

# Surface pressure in solid-on-solid models

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## Abstract

Microscopic models of the solid-on-solid type were considered to describe the surface pressure of monolayers and bilayers on top of another layer in two and three dimensions. The two interfaces, above and below the film, were studied in simultaneous thermal equilibrium without imposing a fixed profile for the first fluid or solid. It is shown that the associated mean field approximation leads to an exact determination of the surface pressure isotherms revealing the possible existence of plateaux, typical of first-order phase transitions.

## 1. Introduction

Consider a thin liquid film which is put on top of another liquid. It follows from Gibb's law that if this situation is stable, the interfacial tension is lower than that of the virgin surface. This difference in interfacial tensions defines the surface pressure [1, 2]:

$$\Pi = \gamma_0 - \gamma \quad (1)$$

where  $\gamma_0$  is the interfacial tension of the virgin surface and  $\gamma$  is the same in the presence of the film.

In the case of very thin films such as monolayers, the standard theories refer to two-dimensional liquid systems, absorbing the details of the underlying layer in some effective parameters. A typical example is given by the van der Waals equation for a two-dimensional fluid,

$$\beta\Pi = \frac{1}{a - a_0} - \frac{a_0}{a^2} \quad (2)$$

where  $a$  is the area per molecule available at the surface,  $a_0$  is the closed packed limit area and  $\beta$  is the inverse of the temperature  $k_B T$ .

Recently, new studies have been developed to take into account the physical and chemical structures of the first medium [3]. This aspect of the problem may indeed be important for rough adsorbates.

It is our aim in this paper to show that the solid-on-solid (SOS) description of the interfaces reproduces at least qualitatively the experimental results. We first review the results which have been obtained so far using the solid-on-solid model in two dimensions. This is

given in Section 2. To obtain explicit expressions for the surface pressure in three dimensions, we also consider the corresponding mean field model for monolayers and bilayers. This aspect of the problem is presented in Section 3. Concluding remarks are presented in Section 4.

## 2. Surface pressure within $d = 2$ SOS models

In two dimensions, an interface with no overhangs may be viewed as a one-dimensional random walk  $h_i$  indexed by  $i$ : this is the SOS model of an interface. If three phases coexist, an interface between two of them may be wetted by bubbles of the third phase. This is described by two random walks  $h_i$  and  $h'_i$  with the restriction that  $h_i \geq h'_i$ : the first phase (A) lies above  $h_i$ , the third phase (C) lies below  $h'_i$ , and the intruding phase (B) is between  $h_i$  and  $h'_i$  and is present at  $i$  only if  $h_i > h'_i$ . The two walks have to be considered as non-crossing and, within restricted SOS models, we impose that

$$h_{i+1} - h_i \in \{-1, 0, 1\} \quad h'_{i+1} - h'_i \in \{-1, 0, 1\} \quad (3)$$

Henceforth, we only allow random walk configurations satisfying all the above restrictions including eqn. (3). This kind of model has already been studied in the literature (see for example refs. 4 and 5 and references cited therein). Here, however, we consider strict monolayers in which the film width is  $\Delta_i = h_i - h'_i = 0$  or 1 as indicated in Fig. 1. The case of bilayers has also been studied in ref. 3.

The couplings  $J$ ,  $J'$  and  $J''$  are associated respectively with the AB, BC and AC interfaces. The energy cost of such interfaces is described by the different lengths of the interfaces AB, BC and AC which characterize the configurations. This leads to the following hamiltonian:

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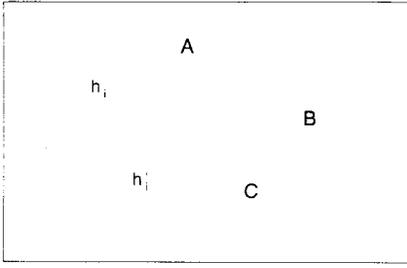


Fig. 1. A typical configuration for a monolayer described by the heights  $h_i$ ,  $i = 0, 1, 2, \dots, N$  on top of a fluid described by the heights  $h'_i$ ,  $i = 1, 2, \dots$ .

$$H = \sum_{i=1}^N G(h_{i-1}, h'_{i-1}; h_i, h'_i) \quad (4)$$

where

$$G(h_{i-1}, h'_{i-1}; h_i, h'_i) = \begin{cases} J''|h_i - h_{i-1}| & \text{if } \Delta_{i-1} = \Delta_i = 0 \\ J|h_i - h_{i-1}| + J'|h'_i - h'_{i-1}| + \frac{\theta(\Delta_{i-1}) + \theta(\Delta_i)}{2} & \text{otherwise} \end{cases} \quad (5)$$

with

$$\theta(\Delta) = \begin{cases} J + J' & \text{if } \Delta \neq 0 \\ J'' & \text{if } \Delta = 0 \end{cases}$$

and

$$\Delta_i = h_i - h'_i$$

where  $\theta$  takes into account the horizontal part of the energy cost.

