PHASE TRANSITIONS AT LIQUID SOLID INTERFACES: PADE APPROXIMANT FOR ADSORPTION ISOTHERMS AND VOLTAMMOGRAMS

by

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1 Introduction

The growth of films on single crystal surfaces is of considerable technological interest which has been discussed extensively in the literature [1]. The occurrence of phase transitions in the adsorbed layers has been known for some time, but the studies, both experimental and theoretical, have been done in either dilute gas-solid interfaces, or vacuum-solid interfaces [2, 3]. The films adsorbed on single crystal surfaces do exhibit a rich variety of phase behavior[2]. There is good reason to think that such a rich phase behavior also exists in liquid-solid interfaces. However, the experiments to detect it are much more difficult to perform, because most of the structural surface analysis is carried out in ultrahigh vacuum, and the observation of adsorption isotherms is possible only for materials, such as graphite, that have a large specific surface, and therefore very irregular. The situation in electrochemistry is different, because there exists a technique, polarography, that is surface sensitive, even for single planar surfaces, and which is capable of detecting the sudden formation of films at electrodes. It has been possible to perform structural analysis of underpotential deposits of metallic monolayers [4] on metal electrode interfaces using X-ray diffraction techniques [5, 6, 7], which yield structural information about ordered phases of adsorbed monolayers on single crystal surfaces. The underpotential deposition (UPD) of monolayers on electrode surfaces occurs suddenly and should be considered as a phase transition at the surface [8, 9]. The adsorption isotherms and voltamograms of systems like the UPD films of Cu on Au(111), Cu on Pt(111), Pb on Ag(111) show very clearly the sudden formation of ordered films. The crystal nature of these films has been observed both in situ and also ex situ. Very recently, scanning tunnel microscope (STM) experiments [10, 11] have shown phase transitions of a complicated nature occur in the underpotential deposition of copper on gold (111) surface. As was hinted by the extended X-ray absorption fine structure (EXAFS) experiments, [12], the anion, in this case the sulfate, plays an important role in the phase formation.

The theory of the UPD [4, 13] has addressed the question of the binding of individual atoms to the metal surface, but has not considered the cooperative effects of the atoms in the adsorbed film. In the present work we discuss the effect of cooperative interactions in the formation of UPD films.
on a triangular lattice, which corresponds to the (111) face of an fcc crystal or the (100) face of an hcp crystal. We propose a Padé approximant that interpolates the adsorption isotherm between the Langmuir isotherm when the lateral interactions of the adsorbate are turned off, and the exact high and low temperature series for the Ising model [14] when the interactions are on. The coefficients of the Padé approximant are generated by a recurrence relation to any arbitrary order in the fugacity $z$, and therefore can be generated for other lattices and multiadsorption isotherms. One drawback of our formalism is that it does not satisfy automatically the symmetry [15] relationship between the high and low temperature series. These relations will be satisfied if we take a large number of terms (perhaps 20 for the triangular lattice), but we can either use a switching function to force duality on our expressions, or alternatively use a two point Padé which will satisfy this relation. We give a brief discussion of this latter approach, which has the disadvantage of requiring the inversion of an $N$ by $N$ matrix, where $N$ is the order of the approximation. We believe that the switching function Padé approximation produces good results even using as few as 8 terms.

In previous work we have proposed a simple model of chemisorption on crystal surfaces [26, 16, 17], in which the binding process of individual atoms is essentially decoupled from the cooperative effects that take place at the surface. This model, which we call the sticky site model (SSM) is a combination of the sticky potential model, first proposed by Boltzmann [18], but solved and discussed in detail by Baxter [19], and the adsorption site model of Langmuir [20]. The sticky potential of Baxter was used by Perram and Smith [21] to study adsorption onto a smooth interface. In that work only the density profile near a smooth hard wall was discussed, and the properties of the adsorbed film were not studied. The properties of this adsorbed film is the central issue of our present work.

