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MONTE CARLO CALCULATIONS FOR THE INTERACTION OF 12-6 ARGON AT 80 K WITH GRAPHITE IN THE REGION OF MONOLAYER ADSORPTION

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Résumé. — La méthode Monte Carlo dans un grand ensemble a été utilisée pour calculer l'adsorption d'argon sur la surface de graphite. L'argon est représenté par un potentiel 12-6 et l'interaction avec le graphite par un potentiel qui varie périodiquement dans le plan de la surface. La méthode grand ensemble permet de distinguer les états stables des états métastables quand ces états sont séparés par une barrière ergotique. Les résultats de ces calculs et de ceux obtenus précédemment pour un modèle en continuum (représenté par un potentiel 9-3) sont comparés avec des résultats expérimentaux. Les isothermes expérimentales semblent être en meilleur accord avec les résultats obtenus avec le modèle en continuum qu'avec ceux obtenus pour le potentiel périodique. De plus, les courbes des chaleurs isostériques sont en accord avec les résultats de l'expérience pour des degrés de recouvrement inférieur à une monocouche mais ils montrent de fortes différences au-delà.

Les résultats de la simulation de Monte carlo sont comparés à plusieurs modèles théoriques (Loi de Henry - isothermes de Hill-de Boer). Seule la loi de Henry est en bon accord avec nos résultats.

Abstract. — The grand ensemble Monte Carlo method has been used to simulate the adsorption of 12-6 argon on a graphite substrate with periodically varying adsorbate-adsorbent potential at 80 K. The grand ensemble method enables stable and metastable states to be distinguished although these may be ergodically separate. The results of these calculations and those carried out earlier for a continuum model, represented by a 9-3 potential, have been compared with experimental data. Experimental isotherms appear to be in better agreement with the continuum results than with those for the periodic potential. Isothermic heat curves on the other hand were in satisfactory agreement with experimental data for coverages of up to a monolayer but showed marked deviations beyond this point.

Tests of theoretical models were restricted to an appraisal of the zero coverage region and of the Hill-de Boer isotherm in its original and modified forms. The latter was in poor agreement with MC data.

1. Introduction. — Extensive computer calculations have established that the 12-6 potential model provides an excellent description of the properties of uniform phases of argon under a very wide range of conditions. Recently we have used the Monte Carlo (MC) method to simulate 12-6 argon as a non-uniform adsorbate in the presence of a 9-3 potential field due to a plane homogeneous continuum solid [1-3] (which will be denoted here by H).

The results of these calculations establish a useful reference base against which adsorption theories can be tested. At the same time it must be appreciated that the 9-3 potential is not expected to be very realistic as an adsorbent potential. This is especially the case at distances of one or two molecular diameters from the surface.

A better approximation to the true adsorbent potential should be obtained by pairwise summation of adsorbate-adsorbent interactions; a procedure which gives rise to a regular periodicity parallel to the surface. For a graphite adsorbent with a rare-gas adsorbate the adsorbate-adsorbent pair potential is also usually represented by a 12-6 function.

The adequacy of the pairwise summation procedure and the use of the 12-6 function are both open to question. In particular it is uncertain whether the compensation for three-body interactions, which appears to be satisfactory in uniform systems, would carry over to non-uniform adsorbate systems.

The MC calculations described in this paper were carried out for 12-6 Ar in the presence of a periodically varying potential due to a model

graphite adsorbent (which will be denoted here by P). The temperature (80 K) has been used previously for the H-adsorbent and is close to those used in many experimental studies. Surface coverages were of the order of a monolayer or less. Such calculations should be useful on the one hand in evaluating model potentials for the description of experimental phenomena. On the other hand they provide detailed information about the adsorbate structure which can be used in testing approximate theories.

