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The RSOS model of wetting of a chemically inhomogeneous, periodic substrate

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Abstract

The two-dimensional RSOS model of adsorption on a chemically inhomogeneous and periodic substrate with point-like interaction between the interface and the substrate is discussed rigorously. We prove that for weakly inhomogeneous substrates critical wetting transitions exist. Their wetting temperatures are higher than in the case of a homogeneous substrate whose interaction parameter is equal to the spatial average of interaction parameters in the inhomogeneous cases.

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1. Introduction

Adsorption on chemically inhomogeneous substrates has been the subject of increasing experimental and theoretical interest [1], in particular because of its relations to nanofluidics [2]. From the theoretical point of view the morphology of fluids adsorbed on patterned substrates has often been investigated via the mean field methods in which fluctuations, say of the order parameter or of the interfacial shapes, are neglected. This type of analysis reveals rich structure of phase diagrams in which different types of adsorbate morphologies are present and transitions between them have been the subject of continuing interest. On the other hand the role of fluctuations—especially in the two-dimensional systems—may be essential not only for the values of the relevant critical indices but also for the very existence and order of such transitions [3]. In this paper we concentrate on the exact solution of such a low-dimensional model of wetting of a planar, chemically inhomogeneous substrate. It consists of adjacent, chemically different segments of varying width and is spatially periodic. The structure of the substrate's part forming the period can be varied within certain limits. We are interested in the rigorous analysis of wetting transitions taking place on such substrates, and—in particular—in the influence of the deviations from the substrate's chemical homogeneity on its wetting properties.

2. Model

We consider the RSOS model of wetting of a chemically inhomogeneous planar substrate. The model is two dimensional: a one-dimensional interface separating the phase adsorbed on the substrate from the phase away from it fluctuates in the presence of a one-dimensional substrate whose chemical constitution varies periodically. The thermodynamics states of the system correspond to bulk coexistence and thus complete wetting is not considered in this paper. The lattice sites of the substrate are enumerated by the index $i = 1, 2, \ldots, \tau N$, where τ is the period, and N is the number of periods in the system. The position of the interface above the ith substrate's site is denoted by the discrete variable $l_i \in \{0, 1, 2, \ldots\}$. The interaction $V_i(l_i)$ between the interface and the substrate at the ith site is point-like

$$V_i(l_i) = -W_i \delta_{l_i,0} \tag{1}$$

and is parametrized by the contact energies $-W_i$, a periodic function of lattice sites

$$W_{i+\tau} = W_i. \tag{2}$$

The RSOS Hamiltonian has the form

$$\mathcal{H}\{l_i\} = \sum_{i=1}^{\tau N} J|l_{i+1} - l_i| - \sum_{i=1}^{\tau N} W_i \delta_{l_i,0}, \tag{3}$$

where J is the positive energy of increasing the length of the interface by one unit. In RSOS model only configurations satisfying

$$|l_{i+1} - l_i| \leqslant 1$$

for $i = 1, 2, \ldots, \tau N$ are considered. For reasons to be explained later we assume certain symmetry of the potential within a single period

$$W_{2+i} = W_{\tau-i} \tag{4}$$

for $i = 0, 1, \ldots, [\tau/2 - 1]$. The above condition allows the substrate to have segment-like structure, with different segments having different widths. A particular case corresponds to only two kinds of segments present, each of different width, and with any rational width ratio.

Finally, periodic boundary conditions

$$l_{\tau N+i} = l_i,$$

for any integer i are imposed on the system.

3. The transfer matrix calculation

The canonical partition function can be found using the transfer matrix method. In the present case the transfer matrix is a linear operator $\mathbf{T}_\tau$ with matrix elements

$$\begin{aligned}\langle v_1|\mathbf{T}_\tau|v_{\tau+1}\rangle = {} & \sum_{v_2=0}^{\infty}\sum_{v_3=0}^{\infty}\cdots\sum_{v_\tau=0}^{\infty}\left(j\delta_{v_1,v_2-1} + \delta_{v_1,v_2} + j\delta_{v_1,v_2+1}\right) \\ & \times \left(j\delta_{v_2,v_3-1} + \delta_{v_2,v_3} + j\delta_{v_2,v_3+1}\right)\cdots\left(j\delta_{v_\tau,v_{\tau+1}-1} + \delta_{v_\tau,v_{\tau+1}} + j\delta_{v_\tau,v_{\tau+1}+1}\right) \\ & \times w_1^{\frac{1}{2}\left(\delta_{v_1,0}+\delta_{v_2,0}\right)} w_2^{\delta_{v_2,0}} w_3^{\delta_{v_3,0}}\cdots w_\tau^{\delta_{v_\tau,0}},\end{aligned} \tag{5}$$

