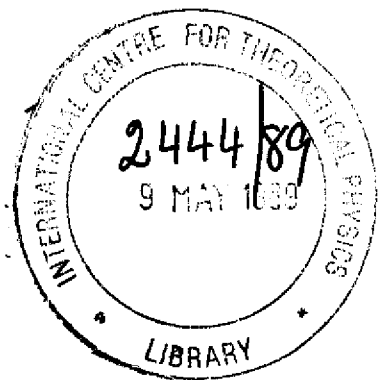


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**INTERNATIONAL CENTRE FOR
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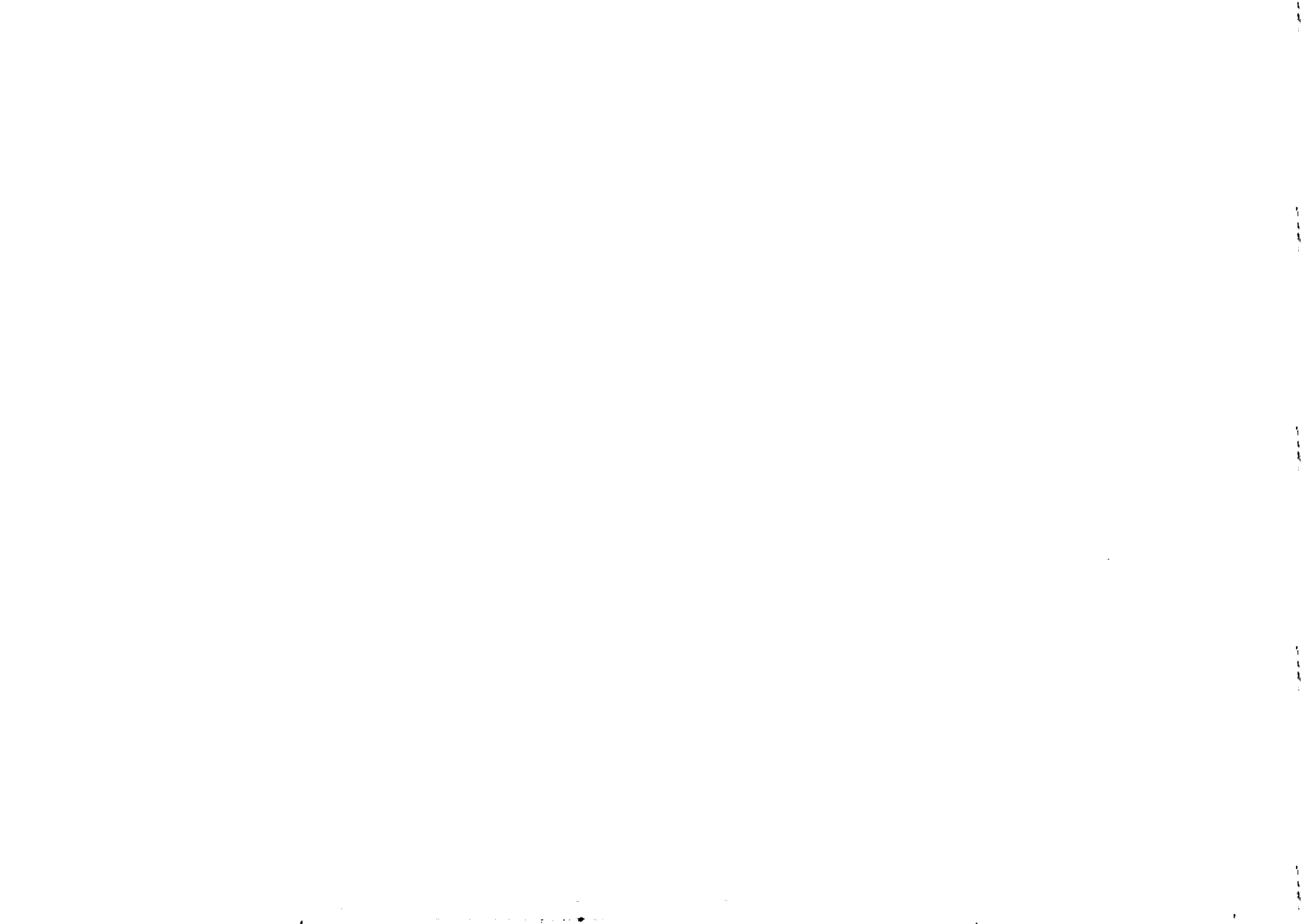
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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

NEW DEVELOPMENTS FOR LOCALIZED ADSORPTION *

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Using the diagrammatic expansion, new developments for localized adsorption are found. It is proved that the correlations in the system, in the absence of the attractive site potential, and the periodicity of the sites play a fundamental role in the adsorption phenomena.