2. Method and calculations. — The 12-6 potential used in this work to represent the argon interactions is,

$$\phi(r) = 4 \varepsilon [(\sigma/r)^{12} - (\sigma/r)^6]$$

with $\varepsilon = 119.8$ K and $\sigma = 0.3405$ nm. Steele [4] and Price [5] have shown that the pairwise summation procedure can be accurately approximated by a truncated Fourier series. The expression given by Steele for rare-gas graphite interactions may be written

$$\psi(\mathbf{r}) = \varepsilon_{gs} [E_0(r_z/a_1) + E_1(r_z/a_1) \mathcal{F}_1(s_1, s_2)] \quad (1)$$

The distance r_z is measured from the centres of the C atoms in the outermost layer of the graphite, writing z^* for (r_z/a_1) we have,

$$E_0(z^*) = \frac{4 \pi A^6}{a_s^*} \sum_{p=0}^{\infty} \left[\frac{2 A^6}{5(z^* + p \Delta z^*)^{10}} - \frac{1}{(z^* + p \Delta z^*)^4} \right] \quad (2)$$

$$E_1(z^*) = \frac{2 \pi A^6}{a_s^*} \left[\frac{A^6}{30} \left(\frac{g_1^*}{2 z^*} \right)^5 K_5(g_1^* z^*) - 2 \left(\frac{g_1^*}{2 z^*} \right)^2 K_2(g_1^* z^*) \right] \quad (3)$$

and

$$\mathcal{F}_1(s_1, s_2) = -2[\cos 2 \pi s_1 + \cos 2 \pi s_2 + \cos 2 \pi (s_1 + s_2)] \quad (4)$$

In these equations a_1 is the a -lattice parameter for graphite ($= 0.417 \sqrt{3}$, measured in σ units which are used for all lengths). The site area $a_s^* = \sqrt{3}/2$; s_1, s_2 are given by

$$r_x/a_1 = \sqrt{3} s_1/2, \quad r_y/a_1 = s_1/2 + s_2;$$

Δz^* is the spacing between graphite lattice planes (0.998); $g_1^* = 4 \pi / \sqrt{3}$; K_2, K_5 are modified Bessel functions of the second kind and $A = 1.38$. The energy parameter $\varepsilon_{gs}/k = 57.8$ K. For the MC calculations $\psi(\mathbf{r})$ and its first derivative were tabulated in length intervals of 0.075 and the potential at $\mathbf{r}$ was calculated from the tables by Lagrange 4-point interpolation. The adsorption minimum which occurs over the centre of a carbon

hexagon was $\psi_s/k = -1118.4$ K with $r_z = 0.979$ and the minimum energy over a carbon atom was $\psi_c/k = -1077.4$ K, at $r_z = 0.996$. The barrier height between these positions is $\beta \Delta \psi = 0.51$ ($\beta = 1/kT$) and may be compared with $\beta \varepsilon = 1.5$. These potentials calculated from eqs. (1), (2), (3) and (4), may be compared with the results obtained by Steele [4]: $\psi_s/k = -1140.4$ K, $\psi_c/k = -1102.8$ K, $\beta \Delta \psi = 0.47$; and by Price [5]: $\psi_s/k = -1135$ K, $\psi_c/k = -1097$ K, $\beta \Delta \psi = 0.47$.

The model graphite surface was placed in the r_x, r_y plane and formed one face of the MC box of length $l_z = 15$. Periodic boundary conditions were imposed in the r_x and r_y directions. The side lengths l_x, l_y were chosen so that either a close-packed monolayer or an expanded site-held (epitaxial) monolayer could be accommodated with the same orientation. The total number of carbon hexagon sites on the surface was 972, but because of hard sphere exclusion only 162 of these would be occupied in a completed epitaxial monolayer. With the Ar atoms closepacked, at the nearest neighbour distance of $2^{1/6}$ ($= 1.122$), there would be 200 atoms in the completed monolayer.

