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# Lattice models for dipolar adsorption at metal/electrolyte interfaces using Bethe approximation

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A two-dimensional lattice model for adsorption of solvent molecules at a metal/electrolyte interface is proposed assuming two configurational states for dipoles. The generalized Ising Hamiltonian incorporating Coulombic effects and nonelectrostatic metal–solvent interaction energies is derived and solved for obtaining the order parameters using the Bethe approximation. The significance of the formalism as well as the extension to adsorption of neutral organic compounds is indicated.

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## I. INTRODUCTION

The statistical mechanical modeling of the metal/electrolyte interface has different facets such as (i) the polarization behavior of solvent dipoles and its contribution to the potential difference and differential capacitance, (ii) the adsorption of ions and neutral organic compounds, and (iii) the structure and dynamics of phase transitions.<sup>1,2</sup> A unified approach for the study of these within a microscopic framework is provided by the generalized Ising (or equivalently lattice gas) model formalism.<sup>3–5</sup> The significance of this approach for the adsorption of dipolar species for a  $(2s+1)$  orientational state model where  $s=1/2$  or 1, has been illustrated *albeit* under the mean field approximation (MFA). However, in view of the qualitative limitations of MFA, especially in the study of phase transitions as well as for a faithful representation of interfacial interactions, approximations superior to MFA need to be investigated in a systematic manner. Further, the study of dipolar interactions plays an important role in other contexts too such as dipolar glasses<sup>6</sup> and thermal desorption kinetics.<sup>7</sup> In this paper, we formulate the total Hamiltonian of the system, taking into account dipole–dipole interactions (permanent and induced), specific metal–solvent nonelectrostatic contributions and solve the same using the *Bethe (or equivalently quasichemical)* approximation. The methodology is illustrated for adsorption of water dipoles in two orientational states at electrochemical interfaces and the qualitative differences with MFA predictions are pointed out. The extension to adsorption of neutral organic compounds in the presence of solvent dipoles is indicated.

## II. MODEL AND ANALYSIS

A two-dimensional lattice of coordination number  $z$  whose sites are occupied by polarizable point dipoles is considered. The spin variable  $s_i=+1$  and  $-1$  denotes the occupancy of the site “ $i$ ” by a water dipole with its oxygen atom either pointing toward or away from the metal surface designated, respectively, as “up” and “down” orientational state. The input parameters of the model are (i) the normal components of permanent dipole moments  $p_{s1}$  and  $p_{s2}$  of the two configurations and the polarizability  $\alpha_s$  of the solvent dipoles (assumed to be equal in the two states). The frac-

tional surface coverage  $\theta^\uparrow$  and  $\theta^\downarrow$  of the two states are given by  $(1+\langle s_i \rangle)/2$  and  $(1-\langle s_i \rangle)/2$ , respectively. The characteristic feature of the Bethe approximation is that the interaction of a chosen central dipole (at site “ $o$ ”) with its nearest neighbors (at site “ $j$ ”) is treated exactly whereas the dipolar interactions outside the first cluster (site “ $i$ ”) are treated as in MFA.

### A. Nonelectrostatic interaction of the solvent states with metal surface

The contribution to the Hamiltonian arising from the nonelectrostatic interaction of the solvent states with electrode surface can be written as,

$$H_{n-e} = \sum_{j=0}^z \left( \frac{1+s_j}{2} \right) U_{s1} + \sum_{j=0}^z \left( \frac{1-s_j}{2} \right) U_{s2}, \quad (1)$$

where  $U_{s1}$  and  $U_{s2}$  represent the interaction energy of the solvent dipoles with the substrate.  $s_o$  and  $s_j$  are the spin variables corresponding to the dipoles at sites  $o$  and  $j$ .

