Annales UMCS Informatica AC 1 (2003) 201-211

Annales UMCS
Informatica
Lublin-Polonia
Sectio AC

http://www.annales.umcs.lublin.pl/

Incommensurate and commensurate phases in adsorbed monolayers: ground state properties

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Abstract

The ground state properties of incommensurate films of domain wall structure formed on the (100) plane of face centered cubic crystals are studied by Monte Carlo simulation. The wall energies, wall structure and the wall-wall interaction are determined for domain walls occurring in films which form the c(2×2) registered structure. The systems characterized by different strength and corrugation of the surface potential and of different misfit between adsorbate and adsorbent are discussed. It is demonstrated that the structure with crossing heavy walls may have higher stability than a simple striped phase with parallel heavy walls.

1. Introduction

The structure of incommensurate phases (IC) and the incommensurate – commensurate (IC-C) transition in adsorbed layers have been a subject of intensive study over the last decades [1-4]. The most widely used theoretical approaches towards the incommensurate phases and the IC-C transition are based on the concept of domain walls. The domain wall theory of IC-C transitions [3-4] assumes that incommensurate phases are described as a collection of commensurate domains separated by different types of walls, which carry all the excess of density. Geometry of domain wall networks is closely related to the symmetry of the commensurate domains, which in turn results from the symmetry of the surface lattice. For the domain wall formalism to apply it is necessary that the commensurate state possesses positional degeneracy.

Possible ground state structures of incommensurate monolayer films adsorbed on the (100) plane of fcc crystals have been recently studied by. Monte Carlo simulation method [5-7]. It has been demonstrated that incommensurate phases with a well developed domain-wall structure may appear in adsorbed films, even

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when the corrugation of the surface potential is strong. That observation has been rather surprising, since it is commonly accepted [1,3] that in continuous space models the IC phases of domain wall structure are most likely to occur for weakly corrugated surfaces.

In this work we discuss the problem of the domain – wall energies and the interaction between walls [1, 3, 8-9]. In particular, we consider the effects of the surface potential properties (its strength and corrugation) on the structure and energy of domain walls and the changes of the structure and properties of domain walls resulting from the changes in the misfit between the adsorbate and the surface lattice.

2. The model and methods

The model of adsorption system has been described in our previous papers [5-7]. Thus, we consider monolayer adsorption on the (100) plane of a perfect face centered cubic crystal and we use the length of the surface unit cell vector ***a*** as the unit of length. The adsorbate - substrate interaction potential is periodic along the *x* and *y* directions, and hence can be represented by the Fourier series [10]

$$V(t,z)=e_{gs}\left[V_0(z)+V_b\sum_q V_q(z)\,f_q(t)\right], \tag{1}$$

where *z* denotes the distance from the surface and τ is the two-dimensional vector τ = *(x,y)* which describes the position of an adsorbed atom over the surface lattice, the Fourier components $V_0(z)$ and $V_q(z)$ as well as the functions $f_q(t)$ can be found in Ref. [10], and V_b is the corrugation parameter [4] which allows to vary the periodic part of the surface potential.

Then the adsorbate - adsorbate interaction is represented by the truncated (12-6) Lennard-Jones potential

$$u(r^*)=\begin{cases}4e\left[\left(s^*/r^*\right)^{12}-\left(s^*/r^*\right)^{6}\right] & r^*\le r^*_{\max}\\ 0 & r^*>r^*_{\max}\end{cases} \tag{2}$$

with e used as the unit of energy and $s^* = s/a$ is a measure of the size of adsorbate atoms. Here we assume that s^* is greater than unity and hence the commensurate phase is the c(2×2) structure of two-fold positional degeneracy. The model is studied using a standard Monte Carlo method in the canonical ensemble [7, 11], for the systems with adsorbate atoms of the size (s^*) ranging between 1.1 and 1.3 and for the gas - solid potential of different strength (measured by the value of the parameter $e^*_{gs}=e_{gs}/e$ and of different corrugation (determined by the magnitude of the parameter V_b). In both *x* and *y* directions we have applied periodic boundary conditions, while in the *z* direction the simulation cell was closed by the reflecting wall placed at $z^* = 10$. Since we have concentrated on the ground state properties of the systems studied, the adsorbed particles have been always confined to the region very close to the surface (monolayer region). The cutoff distance $r^*_{\max}$ has been fixed and equal to 2.5 s^*.

