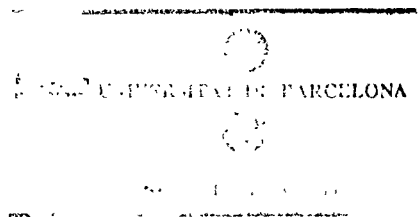


**SIMULACIO MONTE CARLO DE SISTEMES
AMB ACOBLAMENT DE GRAUS DE LLIBERTAT.**



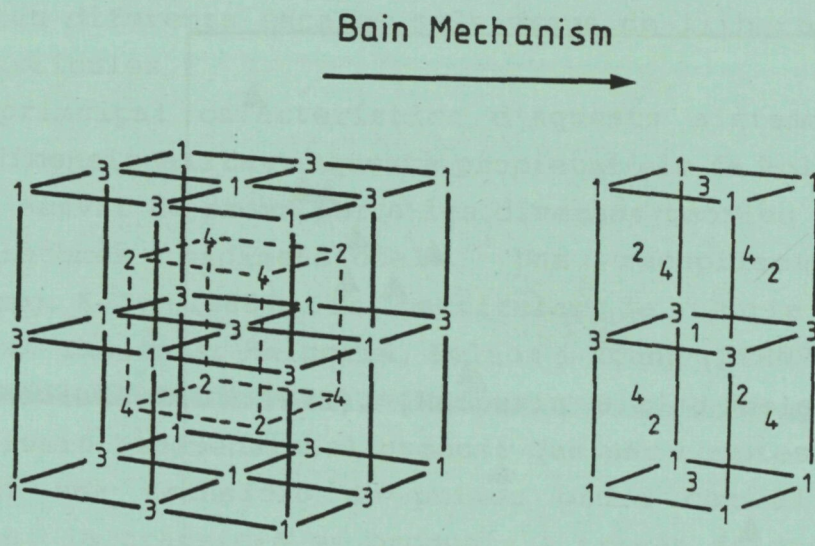


Fig 4. Schematic sublattice representation for the bcc and fcc structures.