### B. Coulombic interactions

The Coulombic contribution to the total Hamiltonian is more involved because of the need to distinguish three different fields viz. (i)  $\xi_o$  at the central dipole (ii)  $\xi_j$  due to the “ $z$ ” nearest neighbors of the central dipole, and (iii)  $\xi_i$  being the contribution by dipoles which are outside the first shell. The field at site  $j$  is given by the sum of the external field and the local field arising from the interaction with dipoles at site  $o$  and  $i$  viz.<sup>8</sup>

$$\begin{aligned} \xi_j = & 4\pi\sigma^M + \sum_{j=1}^z f_{oj} \left( \frac{1+s_o}{2} \right) (p_{s1} - \alpha_s \xi_o) \\ & + \sum_{j=1}^z f_{oj} \left( \frac{1-s_o}{2} \right) (p_{s2} - \alpha_s \xi_o) - \sum_{\langle ij \rangle} f_{ij} \left( \frac{1+s_i}{2} \right) (p_{s1} \\ & - \alpha_s \xi_i) + \sum_{\langle ij \rangle} f_{ij} \left( \frac{1-s_i}{2} \right) (p_{s2} - \alpha_s \xi_i), \end{aligned} \quad (2)$$

where the first term in Eq. (2) is the external electric field due to  $\sigma^M$ , the charge density on the metal surface.  $f_{ij}$  is the potential due to the pair of dipoles at  $i$  and  $j$ , and  $\sum_{\langle ij \rangle} f_{ij}$  is proportional to  $1/d^3$ , with  $d$  being the nearest-neighbor dis-

tance, and the proportionality constant referred to as the ‘‘effective coordination number’’  $C_e$ , is ascribed a value greater than the geometric coordination number  $z$  on account of the field due to infinite imaging of the dipole in the two interfaces. An explicit expression for  $C_e$  in the case of a hexagonal lattice can be obtained from the work of Macdonald and Barlow<sup>9</sup> by imaging the first three plane arrays in each phase and by assuming the dipole layer to be situated at a distance  $d/2$  from each phase as,

$$C_e = 11.0[1 + 0.1612(1 + f) + 0.0522 f + 0.0067f(1 + f) + \dots],$$

where  $f = (\epsilon - 1)/(\epsilon + 1)$ ,  $\epsilon$  being the dielectric constant of bulk water (78.3) which gives  $C_e = 15.2$ .  $f_{oj}$  is the potential due to the pair of dipoles at  $o$  and  $j$  and  $\sum_j f_{oj} = 1/zd^3$ . Note that in *Bethe approximation* the interaction between the dipoles within the first cluster is treated exactly and hence the geometrical coordination number  $z$  arises for  $\sum_j f_{oj}$ .<sup>10</sup> The field at site  $o$  is given by the sum of the field due to the charge density on the metal surface and the field due to the interaction of solvent dipoles at site  $o$  with those at site  $j$  viz.

$$\xi_o = 4\pi\sigma^M + \sum_{j=1}^z f_{oj} \left( \frac{1+s_j}{2} \right) (p_{s1} - \alpha_s \xi_j) + \sum_{j=1}^z f_{oj} \left( \frac{1-s_j}{2} \right) (p_{s2} - \alpha_s \xi_j). \quad (3)$$

Further, since the interaction of the dipole at site  $i$  with the remaining dipoles is treated as in MFA,  $\xi_i$  can be substituted by the mean field  $\langle \xi_i \rangle$  which is hence equal to  $\langle \xi_j \rangle - \xi_o + 4\pi\sigma^M$ . Substituting these conditions we have

$$\langle \xi_j \rangle = A/B, \quad (4)$$

where

$$A = 4\pi\sigma^M \left( 1 - \sum_j f_{oj} \alpha_s s_o \right) + \sum_{\langle ij \rangle} \frac{f_{ij}}{2} (p_{\text{tot}} + \Delta p \langle s_i \rangle) + \sum_j \frac{f_{oj}}{2} (p_{\text{tot}} + \Delta p s_o) + \frac{\alpha_s (p_{\text{tot}} + \Delta p \langle s_j \rangle)}{2} \times \left( \sum_{\langle ij \rangle} f_{ij} \sum_j f_{oj} \langle s_i \rangle - \sum_j f_{oj}^2 s_o \right), \quad (5)$$

