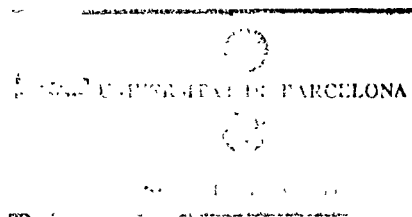


**SIMULACIO MONTE CARLO DE SISTEMES
AMB ACOBLAMENT DE GRAUS DE LLIBERTAT.**



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

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 is a single sum over the lattice sites. R_{ij} represents the vector joining cell centers at sites i and j . 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-Jones¹² 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' results⁶ we have calculated the first few Fourier expansion coefficients for this potential. We find¹¹ that the first six coefficients of the corrugation potential, V_{10} etc., are 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 $V_{1,1}(r)$.

In order to reduce the computer time, we introduce two cuts in the Lennard-Jones potential: Hard core for $r < r_1$, where $r_1 = 2a/\sqrt{3}$ is chosen to prevent particles to occupy the same cell. The interaction is set equal to zero for $r > r_2$ when they are separated more than the 6th neighbour cell, giving $r_2 = 4a/\sqrt{3}$. 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 techniques¹³. 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, 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.

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. Phase diagram as a function of U

The phase diagram has been obtained by studying the evolution of the energy and some other order parameters as a function of temperature. For all U studied we find a transition region. It is not the purpose of this paper to discuss a possible hexatic phase region. For $U \rightarrow \infty$ the model reduces to a 3-state Potts model for which it is known that the transition is a single continuous one. In this paper we study the behavior for much larger U than in ref.11. The result is shown on Fig.1, the inset shows the upper melting transition for U up to U = 200. It is clear that the melting temperature does not rise linearly with increasing U. We still see a transition region at large U, although it is not indicated in the inset.

IV. Scattering properties and real space properties for large U

The static structure factor $S(q)$, which can be measured in X-ray or neutron scattering experiments is defined as

$$S(q) \equiv \frac{1}{N_p^2} \left\langle \left| \sum_{i=1}^{N_p} e^{iq \cdot r_i} \right|^2 \right\rangle \quad (6)$$

where $N_p = N/3$ is the number of particles. It is normalized to 1 for $q = 0$ and approaches $1/N_p$ for $q \rightarrow \infty$. From now on q-vectors will be measured in units of $q_0 = 4\pi/(\sqrt{3}a)$. Fig. 2 shows $S(q)$ for the liquid near the melting temperature for q along different directions of the reciprocal space, for the case of small U (U = 1, T = 4) and large U (U = 200, T = 35). A very similar behavior, at first sight, is

obtained. An important difference is that for large U , the modulation of the intensity of the first ring of scattering in the liquid phase shows a clear memory of the orientation of the underlying lattice. This is as expected. Another very important feature is the persistence of the Bragg peak at $\mathbf{q} = (1,0)q_0$. This is the strongest sign of a lattice modulated liquid. In our simulation we, of course, do not see the substrate Bragg peak, but only the contribution from the surface layer. At the studied potential values we have not found clear sign of peaks from possible secondary liquid rings around the (10) Bragg peaks as indicated in the study by Reiter and Moss⁶; we lack an explanation for this. A systematic study of cases with $c \neq 1/3$ and incommensurate structures might shed some light on that problem. A third important feature is that there is a small, but definite shift to higher q -values of the peak position of the first peak near (above) the melting point in particular for q along the (12) direction. The scattering ring is therefore distorted towards a hexagonal shape. Such an effect has recently been reported observed experimentally for K and Rb intercalated in graphite¹⁴ and it is also detectable in the molecular dynamics simulations¹⁰. The details of the distortion depend on the details of the corrugation potential. The expansion in q -space indicates that the liquid for large U is contracted upon melting. This is in fact directly evident in the snapshot Fig. 3b, which shows considerable regions with low density. One may say that the system melts from a commensurate phase to an incommensurate liquid. The snapshots for $U = 1$, Fig. 3a and $U = 200$, Fig. 3b appear quite similar. The interesting and, at first sight, unexpected feature is that the particles do not reside at the lattice site positions as for a centered Potts model, even for very large U . This partly due to vibrations. A centered Potts model has too low entropy. It is easy to calculate the difference in free energy between a centered Potts model and the observed one with the particle positions relaxed in the potential wells. Neglecting interparticle interactions we find