where parameters

$$j = \exp(-J/(k_B T)), \qquad w_i = \exp(W_i/(k_B T))$$

have been introduced. The vectors $|v_i\rangle$ in equation (5) form an orthonormal base in Hilbert space. The operator $\mathbf{T}_\tau$ is bounded and Hermitian (if interaction with the inhomogeneous wall satisfies the condition in equation (4)) but may be not positive.

The main properties of the model can be deduced from the spectrum Λ of the transfer matrix. Let $|\psi^{(\lambda)}\rangle$ be the eigenvector corresponding to the eigenvalue $\lambda \in \Lambda$. The largest eigenvalue $\lambda_{\max}$ and the corresponding eigenvector $|\psi^{(\lambda_{\max})}\rangle$ define—in the thermodynamic limit—two important quantities: the probability of the interface being located at site 1 on height v_1, i.e.,

$$\rho_1(v_1) = |\langle v_1|\psi^{(\lambda_{\max})}\rangle|^2, \tag{6}$$

and the free energy density

$$f = -k_{\mathrm{B}} T \ln \mu, \tag{7}$$

where

$$\mu = (\lambda_{\max})^{1/\tau}$$

denotes the positive root.

The spectrum Λ contains the continuous part $[(1-2j)^\tau, (1+2j)^\tau]$, and—in addition—there may also be discrete eigenvalues.

It is straightforward to check that the average height of interface is finite only when $\lambda_{\max}$ belongs to the discrete part of the spectrum. The wetting transition occurs when the maximum eigenvalue enters—upon changing the temperature—the continuous part, i.e., when the maximum eigenvalue changes its character from discrete to continuous.

The components of the maximum eigenvector $\psi_v = \langle v|\psi^{(\lambda_{\max})}\rangle$ can be expressed as

$$\psi_v = w_1^{\delta_{v,0}/2} \sum_{k=1}^{\tau} A_k t_k^v,$$

where the parameters t_k satisfy the following conditions,

$$t_k^2 + j^{-1}[1 + \mu \exp(2\pi \mathrm{i} k \tau^{-1})] t_k + 1 = 0, \qquad |t_k| \leqslant 1, \tag{8}$$

and i is the imaginary unit. The above equations follow from the eigenequation for the largest eigenvalue

$$\sum_{v'=1}^{\infty} \langle v|\mathbf{T}_\tau|v'\rangle \psi_{v'} = \lambda_{\max} \psi_v, \tag{9}$$

when one considers $v > \tau$ cases. In the remaining $v \leqslant \tau$ cases one obtains τ linear equations for A_k which depend on the value of τ and the interaction parameters W_i (note that equations obtained for the $v > \tau$ cases do not depend explicitly on the wall interaction parameters W_i). These equations may be symbolically written as

$$\mathbf{M}(\mu, w_1, w_2, \ldots, w_\tau, j)\vec{A} = 0, \tag{10}$$

with $\vec{A} = [A_1, A_2, \ldots, A_\tau]^{\mathrm{T}}$.

Because only non-trivial solutions for A_k are physically interesting the matrix $\mathbf{M}$ must fulfil a condition

$$L(\mu, w_1, w_2, \ldots, w_\tau, j) = \det \mathbf{M} = 0, \tag{11}$$

which constrains possible μ values. It is easy to show that for $\mu > 1 + 2j$ the function L is an analytical function of all its arguments. Because only roots of function L have physical meaning it may be multiplied by any nonzero constant factor. It can be shown that for any period τ there exists complex number c such that cL is a real function—it gives real values for real arguments. From now on we will assume that L is already a real function.

