Phase Transitions and Adsorption Isotherm in Multilayer Adsorbates with Lateral Interactions

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Abstract

We analyze here a model for an adsorbate system composed of many layers by extending a theoretical approach used to describe pattern formation on a monolayer of adsorbates with lateral interactions. The approach shows, in addition to a first order phase transition in the first layer, a transition in the second layer together with evidence of a “cascade” of transitions if more layers are included. The transition profiles, showing a staircase structure, corroborate this picture. The adsorption isotherm that came out of this approach is in qualitative agreement with numerical and experimental results.
1 Introduction

The problem of phase transitions and ordering phenomena in adsorbed films on crystal surfaces has attracted considerable interest for many years (see [1] for a recent review). Formation of ordered structures of particles adsorbed on surfaces due to mutual (lateral) interactions has been observed in many experiments, originating different types of adsorption isotherm [2, 3]. Strong attractive (lateral) interactions lead to phase separation with different coverages, characteristic of first order phase transitions [2, 3].

It is well known experimentally that adsorption on surfaces is not only restricted to the formation of monolayers, but rather a second layer can condensate on the first one, a third on the second, and so on [4]. Numerical simulations also show similar results [5]. The old BET theory [6] considered the possibility of multilayer adsorption but, as it does not include interactions among particles in the same layer, does not yield either a phase transition or ordered structures. So far we are not aware of theoretical models to describe this situation. Other theoretical forms for isotherm intended to describe such a multilayer adsorption phenomenon have been discussed in the literature [7]. However, such models do not seem to be able to describe phase transitions or pattern formation.

The aim of the present work is to introduce a simple model that can describe multilayer adsorption qualitatively and the formation of ordered structures. To reach this goal we exploit a model introduced in Ref.[2] to describe a system of a monolayer of adsorbed particles with lateral attractive interactions leading to the formation of interfaces separating phases with different local coverage. The new aspect is that we extend such a model and go beyond the one layer system considering a multilayer system (however, focusing on the case of only two layers) including also an exchange interaction between different layers. It is worth remarking here that such a “macroscopic” model can be derived from a microscopic one following a procedure similar to that used in [8].

In what follows we present the model, show the form of the isotherm, and discuss briefly some aspects of the critical point and the form of the density profiles of the possible fronts. Finally we draw some conclusions.

2 Adsorptive multilayer system

We adopt here a phenomenological point of view. However, a formal derivation of the macroscopic master equation leading us to the phenomenological equations we present here, is included in the appendix, where we start from a microscopic description closely following the procedure of Ref.[8]).

We adopt a continuous description for the surface, and characterize the adsorptive species through evolution equations for \( c_i(x, t) \), the local coverage in the \( i \)-th layer (see the appendix for the precise definition of these local coverage). The adsorptive contribution is characterized by \( k_a \) (a constant), and the adsorption is only possible in the \( (1 - c_i) \) free sites of the corresponding layer. Hence, the adsorption rate is \( k_a p (1 - c_i) \), where \( p \) is the partial pressure of the gaseous phase. Additionally, for adsorption on the \( i \)-th layer, it is required to have free sites on the \( i + 1 \)-th layer.

The desorption process has a rate \( k_d \), that includes \( k_{d,0} \), the desorption for noninteracting particles, and a correction due to the lateral interactions. The strong local bond induced by the interaction \( U_1(x) \) (\( U_2(x) \) for the second layer, etc), corrects the desorption rate as: \( k_d = k_{d,0} \exp[U_i(x)/kT] \), where \( k \) is the Boltzmann constant and \( T \) the temperature. According to the form we use to introduce such an interaction, we are assuming that it is a substratum mediated interaction. A desorption process in the first layer can happen only if the corresponding site on the second layer is free.
The potential \( U_i(x) \) produces a force \( F_i = -\frac{\partial U_i(x)}{\partial x} \), that affects the adsorbed particles inducing a velocity \( v_i = bF_i \), where \( b \) is the mobility (given by Einstein’s relation \( b = \frac{D}{\mu} \), with \( D \) the diffusion coefficient in the \( i \)-th layer). The associated particle flux is \( j_i \sim c_i v_i \). Because the flux is only possible at the \((1 - c_i)\) free sites, its final form is

\[
j_i = -\frac{D}{kT} c_i (1 - c_i) \frac{\partial U_i(x)}{\partial x},
\]

while the diffusion flux is given by

\[
j_{i\text{diff}} = -D \frac{\partial c_1}{\partial x}, \quad j_{i\text{diff}} = -D \frac{\partial c_2}{\partial x},
\]

for the first and the second layer respectively.

The possible transference interaction between different layers is characterized by a coupling parameter \( k_T \). It involves free sites in the final layer and occupied ones in the original layer. Hence, the form of this contribution is \( k_T c_i (1 - c_{i+1}) \) for transfer from a given layer to the upper one, and similarly in other cases. In Fig. 1 we sketch the different processes entering into our model.

Considering all the above, the evolution equations for the different coverage can be written as

\[
\frac{\partial}{\partial t} c_1(x, t) = k_{a}p(1 - c_1)(1 - c_2) - k_{d,0}(1 - c_2)c_1 \exp[U_1(x)/kT] + c_1(1 - c_2)k_T + \frac{\partial}{\partial x} \left[ \frac{D}{kT} \frac{\partial U_1(x)}{\partial x} c_1(1 - c_1) + D \frac{\partial c_1}{\partial x} \right] \quad (1)
\]

\[
\frac{\partial}{\partial t} c_2(x, t) = k_{a}p c_1(1 - c_2) - k'_{d,0}c_2 \exp[U_2(x)/kT] + k_T c_2(1 - c_1) + \frac{\partial}{\partial x} \left[ \frac{D}{kT} \frac{\partial U_2(x)}{\partial x} c_2(1 - c_2) + D \frac{\partial c_2}{\partial x} \right]. \quad (2)
\]

According to [2], we can employ the following simple approach. In thermal equilibrium the coverage \( c_i(x) \) of the \( i \)-th layer is stationary, that is \( \frac{\partial c_i}{\partial t} = 0 \). The flux induced by the gradient of the potential is balanced by the diffusion one yielding

\[
k_{a}p (1 - c_1)(1 - c_2) - k_{d,0}(1 - c_2)c_1 \exp[U_1(x)/kT] + c_1(1 - c_2)k_T = 0 \quad (3)
\]

\[
k'_{a}p c_1(1 - c_2) - k'_{d,0}c_2 \exp[U_2(x)/kT] + k_T c_2(1 - c_1) = 0. \quad (4)
\]

If we consider the case of constant \( U_i(x) \) as well as no transfer between the layers, we have

\[
k_{a}p (1 - c_1)(1 - c_2) - k_{d,0}(1 - c_2)c_1 \exp[U_1/kT] = 0 \quad (5)
\]

\[
k'_{a}p c_1(1 - c_2) - k'_{d,0}c_2 \exp[U_2/kT] = 0. \quad (6)
\]

We can get \( c_1 \) from the first expression obtaining a result that agrees with the well known form of the Langmuir isotherm for adsorption in a monolayer [2]

\[
c_1 = \frac{1}{1 + \left( \frac{k_{d,0}}{k_a p} \right) \exp[U_1/kT]} \quad (7)
\]

We can also obtain \( c_2 \) from the previous system and consider the total coverage, that can be eventually compared with the results of the usual BET isotherm [3] or similar ones [4]. However, our main interest is to obtain relations and conditions yielding the phase transition, as well as the form of evolution fronts.
For the functional form of \( U_i(\vec{x}) \) we assume an attractive (and as indicated earlier, stratum mediated) potential among particles separated a distance \( r \), that we denote by \( u_i(r) \). The potential acting on a particle located at \( r \) in the first layer is

\[
U_1(r) = -\int u_1(r-r')c(r')dr'.
\]  

(8)

The integration domain is the whole surface. As a first step in our analysis we assume that we have the same potential \( u(r-r') \) among particles in all layers. The function \( u(r) \) depends on the nature of the system. If the interaction radius is small compared with the diffusion length, and the coverage is not much affected by variations in this radius, we can approximate

\[
\int u(r-r')c_1(r')dr' \simeq \int u(r-r')[c_1(r) + (r-r')\frac{\partial c_1}{\partial r} + \frac{1}{2}(r-r')^2\frac{\partial^2 c_1}{\partial r^2} + \cdots]dr'.
\]  

(9)

The spatial derivatives are evaluated at \( r \). Hence we obtain

\[
U_1(r) = -\int u(r-r')c_1(r')dr' \simeq -u_0c_1 - \chi_1\frac{\partial^2 c_1}{\partial r^2},
\]  

(10)

where the coefficients are given by

\[
u_0 = \int u(r)dr,
\]  

(11)

and

\[
\chi_1 = 1/2 \int r^2u(r)dr,
\]  

(12)

and from symmetry considerations we have \( \int ru(r)dr = 0 \).