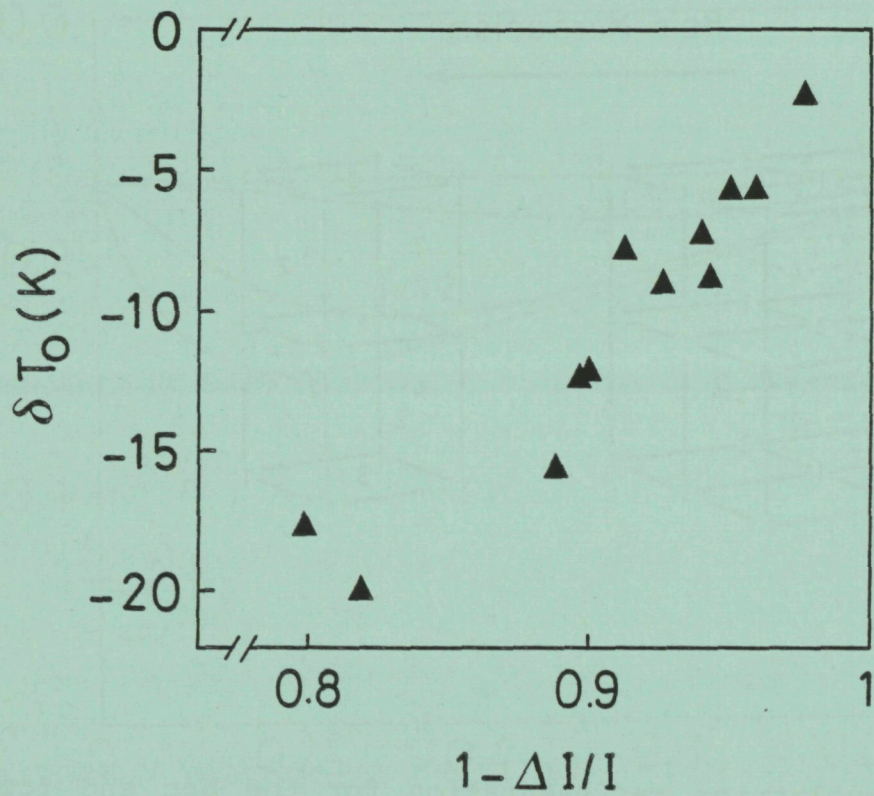


Fig.5 T_0 as a function of $(1 - \Delta I / I)$ for a Cu-16 at% Zn- 16 at% Al alloy. $\Delta I / I$ is the relative change of the X-ray intensity of 111 superlattice reflection.

6. SOLIDS I LIQUIDS SOBRE SUBSTRATS.

La darrera aplicació que s'ha fet ha estat l'estudi de sistemes constituïts per partícules (àtoms o molècules simples) adsorbides sobre substrats com poden ésser els gasos nobles sobre grafit [Birgeneau R.J. i Horn P.M. 1986]. Hem desenvolupat un model que inclou efectes d'acoblament entre diferents variables que representen diferents escales dels graus de llibertat posicionals de les partícules.

La principal característica d'aquests sistemes és la seva quasi-bidimensionalitat. Aquesta propietat els fa molt interessants de cara a servir de prova per a les diverses teories que existeixen sobre sistemes bidimensionals. Una recopilació recent és [Strandburg K.J. 1988]. En particular la teoria anomenada de Kosterlitz, Thouless, Halperin, Nelson i Young (KTHNY), [Kosterlitz J.M. i Thouless D.J. 1973], [Halperin B.I. i Nelson D.R. 1978] sobre la fusió bidimensional proposa que per comptes de produir-se mitjançant una transició de primer ordre com al cas de tres dimensions, la transició es produeix a través de dues transicions contínues consecutives, entre les quals apareix una fase anomenada hexàtica. Aquesta fase té ordre orientacional dels enllaços entre partícules a molt llarg abast sense tenir ordre posicional.

La bidimensionalitat dels sistemes de partícules adsorbides, però, pot ésser fortament qüestionada. Per un costat, a part d'un potencial d'adsorbció molt intens que manté les partícules adherides al substrat, existeix un potencial de corrugació (Corrugation Potential) que modula al sistema bidimensional i que té la periodicitat del substrat. Per exemple en el cas del grafit aquest potencial pot imaginar-se com una sèrie de pous que formen una xarxa hexagonal. Les partícules adsorbides tenen doncs més tendència a ocupar els mínims de potencial.

Aquest potencial de corrugació permet que a baixes temperatures s'estableixi un ordre posicional de llarg abast i es

formi un veritable cristall, que sabem que no pot formar-se mai en el cas de sistemes perfectament bidimensionals. Es per tant molt important conèixer quin és el paper que juga aquest potencial de corrugació en els sistemes de partícules adsorbides i els estudis que hem desenvolupat fan especial èmfasi en aquest aspecte.

Altres raons que qüestionen la bidimensionalitat d'aquests sistemes són: el fet de que el grau de llibertat z en la direcció vertical pot jugar, en alguns casos, un paper rellevant, els intercanvis de partícules amb el gas que normalment hi ha sobre el substrat, etc. Alguns d'aquests problemes desapareixen al fer experiments amb els anomenats compostos d'intercalació ("intercalated compounds"). Per comptes d'adsorbir molècules o àtoms sobre un substrat, s'intercal·len entre dos plans consecutius d'un cristall, usualment també grafit. En aquest cas no hi ha intercanvi de molècules amb cap gas i el grau de llibertat z està molt més restringit, però el potencial de corrugació és molt més important. A més també hi ha la possibilitat que s'estableixin interaccions entre plans consecutius de partícules intercalades.

