EXACT RESULTS FOR THE STRUCTURED LIQUID-SOLID INTERFACE

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EXACT RESULTS FOR THE STRUCTURED LIQUID-SOLID INTERFACE

The theoretical discussion of smooth surfaces is considerably simpler than that of a realistic surface, in which the solid, usually a metal, has a well defined crystal structure. The reason is that in the case of a smooth surface the problem is one dimensional, rather than three dimensional . The analysis of a realistic metal surface potential in contact with an ionic solution is extremely difficult, and requires the use of very large computers. We would like to discuss a simple model of a structured interface which predicts surface phase behavior, for the adsorbed layers, and which is mathematically tractable. In fact, if the correlation functions of the smooth surface model are known to all orders, then the properties and correlation functions of our model can be computed exactly,at least in principle .

The model[1] combines two ideas that have been used a very long time ago : Boltzmann's sticky potential[2], and the adsorption site model of Langmuir[3]. The elegant work of Baxter[4] in which the Percus-Yevick approximation of the sticky hard sphere model is solved and discussed, shows that this model has a particularly simple mathematical solution In Baxter's work the potential has the form

$$\exp [-\beta u(\mathbf{r})] = 1 + \lambda \delta(\mathbf{r} \cdots) \qquad (1)$$

where $\beta = 1/kT$ is the usual Boltzmann thermal factor,$u(\mathbf{r})$ is the intermolecular potential,λ is the stickiness parameter, $\mathbf{r} = (x,y,z)$

is the relative position of the center of the molecules, and σ is the diameter of the molecules. The right hand side term represents the probability of two molecules being stuck by the potential $u(\mathbf{r})$: this occurs only when the two molecules actually touch, 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 stickiness is represented by the parameter λ, which except for a normalization factor ,can be considered as the fugacity of the formation of the pair. $*$

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. For this model, equation (1) has to be changed to

$$\exp[-\beta u_a(\mathbf{r})] = 1 + \lambda_a(\mathbf{R})\delta(z) \qquad (2)$$

with

$$\lambda_a(\mathbf{R}) = \sum_{n_1 n_2} \lambda_a\, \delta(\mathbf{R} - n_1\mathbf{a}_1 - n_2\mathbf{a}_2) \qquad (3)$$

Here $\mathbf{R} = (x,y)$ 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 (3), n_1, n_2 are natural numbers, and $\mathbf{a}_1, \mathbf{a}_2$ are lattice vectors of the adsorption sites on the surface. The number λ_a represents now the fugacity of an adsorbed atom of species a, onto the surface which has a perfectly ordered array of adsorption sites. While this is not a requirement of the model, it makes the mathematical discussion much simpler.

Consider the case of a simple salt dissolved in water, near a metallic electrode: in the SSM there will be three components,the anion, the cation and the solvent,and the lattice atoms. In the limiting case of the SSM, the sizes of the different species play a crucial role in the possible ordering of the ad layers 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 σ_n. The lattice spacing of 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. In the most general case, all three components can be adsorbed competitively, and this situation can give rise to very complex phase diagrams .In most electrochemical situations the electrode surface is polarized either positively or negatively, which means that either the cation or the anion is strongly repelled from the surface, and therefore we need to consider the adsorption of either a or b and the solvent n on the electrode. This implies a drastic simplification in the model, because now we can discuss at least the case of commensurate adsorption in terms of models that have been solved analytically, such as the spin s=1/2 Ising model and the hard hexagon gas model. The phase transitions predicted for these models seem to be reasonable in terms of the currently available experimental evidence.

There are two cases of chemisorption of electrochemical interest: In the first one, the charge of the adsorbate is neutralized by the electrons in the metal, and this means that the interactions between neighbors on the surface is attractive. If we are far from the point of zero charge, and the metal is negatively charged, the contact probability of the anions a is zero for all practical purposes and we have only the cation b or the solvent n on the adsorption sites. The problem is then reduced to a spin s=1/2 Ising model with ferromagnetic interactions. In the second case there is no discharge of the adions by the metal. The interactions between the ions of the same sign is clearly repulsive, so that the nearest neighbor sites to an occupied site are not going to be occupied.

The possible existence of phase transitions was discussed in the work of Huckaby and Blum[5]. The observation is that the SSM model maps the three dimensional interface onto a two dimensional lattice problem. The phase behavior in the interphase is determined by the mapping of the parameters, and exact conditions on the existence of phase transitions can be given.