1. INTRODUCTION

The adsorption of fluids on a solid surface are classified as a localized or non-localized adsorption [1]. In the first approach, fluid particles are adsorbed at discrete sites that the realistic solid surface contains. In the second, the surface is modelled by an attractive smooth wall; the particles may be adsorbed randomly by any of the surface points.

It is clear that the first approach constitutes a more realistic model but, the problem is very difficult to solve.

In this paper, our purpose is to study a fluid system in contact with an ideal crystalline solid. The solid surface, assumed perpendicular to the z-axis, is modelled by a hard wall with periodically located sites (i.e., the sites are distributed on square, triangular lattices etc...). Our aim is to determine the consequence of the particle-particle and the site-particle interactions on the adsorption phenomena.

The case of "a fluid in contact with an ideal hard wall" is chosen as a reference system. The periodic attractive potential is treated as a perturbation using the diagrammatic expansion. It is evident from this study that the correlations in the reference system, and the periodicity of the surface have a central role in the adsorption phenomena.

2. MODELLING

Let us consider a system of N identical particles of hard core diameter, σ , interacting with an adsorbent structured surface situated at $z = -c/2$ by:

$$w(i) = v^*(i) + v(i), \quad (1)$$

where the hard wall and the attractive parts are defined, respectively, as:

$$v^*(i) = \begin{cases} \infty; & z_i < 0, \\ 0; & z_i \geq 0. \end{cases} \quad (2a)$$

$$v(i) = \sum_{\alpha=1}^M v_{\alpha}(\vec{r}_i - \vec{r}_{\alpha}),$$

$$v(i) \begin{cases} \leq 0; & |\vec{r}_i - \vec{r}_{\alpha}| \leq \lambda \text{ and } z_i \geq 0, \\ = 0; & \text{otherwise.} \end{cases} \quad (2b)$$

Here, the sum is extended to all the sites of the surface; λ denotes the range of the site potential; and, \vec{r}_{α} and \vec{r}_i are the coordinate vectors of the α -th site and the i -th particle of the fluid, respectively.

For simplicity, the origin of the coordinates, O , is chosen coinciding with one of the attractive sites. According to the surface periodicity, the potential, v , must satisfy the condition:

$$v(\vec{r}_i + p\vec{a} + q\vec{b}) = v(\vec{r}_i), \quad (3)$$

p and q are two arbitrary integers; and \vec{a} and \vec{b} are two constant vectors contained in the plan x, y and characterising the crystalline structure of the surface.

The particle-particle potential is assumed to be a radial interaction:

$$w(i, j) = w(r_{ij}). \quad (4)$$

The total potential energy of the system under consideration (complete system) is given by:

$$U_M = \sum_{i < j} w(i, j) + \sum_i w(i),$$

$$= U_M^* + \sum_i v(i). \quad (5)$$

U_M^* being the total potential energy of the system in the absence of the attractive potential (reference system).

It has been shown that the complete system may be treated as

two coupled systems [2]. The first is the reference system; the second, called fictitious system, is defined by the pair-potential, W , and the activity, m , as follows:

$$W(i, j) = -kT \ln[\tilde{g}(i, j)], \quad (6)$$

$$m(i) = \rho(i) \varphi(i). \quad (7)$$

$\tilde{g}(i, j) = \tilde{g}(z_{ij}, z_i, z_j)$ and $\rho^*(i) = \rho^*(z_i)$ are, respectively, the pair distribution function (PDF) and the one-particle distribution function (OPDF) in the reference system. $\varphi(i)$ is the Mayer function associated to the external potential by:

$$\varphi(i) = \exp[-\beta v(i)] - 1. \quad (8)$$

The grand partition function (GPF) and the OPDF in the complete system are given, respectively, by [2]:

$\Xi = \Xi^* \chi \exp(\text{sum of all the distinct connected diagrams free of: pure articulated points of type R, reference articulated points, and reference articulation pair of points; consisting of: R field points, at least one } \rho^* \text{ field point, and } \tilde{h} \text{ bonds}).$

$$= \Xi^* \chi \exp(\text{diagrams with root point and R field points}).$$

$$= C \Xi^* \chi. \quad (9)$$

$\rho(l) = \rho^*(l) \exp[-\beta v(l)] Y(l) \exp(\text{sum of all the distinct connected diagrams free of: pure articulated points of type R, reference articulated points and reference articulation pair of points; consisting of: one root point, R field points at least one } \rho^* \text{ field point and } \tilde{h} \text{ bonds such that the root point does not form an articulation point}).$

$$= \rho^*(l) \exp[-\beta v(l)] Y(l) \exp(\text{diagrams with root point and R field points}).$$

