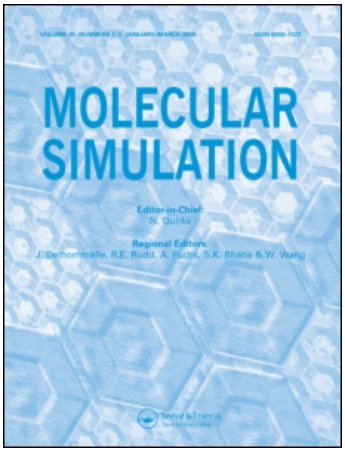

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A Fast-convergent Monte Carlo Method for Surfaces with High Potential Barriers to Movement of Adatoms

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A FAST-CONVERGENT MONTE CARLO METHOD FOR SURFACES WITH HIGH POTENTIAL BARRIERS TO MOVEMENT OF ADATOMS

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A new Monte Carlo method is described that is suitable for studies of adsorption systems in which the movement of adatoms is hindered by large potential barriers. The technique involves the possibility of a "jump" of a particle by one lattice vector of the substrate. The method is tested on a model for studies of commensurate–incommensurate transitions. It is shown that the modification leads to considerable advantages in terms of convergence, as indicated by control charts for the mean potential energy and the mean displacement of the particles from the nearest commensurate site for a system with a potential barrier of 6†. Results are presented for three values of the fractional coverage (θ = 0.667, 0.833 and 0.958 with respect to the commensurate monolayer) and for two values of the inter-particle Lennard-Jones parameter ε^* (ε^* = 3 and 8).

KEY WORDS: Monte Carlo, simulation, adsorption, potential barriers.

INTRODUCTION

A great deal of theoretical work has been devoted to the study of the physisorption of simple gases on the basal plane of graphite [1a]. There are two main reasons for this concentration of effort. First, because of the availability of graphite in very well-characterised form, there is experimental data of very high quality. Secondly, because of the nature of the graphite surface, it approximates well to a completely smooth, or unstructured, surface, for which it is relatively easy to devise theoretical treatments. In the last few years theoretical treatments taking account of the structure of the graphite surface have been developed, and these have further improved the agreement between theory and experiment [2, 3, 4].

Even though the potential barrier opposing movement of the adsorbed molecules is very small and is not at all typical of those to be expected for the large majority of substrates, some sluggishness in equilibration is observed. Furthermore, it has been shown that serious convergence problems, requiring special expensive procedures to show that convergence has been reached, arise for molecular simulation if systems having much larger barriers (as, for example, argon on pseudo-graphites with barriers > 380 k) are considered [4]. Thus, in order to make studies of films adsorbed on a wider range of surfaces it is essential to devise a method that can overcome the problem of the extremely small success rate in surmounting potential barriers.

The present paper introduces and tests a method for making Monte Carlo studies for systems of this kind with arbitrarily high potential barriers. It is demonstrated that

†Throughout this paper all energies are given in units of kT.

the new method has a substantial advantage over the normal procedure in terms of rate of convergence.

METHOD

It is well known that the rate of convergence of Monte Carlo studies of lattice models is much greater, often by an order of magnitude, than that for non-lattice (or continuum) models. However, for physical adsorption it is generally a poor approximation to assume that molecules may be adsorbed only on specific sites. The method adopted here attempts to obtain the convergence advantages of the lattice model, while retaining the realism of the non-lattice models.

In the normal Monte Carlo procedure a change in position is chosen randomly within a limited range (Eq. (1a)), the step-length parameter (a). We here include a chosen proportion of a second type of trial move (a "jump" move) in which the normal randomly chosen shift is combined with a shift equal to one lattice-spacing of the absorbent lattice (Eqs (1b or 1c)). Thus the possible modifications of positions are:

$$\left.\begin{aligned} \delta x &= a \times \xi \\ \delta y &= a \times \xi \end{aligned}\right\} \qquad (1a)$$

$$\left.\begin{aligned} \delta x &= a \times \xi \pm a_x \\ \delta y &= a \times \xi \end{aligned}\right\} \qquad (1b)$$

$$\left.\begin{aligned} \delta x &= a \times \xi \\ \delta y &= a \times \xi \pm a_y \end{aligned}\right\} \qquad (1c)$$

where ξ is a random number in the range -1 to $+1$. a is the usual step-length parameter, and a_x and a_y are the lattice parameters for the x- and y-directions, respectively.