The sticky potential has the form

$$e^{-[\beta u(r)]} = 1 + \lambda \delta (r - \sigma),$$

where $\beta = 1/kT$ is the usual Boltzmann thermal factor, $u(r)$ is the intermolecular potential. $\lambda$ is the stickiness parameter, $r = (x, y, z)$ is the relative position of the center of the molecules, and $\sigma$ is the diameter of the molecules. The right hand side term represents the probability of two molecules being
stuck by the potential $u(r)$: this occurs only when the two molecules are in contact, and for this reason we use the dirac delta function $\delta(r - \sigma^-)$, which is zero when the molecules do not touch, is infinity when they do, but the integral is normalized to one. The parameter $\lambda$ represents the probability of adsorption of an individual molecule onto the surface. It has the form of a fugacity,

$$\lambda = e^{-\beta \mu_A(r)},$$

where $\mu_A$ is the free energy of the adsorption of an individual molecule onto the surface. This quantity is obtained from a quantum mechanical calculation.

The Langmuir adsorption sites can be represented by a collection of sticky sites of the same form as was suggested by Baxter. Only that now we do not have a sphere covered uniformly by a layer of glue, but rather a smooth, hard surface with sticky points, which represent adsorption sites where actual chemical bonding takes place. In this model, Eq. 1 has to be changed to

$$e^{-[\beta u^{+}(r)]} = 1 + \lambda(R)\delta(z).$$

with

$$\lambda(R) = \sum_{n_1, n_2} \lambda \delta(R - n_1a_1 - n_2a_2),$$

Here $R = (x, y)$ is the position at the electrode surface, and $z$ the distance to the contact plane, which is at a distance $\sigma/2$ from the electrode. In 4, $n_1, n_2$ are natural numbers, and $a_1, a_2$ are lattice vectors of the adsorption sites which are the sites of a lattice $\Lambda$ on the surface. The requirement of point adsorption sites rather than extended regions around the sites is not essential to our discussion. It is clear that phase transitions will occur even in smooth surfaces, simply because the two dimensional gas does undergo such phase transitions. Less localized forms of the adsorption potential are equivalent to the soft potential models discussed by Steele and collaborators [22], and models of commensurate-incommensurate adsorption such as the ones discussed by McTague and Novaco [23], and by Shiba [24].

Consider the case of a simple salt dissolved in water, near a metallic electrode: in the general case there will be three species of the liquid phase
that will be adsorbed onto the metal surface: the anion, the cation and the solvent. If the metal is charged, then only the ions of opposite charge will be adsorbed and will compete with the solvent for the adsorption sites. If the metal is neutral, then all three species can compete for the sites. This case corresponds to a three state Ising model in two dimensions: it leads to a very rich and complicated phase diagram for the adsorbate and was discussed in detail recently [25]. When the metal is charged, then the adsorbate consists of ions of the same sign, which repel each other. This situation corresponds to the two dimensional antiferromagnetic Ising model, which for first nearest neighbor interactions has an order-disorder phase transition. In the limiting case of infinite strong repulsion, it is mathematically isomorphic to the hard disk problem on a planar lattice, which is known to undergo second order phase transitions. Alternatively the adions can be neutralized by the electrons of the metal, and form metal bonds between the surface atoms. This occur as in the UPD: the interactions between neighbors are attractive, as in the case of the ferromagnetic Ising model on a two dimensional lattice, and one should expect first order phase transitions in the adsorbed film. We should remark that the existence of phase transitions is not a consequence of the existence of an ordered array of adsorption sites: they occur also in the smooth surface as a phase transition of the two dimensional gas.

In the limiting case of the SSM, the sizes of the different species play a crucial role in the possible ordering of the adlayers at the interface. It will be convenient to picture the ions as having a hard sphere core with a diameter \( \sigma_a, \sigma_b \), and the solvent as having a hard core with diameter \( \sigma_s \). The lattice spacing of the atoms in the metal surface is \( d \), and because it is the most stable surface, we will restrict ourselves to the (111) surface of the fcc crystals, or the (100) face of the hcp crystal, that is, the triangular lattice. When the adions are bigger than the lattice spacing and the adsorption sites are extended rather than point like, then the geometry of the adlayer is different of that of the substrate, and in general incommensurate with it. This case was studied in a separate communication [17].