$$= \rho^*(l) \exp[-\beta v(l)] Y(l) K(l). \quad (10)$$

In these graphical sums, the dashed and the black circles denote the ρ^* and the R field points, respectively; the white circle designates the root point; \tilde{h} is the total correlation function in

the reference system characterized by its GPF Ξ' ; Y and R are, respectively, the GPF and the OPDF in the fictitious system. Y is related to R by the following equation:

$$R(i) = m(i)Y(i), \\ = R(x_i, y_i, z_i). \quad (11)$$

It should be noted that, because $m(i)$, $R(i)$ is non-zero only on the first layer (i.e., region where the potential is non-zero), while $Y(i)$ is propagated beyond this region via the correlations, according to the surface structure periodicity, equation (3) is satisfied by Y and R . We have:

$$R(\vec{r}_i + p\vec{a} + q\vec{b}) = R(\vec{r}_i). \quad (12)$$

In diagrammatic terms, Y and R can be expressed as follows [2]:
 $Y = \exp(\text{sum of all the distinct connected diagrams consisting of } m \text{ field points and } h \text{ bonds}).$

$$Y = \exp(\bullet + \text{---} + \text{---} + \text{---} + \text{---} + \text{---} + \text{---} + \text{---} + \dots). \quad (13)$$

$R(\vec{r}_i) = m(\vec{r}_i) \exp(\text{sum of all the distinct connected diagrams free of articulation points; consisting of: one root point, } R \text{ field points and } h \text{ bonds}).$

$$= m(\vec{r}_i) \exp(\text{---} + \text{---} + \text{---} + \text{---} + \text{---} + \text{---} + \dots). \\ = m(\vec{r}_i) Y(\vec{r}_i). \quad (14)$$

The PDF, g' , can be written as follows:

$$g'(i, j) = g'(r_{ij}, z_i, z_j; \eta, \sigma). \quad (15)$$

This function tends to the Boltzmann factor when the parameter, η , (packing fraction) becomes zero [3]. For any value of η , g' is identical to zero for all r_{ij} less than σ ; and, for homogeneous systems, it contains an oscillating part which converges to unity beyond four or five hard core diameters (fig.1) (see for instance [4-5]). The magnitude of these oscillations increases with η . If we assume that this function remains unchanged when the surface

is introduced, the pair-potential, W , which is infinite for $r_{ij} < \sigma$ and zero for all the distance large values, is alternatively attractive and repulsive for the intermediate values of this variable. Consequently, two fictitious particles may be mutually attracted or repelled according to their respective positions. This mutual interaction vanishes and the particles ignore themselves if their positions correspond to the g' 's extremums. To have this situation, the attractive periodic surface should satisfy the following conditions:

- 1) The distance site-site, l , must be such that $g(l)$ is extremum.
- 2) The site-potential should act only on the particles which have their centers on the plan $z = 0$.
- 3) The distances, r_k , between an adsorbed particle and its neighbours, other than the first (i.e., nearest neighbours), are such that $g'(r_k) = 1$.

This corresponds to two different physical situations. In the first, the structured surface being given with an l parameter greater than σ , we consider a dilute fluid (gas). In the second, the nature of the structured surface and its parameter, l , are chosen according to the parameters, η and σ , of the fluid assumed to be dense.

Therefore, it is clear that the PDF and the external potential have opposite effects. Indeed the external potential tends to increase the adsorption when g' tends to dissociate the adsorbed particles, because of the attractive or repulsive interactions. Nevertheless, the problem may become more complicated when the attractive sites are near each other and/or the external potential range is long. In these cases, as mentioned above, the particles which are at a distance of r nearly equal to σ (i.e., $r \approx \sigma$) are attracted and then the cluster formation is favoured.

3. COUPLING PARAMETERS AND SELF-CONSISTENT APPROXIMATION

The importance of the respective contributions of the coupling terms C and K(1) to the GPF and the OPDF depend on the parameters of the system (i.e., the packing fraction, the periodicity of the surface, the nature of the particle-particle interactions and the range of the site-particle potential as well as its magnitude).

