

## THEORETICAL STUDY OF THE GAS-SOLID INTERFACE

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The gas-solid interface is studied using the formalism of classical liquid theory. In this work the factor correlation function (FCF) is deduced using the Baxter's potential model. This potential model presents the fundamental characteristics of a real interaction potential, i.e., it is attractive in a finite region and strongly repulsive in the core. Additionally it is easily manipulated analytically. The FCF is useful in the calculation of thermodynamic properties of a sticky hard-sphere mixture. The solid is, therefore, modeled as an infinite-radius sticky hard-sphere. One can also evaluate the adsorption isotherms.

## I. Introduction.

Adsorption is certainly one of the most important gas-surface interactions and many technologically important processes are based on it [1].

We present here a statistical model to describe the gas-solid interface using some previous results of the classical theory of liquids [2].

In this work we discuss the statistical mechanics treatment of a polydisperse system of spherical particles whose interaction is due to an attractive short ranged potential. This model is known as sticky hard-spheres or Baxter's model [3]. The present study is made in the (PYA) Percus-Yevick approximation [4]. We present the methodology and preliminary results for a set of interaction potentials that, in general, do not correspond to a particular physical problem. Using them, however, one can show the easiness in applying this technique and the method that will allow us to include parameters with direct physical interpretation.

The sticky hard-sphere system allows us to do the theoretical study of colloidal interfaces and polyelectrolytes with good results and a relatively simple analytical treatment [5]. The Percus-Yevick theory for liquids is inaccurate at high densities. We may thus expect that in this region of monolayer density (i.e. close to the surface close-packing) our theory will be inaccurate [4].

The method here presented has some application in the study of liquid-solid interfaces, in particular in the study of metal-electrolyte interfaces [5]. However, we believe that since the model is simple it is convenient to exploit this approximation for certain explicit potentials that can be considered in the adsorption studies ( $1/z^3$  or Lennard-Jones for example) [6].

In this model, the gas-solid interface is represented by a binary hard-spheres mixture, from which, the first component presents only hard-sphere interaction while the second component has a sticky surface that implies sticky interaction between species 1 and 2 molecules. Taking the limit of zero density ( $\rho \rightarrow 0$ ) and infinite diameter ( $\sigma \rightarrow \infty$ ) for the species-2 molecules one has a flat surface. This problem was studied by Perram and Smith [7] and, at present, it has a great interest [8,9].

In part II of this work a review is made of the fundamental results of the distribution functions theory and its general applications in liquid theory [2]. In part III we discuss the polydisperse sticky hard-sphere system and the limiting case of a hard-sphere mixture on an adherent surface [7]. Part IV is dedicated to obtain the adsorption isotherms for the adsorbed monolayer remarking the coincidence with the BET (Brunauer, Emmett, Teller) model and with experimental results [10,11]. Special attention is placed on the qualitative behavior for very high and low temperatures.

## II. The correlation distribution functions.

The fundamental idea in the distribution functions theory is based on the calculation of the thermodynamic properties of a system beginning from an interaction potential model and the knowledge of a correlation function which, in general, is related to the mean force potential  $v_{ij}(r)$  by  $g_{ij}(r) = e^{-v_{ij}(r)/kT}$  [2].

The radial distribution function  $g_{ij}(r)$  relates directly with the total (or indirect) correlation function  $h(r)$  and the direct correlation function  $c(r)$  [12], which satisfies the Ornstein Zernike (OZ) equation:

$$h_{ij}(r) = c_{ij}(r) + \sum_k \rho_k \int d\mathbf{s} c_{ik}(\mathbf{s}) h_{kj}(|\mathbf{s}-\mathbf{r}|) \quad (1)$$

This equation can be written separately for each of the correlation functions  $h_{ij}(r)$  and  $c_{ij}(r)$  using the Wiener-Hopf factorization technique. The final expressions were deduced by Baxter and, independently, by Wertheim [13]. For a polydisperse system we have

$$rh_{ij}(|r|) = -q'_{ij}(r) + 2\pi \sum_k \rho_k \int_0^{\sigma_{ik}} dt (r-t) q_{ik}(t) h_{kj}(|r-t|) \quad (2)$$

and

$$rc_{ij}(|r|) = -q'_{ij}(r) + 2\pi \sum_k \rho_k \int dt q_{ik}(t) q'_{kj}(r+t) \quad (3)$$

where  $\sigma_{ij} = (\sigma_i + \sigma_j)/2$  and  $s_{ij} = (\sigma_i - \sigma_j)/2$ ,  $\sigma_k$  is the diameter of species  $k$  molecule and  $q'(r) = dq(r)/dr$ . Notice that the functions  $q_{ij}(r)$  are the factor correlation functions and, if they are known, one can evaluate thermodynamic properties of these mixtures [2].

