Solid–on–solid Model for Adsorption on Self–Affine Substrate: a Transfer Matrix Approach

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Abstract

We study a $d = 2$ discrete solid–on–solid model of complete wetting of a rough substrate with random self–affine boundary, having roughness exponent $\zeta_s$. A suitable transfer matrix approach allows to discuss adsorption isotherms, as well as geometrical and thermal fluctuations of the interface. For $\zeta_s \leq 1/2$ the same wetting exponent $\psi = 1/3$ as for flat substrate is obtained for the dependence of the coverage, $\theta$, on the chemical potential, $h$ ($\theta \sim h^{-\psi}$ for $h \to 0$). The expected existence of a zero temperature fixed point, leading to $\psi = \zeta_s/(2 - \zeta_s)$ for $\zeta_s > 1/2$, is verified numerically in spite of an unexpected, very slow convergence to asymptotics.

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1. Introduction

Adsorption of a nearly saturated vapour on a rough substrate has both fundamental and technological relevance. In the case of complete wetting [1], which is the main concern of the present paper, one considers the approach to infinity of the thickness of the adsorbed liquid film in presence of the vapour phase, as the chemical potential tends to the coexistence value. Indicating by \( l \) such thickness and by \( h \) the chemical potential difference, one expects \( l \propto h^{-\psi} \). Once assumed that roughness has well-defined scaling properties, globally characterized by a fractal dimension or a roughness exponent, the power law describing complete wetting should depend on these dimensions [2–9]. For example, a self-affine surface is characterized by a roughness exponent \( \zeta_s \), which gives the average transverse height fluctuation, \( \overline{|\Delta S|} \), sampled on a portion of the surface with projection of linear size \( L \), as \( \overline{|\Delta S|} \propto L^{\zeta_s} \). The full elucidation of the scaling behaviours describing wetting and/or the crossover phenomena possibly affecting their detectability, is a hard problem, whose solution should also suggest useful new ways of probing roughness in experimental samples.

In recent years there have been many attempts to solve such issues, mostly on the basis of relatively simple phenomenological models and scaling considerations [2–7]. Scaling laws describing complete wetting have been proposed for both fractal [2,3] and self-affine substrates [4–7]. Attempts to apply such results to the analysis of recent experiments concerning the adsorption of \( \text{N}_2 \) on deposited Ag [3,10] or cyclohexane vapor on Si substrates [11] have also been made. Many ambiguities however remain in this respect, because, even the recognition of a fractal or self-affine character of the samples seems to be sometimes a matter of controversy [3–5][10]. An important step towards a satisfactory theoretical control of wetting on rough substrates should be made by studying in detail statistical models incorporating all essential features of the problem. Being free of the ambiguities still affecting experiments interpretation, such a study would provide crucial tests of the existing conjectures and of their ranges of validity.

In the case of fractal substrates a model investigation of this kind has been undertaken recently by the present authors [8]. Due to the strong limitations imposed by the presence of overhangs for a fractal boundary, the statistical treatment had to be limited to a mean field approximation. However, neglecting interface fluctuations is not expected to lead to substantial modifications of the asymptotic results in that case. Indeed, as we also confirm below on the basis of our results, wetting of an extremely rough surface, like a fractal, can be considered, in comparison to a self-affine one, as a \( T = 0 \) phenomenon [12]. On the other hand, thermal effects are still adequately described in a mean field treatment of non asymptotic features of adsorption isotherms, such as layering and capillary condensation phenomena. However, the computational complexity inherent even in such mean field description, limits considerably the possibility of detecting asymptotic laws, like the expected power law dependence of the coverage on chemical potential [8].

Self-affine substrates can be modelled by profiles without overhangs. Due to this simplification, they are relatively more accessible to statistical treatment. At least for moderate self-affine roughness, thermal fluctuations of the interface are expected to play a key role in

* Here and in the following the overbar indicates average over disorder
determining wetting exponents, as it is the case for flat substrates when the bulk dimension is lower than 3 \[12\]. Thus, an adequate treatment of self-affine substrates must describe correctly interface fluctuation phenomena. In the present paper we accomplish this task by a transfer matrix study of an interface model of adsorption on self-affine boundary in 2 bulk dimensions. The interface is treated in a solid–on–solid (SOS) approximation and takes the shapes of a directed self-avoiding walk on square lattice. Thermal interface fluctuations are controlled by surface tension and lead to self-affine behavior with a roughness exponent \( \zeta = 1/2 \) [9]. The boundary of the substrate has the same kind of shapes, with quenched fluctuations. Generalization of a method introduced by Mandelbrot [13] enables us to produce random boundaries with preassigned roughness exponents, \( 0 < \zeta_s < 1 \). The liquid in the wetting film is further supposed to feel a van der Waals type of potential from the substrate, and its thickness \( l \) is controlled by the chemical potential.

