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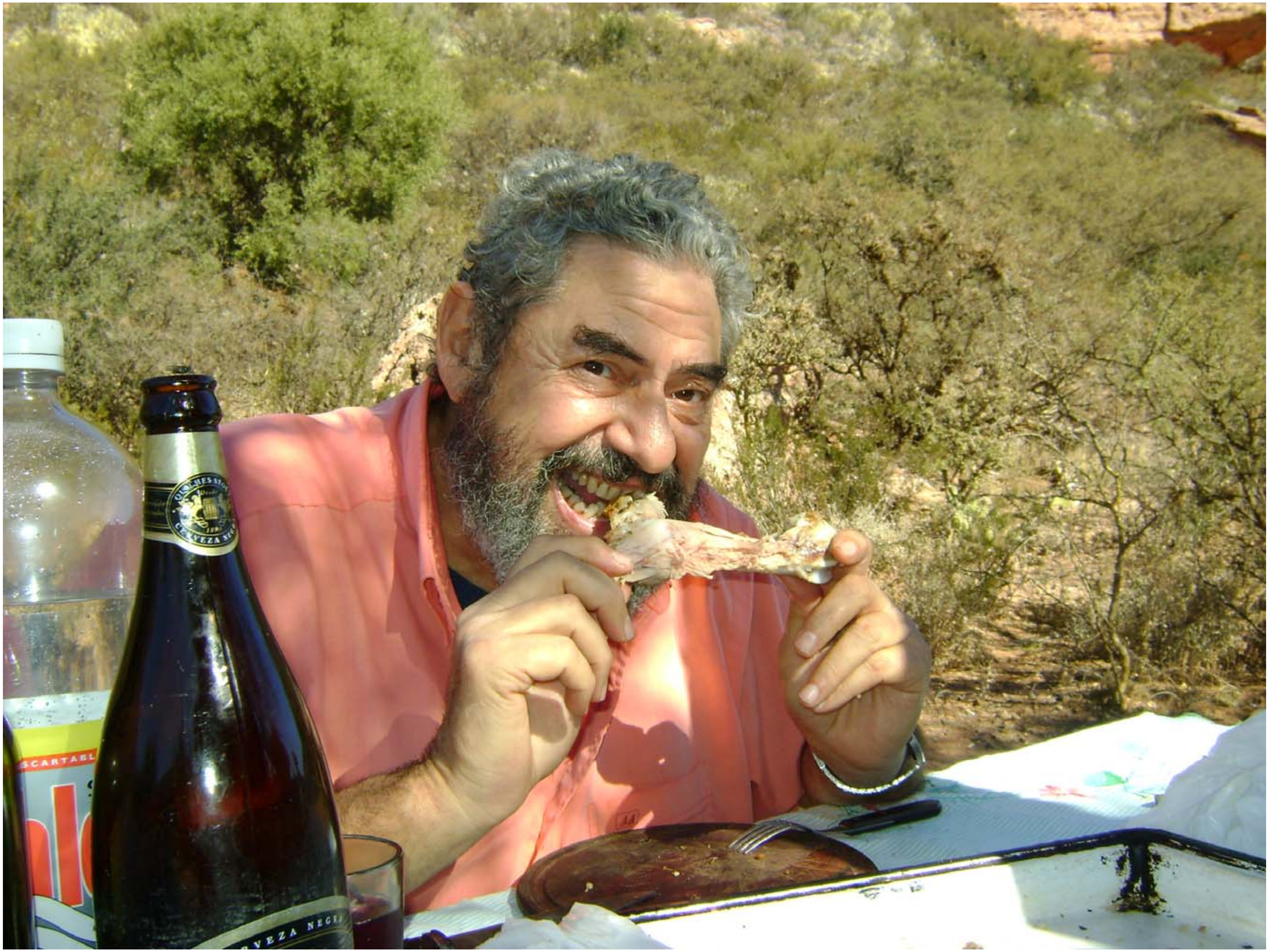
Simposio sobre Adsorción Adsorbentes y sus Aplicaciones


Ya les voy a enseñar yo a organizar congresos!!

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ENANTIOSELECTIVE ADSORPTION BY TEMPLATE SURFACES
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ito de Fisica Aplicada (INFAP), Universidad Nacional de San Luis (UNSL) –
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33 YEARS OF ENERGETIC TOPOGRAPHY IN ADSORPTION ON HETEROGENEOUS DURFACES

Giorgio Zgrablich

Instituto de Física Aplicada (INFAP), CONICET-Universidad Nacional de San Luis

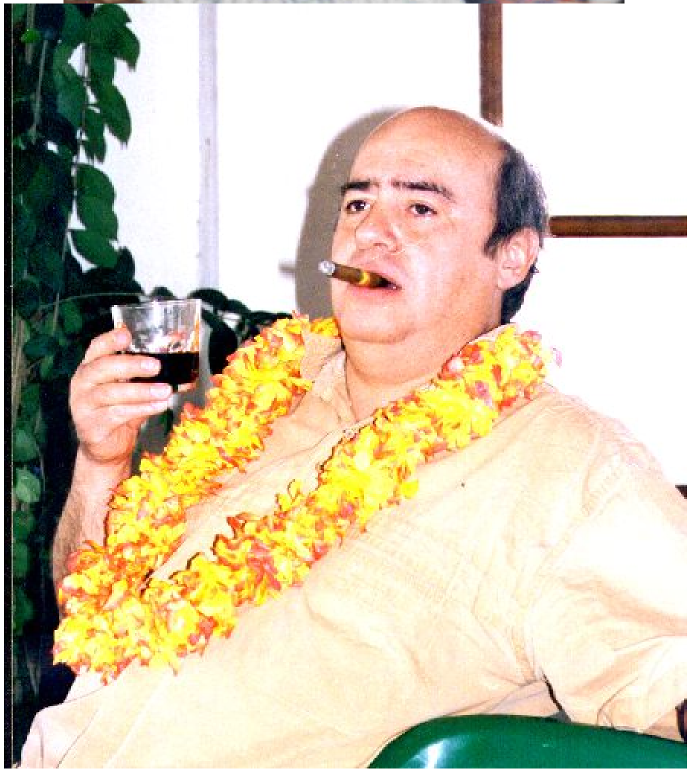
SOME COLLABORATORS

CONFERENCIA DEDICADA A MIS QUERIDOS AMIGOS, SIEMPRE PRESENTES:

PEDRO RIPA

Y

VICENTE MAYAGOITIA



OUTLINE

THE PROBLEM

- ADSORPTIVE ENERGY SURFACE CHARACTERIZATION

CONTINUUM APPROACH

- GENERALIZED GAUSSIAN MODEL

LATTICE-GAS APPROACH

- GENERALIZED GAUSSIAN LATTICE-GAS
- EFFECTIVE STATE APPROXIMATION
- DUAL SITE-BOND MODEL

PATCHWISE APPROACH

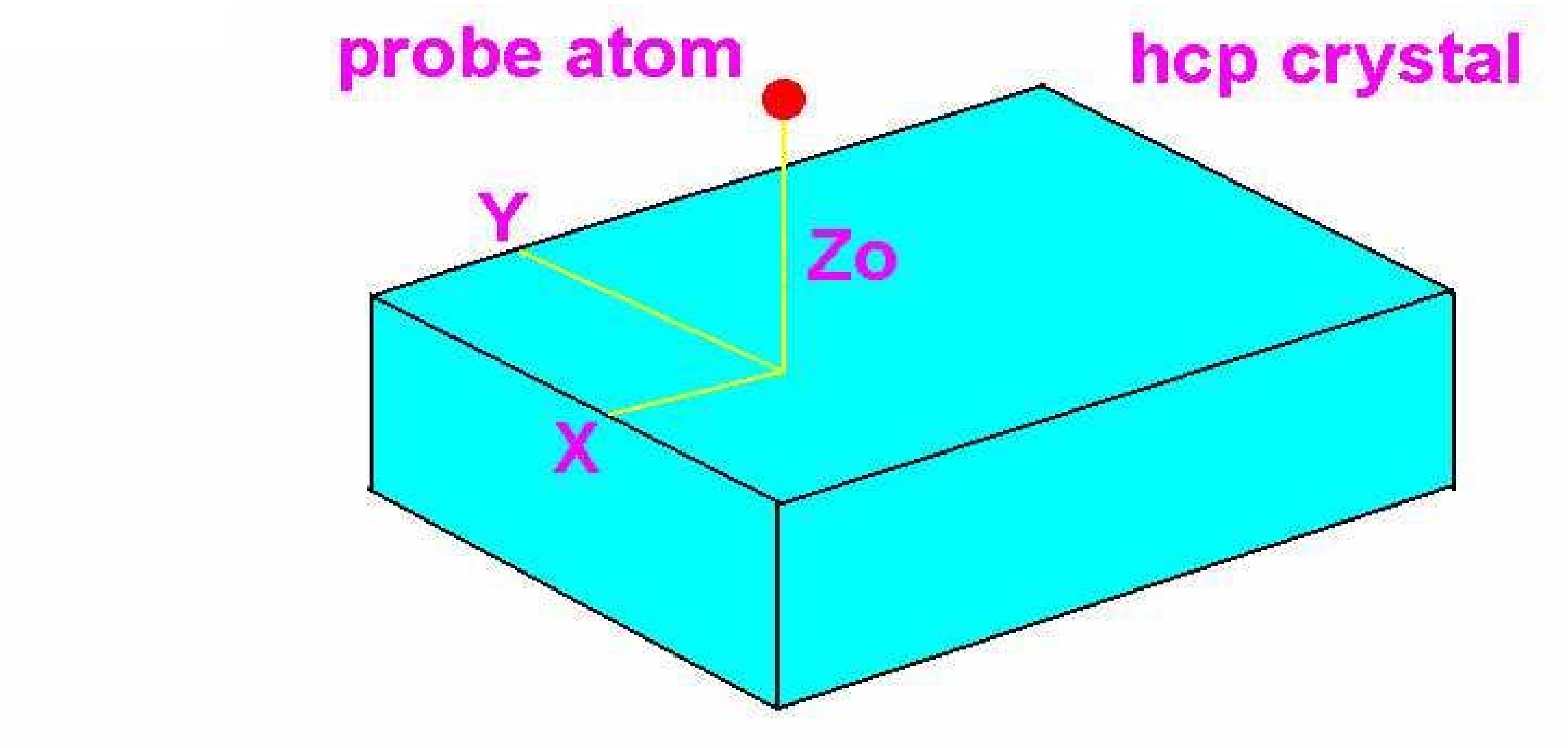
- BIVARIATE SURFACES

CONCLUSIONS

THE PROBLEM

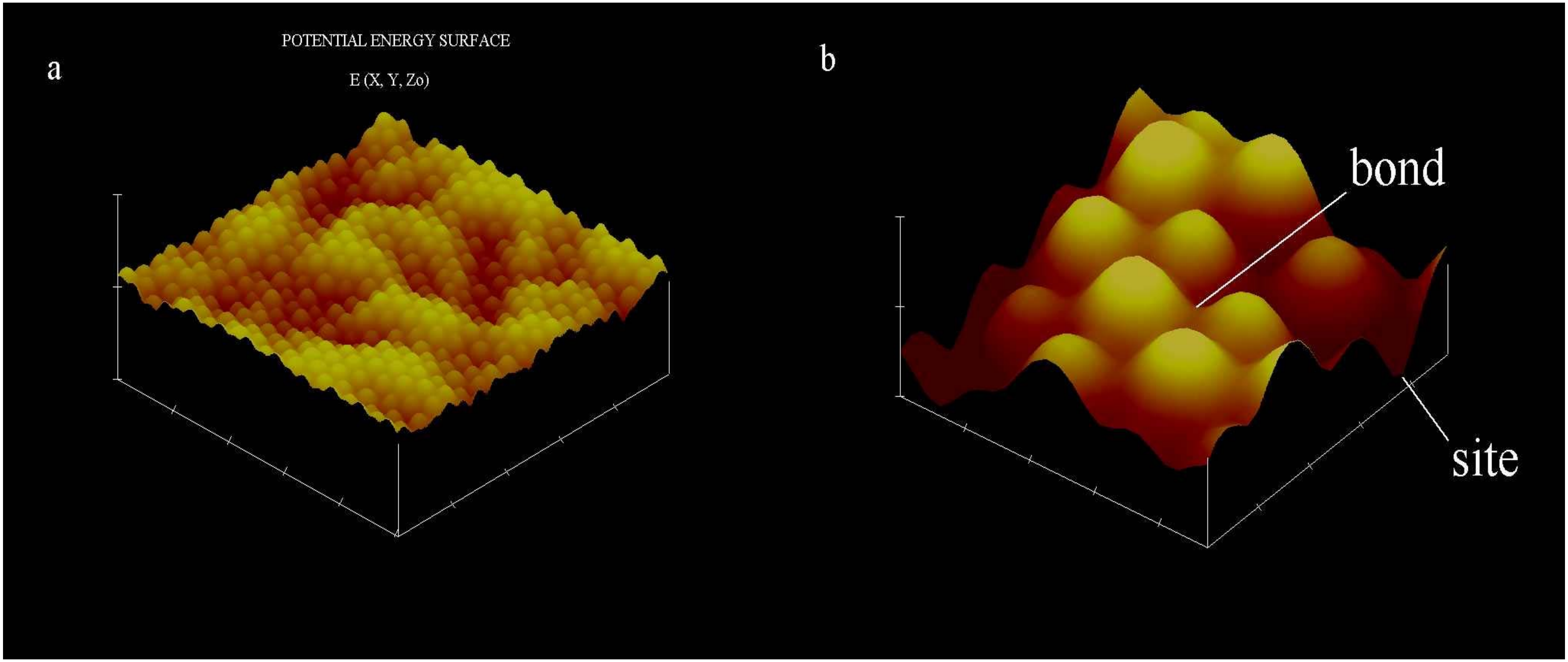
Que problema? Aquí no hay ningún problema!!

ADSORPTIVE ENERGY SURFACE



- Crystal of atoms A with random impurities B
- Gas-Solid Lennard-Jones interaction
- $E(X,Y,Z_0) = \min_Z E(X,Y,Z)$

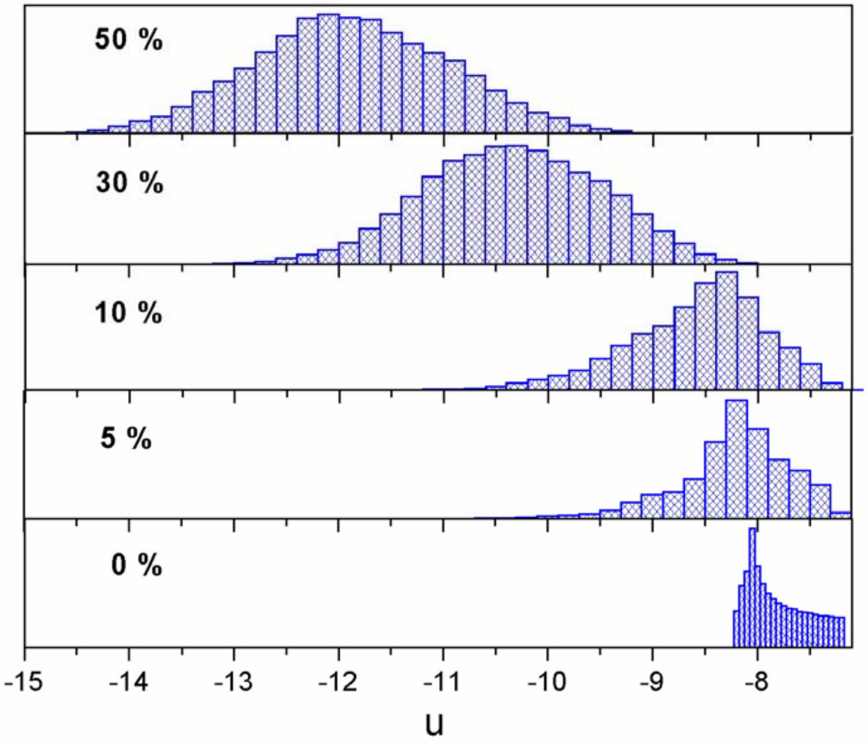
What we get is the "adsorptive energy surface" AES

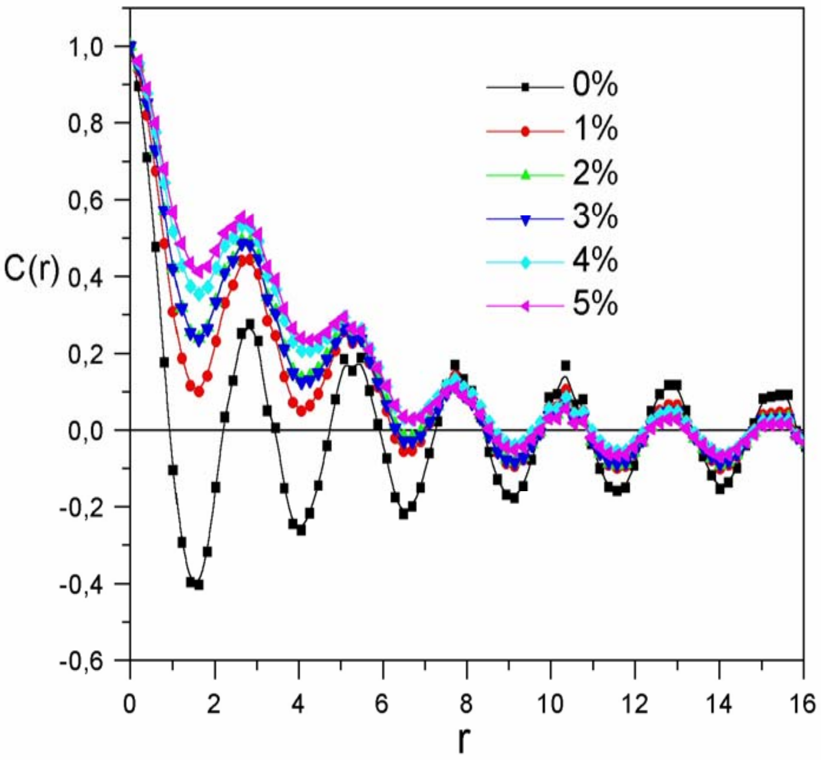


- The potential energy surface seen by the probe atom: ε (X,Y)

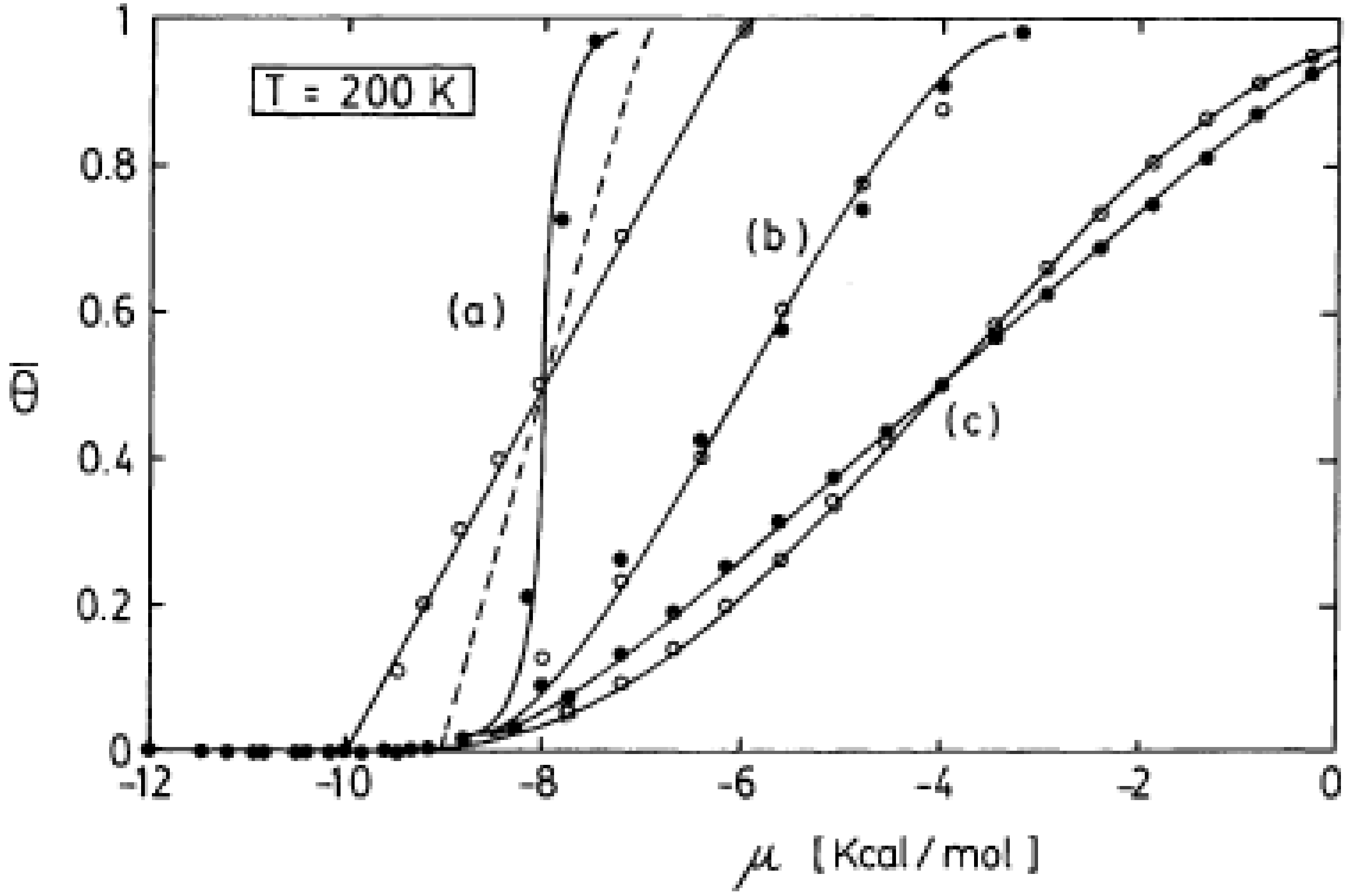
WHAT IS THE ENERGETIC TOPOGRAPHY?