We generally take boundary conditions setting  $h_i = h'_i = 0$  outside of some finite region  $\mathcal{A}$  of length  $N$ . We wish to study the surface tension  $\gamma$  of an insoluble thin film of B between bulk amounts of A and C in which the amount of B has a macroscopic surface density fixed to some value  $c \geq 0$ .

To study this function  $\gamma(c)$ , let us first consider the surface tension as a function of the chemical potential  $\mu$ . We take

$$w = \beta\mu \quad (6)$$

where  $\beta$  is the inverse temperature. We then define

$$\beta\gamma(w) = \lim_{N \rightarrow \infty} -\frac{1}{N} \log \sum_{h_N = h'_N = 0} \exp(-\beta H - w\Omega) \quad (7)$$

where  $\Omega$  is the number of particles in the film

$$\Omega = \sum_{i=1}^N (h_i - h'_i) \quad (8)$$

and  $c$  is related to  $w$  by

$$c = \frac{\hat{c}}{\hat{c}_w} \beta\gamma(w) \quad (9)$$

The sum in eqn. (7) is over configurations of  $h_i$  and  $h'_i$  ( $i = 0, 1, 2, \dots, N$ ) with the indicated constraints of  $h_N$  and  $h'_N$  in addition to those we will always impose ( $h_i \in \mathbb{Z}$ ,  $h'_i \in \mathbb{Z}$ ,  $h_i - h'_i = 0$  or  $1$ ,  $h_0 = h'_0 = 0$ ,  $|h_{i+1} - h_i| \leq 1$  and  $|h'_{i+1} - h'_i| \leq 1$ ).

Using the transfer matrix technique [3, 6], one obtains explicit expressions for  $\gamma(w)$  and  $c(w)$ .

Defining  $\beta\Pi(c) = \beta\gamma(0) - \beta\gamma(c)$ , one then obtains

$$\beta\Pi(c) = \log\left(1 + \frac{cx}{1-2c}\right) \quad (10)$$

with  $x$  given by

$$x = (1-2c) \frac{1}{\epsilon} \times \left\{ \frac{-(1-2c) + [(1-2c)^2 + 4c(1-c)\epsilon]^{1/2}}{2c(1-c)} \right\} \quad (11)$$

where

$$\epsilon = \frac{[1 + 2 \exp(-K'')][1 + 2 \exp(-K - K')]}{[\exp(-K) + \exp(-K')]^2} \quad (12)$$

with  $K = \beta J$ ,  $K' = \beta J'$  and  $K'' = \beta J''$ .

A comparison with the perfect fluid approximation is easily realized by expanding the function  $\Pi(c)$  in powers of  $1/c$ . The virial series is, with  $z = 1/c$

$$\beta\Pi\left(\frac{1}{z}\right) = \frac{1}{z} + v_2 \frac{1}{z^2} + O\left(\frac{1}{z^3}\right) \quad (13)$$

where

$$v_2 = \frac{3}{2} - \epsilon \quad (14)$$

which may be positive or negative.

Let us point out here that there appears in this formula only one parameter  $\gamma/\delta^2$  which is to be related to the molecular interactions at the interfaces,  $K$ ,  $K'$  and  $K''$ . This new type of equation of state for the surface pressure has the advantage that it takes into account the entropy of the surface of the first medium but, as can easily be seen in Fig. 2, it does not allow a possible phase transition to be described.

### 3. Surface pressure within $d = 3$ models

Let us now consider a three-dimensional model. The two random walks have then to be replaced by two random surfaces. Within a lattice  $\mathbb{Z}^3$ , we may model these two random surfaces by two sets of height random variables, namely  $h_i$  ( $i \in \mathbb{Z}^2$ ) which take the values 0 or 1 and  $h'_i$  ( $i \in \mathbb{Z}^2$ ) which take values 0 or  $-1$ . In that case, the restriction  $h_i \geq h'_i$  is automatic. Moreover, we can consider a strict monolayer by imposing that  $\mathcal{A}_i$  has to be 0 or 1 or a bilayer model, in the absence of further