Existing scaling and analytical approaches to this problem [5,14] have strong ties with the work of Fisher and Lipowsky [12], who first discussed the role of the interfacial \( \zeta \) in determining exponents like \( \psi \) in the flat case. The basic idea emerging from such scaling arguments, which will be recalled in the next section, is that for complete wetting the asymptotics should be determined by the maximum between \( \zeta \) and \( \zeta_s \). When \( \zeta > \zeta_s \), the \( \psi \) exponent is the same as in the flat case, and thermal fluctuations control the asymptotics. When \( \zeta < \zeta_s \), control is assumed by the quenched geometrical fluctuations, and the role of \( \zeta \) is taken by \( \zeta_s \) in the formulas. Even if replica based perturbative renormalization group calculations have confirmed this simple scheme [14], and the fact that only \( \zeta_s \) determines scaling in the strong fluctuation regime, with \( \zeta_s > \zeta \), a direct verification did not exist and is one of the goals of our study.

The application of transfer matrix techniques to a model like the one studied here encounters some complications which we explain below, and involves relatively heavy computing. Thus, the approach presented in this paper has some methodological interest and should also constitute a starting point in view of further applications.

This paper is organized as follows. In the next section we introduce the model, discuss some technicalities of the transfer matrix approach, and present a simple derivation of the scaling results which are the object of our numerical investigation. Section 3 is devoted to a discussion of test applications to the case of flat substrate. In section 4 we present the main results for substrates with different degrees of roughness, with particular emphasis on the basic scaling laws involved. The last section contains general conclusions and outlines some open perspectives.

2. SOS Model, Transfer Matrix Approach and Scaling Arguments

In the SOS approximation the separation between condensed and vapour phases of the wetting fluid is described by a sharp interface, which fluctuates without forming overhangs. In 2 bulk dimensions on a square lattice this interface can be represented by a single valued integer function \( Z_x \) of the abscissa \( x \), and fluctuations are controlled by a Hamiltonian of the form:

\[
\mathcal{H} = \sum_x \left[ \frac{\varepsilon}{2} |Z_x - Z_{x+1}| + U_x(Z_x) + hZ_x \right]
\]  (1)
where $x$ also runs over integers. The first term in the sum of eq.(1) represents the energy cost for the interface steps due to surface tension. Indeed, $\varepsilon$ corresponds to the strength of the attractive nearest–neighbor energy between fluid particles in a lattice–gas model, in which particles can be placed at the centers of each elementary square not already occupied by substrate atoms. The second term in the sum is the energy due to long range van der Waals interaction with the substrate and $h$ is the deviation of chemical potential from the coexistence value.

The substrate boundary can be represented by a single valued function $S_x$. Upon averaging over randomness, the following scaling is expected to hold

$$|S_x - S_{x'}| \sim |x - x'|^{\zeta_s},$$

(2)

$\zeta_s$ being the surface roughness exponent, with values in the interval $(0, 1)$.

The interface heights can be written as $Z_x = S_x + z_x$ where $z_x$ is the local thickness of the wetting film, i.e. the distance of the SOS interface from the substrate.

$U_x(Z_x)$ in eq.(1) represents the potential energy, due to the substrate, of a column of fluid with height $z_x$ at $x$. The long range nature of the potential and numerical checks convinced us that the following local approximation for this function

$$U_x(Z_x) = -U_x^{(0)} + c/z^{\sigma-1},$$

(3)

is adequate to reproduce the scaling properties of adsorption in the high coverage regime. In all calculations reported here the choice $\sigma = 4$ has been made. This corresponds to a $1/r^6$ van der Waals interparticle potential.

We thus rewrite Hamiltonian (1) in the form:

$$H = -\sum_x U_x^{(0)} + \sum_x \left[ \frac{\varepsilon}{2}|z_x - z_{x+1} + \Delta S_x| + \frac{c}{z^{\sigma-1}} + h z_x \right]$$

(4)

where $\Delta S_x = S_x - S_{x+1}$ are the substrate surface steps and $L$ is the horizontal linear size of the system. Here and in the following we assume $1 \leq z < \infty$.