where  $p_{\text{tot}} = p_{s1} + p_{s2}$ ,  $\Delta p = p_{s1} - p_{s2}$  and

$$B = 1 + \sum_{\langle ij \rangle} f_{ij} \alpha_s + \sum_{\langle ij \rangle} f_{ij} \sum_j f_{oj} \alpha_s^2 \langle s_i \rangle - \sum_j f_{oj}^2 \alpha_s^2 \langle s_o \rangle. \quad (6)$$

The limit to MFA is obtained by letting the coordination number  $z \rightarrow \infty$  thereby  $\sum_j f_{oj}$  in Eqs. (2) and (3)  $\rightarrow 0$  and hence  $\langle \xi_j \rangle = \langle \xi_i \rangle = \langle \xi \rangle$ . Thus Eq. (4) becomes consistent with the previously known MFA results.<sup>4,11</sup> The Coulombic contribution to the Hamiltonian is given by

$$H_c = \left( \frac{1+s_0}{2} \right) \left( p_{s1} E - \frac{\alpha_s E^2}{2} \right) + \left( \frac{1-s_0}{2} \right) \left( p_{s2} E - \frac{\alpha_s E^2}{2} \right) + \sum_{j=1}^z \left( \frac{1+s_j}{2} \right) \left( p_{s1} \langle \xi_j \rangle - \frac{\alpha_s \langle \xi_j \rangle^2}{2} \right) + \sum_{j=1}^z \left( \frac{1-s_j}{2} \right) \times \left( p_{s2} \langle \xi_j \rangle - \frac{\alpha_s \langle \xi_j \rangle^2}{2} \right). \quad (7)$$

Note that, since the field acting at site  $j$  ( $\langle \xi_j \rangle$ ) includes the interaction of central dipole with its nearest neighbors, the field  $E$  comes in Eq. (7) instead of  $\xi_o$ , in order to avoid double counting. Simplifying and neglecting the terms independent of the spin variables Eq. (7) can be written as

$$H_c = \frac{\Delta p E s_o}{2} + \frac{\Delta p \langle \xi_j \rangle}{2} \sum_{j=1}^z s_j. \quad (8)$$

Equation (8) after substituting for  $\langle \xi_j \rangle$  becomes

$$H_c = \frac{\Delta p E}{2} s_o + \frac{\Delta p E}{2} \sum_{j=1}^z s_j + \frac{\Delta p F}{2} \sum_{j=1}^z s_j + J \sum_{j=1}^z s_o s_j. \quad (9)$$

The renormalized electric fields  $E$ ,  $F$ , and  $J$  are given by

$$E = 4\pi\sigma^M/B, \quad (10)$$

$$F = \frac{1}{2B} \left( \sum_j f_{oj} p_{\text{tot}} + \sum_{\langle ij \rangle} f_{ij} (p_{\text{tot}} + \Delta p \langle s_i \rangle) + \sum_{\langle ij \rangle} f_{ij} \sum_j f_{oj} \alpha_s \langle s_i \rangle (p_{\text{tot}} + \Delta p \langle s_j \rangle) \right), \quad (11)$$

and

$$J = \frac{\Delta p}{2B} \left\{ \sum_j f_{oj} \left( \frac{\Delta p}{2} - \alpha_s (4\pi\sigma^M) \right) - \sum_j \frac{f_{oj}^2 \alpha_s}{2} (\Delta p \langle s_j \rangle + p_{\text{tot}}) \right\}. \quad (12)$$