Un altre efecte important a considerar és el fet que els experiments de partícules adsorbides es realitzen a pressió constant del gas que hi ha sobre el substrat, la qual cosa és equivalent a treballar amb un sistema de partícules adsorbides a potencial químic constant. Els models, en canvi, solen formular-se a nombre de partícules constant, semblantment al que passa als compostos d'intercalació. Aquestes diferències poden donar lloc a confusió a l'hora de interpretar possibles zones de coexistència, metastabilitats, etc...

La idea principal que ha inspirat el model que s'ha elaborat ha estat la d'introduir dues variables diferents per descriure les posicions de les partícules sobre el substrat. En primer lloc una variable S_i que descriu quins pous del substrat estan ocupats per partícules i quins no, i una segona variable r_i que descriu la posició de les partícules dins de cada pou. Ambdues variables estan associades als graus de llibertat posicionals (x,y) però

corresponen a dues escales diferents: una als moviments de salt entre pous i l'altra al moviment dins de cada pou. Evidentment ambdues variables no es poden moure independentment com al cas de l'acoblament orientacional-posicional dels cristalls líquids, sinó que les S_i canvien quan alguna partícula passa d'un pou a un altre a causa d'una petita alteració de la seva r_i .

Aquesta descripció en termes de dues variables es físicament força satisfactòria. La rao d'això és que probablement la interacció entre partícules pot separar-se molt bé en aquests dos termes: una a molt petita escala, que és bàsicament la interacció amb el potencial de corrugació i l'altre a una escala del diàmetre dels pous que depèn de la interacció hard-core de les partícules i que pot aproximar-se per termes de tipus lattice gas (Es a dir dues partícules no poden estar en la mateixa cel.la, i si estan en cel.les massa separades ja no interactuen). En aquest cas, igual que en el cas dels cristalls líquids, l'acoblament entre els dos tipus de variables és conseqüència que no pot produir-se interacció entre les r_i si no hi ha interacció entre les S_i .

En la literatura es troben alguns models per estudiar aquests sistemes. El problema que existeix és que, o bé es fa una descripció en termes de variables lattice gas o Potts (S_i), o bé s'utilitzen models completament continus que són difícilment resolubles. El nostre model inclou les dues variables simultàniament que apareixen de forma natural en la simulació de Monte Carlo com a conseqüència de la introducció d'un algorisme de tipus descripció cel.lular dels que s'utilitzen en els problemes de Dinàmica Molecular.

El model elaborat considera una interacció tipus Lennard-Jones entre les partícules i un potencial de corrugació amb simetria hexagonal i de tipus parabòlic. Els paràmetres més rellevants són la densitat de partícules (número de partícules per pou del substrat) que hem mantingut fixada a 1/3, la posició del mínim de la interacció Lennard-Jones que hem fixat a una distància corresponent a la distància entre segons veïns de la xarxa

hexagonal, i el paràmetre U que ens dona la relació entre la profunditat del pou i l'energia d'interacció Lennard Jones.

Els estudis realitzats s'han centrat en la transició de la fase ordenada a baixa temperatura amb una estructura $\sqrt{3} \times \sqrt{3}$ i la fase líquida, per diferents valors de U (0...200).

Les simulacions s'han realitzat amb un sistema de 2700 partícules sobre un substrat de 8100 pous. La durada de les simulacions ha estat de l'ordre de 6000-12000 MCS.

Per al cas $U=0$ s'han realitzat mesures de l'evolució de l'energia i de diferents paràmetres d'ordre amb la temperatura per tal de discernir entre la teoria de KTHNY i resultats de simulació existents en la literatura que eren contradictoris [Barker J.A., Henderson D. i Abraham F.F. 1981], [Frenkel D. i McTague P. 1979]. Els nostres resultats apunten cap al fet que ambdues descripcions són mes similars del que es pot pensar, sobretot a causa dels efectes de mida finita de les simulacions. La nostra proposta és que existeix una sola transició de fase amb una zona de coexistència dins de la qual existeix ordre orientacional de llarg abast però no posicional. Per tant la zona de coexistència podria assemblar-se a l'anomenada fase hexàtica postulada per la teoria KTHNY. Aquests efectes de mida finita també són importants als experiments, i s'ha comprovat [Abraham F.F. 1980] que les mides dels sistemes que s'utilitzen són suficientment petites per permetre, per exemple, que s'estableixi una veritable estructura cristal·lina bidimensional a baixa temperatura, la qual cosa estaria prohibida d'acord amb la teoria KTHNY..