In this paper we consider the case of a triangular lattice of sticky points. The spacing between the sites of the lattice is \( d \). This surface is in contact with a solution. Only two states of occupation are allowed: the sites are
either occupied by an ion or by the solvent, or alternatively in the case of a pure fluid, by a fluid particle or none. The fluid particles have an exclusion diameter \( \sigma \), which may or may not be associated with a hard core potential. Otherwise the interactions are arbitrary. We assume, however, that the pair correlations on the surface decay sufficiently fast so that we need to take into account first neighbor interactions only. There are two possible situations: If the adsorbate diameter \( \sigma \) is smaller than the lattice spacing \( d \), then there are two possible phases, a dense, crystalline one and a dilute disordered one. There is a first order transition between them. If the adsorbed particles exclude all next nearest neighbors, that is when

\[
d < \sigma < \sqrt{3}d,
\]

then the problem is exactly analogous to the hard hexagon problem of Baxter [15]. In this case there is a second order phase transition between an ordered \( \sqrt{3} \times \sqrt{3} \) phase and a disordered one. This interesting case will not be discussed here.

2 Basic Formalism

Consider a fluid of only one kind of particle of diameter \( \sigma \). near a smooth, hard wall with sticky sites. The fluid has \( N \) particles and the volume of the system is \( V \). The Hamiltonian of the system is

\[
H = H_0 + H_s,
\]

where \( H_0 \) is the Hamiltonian of the system in the absence of the sticky sites on the hard wall, and \( H_s \) is the sticky sites interaction

\[
H_s = \sum_{i=1}^{M} u_i(\mathbf{r}),
\]

where \( u^i(\mathbf{r}) \) is the sticky interaction of Eq. 3. The canonical partition function of this model is

6
\[
Z = (1/N!) \int d\mathbf{r}^N e^{-\beta H_0} \prod_{i=1}^{N} [1 + \lambda(\mathbf{R}_i) \delta(z_i)]. \tag{8}
\]

Expanding the product in Eq.8 and integrating the Dirac delta functions we get, using the single component notation to avoid heavy and unnecessarily complex equations, (with the understanding that in the multi component case \(N\) is a vector quantity with components \(N_1, N_2, ... N_n\), the necessary modifications of \(N!\) and the integrations have to be made).

\[
Z = Z_0 \sum_{n=0}^{N} \frac{\lambda^n}{n!} \sum_{\{\mathbf{R}_i\} \subset \Lambda} \rho^0_n(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_n) \tag{9}
\]

where

\[
\rho^0_n(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n) = (Z_0(N-n)!)^{-1} \int d\mathbf{r}_{n+1} \cdots d\mathbf{r}_Ne^{-\beta H_0}, \tag{10}
\]

\[
= g^0_n(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n) \prod_{i=1}^{N} \rho^0_i(\mathbf{r}_i). \tag{11}
\]

Here \(g^0_n(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n)\) is the n-body correlation function, and \(\rho^0_i(\mathbf{r}_i) = \rho^0_i(z_i)\) is the singlet density of the inhomogeneous smooth wall problem. The partition function is

\[
Z_0 = (1/N!) \int d\mathbf{r}^Ne^{-\beta H_0}. \tag{12}
\]

In the sticky sites model (SSM), the excess properties of the interface depend only on the correlation functions of the smooth interface. Introducing the potentials of mean force \(w_n(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_n)\)

\[
g^0_n(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_n) = e^{-\beta w_n(\mathbf{R}_1, \mathbf{R}_2, ..., \mathbf{R}_n)}, \tag{13}
\]

Combining these expressions we arrive at

\[
\frac{Z}{Z_0} = \sum_{\mathbf{R}_i \subset \Lambda} [\lambda \rho^0_1(0)]^n/n!e^{-\beta w_n(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n)}, \tag{14}
\]

which is the central quantity of our work. The excess free energy is
\[ \Delta f^* = (-1/\beta A) \ln(Z/Z_0). \]  