In a similar way (and remembering that we assume the lateral interaction is stratum mediated) for the second layer we get

\[
U_2(r) = c_1[-\int u(r-r')c_2(r')dr'].
\]  

(13)

After replacing \( c_2(r') \) by its approximation (that is a Taylor expansion around \( r \) as in Eq. (8)), we find

\[
U_2(r) = -c_1\int u(r-r')c_2(r')dr' \simeq -c_1[u_0c_2 + \chi_2\frac{\partial^2 c_2}{\partial r^2}],
\]  

(14)

where \( u_0 \) and \( \chi_2 \) have the same form as before.

Replacing \( U_1(r) \) y \( U_2(r) \) into the equations of motion Eqs.(1,2), we get

\[
\frac{\partial}{\partial t}c_1(r,t) = k_0p(1-c_1)(1-c_2) - k_{d,0}(1-c_2)c_1e^{-u_0c_1/kT} + c_1(1-c_2)k_T
\]

\[
+ \frac{\partial}{\partial r}[D(1 - \frac{u_0}{kT}(1-c_1)c_1)\frac{\partial c_1}{\partial r}],
\]

(15)

\[
\frac{\partial}{\partial t}c_2(r,t) = k'_0pc_1(1-c_2) - k'_{d,0}c_2e^{-u_0c_2/kT} + k_Tc_2(1-c_1)
\]

\[
+ \frac{\partial}{\partial r}[D(1 - \frac{u_0}{kT}c_1(1-c_2)c_2)\frac{\partial c_2}{\partial r}],
\]

(16)

In both equations we have neglected the contribution coming from the terms \( \chi_i\partial^2 c_i \), as we follow Ref. [8], and assume they are only small contributions.
To simplify the notation we assume $D_1 = D_2 = D$, and we scale the variables as follows: 
\[ \xi = x/L_{\text{dif}}, \]
where the diffusion length is $L_{\text{dif}} = (D/k_{d,0})^{1/2}$; $\tau = t/t_d$, with $t_d = 1/k_{d,0}$; $\varepsilon = u_0/kT$. Finally, $\alpha = k_{ap}/k_{d,0}$ characterizes the coverage in equilibrium when $U(x)$ becomes zero. Also, $K = kT/k_{d,0}$ is the exchange parameter.

With the indicated scaling the evolution equations for $c_i(\xi, \tau)$ reduce to
\[
\frac{\partial c_1}{\partial \tau} = \alpha_1 (1 - c_1)(1 - c_2) - (1 - c_2)c_1 \exp[-\varepsilon c_1]
\]
\[
- \frac{\partial}{\partial \xi} [\varepsilon c_1 (1 - c_1) \frac{\partial c_1}{\partial \xi}] + \frac{\partial^2 c_1}{\partial \xi^2} + c_1 (1 - c_2)K
\]
\[
17)
\]
\[
\frac{\partial c_2}{\partial \tau} = \alpha_2 c_1 (1 - c_2) - c_2 \exp[-\varepsilon c_1 c_2]
\]
\[
- \frac{\partial}{\partial \xi} [\varepsilon c_1 (1 - c_2) c_2 \frac{\partial c_2}{\partial \xi}] + \frac{\partial^2 c_2}{\partial \xi^2} + c_2 (1 - c_1)K.
\]
\[
18)
\]

As in [2], we may consider for the stationary regimen or thermodynamic equilibrium (and initially assuming $K = 0$) that
\[
\alpha_1 (1 - c_1) - c_1 \exp[-\varepsilon c_1] = 0 \quad 19)
\]
\[
\alpha_2 c_1 (1 - c_2) - c_2 \exp[-\varepsilon c_1 c_2] = 0. \quad 20)
\]

The dependence of the coverages $c_i$ on $\varepsilon$, $\alpha_1$ and $\alpha_2$ is apparent. The result is analogous to that shown in Fig. 2 of Ref. [2]. It shows that in the plane $(\varepsilon, \alpha_1)$ there are three regions. Two of them correspond to real solutions, with homogeneous coverage, while the intermediate region is bistable and presents a coexistence phase with intermediate coverages. Those regions coalesce in a critical point indicating a second order phase transition.

In equilibrium and from the diffusive term we get equations for $c_1$ and $c_2$:
\[
1 - \varepsilon c_1 (1 - c_1) = 0,
\]
\[
1 - \varepsilon c_1 (1 - c_2)c_2 = 0.
\]

The last expressions indicate that in order to have a high coverage in the first layer we need $\varepsilon > 4$, while for the second layer we find a relation with the coverage of the first one through $\varepsilon > 4/c_1$. This indicates that $c_2$ becomes relevant only after some threshold value of the coverage has been reached in the first layer.

The kind analysis we have just outlined, has been strongly criticized in [3] on the basis that the Maxwell construction in [2] is done assuming that coverages near the interface correspond to the spinodal points. This was discussed and corrected in [10] using the true equilibrium condition, that is that the chemical potentials of both phases should be equal at the transition point. In the next Section we use such an approach in order to determine the correct phase diagram.

### 3 Local Chemical Potential

As indicated in the last part of the previous section and in order to analyze the phase transition we follow [4] defining a local chemical potential for each layer according to
\[
\varphi = - \int u(r - r') c_1(r') dr' + kT \ln \frac{c_1(r)}{1 - c_1(r)}, \quad 21)
\]
\[ \varphi' = -c_1 \int u(r - r')c_2(r')dr' + kT \ln \left[ \frac{c_2(r)}{1 - c_2(r)} \right]. \] (22)

Using these definitions, the equations of motion can be written as

\[ \frac{\partial c_1}{\partial t} = k_a p (1 - c_1) [1 - e^{-\frac{\varphi - \varphi_0}{kT}}] + \partial \frac{D}{\partial r} \left[ \frac{c_1}{kT} (1 - c_1) \frac{\partial \varphi}{\partial r} \right], \] (23)

\[ \frac{\partial c_2}{\partial t} = k_a p c_1 (1 - c_2) [1 - e^{-\varphi' - \varphi'_0}] + \partial \frac{D}{\partial r} \left[ \frac{c_2}{kT} (1 - c_2) \frac{\partial \varphi'}{\partial r} \right], \] (24)

where

\[ \varphi_0 = kT \ln \left[ \frac{k a p}{k_d o} \right], \] (25)

and

\[ \varphi'_0 = kT \ln \left[ \frac{k a p}{k'_d o} c_1 \right]. \] (26)

In equilibrium these chemical potentials are constant on all surface regions corresponding to each layer and equal to \( \varphi_0 \), for the first one and \( \varphi'_0 \), for the second.

For a uniform distribution, according to Eqs. (21) and (22), the chemical potentials are given by

\[ \varphi(c_1) = -u_0 c_1 + kT \ln \left[ \frac{c_1}{1 - c_1} \right], \] (27)

and

\[ \varphi'(c_2) = -u_0 c_1 c_2 + kT \ln \left[ \frac{c_2}{1 - c_2} \right]. \] (28)

In figure 2 we depict the phase diagram that clearly shows three regions: a low and a high coverage region, and a central region corresponding to coexistence. This last region is bistable in both layers and fulfills the conditions \( \frac{d\varphi}{dc_1} = 0; \frac{d\varphi'}{dc_2} = 0; \) that explicitly indicate

\[ \frac{d\varphi}{dc_1} = -u_0 + \frac{kT}{c_1(1 - c_1)} = 0, \] (29)

and

\[ \frac{d\varphi'}{dc_2} = -u_0 c_1 + \frac{kT}{c_2(1 - c_2)} = 0. \] (30)

In order that the interface separating both phases be stationary, the Maxwell condition should be satisfied in both cases. Such a condition can be derived for \( \varphi = \varphi_0 \) and \( \varphi' = \varphi'_0 \), together with the approximation indicated in Eq. (10). This yields the following equations

\[- u_0 c_1 + kT \ln \left( \frac{c_1}{1 - c_1} \right) - \chi_1 \frac{\partial^2 c_1}{\partial r^2} = \varphi_0, \] (31)

and

\[- u_0 c_2 + kT \ln \left( \frac{c_2}{1 - c_2} \right) - \chi_2 \frac{\partial^2 c_2}{\partial r^2} = \varphi'_0. \] (32)