En relació a l'efecte de l'existència d'un substrat hem comprovat com afecta dràsticament a algunes propietats, en particular al factor d'estructura del sistema que presenta un veritable pic de Bragg fins i tot per sobre de la transició de fase, causat per la modulació del líquid pel substrat. La intensitat d'aquest pic ha estat calculada i depèn únicament de les fluctuacions de les partícules al voltant dels pous. En la fase sòlida presenta un comportament exponencial negatiu amb un pendent corresponent al factor de Debye-Waller, com era d'esperar. Aquest

comportament exponencial negatiu es pot estendre a la fase líquida, però amb un canvi molt important en el pendent.

La dependència del factor d'estructura amb U/T obtinguda mitjançant la simulació s'ha comparat amb l'aproximació lineal de la teoria general de [Reiter G. i Moss S.C. 1986]. Ens hem fixat en la intensitat del pic (1,0) corresponent a la modulació del líquid pel potencial de corrugació. L'acord és força bo per a valors intermedis d' U . Per a U molt gran falla ja que la teoria de Reiter i Moss és pertorbativa en U/T . També per a U molt petites hi ha desacord, probablement a causa de que aleshores les fluctuacions posicionals de les partícules al voltant dels centres dels pous són molt grans i això fa que en el punt (1,0) a part del pic de Bragg calgui afegir la intensitat que prové de l'"scattering" incoherent.

El model desenvolupat també s'ha mostrat útil per a l'estudi de la formació de defectes en la solidificació de líquids bidimensionals, camp en el qual s'està treballant actualment però que no s'ha desenvolupat en aquesta tesi.

BIBLIOGRAFIA.

Abraham F.F. (1980), Phys. Rev. Lett. 44, 463-466

Barker J.A., Henderson D. i Abraham F.F. (1981), Physica 106A, 226-238.

Birgeneau R.J. i Horn P.M. (1986), Science 232, 329-336

Frenkel D. i McTague P. (1979), Phys. Rev. Lett. 42, 1632-1635.

Halperin B.I. i Nelson D.R. (1978), Phys. Rev. Lett. 41, 121-124.

Kosterlitz J.M. i Thouless D.J. (1973), Journ Phys. C: Sol. Stat. Phys. 6, 1181-1203.

Reiter G. i Moss S.C. (1986), Phys. Rev. B33, 7209-7217.

Strandburg K.J. (1988), Rev. Mod. Phys. 60, 161-207.

Substrate Influence on Two Dimensional Solids and Liquids: A Monte Carlo Simulation Study

ABSTRACT

A general model for two dimensional solids and liquids on a substrate is studied by means of Monte Carlo simulation. The results can be applied to the case of adsorbed atoms or molecules on surfaces as well as intercalated compounds. We have focused on the study of the melting of a commensurate $\sqrt{3} \times \sqrt{3}$ structure on a triangular lattice with $1/3$ coverage. The evolution of the energy, order parameters and structure factor has been followed in a large range of temperature and substrate potential strength. The phase diagram exhibits a broad transition region between the solid and liquid phase for all the studied cases. We have in particular investigated the contribution from the two dimensional liquid to the Bragg peaks corresponding to the substrate structure. Reiter and Moss et al have demonstrated that this gives valuable information about the substrate potential. A universal dependence is found between this and the particle fluctuations around the substrate potential wells. This dependence may be useful for an experimental determination of the magnitude of the substrate potential from scattering experiments, in particular for weak potentials and large atomic mean square displacements.