We have set up a transfer matrix technique [9,15] for the solution of the problem. In our case, because of roughness, and according to Hamiltonian (4), we can associate to any $x$ two transfer matrices, $T_+(x)$ and $T_-(x)$, with elements

$$[T_+(x)]_{z,z'} = \exp \left[ -\left( \frac{\varepsilon}{2}|z - z' + \Delta S_x| + \frac{c}{z^{\sigma-1}} + h z_x \right)/T \right]$$

(5a)

$$[T_-(x)]_{z,z'} = \exp \left[ -\left( \frac{\varepsilon}{2}|z - z' - \Delta S_{x-1}| + \frac{c}{z^{\sigma-1}} + h z_{x-1} \right)/T \right]$$

(5b)

where $T$ is the temperature measured in units of energy. The first term in eq.(4) does not enter in the definition of (5a–b) since it does not affect adsorption properties. One can see that $[T_+(x)]_{z,z'}$ and $[T_-(x)]_{z,z'}$ represent the Boltzmann weighing factor for a step of the SOS interface from $(x,z)$ to $(x+1,z')$ or $(x-1,z')$, respectively.

A film of adsorbed liquid can be represented by a very long SOS interface with, e.g., its ends pinned by the surface (see Fig.1). The average distance of the interface from the
substrate calculated in its middle point will give a measure of the thickness of the wetting film. The evaluation, at a given temperature, of such thickness as a function of chemical potential \( h \) gives the adsorption isotherms.

Let us consider a SOS interface of length \( L \). This interface can ideally be separated into two parts at the middle point \( x_m \); for example, the left part has the left–end pinned at \((x_m - L/2, 1)\) and the right–end at \((x_m, z)\) (see Fig.1). We begin by treating the two parts as mutually independent. Let us consider first the left one. While its left–end is pinned, as we move to the right, the interface becomes more and more free to fluctuate. The position of the interface at \( x_m \) can be studied in terms of an occupation profile \( \eta_+(x_m, z) \) which is the probability for the interface to be at \((x_m, z)\). It is easy to verify that

\[
\eta_+(x_m, z) \propto [T_+(x_m - L/2) \cdot T_+(x_m - L/2 + 1) \cdots T_+(x_m - 1)]_{1,z} \tag{6}
\]

This follows from iterating the formula:

\[
\eta_+(x + 1, z) = N^+_x \sum_{z'} \eta_+(x, z') [T_+(x)]_{z', z} \tag{7}
\]

where \( N^+_x = 1/\sum_{z'', z'''} \eta(x, z') [T_+(x)]_{z'', z'''} \) is a normalization constant (\( \sum_z \eta_+(x, z) \equiv 1 \)) and \( \eta_+(x_m - L/2, z) \equiv \delta_{z,1} \). In general, the shape of the occupation profile in \( x_m \) will depend not only on \( L \) but also on the shape of the substrate surface between \( x_m - L/2 \) and \( x_m \). However, we expect that for large \( L \) the interface will loose memory of the starting point, and \( \eta_+(x_m, z) \) will depend only on the shape of the substrate within a distance \( \xi_\parallel \), to be defined below.

For the right part of the interface we can obviously repeat similar considerations. The occupation profile in this case will be obtained by iterations of the form:

\[
\eta_-(x - 1, z) = N^-_{x-1} \sum_{z'} \eta_-(x, z') [T_-(x)]_{z', z} \tag{8}
\]

The occupation profiles at \( x_m \) we can get from eqs. (7) and (8) will in general differ from each other (see Fig.1). This is due to the roughness of the substrate which makes the surface asymmetric.

In order to determine a unique, continuous interface on the basis of \( \eta_+ \) and \( \eta_- \), it is natural to impose that the left and right interfaces match at \( x_m \). We thus define a profile:

\[
\eta(x_m, z) = N_{x_m} \eta_+(x_m, z) \eta_-(x_m, z) \tag{9}
\]

where \( N_{x_m} = 1/\sum_z \eta_+(x_m, z) \eta_-(x_m, z) \) is the corresponding normalization factor. Of course, the same procedure discussed for \( x_m \) and leading to eq.(9) can be applied to any \( x \), leading to the construction of a unique profile, as illustrated in Fig. 1.

To obtain macroscopic quantities, two average operations have to be performed. We will distinguish between thermal and disorder averages, marked by brackets and overbars, respectively. The main quantity we are interested in is the coverage, i.e. the thickness of the wetting film, \( \theta \). \( \theta \) is given by

\[
\theta \equiv \langle z(x) \rangle = \sum_z z \eta(x, z) = \sum_z z \overline{\eta(x, z)} \tag{10}
\]
On the other hand, also interface roughness has to be considered. In the case of a flat substrate, interface roughness is due to thermal fluctuations alone. Here, we can not exclude that the interface roughness can also be affected by the self-affine substrate. Information on the interface is given by the difference correlation function

$$\Delta C(x - x') = \frac{1}{2} \langle [z(x) - z(x')]^2 \rangle = \langle z^2(x') \rangle - \langle z(x) z(x') \rangle$$  \hspace{1cm} (11)$$

The last thermal average on the r.h.s of eq.(11) can be defined following lines similar to those discussed above for the case of a quantity depending on one variable alone. An idea of how this can be achieved is given in the following section, where an application to the flat case is discussed.