MC calculations were carried out using the grand ensemble technique [1, 2] and long-range corrections were applied as discussed more fully elsewhere [3]. The grand ensemble method should be advantageous in calculations on non-uniform systems because particles can not only be moved but also created or destroyed thereby ensuring optimum sampling at different densities. A second advantage is that the appropriate free energy of the system can be obtained as

$$\Omega = -kT \ln \Xi = -\frac{1}{2} V(p_{xx} + p_{yy}) \quad (5)$$

where Ξ is the grand partition function and p_{xx}, p_{yy} are MC ensemble averages of the diagonal components of the pressure tensor for the r_x and r_y directions respectively and are obtained directly from the pressure virial. Ω is related to the spreading pressure Φ which enters into the thermodynamic equation

$$dU = T dS - \Phi d\mathcal{A} - pV + \mu dN \quad (6)$$

through the equation [6]

$$\Phi = \int_0^{l_z} (\frac{1}{2}(p_{xx} + p_{yy}) - p) dr_z = [\frac{1}{2}(\bar{p}_{xx} + \bar{p}_{yy}) - p] V/\mathcal{A} \quad (7)$$

In (6) and (7) $\mathcal{A}$ is the area ($= l_x l_y$) and the other symbols have their conventional meanings, we also note the identity $p \equiv p_{zz}$. A third advantage of the grand ensemble method in adsorption systems is that the average number of particles adsorbed is obtained directly as a function of the adsorbate activity.

TABLE I

MC Data for 12-6 Argon on the P-Adsorbent at 80 K. (Figures in brackets are standard deviations)

Run	Initial Conf.	States /10 ⁶	Z /10 ⁻⁴	$\theta^{(e)}$	$\theta_i(1)$	$\theta_i(2)$	βq_{st}	$-\Omega \mathcal{A}^{-1}$ /10 ⁻²	$C/kN^{(e)}$
1	C	3.9	.000362	0.0041	0.004		14.18 (.009)	0.33 (.05)	0.719 (.009)
2	0	2.6	0.0168	0.697	0.697		19.96 (0.36)	52 (11)	1.27 (.05)
3	C	3.3	0.0168	0.675	0.675		20.80 (0.25)	63 (10)	1.35 (.04)
4	0	1.5	0.099	0.836	0.836	0.005	18.7 (0.99)	176 (18)	1.65 (.21)
5	C	6.0	0.132	0.89	0.89	0.005	19.3	361	2.11
6	0	1.4	0.166	0.845	0.84	0.005	17.32 (1.11)	158 (19)	2.15 (.21)
7	S	1.5	0.166	0.830	0.83	0.005	17	136	1.0
8	C	7.4	0.164	0.910	0.905	0.005	16.10 (0.6)	303 (13)	1.90 (.14)
9	F	1.00	0.165	0.833	0.827	0.006	17.5 (1.3)	274 (20)	2.19 (.27)
10	0	2.0	0.198	0.855	0.850	0.005	17.7 (0.21)	169 (20)	1.91 (.18)
11	C	5.0	0.195	0.982	0.980	0.02	20.8	488	2.87
12	C	2.95	0.326	0.996	0.980	0.013	21.5 (0.8)	537 (13)	0.87 (.08)
13	C	2.35	0.650	1.020	0.990	0.030	9.43 (0.21)	516 (15)	1.39 (.15)
14	C	2.85	0.973	1.037	0.990	0.047	9.08 (0.23)	538 (14)	1.85 (.14)
15	C	4.20	1.294	1.062	0.992	0.069	9.08 (0.16)	534 (11)	2.40 (.14)
16	S	6.8	1.304	0.993	0.993	0.059	8.87 (0.19)	342 (16)	1.82 (.13)
17	C	3.25	1.925	1.126	0.991	0.133	9.55 (0.18)	519 (12)	1.62 (.11)
18	CL	4.05	1.927	1.139	0.994	0.140		497 (12)	
19	S	6.05	1.950	1.020	0.899	0.120	10.13 (0.15)	372 (12)	3.52 (.22)
20	C	5.20	3.075	1.54	0.994	0.522	11.75 (0.21)	438 (13)	2.43 (.14)