Is the way a given distribution of adsorptive energies are **spatially distributed.** For example, in the case of the simulated doped cristal we have these adsorption energy distribution and spatial correlation:





The energetic topography produces important effects in all molecular processes on the surface (adsorption, surface diffusion, aggregation, chemical reactions, etc.). For example, adsorption isotherms for a surface with the same AED but different topography are different !!



CHARACTERIZATION

- Obtain the statistical properties of ε(X,Y) from experiments
- Experiments: adsorption isotherms θ(μ ,T)
- Classical approach: neglects the "topography", only valid for non-interacting adsorbates

$$\theta(\mu,T) = \int \theta_L(\mu,T,\varepsilon)\; f(\varepsilon)\, d\varepsilon$$

Correct approach: considers the "topography"

$$\theta(\mu,T) = \int \theta_L(\mu,T,\varepsilon_1,\ldots,\varepsilon_M)\; f(\varepsilon_1,\ldots,\varepsilon_M)\, d\varepsilon_1 \ldots d\varepsilon_M$$

AN IRRESOLUBLE PROBLEM!!!

WHAT CAN WE DO?

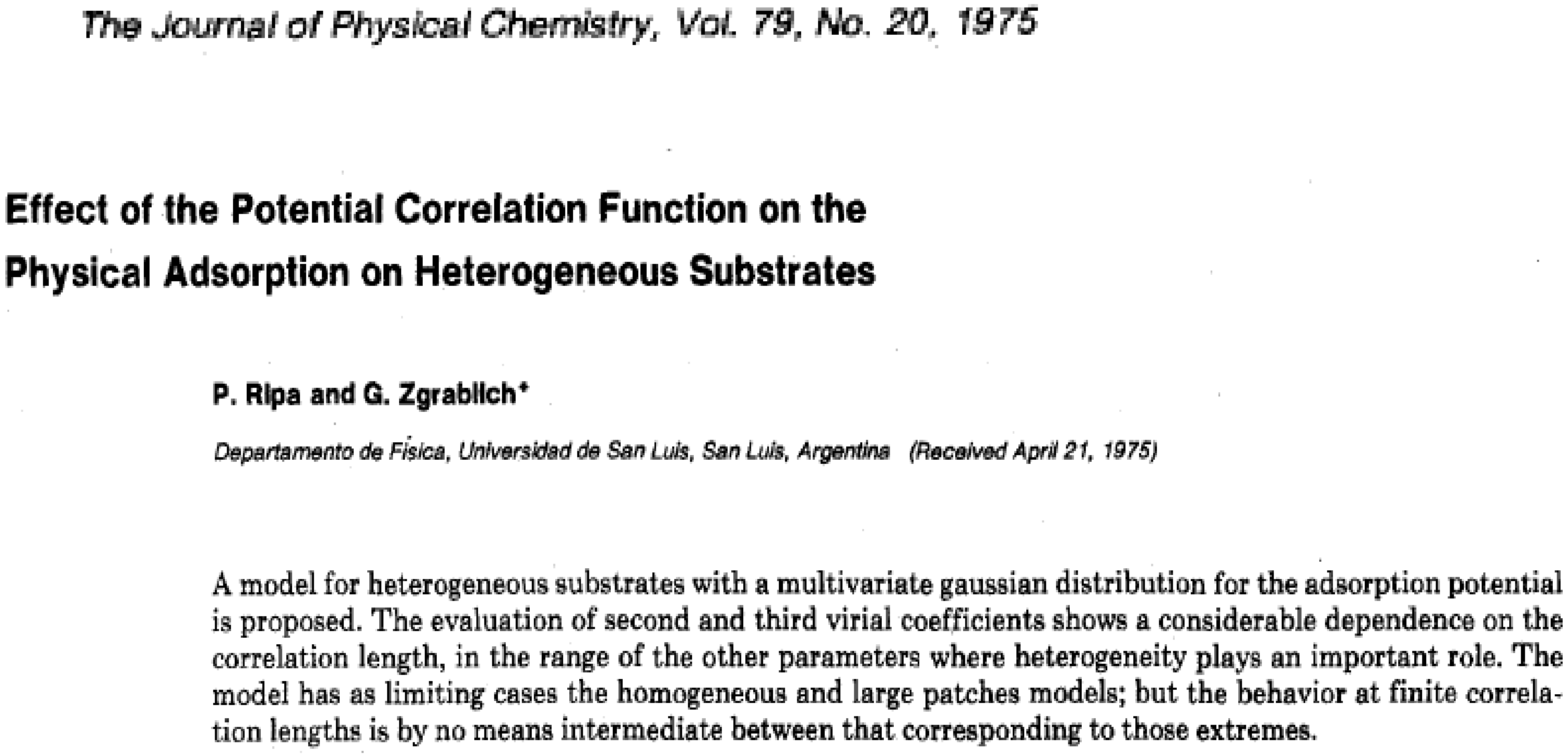
- **Develop simple models taking into account both the AED and the spatial correlation in adsorptive energies in such a away that these can be described by few parameters.**

- **These models will provide us with an adsorption isotherm equation, which can be fitted to experimental data allowing the determinationof those parameters describing the energetic topography.**

Ante la duda siempre es bueno hacer un asado!

CONTINUUM APPROACH

THE GENERALIZED GAUSSIAN MODEL (GGM)



The Journal of Physical Chemistry, Vol. 79, No. 20, 1975

Effect of the Potential Correlation Function on the Physical Adsorption on Heterogeneous Substrates

P. Ripa and G. Zgrablich*

Departamento de Física, Universidad de San Luis, San Luis, Argentina *(Received April 21, 1975)*

A model for heterogeneous substrates with a multivariate gaussian distribution for the adsorption potential is proposed. The evaluation of second and third virial coefficients shows a considerable dependence on the correlation length, in the range of the other parameters where heterogeneity plays an important role. The model has as limiting cases the homogeneous and large patches models; but the behavior at finite correlation lengths is by no means intermediate between that corresponding to those extremes.

Comments of Reviewer: (J)

I think that this paper is an important contribution to a problem which is just now the subject of concern to a number of us. The approach is at once more sensible and sophisticated than any other I have seen. The results are in qualitative accord with my intuition and experimental experience.

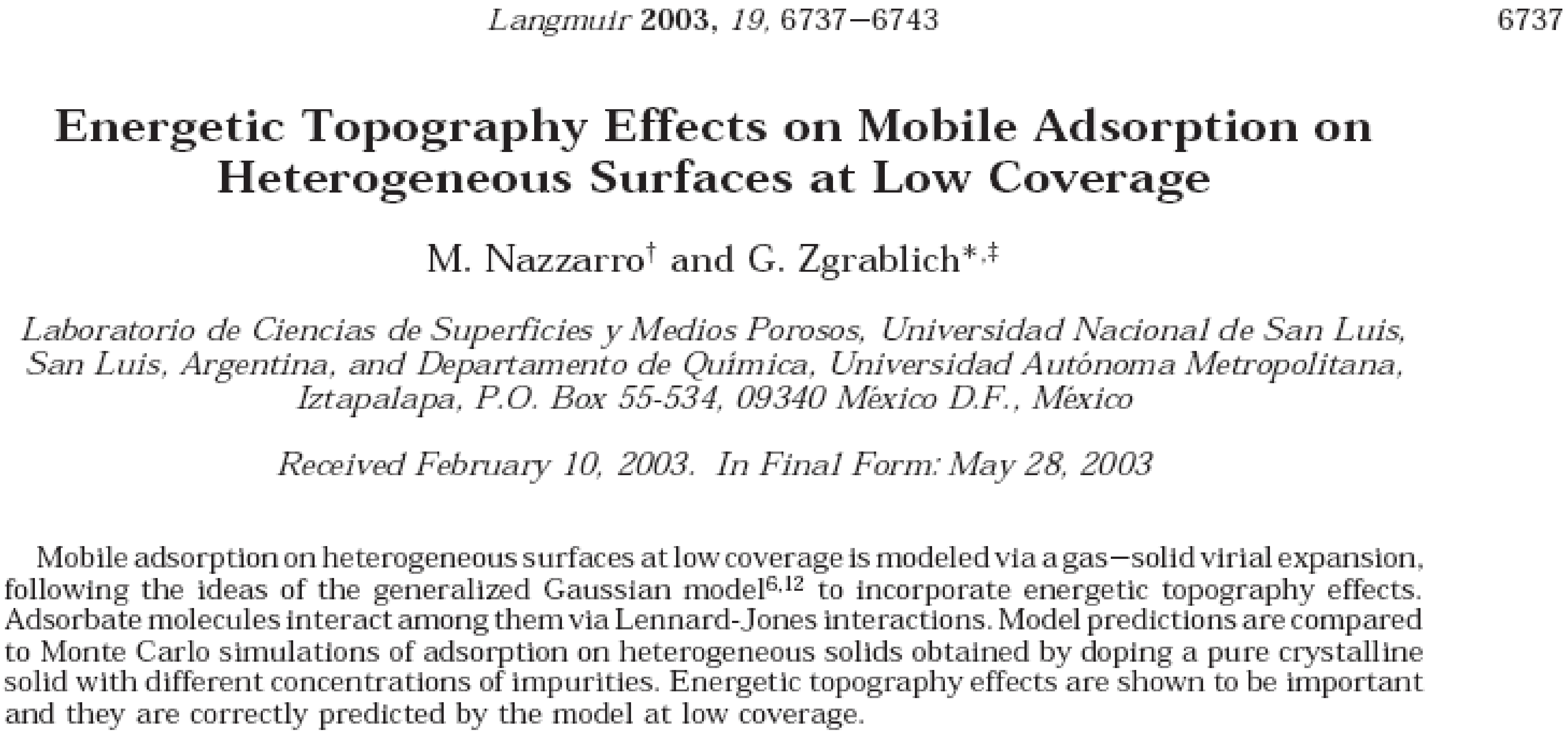
However, the manuscript is rather carelessly prepared, and I do not have the inclination to study the details of the calculation. The results will serve the purpose at any rate to encourage a fresh approach to the problem of surface heterogeniety. It will be left to other workers to interpret the meaning of the parameters and apply the results. As you can see, I am eager to see this paper in print.

Comments of Reviewer: (P)

An original approach to a well-known unsolved problem. Should definitely be published, and I look forward to future work. An obvious mistake is made in Fig. 1, namely, the first diagram in $S'_{1,2,3,4}$ is not a triangle, but is  ; it is undoubtedly a drafting error.

Bill Steele, the first reviewer, discovered by accident!!!

THE LAST VERSION OF THE GGM



Langmuir 2003, 19, 6737−6743 6737

Energetic Topography Effects on Mobile Adsorption on Heterogeneous Surfaces at Low Coverage

M. Nazzarro† and G. Zgrablich*,‡

Laboratorio de Ciencias de Superficies y Medios Porosos, Universidad Nacional de San Luis,
San Luis, Argentina, and Departamento de Química, Universidad Autónoma Metropolitana,
Iztapalapa, P.O. Box 55-534, 09340 México D.F., México

Received February 10, 2003. In Final Form: May 28, 2003

Mobile adsorption on heterogeneous surfaces at low coverage is modeled via a gas−solid virial expansion, following the ideas of the generalized Gaussian model[6,12] to incorporate energetic topography effects. Adsorbate molecules interact among them via Lennard-Jones interactions. Model predictions are compared to Monte Carlo simulations of adsorption on heterogeneous solids obtained by doping a pure crystalline solid with different concentrations of impurities. Energetic topography effects are shown to be important and they are correctly predicted by the model at low coverage.


Esto me costó mis mejores años de juventud!!

GGM : LAST VERSION

- The AES is assumed to be a Gaussian Stochastic Process, with the multivariate distribution function

$$\Phi_n(\varepsilon_1,\ldots,\varepsilon_n)=\left[(2\pi)^n\det H\right]^{-1/2}\exp\left[-1/2\sum_{i,j=1}^{n}\left(\varepsilon(\vec{r}_i)+kT_a\right)\left(H^{-1}\right)_{i,j}\left(\varepsilon(\vec{r}_j)+kT_a\right)\right]$$

with the covariance matrix

$$H_{ij}=\left\langle\left(\varepsilon(\vec{r}_i)+kT_a\right)\left(\varepsilon(\vec{r}_j)+kT_a\right)\right\rangle=(kT_s)^2C(\vec{r}_i-\vec{r}_j)$$