I. Introduction

From a theoretical point of view, the problem of two dimensional solids, liquids and specially the melting transition is very interesting and has been studied intensively the last decades. A comprehensive review has been published recently¹. It is known that a two dimensional (2d) crystal does not have perfect long range positional order, but instead exhibits a logarithmic decay of the positional correlations and only quasi-long range order exists². Kosterlitz and Thouless³ demonstrated that although the true long range positional order is not possible for a 2-dimensional solid, it can exhibit a long range orientational order of the particle bonds. This orientational order is destroyed by dislocations when the temperature is increased. Halperin, Nelson and Young⁴ completed the theory and showed that two consecutive continuous phase transitions may appear between the two dimensional solid phase, with quasi long range positional order and true orientational order, and the liquid phase with no long range order. The intermediate phase, so called hexatic phase, which exhibits quasi long range orientational order but no positional order has been under discussion during the last 20 years¹. Experiments^{5,6,7}, simulations^{8,9} and different theories¹⁰ have been developed, sometimes with contradicting results.

A main reason for the prolonged discussion and lack of consensus is that real experiments are always performed on systems that are not perfectly two dimensional. Most of the experiments are performed with atoms physisorbed on substrates or intercalated between layers. We will focus our discussion on the adsorbed rare-gas atoms¹¹ and alkali metals intercalated in graphite¹². Several factors are contributing to the difficulty in comparing these systems with the ideal two dimensional solids and liquids. First of all there is the influence of the substrate potential, also called the corrugation potential. Depending on the

competition between this interaction and the particle-particle interaction the solid phase at low temperature can be commensurate or incommensurate¹³. This fact is also important in the study of the melting of such systems. In general it is thought that the liquid and melting corresponding to incommensurate solids are less effected by the substrate potential¹⁴. Other factors are the motion of atoms perpendicular to the substrate¹⁵, the exchanges between the gas and the layer¹⁶ in the adsorbed systems and the influence between two consecutive intercalated layers¹⁷ in the intercalated systems. Such effects will here be neglected. In this paper we focus on the substrate influence and limit the discussion to the case which has a commensurate solid phase at low temperatures. Our main aim is to perform a systematic study using Monte Carlo simulation, of the influence of the periodic substrate on the properties of two dimensional solid and liquids, and to emphasize the observable effects on the structure factor, which can be measured in scattering experiments.

Two limiting cases have usually been discussed in order to characterize the substrate influence. The first assumes that the corrugation potential is large, so that the system can be considered as a lattice liquid in which the motion of the particles is restricted to a jumping between neighbouring wells, while the motion within the substrate potential wells is not considered. In this limit several theories concerning modified Potts Models¹⁸ have been developed, discussing mainly the symmetry change between the solid and liquid phase. Some of them¹¹ seem to be in agreement with the phase diagram for Kr adsorbed on graphite⁶. Very few calculations of the structure factors have been performed for these models, the only exception, to our knowledge, being the calculation of the structure factor of the lattice gas model using Monte Carlo simulation²⁰. The second limit studied is based on the assumption that the substrate potential is relatively small and can be considered as perturbing the real continuous liquid. A general perturbation theory of the substrate influence on the structure factor has

been developed by Reiter and Moss²¹ and has been proved to be successful in describing experiments on Rb^{22,23} as well as on K²⁴ intercalated in Graphite. The theory allows the possibility of extracting the corrugation potential from X-ray scattering data. The principal conclusion of the theory is that the 2d liquid produces an important contribution to the Bragg peaks of the substrate, and that the diffuse liquid ring structure factor may be reproduced around all the substrate peaks. The linear approximation of the theory predicts that the contribution to the Bragg peak intensity of the substrate is proportional to $(V_{\text{HK}}/k_{\text{B}}T)^2$ where V_{HK} are the Fourier coefficients of the substrate potential, T is the thermodynamic temperature and k_{B} is the Boltzmann factor. The intensity of the secondary rings is of higher order. A quantitative comparison between these predictions and experiments is however not easy and therefore molecular dynamics calculations have been used^{23,25} for tests. A main problem with this technique is that only relatively small systems can be studied within reasonable computer time, and finite size effects may influence the results, in particular for a quantity like the structure factor. In this paper we propose instead a continuous Monte Carlo method, which allows the possibility of studying systems of 2700 atoms or more, thereby considerably reducing the finite size effects.