(15)

where \( A \) is the area of the interface. We also deduce the the fraction of occupied sites \( \theta \), [26]

\[
\theta = -\frac{A\beta \lambda \partial \Delta f^*}{|\lambda| \partial \lambda} 
\]

(16)

Eq. 14 shows that the SSM model maps the adsorption on a flat surface onto a two dimensional lattice problem of a very general kind, which is in general not amenable to analytic treatment. It can be simplified by introducing the Kirkwood superposition approximation

\[
g^0_n(R_1, R_2, R_n) = \prod_{i,j<n} g^0_2(R_i, R_j), \]

(17)

where

\[
g^0_2(R_i, R_j) = g^0_2(|R_i - R_j|). \]

(18)

is the pair distribution function. Further restriction of the interactions to nearest neighbors makes this problem equivalent to that of the Ising model.

The partition function can be written as

\[
\frac{Z}{Z^0} = \sum_{\{t_i\}} e^{\beta \lambda \sum_i t_i - \beta \mu \sum_{a,a',t_i} t_i} 
\]

(19)

where \( \beta = 1/kT \),

\[
\beta \epsilon = -\ln[g^0_2(d)].
\]

(20)

\[
g^0_2(d) = g^0_2(R_i, R_j) \quad [i, j = nearest \ neighbors]
\]

(21)

\[
\beta \mu = \ln[\lambda \rho^0_1(0)]
\]

(22)

This partition function can be mapped onto an Ising model with spin variables \( s_i = \pm 1 \) by means of the transformation

\[
s_i = 2t_i - 1.
\]

(23)
When we turn off the interactions in the surface then $\epsilon = 0$ and Eq. 19 becomes

$$Z/Z^0 = \sum_{\{i\}} e^{3\mu \sum_{i}}.$$  \hspace{1cm} (24)

or

$$Z/Z^0 = (1 + e^{3\mu})^{|\lambda|}.$$ \hspace{1cm} (25)

and using Eq. 16, we get

$$\theta = \lambda \frac{\partial}{\partial \lambda} \ln[(1 + e^{3\mu})].$$ \hspace{1cm} (26)

Furthermore since

$$e^{3\lambda} = \lambda \rho^0(0),$$ \hspace{1cm} (27)

we get the Langmuir isotherm

$$\theta = \frac{\lambda \rho^0(0)}{1 + \lambda \rho^0(0)}.$$ \hspace{1cm} (28)

3 Phase Transitions at Electrode Surfaces

There is a phase transition in the ferromagnetic Ising model only when the external field is zero [27]. For the two dimensional lattice gas this means that when $w < 0$

$$\mu = \frac{wq}{2}$$ \hspace{1cm} (29)

or

$$\lambda \rho^0(0) = [g_2^0(d)]^{-q/2}.$$ \hspace{1cm} (30)

where $q$ is the number of nearest neighbors of the lattice. 4 for the square lattice and 6 for the triangular lattice. The exact spontaneous magnetization of the ferromagnetic Ising model on the triangular lattice [28] yields the expression

$$\theta = (1/2) \left( 1 \pm \left(1 - \frac{16g_2}{(g_2 - 1)^3(g_2 + 3)} \right)^{1/8} \right).$$ \hspace{1cm} (31)
Setting $\theta = (1/2)$ this equation yields the condition

$$g_2 = g_2^0(d) |_{\text{crit}} = 3.$$  \hspace{1cm} (32)

and the value for the critical sticky parameter $\lambda$ is

$$\lambda \rho^0(0) |_{\text{crit}} = 1/27.$$ \hspace{1cm} (33)

As was mentioned already in the electrochemical case, the contact pair correlation function in the bulk for ions of equal sign is practically zero, because of the Coulomb repulsion which prevents ions of equal sign to approach each other. In the adsorbed layer the interactions of these ions must be attractive, if the formation of a layer occurs suddenly, and therefore the state of chemical bonding, or more precisely the electrovalence, must change during the adsorption process.