The function L determines all possible eigenvalues for $\mu > 1 + 2j$. Their dependence on temperature governs the wetting transition. There are two ways in which the largest eigenvalue can change its character, i.e., the type of spectrum it belongs to. If the largest μ that satisfies equation (11) decreases with temperature and reaches the boundary value $1 + 2j$ the average height of the interface continuously grows to infinity; the system experiences the critical wetting transition. If, on the other hand, two discrete eigenvalues, both $\mu > 1 + 2j$, meet and disappear then the average interfacial height jumps from a finite value to infinity. The critical wetting temperature is the largest temperature for which the equation

$$L(\mu = 1 + 2j, w_1, w_2, \ldots, w_\tau, j) = 0 \tag{12}$$

holds.

4. Results

The case $\tau = 1$ corresponds to a homogeneous substrate for which straightforward calculations show that

$$L(\mu, w_1, j) = w_1 - \mu + \tfrac{1}{2}w_1\big(\mu - 1 - \sqrt{(\mu - 1)^2 - 4j^2}\big).$$

It can be checked that $\frac{\partial L}{\partial \mu} \neq 0$, for any positive j, w_1 and $\mu > 1 + 2j$ and thus function L is monotonic and cannot have more than one root for fixed j and w_1. In consequence the second scenario described at the end of section 3 cannot take place and only critical wetting is allowed.

Condition (12) leads to the previously obtained [4] equation for the wetting temperature

$$w_1^* = \frac{1 + 2j^*}{1 + j^*},$$

where starred symbols are evaluated at the wetting temperature.

In the case $\tau = 2$, the substrate consists of two kinds of segments of the same width and

$$\begin{aligned} L(\mu, w_1, w_2, j) &= 4\mu^2 + \mu\big(\sqrt{(\mu - 1)^2 - 4j^2} + \sqrt{(\mu + 1)^2 - 4j^2} - 2\mu\big)(w_1 + w_2) \\ &\quad + \big(\mu + 1 - \sqrt{(\mu - 1)^2 - 4j^2}\big)\big(\mu - 1 - \sqrt{(\mu + 1)^2 - 4j^2}\big)w_1 w_2. \end{aligned}$$

Although the theory does not exclude the possibility of discontinuous changes of the wetting layer width, we could not find a set of model parameters for which a discontinuous change would actually occur [5]. This suggests that only a continuous wetting transition may take place in this case. For higher periods the analysis of equation (11) becomes even more cumbersome. Nevertheless, our numerical analysis of this equation for the cases up to $\tau = 5$ showed that only continuous wetting transitions are present in such systems. However, the results presented below are purely analytic.

Quite generally we are able to prove that for weakly inhomogeneous substrates of arbitrary period only critical wetting may take place. This is contained in the following theorem proved in the appendix:

Theorem. *Let T_0^* be the temperature of critical wetting transition in the RSOS model (equations (3) and (4)) with homogeneous substrate characterized by interaction potential parameter W_0. For any real $M > 1$ there exists $\varepsilon > 0$ so that for arbitrary temperature $T \in \big(\frac{1}{M}T_0^*, MT_0^*\big)$, and any interaction potential parameters $\{W_i\}$ satisfying $|W_i - W_0| < \varepsilon W_0$*

for $i = 1, 2, \ldots, \tau$ *the transfer matrix operator* $\mathbf{T}_\tau$ *has at most one discrete eigenvalue above its continuous spectrum.*

Thus if the transfer matrix has at most one eigenvalue above its continuous spectrum then only continuous wetting transition may occur.

To gain information about the dependence of the critical wetting temperature on the substrate (weak) inhomogeneity we considered a model in which the interaction parameters have the following form,

$$W_i = W_0(1 + q_i x), \tag{13}$$

where coefficients q_i are numbers and parameter x is small enough (in agreement with the above theorem). In addition we assumed that

$$\frac{1}{\tau}\sum_{i=1}^{\tau} W_i = W_0, \tag{14}$$

and thus

$$\sum_{i=1}^{\tau} q_i = 0 \tag{15}$$

so the (spatial) average of the interaction parameters has the same value as in the case of a homogeneous substrate with the critical wetting temperature equal to T_0^*. We also assumed that

$$\sum_{i=1}^{\tau} q_i^2 = \tau, \tag{16}$$

so the substrate has the same variance density for every period. The third condition for parameters is a consequence of the symmetry of the substrate within one period (see equation (4))

$$q_{2+i} = q_{\tau-i} \qquad \text{for} \quad i = 0, 1, \ldots, [\tau/2 - 1]. \tag{17}$$