These contributions may be evaluated as follows:

$$D(C; p, q) = BpSd(\rho d^3)^{p-1}(\rho u)^q; \quad q > 2, \quad (15a)$$

$$D(K(1); p, q) = B(\rho d^3)^p(\rho u)^q; \quad q > 1. \quad (15b)$$

In these equations, D(X; p, q) denotes the magnitude of a diagram D of the coupling term X = C or K(1); p and q are, respectively, the numbers of ρ^0 and R field points that D contains; S designates the surface area of the system; d is the average range of the correlation function \tilde{h} ; B is a numerical coefficient of order unity depending essentially on the connectivity of the diagram and on the distance site-site, 1, on the surface; and u is defined as:

$$u = M^{-1} \int d\vec{r}_i (\exp[-\rho v(i)] - 1). \quad (17)$$

The contributions of the coupling terms depend on the density of the fluid and on the surface itself. For a dilute fluid or an external potential such that u is very small, only some few terms in (9) and (10) should be retained. Nevertheless, it is interesting to approximate these developments in such a manner that the GPF and the OPDF give the same properties for the system. We use a method completely analogous to the familiar charging process employed in the coulombic potential. The complete system is assumed to be obtained from the reference system by a continuous transformation. This is expressed by introducing the coupling parameter, ν , as:

$$\varphi(i; \nu) = \nu \varphi(i) \quad (18)$$

ν varies continuously from 0 to 1 which corresponds, respectively, to the reference and the complete systems.

The GPF, Ξ , becomes then:

$$\begin{aligned} \Xi(\nu) &= \sum_N (z^N/N!) \int \exp(-\beta U_N^0) \prod_{i=1}^N (1 + \nu \varphi(i)) d\vec{r}_1 \dots d\vec{r}_N, \\ &= C(\nu) \Xi^0 Z(\nu). \end{aligned} \quad (19)$$

Therefore, the grand free energy (GFE) is given by:

$$\begin{aligned} F - F^0 &= \int \partial_\nu F(\nu) d\nu, \\ &= -kT \int_0^1 \int d\nu d\vec{r}_1 \rho_Y(\vec{r}_1; \nu) \varphi(\vec{r}_1), \end{aligned} \quad (20)$$

F, F⁰ and F(ν) are the GFE for the complete, the reference and an intermediate system, respectively. ∂_ν denotes the differentiation with respect to ν; and $\rho_Y(\vec{r}_1; \nu)$ is defined by:

$$\rho(\vec{r}_1; \nu) = \rho_Y(\vec{r}_1; \nu) (1 + \nu \varphi(\vec{r}_1)). \quad (21)$$

Inserting (10) in (21), equation (20) takes the form:

$$\begin{aligned} F - F^0 &= -kT \int_0^1 \int d\nu d\vec{r}_1 \varphi(\vec{r}_1) \rho^0(z_1) Y(\vec{r}_1; \nu) K(\vec{r}_1; \nu), \\ &= -kT \int_0^1 \int d\nu d\vec{r}_1 \varphi(\vec{r}_1) \rho^0(z_1) Y(\vec{r}_1; \nu) \\ &\quad (1 + [K(\vec{r}_1; \nu) - 1]). \end{aligned} \quad (22)$$

Introducing the GPF for the fictitious system, Ξ_ν , (contribution of the first term in (22)), and using the fact that all the sites are equivalent, we obtain:

$$\begin{aligned} F - F^0 &= \Xi_\nu - kTM \int_0^1 \int d\nu d\vec{r}_1 \varphi(\vec{r}_1) \rho^0(z_1) Y(\vec{r}_1; \nu) \\ &\quad [K(\vec{r}_1; \nu) - 1]. \end{aligned} \quad (23)$$

The particle 1 should now be in the domain Δ_0 containing only one site which may be taken at the origin.

According to (9), (23) can be expressed in the following form:

$$F - F^0 = \Xi_\nu - kT \ln C. \quad (24)$$

Consequently, when an approximation is introduced in the calculations of Ξ and $\rho(1)$, Z and C should be chosen such that:

$$\begin{aligned} \Xi_\nu &= -kT \ln Z, \\ &= -kTM \int_0^1 \int d\nu d\vec{r}_1 \varphi(\vec{r}_1) \rho^0(z_1) Y(\vec{r}_1; \nu), \end{aligned} \quad (25a)$$

$$\begin{aligned} -kT \ln C &= -kTM \int_0^1 \int d\nu d\vec{r}_1 \varphi(\vec{r}_1) \rho(z_1) Y(\vec{r}_1; \nu) \\ &\quad [K(\vec{r}_1; \nu) - 1]. \end{aligned} \quad (25b)$$

Introducing the density of sites per unit of area, σ , given by:

$$M = S\sigma, \quad (26)$$

we obtain:

$$\begin{aligned} Z &= \exp(S\sigma \int_0^1 \int d\mathbf{z} \, d\mathbf{z}_1 \, \varphi(\mathbf{z}_1) \rho^0(z_1) Y(\mathbf{z}_1; \mathbf{v})), \\ &= \exp(-\beta S Y_1^*), \end{aligned} \quad (27a)$$

$$\begin{aligned} C &= \exp(S\sigma \int_0^1 \int d\mathbf{v} \, d\mathbf{z}_1 \, \varphi(\mathbf{z}_1) \rho^0(z_1) Y(\mathbf{z}_1; \mathbf{v}) [K(\mathbf{z}_1; \mathbf{v}) - 1]), \\ &= \exp(-\beta S Y_2^*). \end{aligned} \quad (27b)$$

The excess surface tension, γ^e , due to the external potential has two components.

$$\gamma^e = \gamma_1^e + \gamma_2^e \quad (28)$$

The first is the contribution of the adsorbed (fictitious) particles, the second is due to the coupling between adsorbed and non-adsorbed particles.