In the case of incommensurate (striped) phases four types of domain walls can be defined (cf. Fig. 1 a-d). Another possible IC phase has the structure of rectangular commensurate domains separated by domain walls (cf. Fig. 1e), which in the case of heavy walls is called the CRHW structure. Therefore the number of particles in the system (N) has been determined by the assumed initial structure of the film, i.e., by the type and number of domain walls. In the case of striped phases, the starting configuration has been always chosen as the ideal lattice-like structure of the type shown in fig. 1 with specified type and number of walls, the distance between adjacent walls, l_x and the wall length L_y. Similarly, in the calculations performed for IC phases with rectangular domains (CRHW structure) an ideal structure of the assumed l_x, l_y and number of the domains has been used as a starting configuration. Then the system was allowed to relax to the stable state, by monitoring the behavior of its energy.

Each Monte Carlo step (MCS) consisted in N attempts to displace a randomly selected particle by, also randomly chosen, displacement vector within a cube of the side equal to $d_{\max}$ The magnitude of $d_{\max}$ has been dynamically adjusted during the run to keep the acceptance ratio at the level of about 40%.

The number of Monte Carlo steps required to attain steady state ranged between 10^6 and 10^7 The measured quantities have been obtained by averaging $10^6 - 10^8$ configurations spaced by 10 - 30 MCS's.

The basic thermodynamic quantities recorded during the simulation run were the adsorbate - adsorbate and adsorbate - substrate contributions to the system energy, the total energy, $\langle e_t^* \rangle$ and the density profiles $n(z^*)$. In the case of striped IC phases we have also recorded the average displacement fields Δx^*, Δy^* and Δz^* as functions of the distance from the wall core and the energy profiles $e(k)$ along the direction normal to the wall, so that k runs from 1 to L_x . The displacement fields as well as the energy profiles have been averaged over the one-dimensional stripes along the y axis.

In the case of striped phases, the wall energy, $e^{ex}_{2,w}(l_x, L_y)$ (in what follows we neglect the dependence of all wall properties on temperature), can be calculated using the energy profile as

$$e^{ex}_{2,w}\left(l_x, L_y\right) = \sum_{i=1}^{2l_x}\left[e(i) - e_c\right], \qquad (3)$$

where e_c is the energy (per particle) of the perfect c(2×2) commensurate structure.

