gas value, respectively. This implies long-ranged transverse correlations exist at the edge of both films.<sup>13</sup> For smaller temperatures the larger maximum shifts to larger values of  $z$ , as the thick film becomes thicker, and its height increases rapidly and ultimately diverges as  $T \rightarrow T_W$  from above.<sup>13</sup> For higher-temperatures, Fig. 4(b), the heights of both maxima are comparable and in the limit  $T \rightarrow T_{sc}$ , from below, both maxima diverge; this is a signature of the approach to the surface critical point. The behavior of the maxima in  $H(z, 0)$  along the transition line is similar to that found in our earlier calculations<sup>13</sup> for exponential models. However, our present results for  $H(z, 0)$  at small  $z$  are different from those obtained earlier.<sup>13,17</sup> For both the thick and thin films  $H(z, 0)$  exhibits a sharp minimum at  $z \sim 0.94\sigma$ , where  $V(z)$  has its minimum, and, for smaller values of  $z$ ,  $H(z, 0)$  increases rapidly. This latter behavior correlates with the rapid decrease in  $\rho(z)$  for small values of  $z$ . It appears that long-ranged transverse correlations can also develop very close to the substrate where the fluid density is very small. The model potentials employed in our earlier calculations<sup>13,17</sup> do not force  $\rho(z)$  to become very

small at the substrate and the resulting  $H(z, 0)$  do not exhibit the minimum. We note that Foiles and Ashcroft<sup>18</sup> have obtained results for  $H(z, 0)$  for a single thin film which are rather similar to the thin-film result shown in Fig. 3(a).

What conclusions can we draw from our results? We are confident that this particular model system does exhibit a wetting transition and a thick-thin-film transition, but these probably occur at substantially higher temperatures than those predicted by Ebner and Saam.<sup>1</sup> If we assume that our present estimate of the ratio  $T_W/T_c$  is reasonably accurate but use the simulation value  $T_c^* = 1.32$  for the bulk critical temperature, it follows that the wetting transition should occur at  $T_W^* = 1.15$ , and if we scale the surface critical temperature in the same way we obtain  $T_{sc}^* = 1.19$ . These values should be contrasted with those of Ebner and Saam ( $T_W^* = 0.77$  and  $T_{sc}^* = 0.92$ ). It is, of course, possible that our present theory underestimates the ratio  $T_W/T_c$  in which case the wetting transition would occur even closer to  $T_c$ . The Monte Carlo simulations and the calculations<sup>8-10</sup> based on other theories of inhomogeneous fluids for this model system were performed at  $T^* = 1.1$  or at  $T^* = 0.9$ . Both temperatures lie below our above estimate of  $T_W^*$  so we speculate that this is the reason no thick-film formation was observed in this work. We also speculate that if the simulations and calculations were carried out at suitably higher temperatures these should observe both the wetting transition and the thick-thin-film transition. The latter might be very difficult to observe if, as is indicated by our results, the transition line lies extremely close to the bulk coexistence curve and is restricted to a small range of temperature.

It might be more practicable to perform simulations or calculations for a more attractive substrate potential,<sup>19</sup> i.e., for a model with a larger value of  $\epsilon_{0w}$  in Eq. (3).  $T_W$  would then be shifted further below  $T_c$  and the thick-thin transition line might be moved further from the bulk coexistence curve. Further calculations might also search for the long-ranged transverse correlations which are predicted by our simple theory. The observation of a slow decay with  $R$  of the total correlation function  $h(z, z', R)$  for near-bulk coexistence conditions would provide a useful indication of the growth of thick films<sup>13,17</sup> in computer simulations. It would also be useful to extend the calculations of Foiles and Ashcroft<sup>18</sup> to the thick-thin-film transition line and thereby test the predictions of Figs. 3(b) and 4(b).

Finally, we return to the question of why different theories<sup>20</sup> should yield rather different results for  $T_W$  and  $T_{sc}$ . Perhaps this is not too surprising. It is well known that different (mean-field) theories of bulk liquids yield quite different coexistence curves and critical points. We should expect a similar situation for the “surface phase diagram” of inhomogeneous

fluids. Clearly a great deal of further research is required before we can decide what is a "good" theory of inhomogeneous fluids. In this context we remark that the calculations of Ebner and Saam<sup>1,10</sup> have attracted a large amount of criticism.<sup>6-9,21</sup> Most of this is leveled at their use of a density functional approach which requires, as input, the direct correlation function of a uniform fluid in the unstable two-phase region of the phase diagram. Since our present approach<sup>7</sup> does not require such input<sup>22</sup> and yet gives

results which exhibit the same qualitative features as those of Ebner and Saam, we are of the opinion that this particular criticism is not very serious and that Ebner and Saam's description of the wetting and thick-thin film transitions is essentially correct.