A theory unifying the Potts lattice description and the continuous perturbed liquid description is needed in order to understand the influence of the substrate on the two dimensional solids and liquids. Most experimental realizations seem to fall in a class between these limiting descriptions. We will focus on the calculations of the structure factor, because that can be directly compared with detailed scattering experiments. For this purpose it is particularly important to be able to study large systems, since the resolution of details in the structure factor are directly dependent on the spatial extent of the system. The structure factor offers a possibility for a measurement of the corrugation potential, the magnitude of which is under considerable discussion¹.

The structure of the paper is as follows. In section II we present our model and the main characteristics of the Monte Carlo simulation. In section III the pair correlation functions and a number of order parameters are calculated. In section IV we present the phase diagram for our model. In section V the scattering properties are discussed and finally in section VI we summarize and conclude.

II The Model

The model is defined on a 2d triangular reference lattice, with $L \times L$ sites i ($i = 1, \dots, N = L \times L$) and lattice parameter a . Each site in the lattice corresponds to the center of a hexagonal cell representing the substrate, see Fig. 1 with edge length $= a/\sqrt{3}$. Each cell can be occupied by only one atom. This particular symmetry has been chosen because it is the one corresponding to the (0,0,1) graphite surface ($a = 2.456 \text{ \AA}$) which is the most common substrate used for experiments on adsorbed atoms and intercalated compounds. The assumption of only one particle per cell is true for most of the adsorbates due to the large atomic (hard core) radius of the ad atoms compared with the graphite lattice spacing.

On each site of the triangular lattice we define a variable S_i taking the two values 0 or 1 depending on the absence or presence of a particle at the cell i . Further we define r_i which is a 2d continuous vector that measures the position of the center of the atom inside the cell. We neglect the possibility of perpendicular motion of the particles. The total number of particles on the surface is kept constant so that:

$$\sum_{i=1}^N S_i = cN, \quad (1)$$

where c is the coverage of the system. The Hamiltonian of the system is written as:

$$H = \sum_{ij} S_i S_j V(|r_i - r_j - R_{ij}|) + \sum_{i=1}^N S_i U(|r_i|), \quad (2)$$

where the first term represents an isotropic interaction between the particles and the second term the particle substrate corrugation interaction, assumed to be isotropic around each cell centre. The first summation is a sum over all pairs of sites in the lattice and the second summation a single sum over the lattice sites. R_{ij} represents the vector joining cell centers at sites i and j .

It is known that in real systems, in particular for metal surfaces, the interactions are more complicated, usually exhibiting anisotropic particle-particle interactions due to the electronic exchange with the substrate and a breakdown of the pair interaction assumption¹⁴, etc.. Such effects could be included but are neglected for simplicity.

The Hamiltonian allows the possibility of clearly identifying the two limits described in the introduction. On the one hand, when the corrugation potential U is very big, the only effect of the second term is to force the particles to occupy the cell centres and restricting the possible movement to jumps between the sites. The system is then described by the S_i variables only. On the other hand, in the case of no substrate effect, the S_i variables are irrelevant and the first summation is a sum over particles interacting through an isotropic potential. The intermediate case, as demonstrated by Fan et al²⁵, does exhibit interesting coupling phenomena between the r_i and S_i variables in the same way as in other Hamiltonians used for the description of coupled phase transitions²⁶.