4. STICKY POTENTIAL AND ADSORPTION PARAMETERS

In this paragraph, we will try to find the parameters of the system governing the adsorption and explain the importance of each of the PDF and the external potential. Some other additive simplifications are necessary. Here other the surface of periodic structure, the following two assumptions will be taken into account:

* The distance site-site, l , is greater than or equal to σ to have no particle occupying simultaneously more than one site.

* The range of the site potential, λ , is less than or equal to σ to have no more than one particle per site.

When this potential becomes very localized and very peaked, the center of the adsorbed particle coincides with the adsorbent site and, the pair-potential, W , depends only on the two-dimensional distance between the two adsorbed particles (i.e., W is now a radial function). In this limit, the attractive external potential can be written as:

$$\exp(-\beta \sum_{\alpha=1}^M v_\alpha(\mathbf{z}_\alpha)) = 1 + A \sum_{\alpha=1}^M \delta(\mathbf{z}_\alpha - \mathbf{z}_\alpha^*), \quad (29)$$

in which, A is a positive constant characterizing the strength of the adsorption, and δ is the Dirac delta function. This type of potential has been first introduced by Baxter in the case of homogeneous systems [6]. It was extended to the surface case by Carnie and Chan [7].

Inserting (29) in (7), the activity, $m(i)$, becomes:

$$m(\mathbf{z}_i) = A \rho^0(0) \sum_{\alpha=1}^M \delta(\mathbf{z}_i - \mathbf{z}_\alpha^*). \quad (30)$$

As in homogeneous fluids, the average number and the dispersion of adsorbed particles around its average value are given by:

$$\begin{aligned} \bar{N} &= t(\partial_{\lambda} \ln Z), \\ &= \int d\mathbf{z} R(\mathbf{z}). \end{aligned} \quad (31a)$$

$$\bar{N}^2 - \bar{N}^2 = t(\partial_{\lambda} \bar{N}). \quad (31b)$$

t denotes the quantity $A \rho^0(0)$. Equation (30) allows us to write Z and C given by (26a) and (26b), after integration with respect to \mathbf{z}_i , in the form:

$$\begin{aligned} Z &= \exp(S t \sigma \int_0^1 d\mathbf{v} Y(0; \mathbf{v})), \\ &= \exp(S \sigma \int_0^1 d\tau Y(0; \tau)). \end{aligned} \quad (32a)$$

$$\begin{aligned} C &= \exp(S t \sigma \int_0^1 d\mathbf{v} Y(0; \mathbf{v}) [K(0; \mathbf{v}) - 1]), \\ &= \exp(S \sigma \int_0^1 d\tau Y(0; \tau) [K(0; \tau) - 1]). \end{aligned} \quad (32b)$$

The excess properties of the system are related to the fraction of occupied sites.

4.1. OCCUPIED SITE FRACTION AND THE OPDF R

In this case, the occupied site and the adsorbed particle numbers coincide and the fraction of occupied sites, θ , is obtained simply from (31a) by:

$$\theta = \bar{N}/M. \quad (33)$$

Introducing (14) in (33) leads to:

$$\begin{aligned} \theta &= A M^{-1} \int d\mathbf{z} \rho^0(z) Y(\mathbf{z}) \left[\sum_{\alpha=1}^M \delta(\mathbf{z} - \mathbf{z}_\alpha^*) \right], \\ &= t Y(0). \end{aligned} \quad (34)$$

Consequently to our hypothesis concerning the external potential, an adsorbed particle is such that its center coincides with the one of the adsorbent site. Thus $R(\vec{r})$ has the same value if \vec{r} corresponds to a vector site-position, and it is zero in the opposite case. R can then be written as:

$$R(\vec{r}) = tY(0) \sum_{\alpha=1}^M \delta(\vec{r} - \vec{r}_{\alpha}), \quad (35)$$

in which, $Y(0)$ is the value taken by Y in the origin (where an adsorbent site is located).