- We also assume a gaussian decay for the correlation

$$C(\vec{r})=\exp\left[-1/2(r/r_0)^2\right]$$

with a “correlation length” r_0 and a g-g interaction

$$U_{gg}(r)=4k_BT_{gg}\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]$$

EXAMPLE: THE DOPED CRISTAL

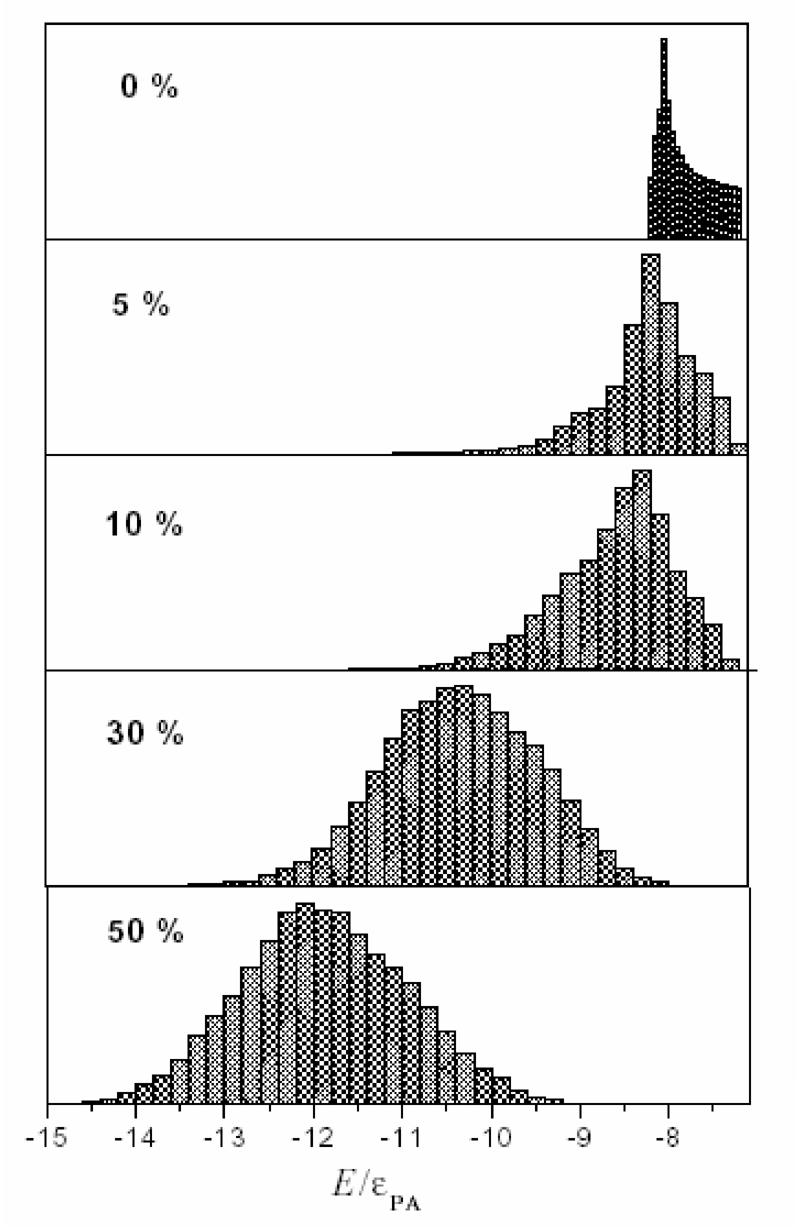


figure 4

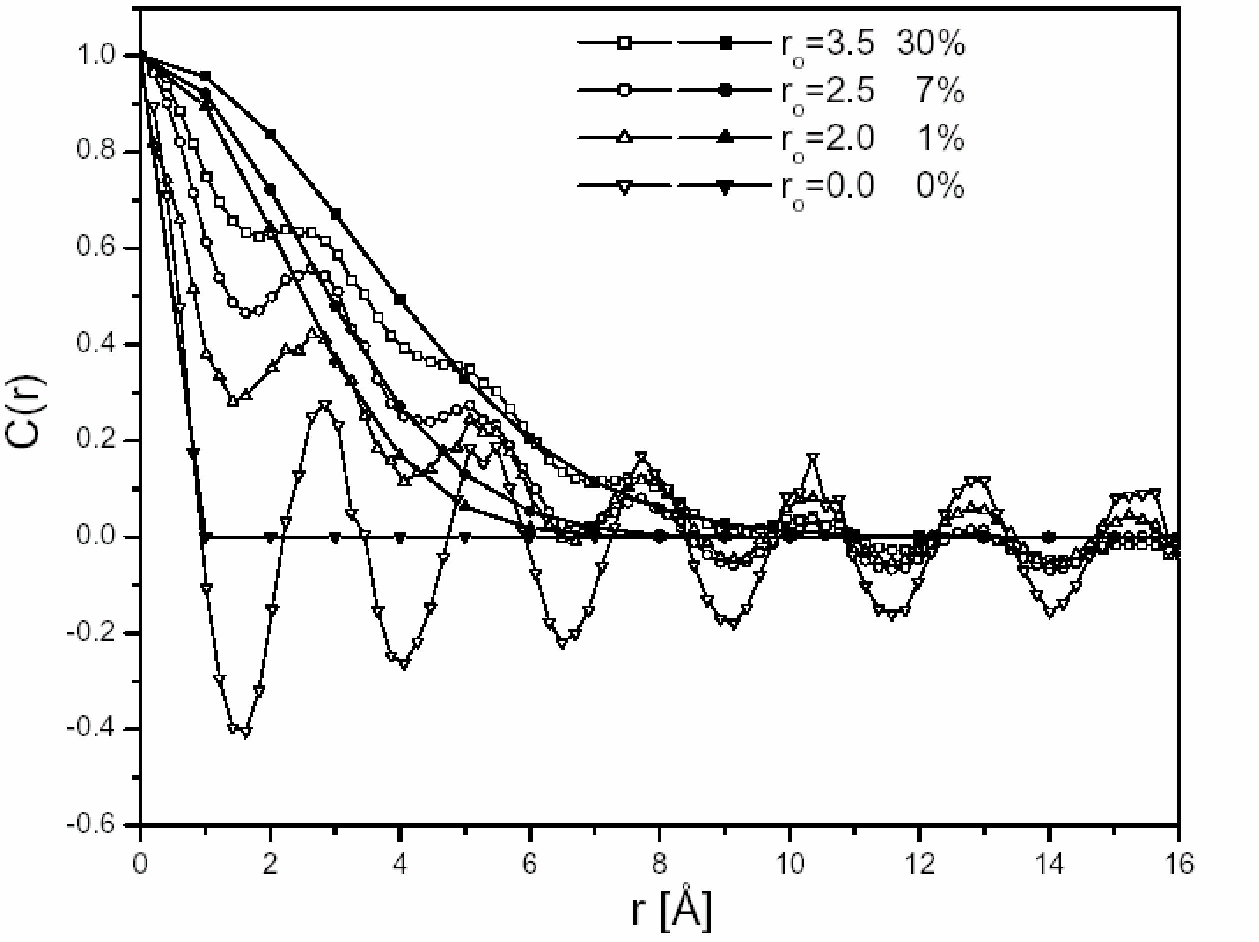
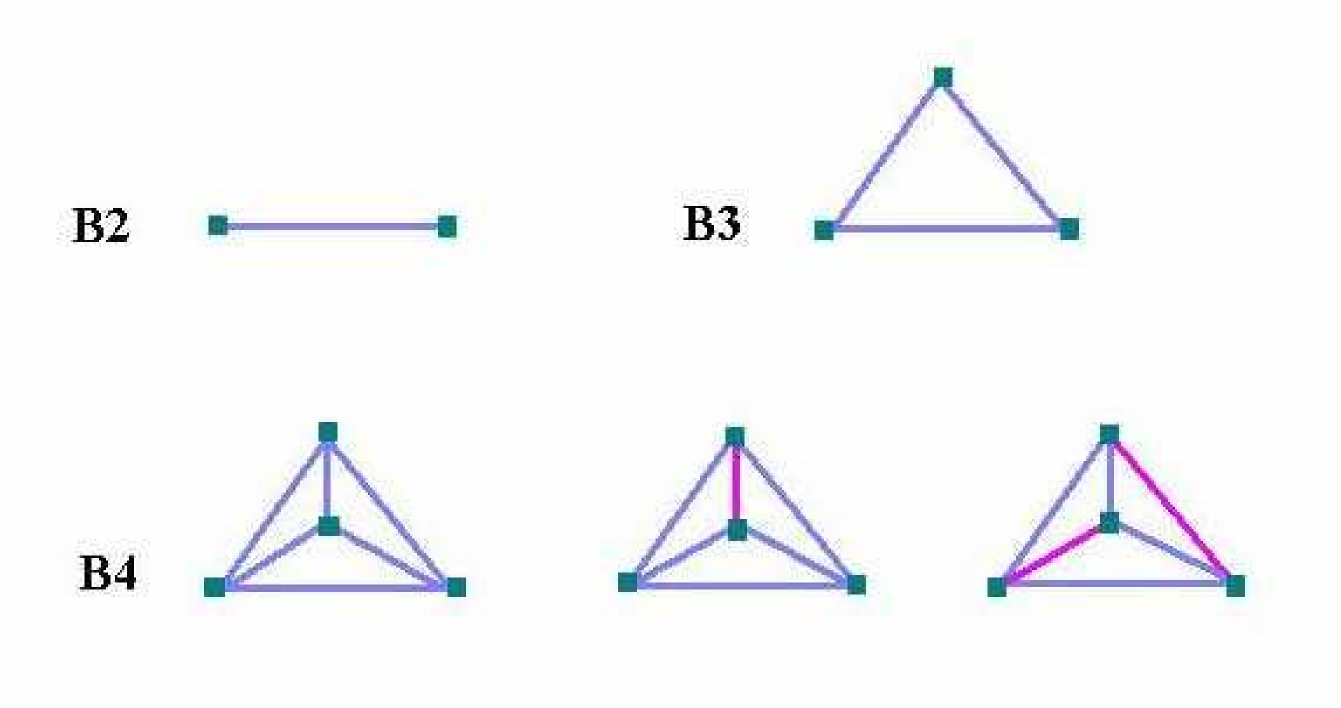


Figure 6

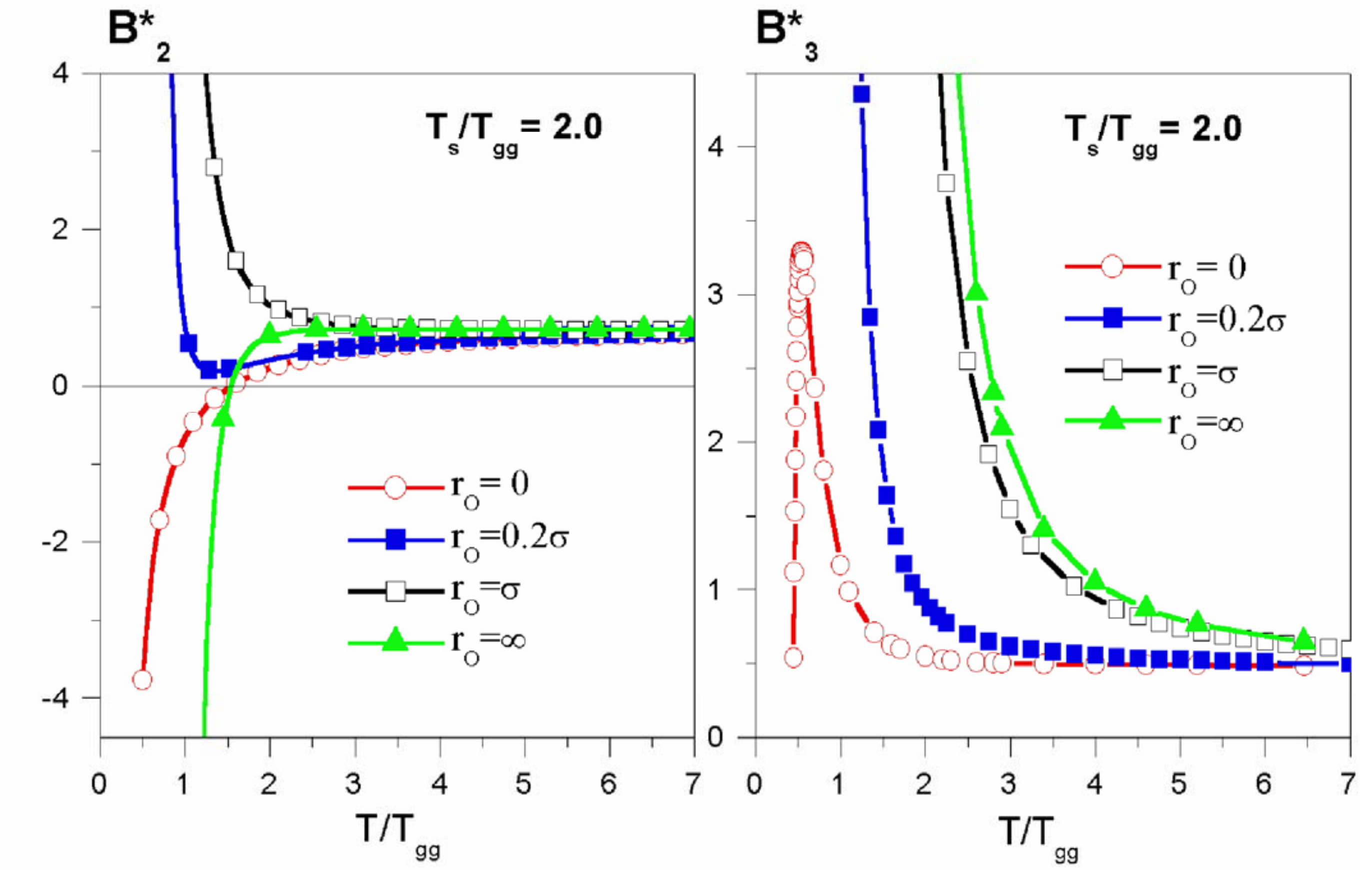
GAS-SOLID VIRIAL EXPANSION

- **Adsorption isotherms ==> gas-solid virial expansion**
- **A blue line represents a factor** $f_{ij} \exp\left[H_{ij}/(kT)^2\right]$
  with $f_{ij} = \exp\left[-U_{gg}(\vec{r}_i - \vec{r}_j)/kT\right] - 1$
- **A red line represents a factor** $\exp\left[H_{ij}/(kT)^2\right]$



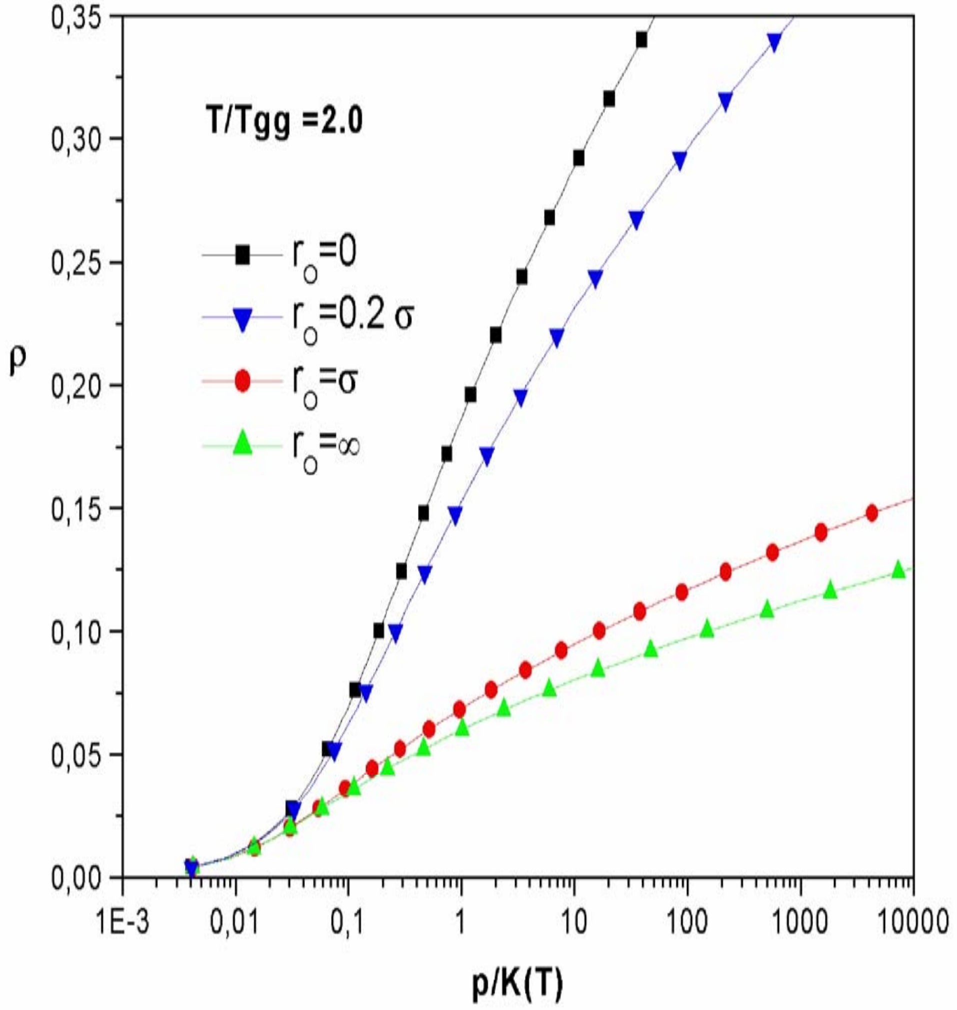
Basta!! Con tantas ecuaciones tengo la cabeza como la de un elefante!!

BEHAVIOR OF VIRIAL COEFFICIENTS



- B_2 and B_3 depend strongly on the correlation length r_0

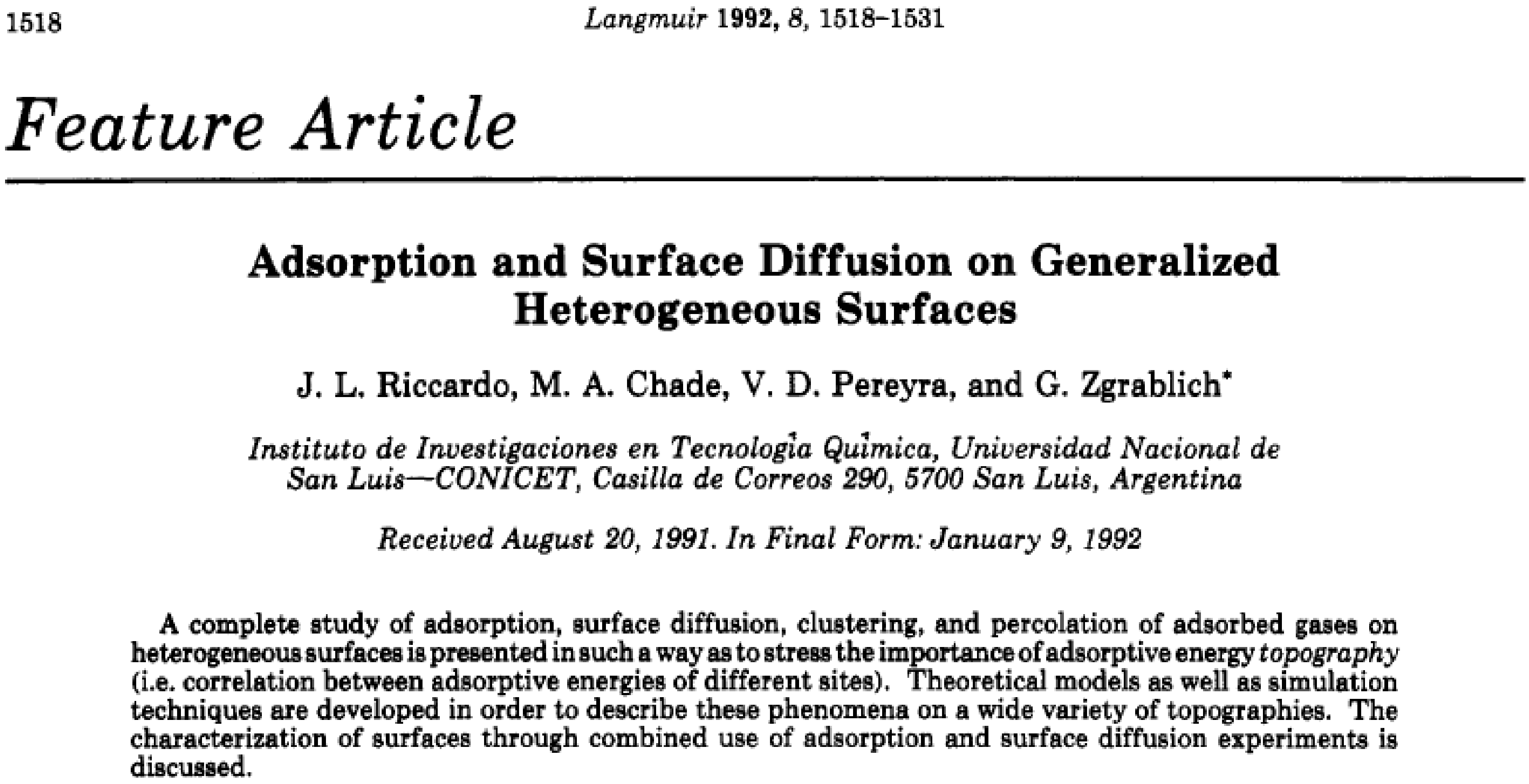
BEHAVIOR OF ADSORPTION ISOTHERM



- Adsorption decreases strongly with increasing correlation length.
- Experimental data for low density can be fitted with 4 parameters characterizing the heterogeneity: K(T) (or T_a), T_s, T_{gg} and r_0.

LATTICE-GAS APPROACH

THE LATTICE-GAS GGM



1518 *Langmuir* **1992**, *8*, 1518–1531

Feature Article

Adsorption and Surface Diffusion on Generalized Heterogeneous Surfaces

J. L. Riccardo, M. A. Chade, V. D. Pereyra, and G. Zgrablich*

Instituto de Investigaciones en Tecnología Química, Universidad Nacional de San Luis—CONICET, Casilla de Correos 290, 5700 San Luis, Argentina

Received August 20, 1991. In Final Form: January 9, 1992

A complete study of adsorption, surface diffusion, clustering, and percolation of adsorbed gases on heterogeneous surfaces is presented in such a way as to stress the importance of adsorptive energy *topography* (i.e. correlation between adsorptive energies of different sites). Theoretical models as well as simulation techniques are developed in order to describe these phenomena on a wide variety of topographies. The characterization of surfaces through combined use of adsorption and surface diffusion experiments is discussed.


Esta tesis me ha hecho dar un hambre feroz !!!

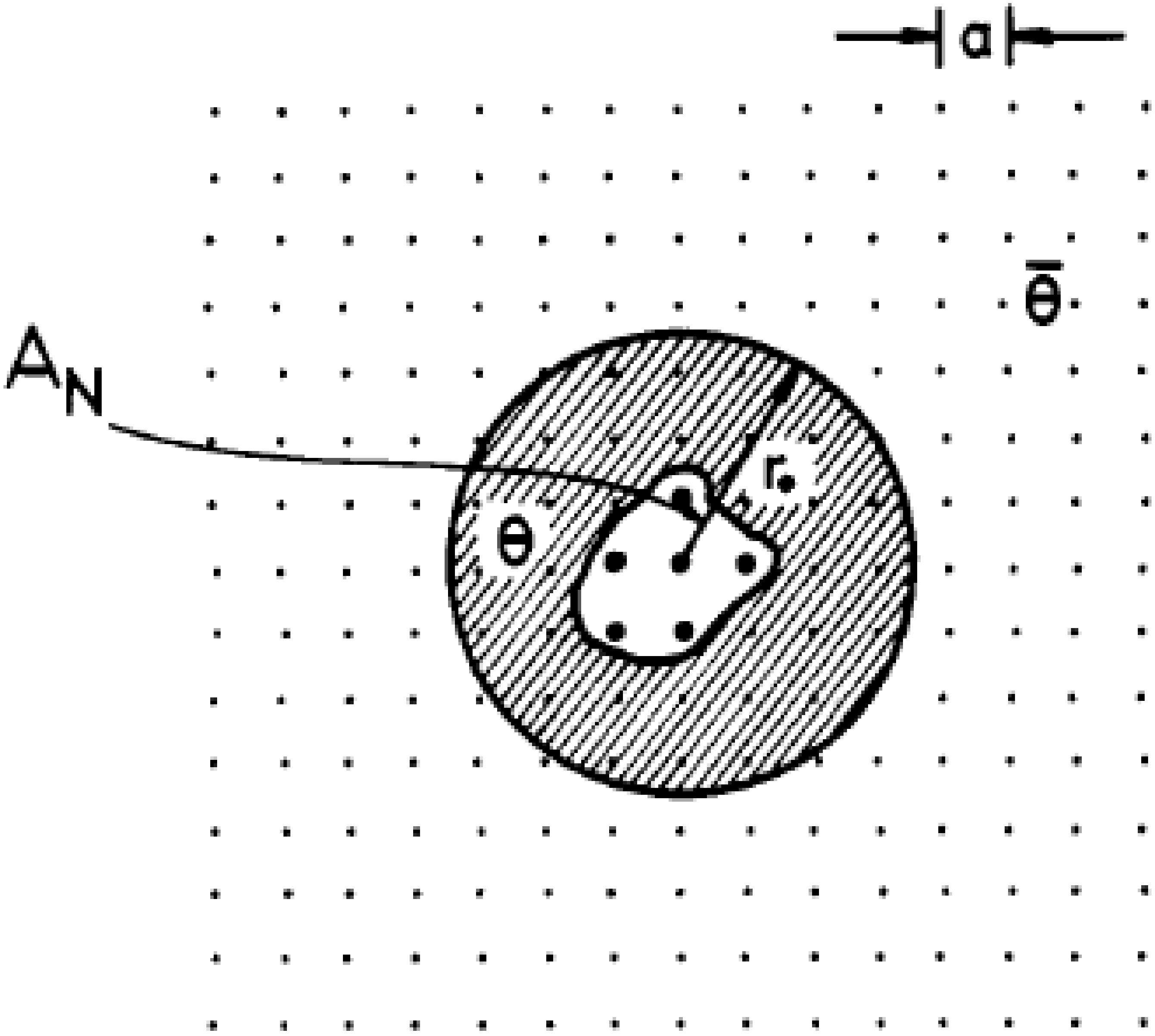


Figure 2. A square lattice of adsorption sites where *N*th order mean field approximation zones are shown.