Although the formulation of the model is general, we have focused on a simple case with $U(r)$ being a parabolic potential and $V(r)$ being a Lennard-Jones²⁷ like

interaction. $U(r)$ is defined in such a way that it takes a zero value at the corners of the hexagonal cell and $-\epsilon U$ ($U > 0$) at the centre of the cell, where ϵ is an energy unit.

$$U(r) = -\epsilon U (1 - 3(r/a)^2) \quad (3)$$

In order to compare with Reiter and Moss' results²¹ we have calculated the first few Fourier expansion coefficients for this potential

$$U(x,y) = \epsilon U \sum_{H,K} V_{HK} e^{2\pi i \left(\frac{x}{a} \frac{K}{\sqrt{3}} + \frac{y}{a} \frac{K+2H}{\sqrt{3}} \right)} \quad (4)$$

where H, K are integer numbers indexing the sites in the reciprocal lattice. The first coefficients are

$$V_{0,0} = -0.58329264$$

$$V_{1,0} = V_{0,1} = V_{-1,1} = V_{-1,0} = V_{0,-1} = V_{1,-1} = -0.09428979$$

$$V_{1,1} = V_{2,-1} = V_{1,-2} = V_{-1,-1} = V_{-2,1} = V_{-1,2} = 0.02540826$$

Note that the first coefficient of the corrugation potential is in this case only -9.4% of ϵU .

The Lennard-Jones potential has been extensively used for the study of the rare gas atomic interaction. It is defined as

$$V_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma a}{r} \right)^{12} - \left(\frac{\sigma a}{r} \right)^6 \right] \quad (5)$$

Here ϵ is the energy scale of the Lennard-Jones potential. All energies will be given in units of ϵ and the temperatures as $T = k_B T/\epsilon$. The depth of the attractive well is ϵ and σa is proportional to the position of the potential minimum ($r_{\min} = 2^{1/6}\sigma a$) for $V_{1,j}(r)$.

In order to reduce the computer time, we introduce two cuts in the Lennard-Jones potential:

$$\begin{aligned} V(r) &= \infty \text{ if } r < r_1 \\ V(r) &= 0 \text{ if } r > r_2 \\ V(r) &= V_{1,j}(r) \text{ for } r_1 < r < r_2. \end{aligned} \tag{6}$$

Here r_1 is chosen to prevent particles to occupy the same cell by assuming that the interaction energy of two particles is infinite if they are in the same cell. This gives $r_1 = 2a/\sqrt{3}$, i.e. the maximum distance between two points inside of a cell. The distance r_2 is chosen so that the interaction is zero when they are separated more than the 6th neighbour cell, giving $r_2 = 4a/\sqrt{3}$, i.e. the minimum distance between two 6th neighbours cells, see Fig. 1. With these definitions the first summation over lattice pairs in (2) can be performed including the 5th neighbours without losing the isotropy of the potential. A further restriction of the summation over the pairs in (2) without reducing the potential cut r_2 will lead to an anisotropy in the system even in the case $U = 0$. With our choice we maintain the complete isotropy of the liquid also in the limit $U = 0$. Therefore the influence of the reference lattice vanishes when the corrugation disappears. Let us define the Hamiltonian H_0 for the cut potential and that for the tail ΔH , giving $H = H_0 + \Delta H$.

In this paper we study the commensurate case with $2^{1/6}\sigma = \sqrt{3}$ and $c = 1/3$, so that the minimum of the particle-particle interaction is exactly at the second neighbour distance on the substrate lattice. With these definitions the ground

state of the system is a commensurate structure (usually called a $\sqrt{3} \times \sqrt{3}$ structure) with degeneracy 3 in the case of $U > 0$. For $U = 0$ the system has continuous translational and rotational symmetry.

The simulation of this system is performed using standard Monte Carlo techniques²⁸. We use a 90×90 triangular lattice with periodic boundary conditions in order to minimize the boundary effects. This represents a lattice with 8100 sites and 2700 particles when $c = 1/3$. The position of the molecules is updated sequentially on the lattice, and the new proposed position is obtained performing uniformly distributed random steps inside of a circle of radius r_d around the old position. When the new proposed position is outside of the original cell, the change is considered as an attempt to jump to a new cell, and if the movement is accepted the variables S_i are updated. By this method we assure that the particle diffusion is isotropic for $U = 0$, which has been tested. The size of r_d will determine the speed of the Monte Carlo simulation. We have chosen $r_d = 0.2a$ which gives an acceptance ratio of 0.5 in a large range of intermediate temperatures. Considering that we are not particularly interested in the dynamics of the system, but in the equilibrium properties, this value is quite good.