From these expressions we can obtain the Maxwell condition corresponding to the coexistence of both phases. For the first layer we have

\[ \int_{c_{11}}^{c_{12}} (\varphi(c_1) - \varphi_0) dc_1 = 0, \] (33)

where \( \varphi(c_1) \) is given by Eq. (27), and \( c_{11}, c_{12} \) are the coverage values in the equilibrium phases on the first layer. For the second layer we have

\[ \int_{c_{21}}^{c_{22}} (\varphi'(c_2) - \varphi'_0) dc_2 = 0, \] (34)

where \( \varphi(c_2) \) is given by Eq. (28), and \( c_{21}, c_{22} \) are the coverage values in the equilibrium phases.
4 Stationary coexisting states

4.1 First layer

As seen above, the coexistence line between the dense and diluted phases on the first layer is given by the Maxwell condition in Eq. (33), where

\[ \varphi(c_1) = -u_0 c_1 + kT \ln \left( \frac{c_1}{1 - c_1} \right), \]  
\[ \varphi_0 = kT \ln \left( \frac{k_a p}{k_{d,0}} \right). \]  

After integrating we find

\[ -\frac{u_0 c_1^2}{2} + kT \ln(1 - c_1) + kT c_1 \ln\left( \frac{c_1}{1 - c_1} \right) - \varphi_0 c_1 = \]
\[ = \frac{-u_0 c_1^2}{2} + kT \ln(1 - c_1) + kT c_1 \ln\left( \frac{c_1}{1 - c_1} \right) - \varphi_0 c_1. \]  

Here, \( c_{11} \) and \( c_{12} \) are the equilibrium coverages of both phases on the first layer. They satisfy the equations

\[ -u_0 c_{11} + kT \ln\left( \frac{c_{11}}{1 - c_{11}} \right) = \varphi_0, \]  
\[ -u_0 c_{12} + kT \ln\left( \frac{c_{12}}{1 - c_{12}} \right) = \varphi_0, \]  

with \( \varphi_0 \) given by

\[ \varphi_0 = kT \ln \left( \frac{k_a p}{k_{d,0}} \right). \]  

After some algebra, where the condition \( c_{11} + c_{12} = 1 \) arises, we get

\[ -u_0 c_{11} + kT \ln\left( \frac{c_{11}}{1 - c_{11}} \right) = -\frac{1}{2} u_0. \]  

When comparing Eqs. (38) and (41), we see that

\[ \varphi_0 = \frac{1}{2} u_0. \]  

Replacing \( \varphi_0 \) by Eq. (40) we finally obtain the coexistence condition on the first layer

\[ \frac{k_a p}{k_{d,0}} = e^{-\frac{u_0}{2kT}}. \]  

4.2 Second layer

In a similarly way for the second layer, we consider Eq. (34), where

\[ \varphi' = -u_0 c_1 c_2 + kT \ln\left( \frac{c_2}{1 - c_2} \right), \]  

and

\[ \varphi'_0 = kT \ln \left( \frac{k'_a p}{k'_{d,0} c_1} \right). \]
After integrating we get

\[-\frac{u_0 c_1 c_{21}^2}{2} + kT \ln(1 - c_{21}) + kT c_{21} \ln\left(\frac{c_{21}}{1 - c_{21}}\right) - \varphi'_0 c_{21} =\]

\[= -\frac{u_0 c_1 c_{22}^2}{2} + kT \ln(1 - c_{22}) + kT c_{22} \ln\left(\frac{c_{22}}{1 - c_{22}}\right) - \varphi'_0 c_{22}.\] (46)

Here \(c_{21}\) and \(c_{22}\) are the equilibrium coverages in both phases of the second layer. They fulfill the equations

\[- u_0 c_1 c_{21} + kT \ln\left(\frac{c_{21}}{1 - c_{21}}\right) = \varphi'_0,\] (47)

and

\[- u_0 c_1 c_{22} + kT \ln\left(\frac{c_{22}}{1 - c_{22}}\right) = \varphi'_0,\] (48)

and \(\varphi'_0\) is given by

\[\varphi'_0 = kT \ln\left(\frac{k'_{\alpha p}}{k'_{d,0}}\right).\] (49)

As in the previous subsection, after some algebra where the condition \(c_{21} + c_{22} = 1\) arises, we get

\[- u_0 c_1 c_{21} + kT \ln\left(\frac{c_{21}}{1 - c_{21}}\right) = -\frac{1}{2} u_0 c_1.\] (50)

Comparing Eqs. (47) and (50), we see that

\[\varphi'_0 = -\frac{1}{2} u_0 c_1.\] (51)

Replacing \(\varphi'_0\) by Eq. (49) we get

\[\frac{k'_{\alpha p}}{k'_{d,0}} = \frac{1}{c_1} e^{-\frac{\varphi'_0}{kT}}.\] (52)

For the first layer we denote

\[\varepsilon = \frac{u_0}{kT},\] (53)

while for the second

\[\varepsilon' = \frac{u_0 c_1}{kT}.\] (54)

5 Adsorption isotherm and Critical behaviour

The adsorption isotherm can be obtained from Eqs. (13) and (52). The result for \(\theta\), that is the total coverage \((\theta = c_1 + c_2)\), is shown in Fig. 3. We only show \(\theta\) as a function of the chemical potential (the difference with the representation \(\theta\) vs. \(p (\propto \alpha)\) amounts to a logarithmic scale change).

The staircase form is apparent. The first step corresponds to the filling of the first layer, the second one to the filling of the second layer, and so on. It is clear that if we consider more layers the structure will persist, but with a progressive collapse of the step size [4, 5]. It is of interest to determine how the step size for different layers depends on the system parameters, in particular on \(\varepsilon\). The analysis indicates that, for the first layer, \(\Delta \varphi\), the step’s size, as a function of \(\varepsilon\), scales as \(\Delta \varphi \sim \varepsilon^\nu\) with \(\nu \approx 2.0\). A similar analysis for the second step indicates that \(\nu \approx 1.9\), showing a decrease in step’s size, in qualitative agreement with known data [4, 5].

It is also possible to analyze the behaviour of the order parameters (that is \(\Delta c_i = c_i^+ - c_i^-\)) near the critical point, considering their dependence on \(\alpha_i\) (that are related with the partial
pressure, i.e. $\alpha_i \sim p$). The characterization of such critical behaviour is certainly of interest \[11\]. In our case, from Eqs. (38,39) and (48,49) and near the critical point, we have

$$c_1^+ - c_1^- = \frac{1}{(\varepsilon)^{1/2}}(\varepsilon - 4)^{1/2} = \frac{1}{2}\eta^{1/2}$$

with $\eta = \varepsilon - 4$ (with $\varepsilon \sim 4$); and

$$c_2^+ - c_2^- = \frac{1}{(\varepsilon_0)^{1/2}}(\varepsilon - \varepsilon_0)^{1/2} = \eta'^{1/2}$$

where $\eta' = \varepsilon - \varepsilon_0$ (with $\varepsilon_0 \sim 1$). For both layers, we see that the critical behaviour, as could be expected, corresponds to the typical mean field one with a critical exponent 1/2.

6 Density Profiles

In this section we show how to get the form of the density profile of a propagating interface with constant velocities $v_1$ for the first layer and $v_2$ for the second layer. They can be obtained considering the following change of variables in Eqs. (17): $c_1(\xi_1)$; with $\xi_1 = \xi - v_1\tau$ and $c_2(\xi_2)$; with $\xi_2 = \xi' - v_2\tau$. Where $c_1(\xi_1) \to c_1$ when $\xi_1 \to \infty$, $c_1(\xi_1) \to c_3$ when $\xi_1 \to -\infty$, and also $c_2(\xi_2) \to c_5$ when $\xi_2 \to \infty$ $c_2(\xi_2) \to c_7$ when $\xi_2 \to -\infty$.

With the indicated change of variables, the partial differential equations (17) transform into ordinary differential equations

$$-v_1 \frac{dc_1}{d\xi_1} = g_1(c_1) + D(c_1) \frac{dc_1}{d\xi_1},$$

$$-v_2 \frac{dc_2}{d\xi_2} = g_2(c_2) + D(c_2) \frac{dc_2}{d\xi_2},$$

where

$$g(c_1) = \alpha_1(1 - c_1) - c_1 \exp(-\varepsilon c_1)$$

$$D(c_1) = 1 - \varepsilon c_1(1 - c_1),$$

for the first layer, and

$$g(c_2) = \alpha_2(1 - c_2) c_1 - c_2 \exp(-\varepsilon c_1 c_2),$$

$$D(c_2) = 1 - \varepsilon c_2(1 - c_2) c_1,$$

for the second layer.