Now, it is clear that $Y(0)$ (and then $R(\vec{r})$) can be expressed in term of Θ as:

$$Y(0) = \exp\left(\sum_{n=1}^{\infty} a_n \Theta^n\right), \quad (36)$$

we have now a combinatorial problem. For example, the coefficient a_1 , arising from the first graph in (14) may be written in the following form:

$$a_1 = \sum_{k=0}^{\infty} c_k h^k(r_k). \quad (37)$$

Here, c_k is the number of sites located on the k -th ring of radius $r_k \geq 0$ centered on the site 0. In this equation, h^k depends on the reference system (because of the density) and on the periodicity of the surface (because of r_k) whereas c_k is a function of the type of structured surface only.

The total correlation function $h^k(r)$ can certainly be approximated by its value $h(r)$ in homogeneous system for the same distance r and the same bulk density, ρ . Indeed, h^k has a functional dependence of the local density, $\rho^k(z)$, in the fluid. This property is different of its bulk value only near the wall (i.e. $0 \leq z \leq 3\sigma$); the average value of $\rho^k(z)$ within the layer $0.5\sigma < z < 3\sigma$ is approximately equal to ρ ; and it does not seem that this function has an important consequence on the calculation of $h^k(r)$. On the other hand, the approximation $h^k(r_i, z_i, z_j) = h(r_{ij})$ has been used in another field, (see for example [8]); the results obtained are in good agreement with those given by thermodynamic equations.

The phase transition can be obtained in two different ways. The first is when the packing fraction increases and attains its crystallization value. The second is when for a given η , the magnitude of the external potential becomes very strong such that t corresponds, for the adsorbed fluid, to its crystallization value. This second ordered phase is localized in the neighbourhood of the surface. Nevertheless the pair-potential, W , is attractive for the short distances (r nearly equal to σ) and, consequently, for dense fluids, this ordered phase may be spread to the second, third layer. For a pressure and a temperature near their critical values, the correlations become very long range, and the phase transition induced by the external potential can be generalized to the hole system. In this limit, the coupling terms cannot be neglected.

The profile density of a simple fluid near a wall is a continuous function of η [8]; hence Θ varies continuously from 0 to 1 when the factor t increases.

4.2. ADSORPTION PARAMETERS

In the case of simple fluids, the adsorption properties are function of η , σ , l , and A through t . g^0 depends only on r/σ and η . If for a given type of structured surface (triangular lattices for example), σ , ρ and l vary such that η and l/σ remain unchanged, then the coefficients, $a_n = a_n(\eta, l/\sigma)$, in (36) are constant. Therefore, χ may be written as:

$$\chi = \chi(t, \eta, l/\sigma). \quad (38)$$

It is clear that the adsorption increases with A . Indeed,

$$\partial_A \chi = \sqrt{A} \chi / A \geq 0. \quad (39)$$

This is a predictable result. In fact, the system is more orderly for higher potential.

Using the fact that ζ is the GPF of a fluid in which the activity and the pair-potential depend on η , the variations of ζ with the packing fraction can be expressed as:

$$\begin{aligned} \partial_{\eta} \zeta &= (\partial_{\eta} \zeta) (\partial_{\eta} t)_{g(r)} + \int d\vec{r}_1 d\vec{r}_2 (\delta_{g(r_{12})} \zeta)_{,t} \partial_{\eta} g^{\circ}(r_{12}), \\ &= \zeta (\bar{W}(\partial_{\eta} \ln t)_{g(r)}) + 1/2 \int d\vec{r}_1 d\vec{r}_2 R(\vec{r}_1, \vec{r}_2) \partial_{\eta} \ln(g^{\circ}(r_{12})). \end{aligned} \quad (40)$$

$\delta_{g^{\circ}(r_{12})}$ denotes the functional derivative with respect to g° .

It should be noted that:

* The first term in this equation is due to the fact that the OPDF contact value, $\rho^{\circ}(0)$, varies with η . The second is due to the variations of the PDF, $g^{\circ}(r)$, with the same parameter. Hence, they are of first and second order, respectively.

* When the surface parameter, $1/\sigma$, is such that $g^{\circ}(r)$ is equal to 1 for all r greater than 1, the adsorbed fluid becomes identical to an adsorbed ideal gas (i.e., non-interacting particles).

Now the first contribution in (40) arising from t , which increases with η [8], tends to increase ζ . The last one has, certainly, a non-constant effect. Indeed, for η going to zero, g° vanishes for $r < \sigma$ and it is equal to unity otherwise. When η increases, an oscillating g° 's part, converging rapidly to 1 and containing a very pronounced first peak near σ , arises. The magnitude of these oscillations increases with η [4,9,10]. Therefore this contribution can be positive or negative according to the particular value of $1/\sigma$. For the large values of this parameter, the second contribution vanishes, and (40) is reduced to the adsorbed ideal gas term.

Consequently, for 1 less than the range of h° , η may favour the adsorption or the desorption. For the large 1 values, the adsorption is always favoured.