The averages of the interesting quantities are taken over 3000-6000 MCS (1 MCS = 1 Monte Carlo step = 1 attempt per particle) after discarding the first 4000-8000 MCS's in order to equilibrate the system. Averages over different runs, using different random number generator seeds, are also taken in order to improve the statistics of the results.

III. The pair correlation function $g(r)$ and energy $E(T)$ at $U = 0$

In order to reach firm conclusions about the effects of the corrugation potential U , it is important to test the liquid structure for $U = 0$. Firstly, that the structure is not influenced by the underlying reference lattice and secondly that no unphysical features are introduced by the truncated Lenard-Jones potential. Fig. 2 shows the structure at "full coverage" $c=1/3$ obtained after melting a perfect $\sqrt{3} \times \sqrt{3}$ structure on the reference lattice and letting it reach equilibrium in 7000 MCS. It is isotropic with no obvious signs of memory of the orientation of the initial ordered structure. Both pictures show the same structure, but to the right an analysis is made showing the number of neighbors each particle has. It is evident that the liquid has a fluctuating density with open areas and denser crystalline-like patches of various orientations. The pair correlation, averaged over direction, $g(r)$ is calculated directly including r up to $13a$. As expected for high coverages, there is no sign in $g(r)$ of the truncation of the potential V_{LJ} at $r = 4a/\sqrt{3}$. Assuming *a priori* that $g(r)$ is correct, we can calculate the effect of the truncation on the internal energy per particle E and the free energy at high T . Using $F = -T \ln Z$ with $Z = Tr\{\exp [-(H_0 + \Delta H)/T]\}$ and expanding to first order in $\Delta H/T$ one obtains

$$F_{LJ} = F_0 - \langle \Delta H \rangle_0 + o(1/T), \quad (7)$$

where the index 0 indicates properties obtained in the Monte Carlo simulation with the truncated $V_{LJ}(r)$ potential. The main effect of the cut is a correction to the internal energy per particle. Eq. (7) is valid also at $T \rightarrow 0$. The calculated $E(T)$ is shown on Fig. 3, and it is demonstrated that the energy, corrected for the neglected contribution from the tail according to (7) using the calculated $g(r)$, agrees excellently with that obtained by Abraham²⁷. Fig. 4a shows furthermore

that our $g(r)$ for the liquid agrees in all details with that obtained by Abraham²⁷ and so does that for the solid, Fig. 4b.

We conclude that our Monte Carlo scheme gives results in good agreement with previous calculations and shows no anisotropy for $U = 0$.

IV. Phase diagram as a function of U

In the following we study mainly the case of coverage $c = 1/3$ with variable corrugation potential and with the LJ-potential favoring the $\sqrt{3} \times \sqrt{3}$ structure with the same lattice constant i.e. with $\sigma = 3^{1/2}2^{-1/6}$. For all U studied we find a transition region. Because the pressure is increasing rapidly in this region, it most probably can be characterized as a mixed phase region. It is not the purpose of this paper to discuss a possible hexatic phase region. For very large U the model reduces to a 3-state Potts model for which it is known that the transition is a single continuous one. We have not have aimed at studying sufficiently high U to observe this. The phase diagram was obtained by starting from a single domain $\sqrt{3} \times \sqrt{3}$ structure and also by cooling from the liquid phase. In the latter case one reaches a (probably) metastable multidomain structure shown on Fig. 5 for $U = 0$, $T = 0.1$ and $c = 0.32333$. It has clearly no preferred orientation of the crystalites. To the right is seen an analysis showing that particles with 5 and 7 neighbours are concentrated along the grain boundaries. We return to a more detailed discussion of the possibility that this is a Kosterlitz-Thouless phase and of a possible hexatic phase elsewhere.

The following several parameters were monitored in order to display the transition.