We thank Dr. T. J. Sluckin and Dr. M. M. Telo da Gama for useful conversations. This research was supported by the United Kingdom Science and Engineering Research Council.

<sup>1</sup>C. Ebner and W. F. Saam, *Phys. Rev. Lett.* **38**, 1486 (1977).

<sup>2</sup>J. W. Cahn, *J. Chem. Phys.* **66**, 3667 (1977).

<sup>3</sup>See, e.g., R. Pandit and M. Wortis, *Phys. Rev. B* **25**, 3226 (1982).

<sup>4</sup>M. R. Moldover and J. W. Cahn, *Science* **207**, 1073 (1980); D. W. Pohl and W. I. Goldberg, *Phys. Rev. Lett.* **48**, 1111 (1982), and references therein.

<sup>5</sup>For a review, see B. Widom, in *Perspectives in Statistical Physics*, edited by H. Raveché (North-Holland, Amsterdam, 1981), p. 273.

<sup>6</sup>J. E. Lane, T. H. Spurling, B. C. Freasier, J. W. Perram, and E. R. Smith, *Phys. Rev. A* **20**, 2147 (1979).

<sup>7</sup>D. E. Sullivan, *Phys. Rev. B* **20**, 3991 (1979).

<sup>8</sup>R. M. Nieminen and N. W. Ashcroft, *Phys. Rev. A* **24**, 560 (1981).

<sup>9</sup>G. F. Teletzke, L. E. Scriven, and H. T. Davis, *J. Colloid Interface Sci.* **87**, 550 (1982).

<sup>10</sup>W. F. Saam and C. Ebner, *Phys. Rev. A* **17**, 1768 (1978).

<sup>11</sup>C. Ebner, *Phys. Rev. A* **23**, 1925 (1981). Note that in this paper "partial and complete wetting" are used in a different sense from the present.

<sup>12</sup>C. Ebner, *Phys. Rev. A* **22**, 2776 (1980).

<sup>13</sup>P. Tarazona and R. Evans, *Mol. Phys.* (in press).

<sup>14</sup>This approximation (see Ref. 7) neglects short-ranged correlations so the density profiles calculated from the theory do not exhibit oscillatory behavior near the substrate; they are the "long-range profiles"  $\rho_L(z)$  of Sullivan (Ref. 7).

<sup>15</sup>N. F. Carnahan and K. E. Starling, *Phys. Rev. A* **1**, 1672 (1970).

<sup>16</sup>J. A. Barker and D. Henderson, *J. Chem. Phys.* **47**, 4714 (1967).

<sup>17</sup>P. Tarazona and R. Evans, *Mol. Phys.* **47**, 1033 (1982).

<sup>18</sup>S. M. Foiles and N. W. Ashcroft, *Phys. Rev. B* **25**, 1366 (1982). These authors calculate the total pairwise correlation function and  $H(z, 0)$  using a modified hypernetted chain closure of the Yvon-Born-Green hierarchy. They do not consider films as thick as those discussed here, nor do they discuss the wetting or thick-thin-film transitions.

<sup>19</sup>Ebner (Ref. 12) also makes this suggestion and points out that the lattice-gas model of the Lennard-Jones system requires a considerably larger value of  $\epsilon_{0w}$  to produce the wetting transition than the density functional treatment (Ref. 1) of the same (continuum) system.

<sup>20</sup>A comparison of the results of our theory with those of Ref. 9 based on the square-gradient approximation to the free-energy functional shows that, for the same model potentials,  $T_W$  and  $T_{sc}$  are much higher in the square-gradient approximation. We suspect that the latter overestimates  $T_W$  but this remains to be proved.

<sup>21</sup>M. J. Grimson and G. Rickayzen, *Mol. Phys.* **42**, 767 (1981).

<sup>22</sup>We note further that our approach does not require any parametrization of the density profiles. Ebner and Saam's parametrization scheme has also been criticized (Refs. 6 and 8).