There exist different approximations to obtain the explicit FCF's. Here we consider the Percus-Yevick approximation (PYA) that can be written as [2,4]

$$c_{ij}(r) = g_{ij}(r) \left[ 1 - e^{\beta u_{ij}(r)} \right] \quad (4)$$

where  $u_{ij}(r)$  is the interaction potential

between species  $i$  and  $j$  particles,  $\beta = 1/kT$  with  $k$  being Boltzmann's constant and  $g_{ij}(r)$  is the radial distribution function defined before.

## III. Polydisperse sticky hard-sphere system.

The sticky interaction potential for a monodisperse system is

$$u(r)/kT = \begin{cases} +\infty & 0 < r < \sigma^- \\ \log[12\tau(\sigma - \sigma^-)/\sigma] & \sigma^- < r < \sigma \\ 0 & r > \sigma \end{cases} \quad (5)$$

where  $\sigma$  is the molecule diameter.

The generalization of this potential for a mixture of sticky hard-spheres is

$$u_{ij}(r)/kT = \begin{cases} -\log \frac{\sigma_{ij}}{12\tau_{ij}(\sigma_{ij} - \sigma_{ij}^-)} & r < \sigma_{ij}^- \\ 0 & \sigma_{ij}^- < r < \sigma_{ij} \\ 0 & r > \sigma_{ij} \end{cases} \quad (6)$$

where  $\tau_{ij}$  is a dimensionless parameter which is proportional to temperature. This parameter, in the form  $\tau_{ij}^{-1}$ , corresponds to a "bare" association (stickiness) parameter [9,11].

A sensible temperature dependence is introduced in the problem by making the second virial coefficient for the potential in equation (6) equal to the second virial coefficient for a physical potential. As  $\sigma_{N+1}$  becomes large, the parameter  $\tau_{1,N+1}$  is then given by

$$\tau_{1,N+1} = \sigma_{1,N+1} / 12S_1(T) + O(1) \quad (7)$$

where

$$S_1(T) = \int_0^{\infty} (e^{-\beta u_1(z)} - 1) dz \quad (8)$$

where  $u_1(z)$  is some potential which we wish to model for the adsorption of particles of species  $i$  on the plane surface.

The FCF is obtained by obtaining a set of algebraic equations from (2) and (3), and considering the Percus-Yevick closure (eq.(4)). Using now the expression [3,7]

$$h_{ij}(r) = -1 + \frac{\lambda_{ij}\sigma_{ij}}{12} \delta(r - \sigma_{ij}^-) \quad r < \sigma_{ij} \quad (9)$$

for the condition  $\sigma_{ij}^- \rightarrow \sigma_{ij}$ , one can write the interaction potential as

$$e^{-\beta u_{ij}(r)} = \begin{cases} \frac{\sigma_{ij}}{12\tau_{ij}} \delta(r - \sigma_{ij}^-), & r < \sigma_{ij} \\ 1, & r > \sigma_{ij} \end{cases} \quad (10)$$

Here  $\sigma_{1j}^-$  is infinitesimally close to  $\sigma_{1j}$  from the left.

The new parameter  $\lambda_{1j}$  that appears in eq. (7) is the mean association parameter for the system at arbitrary density. It reduces to  $1/\tau_{1j}$  in the dilute-system limit and its relationship with  $\tau_{1j}$  is given by [7]

$$\lambda_{1j} \tau_{1j} = a_1 + b_1/\sigma_{1j} + \frac{\pi}{6} \sum \rho_k \frac{\lambda_{jk} \sigma_{jk}^2}{\sigma_{1j}} q_{1k}(s_{1k}) \quad (11)$$

The factor correlation function,  $q(r)$ , was obtained by Perram and Smith [7], and is given by

$$q_{1j}(r) = \frac{1}{2} a_1 (r^2 - \sigma_{1j}^2) + b_1 (r - \sigma_{1j}) + \lambda_{1j} \sigma_{1j}^2 / 12 \quad (12)$$

with

$$a_1 = \frac{1 - \xi_3 + 3\sigma_1 \xi_2}{(1 - \xi_3)^2} - \frac{X_1}{1 - \xi_3}$$

$$b_1 = \frac{-3\sigma_1^2 \xi_2}{2(1 - \xi_3)^2} + \frac{\sigma_1 X_1}{2(1 - \xi_3)} \quad (13)$$

and

$$\xi_j = \frac{\pi}{6} \sum \rho_k \sigma_k^j$$

$$X_1 = \frac{\pi}{6} \sum \rho_k \lambda_{1k} \sigma_{1k}^2 \sigma_k \quad (14)$$