For convenience we assume that the concentration jump is localized at $\xi = 0$. It is worth noting that with this change of variables the coverage behaves as

$$c_1(\xi_1) = c_1^- - qx_{\xi_1}^{1/2}, \quad \xi_1 \to +0,$$

and

$$c_1(\xi_1) = c_1^+ - qx_{\xi_1}^{1/2}, \quad \xi_1 \to -0,$$

with $q$ some constant. Similarly, for the second layer

$$c_2(\xi_2) = c_2^- - ax_{\xi_2}^{1/2}, \quad \xi_2 \to +0,$$

and

$$c_2(\xi_2) = c_2^+ - ax_{\xi_2}^{1/2}, \quad \xi_2 \to -0.$$
with a some constant.

The mass balance requires that the flux be the same on both sides of the profiles moving with velocities \(v_1\) and \(v_2\), respectively. Hence, we consider the equation

\[
D(c_1) \frac{dc_1}{d\xi_1} \bigg|_{\xi_1 \to +0} - D(c_1) \frac{dc_1}{d\xi_1} \bigg|_{\xi_1 \to -0} = -v_1(c_1^+ - c_1^-),
\]

\[
D(c_2) \frac{dc_2}{d\xi_2} \bigg|_{\xi_2 \to +0} - D(c_2) \frac{dc_2}{d\xi_2} \bigg|_{\xi_2 \to -0} = -v_2(c_2^+ - c_2^-).
\]

We multiply by \(D(c_i) \frac{dc_i}{d\xi_i}\), with \(i = 1, 2\), respectively. After integrating from \(-\infty\) to \(\infty\); we obtain for the velocity of the first layer

\[
v_1 = \frac{G(c_3) - G(c_1^+) - G(c_1) + G(c_1^+)}{\int_{-\infty}^{\infty} \left(\frac{dc}{d\xi}\right)^2 D(c) d\xi_1},
\]

while for the second layer we have

\[
v_2 = \frac{G(c_7) - G(c_2^+) - G(c_5) + G(c_2^+)}{\int_{-\infty}^{\infty} \left(\frac{dc}{d\xi}\right)^2 D(c) d\xi_2},
\]

that in general is different from the velocity in the first layer. Note that the propagation velocity goes to zero if the numerator of the previous expressions goes to zero. This allows us to represent the Maxwell conditions for the coexistence in stationary conditions, for phases subject to first order transitions

\[
G(c_3) - G(c_1) = G(c_1^+) - G(c_1^-)
\]

(67)

\[
G(c_7) - G(c_5) = G(c_2^+) - G(c_2^-)
\]

(68)

The profile in the first layer is described by the following integral

\[
\xi(c) = \frac{\int_{c_1^-}^{c_1} D(c) dc}{[2x(G(c_1) - G(c))]^{0.5}}
\]

for \(c_1^- > c > c_1\), and

\[
\xi(c) = -\frac{\int_{c_1}^{c_3} D(c) dc}{[2x(G(c_3) - G(c))]^{0.5}}
\]

for \(c_3 > c > c_1^+\).

For the second layer we have

\[
\xi'(c) = \frac{\int_{c_2^-}^{c_2} D(c) dc}{[2x(G(c_5) - G(c))]^{0.5}}
\]

for \(c_2^- > c > c_5\), and

\[
\xi'(c) = -\frac{\int_{c_2}^{c_7} D(c) dc}{[2x(G(c_7) - G(c))]^{0.5}}
\]

for \(c_7 > c > c_2^+\). For \(\xi = 0\) the coverage jumps at \(c_1 = c_1^-\) at \(c_1 = c_1^+\), or in the second layer for \(c_1 + c_2 = c_1^+ + c_2^+\) at \(c_1 + c_2 = c_1^+ + c_2^+\).

Figure 5 shows an example of a typical form of the density profiles. It is worth remarking here that the form of these profiles is reminiscent of those found in the problem of layering in wetting \[15\]. However, such an analogy requires further study.
7 Conclusions

We have introduced a simple model able to describe qualitatively multilayer adsorption and the formation of ordered structures. It is an extension of an early model describing a system of a monolayer of adsorbed particles with lateral attractive interactions leading to the formation of interfaces separating phases with different local coverages. However, for sake of simplicity, we have focused in the case of two layers. Such a case show evidences indicating the occurrence of a “cascade” of first order phase transitions in the successive layers. Such a result is in agreement with some experimental measurements as well as simulations.

Lateral interactions play a key role in the whole picture. Also the possibility of transfer interactions among different layers can strongly affect the results, particularly the position of the phase transition and the scaling of the step size $\Delta \alpha$ as a function of $\varepsilon$. The study of this exchange effect will be done in a forthcoming work. Here we have found that $\Delta \alpha \sim \varepsilon^\nu$ with $\nu \approx 2.0$ for the first step while $\nu \approx 1.92$ for the second. We have also found that the critical behaviour corresponds to a mean field one, indicating that the analysis of critical properties requires a more detailed study.

The study of the fronts connecting different stationary states, for instance the dependence of the front velocity on system’s parameters, as well as the comparison of isotherm with simulations and experiments, is under way. Also, the connection of this problem with the determination of more realistic adsorption isotherm as well as with cases involving reactions or layering problems in wetting will be the subject of further work.

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8 Appendix

In this appendix we show how to derive the macroscopic master equation starting from a microscopic analysis. To reach such a goal we closely follow the procedure of Ref. [8], however with the adequate changes for the actual situation. The basic step is to consider that the system is composed of a given number of particles enclosed in a box and that this number is so large that the local coverage, defined as the ratio between occupied sites to the total number of sites, should not suffer an appreciable change due to individual adsorption, desorption, or diffusion processes.

8.1 Microscopic approach to the system’s evolution equations

For a box containing \( n_j \) particles, the probability per unit time that an adsorption or desorption occurs in the first layer is proportional to the number of sites occupied or free in the first and those free in the second layer. Hence, for the first layer we have

\[
\tilde{w}_a(n_j) = w^a(N - n_j)(1 - n'_j/N'),
\]

\[
\tilde{w}_d(n_j) = w^d_d n_j (1 - n'_j/N').
\]

Where \( w^a = k_a p \) and \( w^d_d = k_{d,0} \exp(U_i/k_B T) \), and \( N' \) is the maximum number of sites.

Here \( \tilde{w}^\pm_j \) the transition probability per unit time for transitions between neighbor boxes (diffusion) is proportional to \( n_j \), the particle number in the box \( j \), and the fraction of free sites in the box towards which the transition occurs

\[
\tilde{w}^\pm_j = w^\pm_j (1 - n_{j \pm 1}/N)n_j.
\]

Where

\[
w^\pm_j = \begin{cases} w^{\pm}_{l} & U_j < U_{j \pm 1}, \\ w^{\pm}_{r} & U_j > U_{j \pm 1}. \end{cases}
\]

Similarly, for the second layer we can write

\[
\tilde{w}'_a(n'_j) = w'^a(N' - n'_j)n_j/N,
\]

\[
\tilde{w}'_d(n'_j) = w'^d_{j} n'_j.
\]

Where \( w'^a = k'_a p, \ w'^d_{j} = k'_{d,0} \exp(U'_i/k_B T) \), and \( N' \) is the maximum number of sites in the second layer \( (N < N') \).

\[
\tilde{w}'^\pm_j = w'^\pm_j (1 - n'_{j \pm 1}/N'n'_j).
\]

Where

\[
w'^\pm_j = \begin{cases} w'^{\pm}_{l} & U'_j < U'_{j \pm 1}, \\ w'^{\pm}_{r} & U'_j > U'_{j \pm 1}. \end{cases}
\]

For the first layer we assumed \( N = N_{\text{max}} \gg 1 \), a number of particles \( n_j \) and \( x_j \) sites with \( j = 1, \ldots, m \). The concentration is defined as \( c_j = n_j/N \). For the second layer we consider \( N' = \sum n'_j \), with \( N' < N_{\text{max}} \) and \( N' \gg 1 \). Here we have a number of particles \( n'_j \) and \( x_j \) sites with \( j = 1, \ldots, m \), and the concentration is defined as \( c'_j = n'_j/N' \).