Condensed phases in the ad layers are observed in electrochemistry. In particular the under potential deposition of some metals on electrodes occurs at certain very well defined values of the potential bias [8]. For example, the deposition of Cu on the Au(111) face forms two phases according to the deposition potential. These phases have been observed ex-situ [8] and in situ [5] [29] [30], [10], [11]. At a lower potential a dilute ordered phase is formed. At a higher potential a dense commensurate phase is formed. It is clear from the above considerations that in the dense ad layer case the ions must be discharged, because then they would form a metallic bond, which makes $w$ negative, and therefore ferromagnetic. This is supported by the features of the EXAFS spectra. In the high density phase the near edge structure corresponds to that of metallic copper, which has a characteristic double peak.

In the electrosorption of ions, the charge of the ions can be neutralized by the electons in the metal electrode substrate. If this happens then the normally repulsive effective interaction between equally charged ions can become attractive because of the formation of a metallic bond. The change is known as the electrosorption valency, and has been studied extensively by Schultze and coworkers [31]. From the structure of the Eqs.30 and Eq. 31 it is clear that no phase transition will occur if the adsorbed ions keep their charge, and their repulsive interaction as the potential changes. The conclusion is that the adions , in this case Cu, attract each other in the adsorbed
layer, and therefore are chemically different in the adlayer than in the bulk solution.

The contact probability parameter \( \rho_i(0) \) is a function of the electric potential: an estimate of the contact can be obtained using the Poisson-Boltzmann expression used by the classic Gouy-Chapman theory\[32\]

\[
\rho_i(0) = e^{-z_i \Psi} \rho_i, \tag{34}
\]

where \( z_i \) is the electrovalence and \( \rho_i \) is the bulk density of ion \( i \). \( \Psi \) is the adimensional potential bias with reference to the so called potential of zero charge, and is given by

\[
\Psi = \beta e[\psi(0) - \psi^{pzc}]. \tag{35}
\]

where \( e \) is the elementary charge, \( \beta = 1/kT \), \( \psi(0) \) is the potential at the electrode surface, and \( \psi^{pzc} \) is the potential of zero charge. Empirically, recent experiments by Anderson\[33\] have shown that Eq. 34 works in systems where the assumptions of the Gouy-Chapman theory do not apply, and where we know that the discrete nature of the solvent will produce oscillatory charge profiles\[34\]. Yet contact theorems of the type

\[
kT \sum \rho_i(0) = \frac{e}{8\pi} E_0^2 + kT \sum \rho_i, \tag{36}
\]

are valid for irregular surfaces with arbitrary interactions\[12\] in the mean field sense. The reason is that the contact density \( \rho_i(0) \) given by Eq.34, for a particular value of the potential of zero charge \( \psi^{pzc} \), is accurate is presumably that the pair interactions cancel out at the surface, where only the particle-wall interactions exist, and in the mean field limit a relation like Eq.36 is satisfied by this ansatz.

The fraction of occupied sites \( \theta \) Eq. 16 can be represented by a series\[14\], at both low temperature (high fugacity \( z \)) and high temperature (low fugacity \( z \)). We consider the adsorption of a single ion only, (always the counterion),

\[
z = e^{-z_i \Psi} \rho_i \lambda = \rho_i(0) \lambda, \tag{37}
\]

and in Domb’s notation

\[
y = u^3/(z), \tag{38}
\]
\[ u = e^{\tau^3} = [g_2^B(d)]^{-1}. \quad (39) \]

\( \theta \) at low fugacity is given by

\[ 1 - \theta = \sum_{r=1}^{\infty} r y^r g_r(u). \quad (40) \]

and at high fugacity is given by

\[ \theta = \sum_{r=1}^{\infty} r y^{-r} g_r(u). \quad (41) \]

Here \( g_r(u) \) are polynomials, obtained from graph theory [14] (there are not to be confused with the distribution functions). The first polynomials are

\[ g_1(u) = u^3, \quad (42) \]

\[ g_2(u) = (1/2)(6u^5 - 7u^6), \quad (43) \]

\[ g_3(u) = (1/3)(6u^6 + 27u^7 - 90u^8 + 58u^9). \quad (44) \]