It can be noted that  $J \rightarrow 0$  in the mean field limit with the corresponding expressions for  $E$  and  $F$ . The total Hamiltonian incorporating nonelectrostatic and Coulombic contributions becomes,

$$H_T = (\Delta U + \Delta p E) \sum_{j=0}^z \frac{s_j}{2} + \Delta p F \sum_{j=1}^z \frac{s_j}{2} + J \sum_{j=1}^z s_o s_j, \quad (13)$$

where  $\Delta U = U_{s1} - U_{s2}$ . When  $\Delta U = 0$  and  $p_{s1} = p_{s2} = p$ , Eq. (13) becomes,

$$H_T = -pE \sum_{j=0}^z s_j - pF \sum_{j=1}^z s_j - J \sum_{j=1}^z s_o s_j, \quad (14)$$

which is isomorphic with the Hamiltonian customarily employed<sup>12,13</sup> while using Bethe approximation in the cooperative phenomena of magnetism. However, in the context of dipolar adsorption at electrochemical interfaces, the fields  $E$ ,  $F$ , and  $J$  contain molecular constants as well as spin variables.

### III. RESULTS AND DISCUSSION

#### A. Order parameters

For the Hamiltonian given by Eq. (13), the long-range order parameter  $R$  denoting the net orientation of the solvent dipoles, i.e.,  $(N\uparrow - N\downarrow)/N_T$  becomes<sup>12-14</sup>

$$R = \langle s_o \rangle = \frac{a-b}{a+b}, \quad (15)$$

where

$$a = \exp(k_1 + k_2) [2 \cosh(k_1 + k_2 + k_3 + \gamma)]^z, \\ b = \exp[-(k_1 + k_2)] [2 \cosh(k_1 + k_2 + k_3 - \gamma)]^z \quad (16)$$

and  $k_1$ ,  $k_2$ ,  $k_3$ , and  $\gamma$  are as follows:

$$k_1 = -\frac{\Delta U}{2kT}, \quad k_2 = -\frac{\Delta p E}{2kT}, \quad k_3 = -\frac{\Delta p F}{2kT}, \\ \gamma = -\frac{J}{kT}. \quad (17)$$

The short-range order parameter defined by  $2[(N\uparrow\uparrow + N\downarrow\downarrow) - 2N\downarrow\uparrow]/zN$  is

$$Q = \langle s_j \rangle \\ = \frac{a \tanh(k_1 + k_2 + k_3 + \gamma) + b \tanh(k_1 + k_2 + k_3 - \gamma)}{a + b}. \quad (18)$$

$k_3$  can be obtained self-consistently by equating Eqs. (15) and (18) viz.

$$\exp\left(\frac{2k_3}{z-1}\right) = \frac{1 + \exp[-2(k_1 + k_2 + k_3 + \gamma)]}{\exp(-2\gamma) + \exp[-2(k_1 + k_2 + k_3)]}. \quad (19)$$

Substituting Eq. (19) into Eqs. (15) and (18) we have

$$\langle s_o \rangle = R = \tanh[k_1 + k_2 + k_3 z / (z-1)] \quad (20)$$

and

$$\langle s_j \rangle = Q = \frac{\tanh(k_1 + k_2 + k_3 + \gamma) + \exp[-2[k_1 + k_2 + k_3 z / (z-1)]] \tanh(k_1 + k_2 + k_3 - \gamma)}{1 + \exp[-2[k_1 + k_2 + k_3 z / (z-1)]]}. \quad (21)$$