3. Results and discussion. — **3.1 MC RESULTS AND ADSORBATE STRUCTURE.** — Some properties of the system obtained from the MC runs are given in table I. The initial configuration for a run was the empty box (0), a close packed monolayer (C) or an epitaxial monolayer (S). Run 9 was a continuation of run 8 in which a transition to lower occupation had occurred. In run 18 the cut-off distance was extended from its usual value of 3.0 to 5.5. Z is the activity after correction for long-range

interactions [2, 3]. $\theta^{(e)}$ is the Gibbs excess number of particles in the system divided by the number in a statistical monolayer, $\mathcal{A}\sigma_m$. If the monolayer is assumed to be close-packed with nearest neighbour distance 1.122 5 then $\sigma_m = 0.916$ 5. $\theta(i)$ is the fractional filling of layer i , i.e., the number of particles in the i th layer divided by $\mathcal{A}\sigma_m$. The number in the i th layer was calculated from an integral of the density distribution with respect to r_z with the limits corresponding to the spacing

between (111) planes in an f.c.c. lattice. q_{st} is the isosteric heat and C is the heat capacity at constant area and surface excess. Further details of the calculations have been given elsewhere [1, 2].

Usually a run at a given activity from one initial configuration was ergodically separate from another run at the same activity which had been started from a different initial configuration. This difficulty can be met by comparing $-\Omega/\mathcal{A}$ values for different initial configurations at the same activity to determine the most stable system. It is well known that *crystallization* is very difficult to obtain in simulation calculations [7] so that, for example, a transition from the configurations of run 19 starting from an epitaxial monolayer to those of run 17, (18) starting from a close-packed monolayer would not be expected. Nevertheless the very considerable difference in $-\Omega/\mathcal{A}$ between these runs establishes that the close-packed starting point provides the more stable system. A similar conclusion emerges from a comparison of runs 15 and 16 where the close-packed configuration is again preferred to that of the epitaxial system. At low activities the close-packed arrangement becomes less stable. Thus runs 11 and 5 must be regarded with some caution because even after 5 and 6×10^6 configurations respectively convergence was not good. Run 8 on the other hand did appear to converge but then showed a rapid fluctuation to the less stable system of lower density which is labelled as run 9. Since $\theta^{(e)}$ would be ~ 0.8 for an epitaxial monolayer it is possible that this structure might be stable when the coverage is close to this value. However in run 7, which was started from an S configuration, the coverage increased rapidly towards that found in runs 6, 8 and 9. Furthermore the pair distribution function for run 7 retained none of the characteristics of the epitaxial structure after a few thousand configurations had been sampled. At lower activities the close-packed structure broke down quite rapidly and the ergodic barrier between 0 and C initial configurations appeared to have vanished at $Z \approx 1 \times 10^{-5}$.

The structure of some of these adsorbates is indicated by the pair distributions $\rho^{(2)}(r_{12}; 1)$ averaged over the region of the first layer in the manner previously described [1, 2]. They are plotted as functions of the pair separation r_{12} in figure 1. The characteristic double maximum at $r_{12} \sim 1.95$ and ~ 2.20 is a feature of random dense packing of spheres [8] and is well resolved in run 14. At the lower densities reached in runs 11 and 5 the resolution of these peaks is less clear and is absent in run 3 where $\rho^{(2)}$ is now characteristic of low density liquids. Although complete convergence was not achieved in runs 5 and 11 it is clear that the trend in $\rho^{(2)}$ is away from that of the close-packed structures and towards that of a liquid-like structure.