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 σ, 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 σ 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[5] of Baxter. In this case there is a second order phase transition between an ordered $\sqrt{3}$x$\sqrt{3}$ phase and a disordered one. The partition function is in this case

$$Z/Z^0 = \sum_{\{t_i\}} \exp\left[-\beta w \sum_{nn} t_i t_j + \beta\mu \sum_i t_i \right] \qquad t_i=0,1$$

where $\beta=1/kT$ and $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (4)

$$\beta w=-\ln g_2^0(d) \qquad\qquad (5)$$
$$\beta\mu=\ln\left[\lambda\rho^0(0)\right] \qquad\qquad (6)$$

This partition function can be mapped onto an Ising model with spin variables $s_i=\pm 1$ by means of the transformation
$$s_i=2t_i-1 \quad \text{or} \quad t_i=(s_i+1)/2 \qquad (7)$$

and using the above definitions we get the exact condition
for phase transitions when w<0

$$\lambda\rho^0(0)=[g_2^0(d)]^{-3} \qquad (8)$$

The preceding analysis can be illustrated by a fluid of hard

spheres in contact with a sticky triangular lattice of spacings $d=\sigma$. In this case a good estimate of both the contact density and the pair distribution function are obtained from the Percus-Yevick theory

$$\rho^0(0) = \rho \, \frac{(1+2\eta)}{(1-\eta)^2} \qquad (9)$$

$$g_2^0(\sigma) = \frac{(1+\eta/2)}{(1-\eta)^2} \qquad (10)$$

$$\eta = (1/6)\,\pi\rho\sigma^3$$

where η is the fraction of occupied volume. Replacing into the previous expression we get

$$\lambda = (1/6)\,\pi\sigma^3 \frac{(1-\eta)^8}{\eta\,(1+2\eta)\,(1+\eta/2)^3} \qquad (11)$$

This relation is a necessary but not sufficient condition for the occurrence of phase transitions.

A sufficient condition for the occurrence of a phase transition can be obtained from the work of Potts on the magnetization of the ferromagnetic Ising model on the triangular lattice[6]. We use the variable

$$x = e^{\beta w/2} = 1/\left(g_2^0(d)\right)^{1/2} \qquad (12)$$

Solving now the magnetization equation with this variable we obtain for the contact pair correlation function the condition

$$g_2^0(d)\Big|_{crit} = 3 \qquad (13)$$

and the value for the critical sticky parameter λ is

$$\lambda \rho^0(0)\Big|_{crit} = 1/27 \qquad (14)$$

These are exact results, that are model independent. In our example of hard core fluid in the Percus-Yevick approximation, we get the critical value of the excluded volume fraction

$$\eta_{crit} = 0.371$$

and the sticky parameter

$$\lambda_{crit} = 0.0118 \ \sigma^3$$

These exact results are in qualitative agreement with the mean field theory of Badiali et al.[1], where the first order phase transition is also predicted. But the quantitative agreement is not good, which illustrates the pitfalls of mean field theory. In the computer simulations of Caillol et. al.[7] the conditions for the occurrence of a first order phase transition are not met, because the adsorption sites are of finite size, and for that reason the occupancy of a site may prevent nearest neighbor occupation. In this case we expect a second order phase transition to occur.

When there are longer ranged interactions, beyond the nearest neighbor interactions, Dobrushin[8] has shown that the first order phase transition still occurs. However, an exact relation is not available.

As was mentioned already in the electrochemical case the contact pair correlation function of ions of equal sign is practically zero, because of the Coulomb repulsion which prevents ions of equal sign to approach each other. However 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[9]. 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[10] and in situ[11] [12] [13]. At a lower potential a dilute ordered √3x√3 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 . The dilute √3x√3 phase has the white line characteristic of the charged ions. We may assume then that in this case the Cu retains part of its charge, so that the interactions are in this case repulsive. If the occupation of one site in the triangular

lattice also excludes the nearest neighbors, then the problem is equivalent to the hard hexagon problem of Baxter[14]. This problem can be solved when the interactions between the hard hexagons are neglected.

The thermodynamics of the hard hexagon model was recently worked out by Joyce[15]. In terms of the lattice fugacity

$$\gamma = \lambda \rho^0 (0) \tag{15}$$

The system undergoes a second order phase transition between an ordered solid like phase and a disordered one. The transition occurs when

$$\gamma_{crit} = (11 + 5\sqrt{5})/2 = 11.09$$

The fraction of occupied sites is

$$\theta_{crit} = (5 - \sqrt{5})/10 = 0.2764$$

We remark that in the limit of highest possible density the occupied sites fraction is $\theta = 1/3$.

Consider again the model of hard spheres of equal size but larger than the lattice spacing. Then we can draw the adsorption isotherm for different values of the sticky parameter . See figure 1.

Figure 1: Adsorption isotherm for $\sigma > d$. The fraction of occupied sites is given as a functin of the bulk density $\rho \sigma^3$, fot the following values of the stickiness parameters λ/σ^3: (a) 0.2, (b) 1.0, (c) 2.0, (d) 10 and (e) 40. An order disorder transition occurs at $\theta_c = 0.2764$.

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$\rho \sigma^3$