The roughness of the interface can be measured by the perpendicular correlation length $$\xi_\perp$$ which is extracted from $$\Delta C$$ in the $$|x - x'| \to \infty$$ limit

$$\xi_\perp^2 = \Delta C(\infty) = \langle z^2(x) \rangle - \langle z(x) \rangle^2$$  \hspace{1cm} (12)$$

It is interesting to note that, by summing and subtracting the quantity $$\langle z(x) \rangle^2$$ to eq.(12), $$\xi_\perp$$ can be expressed in the form

$$\xi_\perp^2 = \xi_{\perp,T}^2 + \xi_{\perp,R}^2$$  \hspace{1cm} (13)$$

with

$$\xi_{\perp,T}^2 = \langle z^2(x) \rangle - \langle z(x) \rangle^2 = \langle z^2(x) \rangle - \langle z(x) \rangle^2$$  \hspace{1cm} (14a)$$

and

$$\xi_{\perp,R}^2 = \langle z(x) \rangle^2 - \langle z(x) \rangle^2$$  \hspace{1cm} (14b)$$

Thus the width of the interface is the sum of a thermal term ($$\xi_{\perp,T}$$), which is just the quenched average of the local mean square fluctuation around the mean position of the interface, and a geometrical one, i.e. the mean square fluctuation, induced by the surface geometrical disorder, of the average mean position ($$\xi_{\perp,R}$$). The second term clearly vanishes when a flat surface is considered.

The parallel correlation length $$\xi_\parallel$$ can also be calculated from $$\langle z(x) z(x') \rangle$$. Indeed one expects [9]

$$\Delta C(\infty) - \Delta C(x - x') \sim \exp(-|x - x'|/\xi_{\parallel})$$  \hspace{1cm} (15)$$

in the $$|x - x'| \to \infty$$ limit.

As we verify in the next section, for an interface bound near a flat substrate,

$$\xi_\perp \sim \xi_{\parallel}^\zeta$$  \hspace{1cm} (16)$$

with $$\zeta = 1/2$$ in $$d = 2$$. This interface wandering exponent in $$d = 2$$ is explained by the fact that a free interface performs a random walk in the vertical direction [9].

Following Lipowsky and Fisher [12], we can separate into two terms the free energy of a wetting film of average depth $$l$$. The first one is $$U(l) = hl + c/l^{d-1} + \text{const.}$$, and represents the free energy contribution due to the last two terms of the second sum in eq.(4). The second term can be written on the basis of the standard continuum interface Hamiltonian, which replaces the first term in the above mentioned sum by a gradient squared of the local
depth. For our interface, this gradient can be represented by $\xi/\xi_\parallel \sim \xi^{(\zeta-1)/\zeta}$. Moreover, since for a bound interface it is natural to expect $l \approx \xi_\perp$, the free energy density due to interface roughness, takes the form:

$$f_I \simeq vl^{2(\zeta-1)/\zeta}. \quad (17)$$

In the case of a flat substrate, and in the absence of any kind of randomness, for $d = 2$, $\zeta = 1/2$ has to be assumed in eq.(17), and minimization of $U + f_I$ gives

$$\frac{d}{dl}(U + f_I) = h - \frac{(\sigma - 1)c}{l^2} - 2vl^{-3} \simeq h - vl^{-3} = 0 \quad (18)$$

for $\sigma > 3$, which leads to $l \sim \theta \propto h^{-1/3}$, i.e. $\psi = 1/3$.

If the substrate is rough, with exponent $\zeta_s$, the problem arises to establish which $\zeta$ should actually enter in eq.(17). It is rather natural to expect that, as long as $\zeta_s < 1/2$, the intrinsic thermal roughness of the interface determines $f_I$. Thus $\zeta = 1/2$ has to be chosen in eq.(17) and the flat case $\psi = 1/3$ still holds. On the other hand, for $\zeta_s > 1/2$, the geometrical substrate roughness induces a corrugation energy for the interface, which can still be estimated via eq.(17), this time with $\zeta = \zeta_s > 1/2$.

This energy term becomes now asymptotically dominant in the minimum condition:

$$\frac{d}{dl}(h - vl^{2(\zeta_s-1)/\zeta_s}) = 0 \quad (19)$$

yielding $\psi = \zeta_s/(2 - \zeta_s)$, $\zeta_s \geq 1/2$. In eq.(19) we again exploited the fact that $l \approx \xi_\perp$.