Concerning $1/\sigma$, ζ depends on this parameter through interactions between adsorbed particles of distance r_k , $g^{\circ}(r_k)$, and the density of sites, σ° ; because of the oscillations of g° , $\zeta(1/\sigma)$

should be an oscillating function. When $1/\sigma$ increases, the magnitude of these oscillations decrease and ζ goes to its limiting value (i.e., the GPF of an adsorbed ideal gas, reached for 1 such that $g^{\circ}(r) = 1$ for all r greater than 1). However for a given type of structured surface, when $1/\sigma$ increases, σ° decreases and tends to attenuate the magnitude of the oscillations in ζ . Hence, the convergence of this function is accelerated. Consequently, the adsorption increases when $1/\sigma$ decreases. In the limit case when the sites become very close each other, clusters of adsorbed particles should be obtained. This result is reasonable. Indeed, the more numerous attractive sites the more important is the adsorption.

Note that when, for a given fluid and value of $1/\sigma$, the type of structured surface changes, the adsorption is maximum for the triangular lattice surface which has the greater density σ° .

5. RESULTS

The structure and the thermodynamic properties of the system are given by equations (9), (10), (32a), (32b) and (35) using (34) and (36). Here, we are mainly interested in qualitative results which prove our theory. The parameter, 1 , of the surface is chosen in such a manner that the pair-potential $W(i,j)$ in (6) satisfy the condition:

$$\begin{aligned} \exp(-\beta W(i,j)) &= g^{\circ}(r_{ij}), \\ &= \begin{cases} 0, & \text{if } i \text{ and } j \text{ are on the same site,} \\ g^{\circ}(r), & \text{if } i \text{ and } j \text{ are nearest neighbours,} \\ 1, & \text{otherwise.} \end{cases} \end{aligned} \quad (41)$$

Consequently to the adsorbed-non adsorbed particle interactions, this condition only cannot allow us to find a good approximation for C and $K(1)$. In contrast, if one (at least) of the two fluids (reference and fictitious) is dilute, an accurate approximation

can easily be found. We first consider an extremely dilute hard sphere fluid in front of a structured triangular lattice surface. $g^*(r)$ is equal to the analytical known $g(r)$ [11]:

$$g(r) = \begin{cases} 0; & 0 < r/\sigma < 1, \\ 1 + 4\eta[2 - 3r/2\sigma + (r/2\sigma)^3]; & 1 < r/\sigma < 2, \\ 1; & r/\sigma > 2, \end{cases} \quad (42)$$

Then, $\eta \approx 0.21$, for which $g^*(r)$ is approximated by its homogeneous value given in [10], is taken. The coupling terms C and $K(l)$ may be approximated by 1; hence, equations (27b) is automatically satisfied. In (36), only the two first graphs of Y are retained. We have:

$$a_1 = -1 + c_1 h^c(r_1), \quad (43a)$$

$$a_2 = -0.5 - 1.5c_1 h^2(r_1) + c_1 (c_1 - 1) h^3(r_1). \quad (43b)$$

The results, for various values of l/σ , are summarized in table 1. The calculations of the fraction of occupied sites are given in table 2. According to equation (32a), χ and θ have the same variations. Therefore, as provided by the theory, the GPF of the adsorbed fluid increases with l and, it is an oscillating function of l/σ , converging to its limiting value, when this parameter becomes greater than the range of h^* . χ and η have the same variations (i.e., they increase and decrease simultaneously) if l is in a region, approximately centered around $n\sigma$, where $g^*(r)$ reached one of its maximums. They have opposite variations when l is in a region, approximately centered around $(2n+1)\sigma/2$, corresponding to one of the minimums of $g^*(r)$. n is an integer number generally small, $n \approx 3$ or 4.

6. CONCLUDING REMARKS

The purpose of this work has been to prove that the structure of the surface and the correlations in the system without the attractive external potential play a central role in the adsorption

phenomena. It has been shown that the adsorption increases with the magnitude of the site-particle potential. The packing fraction may favour the adsorption or the desorption according to the value of l when this parameter is less than the range of h^* ; for large values of this parameter, it always favours the adsorption. In contrast, when for a given hard core diameter, the site-site distance increases the adsorption is an oscillating function of this parameter; its magnitude decreases rapidly to its limiting value.

For simple fluids, the potential site-particle favours the adsorption when the correlations particle-particle may favour the adsorption or the desorption according to the site-site distance. Indeed, the hard sphere systems constitute a good approximation for such fluids.

These developments can be used to study the phenomenon of selective wetting. Hence a more realistic external potential sensitive to the nature of the fluid should be taken. Such interaction may be introduced by considering an anisotropic potential surface particle. The model of particle with fixed site can be used. Therefore, only some orientations of the particles are selected by the surface. This is however beyond the scope of the present study.