We will try to obtain the master equation from the multidimensional probability distribution \( p(n_1, \ldots, n_m, t) \). Such a distribution corresponds to the probability of finding \( n_1, \ldots, n_m \) particles in the box located at \( x_1, \ldots, x_m \), at time \( t \). Let us see what we obtain from such an analysis for the first and second layers.
8.2 Equation of motion for the first layer

The analysis of the time derivative of the probability distribution \( p(n_1, \cdots, n_m, t) \) for the first layer gives

\[
\frac{\partial p(\{n_j\}, t)}{\partial t} = \sum_{j=1}^{m} \frac{(N' - n'_j)}{N'} [(N - n_j + 1)\dot{p}^+_j - (N - n_j)p(\{n_j\}, t)] + \\
+ \sum_{j=1}^{m} \frac{w_j'(N' - n'_j)}{N'} [(n_j + 1)\dot{p}^-_j - n_jp(\{n_j\}, t)] + \\
+ \sum_{j=1}^{m} \sigma_j(n_j + 1)[(1 - \frac{n_j+1-1}{N})p^+_j + (1 - \frac{n_j-1}{N})p^-_j] - \\
- \sum_{j=1}^{m} \sigma_jn_j[2 - \frac{n_j+1+n_j-1}{N}]p(\{n_j\}, t) + \\
+ \sum_{j=1}^{m} \gamma_j(n_j + 1)[(1 - \frac{n_j+1}{N})p^+_j - (1 - \frac{n_j-1}{N})p^-_j] + \\
+ \sum_{j=1}^{m} [\gamma_jn_j(\frac{n_j+1}{N} - \frac{n_j-1}{N})]p(\{n_j\}, t). \quad (79)
\]

Replacing this into Eq. (79) we get

\[
\frac{\partial}{\partial t} = w^a \sum_{j=1}^{m} \frac{(N' - n'_j)}{N'} [(N - n_j + 1)\dot{p}^+_j - (N - n_j)p(\{n_j\}, t)] + \\
+ \sum_{j=1}^{m} \frac{w_j'(N' - n'_j)}{N'} [(n_j + 1)\dot{p}^-_j - n_jp(\{n_j\}, t)] + \\
+ \sum_{j=1}^{m} \sigma_j(n_j + 1)[(1 - \frac{n_j+1-1}{N})p^+_j + (1 - \frac{n_j-1}{N})p^-_j] - \\
- \sum_{j=1}^{m} \sigma_jn_j[2 - \frac{n_j+1+n_j-1}{N}]p(\{n_j\}, t) + \\
+ \sum_{j=1}^{m} \gamma_j(n_j + 1)[(1 - \frac{n_j+1}{N})p^+_j - (1 - \frac{n_j-1}{N})p^-_j] + \\
+ \sum_{j=1}^{m} [\gamma_jn_j(\frac{n_j+1}{N} - \frac{n_j-1}{N})]p(\{n_j\}, t). 
\]

Remembering that

\[
N' = \sum_{j=1}^{m} n_j, \quad (80)
\]

the local coverage in the second layer is related to

\[
c'_j = \frac{n'_j}{N'}, \quad (81)
\]

where \( N' > > 1 \). These are the available sites for adsorption on the second layer. Also \( N > > 1 \) and the local coverage for the first layer is \( c_j = \frac{n_j}{N} \).

Assuming that \( c_j \) changes only slightly with an adsorption or desorption process, we can expand

\[
\dot{p}^\pm \simeq p \pm \frac{1}{N} \frac{\partial p}{\partial c_j} + \frac{1}{2N^2} \frac{\partial^2 p}{\partial c_j^2}, \quad (82)
\]

hence,

\[
p_j^\pm \simeq p \pm \frac{1}{N} \left[ \frac{\partial p}{\partial c_j} - \frac{\partial p}{\partial c_{j+1}} \right] + \frac{1}{2N^2} \left[ \frac{\partial^2 p}{\partial c_j^2} + \frac{\partial^2 p}{\partial c_{j+1}^2} - \frac{\partial^2 p}{\partial c_j \partial c_{j+1}} \right]. \quad (83)
\]

Replacing this into Eq. (79) we get

\[
\frac{\partial p(\{c_j\}, t)}{\partial t} = - \sum_{j=1}^{m} w^a(1 - c'_j) \frac{\partial}{\partial c_j} [(1 - c_j)p] + \frac{1}{2N} \sum_{j=1}^{m} w^a(1 - c'_j) \frac{\partial^2 p}{\partial c_j^2} [(1 - c_j)p] - \\
- \sum_{j=1}^{m} w'_j(1 - c'_j) \frac{\partial}{\partial c_j} [-c_jp] + \frac{1}{2N} \sum_{j=1}^{m} w'_j(1 - c'_j) \frac{\partial^2 p}{\partial c_j^2} [c_jp] - \\
- \sum_{j=1}^{m} \frac{\partial}{\partial c_j} [(\sigma_{j+1}c_{j+1} + \sigma_{j-1}c_{j-1} - 2c_j\sigma_j)(1 - c_j)p] - \\
- \sum_{j=1}^{m} \frac{\partial}{\partial c_j} [(c_{j+1} + c_{j-1} - 2c_j)\sigma_jc_jp] + \]

13
\[ + \frac{1}{2N} \sum_{j=1}^{m} \frac{\partial^2}{\partial c_j^2} \left\{ \left( \sigma_{j+1} c_{j+1} + \sigma_{j-1} c_{j-1} - 2c_j \sigma_j \right)(1 - c_j) - \\
- \left( c_{j+1} + c_{j-1} - 2c_j \right) \sigma_j c_j \right\} - \\
- \frac{1}{N} \sum_{j=1}^{m} \frac{\partial}{\partial c_j} \left[ \frac{\partial}{\partial c_{j+1}} (1 - c_{j+1}) + \frac{\partial}{\partial c_{j-1}} (1 - c_{j-1}) - \\
- 2 \frac{\partial}{\partial c_j} (1 - c_j) \right] \sigma_j c_j \right\} - \\
- \sum_{j=1}^{m} \frac{\partial}{\partial c_j} \left[ \gamma_j c_j (c_{j+1} - c_{j-1}) + (c_j - 1) \left( \gamma_{j+1} c_{j+1} - \gamma_{j-1} c_{j-1} \right) \right] - \\
- \frac{1}{2N} \sum_{j=1}^{m} \frac{\partial^2}{\partial c_j^2} \left[ \gamma_j c_j (c_{j+1} - c_{j-1}) + (1 - c_j) \left( \gamma_{j+1} c_{j+1} - \gamma_{j-1} c_{j-1} \right) \right] - \\
- \frac{1}{N} \sum_{j=1}^{m} \frac{\partial}{\partial c_j} \left[ \frac{\partial}{\partial c_{j+1}} (1 - c_{j+1}) - \frac{\partial}{\partial c_{j-1}} (1 - c_{j-1}) \right] \gamma_j c_j \right\}. \tag{84} \]

As indicated above, the size of an individual box is much smaller than the characteristic length scale of the spatial patterns. Therefore, both coverage, \( c_j \) and \( c_j' \), do not significantly change between neighbor boxes, and we can assume that the coverage \( c(x) \) is continuous. Hence we consider a continuous version of the equation in terms of \( c(x) \). These transformation also transform the multidimensional distribution \( p(\{c_j\}, t) \) into the functional \( p(c(x), t) \). The evolution equations for such a functional become

\[
\frac{\partial p}{\partial t} = - \int dx \frac{\delta}{\delta c(x)} \left[ (1 - c') \left( w^o (1 - c) - w^d c \right) + 2l_o \frac{\partial}{\partial x} (\gamma c (1 - c)) \right] p(c(x), t) \\
- \int dx \frac{\delta}{\delta c(x)} \left[ (1 - c) \frac{\partial^2 (\sigma c)}{\partial x^2} + \sigma c \frac{\partial^2 c}{\partial x^2} \right] p(c(x), t) \\
+ \frac{1}{2N} \int dx \frac{\delta^2}{\delta c(x)^2} \left[ (1 - c') \left( w^o (1 - c) + w_c c + \sigma l_o c (1 - c) \frac{\partial^2 (\sigma c)}{\partial x^2} + \sigma l_o c \frac{\partial^2 c}{\partial x^2} \right) \right] p(c(x), t) \\
+ \frac{l_o}{2} \int dx \frac{\delta^2}{\delta c(x)^2} \left[ 2 \gamma c \frac{\partial c}{\partial x} - 2 \left( 1 - c \right) \frac{\partial (\gamma c)}{\partial x} \right] p(c(x), t) \\
- \frac{l_o}{N} \int dx \frac{\delta}{\delta c(x)} \frac{\partial}{\partial x} \left[ \frac{\delta}{\delta c(x)} \left( 1 - c \right) \right] \gamma c p(c(x), t) \\
- \frac{l_o}{l_o} \int dx \frac{\partial}{\partial x} \left( \left( \frac{\delta}{\delta c(x)} \right)^2 \gamma (1 - c) p(c(x), t) \right). \tag{85} \]

Here we have introduced the parameter \( \mu = \frac{l_o}{l_o} \), where \( l_o \) is the typical size of each box. This value of \( \mu \) gives us the number of lattice sites per unit area.