These results were first derived by Kardar and Indekeu [5] on the basis of similar scaling arguments. An important remark to be made concerns the fact that the replacement of $\zeta = 1/2$ by $\zeta = \zeta_s > 1/2$ in eq.(17), leads to an $f_I$ which violates hyperscaling. Indeed, since $f_I$ is a free energy per unit horizontal length, it should scale like $\xi_\parallel^{-1} \sim \xi_\perp^{-1/\zeta}$. For $\zeta = 1/2$, taking into account that $l \sim \xi_\perp$, $f_R \sim l^{-2}$ is indeed consistent with hyperscaling. For $\zeta = \zeta_s > 1/2$, the roughness free energy in eq.(19) does not scale as $\xi_\parallel^{-1}$. The hyperscaling violation is consistent with a zero temperature fixed point describing complete wetting. In the regime $\zeta_s > 1/2$, interface fluctuations are of a quenched geometrical, rather than thermal nature. A direct verification of this will be obtained in section 4, where it will be shown that while $\xi_\perp \simeq \xi_{\perp,T} >> \xi_{\perp,R}$ for $\zeta_s \leq 1/2$, $\xi_\perp \simeq \xi_{\perp,R} >> \xi_{\perp,T}$ for $\zeta_s > 1/2$.

3. Flat Substrate

As a preliminary test of the transfer matrix approach, we have considered the case of a flat substrate. The absence of geometrical disorder determines here several simplifications. In particular, the transfer matrices $T_+(x)$ and $T_-(x)$ in eqs. (5a–b) are equal to each other. Thus, a unique $x$–independent matrix, $T$, has to be considered. As a consequence, the occupation profiles $\eta_+$ and $\eta_-$ also coincide, and $\eta_+(x, z) = \eta_-(x, z) \equiv \eta_0(z)$.
One should note that the present case could be treated, equivalently, by computing directly the partition function of the system, i.e. \( Z = Tr[T^L] \). For large sizes, \( L \), of the system, \( Z \) can be approximated by the quantity \( \lambda^L \) where \( \lambda \) is the largest eigenvalue of \( T \). The relation with our approach is due to the fact that \( \eta_0 \) is the eigenvector of \( T \) associated to \( \lambda \) [15].

Thus, the above defined occupation profile \( \eta \) is now given by \( \eta(z) = N\eta_0^Z(z) \). In spite of the absence of disorder, \( \eta_0 \) cannot be calculated analytically. So, we evaluated it numerically by iterating eq.(7) until convergence. The coverage \( \theta \) is then obtained by eq.(10), in which obviously disorder averaging does not apply. \( \xi_\perp \) follows from eq.(12) or (14) \( (\xi_{\perp,R} \equiv 0) \). The limited complexity of the numerical calculations makes also the evaluation of the interface correlation length, \( \xi_\parallel \), feasible. In fact, for the calculation of \( \langle z(x)z(x') \rangle \), which is now equal to \( \langle z(x)z(x') \rangle \), we can use the expression

\[
\langle z(x)z(x') \rangle = \frac{\sum_{z,z'} z\eta(z)[T|x-x'|]_{z,z'} \eta(z')z'}{\sum_{z,z'} \eta(z)[T|x-x'|]_{z,z'} \eta(z')},
\]

(20)

which straightforwardly follows from extending considerations made in the previous section.

To work in complete wetting conditions the parameters \( \varepsilon, c \) and \( T \) have to be conveniently fixed. In particular we have chosen the values \( c/\varepsilon = 2 \), for which the system is wetted at any temperature (i.e. \( T_w = 0 \)). Our choice is meant to represent a typical situation for complete wetting and is not far from values appropriate for real adsorption experiments, like krypton on graphite [16], argon on solid xenon [17], or \( N_2 \) on \( Ag \) [3].

To test the asymptotics of adsorption, which corresponds to consider very thick adsorbed films, the size of \( T \) should be made as large as possible. Of course, in a numerical calculation a reasonable matrix size \( z_{\max} \times z_{\max} \) has to be considered, realizing a compromise between the necessity of avoiding finite size effects and that of reducing computation times. In our runs \( z_{\max} \) ranged from a minimum of 300 (low coverage) to a maximum of 800 (high coverage), in this flat case.

As discussed in the previous section, due to the dominance of interfacial thermal fluctuations, adsorption isotherms should follow the law \( \theta \sim h^{-1/3} \) for \( h \to 0 \). On the other hand, at very low \( \theta \), the effects of the attractive potential, \( U(l) \), possibly dominate with respect to \( f_l \), and a behaviour \( l \sim \theta \sim h^{-1/\sigma} \) (see eq.(18)) could hold before the thermal fluctuation effects are able to impose the asymptotic regime. This \( \psi = 1/\sigma \) is strictly a \( T = 0 \) exponent, of the FHH type (see Ref. [18]), and the low coverage window in which it can manifest itself will be the narrower, the higher the temperature.