Further,  $\langle s_i \rangle = (\langle s_j \rangle + \langle s_o \rangle)/2$ . In MFA, since the central dipole is not given any special status,  $\langle s_o \rangle = \langle s_j \rangle$  thus  $\langle s_i \rangle = \langle s_j \rangle = \langle s \rangle$  which implies that local correlations are ignored. Introducing the definition for  $\sum_{\langle ij \rangle} f_{ij}$  and  $\sum_j f_{oj}$  as mentioned earlier, the equations for  $E$ ,  $F$ , and  $J$  become,  $E = 4\pi\sigma^M/B$ , and Eqs. (11) and (12) can now be written as

$$F = \frac{1}{2B} \left\{ \frac{p_{\text{tot}}}{zd^3} \left( 1 + C_e \left[ z + \frac{\alpha_s(R+Q)}{2d^3} \right] \right) + \frac{C_e(R+Q)\Delta p}{2d^3} \left( 1 + \frac{\alpha_s Q}{zd^3} \right) \right\}, \quad (22)$$

$$J = \frac{\Delta p}{2zd^3 B} \left\{ \frac{\Delta p}{2} - \alpha_s 4\pi\sigma^M - \frac{\alpha_s(\Delta p Q + p_{\text{tot}})}{2zd^3} \right\}, \quad (23)$$

where  $B$  is given by

$$B = 1 - \frac{\alpha_s^2 R}{z^2 d^6} + \frac{\alpha_s C_e}{d^3} \left( 1 + \frac{\alpha_s(R+Q)}{2zd^3} \right). \quad (24)$$

From Eqs. (15), (18), and (19), it is clear that the general form for  $\langle s_o \rangle$ ,  $\langle s_j \rangle$ , and  $F$  obtained using the Bethe approximation in the context of magnetism is retained [cf. Eqs. (4), (5), and (7) of Ref. 13]. It can be noted that when the coordination number  $z \rightarrow \infty$ —limit to MFA—Eqs. (20) and (21) become identical as expected. Thus Eq. (20) obviously is a first-order correction to the conventional MFA in the case of adsorption of two state solvent dipoles at electrode/electrolyte interfaces. In general  $E$ ,  $F$ , and  $J$  are dependent upon  $R$  as well as  $Q$ , hence Eqs. (20) and (21) are to be solved simultaneously to obtain the order parameters. How-

ever, when  $\alpha_s = 0$ ,  $E$  and  $J$  become independent of  $R$  and  $Q$  thus simplifying the analysis. In what follows, we restrict ourselves to this special case.

#### B. Dipole potential and its temperature coefficient

The analysis of water structure at an electrochemical interface is usually centered around the experimental differential capacitance–potential data of Grahame<sup>15</sup> at Hg/NaF solution interface—a prototype of an ideally nonpolarizable interface. Nevertheless, a sensitive test for the validity of any solvent model is provided by the sign of temperature coefficient of dipole potential when the external electric field is absent. The potential drop due to the adsorbed solvent molecules is<sup>11</sup>

$$g_{\text{dip}} = 2\pi N_T (\Delta p R + p_{\text{tot}}) / \epsilon, \quad (25)$$

where  $\epsilon$  is the dielectric constant of the medium. However, when  $p_{s1} = -p_{s2} = p$ ,

$$g_{\text{dip}} = -4\pi N_T p R / \epsilon. \quad (26)$$

From the expression for dipole potential, it is clear that the sign of  $g_{\text{dip}}$  is dictated by the sign of the order parameter  $R$  and a negative value of  $R$  indicates that  $g_{\text{dip}}$  is positive in accordance with the experimental data for Hg/NaF solution interface.<sup>16</sup> The following set of molecular constants are employed in the calculations.  $p = 2 \times 10^{-30}$  C m,  $z = 4$ ,  $d = 3.8 \times 10^{-10}$  m. Since exact estimates of  $\Delta U_{s1}$ ,  $\Delta U_{s2}$  representing the nonelectrostatic interaction of solvent dipoles with the metal surface are not available, we have chosen, to