These observations are consistent with the

FIG. 1.— Examples of pair distribution functions angle averaged over the thickness of the first layer. The lines are drawn through data points to 100 equal intervals in $1/r_{12}^2$ (see Ref. [1]). Successive examples are shifted vertically by 0.2 which is the spacing of the intervals on the vertical axis. Curves are labelled according to the run number in table I.

two-dimensional character of the adsorbate. In 2 D systems a gradual decrease from regular packings of high density to irregular packings of lower density is possible. This contrasts with 3 D systems where there is a gap in the range of possible packings of hard spheres which is thought to be a fundamental property of three-dimensional space filling [8].

The position of the first maximum in $\rho^{(2)}$ is close to $r_{12} = 1.10$ and tends towards a lower position as coverage decreases. This may be compared with the nearest neighbour distance for close-packing (~ 1.11 when allowance is made for relaxation in a 2 D crystal [9]), the position of the maximum in liquid Ar (~ 1.08) and the separation of adsorption sites (1.25). In earlier calculations with the structureless (H) adsorbent the first maximum was always close to 1.08. There is some evidence therefore of a tendency for the adsorbate to be perturbed by the periodicity of the substrate even at the relatively low energy barriers in this system.

3.2 COMPARISON WITH EXPERIMENTAL RESULTS.

— For the purpose of comparison with experimental results the MC data were shifted to 77 K using the heat capacities to obtain new isosteric heats and the heats to obtain new values of Z . The increase in q_{st} was of the same order of magnitude as the standard deviation. The change in Z was much greater; but a change of similar magnitude also occurs in Z_0 (the vapour activity of the adsorptive). The overall effect is to produce a slight increase ($< 3\%$) in $\theta^{(e)}$ at a given value of Z/Z_0 . The resulting isotherms and heat curves are shown in figures 2 and 3. Points from the previously investigated (H) system, likewise shifted to 77 K, are also shown. The monolayer capacities of the experimental systems

were taken as the *point B* values given by the authors [10, 11]. It is notable that the *point B* method, applied to the MC data, would also give excellent monolayer values for both model adsorbents. For the purpose of comparison Z/Z_0 was assumed to be equivalent to p/p_0 , this assumption should introduce no serious error.

FIG. 2. — Isotherms for argon at 77 K. MC data for 12-6 Ar on the P-adsorbent $\square$, H-adsorbent $\circ$. Only stable configurations are shown. Experimental data — Rouquerol *et al* [10] on Sterling MT, — Goellner *et al*, --- Hegde (from ref. [11] on graphoil).

It is clear from figure 2 that adsorption is greater on the P-adsorbent than on the H-adsorbent. Moreover the adsorbate on the H-adsorbent showed evidence of a transition from a liquid-like monolayer structure of low density to a solid-like structure of higher density between $Z/Z_0 \sim 0.05$ and $Z/Z_0 \sim 0.10$. This behaviour may be contrasted with that of the P-adsorbent where close packed structures were still the most stable at down to $Z/Z_0 \cong 0.01$. The experimental results of Rouquerol and co-workers [10] on Sterling MT graphite also showed a transition at $Z/Z_0 \sim 0.07$, although previous experiments on graphoil [11] have failed to do so. As already noted the existence of the potential wells at sites counteracts the tendency of the adsorbate molecules to pack at hard sphere distances. Consequently the randomly packed hard sphere configurations, which underly liquid structure, and which result in a distribution function maximum at $r \sim 1.08$, would be less favoured on the P-adsorbent than on the H-adsorbent. The persistence to low Z/Z_0 of a close-packed structure for the Ar on the P-adsorbent might be attributed to this cause. Although there is a somewhat higher adsorption in the second layer on the P-adsorbent, due to differences in the shape of the potential well, this would not affect the sub-monolayer points (c.f. table I).