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Pure articulated point of type R consists in an ensemble of n ($n \geq 1$) R field points attached to the diagram by only one R field point [2,12,13].

Reference articulated points are defined as an ensemble of n ($n \geq 1$) ρ' field points attached to the rest of the diagram by only one point [2,12,13].

A reference articulation pair of points is defined such that upon its removal from a connected diagram the diagram splits into two or more components, at least one will contain K bonds, at least one ρ' field point and no R field point [5,14].

An articulation point is defined such that upon its removal from a connected diagram, the diagram splits into two or more components. Of the resulting components, at least one will contain no root point [5,14].

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$1/\sigma \backslash \eta$	0.05		0.21	
	a_1	a_2	a_1	a_2
1.5	-0.795	-0.946	-0.832	-0.506
1.75	-0.807	-0.501	-1.432	-0.558
2	-1	-0.5	-1.228	-0.515
2.5	-1	-0.5	-1	-0.5

Table 1: Variations of a_1 and a_2 with η and $1/\sigma$.

$1/\sigma \backslash t$	0.3	0.5	1	1.5	2	2.5	3	3.5
	1.5	0.236	0.342	0.516	0.628	0.709	0.772	0.823
1.75	0.240	0.353	0.551	0.684	0.783	0.861	0.926	0.981
2	0.232	0.337	0.520	0.642	0.734	0.807	0.867	0.918
2.5	0.232	0.337	0.520	0.642	0.734	0.807	0.867	0.918
1.5	0.239	0.351	0.546	0.677	0.775	0.852	0.916	0.970
1.75	0.215	0.306	0.460	0.562	0.639	0.700	0.750	0.793
2	0.223	0.320	0.487	0.599	0.682	0.748	0.803	0.850
2.5	0.232	0.337	0.520	0.642	0.734	0.807	0.867	0.918

Table 2: Variations of θ and with η , $1/\sigma$ and t .

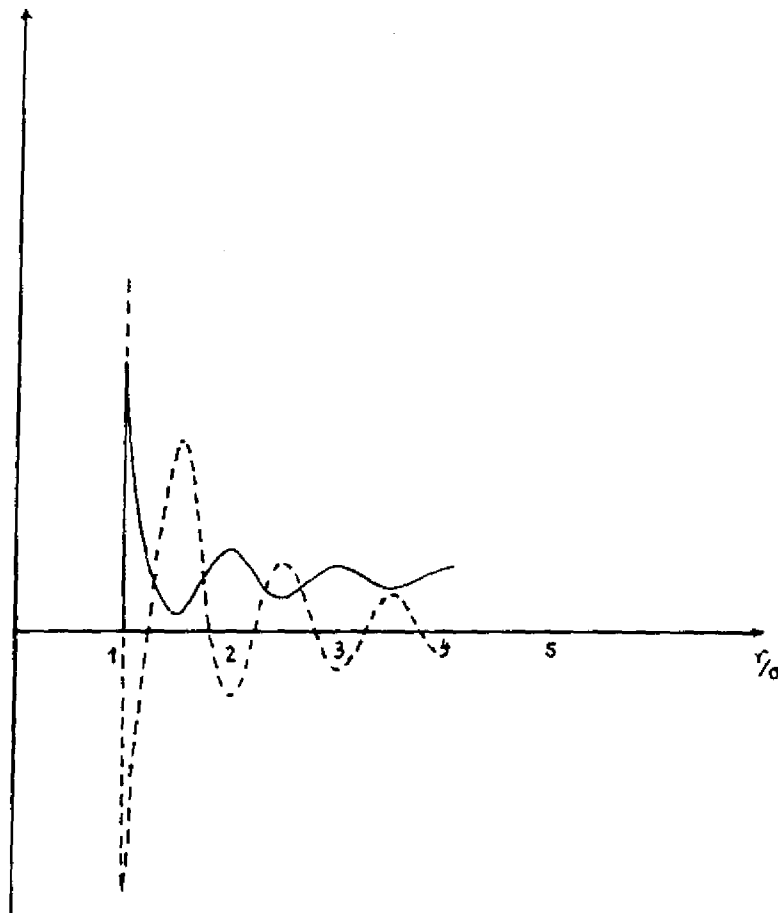


Fig-1 The solid curve: the PDF $g(r)$, the dashed curve: the pair-potential $W(r)$.

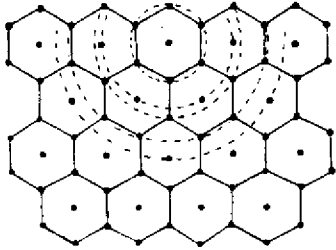


Fig.2 Structured triangular lattice surface.

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