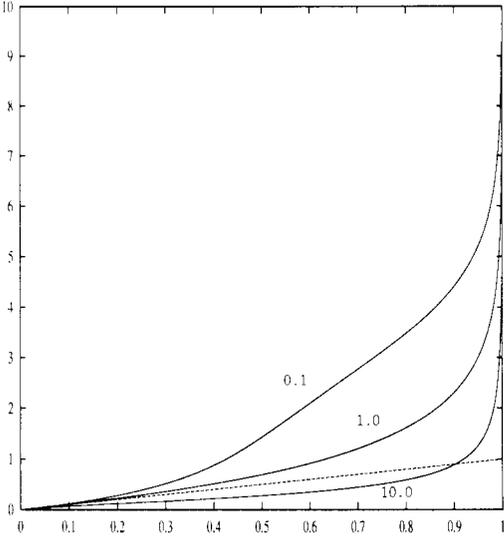


Fig. 2. The surface pressure given by eqn. (10) in units of  $kT$  as a function of the concentration  $c$  and different values of the parameter  $\epsilon$ : 0.1, 1.0 and 10.0. The perfect gas approximation is given by the dashed line.

restrictions, since then  $\Delta_i$  may be 0, 1 or 2. These models are of interest in that they undergo a phase transition.

More specifically, we show below that our model of two random surfaces leads to the existence of flat regions in  $\Pi(c)$ . Such flat regions are well known experimentally (see for example ref. 7).

The hamiltonian which describes the energetic cost of such an interface is given by

$$J \sum_i \left[ 1 + \frac{1}{2} \sum_{j \in n \cdot i} |h_i - h_j| \right] + J' \sum_i \left[ 1 + \frac{1}{2} \sum_{j \in n \cdot i} |h'_i - h'_j| \right] + (J'' - J - J') \sum_i \delta_{h_i, 0} \delta_{h'_i, 0} \quad (15)$$

Let us associate with each height  $h_i$  or  $h'_i$  a spin variable which takes the value  $-1$  or  $1$ , by

$$h_i = \frac{\sigma_i + 1}{2}$$

and

$$h'_i = \frac{\sigma'_i + 1}{2} \quad (16)$$

With this change of variables, we obtain the equivalent of a “two-sheeted” Ising model in two dimensions:

$$\mathcal{H} = \text{constant} - \frac{J}{2} \sum_{\langle i, j \rangle} \sigma_i \sigma_j - \frac{J'}{2} \sum_{\langle i, j \rangle} \sigma'_i \sigma'_j - \frac{J'' - J - J'}{4} \sum_i (\sigma_i + \sigma'_i) + \frac{J'' - J - J'}{4} \sum_i \sigma_i \sigma'_i \quad (17)$$

where in  $\Sigma_{\langle i, j \rangle}$ , each nearest neighbor bond is counted only once. The corresponding free energy is thus given by

$$\beta f(H, \beta) = \lim_{A \uparrow \mathbb{Z}^2} -\frac{1}{|A|} \log Z_A(K, K', \Delta J, H) \quad (18)$$

where

$$Z_{\cdot, 1}(K, K', \Delta J, H) = \sum_{(\sigma, \sigma')} \exp \left[ (K/2) \sum \sigma_i \sigma_j + (K'/2) \sum \sigma'_i \sigma'_j + H \sum_i (\sigma_i + \sigma'_i) - \Delta J \sum_i \sigma_i \sigma'_i \right] \quad (19)$$

where the sum is over all the configurations  $(\sigma, \sigma')$ . In our case, when the chemical potential  $\mu = 0$ , we have

$$H = \Delta J = \beta \frac{J'' - J - J'}{4} \quad (20)$$

A qualitative discussion of the phase diagram associated with this model has already been given in ref. 3 using the Pirogov–Sinai theory. We are here interested in exact results for the surface pressure but this requires some simplification of the hamiltonian. Let us then consider the corresponding mean-field approximation given by the Curie–Weiss model [8] associated with this hamiltonian.