(b) The second-order approximation ($N = 2$) is a more interesting one inasmuch as explicit pair interactions are taken into account and site correlation effects may be investigated. In this case we have the pair of coupled equations

$$\begin{aligned} \theta_1 &= \frac{\exp[-\beta(\epsilon_1 + U_{12}\theta_2 + \lambda_0\theta + \lambda\bar{\theta} - \mu)]}{1 + \exp[-\beta(\epsilon_1 + U_{12}\theta_2 + \lambda_0\theta + \lambda\bar{\theta} - \mu)]} \\ \theta_2 &= \frac{\exp[-\beta(\epsilon_2 + U_{12}\theta_1 + \lambda_0\theta + \lambda\bar{\theta} - \mu)]}{1 + \exp[-\beta(\epsilon_2 + U_{12}\theta_1 + \lambda_0\theta + \lambda\bar{\theta} - \mu)]} \end{aligned} \tag{12}$$

Local coverage on a pair of sites with energies (ϵ_1, ϵ_2) is given by

$$\theta(\epsilon_1,\epsilon_2,\mu) = (\theta_1 + \theta_2)/2 \tag{13}$$

and the overall isotherm is

$$\bar{\theta} = \int\int f_2(\epsilon_1,\epsilon_2)\, \theta(\epsilon_1,\epsilon_2,\mu)\, \mathrm{d}\epsilon_1\, \mathrm{d}\epsilon_2 \tag{14}$$

$$f_2(\epsilon_1,\epsilon_2) = [(2\pi)^2 \det\mathbf{H}]^{-1/2} \times \exp\left[-\frac{1}{2} \sum_{i,j=1}^{2} (\epsilon_i - \bar{\epsilon})(\mathbf{H}^{-1})_{ij}(\epsilon_j - \bar{\epsilon}) \right] \tag{15}$$

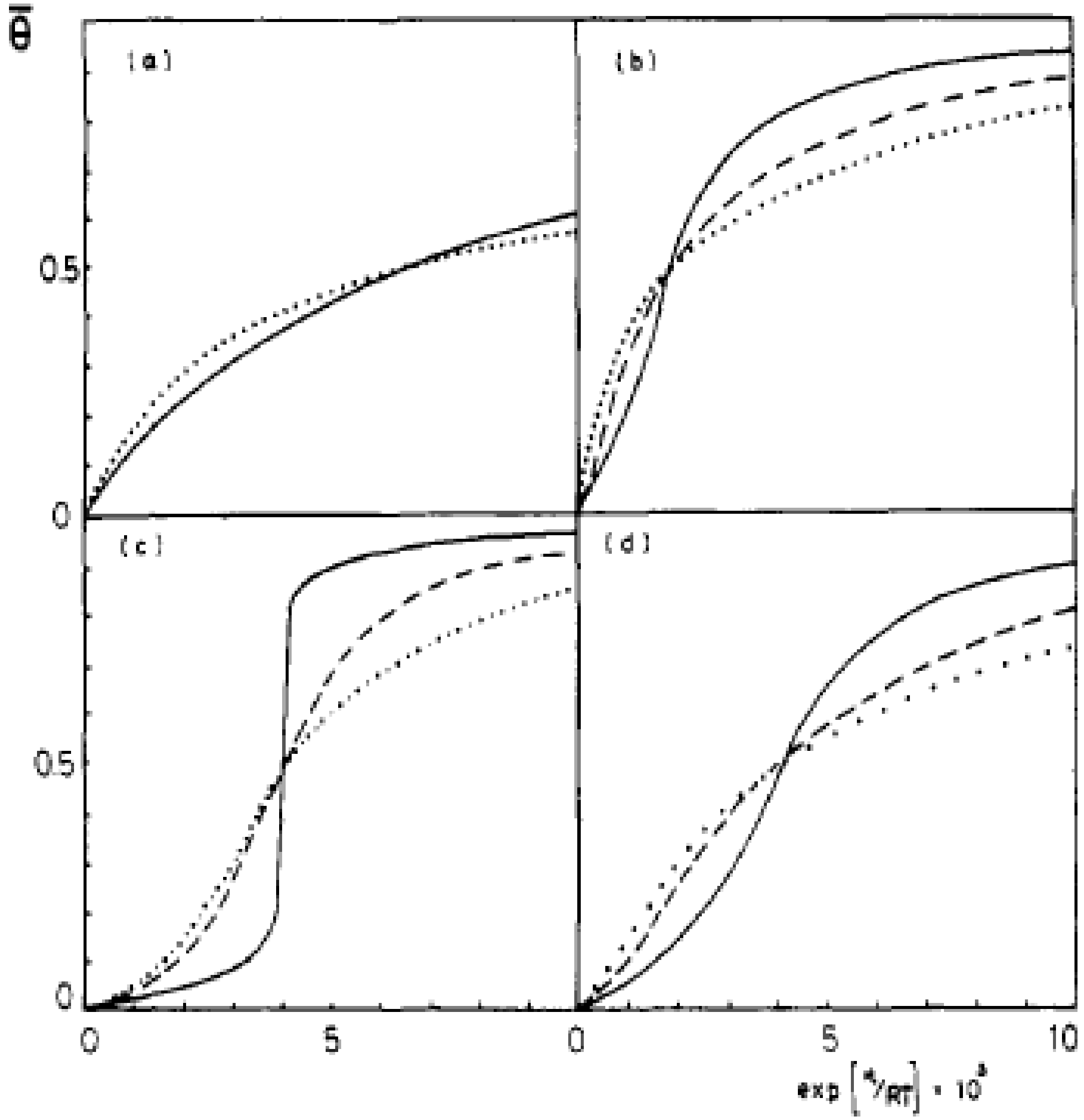


Figure 3. Adsorption isotherms predicted by the MRF model for three correlation lengths: ——, $r_o = 0$; - - -, $r_o = 1$; · · ·, $r_o = 2$. (a) T = 400 K, $T_{gg}/T = 0.5$, $T_s/T = 1.5$; (b) T = 400 K, $T_{gg}/T = 1$, $T_s/T = 1.5$; (c) T = 500 K, $T_{gg}/T = 1$, $T_s/T = 0.7$; (d) T = 500 K, $T_{gg}/T = 1$, $T_s/T = 1.5$.

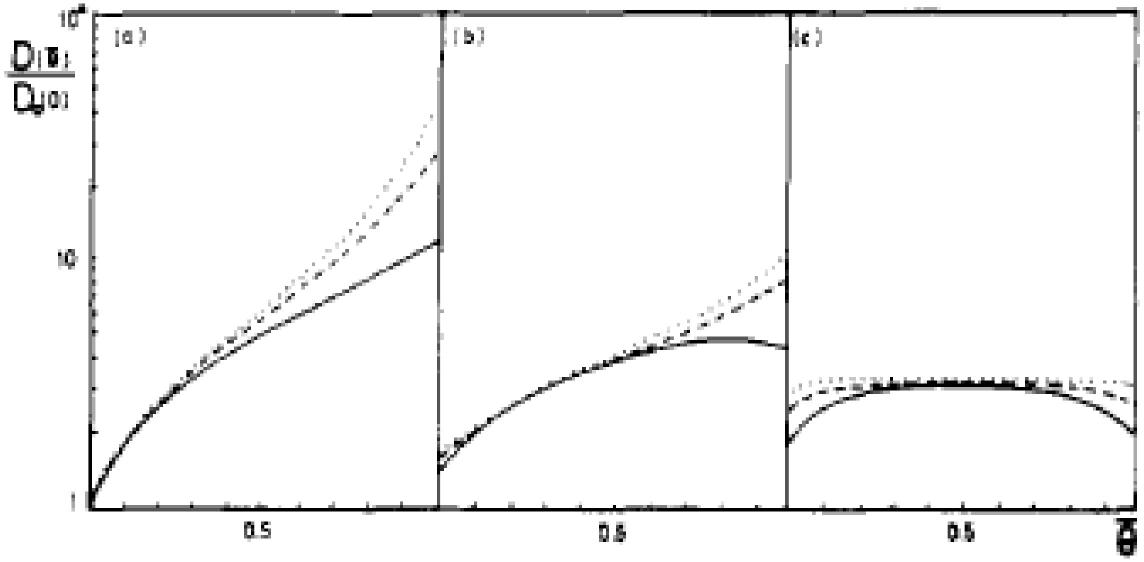


Figure 24. Surface diffusion coefficient for a noninteracting adsorbate, $T_{gg}/T = 0$: ——, $r_0 = 0$; - - -, $r_0 = 1$; · · ·, $r_0 = 2$. (a) $\alpha = 0$; (b) $\alpha = {}^1/_4$; (c) $\alpha = {}^1/_2$.

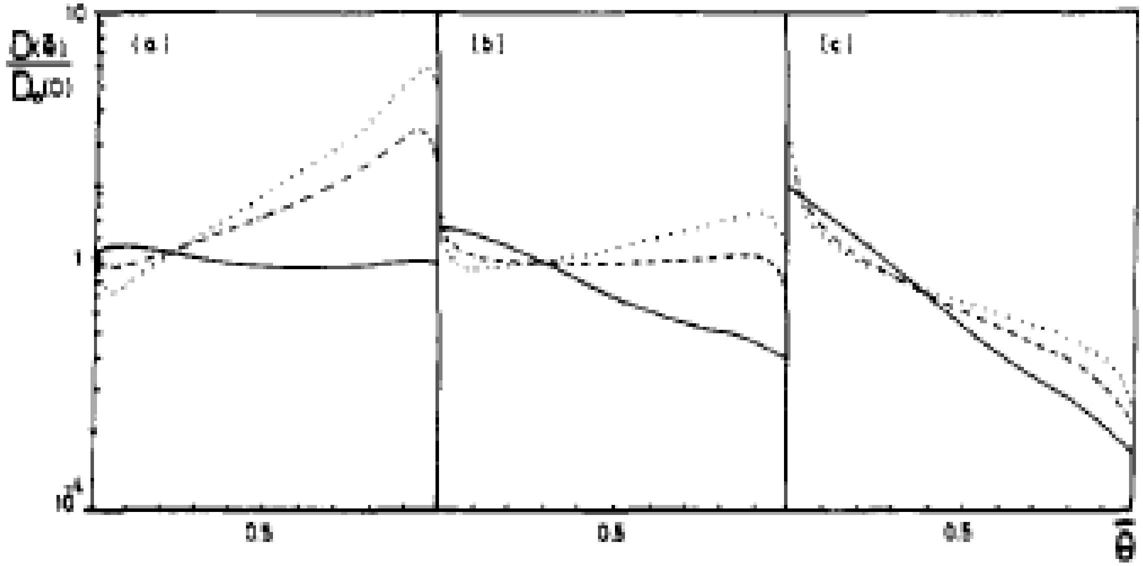
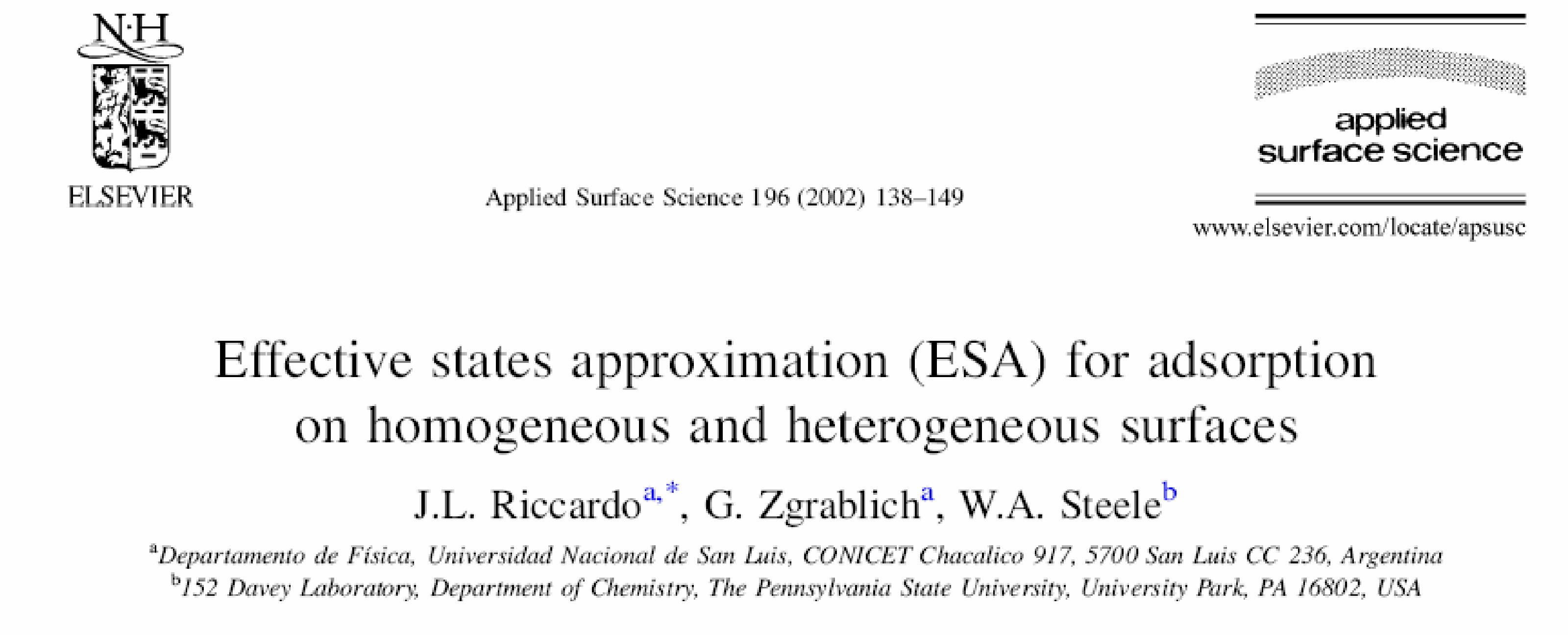


Figure 25. Same as Figure 24 for an interacting adsorbate, $T_{gg}/T = 0.5$.

EFFECTIVE STATE APPROXIMATION (ESA)



ELSEVIER

Applied Surface Science 196 (2002) 138–149

applied surface science

www.elsevier.com/locate/apsusc

Effective states approximation (ESA) for adsorption on homogeneous and heterogeneous surfaces

J.L. Riccardo[a,*], G. Zgrablich[a], W.A. Steele[b]

[a]*Departamento de Física, Universidad Nacional de San Luis, CONICET Chacalico 917, 5700 San Luis CC 236, Argentina*
[b]*152 Davey Laboratory, Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA*

I-SISA (SIMPOSIO SUDAMERICANO DE ADSORCION)
Campina Grande, Pernambuco, Brasil, Junio 2008

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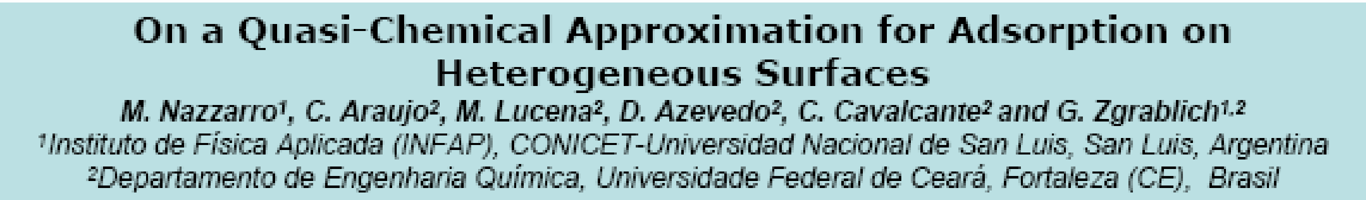


On a Quasi-Chemical Approximation for Adsorption on Heterogeneous Surfaces

M. Nazzarro[1], C. Araujo[2], M. Lucena[2], D. Azevedo[2], C. Cavalcante[2] and G. Zgrablich[1,2]
[1]Instituto de Física Aplicada (INFAP), CONICET-Universidad Nacional de San Luis, San Luis, Argentina
[2]Departamento de Engenharia Química, Universidade Federal de Ceará, Fortaleza (CE), Brasil

UFC

Campina Grande, Junio 2008

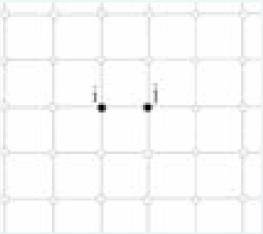


Figure 1 – Heterogeneous lattice where two NN sites are chosen.

$$\frac{P_{++}\,P_{--}}{P_{+-}^2} = \frac{1}{4}\chi(w,\varepsilon_i,\varepsilon_j)$$

$$\chi(w,\varepsilon_i,\varepsilon_j) = \frac{2\exp(-\beta w)}{1+\cosh[\beta(\varepsilon_i-\varepsilon_j)]} \qquad w = kT_{gg}$$

$$P_{++} = \theta - \xi \quad ; \quad P_{+-} = 2\,\xi \quad ; \quad P_{--} = 1-\theta-\xi$$

where $\xi = \{1-[1-2\eta\theta(1-\theta)]^{1/2}\}/\eta \;\; ; \;\; \eta = 2(1-\chi)$

The probability of finding a site of adsorption energy ε with a neighborhood α (α occupied sites out of nearest-neighbor sites) characterized by adsorption energy ε', is:

$$P_\alpha = \binom{c}{\alpha}[P_+(\varepsilon,\varepsilon',\theta)]^\alpha\,[P_-(\varepsilon,\varepsilon',\theta)]^{c-\alpha}$$

The conditional probabilities of finding an occupied (empty) NN site with energy ε' given an occupied site with energy ε is given by:

$$P_+(\varepsilon,\varepsilon',\theta) = \frac{P_{++}(\varepsilon,\varepsilon',\theta)}{\theta} \quad ; \quad P_-(\varepsilon,\varepsilon',\theta) = \frac{1}{2}\frac{P_{+-}(\varepsilon,\varepsilon',\theta)}{\theta}$$

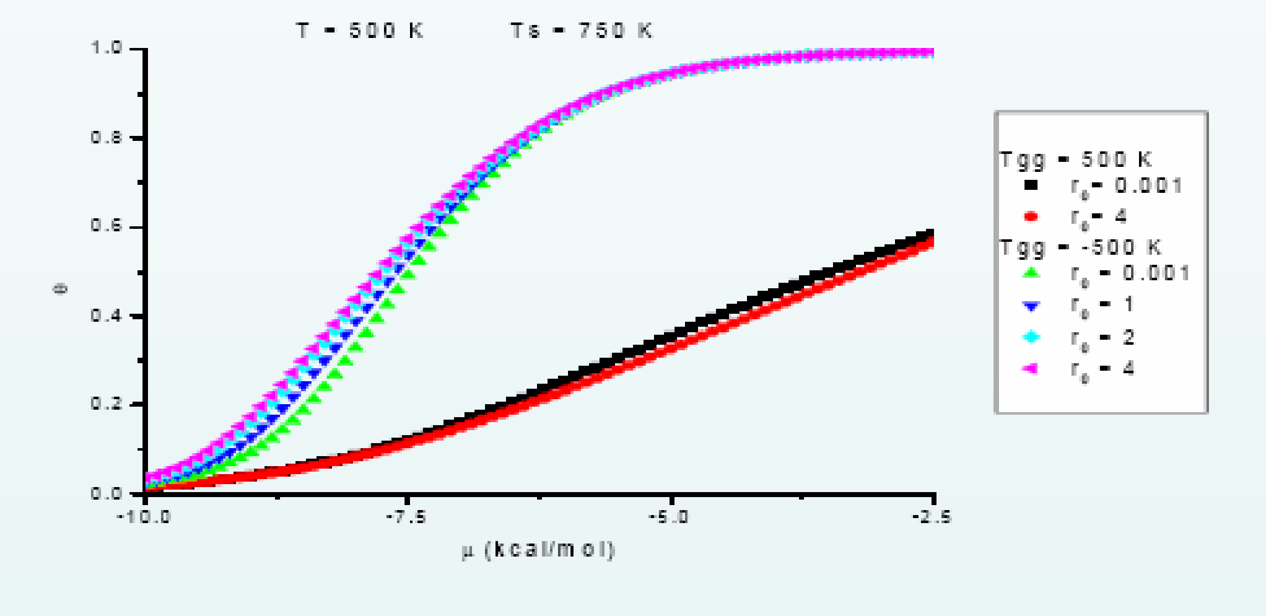
The coverage of the site with energy ε and a neighborhood α is given by:

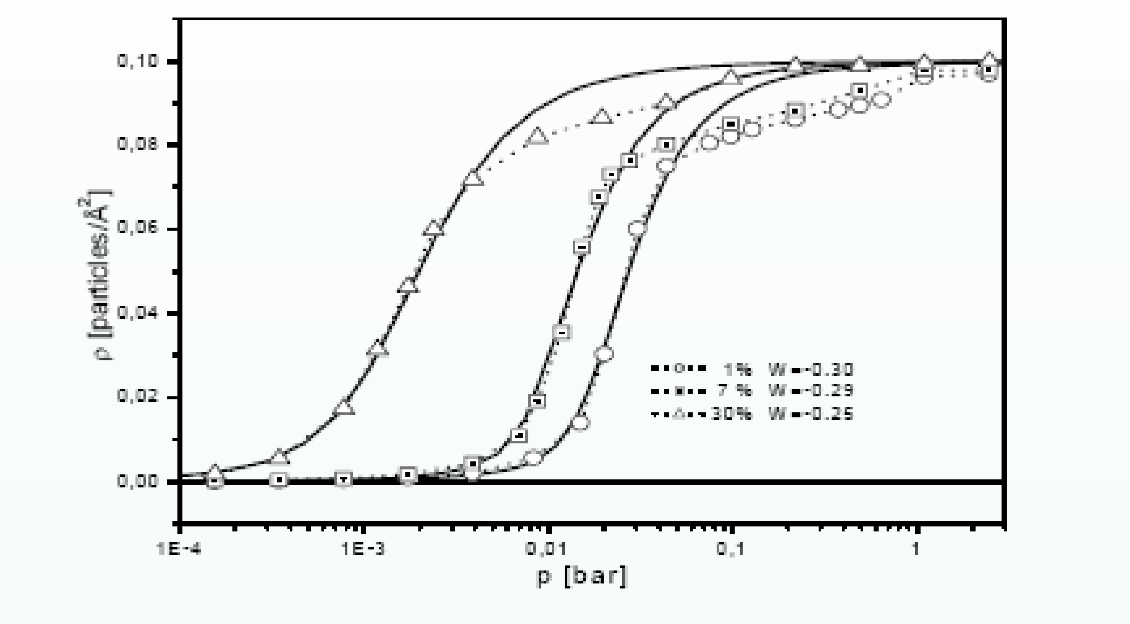
$$A_\alpha(\varepsilon,\mu) = \frac{\exp[-\beta(\varepsilon+W_\alpha-\mu)]}{1+\exp[-\beta(\varepsilon+W_\alpha-\mu)]}$$

So, the local isotherm becomes: $\theta_L(\varepsilon,\varepsilon',\theta,\mu,T) = \sum_\alpha P_\alpha(\varepsilon,\varepsilon',\theta,T)\,A_\alpha(\varepsilon,\mu)$

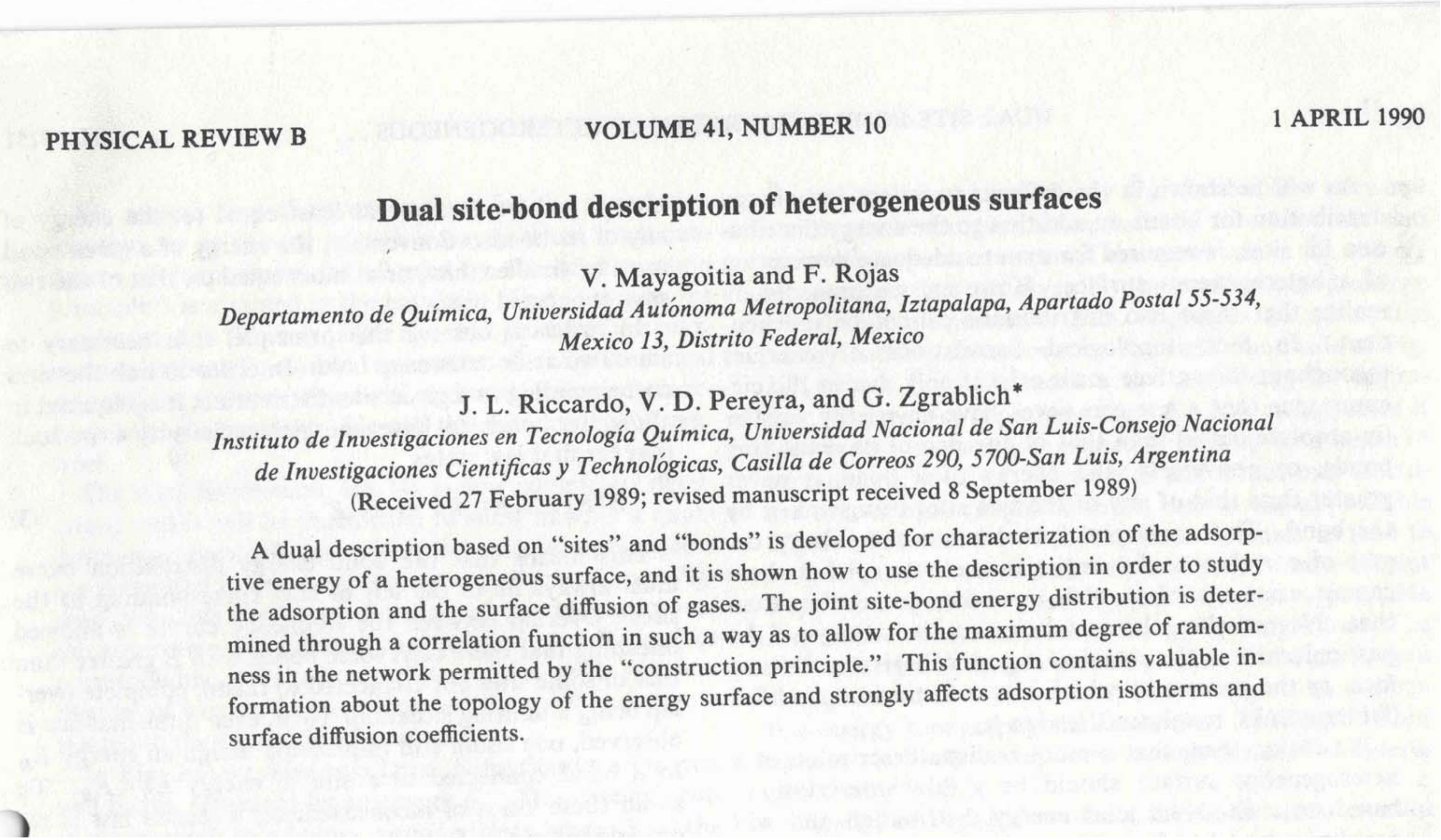
Therefore the mean surface coverage, representing the total adsorption isotherm is:

$$\theta(\mu,T) = \iint \theta_L(\varepsilon,\varepsilon',\theta,\mu,T)\,f_2(\varepsilon,\varepsilon')\,d\varepsilon\,d\varepsilon'$$


T = 500 K
Ts = 750 K
θ
1.0
0.8
0.6
0.4
0.2
0.0
-10.0
-7.5
-5.0
-2.5
μ (kcal/mol)
Tgg = 500 K
r_0 = 0.001
r_0 = 4
Tgg = -500 K
r_0 = 0.001
r_0 = 1
r_0 = 2
r_0 = 4


ρ [particles/Å^2]
0,10
0,08
0,06
0,04
0,02
0,00
1E-4
1E-3
0,01
0,1
1
p [bar]
1% W=-0.30
7 % W=-0.29
30% W=-0.25

THE DUAL SITE-BOND MODEL (DSBM)



PHYSICAL REVIEW B VOLUME 41, NUMBER 10 1 APRIL 1990

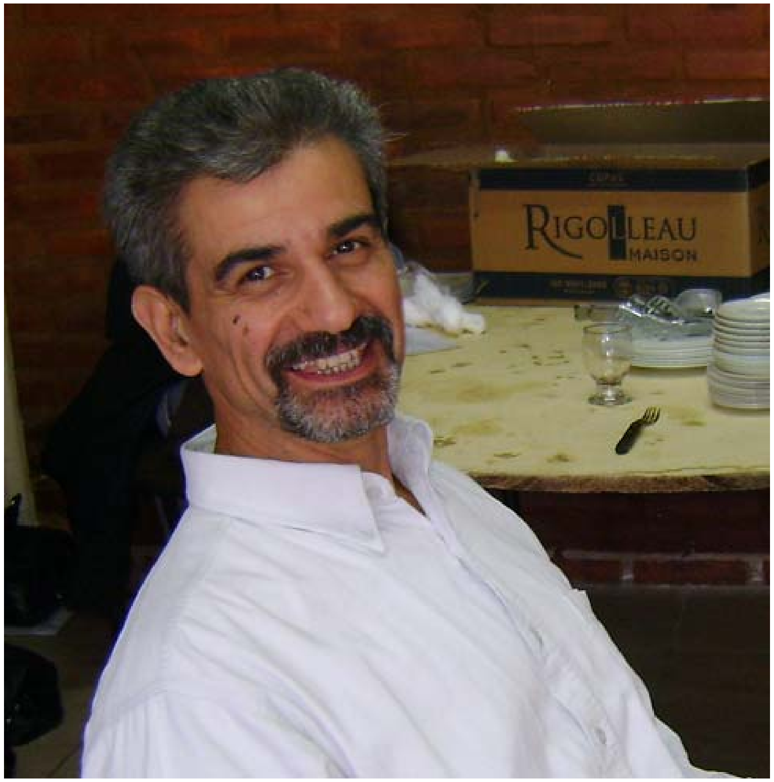
Dual site-bond description of heterogeneous surfaces

V. Mayagoitia and F. Rojas
Departamento de Química, Universidad Autonoma Metropolitana, Iztapalapa, Apartado Postal 55-534,
Mexico 13, Distrito Federal, Mexico

J. L. Riccardo, V. D. Pereyra, and G. Zgrablich*
Instituto de Investigaciones en Tecnología Química, Universidad Nacional de San Luis-Consejo Nacional
de Investigaciones Cientificas y Technológicas, Casilla de Correos 290, 5700-San Luis, Argentina

(Received 27 February 1989; revised manuscript received 8 September 1989)

A dual description based on "sites" and "bonds" is developed for characterization of the adsorptive energy of a heterogeneous surface, and it is shown how to use the description in order to study the adsorption and the surface diffusion of gases. The joint site-bond energy distribution is determined through a correlation function in such a way as to allow for the maximum degree of randomness in the network permitted by the "construction principle." This function contains valuable information about the topology of the energy surface and strongly affects adsorption isotherms and surface diffusion coefficients.


RIGOLLEAU
MAISON

Langmuir 1996, *12*, 4272−4280

Simulation of Model Heterogeneous Surfaces in the Presence of Correlation

Alessandra Adrover, Massimiliano Giona,* and Manuela Giustiniani

Centro Interuniversitario sui Sistemi Disordinati e sui Frattali nell'Ingegneria Chimica,
c/o Dipartimento di Ingegneria Chimica, Università di Roma "La Sapienza" via
Eudossiana 18, 00184 Roma, Italy

Received January 16, 1996. In Final Form: May 14, 1996$^{\otimes}$

We propose a general method to generate correlated energy landscapes for model heterogeneous surfaces. It is based on the representation of an energy landscape as a superposition of exponentially correlated Gaussian processes. This method is the extension of a previous work of Giona and Adrover to reconstruct binary lattice models of porous structures to a random energy field with values between 0 and ∞. The application to dual bond−site models is also developed.

Langmuir 1999, *15*, 5961−5969

Probabilistic Analysis of the Dual Site−Bond Model: The Self-Consistent Case[†]

Alessandra Adrover

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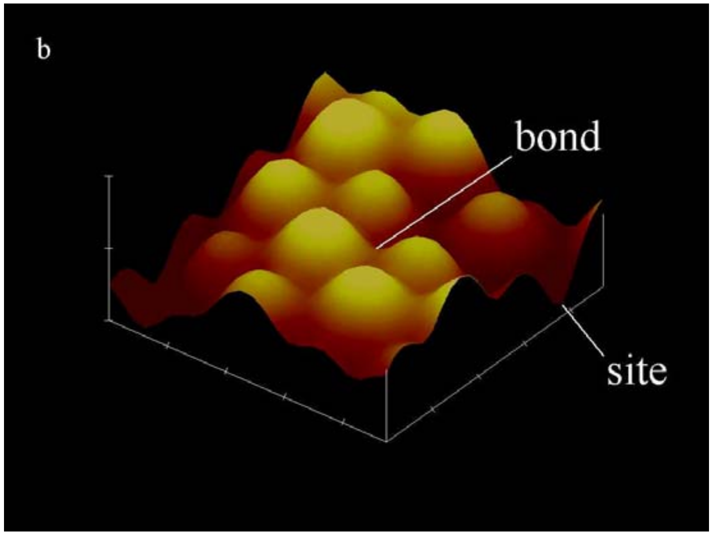
00184 Roma, Italy

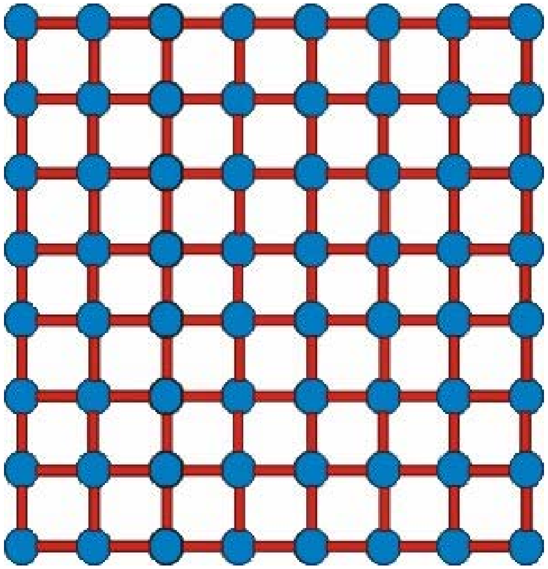
Received September 25, 1998. In Final Form: December 4, 1998

A probabilistic analysis of the generation of dual site−bond models for the energy landscape of adsorbents is presented, focusing attention on the self-consistent case. To generate an uncorrelated site−bond energy landscape with prescribed distribution functions $F_S^*(E)$ and $F_B^*(E)$ consistent with the two basic laws of the dual site−bond model, the random variables associated with the site and bond energies should possess the local distribution functions $F_S(E)$ and $F_B(E)$, which are related to $F_S^*(E)$ and $F_B^*(E)$ through a nonlinear integral equation. In particular, the inverse problem in two dimensions is solved in closed form. The analytical solution for the inverse problem provides a clear description of the intrinsic correlation in the energy landscape induced by the fulfillment of the construction principle.

Alex Adrover and Max Giona with friends in Roma

THE SITE-BOND LATTICE REPRESENTATION

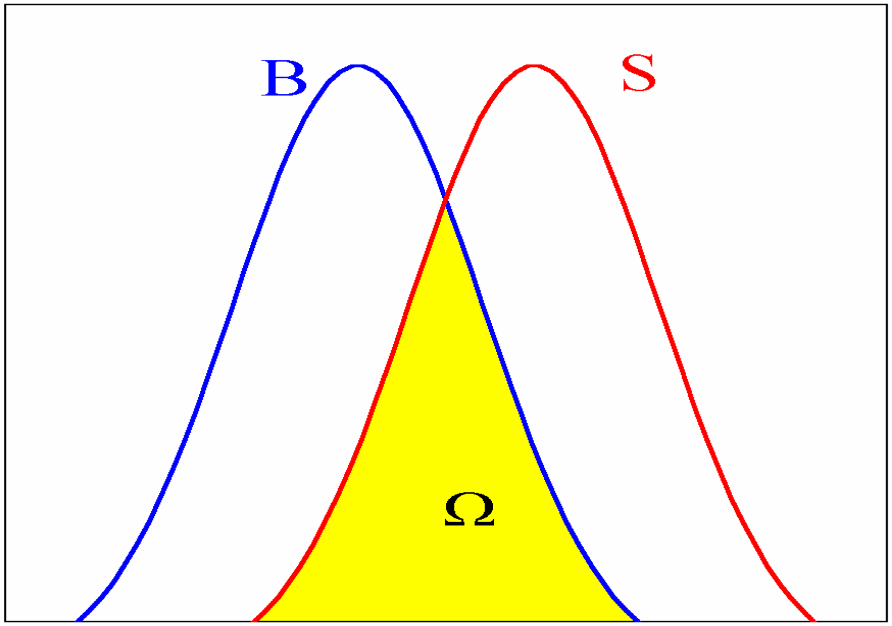




- The surface is represented by a lattice of sites and bonds.
- Each site can be either empty or occupied by an adsorbed particle.
- The lattice-gas approach is equivalent in magnetism to the Ising problem in a randomly inhomogeneous magnetic field.

Muse of Inspiration for the DSBM

THE DUAL SITE-BOND DISTRIBUTION



- $F(E_S, E_B) = F_S(E_S)\, F_B(E_B)\, \Phi(E_S, E_B)$
- **Correlation function**: $\langle [E(r)\, E(r+l)] \rangle \sim C(l)$
- **Correlation length**: $C(l) \sim \exp(-l/l_0)$; $l_0 = 2\,\Omega^2 / (1-\Omega)^2$

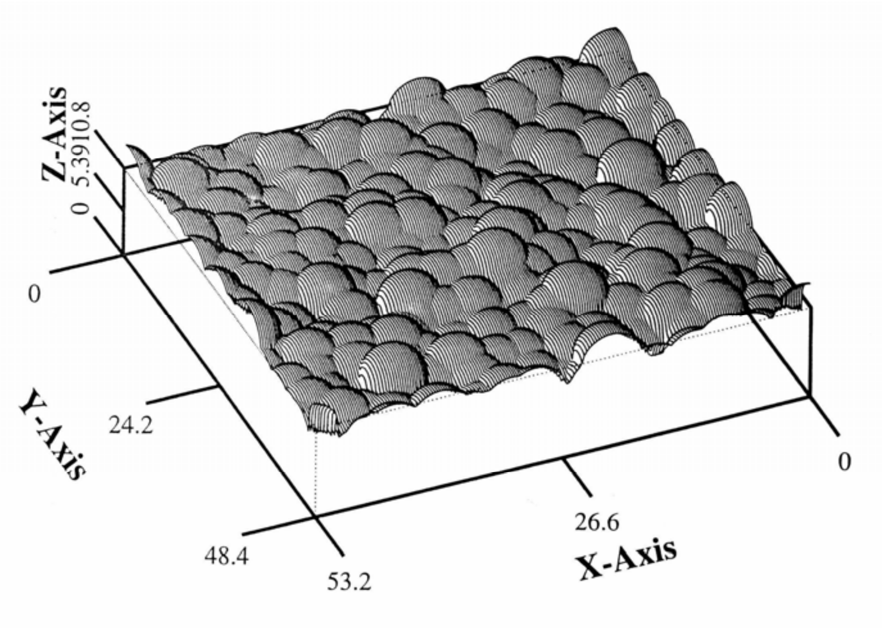
ADSORPTION ISOTHERM

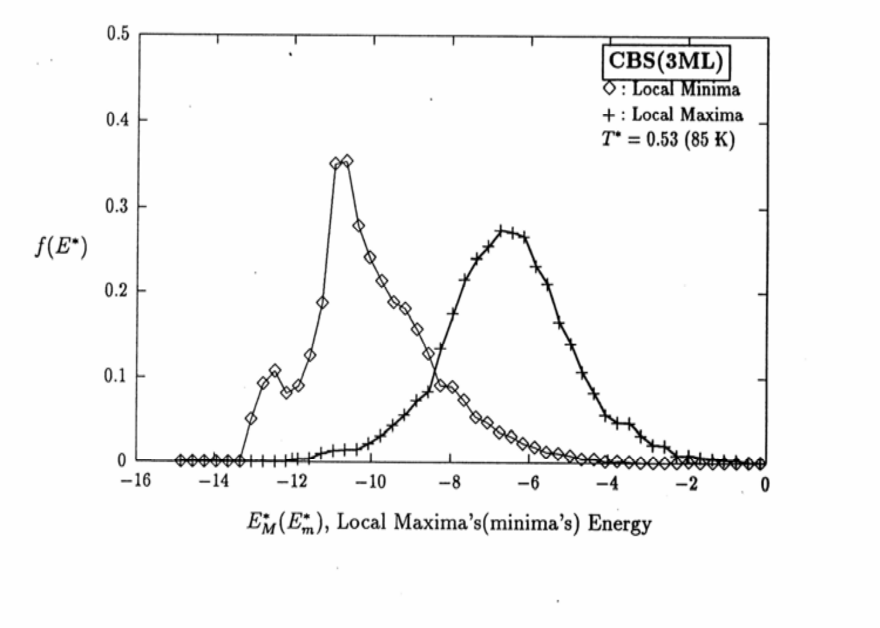
$$\theta(\mu,T)=\int\theta_L(E_{S_1},E_{S_2},\mu,T)\; f_2(E_{S_1},E_{S_2})\,dE_{S_1}\,dE_{S_2}$$

$$f_2(E_{S_1},E_{S_2})=F_S(E_{S_1})\,F_S(E_{S_2})\int F_B(E_B)\,\Phi(E_{S_1},E_B)\,\Phi(E_{S_2},E_B)\,dE_B$$

θ_L is calculated through a mean-field approximation, valid outside of phase transition regions.