From  $q_{1j}(r)$  one can find  $h_{1j}(r)$  and  $c_{1j}(r)$  from eqs. (2) and (3) respectively. Note that the factor correlation function  $q_{1j}(r)$  satisfies two important conditions:

- $q_{1j}(r)$  is of finite range and
- is a symmetric function respect to  $s_{1j}$ , i.e.

$$q_{1j}(s_{1j}) = q_{1j}(s_{j1})$$

#### IV. Adsorption isotherms.

We will find here the general expressions that describe the behavior of a mixture of hard-spheres and/or sticky hard-spheres (in accordance with the classical theory of liquids) and we will consider which are the suitable parameters for a particular system. We assume that the interactions between

molecules species 1 to N is a hard-sphere one, while the interaction between a molecules of the species N+1 and one of any other species is given by eq. (8). This model corresponds to a negligible adsorbate-adsorbate interaction.

Taking the limit  $\rho_{N+1} \rightarrow 0$ , the total excess number of species i particles respect to the isolated species N+1 particle is [7, 11]

$$N_1 = 4\pi\rho_1 \int r^2 h_{1,N+1}(r) dr \quad (15)$$

where, as before,  $h_{1,N+1}(r)$  is the total correlation function between particles of species i and of species N+1.

The excess number of species i particles per unit area of species N+1 particle will be

$$n_1 = \frac{\rho_1}{\sigma_{1,N+1}^2} \int_0^\infty r^2 h_{1,N+1}(r) dr + \frac{1}{3} \rho_1 \sigma_{1,N+1} \quad (16)$$

The integral in expression (15) is proportional to the three dimensional Fourier transform of  $h_{1,N+1}(r)$  at  $|k|=0$ . For  $h_{1j}$  as defined in (9), this fourier transform is

$$[\tilde{H}(k)]_{1j} = \frac{4\pi}{k} (\rho_1 \rho_j)^{1/2} \int r \sin(kr) h_{1j}(r) dr$$

so that

$$\int r^2 h_{1,N+1}(r) dr = [\tilde{H}(0)]_{1,N+1} / 4\pi (\rho_1 \rho_{N+1})^{1/2} \quad (17)$$

For  $N=1$  (i.e. only one component in the adsorbate) and in the limit  $\rho_2 \rightarrow 0$  the evaluation yields

$$n_1 = \rho_1 \sigma_1 \left[ \frac{3\xi_3/2}{1+2\xi_3} + 1 + \frac{(1-\xi_3)S_1(T)/\sigma_1}{[6S_1(T)/\sigma_1 - 1]\xi_3} \right]$$

For the case of the adsorbed monolayer, one considers that the species  $i=1$  particles are touching the plane surface (species 2 particle). In that case

$$n_{\text{monolayer}} = \frac{\rho_1 S_1(T)(1+2\xi_3)}{(1-\xi_3)(1+[6S_1(T)/\sigma_1 - 1]\xi_3)} \quad (18)$$

We have calculated  $n_{\text{monolayer}}$  for three different hypothetical interaction potentials:

- triangular potential or

$$u(z) = -\epsilon(\sigma_1 - z)/\sigma_1, \quad 0 < z < \sigma_1; \\ = 0, \quad z > \sigma_1 \quad (19)$$

where  $\epsilon$  is the well depth.  
In this case we have

$$S_1(T)/\sigma_1 = \frac{kT}{\epsilon} [e^{\beta\epsilon} - 1] - 1 \quad (20)$$

Figure 1 shows results for the adsorbed monolayer density for this case with the limiting cases of high and low temperatures and different values of the parameter  $A = \epsilon/kT$ .