The heat curves in figure 3 show the main characteristics of the experimental curve obtained by Rouquerol *et al* [10]. It is especially notable that

FIG. 3. — Isoteric heats at 77 K. The symbols are the same as those for figure 2.

the MC results support the existence of two maxima separated by a sharp minimum which occurs at just below monolayer coverage. The few points available for the H-adsorbent are also consistent with this pattern. The experimental data have been interpreted in terms of a gradual (high order?) transition from a fluid to a close-packed solid state in the range $0.7 \cong \theta^{(e)} \cong 1.0$. Since βq_{st} is plotted against $\theta^{(e)}$ and not Z the discrepancies arising between the isotherms do not appear in the heat curves. Quantitatively the agreement up to $\theta^{(e)} = 1.0$ appears to be quite good. Either heterogeneity in the experimental system or inadequacy in the adsorbent potential used in these calculations might be responsible for the difference of 0.75 in the initial heats. The first explanation appears to be improbable because there is no initial decrease in βq_{st} . A quantum mechanical correction to the MC value would increase βq_{st} by 0.16, and is therefore insufficient to account for the observed difference. The uncertainty in the MC results in the region of the minimum and second maximum would be rather larger than the standard deviation error bars shown because of poor convergence for the runs 5 and 11. Beyond $\theta^{(e)} = 1.0$ both model systems fail entirely to account for the experimental curve. This suggests that this stage of the adsorption may be especially sensitive to the limitations of the pairwise 12-6 potential.

3.3 THEORETICAL MODELS. — If we define a Henry's law constant K_H by

$$K_H = \theta^{(e)}/Z \quad (\text{Lt. } Z \rightarrow 0) \quad (8)$$

it can be shown [12] that K_H is related to the potential in eq. (1) by

$$K_H = \frac{1}{\sigma_m} \int_0^1 \int_0^1 \int_0^\infty [\exp(-\beta\psi(r)) - 1] ds_1 ds_2 dr_z \quad (9)$$

The very low coverage result of run 1 gives $\theta^{(e)}/Z = 1.1_3 \times 10^5$. Eq. (9) was evaluated in three ways. (i) Using $\psi(r) \equiv E_0(z^*)$, the unweighted average energy given by eq. (1). ($K_H = 0.96_7 \times 10^5$). (ii) Using a 3 D translator model with full allowance for the periodicity of the potential from eqs. (3) and (4). ($K_H = 1.16 \times 10^5$). (iii) Using the assumption that the adsorbate is a layer of 2 D translators with classical vibration in the r_z direction. Here

$$K_H = \exp(-\beta\psi_M) (2\pi/\beta k_z)^{1/2} / \sigma_m \quad (10)$$

where ψ_M is the minimum with respect to r_z of the weighted mean energy $\bar{\psi}(r_z)$ averaged over the $r_x r_y$ plane and $k_z = (\partial^2 \bar{\psi}(r_z) / \partial r_z^2)$ evaluated at the minimum in r_z . ($K_H = 1.1_2 \times 10^5$).

The limiting values of $\beta q_{st}(\theta^{(e)}) (\equiv \beta q_{st}(0))$ may also be compared with the value of 14.18 given in the table. The mean energy calculated from

$$\beta \langle \psi \rangle = \int \beta \psi(r) \exp(-\beta\psi(r)) \times dr / \int \exp(-\beta\psi(r)) dr \quad (11)$$

is -13.72 which leads to values for $\beta q_{st}(0)$ of ; 14.72 (3 D translator), 14.22 (2 D translator and r_z vibrator), and 13.48 (3 D vibrator).

It may be concluded that the 2 D gas model provides a satisfactory representation of the MC result at very low coverage.

Mobile two-dimensional monolayers are often discussed in terms of the Hill-de Boer isotherm, in the present notation this may be written

$$\ln(ZK_H/\theta^{(e)}) = \theta^{(e)}/(1 - \theta^{(e)}) - \ln(1 - \theta^{(e)}) - a\beta\epsilon\theta^{(e)}. \quad (12)$$

The first two terms on the right hand side of eq. (12) give the entropy contribution according to the van der Waals model due to hard discs, while the third term arises from a mean field treatment of the attractive interactions. The constant a is usually obtained from an integration over 2 D space with the assumption that the pair correlation function is unity and for the 12-6 potential this leads to $a = 2.4$.