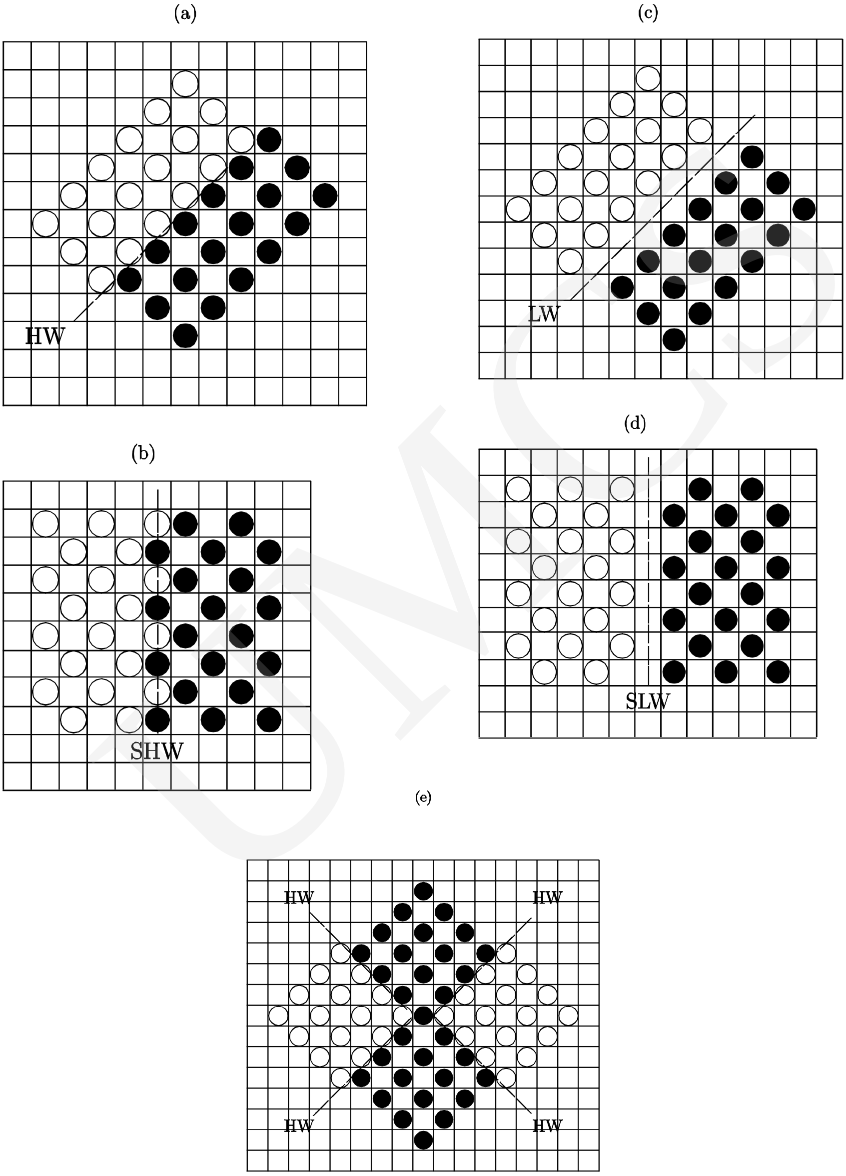

Fig. 1. Schematic representation of different domain walls that can appear in the system which orders into the c(2×2) registered structure

Alternatively, the wall energy can be computed from the known average energy $\left\langle e_t^* \right\rangle$ using the equation

$$e_{2,w}^{ex} = 2l_x\left[\left\langle e_t^* \right\rangle - e_c\right]. \tag{4}$$

Then, a single wall energy as well as the wall − wall interaction energy can be estimated.

In the case of the CRHW structures, the wall energy (per the unit of the wall length), $e_{CRHW,w}$ can be evaluated from the following equation

$$e_{CRHW,w} = \frac{l_x l_y}{l_x + l_y}\left[\left\langle e_t^* \right\rangle - e_c\right]. \tag{5}$$

Of course, $e_{CRHW,w}$ contains contributions due to a single wall energy, the wall - wall interaction energy as well as the energy due to the wall crossings, and a direct calculation of all those contributions is not possible. If, however, the wall energy and the wall - wall interaction energies are assumed to be the same as in the case of a striped phase, then it is possible to extract the information about the energy resulting from a single wall crossing, $\left\langle e_{cr}^* \right\rangle$, as

$$e_{cr}^*\left(l_x, l_y\right) = 0.5 * \left[e_{CRHW,w} - \frac{l_x e_{2,w}\left(l_x\right) + l_y e_{2,w}\left(l_y\right)}{l_x + l_y}\right]. \tag{6}$$

Following the results of our previous works [5,7], where it has been shown that only heavy walls are stable, we restrict the calculations to the striped phases with heavy walls and the CRHW structure. In the case of striped phases, the distance between walls, l_x, has been varied between 3 and 50, while in the case of CRHW phase both l_x and l_y have been changed between 4 and 16.

3. Results and discussion

At first the energies of single walls for the systems characterized by different surface field strength, e_{gs}^*, the corrugation parameter V_b and the size of adsorbed atoms s^* have been determined (see Tables 1).

In the case of striped phases with heavy domain walls the stability region of the commensurate phase depends strongly on both the corrugation of surface potential and the diameter of adsorbed atoms. When the misfit between the size of adsorbate atoms and the substrate lattice increases, then a higher potential barrier between adsorption sites V_D^* is needed to stabilize the commensurate phase.