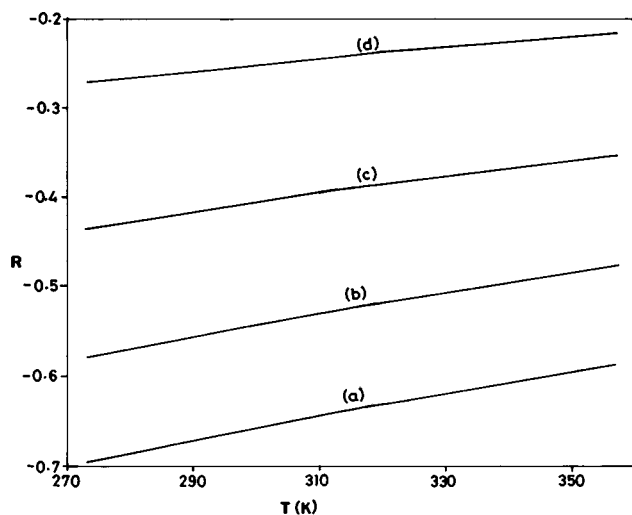


FIG. 1. The variation of long-range order parameter with temperature for the following set of parameters:  $p_{s1} = -p_{s2} = 2 \times 10^{-30}$  C m,  $\sigma^M = 0$ ,  $z = 4$ ,  $d = 3.8 \times 10^{-10}$  m,  $(U_{s1} - U_{s2})/k =$  (a) 178.8 K, (b) 298.0 K, (c) 417.2 K, (d) 536.4 K.

begin with, a particular value of  $\Delta U$ , i.e.,  $(\Delta U_{s1} - \Delta U_{s2})$  using which  $k_1$  is evaluated at various temperatures. Substituting this  $k_1$  and the corresponding  $J$  from Eq. (23) in Eq. (19),  $k_3$  can be estimated. Subsequently  $R$  from Eq. (20) is evaluated [line (a) of Fig. 1]. The same procedure is repeated for other values of  $\Delta U$  and lines (b), (c), and (d) of Fig. 1 are obtained. A positive temperature coefficient of  $R$  results from the above calculations, which on account of Eq. (26) denotes a negative temperature coefficient of dipole potential and is consistent with experimental data pertaining to Hg/NaF solution interface. This implies that the negative end of the water dipole is oriented toward the metal surface at the potential of zero charge. We reiterate here that conventional two-state models previously investigated using MFA are at variance with the experimental data concerning the temperature dependence of the dipole potential at  $\sigma^M = 0$ . It appears that this may be due to the overestimation of the order parameters in MFA. In hindsight, such an improvement is not entirely fortuitous since the Bethe approximation does provide more accurate estimates of critical temperature in various contexts when compared with the Bragg–Williams approximation. While the values chosen for the molecular constants are only plausible estimates, it is gratifying to note that a simple two state nonpolarizable point dipole model is able to account for the experimentally observed behavior. It can be recalled that the Bethe approximation carried out here is equivalent to the periodic cluster model when a square lattice is chosen as the basic unit.

Several comments concerning this approach are in order here. First, the structure of the Hamiltonian (13) is invariant even for adsorption of two different dipolar species (organic adsorbate and solvent dipoles each having one orientational state) with different interpretations of  $E$ ,  $F$ , and  $J$ . However the order parameter is still given by Eq. (20), which can be converted into an adsorption isotherm, after incorporating chemical potential effects. Even the mean field version of the

above two-state model has been shown<sup>17</sup> to be useful in rationalizing a large number of experimental observations. This is not all. The availability of the Hamiltonian such as Eq. (13) in the case of physisorbed organic compounds makes the systematic analysis of a variety of two-dimensional phase transitions<sup>2</sup> feasible at electrochemical interfaces. This in turn enables one to comprehend the limitations of the mean field approximation in the prediction of transition temperatures at such interfaces.<sup>18</sup> Second, the formulation of the Hamiltonian plays a central role in deriving nonsteady state descriptions using kinetic Ising model formalism, as shown in Ref. 19 in a different context. Consequently, the formulation of the Hamiltonian derived above may also have interesting implications in solving time-dependent adsorption problems. Finally, though the postulate of only two orientational states for solvent dipoles is restrictive, the present methodology provides a framework whereby additional orientational states can be included within the Bethe approximation for a more sophisticated description. However, while classical infinite orientational state models for dipoles lead to a Langevin function<sup>20</sup> for the long-range order parameter under MFA the corresponding result pertaining to the Bethe approximation is unclear and may even be tedious, when polarizability effects are introduced. This is now being investigated. These models when coupled with a satisfactory formalism for metal surfaces using jellium models<sup>21–23</sup> will hopefully provide a complete description of the inner part of the electrical double layer.