We obtain

$$\beta f_{\text{MF}}(H, \beta) = \lim_{A \uparrow \mathbb{Z}^2} -\frac{1}{|A|} \log Z_A^{\text{MF}}(K, K', \Delta J, H) \quad (21)$$

where

$$Z_A^{\text{MF}}(K, K', \Delta J, H) = \int \exp \left[ \frac{K}{4} \frac{\left( \sum_i \sigma_i \right)^2}{|A|} + \frac{K'}{4} \frac{\left( \sum_i \sigma'_i \right)^2}{|A|} \right] \prod_i d\rho_H(\sigma_i, \sigma'_i) \quad (22)$$

with

$$d\rho_H(\sigma_i, \sigma'_i) = \exp[-\Delta J \sigma_i \sigma'_i + H(\sigma_i + \sigma'_i)] d\nu(\sigma_i) d\nu(\sigma'_i) \quad (23)$$

where  $d\nu(\sigma)$  stands for the measure  $\frac{1}{2}[\delta(\sigma - 1) + \delta(\sigma + 1)]$ .

This expression is equivalent to

$$\beta f_{\text{MF}}(H, \beta) = \lim_{A \uparrow \mathbb{Z}^2} -\frac{1}{|A|} \log \frac{1}{2\pi} \int_{-\infty}^{+\infty} dz \exp \left( -\frac{1}{2} z^2 \right) \times \int_{-\infty}^{+\infty} dz' \exp \left\{ -\frac{1}{2} z'^2 + |A| \Phi_H \left[ \left( \frac{K}{2|A|} \right)^{1/2} z, \left( \frac{K'}{2|A|} \right)^{1/2} z' \right] \right\} \quad (24)$$

where

$$\begin{aligned} \exp[\Phi_H(u, u')] &= \int \exp(u\sigma + u'\sigma') \, d\rho_H(\sigma, \sigma') \\ &= \exp[\Phi_0(u + H, u' + H)] \end{aligned} \tag{25}$$

$$\begin{aligned} \beta f_{MF}(H, \beta) &= \lim_{|A| \rightarrow \infty} -\frac{1}{|A|} \log \frac{|A|}{\pi(KK')^{1/2}} \\ &\quad \times \int_{-1}^1 dv \int_{-1}^1 dv' \exp\left\{-|A| \left[\frac{v^2}{K} + \frac{v'^2}{K'} - \Phi_H(v, v')\right]\right\} \end{aligned} \tag{26}$$

which leads to

$$\beta f_{MF}(H, \beta) = \min_{v, v'} \left\{ \frac{v^2}{K} + \frac{v'^2}{K'} - \Phi_H(v, v') \right\} \tag{27}$$

Now, we use in the monolayer case

$$\begin{aligned} \exp[\Phi_H^{\text{monolayer}}(v, v')] &= \frac{1}{4} \sum_{(\sigma, \sigma') = (-1, -1), (-1, 1), (1, -1)} \exp[-\Delta J \sigma \sigma' + H(\sigma + \sigma') \\ &\quad + v\sigma + v'\sigma'] \\ &= \frac{1}{4} [\exp(-\Delta J - 2H - v - v') \\ &\quad + 2 \exp(\Delta J) \cosh(v - v')] \end{aligned} \tag{28}$$

and in the bilayer case

$$\begin{aligned} \exp[\Phi_H^{\text{bilayer}}(v, v')] &= \frac{1}{4} \sum_{\sigma = \pm 1} \sum_{\sigma' = \pm 1} \exp[-\Delta J \sigma \sigma' + H(\sigma + \sigma') + v\sigma + v'\sigma'] \\ &= \frac{1}{2} [\exp(-\Delta J) \cosh(v + v' + 2H) \\ &\quad + \exp(\Delta J) \cosh(v - v')] \end{aligned} \tag{29}$$

To introduce the concentration  $c$ , let us consider the grand canonical ensemble and its partition function (cf. eqn. (7))

$$\begin{aligned} \beta_i(\beta\mu) &= \lim_{|A| \rightarrow \infty} -\frac{1}{|A|} \log \sum_{\text{conf.}} \exp\left[-\beta \mathcal{H} \right. \\ &\quad \left. - \frac{\beta\mu}{2} \sum_i (\sigma_i + \sigma'_i + 2) \right] \end{aligned} \tag{30}$$

we then obtain

$$\begin{aligned} \beta_i(\beta\mu) &= \text{constant} + \beta\mu \\ &\quad + \beta f_{MF}\left(-\frac{\beta\mu}{2} + \frac{K'' - K - K'}{4}, \beta\right) \end{aligned} \tag{31}$$