MD SIMULATIONS ON TiO_2





Site and Bond distributions arising from Molecular Dinamics simulations of Ar on TiO_2

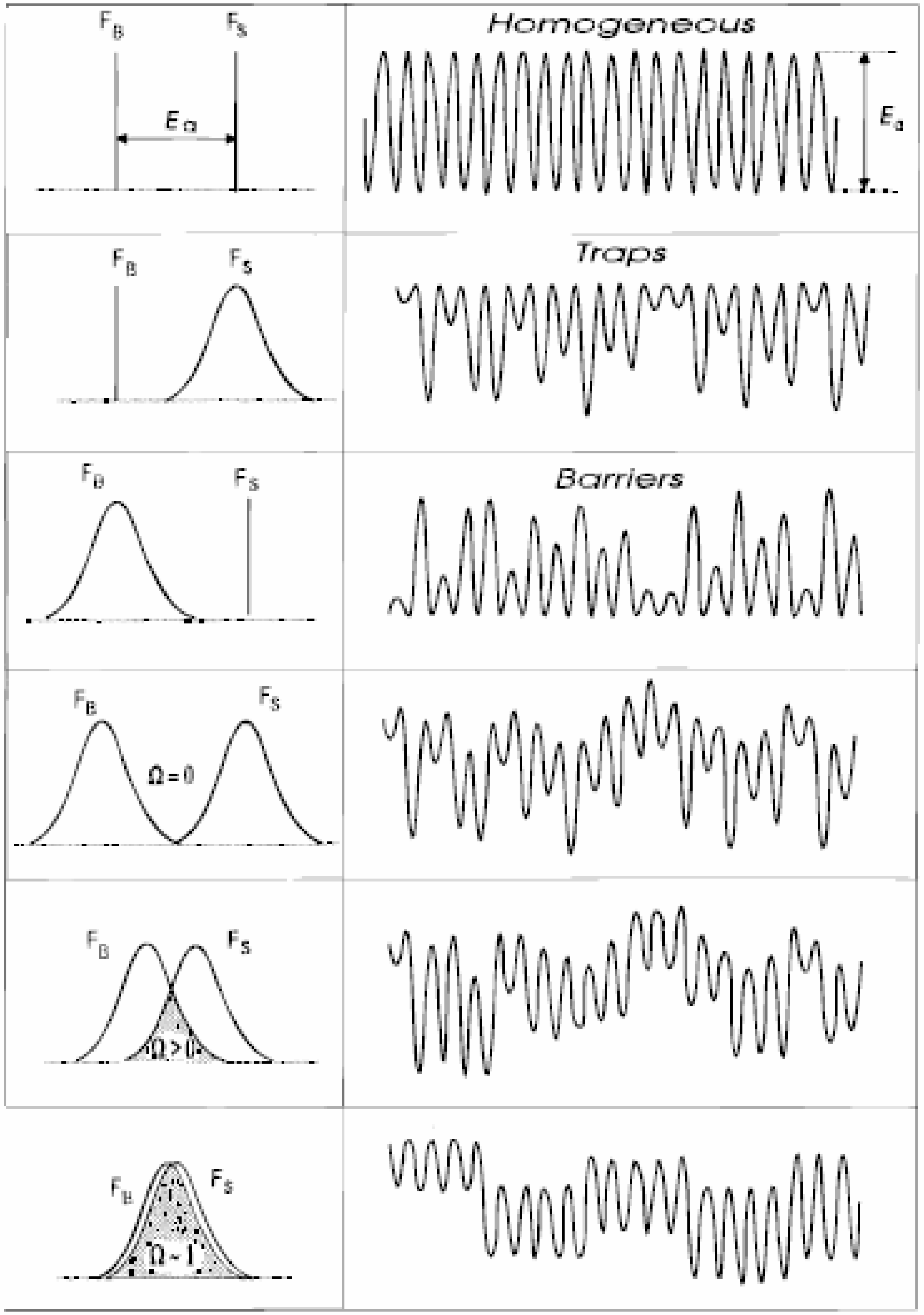
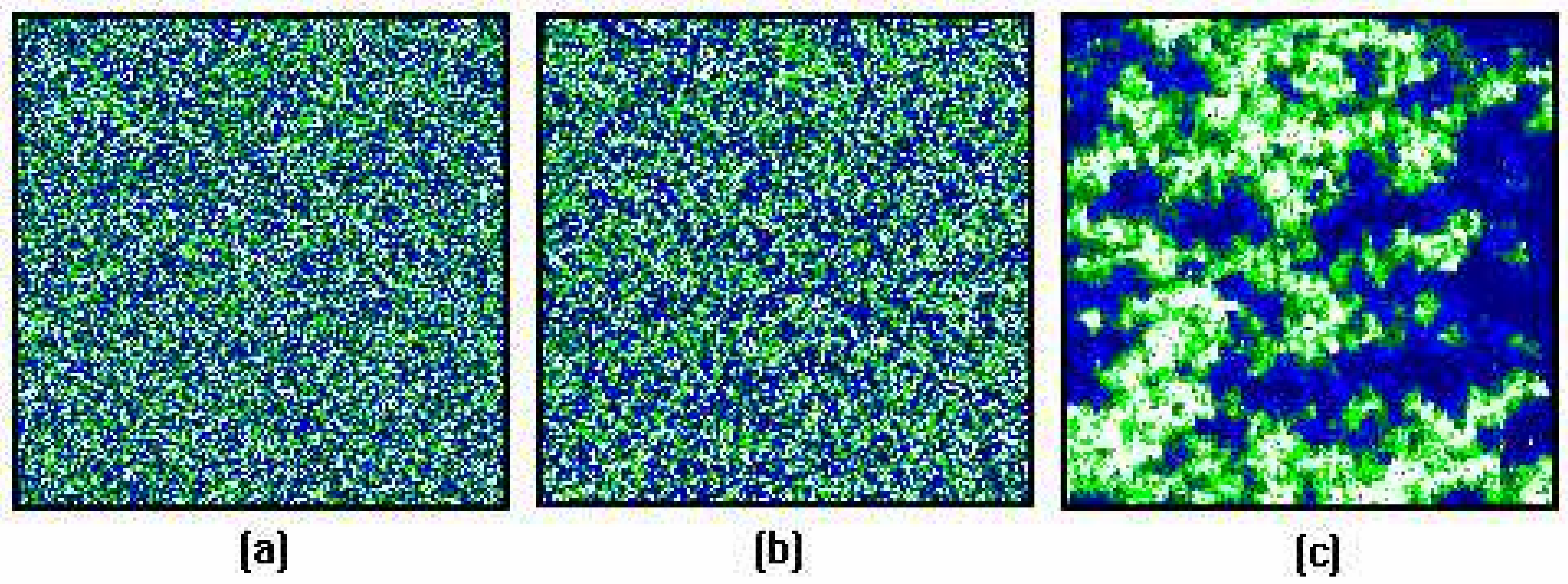


Figure 1. One-dimensional representation of different topographies obtained in the SBM.

THE DSB MODEL TOPOGRAPHY



a) Ω = 0.3; b) Ω = 0.5; c) Ω = 0.8

Site energies are represented by 4 colors, darker colors represent more energetic (stronger) sites

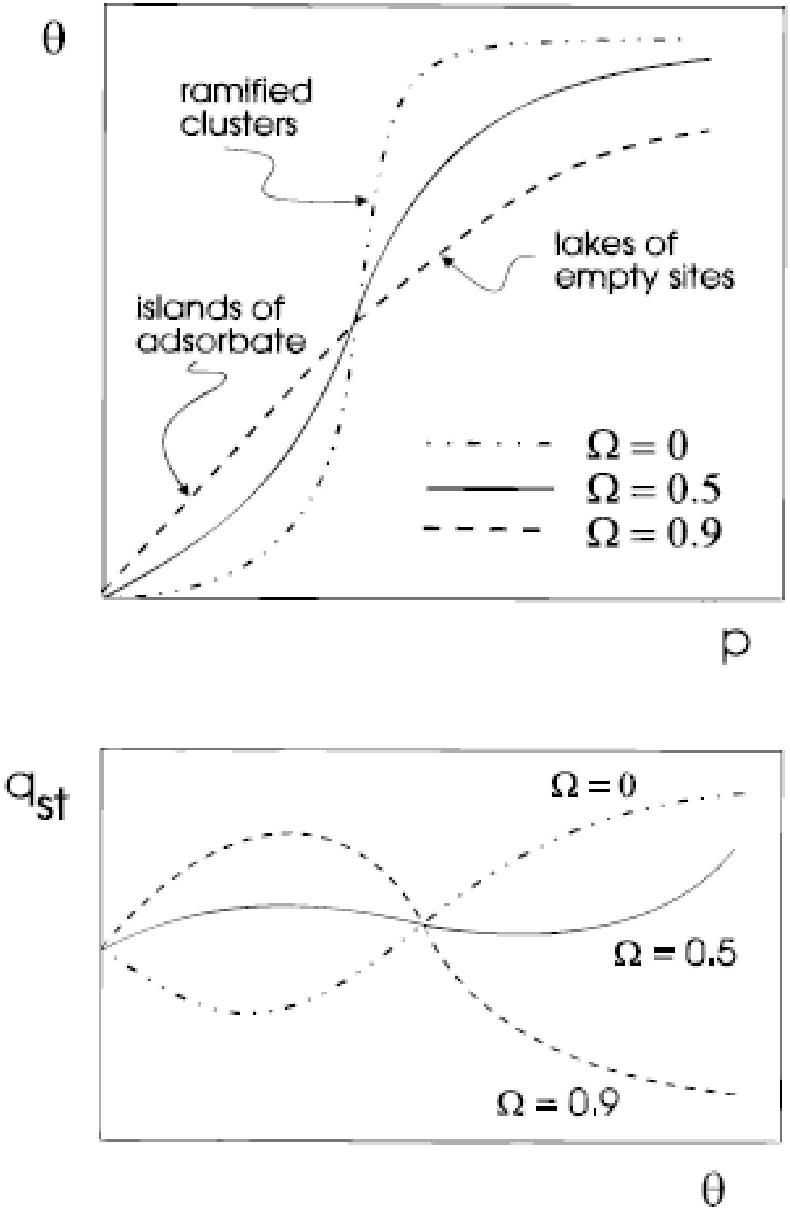


Figure 3. Adsorption isotherm and isosteric heat of adsorption for three surfaces with different topographies. Adsorbate–adsorbate interactions are described by a Lennard-Jones potential. The dimensionless temperature is $kT/U_0 = 1$, where U_0 is the depth of the intermolecular potential.

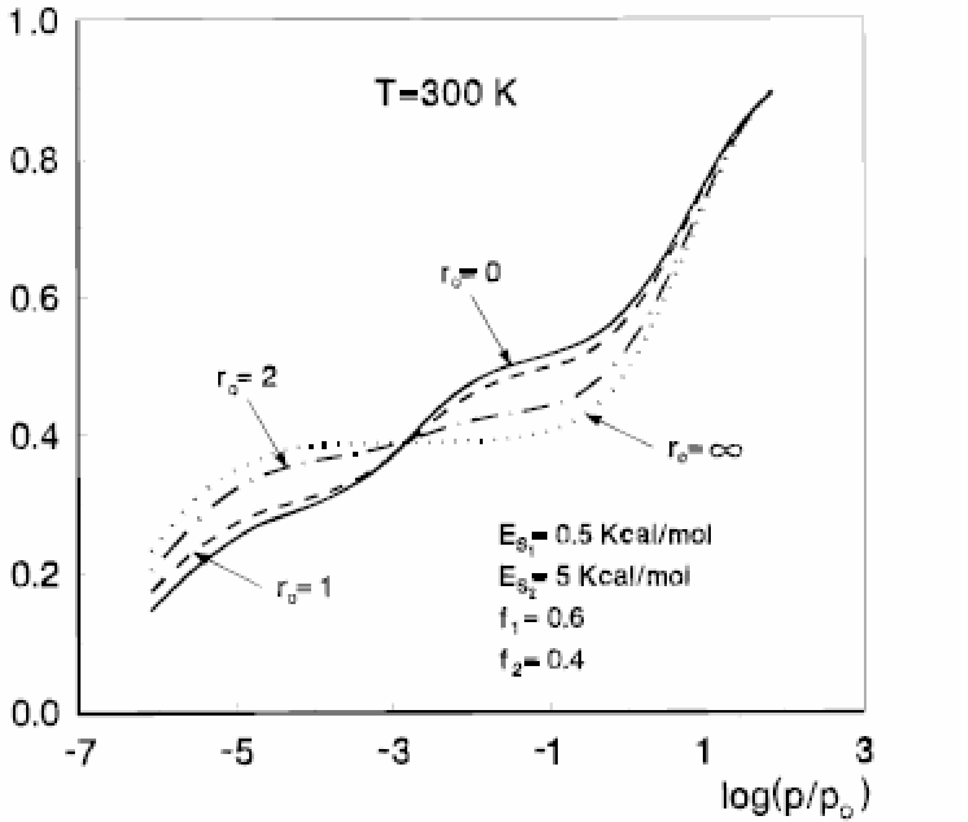


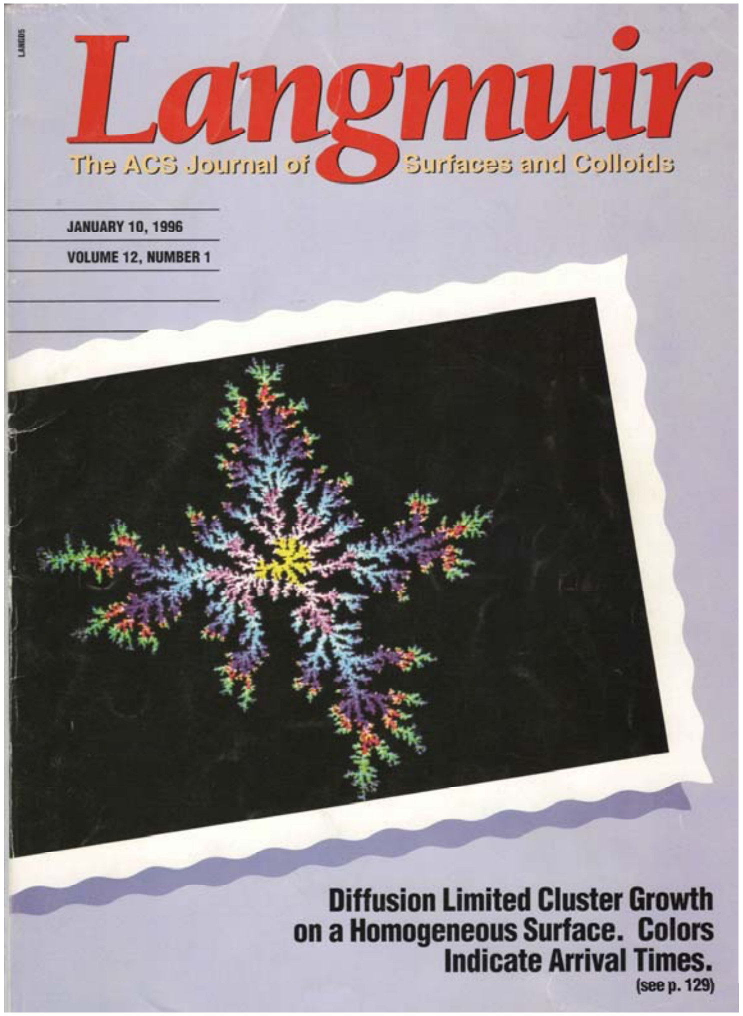
Figure 4. Adsorption isotherms of dimers on surfaces with two kinds of sites S_1 and S_2 with energies E_{S_1} and E_{S_2} forming patches with mean size r_0. Relative abundances of sites are f_1 and f_2, respectively.

TOPOGRAPHY EFFECTS ON ADSORPTION

Molecular Processes on Heterogeneous Solid Surfaces

G. Zgrablich, V. Mayagoitia, F. Rojas, F. Bulnes, A. P. Gonzalez, M.
Nazzarro, V. Pereyra, A. J. Ramirez-Pastor, J. L. Riccardo, and K. Sapag

Langmuir, **1996**, 12 (1), 129-138• DOI: 10.1021/la9408782 • Publication Date (Web): 10 January 1996



Langmuir

The ACS Journal of Surfaces and Colloids

JANUARY 10, 1996

VOLUME 12, NUMBER 1

Diffusion Limited Cluster Growth on a Homogeneous Surface. Colors Indicate Arrival Times.

(see p. 129)

Este trabajo costó muchos asados para tantos autores !!

