COMPUTER SIMULATION OF THE DIFFUSION BEHAVIOR OF AN ORDERED ADSORBATE

MASTER

by

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Prepared for

International Conference

on

Ordering in Two Dimensions

Lake Geneva, Wisconsin

May 28-30, 1980

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

U of C-AUA-USDOE

Operated under Contract W-31-109-Eng-38 for the

U. S. DEPARTMENT OF ENERGY

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COMPUTER SIMULATION OF THE DIFFUSION BEHAVIOR
OF AN ORDERED ADSORBATE

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ABSTRACT

This paper reports on new Monte Carlo results for the "chemical" diffusivity of an
ordered adsorbate. The model used is the square planar lattice gas with repulsive
nearest neighbor interactions and attractive next nearest neighbor interactions.
The simulation is based on the recently formulated rigorous Darken equation.
Within the ordered c (2 x 2) region a strong maximum in the diffusivity as a
function of coverage is observed. It is demonstrated that this maximum is a direct
consequence of the large gradient in the adsorption isotherm within the ordered
region.

INTRODUCTION

It has been usual for many properties of
chemisorbed species on metal surfaces to be
discussed in the light of the lattice gas model.
This model is valid to the extent that
adsorption occurs at particular localized sites
relative to the substrate atoms and that
magnetic and dipole-dipole, etc., interactions
are negligible. Recently, the diffusivity of an
adsorbed species (O on W {110}) has been studied
as a function of coverage at temperatures less
than desorption temperatures [1,2]. This work
inspired Bowker and King [3] to make a Monte
Carlo study of a lattice gas in order to
investigate specifically the effect of lateral
interactions on the diffusion behavior. Using
experimentally derived nearest and next nearest
neighbor interaction energies [4], Bowker and
King were able to demonstrate semiquantitatively
the experimentally observed strong maximum in
the diffusivity as a function of coverage [1,2].
We should note, however, that good agreement
should not necessarily be expected since the
simulation study was in a square planar lattice
while the lattice gas appropriate to O on W
{110} should be triangular with anisotropic
interactions. More importantly, however, the
simulation was not sufficiently transparent for
any insight to be made into the atomistic
reasons for the maximum except that it was
reported to be associated with ordering.

In view of the importance of the result for
other adsorption systems and the development
of a theory of diffusion in ordered structures,
two dimensional or otherwise, we have
undertaken a new Monte Carlo study on the same
model that Bowker and King have employed. The
nature of our method, in which the diffusivity
is built up from its component parts, permits
valuable insight to be made into the reason for
the maximum in the diffusivity.

THEORY

The Lattice Gas

We consider a lattice gas of N adsorbed species
on B lattice sites where the coverage, θ, is
defined by N/B. Introducing the index i for
the labeling of lattice sites and a local
occupation number c_i such that $c_i = 1$ if the

site is occupied and $c_i = 0$ if vacant, we may also designate the coverage by $\theta = \langle c_i \rangle$. We may write down the Hamiltonian of the lattice gas in the following general way [5]:

$$\mathcal{H} = \sum_{i \neq j} c_i c_j \phi(r_i - r_j) + \sum_i \varepsilon_i c_i + \mathcal{H}_o \qquad (1)$$

where ϕ denotes lateral interactions between adatoms, ε_i represents the binding force between the adatom and the substrate, and $\mathcal{H}_o$ represents separable contributions from lattice vibrations of the adsorbed layer, etc. For the case of the square planar lattice gas with nearest neighbor (nn) repulsive interactions and next nearest neighbor (nnn) attractive interactions, one generates a phase diagram with an ordered structure c (2 x 2) centered around $\theta = 0.5$ and two two-phase regions at lower temperatures, see [5].

With these interaction conditions and writing, $c_i = (1 + s_i)/2$; where s_i denotes a spin, we may transform to an Ising model [5]:

$$\mathcal{H} = - \sum_{i \neq j} J_{nn} s_i s_j - \sum_{i \neq j} J_{nnn} s_i s_j - H \sum_i s_i + \mathcal{H}_o' \qquad (2)$$

where $J(r_i - r_j) = -\frac{1}{4} \phi(r_i - r_j)$

and $H(r_i) = -\frac{1}{2} \sum \varepsilon_i + \sum_{j \neq i} \phi(r_i - r_j)$

where H is the imposed magnetic field and J is the exchange coupling between spins. The zero field critical temperature, i.e. at $\theta = 0.5$, for this Ising model has been obtained in an accurate [6] approximate solution by Fan and Wu [7]. They write for the critical condition in the square planar lattice:

$$\exp(|J_{nn}|/kT_c) = \sqrt{2} \exp(-2J_{nnn}/kT_c)$$

$$+ \exp(-4J_{nnn}/kT_c) \qquad (3)$$

where T_c is the critical temperature (at $\theta = 0.5$). Now, in their simulation Bowker and King used values of 14.4 kJ mol^{-1} for the nn repulsion interaction and 6.7 kJ mol^{-1} for the

nnn attraction interaction with a temperature of 1153 K. These parameters lead to $T_c = 1615$ K. Thus, the ordered region is indeed entered during the simulation.