The coefficients \( \sigma \) and \( \gamma \) in the previous equation represent functions of the coordinate \( x \) given by

\[
\sigma_j = \frac{w_j^+ + w_j^-}{2}. \tag{86} \]

and

\[
\gamma_j = \frac{w_j^+ - w_j^-}{2}. \tag{87} \]

Here

\[
w_j^+ = \nu e^{-\frac{U_j - U_j+1}{2k_B T}} \quad U_j < U_{j+1}, \tag{88} \]
and
\[ w_j^- = \nu U_j > U_{j \pm 1}. \]  

(89)

Hence,
\[ \sigma(x) = \frac{\nu}{2} [1 + e^{-\frac{\nu}{K_BT} \frac{\partial U}{\partial x}}], \]

(90)

and
\[ \gamma(x) = -\frac{\nu}{2} [1 - e^{-\frac{\nu}{K_BT} \frac{\partial U}{\partial x}}] \Re, \]

(91)

with \( \Re \) indicating the sign of \( \frac{\partial U}{\partial x} \).

Considering the limit \( l_\circ \to 0 \), we get
\[ \lim_{l_\circ \to 0} (\gamma(x) l_\circ^2) = D, \]

(92)

where \( D \) is the diffusion constant
\[ D = \lim_{l_\circ \to 0} (\nu l_\circ^2), \]

(93)

and
\[ \lim_{l_\circ \to 0} [\gamma(x) l_\circ] = \lim_{l_\circ \to 0} \left[ -\frac{\nu l_\circ^2}{2K_BT} \frac{\partial U}{\partial x} \right] = -\frac{1}{2} \frac{D}{K_BT} \frac{\partial U}{\partial x}. \]

(94)

Introducing the functional differential operator
\[ \hat{A}(x) = \frac{\delta}{\delta c(x)}, \]

(95)

considering the evolution equation in the limit \( l_\circ \to 0 \), and using the previous equations we obtain
\[
\frac{\partial p}{\partial t} = -\int dx \hat{A}(x) [(1 - c)[w^a(1 - c) - w^d c] + \frac{\partial}{\partial x} \left( \frac{D}{K_BT} \frac{\partial U}{\partial x} (1 - c) \right) + D \frac{\partial^2 c}{\partial x^2}] p + \\
+ \frac{1}{2\mu} \int dx \hat{A}^2(x) [(1 - c')[w^a(1 - c) + w^d c] + (1 - 2c) \frac{\partial^2 c}{\partial x^2}] \\
- \frac{Dc}{K_BT} \frac{\partial c}{\partial x} + (1 - c) \frac{\partial}{\partial x} \left( \frac{Dc}{K_BT} \frac{\partial U}{\partial x} \right) p - \\
- \frac{D}{\mu} \int dx [\hat{A}(x) \frac{\partial^2}{\partial x^2} (\hat{A}(x)(1 - c))c - \frac{1}{2} \frac{\partial}{\partial x} (\hat{A}(x)^2) \frac{1}{K_BT} c(1 - c) \frac{\partial U}{\partial x}] p. \]

(96)

We now consider those terms inversely proportional to \( \mu \) and independent of the potential \( U \),
\[
F_d = \frac{D}{\mu} \int dx [\hat{A}(x) \left[ \frac{1}{2} (1 - 2c) \frac{\partial^2 c}{\partial x^2} \right] - \hat{A}(x) \frac{\partial^2}{\partial x^2} (\hat{A}(x)(1 - c))c] p. \]

(97)

This expression can be further transformed into
\[
F_d = \frac{D}{\mu} \int dx [\hat{A}(x) \left[ \frac{1}{2} (1 - 2c) \frac{\partial^2 c}{\partial x^2} + c \frac{\partial^2 c}{\partial x^2} + 2 \hat{A}(x) \frac{\partial^2}{\partial x^2} c - \hat{A}(x) \frac{\partial^2}{\partial x^2} (\hat{A}(x)(1 - c))c \right] p + \\
= \frac{D}{\mu} \int dx [\hat{A}(x) \left[ \frac{1}{2} \frac{\partial A}{\partial x^2} + c \frac{\partial^2}{\partial x^2} + 2 \hat{A}(x) \frac{\partial^2}{\partial x^2} c - \frac{1}{2} \frac{\partial^2}{\partial x^2} (\hat{A}(x)(1 - c))c + \frac{\partial A}{\partial x} \frac{\partial A}{\partial x} c(1 - c) \right] p + \\
= \frac{D}{\mu} \int dx [\hat{A}(x) \left[ \frac{1}{2} \frac{\partial A}{\partial x^2} + c \frac{\partial^2}{\partial x^2} + \frac{\partial A}{\partial x} \right] (1 - c) \right] p, \]

(98)

\[ F_d = \frac{D}{\mu} \int dx (\frac{\partial A}{\partial x})^2 c(1 - c) p, \]

(99)
\[ F_d = \frac{D}{\mu} \int dx \int dy \left( \frac{\partial A(x)}{\partial x} \right) \left( \frac{\partial A(y)}{\partial y} \right) c(x)(1 - c(x)) \delta(x - y)p, \]  

\[ F_d = \frac{1}{2\mu} \int dxdy \tilde{A}(x) \tilde{A}(y) \frac{\partial^2}{\partial x \partial y} (2Dc(x)(1 - c(x)) \delta(x - y))p. \]  

Now we consider in Eq. (100) the terms of order \( O(\mu^{-1}) \), that are proportional to the gradient of the potential \( U \). We find that such terms cancel each other, i.e.

\[ F = \frac{D}{2\mu k_B T} \int dx [\tilde{A}^2(x) \left( \frac{\partial U}{\partial x} \frac{\partial c}{\partial x} + (1 - c) \frac{\partial U}{\partial x} (c(1 - c) \frac{\partial U}{\partial x}) \right) + \frac{\partial}{\partial x} (\tilde{A}^2(x) c(1 - c) \frac{\partial U}{\partial x})]p \]

\[ = \frac{D}{2\mu k_B T} \int dx \tilde{A}^2(x) \left( \frac{\partial U}{\partial x} \frac{\partial c}{\partial x} + (1 - c) \frac{\partial U}{\partial x} (c(1 - c) \frac{\partial U}{\partial x}) \right) - \frac{\partial}{\partial x} (\tilde{A}^2(x) c(1 - c) \frac{\partial U}{\partial x})]p = 0. \]  

Using the previous results the evolution equation can be written as

\[ \frac{\partial p}{\partial t} = -\int dx \frac{\delta}{\delta c(x)} \left[ w^n(1 - c') (1 - c) - w^d(1 - c') c + \frac{D}{k_B T} \frac{\partial}{\partial x} (c(1 - c) \frac{\partial U}{\partial x}) \right] + \frac{\partial^2 c}{\partial x^2} ]p + \frac{1}{2\mu} \int dx \int dy \frac{\delta^2}{\delta c(x) \delta c(y)} \left[ (1 - c') [w^n(1 - c) + w^d c] \delta(x - y) + \frac{\partial^2}{\partial x \partial y} (2Dc(1 - c) \delta(x - y))]p. \]  

The last expression corresponds to the functional Fokker-Planck equation for the probability distribution functional \( p(c(x), t) \). From the theory of stochastic processes, this Fokker-Planck equation is equivalent to a stochastic partial differential \( 17 \) (Langevin-like) equation for the fluctuating field \( c(x, t) \). It has the form

\[ \frac{\partial c}{\partial t} = w^n(1 - c')(1 - c') - w^d(1 - c') c + \frac{D}{k_B T} \frac{\partial}{\partial x} [c(1 - c) \frac{\partial U}{\partial x}] + \frac{1}{\mu^2} \left[ w^n(1 - c')(1 - c') \right]^2 f_a(x, t) + \frac{1}{\mu^2} \left[ w^d c(1 - c') \right]^2 f_d(x, t) + \frac{1}{\mu^2} \frac{\partial}{\partial x} [(2Dc(1 - c)) \frac{1}{2} f(x, t)]. \]  

Here \( f_a(x, t), f_d(x, t) \) and \( f(x, t) \), are independent noise sources, with intensity one according to the Ito interpretation. Those three noise sources correspond to internal noises associated to adsorption, desorption and diffusion respectively. When studying the equation in the macroscopic limit, such noise sources are neglected.