This series must satisfy certain limiting conditions: when \( y = 1 \), the critical line should be obtained, for which an exact expression is known. For the triangular lattice Potts found [28]

\[ \theta = (1/2) \left[ 1 - \left( 1 - \frac{(16u^3)}{(1 - u)^2(1 + 3u)} \right)^{1/8} \right]. \quad (45) \]

A similar expression exists also for the square lattice. From the high and low temperature series the correct critical exponent \( \theta = 1/8 \) can be extracted. However the series has poor convergence properties. Furthermore Eq. 45 diverges when the lateral interactions between the adions is turned off, that is, from Eq. 38 when \( w = 0 \) or \( u = 1 \). The observation is that in this limit both series Eqs. 40 and 41 yield the series

\[ \theta = y^{-1} - y^{-2} + y^{-3} - \ldots = \frac{y^{-1}}{1 + y^{-1}} = \frac{z}{1 + z}, \quad (46) \]

\[ \theta = 1 - y + y^2 - y^3 - \ldots = \frac{1}{1 + y} = \frac{z}{1 + z}, \quad (47) \]
The resummed series is just Langmuir’s adsorption isotherm, which is indeed the correct physical limit of \( \theta \) obtained from Eqs.15, 16, and 19 when the lateral interactions are turned off. This immediately suggests the form of the Padé approximant for general \( z \) and \( w = 1/u = g_2 \). For low fugacities

\[
\theta_l = \frac{z + z(w - 1)P(w, z)}{1 + z + z(w - 1)P(w, z)},
\]

and for high fugacities

\[
\theta_h = \frac{1}{1 + 1/[zw^6] + (1/[zw^6])(w - 1)P(w, 1/[zw^6])},
\]

The Polynomial \( P(w, \alpha) \) and the details of this Padé approximation are discussed in appendix A, where we give explicit formulas up to order 8. As mentioned in the introduction, this approximation does not satisfy the duality symmetry relation. An alternative Padé which does satisfy this relation is discussed in Appendix B. Our approximation here will consist in adding the two expressions for the high and low fugacity limits with a smooth switch function, which we have taken to be

\[
\eta(y, s) = (1/\pi)[\frac{\pi}{2} + \arctan(ys)],
\]

where \( s \) is 0.01 for \( w > 3 \) and \( s = (3.001 - w)/5 \) when \( w < 3 \). This averaging procedure produces an isotherm that has the correct shape for both the region above the critical value of \( w = 3 \) and for the region below, where no sharp transition is expected to occur. In figure 1 we show a series of isotherms for different values of \( w \), and we show, for comparison, the critical line from the exact solution of Potts. Since the calculation was done with only 8 terms, we think that the agreement is satisfactory. We could, with the published expressions of \( g_r(u) \) go up to order 20, but this is certainly beyond the accuracy of our current needs. The final expression for the fraction of occupied sites is

\[
\theta = \eta(y, s)\theta_l + [1 - \eta(y, s)]\theta_h.
\]

A final observation is that the mean field result [35] can also be cast in the form of a modified Langmuir adsorption isotherm:

\[
\theta_l = \frac{zw^{\theta}}{1 + zw^{\theta}},
\]
We also quote the results of the two point Padé approximant, which is discussed in Appendix B. The advantage of this approximant is that it satisfies automatically the duality theorem. The disadvantage is that it requires the inversion of an \( N \times N \) matrix, where \( N \) is the order of the approximant. We have computed this Padé up to order 5, and found that this is not enough since the adsorption isotherm near the critical line deviates strongly from the exact result for the triangular lattice. And also, even the order 5 Padé yields an expression that takes about 20 pages to write down. Above the critical point a [2, 2] two point Padé approximant yields

\[
\theta_P = \frac{(-7 + 6g_2 + g_2^6)z + 6(-1 + g_2)g_2^6z^2}{6(-1 + g_2)g_2^6z^2 + (-1 + g_2^6)(1 + z)},
\]