It turns out that the wetting temperature of the (weakly) inhomogeneous system which fulfils equation (12) depends on x in the following way:

$$T^* = T_0^* + \beta T_0^* x^2 + O(x^3). \tag{18}$$

Evaluation of factor β for all periods up to $\tau = 5$ shows that $\beta > 0$ which means that for weakly inhomogeneous substrates with the same average value of the interaction parameters as in equation (14), the wetting temperature is the smallest in the homogeneous case ($x = 0$ in equation (13)), see figures 1 and 2. Thus, introducing weak chemical inhomogeneity of the substrate—provided that the substrate does not change on average—leads to the presence of critical wetting with the wetting temperature increased compared with the homogeneous case. Similar results were obtained for a SOS model with random substrate [6]. This is in contrast with the case of a chemically homogeneous and corrugated wall; there the wetting temperature is smaller than in the planar substrate case [7].

We have also analysed the dependence of wetting temperature on the substrate interaction for a continuous SOS model. In this model the distance between the wall and the interface l_i at the ith lattice site can take any non-negative real value (while the substrate remains discrete). For homogeneous case this model was discussed in [8].

Here we concentrate on the $\tau = 2$ case and step-like wall potential. In this case the Hamiltonian has the form

$$\mathcal{H}\{l_i\} = \sum_{i=1}^{2N} J|l_{i+1} - l_i| - \sum_{i=1}^{2N} V(l_i), \tag{19}$$

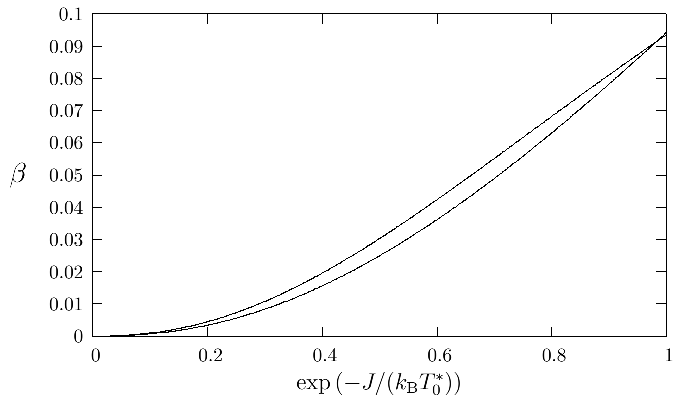

Figure 1. The β function (see equation (18)) for $\tau = 2$ (lower curve) and $\tau = 3$ (upper curve). For these periods interaction parameters q_i are determined uniquely by conditions (15), (16) and (17).

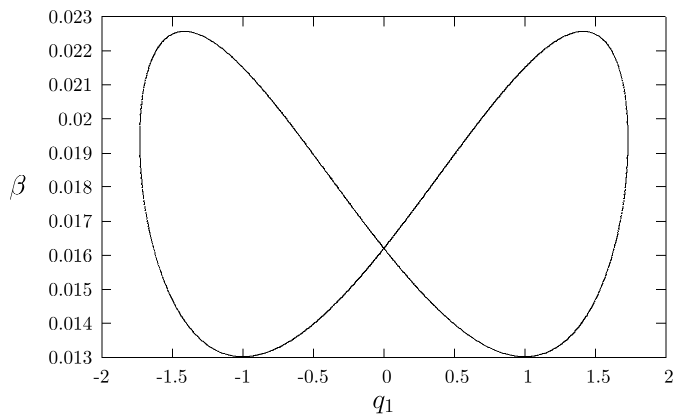

Figure 2. For period $\tau = 4$ conditions (15), (16) and (17) give two solutions for any $-\sqrt{3} < q_1 < \sqrt{3}$. This figure presents the dependence of β on parameter q_1 for $J = k_B T_0^*$.

where

$$V(l_i) = \begin{cases} V_1(l_i) & \text{for odd } i, \\ V_2(l_i) & \text{for even } i, \end{cases} \qquad V_n(l_i) = \begin{cases} W_n & \text{for } l_i < r, \\ 0 & \text{for } l_i \geqslant r, \end{cases}$$

where W_i are constant and r is the interaction length (the same for each lattice site).