Diffusion

We are interested in the calculation of the intrinsic diffusivity, D^i, which is synonymous with the chemical diffusivity, $\tilde{D}$, for the one component lattice gas.

$$D^i = \tilde{D} = - J\left(\frac{d\theta}{dx}\right)^{-1} \tag{4}$$

where J is the diffusive flux and x is the distance. There are three simulation methods available to calculate $\tilde{D}$. The first, an non-steady state method [8], provides a direct means for calculating $\tilde{D}$ from concentration profiles. But this method is prone to statistical uncertainty. The second method makes use of a steady-state technique [9] and is considerably more precise. But both these methods give no real insight into the detailed makeup of $\tilde{D}$. In the third method, however, one can make use of the recently formulated rigorous 'Darken' equation for the one component lattice gas [10].

$$\tilde{D} = D \left(\frac{d\ln a}{d\ln\theta}\right) \tag{5}$$

where D is the self diffusivity of unmarked atoms and a is the thermodynamic activity defined by

$$\mu = kT\ln a + \mu^o \tag{6}$$

and the chemical potential, μ by

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{B,T} \tag{7}$$

where A is the configurational free energy.

D is not measurable experimentally itself, but is related to the familiar tracer diffusivity by

$$D = D^* f_I/f \tag{8}$$

where f_I is the physical correlation factor [10-11] and f is the tracer correlation factor. D may be expanded as [12].

$$D = \frac{1}{2} \lambda^2 f_I [\nu z V W \exp(-E°/kT)] \qquad (9)$$

where the adatom jump frequency, [ ] in eqn 9 depends on the surroundings *before* the jump. V is the availability of vacant nn sites to a diffusing atom, $E°_m$ is the diffusion activation energy of an *isolated* atom, λ, ν, and z are the jump distance and vibrational frequency and co-ordination, respectively, and W, the effective frequency factor is of the form

$$W_i = \exp[(4Z^i_{nn} J_{nn} + 4Z^i_{nnn} J_{nnn})/kT)] \quad V_i \neq 0 \quad (10)$$

and Z^i is the number of occupied neighboring sites around an atom i which is in a position to jump.

In a lattice gas treatment where hopping-like motion is assumed, it is sufficient to calculate V, W, f_I and $d\ln a/d\ln\theta$ in order to access $\tilde{D}$ (θ, T). We used an array of 10^4 sites and divided the calculation into two parts. Specifying J_{nn}, J_{nnn}, and T, we attained equilibrium with the grand canonical ensemble and calculated $V(\theta,T)$, $W(\theta,T)$, and $\mu(\theta,T)$ (the latter is trivially known in this ensemble) by averaging over 10^5 configurations. Then we switched to the petit canonical ensemble in order to calculate f_I for 100 steps per atom [13]. Further details are described elsewhere [14].

RESULTS

In Fig. 1 we display the μ/θ isotherm at 1153 K. We have denoted the entry and exit (second order transitions [14]) to the ordered, c (2 x 2) phase by arrows. We note in particular the very steep rise of the isotherm within the ordered region. We will return to this observation below.

For reasons of space, we do not present detailed results for V, W, and f_I. They will be discussed elsewhere [14]. Our results for $\tilde{D}$ (normalized to unity) after numerical

differentiation of the μ/θ isotherm are shown in
Fig. 2. There is only a rather superficial
resemblance with the results of Bowker and King
[3]. But the rather large statistical
uncertainty in their work, coupled with the
unlikelihood of generating well-behaved
concentration profiles within the ordered
region, probably accounts for any discrepancy.
We note in particular that when $\theta \to 1$, then
$f_I \to 1$, $V \to (1-\theta)$, $d\ln a/d\ln\theta \to (1-\theta)^{-1}$ and
$\tilde{D} \to W$ $(\theta=1)$. This is verified in our work, but
while Bowker and King do not examine coverages
> 0.9, the terminal point just mentioned seems
unlikely to be obtained on the basis of any
reasonable extrapolation.

It is clear that the maximum in $\tilde{D}$ is associated
with the ordered region. The dotted line in
Fig. 2 was obtained by substituting $(1-\theta)^{-1}$,
i.e. the *ideal* mixing case instead of the
derivative of Fig. 1. We see now that the
maximum completely disappears. This implies
that the maximum is dictated only by the very
sharp rise in the μ/θ isotherm within the
ordered region. That is to say, the ordered
region provides a very large thermodynamic
driving force over and above that for random
mixing alone.