The fraction of occupied sites as a function of applied potential is shown in figure 2 for two values of \( w = 2.3 \), well below the critical value for film formation, and for \( w = 3.1 \), which is above the critical point. Clearly a phase transition occurs when \( y = 1/zw^3 = 1 \). This shows also in the voltamogram as a sharp peak. The charge potential curve of the voltamogram can be obtained by differentiation:

\[
I(\psi) = \frac{\partial \theta}{\partial \psi} \frac{d\psi}{dt},
\]

If the scanning rate is constant and we neglect diffusion and double layer effects [32] the derivative of \( \theta \) with respect to the applied potential should give a representation of the voltamogram.

The curves are shown in figure 3, and show a sharp peak for the first case, and a rather broad peak in the case \( w = 2.3 \).

We believe that the procedure discussed in this work can be extended to other systems, and in particular to multicomponent adsorption, where the location of the critical points is known, and where sufficient terms of the high and low fugacity series are known.
4 Appendix A: The Saturation Padé Approximant

In this appendix we discuss the Padé approximant that has the general form

\[ \theta = \frac{A(z)}{1 + A(z)}, \]  

(55)

where

\[ A(z) = \sum_{i=1}^{N} A_i z^i, \]  

(56)

and we have to find the coefficients \( A_i \) in this equation. We remark first that this equation is the natural generalization of Langmuir's adsorption isotherm to the case of interacting films, since for real and positive \( A(z) \), \( 1 > \theta > 0 \). The low fugacity series Eq. 40 can be written as

\[ B(z) = \sum_{i=1}^{N} B_i z^i, \]  

(57)

where the coefficients \( B_i \) are functions of \( w \) and can be obtained directly from the work of Domb [14]: The first few are

\[ B_1 = 1, \]  

(58)

\[ B_2 = -7 + 6w, \]  

(59)

\[ B_3 = 58 - 90w + 27w^2 + 6w^3, \]  

(60)

\[ B_4 = -519 + 1152w - 714w^2 + 20w^3 + 48w^4 + 12w^5, \]  

(61)

\[ B_5 = 4856 - 13980w + 13185w^2 - 3400w^3 - 885w^4 + 90w^5 + 105w^6 + 30w^7, \]  

(62)

\[ B_6 = -46780 + 165330w - 209520w^2 + 100842w^3 - 819w^4 - 7920w^5 - 1668w^6 + 198w^7 + 252w^8 + 84w^9, \]  

(63)

\[ B_7 = 460027 - 1926288w + 3065979w^2 - 2152332w^3 + 447090w^4 + 148176w^5 - 21049w^6 - 18774w^7 - 3948w^8 + 168w^9 + 735w^{10} + 210w^{11} + 7w^{12}, \]  

(64)
The Padé equation

\[
\sum_{i=1}^{N} A_i z^i = \left[ 1 + \sum_{i=1}^{N} A_i z^i \right] \sum_{j=1}^{N} B_j z^j,
\]

(66)
yields a recurrence relation for the coefficients \( A_i \). We get

\[ A_1 = 1, \]

(67)

\[ A_2 = B_1^2 + B_2 = 6(w - 1), \]

(68)

\[ A_3 = 3(-1 + w)(-15 + 11w + 2w^2). \]

(69)

and so on. After some straightforward algebra we find

\[ \theta_t = \frac{z + z(w - 1)P(w, z)}{1 + z + z(w - 1)P(w, z)}, \]

(70)

where

\[ P(w, z) = \sum_{i=1}^{N} p_i z^i, \]

(71)

and

\[ p_1 = 6, \]

(72)

\[ p_2 = 3(-15 + 11w + 2w^2), \]

(73)

\[ p_3 = 2(187 - 266w + 46w^2 + 30w^3 + 6w^4), \]

(74)

\[ p_4 = 3(-1100 + 2306w - 1190w^2 - 156w^3 + 83w^4 + 45w^5 + 10w^6), \]