### 8.3 Equation of motion for the second layer

Next, we analyze the time derivative of the probability density \( p(n_j', t) \) for the second layer. With similar arguments as before we get

\[ \frac{\partial p(\{n_j'\}, t)}{\partial t} = w^a \sum_{j=1}^{m} \frac{n_j}{N} (N' - n_j + 1) \tilde{p}^- - (N' - n_j') p'(\{n_j'\}, t) + \sum_{j=1}^{m} w^d (n_j + 1) \tilde{p}^+ - n_j p'(\{n_j\}, t) + \sum_{j=1}^{m} (\sigma'_j (n_j + 1) [(1 - n'_j + 1 \frac{1}{N'}) p_j^+ + (1 - n'_j - 1 \frac{1}{N'}) p_j^-] - \]
\[- \sum_{j=1}^{m} \sigma_j n_j' (2 - \frac{n_{j+1}' + n_{j-1}'}{N'}) p'(\{n_j'\}, t) + \]
\[+ \sum_{j=1}^{m} \sigma_j n_j' (n_j' + 1) ((1 - \frac{n_{j+1}' - 1}{N'}) p_{j^+} - (1 - \frac{n_{j-1}' - 1}{N'}) p_{j^-}) + \]
\[+ \sum_{j=1}^{m} \gamma_j n_j' \frac{n_{j+1}' - n_{j-1}'}{N'} p'(\{n_j'\}, t). \quad (105)\]

We should remember that
\[N' = \sum_{j=1}^{m} n_j, \quad (106)\]

and the coverage of the second layer is related to
\[c_j' = \frac{n_j'}{N'}, \quad (107)\]

where \(N' \gg 1, N' < N_{\text{max}}\); and \(N'\) are the available sites on the second layer (that is the occupied sites in the first layer).

As in the case of the first layer we approximate
\[\tilde{p}_j^\pm \approx p' \pm \frac{1}{N'} \frac{\partial p'}{\partial c_j'} + \frac{1}{2N'^2} \frac{\partial^2 p'}{\partial c_j'^2}, \quad (108)\]

and
\[p_j^\pm \approx p' + \frac{1}{N'} \frac{\partial p'}{\partial c_j'} - \frac{\partial p'}{\partial c_j'_{\pm 1}} + \frac{1}{2N'} \frac{\partial^2 p'}{\partial c_j'^2} + \frac{1}{2} \frac{\partial^2 p'}{\partial c_j'^2} + \frac{\partial^2 p'}{\partial c_j' \partial c_j'_{\pm 1}}. \quad (109)\]

Replacing into Eq. (103) we obtain
\[
\frac{\partial p'_{\{c_j'\}}}{\partial t} = - \sum_{j=1}^{m} c_j w^a \frac{\partial}{\partial c_j'} [(1 - c_j') p'] + \frac{1}{2N'} \sum_{j=1}^{m} w^a c_j \frac{\partial^2}{\partial c_j'^2} [(1 - c_j') p'] - \]
\[\sum_{j=1}^{m} \frac{\partial}{\partial c_j'} (w_j^d c_j' p') + \frac{1}{2N'} \sum_{j=1}^{m} \frac{\partial^2}{\partial c_j'^2} (w_j^d c_j' p') + \]
\[\sum_{j=1}^{m} \frac{\partial}{\partial c_j'} [\sigma_j c_j' p' (c_{j+1}' - 2 c_j' + c_j')] + \]
\[+ \frac{1}{2N'} \sum_{j=1}^{m} \frac{\partial^2}{\partial c_j'^2} [\sigma_j c_j' p' (c_{j+1}' + c_{j-1} - 2 c_j' \sigma_j c_j') (1 - c_j') - \]
\[\frac{1}{N'} \sum_{j=1}^{m} \frac{\partial}{\partial c_j'} (1 - c_{j+1}) + \frac{\partial}{\partial c_j'} (1 - c_{j-1}) - 2 \frac{\partial}{\partial c_j'} (1 - c_j') [\sigma_j c_j' p'] - \]
\[\frac{1}{N'} \sum_{j=1}^{m} \frac{\partial}{\partial c_j'} (c_j' - 1) (c_j' - 1)(c_{j+1}' c_{j+1}' - c_{j-1}' c_{j-1}')) p' - \]
\[\frac{1}{2N'} \sum_{j=1}^{m} \frac{\partial^2}{\partial c_j'^2} [\gamma_j c_j' (c_{j+1}' - c_{j-1}') + (c_j' - 1)(c_{j+1}' c_{j+1}' - c_{j-1}' c_{j-1}')) p' - \]
\[\frac{1}{2N'} \sum_{j=1}^{m} \frac{\partial^2}{\partial c_j'^2} [\gamma_j c_j' (c_{j+1}' - c_{j-1}') + (1 - c_j') (c_{j+1}' c_{j+1}' - c_{j-1}' c_{j-1}')) p' - \]
\[\frac{1}{N'} \sum_{j=1}^{m} \frac{\partial}{\partial c_j'} (1 - c_{j+1}) - \frac{\partial}{\partial c_j'} (1 - c_{j-1}) [\gamma_j c_j' p']. \quad (110)\]
As for the first layer we consider a uniform coverage implying

\[ c(x_j) \rightarrow c(x), \]  
\[ (111) \]
\[ c'(x_j) \rightarrow c'(x). \]  
\[ (112) \]

Also

\[ p\{c_j\}, t \rightarrow p(c(x), t), \]  
\[ (113) \]
\[ p'(\{c'_j\}, t) \rightarrow p(c'(x), t). \]  
\[ (114) \]

The continuous version of the equation of motion, assuming the uniform coverage of the system as before, is again a functional equation for \( p(c'(x), t) \). This equation is

\[
\frac{\partial p(c'(x), t)}{\partial t} = - \int dx \frac{\delta}{\delta c'(x)} \left[ c w'(1 - c') - w'dc' + 2l_o \frac{\partial(\gamma'c'(1 - c'))}{\partial x} \right] p\{c'(x), t\} - l_o^2 \int dx \frac{\delta}{\delta c'(x)} \left[ (1 - c') \frac{\partial^2 (\sigma'c')}{\partial x^2} + \sigma'c' \frac{\partial^2 c'}{\partial x^2} \right] p\{c'(x), t\} + \frac{1}{2\mu'} \int dx \frac{\delta}{\delta c'(x)} \left[ (1 - c')w'c + w'dc' + l_o^2 (1 - c') \frac{\partial^2 (\sigma'c')}{\partial x^2} - \sigma'l_o^2 c' \frac{\partial^2 c'}{\partial x^2} \right] p\{c'(x), t\} + l_o \int dx \frac{\delta}{\delta c'(x)} \left[ (1 - c') \frac{\partial (\gamma'c')}{\partial x} - 2(1 - c') \frac{\partial (\gamma'c')}{\partial x} \right] p\{c'(x), t\} - l_o \int dx \frac{\delta}{\delta c'(x)} \left( (1 - c') \left[ \sigma'c' \right] p\{c'(x), t\} \right) - l_o \int dx \frac{\partial}{\partial x} \left( (\frac{\delta}{\delta c'(x)})^2 \right) \left[ (\gamma'c') (1 - c') \right] p\{c'(x), t\}.
\]  
\[ (115) \]

Again as in the first layer case, we have introduced here the parameter \( \mu' = \frac{N'}{l_0} \), where \( l_o \) is the size of each box. The value of \( \mu' \) gives the number of sites per unit of area.

The coefficients \( \sigma', \gamma' \) in the last equation differ from those in the first layer by a factor of \( \mu' \). Hence,

\[
\sigma'(x) = \frac{\nu'}{2} \left[ 1 + e \frac{l_o}{K_B T} \frac{\partial U}{\partial x} \right],
\]  
\[ (116) \]
\[
\gamma'(x) = -\frac{\nu'}{2} \left[ 1 - e \frac{l_o}{K_B T} \frac{\partial U}{\partial x} \right] N,
\]  
\[ (117) \]

where \( N \), as before, indicate the sign of \( \frac{\partial U}{\partial x} \).