Whenever the wall energy becomes negative and the stable state is the IC phase the walls form spontaneously.

Table 1. Energies of HW for systems characterized by different size of adsorbate atoms and different corrugation of the surface potential ($e_{gs}^* = 3$)

	$s^*=1.10$		$s^*=1.15$		$s^*=1.20$		$s^*=1.25$		$s^*=1.30$	
V_b	V_D^*	e_w^{ex}	V_D^*	e_w^{ex}	V_D^*	e_w^{ex}	V_D^*	e_w^{ex}	V_D^*	e_w^{ex}
0.3	0.539	-	0.564	-1.537	0.585	-0.962	0.601	0.000	0.613	1.600
0.4	0.776	-1.800	0.808	-1.337	0.833	-0.670	0.852	0.330	0.865	2.490
0.5	1.055	-1.590	1.092	-1.111	1.121	-0.355	1.138	1.050	1.150	3.200
0.6	1.390	-1.416	1.428	-0.858	1.454	-0.004	1.470	1.210	1.476	3.826
0.7	1.802	-1.200	1.835	-0.553	1.853	0.405	1.858	1.700	1.854	4.490
0.8	2.326	-0.918	2.341	-0.177	2.340	0.900	2.327	2.365	2.301	5.240
0.9	3.029	-0.526	3.001	0.328	2.961	1.535	2.907	3.130	2.844	6.140
1.0	4.070	-0.090	3.932	1.077	3.797	2.400	3.663	4.129	3.530	7.260

Calculations of the displacement fields (Δx^*, Δy^* and Δz^*) have demonstrated that the walls are rather narrow, even when the surface potential corrugation becomes small and corresponds to the region of spontaneous formation of walls. Figure 2 presents the displacement fields Δx^* (part a) and Δz^* (part b) plotted against the distance from the wall core, for the systems with adsorbed atoms of the size $s^* = 1.2$ and characterized by $e_{gs}^* = 3.0$ and different corrugation parameter V_b. The displacement field Δy^* is not shown as it is practically equal to zero everywhere. It is quite evident that the decrease of the surface potential corrugation leads to a gradual widening of walls. From the results shown in Fig. 2a we find that in the case of strongly corrugated ($V_b = 1$) surface potential the wall involves only three rows of adatoms at each side of the wall, while in the case of weakly corrugated surface potential ($V_b = 0.3$) the wall is two times wider. In the case of Δz^*, only the first two rows of atoms, at both sides of the wall, show visible deviations from zero (Fig. 2b).

It follows from the fact that small shifts along the x axis induce still smaller changes in the location of the potential minimum along the z-axis. Quite similar results have been found for systems characterized by different s^*. Strong localization of heavy walls leads to a very fast decay of the displacement field Δx^* with the distance from the core of the wall. In fact, in systems of sufficiently small adsorbate atoms (large negative misfit) and characterized by strongly corrugated surface potential, only the first two, or three, rows of atoms adjacent to the wall core show nonzero displacement field Δx^*. In the systems of lower corrugation of the surface potential, we have found that the decay of Δx^* with x is exponential

$$\Delta x^* \propto \exp\left[-x^*/x_w\right], \tag{7}$$

where the parameter x_w can be treated as a measure of the wall thickness. For larger negative misfit ($s^* \leq 1.2$) the walls become very well localized and only the first two rows of atoms adjacent to the wall exhibit nonzero displacement field Δx^*. Exponential decay of Δx^* with the distance from the wall core agrees with the predictions stemming from the theory of Bak *et al*. [12] applied to a simple striped IC phase, when the wall-wall separation is sufficiently large and the displacement field $\Delta y^* = 0$. Also, the one-dimensional theories of Frankel and Kontorova [13] and of Frank and Van der Merwe [14] shows that over a certain range of the distance from the wall core, the displacement field Δx^* can be approximated by the exponential curve.