$$\Delta F/\epsilon = -T \ln Z,$$

$$Z = \int e^{-U(\mathbf{r})/k_B T} d\mathbf{r} \sim A T^{d/n}, \quad (7)$$

where $A > 0$ is a constant slightly dependent on temperature, d is the dimension of the system and n the exponent in a potential of polynomial form, $U(r) \sim r^n$, here $n=2$ and $d=2$. The free energy is therefore favoring the relaxed liquid, as observed, for any $n > 0$. Only for infinitely deep potential wells ($n < 0$) one obtains the centered Potts model. The Potts model must, for $n > 0$, be understood as a model showing the occupied cells. However, due to the interactions the particles are quasi-statically displaced relative to the centers and the deviations are not just a sign of independent vibrations around these. Fig. 4. shows the occupied cell picture is in agreement with that expected for a Potts lattice gas description of a liquid having large ordered crystallites of different registry imbedded. The $g(r)$ for this liquid is very unusual as shown in Fig.5, where a) shows the weakly modulated case with $U = 1$, and b) the large U case with $U = 200$. It demonstrates that the particles for $U = 200$ form at least up to 12 rings around each other. This feature does not show up clearly in $S(q)$, Fig. 2. However, the induced contribution to the substrate Bragg peak $S(q_{10})$ has a number of interesting features: A main one is illustrated by the Debye-Waller factor plot, Fig. 6., which shows that the peak intensity $S(q_{10})$ is an universal function of the mean square fluctuation $\langle r^2 \rangle / a^2$. Fig. 6. shows the same behavior irrespective of the relative values of U and T . The arrow at L indicates the Lindemann criterion¹ for melting in the case of $U = 0$. The value of $\langle r^2 \rangle$ at the melting temperature is substantially smaller for large U .

IV Conclusion

The problem of two dimensional solids, liquids and melting has previously been investigated in the limits of either strong or weak interaction with a supporting substrate and for various coverage. In this paper we have instead studied a plane in phase space spanned by temperature T and a large interval of corrugation potentials U , restricting the coverage to being fixed at $1/3$, corresponding to a perfect $\sqrt{3} \times \sqrt{3}$ structure. The melting transition is found to occur in a

monotonically increasing, relatively broad strip in the plane. The effect of a finite corrugation potential is most clearly seen in the persistence of a Bragg peak at $q = (1.0)q_0$ even in the liquid phase. This is due to the increased probability for (randomly) occupying the imaginary substrate lattice sites. As already emphasized by Reiter and Moss⁶ this induced Bragg peak offers important possibilities for measuring the substrate potential U from the scattering data. We have here extended the study to a larger region of U and T . The linear approximation of the theory fits the data excellently at intermediate U , close to the melting temperature, T_M . For small U the fit is less satisfactory. This seems at first sight surprising. The reason is that for small U the positional fluctuations $\langle r^2 \rangle$ around the lattice sites increase rapidly above T_M . This strongly influences the determination of a Bragg peak and its peak intensity. We have found that the logarithm of the intensity decreases linearly with increasing temperature beyond the transition region. We have further found that this intensity is an universal function, for various U and T , of the mean square displacement $\langle r^2 \rangle$ from the lattice sites. In the solid the exact Debye-Waller factor is found. In the weakly modulated liquid another characteristic smaller factor is found. For large U a contracted, incommensurate liquid is found, which is not resembling a centered Potts Model. A calculation of the free energy shows that a relaxed liquid with the particles displaced in the potential wells is preferable due to the entropy gain. Nevertheless this liquid can in a cellular sense be described as a Potts lattice gas liquid. The relevant interaction parameters for such an effective Potts model are not simply related to the interactions in the present model, since they must include a certain degree of renormalization, representing the interaction between the strongly vibrating particles.