For reference purposes, $\tilde{D}$, for the assumption of
ideal mixing, is given by the dashed line in
Fig. 2. In this case, $V = 1-\theta$, $W = 1$, $f_I = 1$,
and $d\ln a/d\ln\theta = (1-\theta)^{-1}$ and $\tilde{D}$ is accordingly
independent of coverage.

As we pointed out above, the present study was
intended as an examination of a model system
which permitted direct comparison with another
simulation. Both arrays were square planar,
and, despite the comments of Bowker and King
[3], diffusion in this array is unlikely to
bear more than a passing resemblance to the
undoubtedly *anisotropic* diffusion behavior for
O on W [110]. This should be 'modeled' as a
triangular lattice gas with anisotropic
interactions [4]. Results using our procedure
for that lattice gas will be reported elsewhere
[14].

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FIGURE CAPTIONS

Fig. 1. The adsorption isotherm for the square planar lattice gas with $J_{nnn}/J_{nn} = 0.465$ and $J_{nn} > 0$.

Fig. 2. The chemical diffusivity, $\tilde{D}$, as a function of coverage, θ, for the square planar lattice gas with $J_{nnn}/J_{nn} = 0.465$, $J_{nn} > 0$, and $T/T_c = 0.7136$. Monte Carlo results: ————.
Monte Carlo results with $d\ln a/d\ln\theta$ replaced by $(1-\theta)^{-1}$: ....
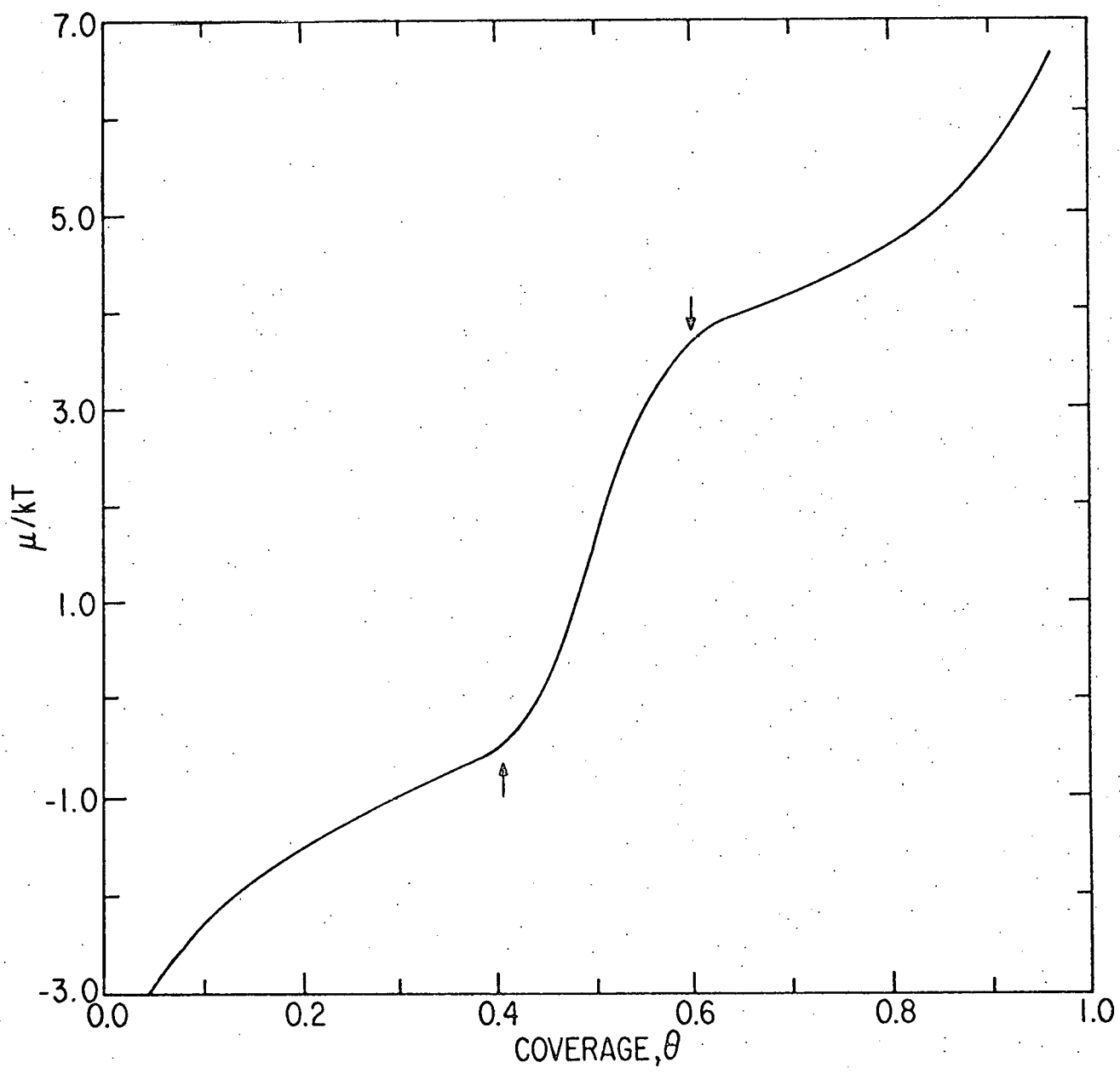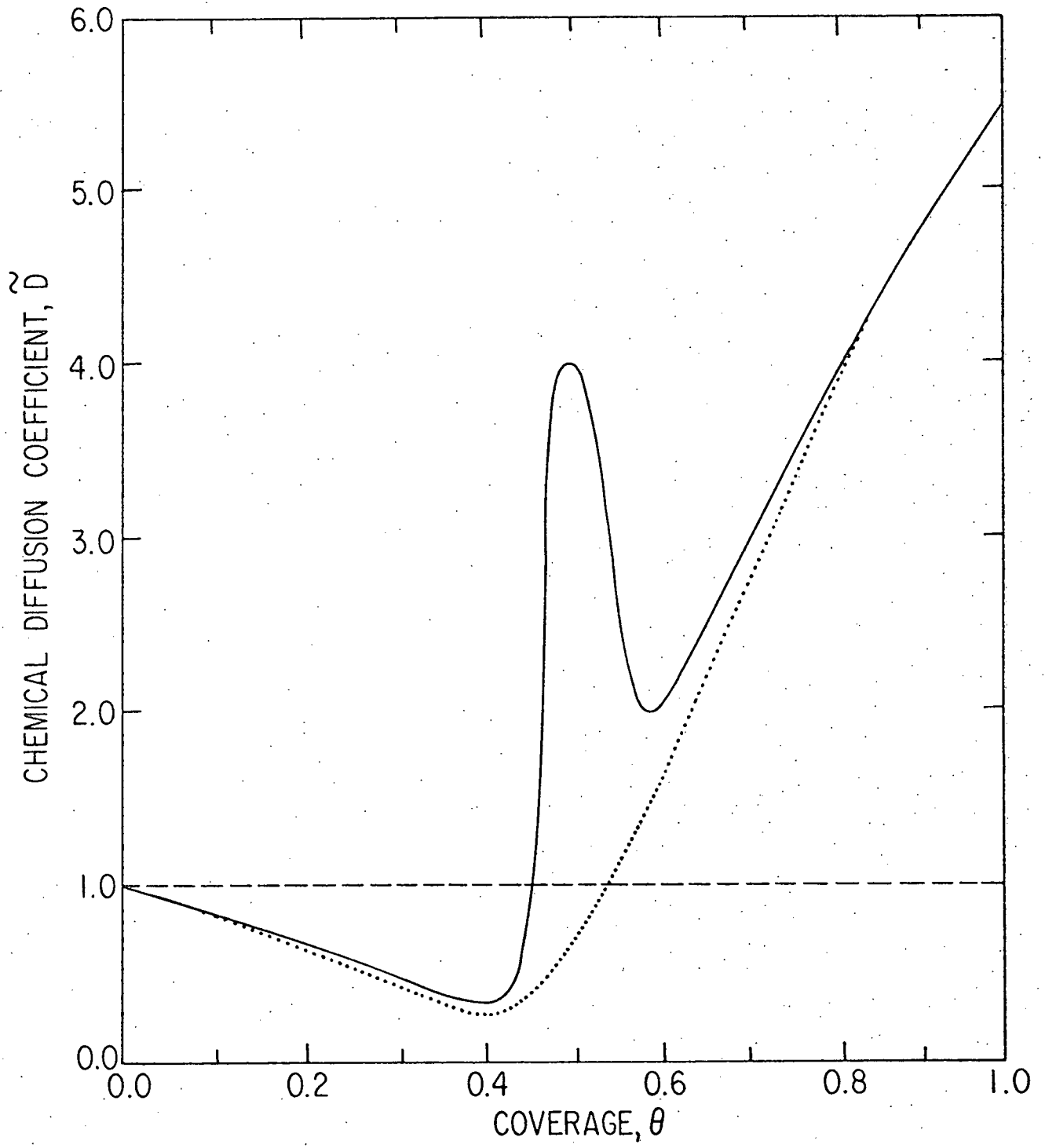Ideal mixing case: — — — —.

Fig 1

Fig 2.