In Fig. 2a) we report three isotherms at temperatures \( T/\varepsilon = 0.2 \) (open squares), \( T/\varepsilon = 0.4 \) (open circles) and \( T/\varepsilon = 0.8 \) (heavy circles). In the isotherm at higher \( T \) the interface fluctuations are dominating already at very low \( \theta \), and the log–log plot of \( \theta \) versus \( h \) (heavy circles) is everywhere consistent with \( \psi = 1/3 \) (slope of the dashed line). To further confirmation of this scaling behaviour, a fit of the isotherm with a function of the type \( Ah^{-\psi} + B \) yielded \( \psi = 0.327 \pm 0.004 \). For this case, the plot in the insert shows also that \( \xi_\perp \) follows the same scaling law and essentially \( \xi_\perp \sim \theta \) which is consistent with the assumptions made at the end of the previous sections. In Fig. 2b), for the two cases at higher temperatures reported in Fig.2a), the corresponding \( \xi_\perp \) are plotted versus the respective \( \xi_\parallel \).
obtained by eq. (20). The log–log plot shows that eq. (16) is obeyed with $\zeta = 1/2$ (dashed line slope), as expected. Fitting of the data for the higher temperature case, with a function of the type $A\xi^\nu$ resulted in a $\nu = 0.478 \pm 0.002$. The two isotherms represented by open circles and squares in Fig. 2(a) demonstrate that, the lower is the temperature, the wider is the preasymptotic region of $\theta$ for which the scaling behaviour is not far from the law $\theta \sim h^{-1/\sigma}$ ($\sigma = 4$ in the actual example). The above results show that, at least in the case of flat substrate, complete wetting is correctly described by our transfer matrix approach.

4. Complete Wetting of Self–Affine Surfaces

As mentioned in the introduction, our self-affine boundaries are obtained by a random generalization of an algorithm introduced by Mandelbrot [13]. This consists in applying a recursive transformation to an initially staircase shaped lattice walk. In practice, given an even number $n$, we consider a starting directed walk of $2n^k$ steps, obtained by alternating elementary forward and upward steps on a 2–$d$ square lattice. Then, given a second even number $m$, with $m < n$, the walk is divided in $n$ equal parts and in $(n-m)/2$ of them, chosen at random, all the vertical steps are reversed. The same procedure is then applied to each of the $n$ parts of the walk obtained after the first stage, and all proceeds for $k$ times. It is easy to check that the profile obtained in this way has a roughness exponent $\zeta_s = \frac{\ln m}{\ln n}$. We checked numerically that the average height–height correlation of relatively small samples of boundary profiles obtained as above satisfied the scaling law (2), with the expected $\zeta_s$ up to a percent, or so.

Since our self–affine boundaries are random, quenched averaging is needed in our evaluation of the wetting film properties. In practice we were careful to use in each actual calculation big enough $L$’s, so as to guarantee a high degree of self–averaging in each individual realization of the random profile. Another technical difference, compared to the flat case, concerns the size of the transfer matrices. Due to the higher coverage induced by surface roughness, a larger $z_{max}$ has to be considered. Of course, $z_{max}$ increases with increasing $\zeta_s$. The results we obtained required to consider matrices with $z_{max}$ between 1000 and 1500, with lengths $L$ up to $6 \cdot 10^4$.

To test the effects of surface roughness on adsorption properties, we have considered three values of $\zeta_s$, $\zeta_s = 1/4$, 1/2 and 3/4. According to the scaling arguments of the previous section, the first and third values are representative of the low and high roughness regimes, respectively. $\zeta_s = 1/2$ marks the border line between the two regimes. For all $\zeta_s$, occupation profiles were obtained by eqs. (7–9). The coverage $\theta$ and $\xi_\perp$, $\xi_{\perp,T}$ and $\xi_{\perp,R}$ were also computed, and, for $\theta$, the asymptotic scaling exponent $\psi$ was extrapolated. Computing time limitations did not allow a direct evaluation of $\xi_\parallel$, at variance with the flat case. The choice $c/\varepsilon = 2$ discussed in the previous section was made in all cases.