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- <sup>1</sup> S. K. Rangarajan, in *Specialist Periodical Reports, Electrochemistry*, edited by H. R. Thirsk (The Chemical Society, London, 1980), Vol. 7.
- <sup>2</sup> R. de Levie, *Chem. Rev.* **88**, 599 (1988).
- <sup>3</sup> S. K. Rangarajan, *J. Electroanal. Chem.* **82**, 93 (1977).
- <sup>4</sup> M. V. Sangaranarayanan and S. K. Rangarajan, *J. Electroanal. Chem.* **176**, 119 (1984).
- <sup>5</sup> C. A. Basha and M. V. Sangaranarayanan, *J. Electroanal. Chem.* **291**, 261 (1990).
- <sup>6</sup> M. W. Klein, C. Held, and E. Zuroff, *Phys. Rev. B* **13**, 3577 (1976).
- <sup>7</sup> B. L. Masschhoff and J. P. Cowin, *J. Chem. Phys.* **101**, 8137 (1994), and references therein.
- <sup>8</sup> The cancellation of terms involving  $\alpha_s$  is not carried out at this stage, for brevity.
- <sup>9</sup> J. R. Macdonald and C. A. Barlow, *Surf. Sci.* **4**, 381 (1966).
- <sup>10</sup> Since, the summation here extends only for  $j$ ,  $z$  comes in the denominator in contrast to  $\sum_{(ij)} f_{ij}$ .
- <sup>11</sup> S. Levine, B. M. Bell, and A. L. Smith, *J. Phys. Chem.* **73**, 3534 (1969).
- <sup>12</sup> R. Kubo, *Statistical Mechanics* (Elsevier Science, New York, 1965), Chap. 5.
- <sup>13</sup> M. Plischke and B. Bergersen, *Equilibrium Statistical Physics* (Prentice Hall, Englewood Cliffs, 1989), Chap. 3.
- <sup>14</sup> R. J. Baxter, *Exactly Solved Models in Statistical Mechanics* (Academic, London, 1982), Chap. 4.

- <sup>15</sup>D. C. Grahame, *Chem. Rev.* **41**, 441 (1947).
- <sup>16</sup>S. Trasatti, *J. Electroanal. Chem.* **91**, 293 (1978).
- <sup>17</sup>M. V. Sangaranarayanan and S. K. Rangarajan, *J. Electroanal. Chem.* **176**, 1, 65, 97 (1984).
- <sup>18</sup>R. Sridharan, R. deLevie, and S. K. Rangarajan, *Chem. Phys. Lett.* **142**, 43 (1987).
- <sup>19</sup>R. Aldrin Denny and M. V. Sangaranarayanan, *Chem. Phys. Lett.* **239**, 131 (1995).
- <sup>20</sup>D. C. Mattis, *The Theory of Magnetism, An Introduction to the Study of Cooperative Phenomena* (Harper and Row, New York, 1965), Chap. 8.
- <sup>21</sup>W. Schmickler and D. Henderson, *J. Chem. Phys.* **85**, 1650 (1986).
- <sup>22</sup>W. Schmickler and D. Henderson, *Phys. Rev. B* **30**, 3081 (1984).
- <sup>23</sup>S. Amokrane, V. Russier, and J. P. Badiali, *Surf. Sci.* **217**, 425 (1989).