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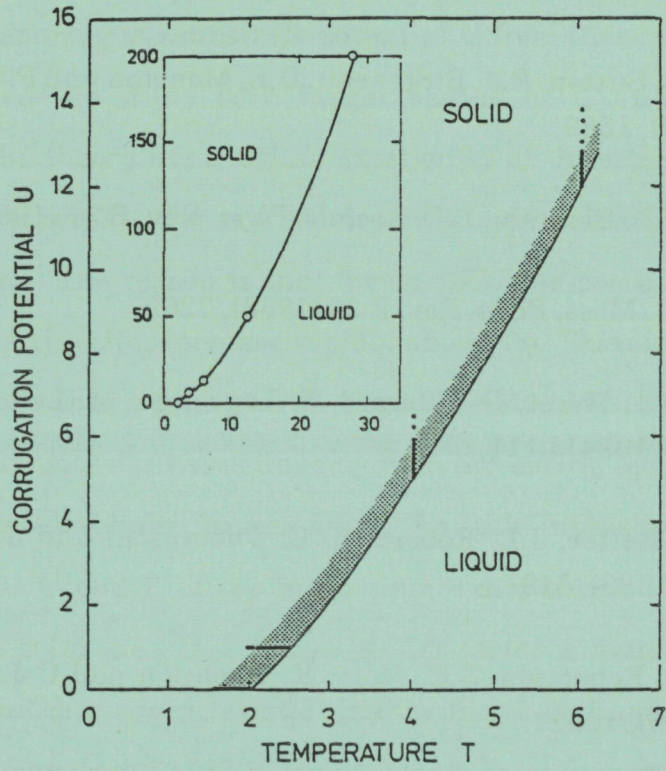


Fig.1. Phase diagram showing the solid and liquid phases and the transition region as obtained by Monte Carlo simulation of the presented model. The inset shows the upper transition temperature T_M for U up to U = 200.

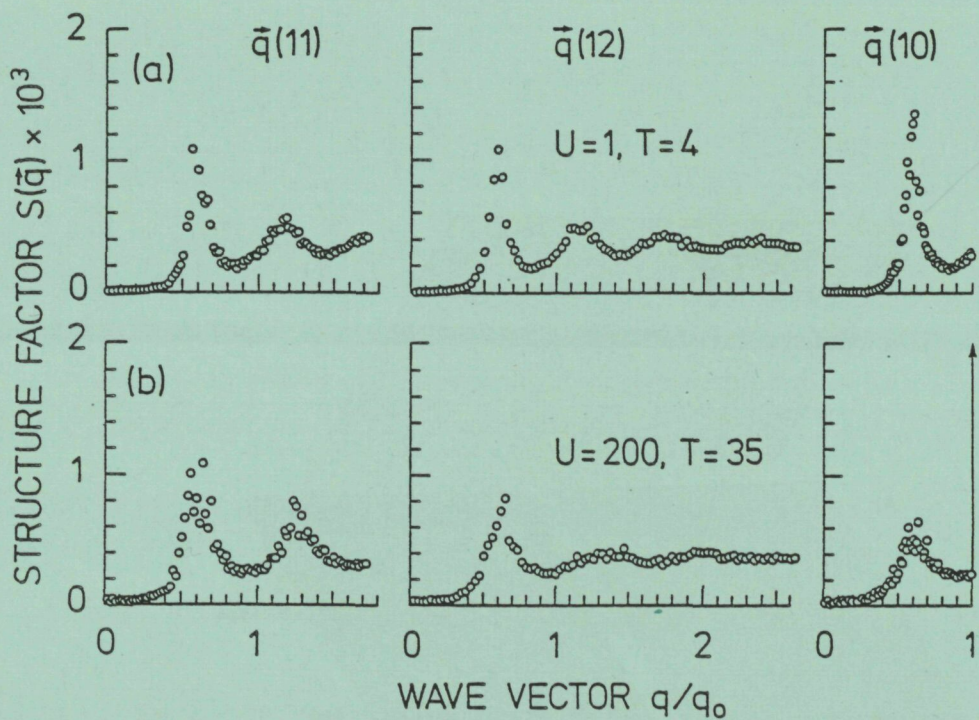


Fig. 2. The liquid structure factor $S(q)$ for q along three different directions in reciprocal space. (a) $U = 1, T = 4$ and (b) $U = 200, T = 35$. For large U a shift of the first peak is clearly detectable for q along the (12) direction, whereas there is no, or very small, shift in the other directions.