(75)

\[ p_5 = 6(5047 - 13944w + 11897w^2 - 1778w^3 - 1276w^4 - 114w^5 + 99w^6 + 56w^7 + 14w^8), \]

(76)
\[ P_6 = -285682 + 978458w - 1161412w^2 + 459060w^3 + 67758w^4 - 41124w^5 - 17876w^6 - 1652w^7 + 1288w^8 + 952w^9 + 217w^{10} + 7w^{11}, \] (77)

\[ P_7 = 2751258 - 11237190w + 17065398w^2 - 10735704w^3 + 1150716w^4 + 1126218w^5 + 41376w^6 - 117342w^7 - 43824w^8 - 7788w^9 + 3810w^{10} + 2430w^{11} + 600w^{12} + 48w^{13}, \] (78)

5 Appendix B: The two Point Padé Approximant

Consider the lattice gas with first neighbor attractions on the triangular lattice. Following the work of Domb [14] we have high density and low density expressions for the excess free energy and the fraction of occupied sites \( \theta \) of the lattice gas. For low \( z \) we have

\[ \theta = z + (-7 + 6g_2)z^2 + \left(58 - 90g_2 + 27g_2^2 + 6g_2^3\right)z^3 \ldots \] (79)

\[ \theta = A(z) = \sum_{i=1}^{N} A_i z^i, \] (80)

For high \( z \)

\[ 1 - \theta = \frac{1}{(zg_2^6)} + (-7 + 6g_2)/(zg_2^6)^2 + \left(58 - 90g_2 + 27g_2^2 + 6g_2^3\right)/(zg_2^6)^3 \ldots \] (81)

or

\[ 1 - \theta = B(z) = \sum_{i=1}^{N} B_i/z^i. \] (82)

The adsorption isotherm can be constructed from both these series by a two point Padé approximant, which is required to satisfy both Eqs. 5 and 82 simultaneously. In fact, consider the Padé

\[ \theta = \frac{a(z)}{1 + b(z)}. \] (83)
where

\[ a(z) = \sum_{i=1}^{N} a_i z^i, \]  

\[ b(z) = \sum_{i=1}^{N} b_i z^i, \]  

which for \( z \rightarrow 0 \) must satisfy, to order \( N \)

\[ A(z) = \frac{a(z)}{1 + b(z)}, \]  

and for \( z \rightarrow \infty \) must satisfy to order \( N \)

\[ B(z) = \frac{a(z)/z^N}{(1 + b(z))/z^N}, \]  

This forms a system of \( 2N \) linear equations that can be solved in closed form: Defining the matrices

\[
W = \begin{bmatrix}
1 & B_1 & B_2 \\
-A_1 & 1 & B_1 \\
-A_2 & -A_1 & 1
\end{bmatrix}
\]  

\[
B = \begin{bmatrix}
1 & B_1 & B_2 \\
0 & 1 & B_1 \\
0 & 0 & 1
\end{bmatrix}
\]  

\[
\tilde{A} = \begin{bmatrix}
A_1 \\
A_2 \\
A_3
\end{bmatrix}
\]

we get

\[
\tilde{a} = W^{-1} \cdot \tilde{A},
\]  

and

\[
\tilde{b} = B \cdot \tilde{a},
\]

which are vectors of the coefficients of the Padé Eq. 83 \( \tilde{a} = (a_1, a_2, ...) \) and \( \tilde{b} = (b_1, b_2, ...) \).

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Figure 1: $\theta$ as a function of the fugacity $z$ for $w = 3.5, 3.1, 3.0$ (critical value), $2.95, 2.9, 2.8$, and $2.6$. The squares are the spontaneous transition curve of Potts.

Figure 2: Adsorption isotherm as a function of the reduced potential $\Psi$, for two values of $w = 2.3$ and 3.1. Here $z_0 = 0.1$.

Figure 3: Ideal voltamogram with no diffusion effects. We show a reduced intensity in units of $\theta/\Psi$ for the same parameters of Figure 2.

Figure 4: The case with $w = 3.1$ blown up 10 times. This is a crude way to picture the effect of diffusion broadening on the voltamogram.
References