SURFACE DIFFUSION

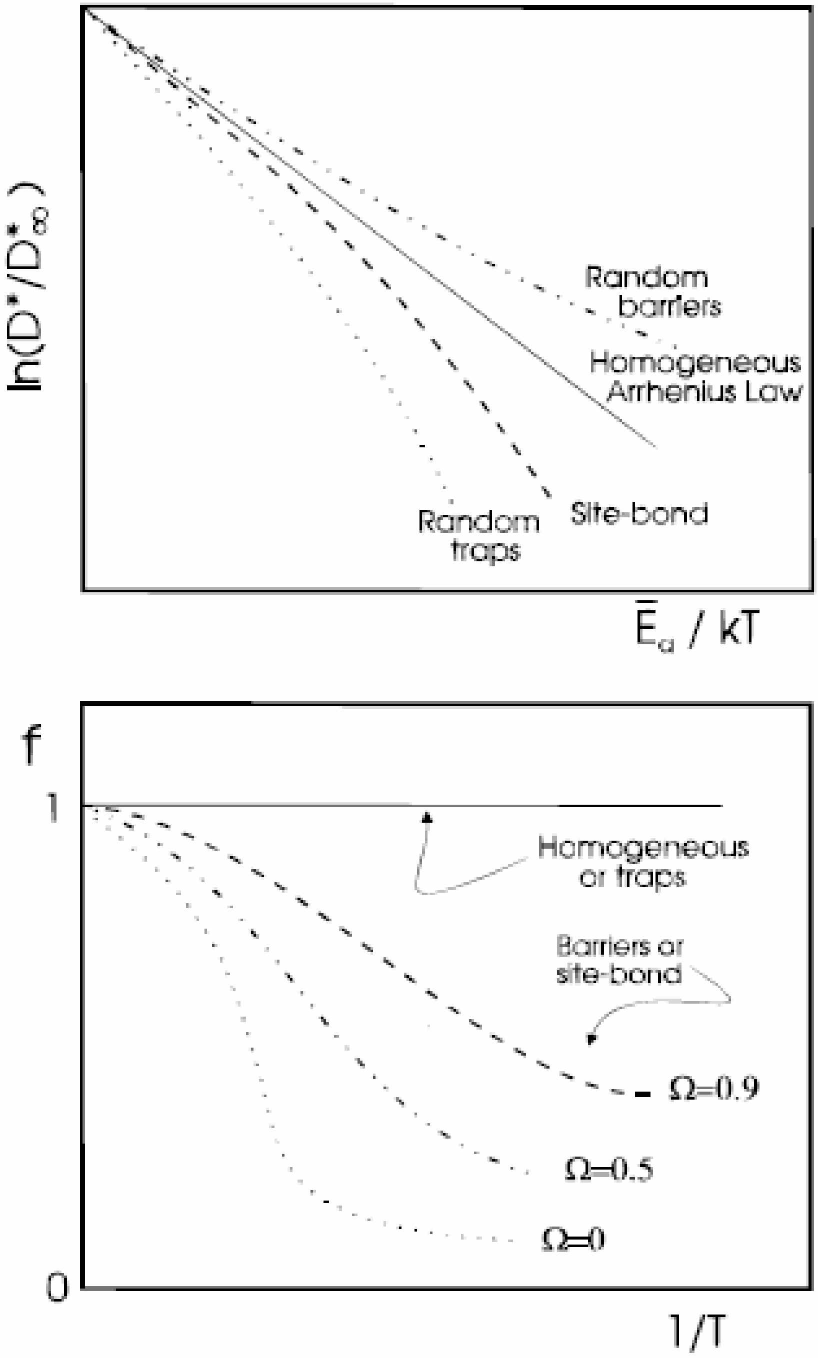
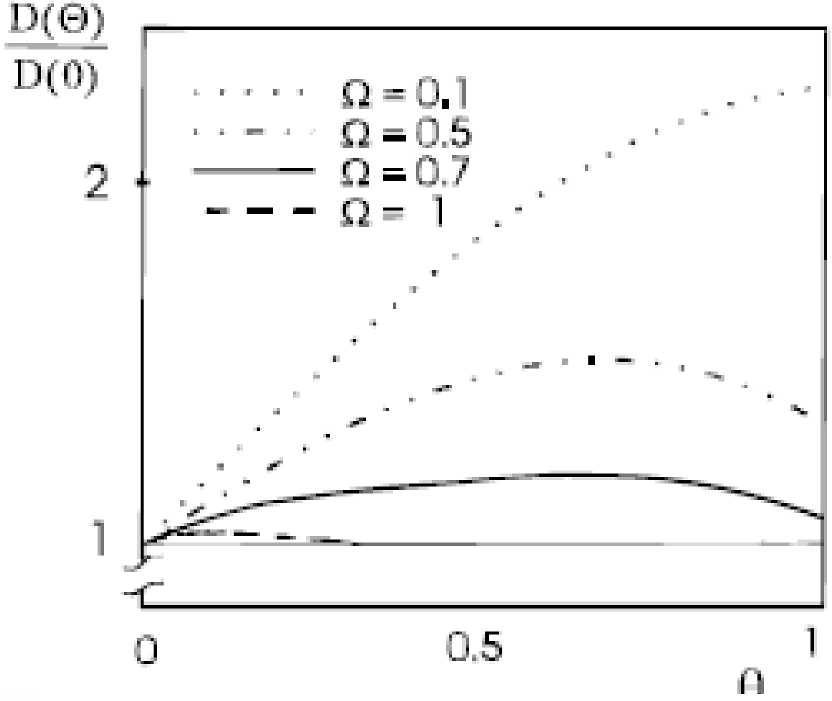


Figure 5. Tracer diffusion coefficient (a) and jump correlation factor (b) for surfaces with different topographies.



Chemical Diffusion Coefficient

ANIQUILATION REEACTION: A+ A→ 0

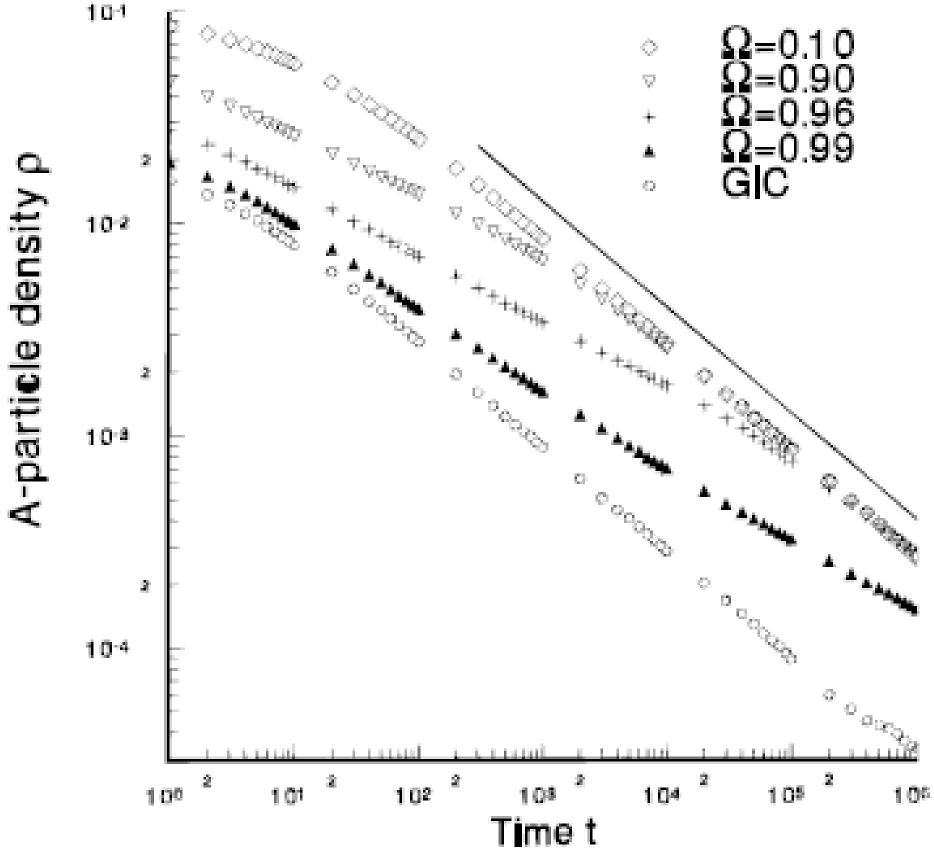
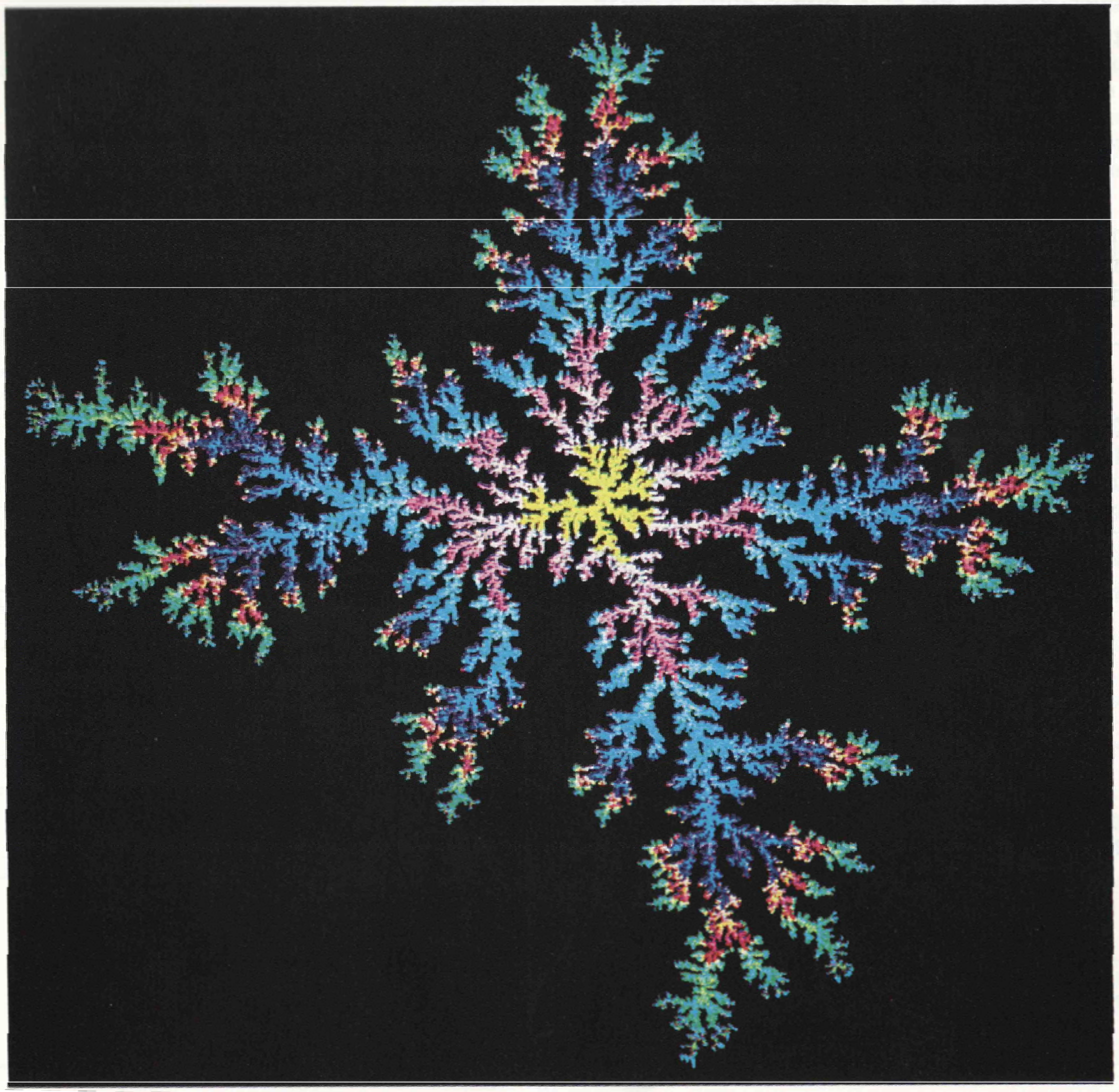


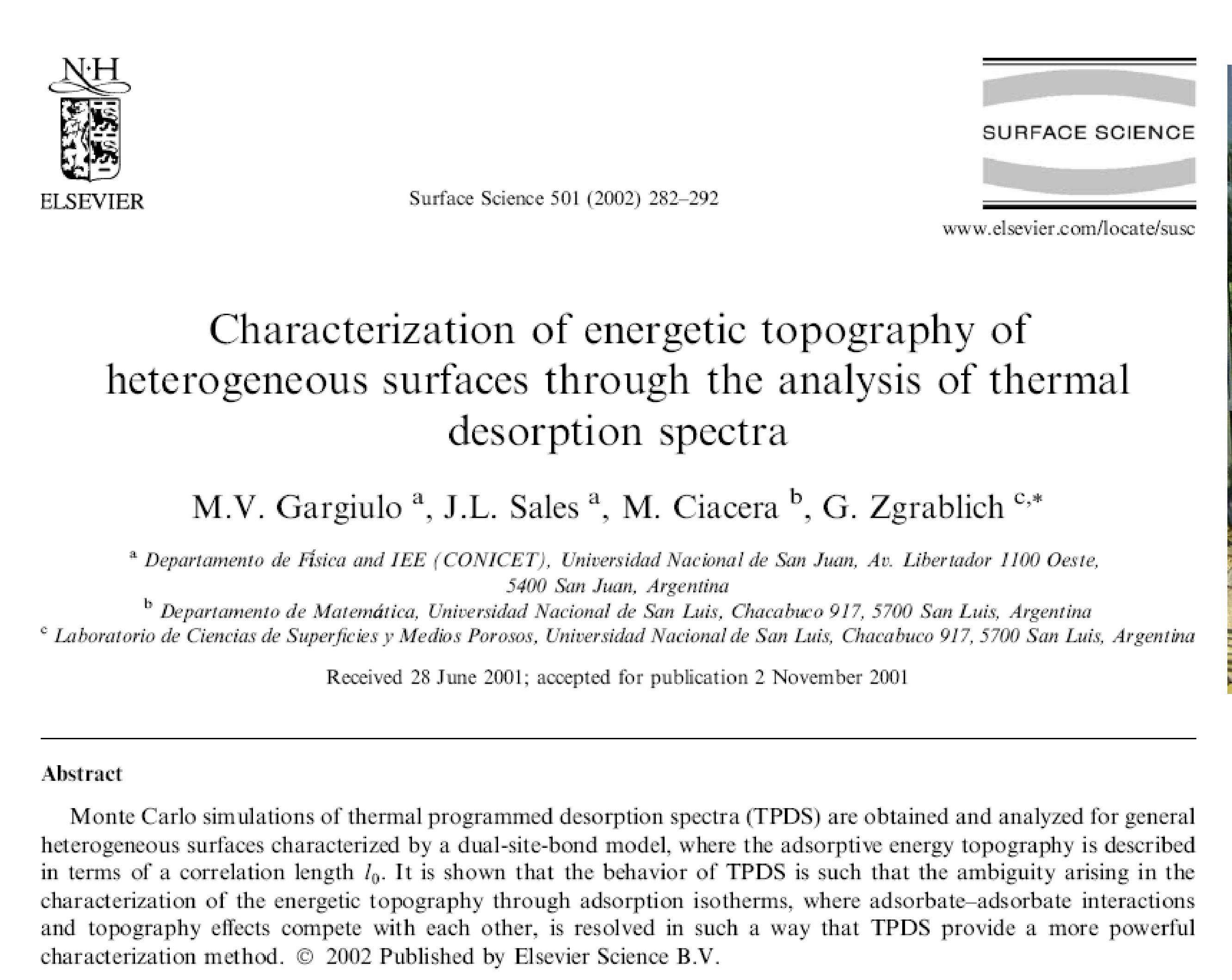
Figure 7. Density of *A* particles as a function of time for surfaces with different topographies.

DIFFUSION LIMITED AGGREGATION (DLA)

FRACTAL DIMENSION DECREASES WITH INCREASING Ω



THERMAL PROGRAMMED DESORPTION (TPD) CAN ALSO BE USED IN THE CHARACTERIZATION OF ENERGETIC TOPOGRAPHY



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Surface Science 501 (2002) 282–292

SURFACE SCIENCE

www.elsevier.com/locate/susc

Characterization of energetic topography of heterogeneous surfaces through the analysis of thermal desorption spectra

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Received 28 June 2001; accepted for publication 2 November 2001

Abstract

Monte Carlo simulations of thermal programmed desorption spectra (TPDS) are obtained and analyzed for general heterogeneous surfaces characterized by a dual-site-bond model, where the adsorptive energy topography is described in terms of a correlation length l_0. It is shown that the behavior of TPDS is such that the ambiguity arising in the characterization of the energetic topography through adsorption isotherms, where adsorbate–adsorbate interactions and topography effects compete with each other, is resolved in such a way that TPDS provide a more powerful characterization method. © 2002 Published by Elsevier Science B.V.

La rama Sanjuanina

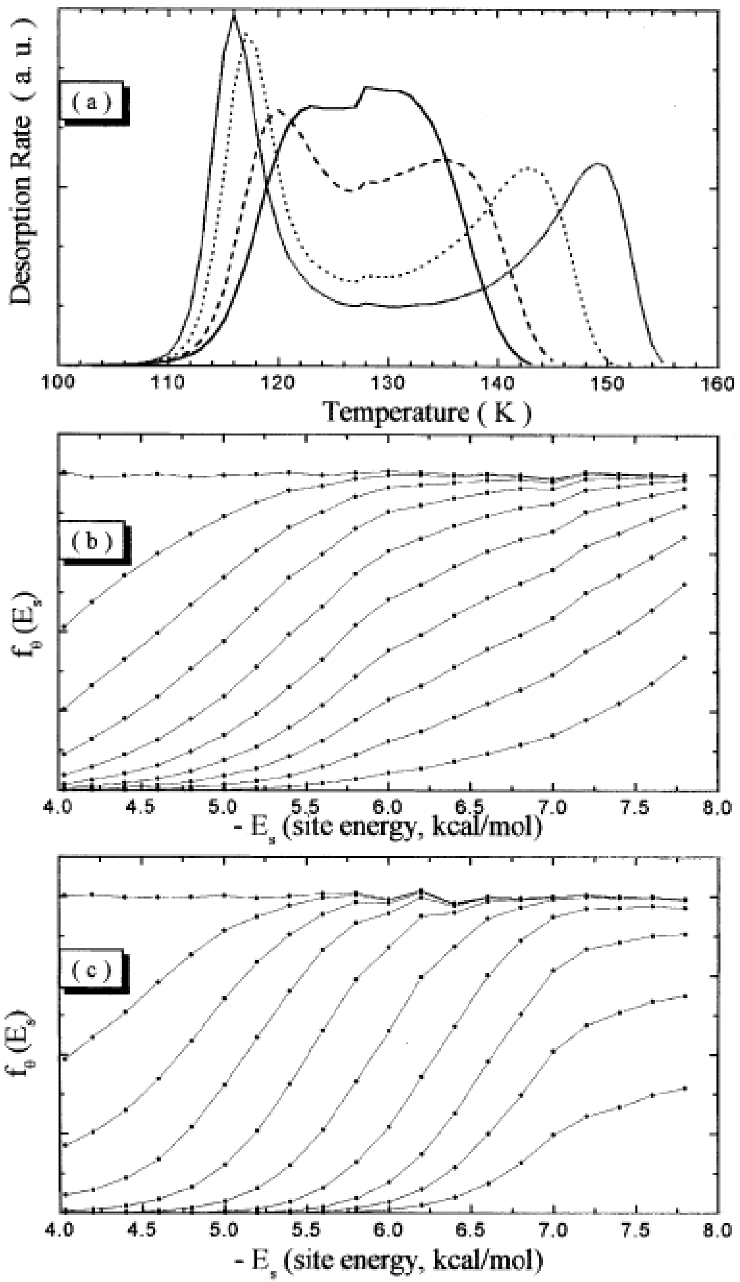

Fig. 2. Attractive interaction energies: $w_1 = w_2 = -0.5$ Kcal/mol. (a) TPD spectra for different values of Ω: (—) $\Omega = 0.5$, (– – –) $\Omega = 0.6$, (- - -) $\Omega = 0.7$, (···) $\Omega = 0.8$. (b) and (c) energy distribution of occupied sites at different coverages for $\Omega = 0.5$ and $\Omega = 0.8$, respectively: coverage ranges from 1.0 (top) to 0.1

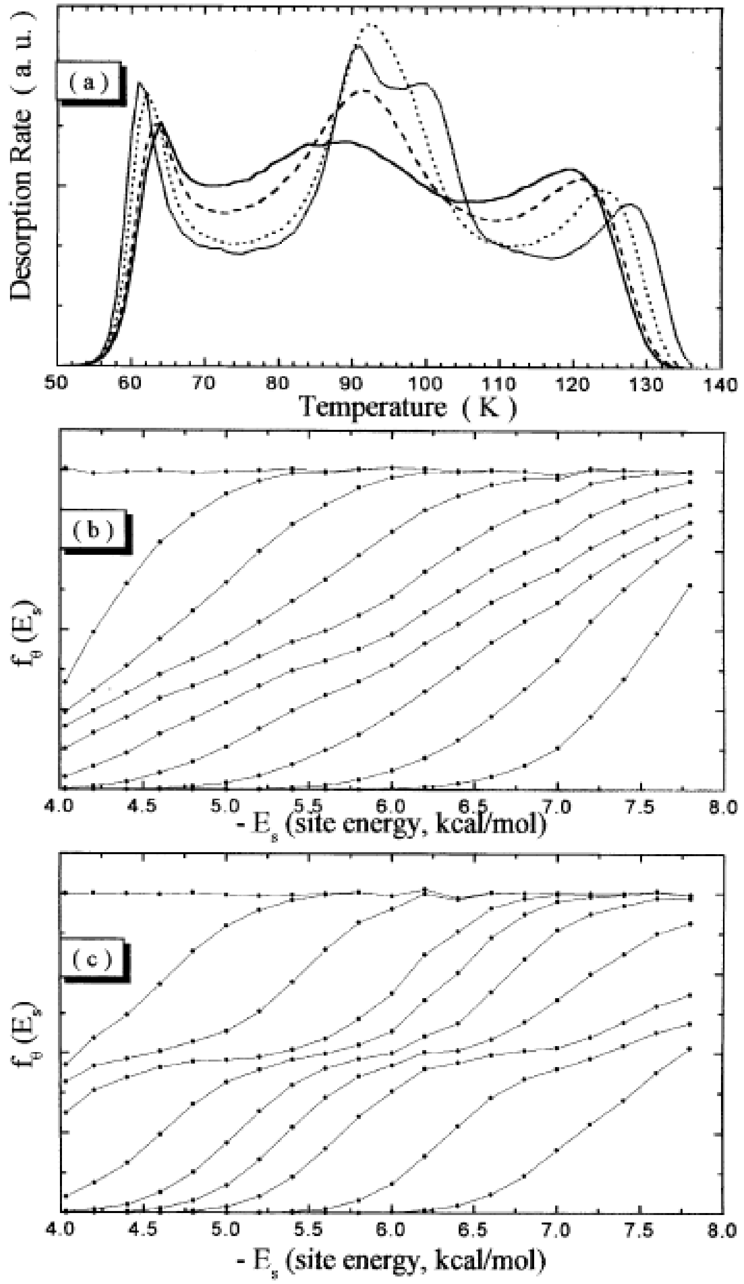

Fig. 3. The same as Fig. 2 for mixed interaction energies: $w_1 = +0.5$ Kcal/mol, $w_2 = -0.5$ Kcal/mol.