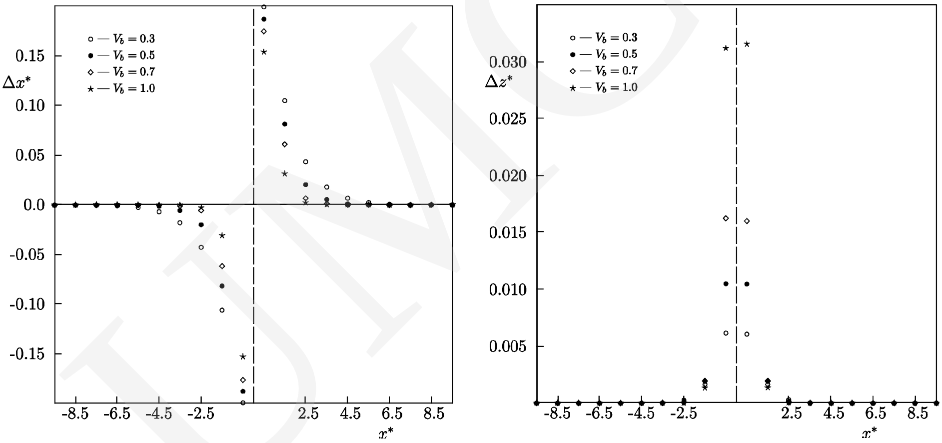

Fig. 2. The displacement fields Δx^* (part a) and Δz^* (part b) versus the distance from the wall core for the striped phase with heavy walls, obtained for a series of systems characterized by s^* = 1.2, e^*_{gs} = 3.0, l_x = 30 and different corrugation

Since the walls are strongly localized, one expects that the wall − wall interaction energy

$$g_{ww}(l_x) = \left[e^{ex}_{w,o}(l_x) - e^{ex}_{w,o}(\infty) \right] \qquad (8)$$

should vanish for sufficiently large distances between walls (l_x), and our calculations confirm that prediction very well. In general, the wall - wall interaction is repulsive and exponentially decays with the wall - wall separation

$$g_{ww}(l_x) \propto exp\left[-l_x / x_{ww} \right], \qquad (9)$$

where the constant x_{ww} is interpreted as another measure of the wall width.

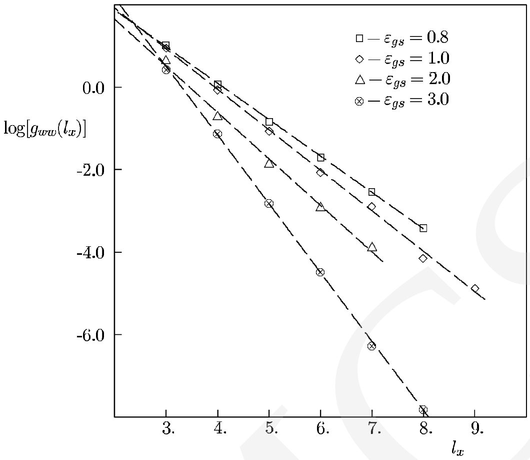

Fig. 3. Plots of the logarithm of the wall - wall energy versus the wall - wall separation for the striped phases with heavy walls, obtained for the systems with $s^* = 1.27$, $V_b = 1.0$ and different e^*_{gs} (shown in the figure)

Figure 3 presents the plots of $\log g_{ww}(l_x)$ versus l_x for a series of systems with a fixed values of $s^* = 1.27$ and $V_b = 1.0$ and with different strength of the surface potential. Obviously, the above eq. (9) is satisfied and the wall thickness decreases with e^*_{gs} as expected. Our results are in agreement with other theoretical predictions [2, 8-9]. Of course, the above relation holds only when the wall – wall interaction is repulsive and sufficiently long ranged. In some systems with strongly corrugated surface potential the wall - wall interaction drops to zero at very small wall – wall separations of four or five lattice spacings. In such cases, eq. (9) can not be used, quite the same as in the case of eq. (7) which describes the behavior of Δx^*.