Similarly to [8] we used the transfer matrix technique and obtained the following equation for eigenfunction ϕ and eigenvalue λ:

$$\int_0^\infty \mathrm{d}y \int_0^\infty \mathrm{d}z \exp\left[\frac{1}{2}\tilde{V}_1(x) - \tilde{J}|x-y| + \tilde{V}_2(y) - \tilde{J}|y-z| + \frac{1}{2}\tilde{V}_1(z)\right]\phi(z) = \lambda\phi(x),$$

where a tilde denotes that this quantity contains the factor $1/k_B T$, e.g. $\tilde{V}_1(x) = \frac{V_1(x)}{k_B T}$. It is straightforward to obtain equations for eigenfunction $\phi(x)$

$$\frac{\mathrm{d}^4\phi_<(x)}{\mathrm{d}x^4} - 2\tilde{J}^2\frac{\mathrm{d}^2\phi_<(x)}{\mathrm{d}x^2} + \left(\tilde{J}^4 - \frac{4\tilde{J}^2}{\lambda}\,\mathrm{e}^{\tilde{W}_1+\tilde{W}_2}\right)\phi_<(x) = 0,$$

$$\frac{\mathrm{d}^4\phi_>(x)}{\mathrm{d}x^4} - 2\tilde{J}^2\frac{\mathrm{d}^2\phi_>(x)}{\mathrm{d}x^2} + \left(\tilde{J}^4 - \frac{4\tilde{J}^2}{\lambda}\right)\phi_>(x) = 0,$$

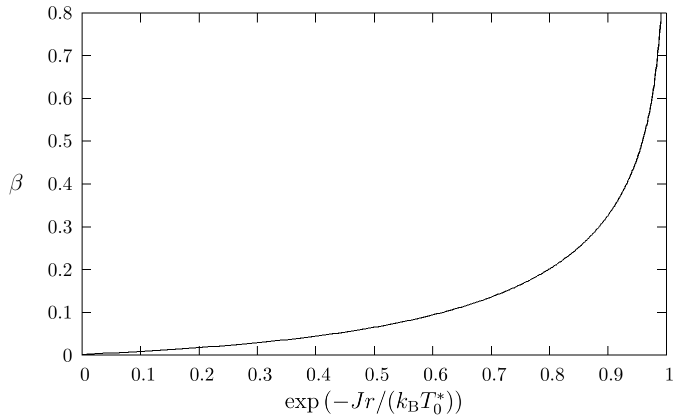

Figure 3. β function for continuous model for $\tau = 2$.

where

$$\phi(x) = \begin{cases} \phi_<(x) & \text{for } x < r, \\ \phi_>(x) & \text{for } x > r, \end{cases}$$

and the corresponding boundary conditions

$$\tilde{J}\phi_<(0) = \frac{d\phi_<}{dx}(0), \qquad \tilde{J}\frac{d^2\phi_<}{dx^2}(0) = \frac{d^3\phi_<}{dx^3}(0),$$
$$\phi_<(r) = e^{\tilde{W}_1/2}\phi_>(r), \qquad \frac{d\phi_<}{dx}(r) = e^{\tilde{W}_1/2}\frac{d\phi_>}{dx}(r),$$
$$\tilde{J}^2\phi_<(r) - \frac{d^2\phi_<}{dx^2}(r) = \exp\left(\frac{\tilde{W}_1}{2} + \tilde{W}_2\right)\left(\tilde{J}^2\phi_>(r) - \frac{d^2\phi_>}{dx^2}(r)\right),$$
$$\tilde{J}^2\frac{d\phi_<}{dx}(r) - \frac{d^3\phi_<}{dx^3}(r) = \left(\frac{\tilde{W}_1}{2} + \tilde{W}_2\right)\left(\tilde{J}^2\frac{d\phi_>}{dx}(r) - \frac{d^3\phi_>}{dx^3}(r)\right).$$

The values λ for which nonzero solution of the above equations exists define the spectrum of the transfer matrix. We found that it consists of a continuous part for $\lambda \in [0, 4/\tilde{J}]$, and—for low temperatures—additional discrete eigenvalues above the continuous part. When the temperature becomes high enough, there are no discrete eigenvalues. Just like in the discrete RSOS model, the wetting transition takes place when the last discrete eigenvalue disappears.