PATCHWISE APPROACH

JOURNAL OF CHEMICAL PHYSICS VOLUME 115, NUMBER 3 15 JULY 2001

Scaling behavior in adsorption on bivariate surfaces and the determination of energetic topography

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(Received 5 October 2000; accepted 26 April 2001)

Adsorption of particles with repulsive nearest-neighbor interactions is studied through Monte Carlo simulation on bivariate surfaces characterized by patches of weak and strong adsorbing sites of size l. Patches can be either arranged in a deterministic chessboard structure or in a random way. Quantities are identified which scale obeying power laws as a function of the scale length l. Consequences of this finding are discussed for the determination of the energetic topography of the

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PCCP

Temperature dependence of scaling laws in adsorption on bivariate surfaces

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PCCP

Temperature dependence of scaling laws in adsorption on bivariate surfaces

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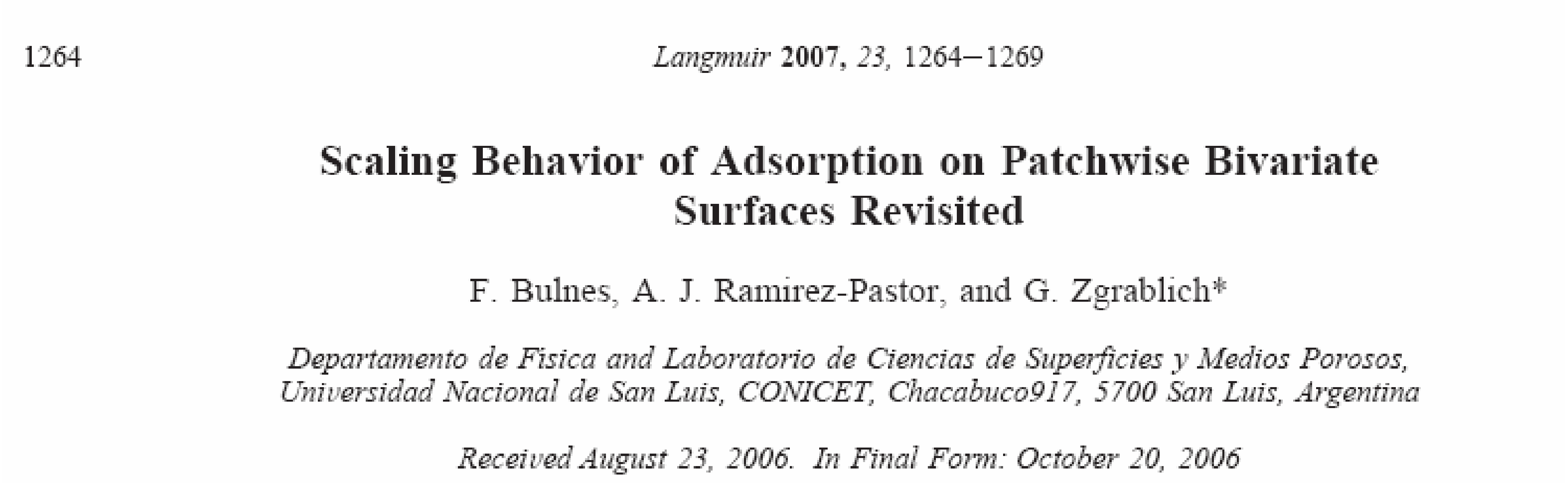

1264 *Langmuir* **2007**, *23*, 1264–1269

Scaling Behavior of Adsorption on Patchwise Bivariate Surfaces Revisited

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Received August 23, 2006. In Final Form: October 20, 2006

Los autores tomando un merecido descanso

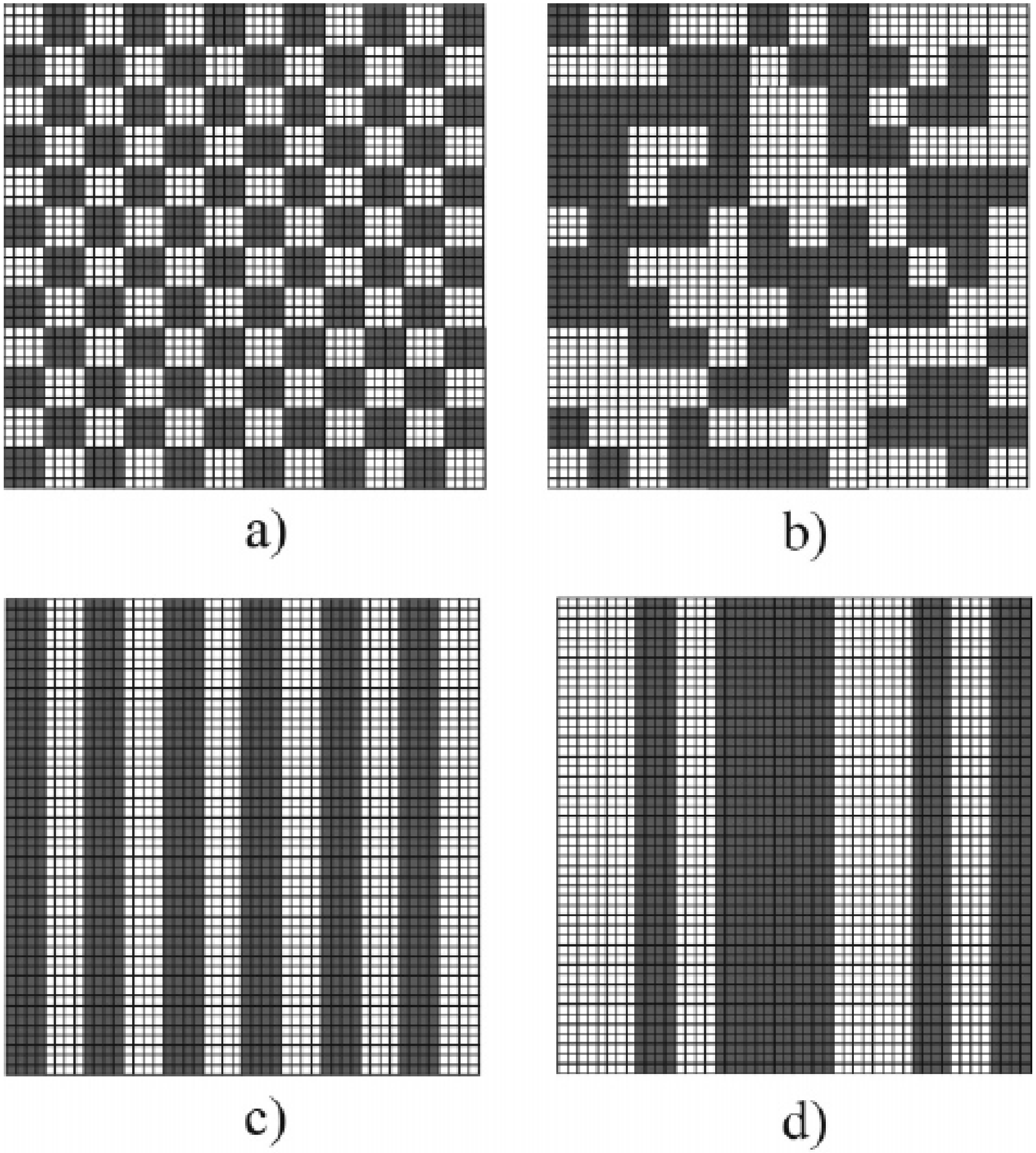


Figure 1. Schematic representation of heterogeneous bivariate surfaces with chessboard (a), random square patches (b), ordered strips (c), and random strips (d) topography. The patch size in the figure is $l = 4$.

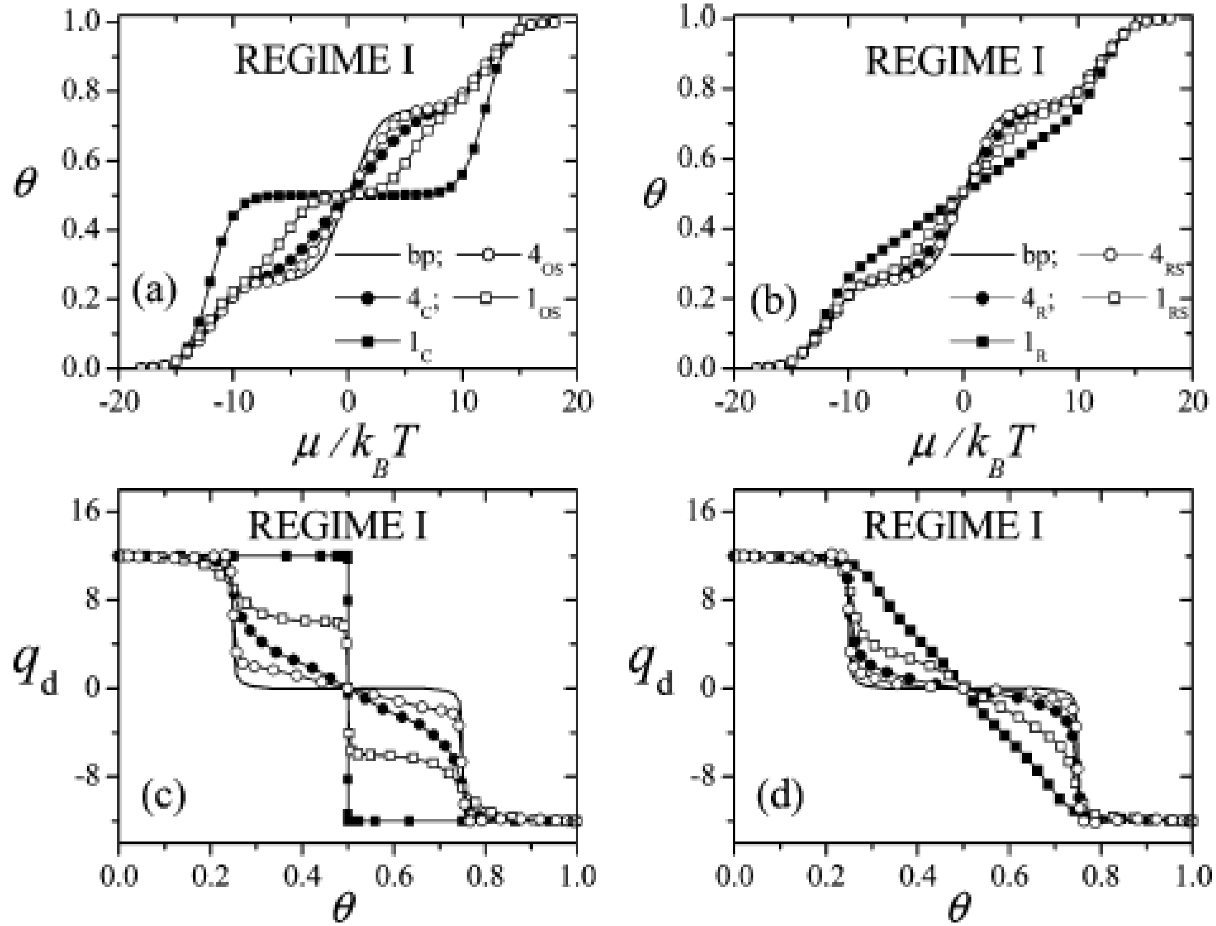


Figure 2. Adsorption isotherms (a−b) and differential heats of adsorption (c−d) for different square patch topographies corresponding to Regime I (in this case $\Delta E = 12$, $w = 3$). Symbols in (c) and (d) are as in (a) and (b), respectively.

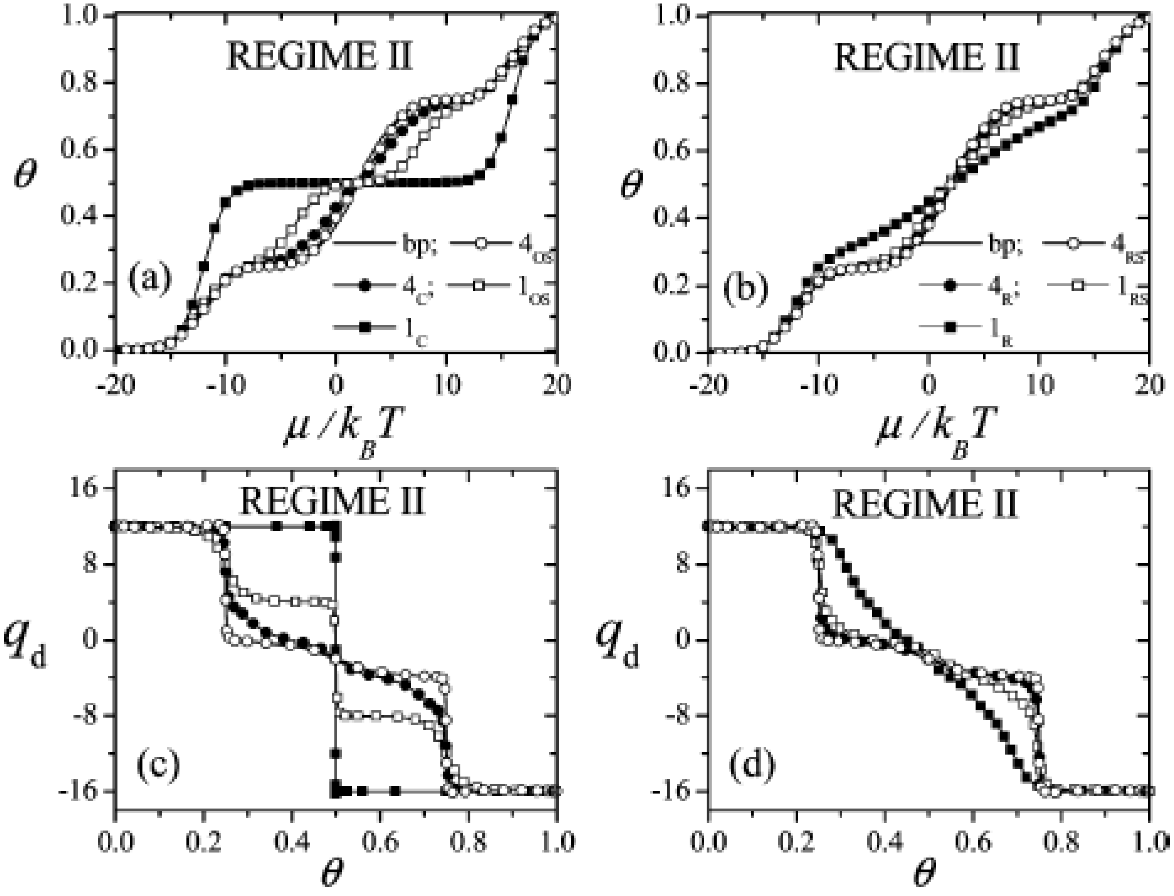


Figure 3. Adsorption isotherms (a−b) and differential heats of adsorption (c−d) for different square patch topographies corresponding to Regime II (in this case $\Delta E = 12$, $w = 4$). Symbols in (c) and (d) are as in (a) and (b), respectively.

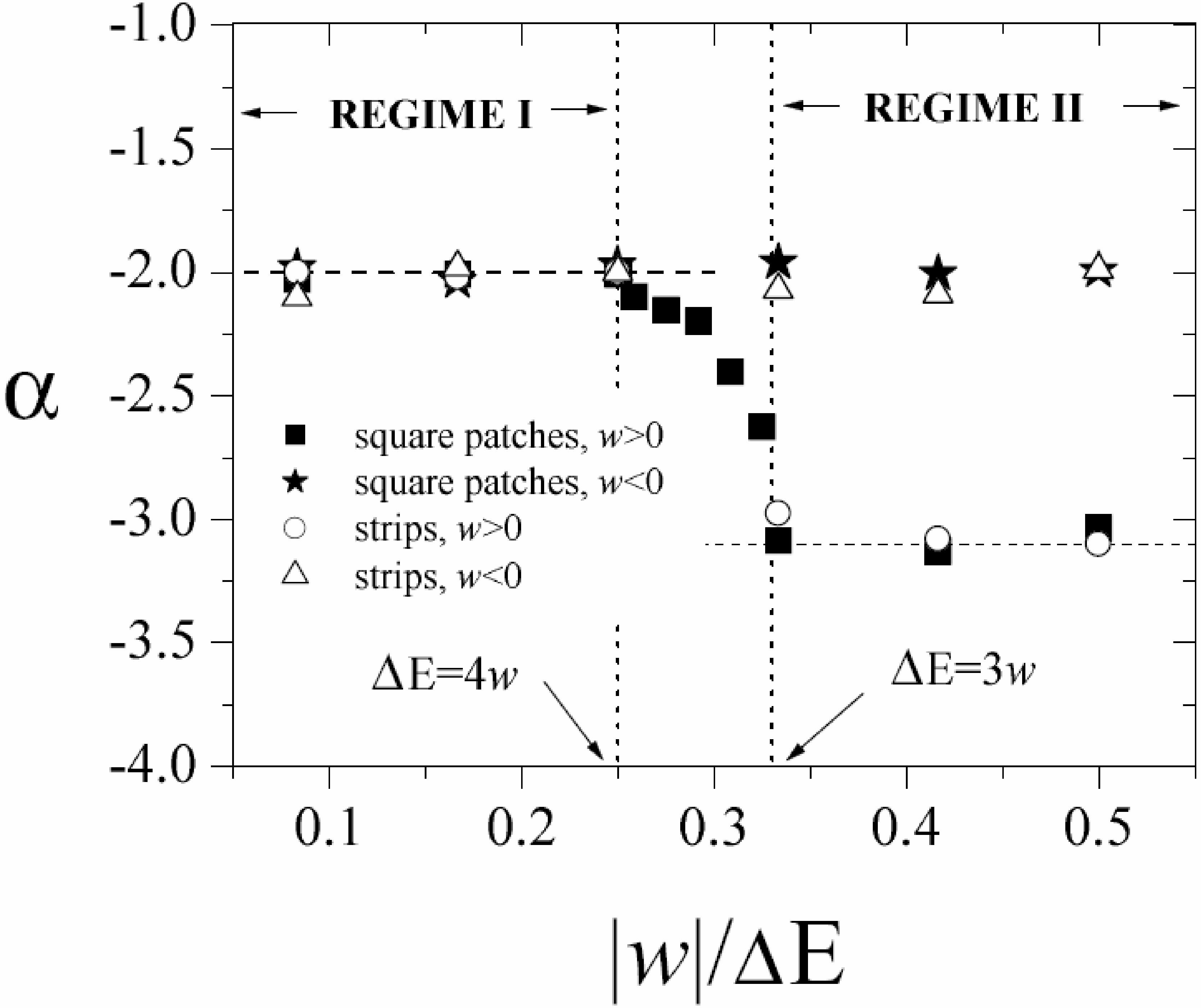
UNIVERSAL SCALING LAW

$$\chi_{\mathrm{a}} = \int_{-\infty}^{+\infty} |\theta(\mu) - \theta^{\mathrm{R}}(\mu)|^2 \, \mathrm{d}\mu$$

$$\ln \chi = \mathrm{const} + \alpha \ln l_{\mathrm{eff}}$$

$$l_{\mathrm{eff}} = \sigma l$$

α presents *universality properties*.



REGIME I
REGIME II
α
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
0.1
0.2
0.3
0.4
0.5
|w|/ΔE
■ square patches, w>0
★ square patches, w<0
○ strips, w>0
△ strips, w<0
ΔE=4w
ΔE=3w

CONCLUSIONS


Aquí hace falta un poco de seriedad académica !!

- **Continuum approach**: virial expansion limited to low adsorbate density, 4 fitting parameters.
- **Lattice-Gas approach**: mean field approximation valid outside phase transitions, 5 or 6 fitting parameters.
- **Patchwise approach**: promising, but must be extended to multivariate surfaces. No fitting parameters ?

AL FIN! YA PODEMOS DEDICARNOS A HACER SOCIALES!