In an improved form of this theory the hard disc terms were replaced by a scaled particle equation and a first order correction to the pair correlation function [12] was used in the evaluation of the attractive term. The resulting equation reads

$$\ln(ZK_H/\theta^{(e)}) = \frac{\theta^{(e)}(3 - 2\theta^{(e)})}{(1 - \theta^{(e)})^2} - \ln(1 - \theta^{(e)}) - \beta\epsilon[4.8\theta^{(e)} + 5.76\theta^{(e)2}] \quad (13)$$

A comparison between the MC results and these equations is given in figure 4. The isosteric heats were obtained by adding the final term from (12) or (13) to $\beta q_{st}(0)$. Neither equation is very successful in representing the MC data obtained in this work.

Further modifications to this type of equation were introduced by Lee and O'Connell [13] to account for the inhibition of mobility caused by lateral periodicity in the adsorbent-adsorbate potential but the effect of these modifications is too small to be shown on the scale of figure 4.

FIG. 4. — Comparison of MC data with mobile two-dimensional models. I calculated using eq. (12), II calculated using eq. (13).

4. Conclusions. — MC calculations at 80 K for 12-6 Ar adsorbed on a model graphite with periodic variation of the potential field have shown that the adsorbate undergoes a gradual transition from a solid-like to a liquid-like structure as activity is decreased. This behaviour is similar to that observed experimentally and for the previously investigated homogeneous substrate, but the transition now occurs at lower activities. Isosteric heat curves on the other hand were in satisfactory agreement with experimental data for βq_{st} against $\theta^{(e)}$ up to $\theta^{(e)} = 1.0$ but showed marked deviations beyond this point.

The Henry's law constant and zero coverage heat from the MC data both support a 2 D gas model but it is necessary to include the laterally periodic part of the adsorbate-adsorbent potential in order to obtain good agreement with the model. Although it would be unwise to draw extensive conclusions from a single temperature study, it would appear that the potential of eqs. (1) to (4) is quite adequate as a graphite-argon potential. At the same time it must be borne in mind that these equations are in effect based on a pairwise summation of 12-6 interactions and the disagreement between MC and experimental heats at $\theta^{(e)} > 1.0$ suggest that this procedure may not be adequate for the description of adsorbate properties.

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DISCUSSION

M. BIENFAIT. — For coverage larger than 1, your theoretical results don't fit the experimental curves. You suggest that your model is not adequate for the description of the system in this coverage range. One can also assume that at high coverages intergranular condensation could perturb the experimental results. Anyway there is a better agreement between your calculation and the latest results of Rouquerol given in these Proceedings.

D. NICHOLSON. — It is true that adsorption in intergranular spaces would have the effect you suggest but the pore sizes would have to be very small (micropores) for this to be important at low relative pressures. The more recent results from Rouquerol's group do show much better agreement with our MC calculations than the earlier measurements. However, the relative pressure at which the transition occurs (~ 0.024) is higher than

that found in our calculations on the P-adsorbent (~ 0.01) and the experimental heats remain higher than the MC heats at coverages beyond a monolayer although this difference is now reduced with the new experimental data.

J. A. VENABLES. — It is very interesting that the L - J potential predicts isosteric heats near monolayer coverage which are slightly too small by comparison with experiment. We also find (J. A. Venables and P. Schabes-Retchkiman, these proceedings, and G. L. Price and J. A. Venables, *Surf. Sci.* **59** (1976) 509) that the L - J adsorbed layer is underbound for Kr and Xe on graphite. This must be due to the fact that (repulsive) manybody forces are smaller in the 2D than in 3D situation, so that the L - J potential overcompensates for many-body effects in 2D applications.