In the limit \( l_o \rightarrow 0 \), we get

\[ \lim_{l_o \rightarrow 0} (\gamma' l_o^2) = D', \]  
\[ (118) \]

where \( D' \) is the diffusion constant on the second layer,

\[ D' = \lim_{l_o \rightarrow 0} (\nu' l_o^2), \]  
\[ (119) \]

and

\[ \lim_{l_o \rightarrow 0} (\gamma' l_o) = \lim_{l_o \rightarrow 0} \left[ -\frac{\nu' l_o^2}{2K_B T} \frac{\partial U}{\partial x} \right] = -\frac{1}{2} \frac{D'}{K_B T} \frac{\partial U}{\partial x}. \]  
\[ (120) \]

We will adopt \( D' \simeq D \), as they differ by a constant.
We introduce now the differential operator
\[ \hat{B}(x) = \frac{\delta}{\delta c'(x)}. \] (121)

Introducing it into the evolution equation and considering the limit \( l_o \to 0 \), we get
\[
\frac{\partial p}{\partial t} = - \int dx \hat{B}(x)[(cw'' - w''d) + \frac{\partial}{\partial x}(\frac{D}{K_BT} \frac{\partial U}{\partial x} c'(1 - c'))] +
\]
\[
+ D \frac{\partial^2 c'}{\partial x^2} [p(c'(x), t) +
\]
\[
+ \frac{1}{2\mu} \int dx \hat{B}^2(x)[(cw'' - w''d) + D(1 - 2c') \frac{\partial^2 c'}{\partial x^2} -
\]
\[
- \frac{Dc'}{K_BT} \frac{\partial U}{\partial x} c' + (1 - c') \frac{\partial}{\partial x} \frac{Dc'}{K_BT} \frac{\partial U}{\partial x} ]p(c'(x), t) -
\]
\[
- \frac{D}{\mu'} \int dx \hat{B}(x) \frac{\partial^2}{\partial x^2} (\hat{B}(x)(1 - c'))c' -
\]
\[
- \frac{1}{2} \frac{\partial}{\partial x} (\hat{B}(x)^2) \frac{1}{K_BT} (1 - c') \frac{\partial U}{\partial x} p(c'(x), t). \quad (122)
\]

As for the previous first layer case, we consider the terms inversely proportional to \( \mu' \) and those independent of the potential \( U \).
\[
F'_d = \frac{D}{\mu'} \int dx [\hat{B}^2(x)[\frac{1}{2}(1 - 2c') \frac{\partial^2 c'}{\partial x^2}] - \hat{B}(x) \frac{\partial^2}{\partial x^2} (\hat{B}(x)(1 - c'))]p(c'(x), t). \quad (123)
\]

This expression can be transformed into
\[
F'_d = \frac{D}{\mu'} \int dx [\hat{B}^2(x)[\frac{1}{2}(1 - 2c') \frac{\partial^2 c'}{\partial x^2} + c' \frac{\partial^2 c'}{\partial x^2}] + 2\hat{B}(x) \frac{\partial^2}{\partial x^2} (\hat{B}(x) \frac{\partial c'}{\partial x} c' -
\]
\[
- \hat{B}(x) \frac{\partial^2}{\partial x^2} (\hat{B}(x)(1 - c'))p] +
\]
\[
F'_d = \frac{D}{\mu'} \int dx [\hat{B}^2(x)[\frac{1}{2} \frac{\partial^2 c'}{\partial x^2}] + \frac{1}{2} \frac{\partial^2}{\partial x^2} \hat{B}(x) \frac{\partial c'}{\partial x} c' - \frac{1}{2} \frac{\partial^2}{\partial x^2} (\hat{B}^2(x)(1 - c')) +
\]
\[
+ [\frac{\partial \hat{B}}{\partial x}]^2 (1 - c')c'p] +
\]
\[
F'_d = \frac{D}{\mu'} \int dx \hat{B}(x) \frac{\partial^2}{\partial x^2} [(1 - c')c'p]. \quad (124)
\]
\[
F'_d = \frac{D}{\mu'} \int dx \hat{B}(x) \frac{\partial}{\partial x} (1 - c')c'p, \quad (125)
\]
\[
F'_d = \frac{D}{\mu'} \int dy \hat{B}(y) \frac{\partial}{\partial y} [(1 - c')c'(x)(1 - c'(x))\delta(x - y)p, \quad (126)
\]
\[
F'_d = \frac{D}{2\mu'k_BT} \int dy \hat{B}(y) \frac{\partial}{\partial x} [(2Dc'(1 - c'(x))\delta(x - y)p]. \quad (127)
\]

Now we consider in Eq. (122) the terms of order \( O(\mu^{-1}) \), that are proportional to the gradient of the potential \( U \). We find that such terms cancel each other, i.e.
\[
F' = \frac{D}{2\mu'k_BT} \int dx [\hat{B}^2(x)[\frac{\partial}{\partial x} c'(1 - c') + (1 - c') \frac{\partial}{\partial x} (c' \frac{\partial U}{\partial x})]].
\]
\[
\frac{\partial}{\partial x} \left( \hat{B}^2(x)c'(1-c') \frac{\partial U}{\partial x} \right) p = \frac{D}{2\mu'k_BT} \int dx \hat{B}^2(x) \left[ -\frac{\partial U}{\partial x} c' \frac{\partial}{\partial x} + (1-c') \frac{\partial}{\partial x} (c' \frac{\partial U}{\partial x}) \right] \]
\[
- \frac{\partial}{\partial x} (c'(1-c') \frac{\partial U}{\partial x}) \]p = 0.
\]

Taking into account our previous results, the evolution equation becomes
\[
\frac{\partial p}{\partial t} = - \int dx \frac{\delta}{\delta c'}(x) \left[ w^a(1-c')c - w^d c' \right] + \frac{D}{k_BT} \frac{\partial}{\partial x} (c'(1-c') \frac{\partial U}{\partial x}) + D \frac{\partial^2 c'}{\partial x^2} p + \frac{1}{2\mu'} \int dxdy \frac{\delta^2}{\delta c'(x) \delta c'(y)} \left[ [(1-c')w^a c + w^d c'] \delta(x-y) \right] + \frac{\partial^2}{\partial x \partial y} (2Dc'(1-c') \delta(x-y)) p.
\]

The last equation is the functional Fokker-Planck equation for the probability distribution \(p(c'(x), t)\) for the second layer. Similarly to the discussion for the first layer, we can obtain the related stochastic partial differential equation
\[
\frac{\partial c'}{\partial t} = w^a c(1-c') - w^d c' + \frac{D}{k_BT} \frac{\partial}{\partial x} [c'(1-c') \frac{\partial U}{\partial x}] + \frac{D}{\mu^2 x^2} \left[ \frac{1}{2} w^a (1-c') c \frac{1}{2} f'_a(x,t) + \frac{1}{\mu^2} [w^d c']^2 \right] f'_d(x,t) + \frac{1}{\mu^2 y^2} \frac{\partial}{\partial x} [(2Dc'(1-c'))^2 f'(x,t)].
\]

Here, as before, \(f'_a(x,t), f'_d(x,t)\) and \(f'(x,t)\), are independent noise sources, with intensity one according to the Ito interpretation. These three noise sources correspond to internal noises associated to adsorption, desorption and diffusion respectively, but now in the second layer. Also, when studying the equation in the macroscopic limit, such noise sources are neglected.

The previous analysis leads us to Eqs.\(\text{[17]}\) and \(\text{[18]}\).
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Figure 1: Sketch of the different processes included in the model.

Figure 2: Phase diagrams in the planes $\varepsilon$ vs. $\alpha_i$. a) first layer, b) second layer. Region I corresponds to the dilute (vapor-like) phase, region III to the dense (liquid-like) phase, while II corresponds to the region of phase coexistence.

Figure 3: Typical form of the isotherm. We depict the total coverage $\theta(=c_1 + c_2)$ vs. $\varphi$, the chemical potential.

Figure 4: Here we depict the relation between the step size and the potential parameter $\varepsilon$: $\Delta \varphi$ vs. $\varepsilon$, yielding a linear dependence in logarithmic scale. The result here corresponds to the 1st step.

Figure 5: Typical form of the density profile. Here we have used $\varepsilon = 5.6$, $\alpha_1 = 0.08$ and $\alpha_2 = 0.096$
\[ \ln[\Delta \phi] \quad \ln[\varepsilon] \]