For $W_1 = W_0(1 + x)$ and $W_2 = W_0(1 - x)$ the dependence of the wetting temperature on x was tested and we discovered that it has a minimum for $x = 0$. This means that—as in the discrete RSOS model—the wetting temperature takes the lowest value for a homogeneous substrate. The function β for this model is presented in figure 3.

5. Conclusions

In this paper we discussed a two-dimensional RSOS model of wetting of a planar, chemically inhomogeneous wall with periodic structure. Within rigorous analysis the exact formula for the system partition function was found. Although we were not able to rigorously exclude the existence of the first-order wetting transitions no such transitions were found upon analysing the system. It looks thus as if only critical wetting transitions are present. Moreover, for weak periodic inhomogeneities that keep the average substrate properties intact we analytically proved the existence of critical wetting transitions. The temperature at which the critical wetting transition takes place turned out to be higher than in the homogeneous case. The same dependence of critical wetting temperature on substrate inhomogeneities was found for the continuous model.

Appendix

In this appendix the following theorem will be proved:

Theorem. *Let T_0^* be the temperature of critical wetting transition in the RSOS model (equations (3) and (4)) with homogeneous substrate characterized by interaction potential parameter W_0. For any real $M > 1$ there exists $\varepsilon > 0$ so that for arbitrary temperature $T \in \left(\frac{1}{M}T_0^*, MT_0^*\right)$, and any interaction potential parameters $\{W_i\}$ satisfying $|W_i - W_0| < \varepsilon W_0$ for $i = 1, 2, \ldots, \tau$ the transfer matrix operator $\mathbf{T}_\tau$ has at most one discrete eigenvalue above its continuous spectrum.*

First we consider the system with a homogeneous wall characterized by potential parameter W_0. This homogeneous case corresponds to arbitrary values of τ and $W_i = W_0$, for $i = 1, 2, \ldots, \tau$. Although the formula for function L depends on the chosen τ, the system properties do not. Comparing formulae for free energy (before the thermodynamic limit is taken) for different widths of the system it is straightforward to see the correspondence between eigenvalues of the transfer matrix in both descriptions

$$\lambda_1^{(i)} = \left(\lambda_\tau^{(i)}\right)^{\frac{1}{\tau}}, \tag{A.1}$$

where $\lambda_n^{(k)}$ is the kth eigenvalue of the transfer matrix operator for the model with period n.

The proof of the theorem is indirect. Suppose that this theorem is not true. This leads to the existence of sequences of temperatures T_n, interacting potential parameters $W_{i,n}$ and two μ values: $a_n > b_n > 1 + 2j_n$ for which

$$L(a_n, w_{1,n}, \ldots, w_{\tau,n}, j_n) = L(b_n, w_{1,n}, \ldots, w_{\tau,n}, j_n) = 0,$$

where $w_{i,n} = \exp\left(\frac{W_{i,n}}{T_n}\right)$ and $j_n = \exp\left(-\frac{J}{T_n}\right)$. The Rolle theorem shows that for any n there exists c_n such that $a_n > c_n > b_n$ and

$$\frac{\partial L}{\partial \mu}(c_n, w_{1n}, \ldots, w_{\tau n}, j_n) = 0.$$

It is straightforward to show that there exist subsequences such that

$$T_{n_k} \to T, \quad a_{n_k} \to a, \quad b_{n_k} \to a, \quad c_{n_k} \to a, \quad w_{i,n_k} \to w = \exp\left(\frac{W_0}{T}\right),$$

where $a = 1 + 2j$, $j = \exp\left(-\frac{J}{T}\right)$. Thus, analyticity of L leads to two equalities

$$L(a, w, \ldots, w, j) = 0, \qquad \frac{\partial L}{\partial \mu}(a, w, \ldots, w, j) = 0.$$

This means that L has—in the homogeneous limit—at least a double root at $\mu = a$. This contradicts—via equation (A.1)—the previously stated properties of function L in the homogeneous case.

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