Moreover,

$$c = \hat{c}_{\beta\mu} \beta_i \tag{32}$$

is therefore equal to

$$c = 1 - \frac{1}{2} \frac{\hat{c} \beta f_{MF}}{\hat{c} \beta \mu} = 1 + \left( \frac{v_*}{K} + \frac{v'_*}{K'} \right) \tag{33}$$

where  $f_{MF}$  is evaluated at the inverse temperature  $\beta$  and the field  $H = -\beta(\mu/2) + (K'' - K - K')/4$ ,  $v_*$  and  $v'_*$  insures the minimum of the right-hand side of eqn. (27), i.e.  $v_*$  and  $v'_*$  are the appropriate solutions of

$$\begin{aligned} \frac{2}{K} v_* &= \frac{\hat{c} \Phi_H}{\hat{c} v}(v_*, v'_*) \\ \frac{2}{K'} v'_* &= \frac{\hat{c} \Phi_H}{\hat{c} v'}(v_*, v'_*) \end{aligned} \tag{34}$$

Solving this set of implicit equations using some fixed point procedure, we find  $\beta_i(\beta\mu)$  and  $c(\beta\mu)$  out of which we may eliminate  $\mu$  and represent  $\beta\Pi = \beta_i(0) - \beta_i(c)$  as a function of  $c$ .

Let us first present the results associated with the monolayer. Typical graphs of  $\beta\Pi$  as a function of  $c$  are given in Fig. 3. As a function of the couplings  $J''$ ,  $J$  and  $J'$  we obtain isotherms which present no plateau or one plateau corresponding to a phase transition of the first order.

For the bilayer case, two different cases may appear as a function of  $\Delta J$ . There could be one or no plateau as in the preceding case for negative or small values of  $\Delta J$ , or there could appear two plateaux for high values of  $\Delta J$ . This corresponds to successive transitions: no layer  $\rightarrow$  monolayer and monolayer  $\rightarrow$  bilayer. When  $J$  is

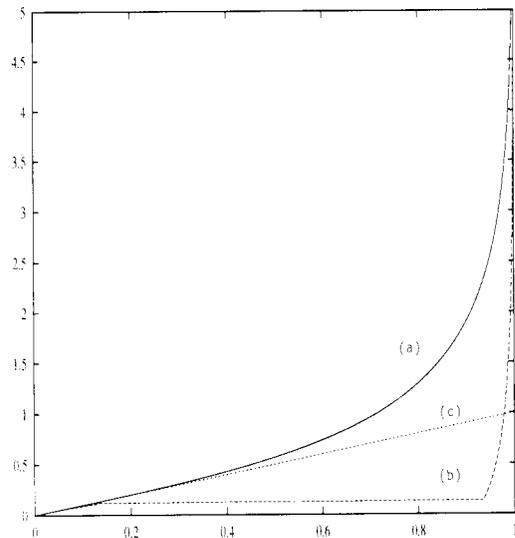


Fig. 3. Isotherms of the surface pressure  $\beta\Pi$  given by eqn. (27) in the monolayer case as a function of the concentration  $c$ . Different values of parameters  $K$ ,  $K'$  and  $\Delta J$  have been considered: curve a, (1.0, 1.0, 0.0); curve b, (3.0, 3.0, -5.0). The perfect gas approximation is denoted by curve c in the figure.

different from  $J'$ , a third plateau could also appear associated with the transition between the two different monolayers. The associated isotherms show once more the possible appearance of first-order phase transitions for bilayer films.

To understand the origin of these properties of  $\beta\Pi$  in terms of  $c$ , it is equivalent to consider the behavior of the free energy  $f_{\text{MF}}$  in terms of the magnetization  $-(v_*/K + v'_*/K')$  defined as the partial derivative of  $f_{\text{MF}}$  (given in eqn. (27)) with respect to the external field  $H$ . Phase transitions correspond therefore to discontinuities of the magnetization. There will be three different cases according to the value of  $\Delta J$ : negative, zero or positive. In the two first cases, we know that there will be a discontinuity in the magnetization for low enough temperature and zero external field (this can be proved rigorously using the Pirogov–Sinai theory [9] for instance). In the antiferromagnetic case (when  $\Delta J$  is positive), the numerical results indicate that when  $\Delta J$  is small enough with respect to  $J$  and  $J'$ , there could be a phase transition.

#### 4. Concluding remarks

We have shown in this paper that the solid-on-solid class of models may be used to model the equilibrium properties of monolayers and bilayers on top of a fluid in two or three dimensions. Exact results have been obtained in three dimensions using the mean field approximation which are in good agreement qualitatively with known experimental observations.

Let us here point out that a direct comparison with the experimental data would require some extension of this work to take into account for instance that the molecular

couplings parallel and perpendicular to the interface may be different. Other approximations could also be usefully considered such as the Bethe lattice approximation. These extensions are now under consideration.

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