Fig. 3 reports the results for $\zeta_s = 1/4$ boundaries. Temperature was fixed at $T/\varepsilon = 0.8$. The coverage $\theta$ (heavy circles) follows in the whole range of $h$ values (about 6 decades), a scaling behaviour consistent with $\psi = 1/3$ (see dashed line). As a confirmation, a fit encompassing the whole data range with a function of the form $Ah^{-\psi} + B$ gave $\psi = 0.319 \pm$
Heavy squares represent data for $\xi_{\perp}$, which clearly follows the same behaviour as $\theta$ ($\theta \sim \xi_{\perp}$). In addition, the thermal part $\xi_{\perp,T}$ (open squares) gives the entire $\xi_{\perp}$, the geometrical one being much lower (open rhombs). Thus, as expected, interface roughness is dominated by thermal fluctuations.

Fig. 4 shows the results for the case of boundaries with $\zeta_s = 1/2$, again at $T/\varepsilon = 0.8$. In spite of the higher roughness of the substrate, $\theta$ (heavy circles) and $\xi_{\perp}$ (heavy squares) still follow the same scaling as for flat substrate. A fit of the type described above gave $\psi = 0.327 \pm 0.002$, still very close to the expected $\psi = 1/3$. In this case $\xi_{\perp,T}$ and $\xi_{\perp,R}$ follow essentially the same scaling law, but, still, $\xi_{\perp,R} \ll \xi_{\perp,T}$.

In the case of high substrate roughness, it turns out that the asymptotic scaling law expected on the basis of the $T = 0$ fixed point mentioned in the second section, does not show up easily, even at prohibitively high coverages. For high coverages thermal fluctuations are still very important and seem to induce a behaviour close to the $\psi = 1/3$ law. In order to reduce the role of thermal fluctuations and to obtain evidence of a crossover to the expected $\psi = \zeta_s/(2 - \zeta_s)$, we had to reduce the temperature to $T/\varepsilon = 0.5$ this time, and to consider $L = 6 \cdot 10^4$ and $z_{max} = 1500$. With such choices, somehow at the limit of our computational possibilities, one detects a sort of saturation of the coverage (heavy circles in Fig. 5) at very low $h$. This saturation is due to truncation of the transfer matrices. On the other hand, our numerical checks indicate that truncation effects are essentially absent up to $h \geq 6 \cdot 10^{-7}$.

An interesting feature of the isotherm is that, for $h$ just above this limit, the slope has a clear increase, and, for about one decade, seems to be consistent with a $\psi = 0.632 \pm 0.021$. This estimate is reasonably close to the value $\psi = \zeta_s/(2 - \zeta_s) = 0.6$ implied by the scaling arguments. We interpret these results as an indication that, after a preasymptotic regime of lower effective $\psi$, the system tends to follow the expected law at very high coverages. In the preasymptotic regime the slope of the log-log plot of $\theta$ is definitely lower, and rather close to the flat case one (dashed line).

Fig. 5 also shows that $\xi_{\perp}$ (heavy squares) follows the same law as $\theta$. Now, however, interface roughness is almost completely due to geometry, rather than temperature, and the roles of $\xi_{\perp,T}$ and $\xi_{\perp,R}$ are interchanged with respect to the previous cases. $\xi_{\perp,T}$ (open squares) is much lower than $\xi_{\perp,R}$ (open rhombs). It also turns out that, in the preasymptotic regime, $\xi_{\perp,T}$ obeys rather closely the $h^{-1/3}$ law, as in the flat substrate case (dashed line). As $\theta$ reaches its expected asymptotic slope, also $\xi_{\perp,R}$ rises more rapidly, and, before saturation, assumes a slope comparable with that of $\theta$, as well.

5. Concluding Remarks

In this paper we performed a systematic study of the effects of self-affine substrate roughness on complete wetting properties of a fluid. This study was based on a discrete, $d = 2$ statistical model genuinely incorporating the essential features of the problem, namely interface fluctuations, long range substrate potential, and geometrical disorder of the surface.

Up to now, existing studies of complete wetting on self-affine substrates all relied on essentially continuum descriptions, so that the problem of testing their scaling [4,5] on discrete
models remained open, together with that of precisely establishing the ranges of validity of various regimes and of locating their crossovers.

We applied to our model a transfer matrix technique which allowed to make a useful distinction between thermally and geometrically driven interface fluctuations, and to relate them to the coverage properties.