The results of our study have clearly demonstrated that in the case of strongly corrugated surface potential the adsorbed layer forms the incommensurate structures with rectangular domains separated by heavy walls (Fig. 4). Therefore it is of interest to estimate the contributions to the system energy resulting from the wall crossings, e^*_{cr}. The calculations have been performed for square domains of different size (l_x, l_x) for a series of systems with different size of the adsorbate atoms and with the fixed values of $e^*_{gs} = 3.0$ and $V_b = 1.0$. The results are presented in figure 5, which shows the plots of e^*_{cr} against l_x^{-1}. For the systems with $s^* \geq 1.20$ the energy due to the wall crossing is negative and hence the formation of domains with crossing walls is energetically favored with respect to the striped phase with parallel orientation of walls. Of course, when the domain size increases the energy $e^*_{cr}(l_x,l_x)$ decays to zero proportionally to l_x^{-1}. Therefore, we can write

$$c^*_{cr}\left(l_x,l_x\right) = 0.5\cdot c^*_{cr,o}/l_x \tag{10}$$

and consider $c^*_{cr,o}$ as the energy due to a single wall crossing. The multiplier 0.5 results from the fact that e^*_{cr} represents the energy due to a pair of walls crossings. The inset to fig. 5 shows the plot of $c^*_{cr,o}$ against s^*.

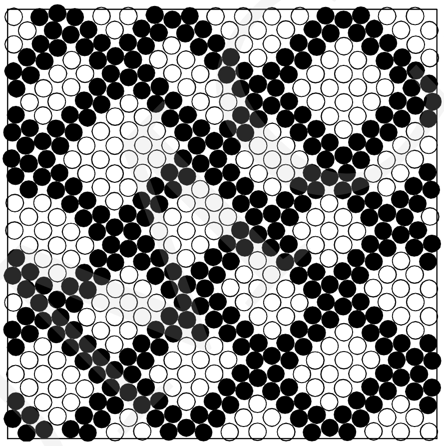

Fig. 4. A typical low temperature configuration obtained for the system characterized by e^*_{gs} = 2.0 and the density ρ = 0.6. The configuration shown in the figure has been recorded during the canonical ensemble simulation at T^* = 0.05 for the system of the size 30×30×10. The particles which belong to the commensurate domains are represented as white circles and those which form walls are shown as black circles. The distinction between the particles belonging to the commensurate domains and to the walls has been possible owing to the bimodal character of the density profile $n_{\perp}(z^*)$. The low-lying particles belong to the commensurate domains while the particles in the walls exhibit a larger distance from the surface

One readily notes that for small domains the relation (10) is not satisfied. In such systems the wall − wall interaction between parallel and perpendicular walls is nonnegligible and contributes to the total energy. The procedure used to extract the energy of the wall crossing neglected those terms and hence it is not surprising that large deviations from eqn. (10) occur.

The demonstration that the energy due to wall crossings for the adsorbed layers formed by atoms of s^* = 1.2 and larger is negative is surely the most interesting result of our study. It cofirms that the CRHW structure has higher stability than the striped structure with parallel heavy walls in agreement with our earlier Monte Carlo studies [5-6], where it was shown that the CRHW structures of different domain sizes form spontaneously during a slow cooling of an initially disordered adsorbed film. It is noteworthy that the negative contribution to the energy, resulting from the wall intersection has been also found by Schöbinger and Abraham [16], who performed molecular dynamics study of incommensurate phases of krypton adsorbed on graphite. At this point we should note that the stability of the CRHW IC phase can not be attributed to entropic effects, as it occurs in the case of honeycomb wall networks [16-17]. Rectangular wall networks can not 'breathe' and hence the corresponding entropic contribution (breathing entropy) [3] is not present. In the case of a rectangular wall network an attempted breathing of a single domain inevitably leads to the development of dislocations followed by coalescence of different domains. In order to preserve the domain structure, in particular the total length of walls and the number of wall crossings, the system would have to exhibit a sort of “collective breathing”, which involves all domains along a given wall.