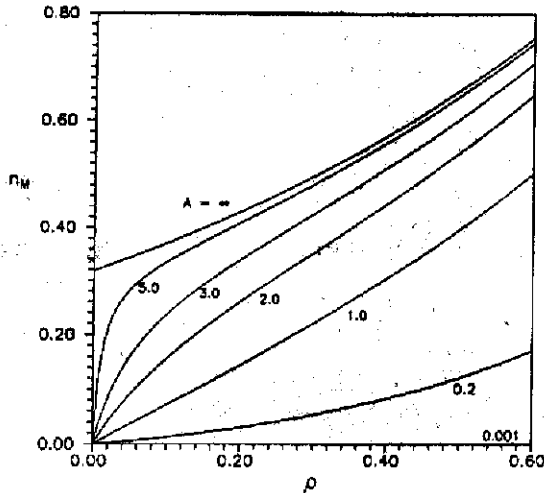


Fig. 1. Monolayer surface density,  $n_{M \text{ monolayer}}$ , as a function of adsorbate density  $\rho_1$  (with  $\sigma_1=1$ ) for different values of  $A$ , using the triangular potential (eq. (19)).

ii) square well potential, i.e.

$$u(z) = -\epsilon, \quad 0 < z < \omega \\ = 0, \quad z > \omega \quad (21)$$

so that

$$S_1(T)/\sigma_1 = \omega^* [e^{-A} - 1] \quad (22)$$

Here  $\omega^* = \omega/\sigma_1$ ,  $\omega$  is the well width, and  $\sigma_1$  is the scaling parameter. Figure 2 shows the corresponding adsorption isotherms.

iii) parabolic potential:

$$u(z) = -\epsilon + z^2, \quad 0 < z < \sqrt{\epsilon} \\ = 0, \quad z > \sqrt{\epsilon} \quad (23)$$

the isotherms are calculated with

$$S_1(T) = \sqrt{\epsilon} (e^A - 1) + \sqrt{\epsilon/A} \quad (24)$$

In this latter case the evaluation was made in the regime of low temperature (see figure 3).

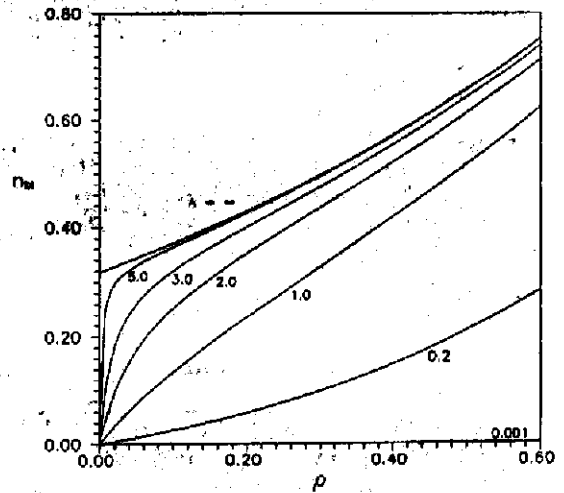


Fig. 2. Monolayer surface density,  $n_M$ , as a function of adsorbate density  $\rho_1$  (with  $\sigma_1=1$ ) for different values of  $A$ , using the square well potential (eq. (21)).

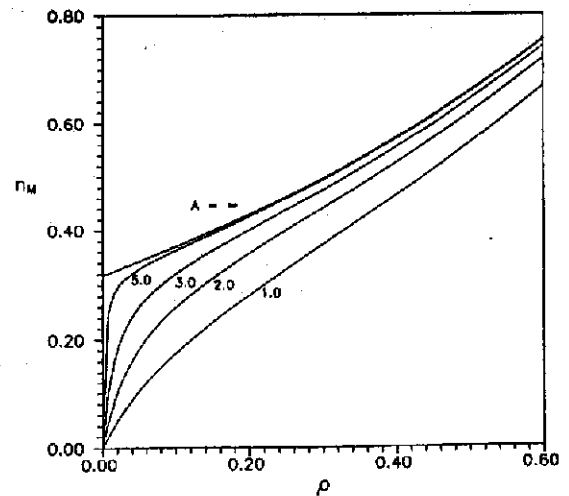


Fig. 3. The same as in figures 1 and 2 but for a parabolic potential (eq. (23)). This isotherms are considered at low temperatures only.

## V. Conclusions.

The results for the three different potentials assumed in the calculations have an analogous behavior. Particularly at very low temperatures ( $A \rightarrow \infty$ ) they converge to the same value. In this limit one can see an accumulation isotherm that does not depend on the chosen interaction potential: this curve is exactly the same for the three potentials (triangular, square and parabolic). This result is due to the approximations made and not to the features of the potentials used.

Finally, it is convenient to say that this treatment can be extended to more complex systems such as adherent surfaces in contact with an electrolyte [14].

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