With a rather high level of accuracy we could verify that power law behaviours expected on the basis of scaling arguments are verified already at relatively low coverages, and for different temperature choices, in the case of moderately rough substrates ($\zeta_s \leq 1/2$). The case $\zeta_s = 3/4$ was expected to constitute an example of complete wetting exclusively controlled by geometrical disorder through a $T = 0$ fixed point. As a matter of fact, a satisfactory treatment of this relatively high substrate roughness revealed a real computational challenge within our model. We could verify that with $\zeta_s = 3/4$ a very wide preasymptotic scaling regime with $\psi$ slightly larger than $1/3$ exists. Only by suitably reducing the effects of thermal fluctuations, responsible for the preasymptotic behaviour, it becomes possible to detect crossover to the expected $\psi = 0.6$, with an effort reaching almost the limits of our computational capabilities. Such slow set up of the asymptotic regime indicates the existence of important scaling corrections, and was not a priori expected. This should constitute a warning with respect to attempts to interpret numerical or experimental results in the field.

The proof that a $T = 0$ fixed point indeed controls asymptotics in the case of high roughness is an indirect confirmation that studies of complete wetting on fractally rough substrates can be correct in predicting the asymptotics, even if disregarding thermal fluctuations of the interface. This applies to our previous study of adsorption on a fractal substrate by mean field methods [8].

The problem of complete wetting does not at all exhaust the range of applicability of methods like those we applied in this paper. The natural further step, already undertaken by us, is the study of the critical wetting transition [1,9,19], possibly occurring when in models of the kind discussed here the temperature approaches from below some critical value, $T_w$. The role of self–affine roughness in this case can not be discussed in terms of simple scaling ideas, and more sophisticated, albeit approximated, renormalization group methods have been produced to elucidate it [14]. In this context the role of our model studies will reveal even more crucial, also because, we anticipate, surface roughness can lead to new features of wetting, at low temperature, which do not seem to be easily caught by continuum descriptions.

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**FIGURE CAPTIONS**

Fig. 1 Shape of a SOS interface on a rough self-affine surface with $\zeta_s = 1/2$ (represented by the stepped curve bounding the shaded area). The heavy continuous line represents the mean shape of the interface with the ends pinned at $A$ and $B$ on the substrate and obtained by applying at each $x$ a matching condition of the form (9). Dashed and long-dashed lines represent the mean shapes of the right and left interfaces discussed in the text. In the upper plot, the occupation profiles $\eta, \eta_+, \eta_-$ at the middle point (see arrow) are shown. The calculation were performed with $c/\varepsilon = 2$, $T/\varepsilon = 0.5$ and $h = 2.44 \cdot 10^{-4}$.

Fig. 2 Adsorption on a flat surface. Calculations were done with $c/\varepsilon = 2$. a) Adsorption isotherms for $T/\varepsilon = 0.2$ (open squares), $T/\varepsilon = 0.4$ (open circles) and $T/\varepsilon = 0.8$ (heavy circles). Dashed and long dashed lines express a $h^{-1/3}$ and $h^{-1/4}$ scaling laws, respectively. In the insert $\xi_\perp$ (heavy squares) for $T/\varepsilon = 0.8$ is plotted versus $h$. Also in this case the dashed line expresses a $h^{-1/3}$ scaling law. b) $\xi_\perp$ versus $\xi_\parallel$ for the two cases at higher temperature reported in a). Dashed line expresses a $\xi_\parallel^{1/2}$ scaling law.

Fig. 3 Adsorption on a rough self-affine surface with $\zeta_s = 1/4$. The calculation were done with $c/\varepsilon = 2$ and $T/\varepsilon = 0.8$. Heavy circles and squares represent the value of coverage $\theta$ and $\xi_\perp$ as functions of $h$, respectively. Open squares (partially hidden by heavy squares) and open rhombs represent $\xi_\perp,T$ and $\xi_\perp,R$ values, respectively. The dashed line obeys the $h^{-1/3}$ scaling law.

Fig. 4 Adsorption on a rough self-affine surface with $\zeta_s = 1/2$. The choice $c/\varepsilon = 2$ and $T/\varepsilon = 0.8$ was made in this case. Heavy circles and squares represent $\theta$ and $\xi_\perp$ as function of $h$, respectively. Open squares (partially hidden by heavy squares) and open rhombs represent $\xi_\perp,T$ and $\xi_\perp,R$, respectively. The dashed line gives again the a $h^{-1/3}$ power law.

Fig. 5 Adsorption on a rough self-affine surface with $\zeta_s = 3/4$. The calculation were done with $c/\varepsilon = 0.5$ and $T/\varepsilon = 0.5$. Heavy circles and squares represent $\theta$ and $\xi_\perp$ as functions of $h$, respectively. Open squares and open rhombs give $\xi_\perp,T$ and $\xi_\perp,R$ values, respectively. The solid line results from fitting $\theta$ with a function of the form $Ah^{-\psi} + B$ in the range $6 \cdot 10^{-7} < h < 3 \cdot 10^{-6}$. This gives $\psi = 0.632 \pm 0.021$. The dashed line gives the $h^{-1/3}$ scaling law.