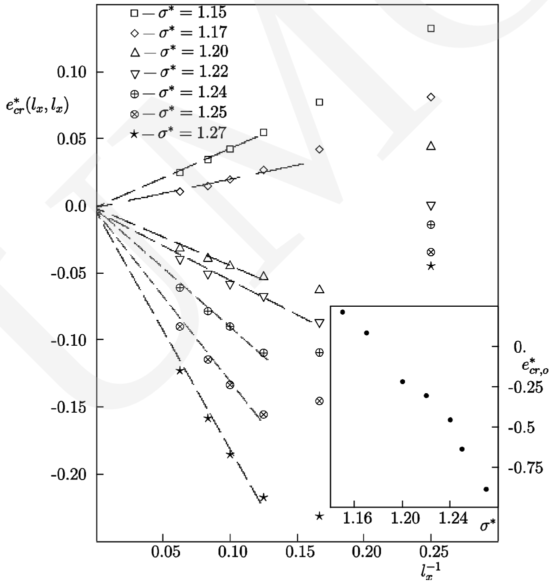

Fig. 5. The energy contribution due to the crossing of heavy walls as a function of l_x^{-1} for a series of systems characterized by e_{gs} = 1.0, V_b = 1.0 and different size of adsorbate atoms (shown in the figure). The inset shows the plot of $e^*_{cr,o}$ versus s^*

Such a process may occur at elevated temperatures, as a consequence of wall meandering, but only if the wall-wall distance is sufficiently large. Note that for the systems with $s^* \geq 1.2$ the energy contribution due to wall crossing is negative and it may be energetically expensive to change its position. Whenever the energy of wall crossing is negative, the network is stabilized and hence prevents meandering. In particular, the system can be expected to preserve the number of wall crossings, which is determined by the density of the adsorbed monolayer. Since, in most cases, the wall-wall interaction is very small and rapidly decays with the wall-wall distance, the CRHW structure of a given density is expected to show large degeneracy due to the presence of commensurate domains of different size, while the total length and the number of wall crossings in the system remain fixed. On the other hand, in the systems which show attractive wall-wall interaction a regular pattern of domains is likely to produce the state of the lowest energy at the ground state, which may be rather difficult to detect in simulations due to metastability and finite size effects.

References

[1] Villain J., *Ordering in Strongly Fluctuating Condensed Matter Systems*, Ed. T. Riste, Plenum, New York, (1980) 221.
[2] Bak P., Rep. Prog. Phys., 45 (1982) 587.
[3] den Nijs M., *Phase Transitions and Critical Phenomena*, Eds. C. Domb and J. L. Lebowitz, Academic Press, London, 12 (1988) 219.
[4] Patrykiejew A., Sokołowski S., Binder K., Surf. Sci. Rep., 37 (2000) 207.
[5] Patrykiejew A., Sokołowski S., Binder K., J. Chem. Phys., 115 (2001) 983.
[6] Patrykiejew A., Sokołowski S., Binder K., *Computer Simulation Studies in Condensed Matter Physics, XIV*, (Eds. D. P. Landau, S. P. Lewis and H.-B. Schüttler), Springer, Berlin, (2001).
[7] Patrykiejew A., Sokołowski S., Binder K., Surface Sci. ****
[8] Houlrik J. M., Landau D.P., Phys. Rev. B, 44 (1991) 8962.
[9] Fisher M.E., Szpilka A.M., Phys. Rev. B, 36 (1987) 644.
[10] Steele W.A., Surf. Sci., 36 (1976) 317.
[11] Landau D.P., Binder K., *A Guide to Monte Carlo Simulation in Statistical Physics*, Cambridge Univ. Press, Cambridge, (2000).
[12] Bak P., Mukamel D., Villain J., Wentowska K., Phys. Rev. B, 19 (1979) 1610.
[13] Frenkel Y.I., Kontorova T., Zh. Eksp. Teor. Fiz., 8 (1938) 1340.
[14] Frank F.C., Van der Merwe J.H., Proc. Royal Soc., 198 (1949) 205, 216.
[15] Bak P., Emery V.J., Phys. Rev. Lett., 36 (1976) 978.
[16] Schöbinger M., Abraham F.F., Phys. Rev. B, 31 (1985) 4590.
[17] Villain J., Surf. Sci., 97 (1980) 219.