In the work described here, 84% of tries were of the normal kind (as Eq. 1a) and the remainder were of the "jump" type (as Eqs 1b and 1c). The choice of the type of trial move was made randomly between the five (one normal and four "jump") types of move represented by Eq. 1 in such a way as to give the desired proportion of normal moves.

It is expected that the inclusion of the "jump" moves will facilitate movements of molecules over large distances and over large barriers and hence greatly speed up the development of large-scale structures. Where large barriers are involved, even movements over a single lattice spacing may be exceedingly slow by the normal method, so that a considerable advantage would then be expected even for quite small-scale structural changes.

MODEL

Since we are here testing the method and, at the same time, aiming towards a general understanding of commensurate–incommensurate (C–IC) transitions, we have chosen the simplest structure for the adsorbent surface, namely a square lattice of lattice parameter unity. For the potential of interaction between an adsorbate molecule and

the adsorbent (u_{iw}) we adopt the form:

$$u_{iw} = BR_{min} \tag{2}$$

where R_{min} is the distance of the adsorbate particle from the nearest site. The difference between the minimum value of u_{iw} (zero at $R_{min} = 0$) and the maximum value is $B/\sqrt{2}$; the difference between u_{iw} at a saddle-point between two sites and the potential at the sites is $B/2$. The results presented here are for $B = 10\,\mathrm{kT}$. The value of the quantity barrier/kT† in the present simulations are $\sim 10\times$ those used in the most commonly studied real system, argon on graphite at 80 K. For this system Steele has given a value for the barrier of ~ 38 k, which at 80 K, in the middle of the temperature range for which these adsorption studies are usually carried out, leads to a value for barrier/kT = 0.35 [5].

The interaction between adsorbate molecules is represented by the Lennard-Jones potential:

$$\varepsilon = 4\varepsilon^* [(\sigma/r)^{12} - (\sigma/r)^6] \tag{3}$$

The minimum image method was adopted for dealing with the spurious periodicity introduced by the application of periodic boundary conditions [1b].

Computations have been carried out for a simulation box of size 12×12. This size indicates the number of unit squares (and the number of commensurate sites) (N_s) in the simulation box. The values of the number of particles ($N = 120$, 96 and 138) correspond to fractional coverages with respect to the commensurate lattice of 0.833, 0.667, and 0.958, respectively. The designation of each run incorporates the value of N.

RESULTS

Figures 1a and b show partial sum averages for the mean potential energy ($\langle U \rangle$) for $N = 120$ as a function of the length of runs up to that point. The partial sum averages are each taken at intervals of 100 K configurations. In each of these cases the starting configuration is remote from the equilibrium configuration. Thus the starting configuration for run 120A (described in Figure 1a) was incommensurate (IC), but the parameters are such that the final configuration is commensurate (C), and vice versa for run 120B (Figure 1b). It will be seen that the new modified method approaches equilibrium much more rapidly than the normal method. In Figure 1a, $\langle U \rangle$ reaches a steady value after ~ 2600 K moves with the modified method, but is still drifting upwards after 5000 K moves with the normal technique. A longer run (> 15 M moves) using the normal method settled to a value of -1.845×10^{-18} for $\langle U \rangle$ and 0.106 for the mean displacement of the particle from the nearest commensurate site ($\langle R \rangle$), supporting the correctness of the values found by the modified method and shown here and in Figure 4 as against those suggested by the shorter normal run.

In Figure 1b, over the first 400 K moves of the normal system the modification leads

†The term "barrier height" is sometimes applied to the minimum energy required for the particle to be able to move to the next cell, and sometimes to the energy required to reach the peaks of the potential energy surface. The former definition is clearly appropriate for studies on rates of motion over the surface, but the latter is probably more appropriate for studies of static properties, where one is interested in the accessibility of all the surface. In many papers the mean of these two values is referred to as the barrier height, and this is the definition adopted here.

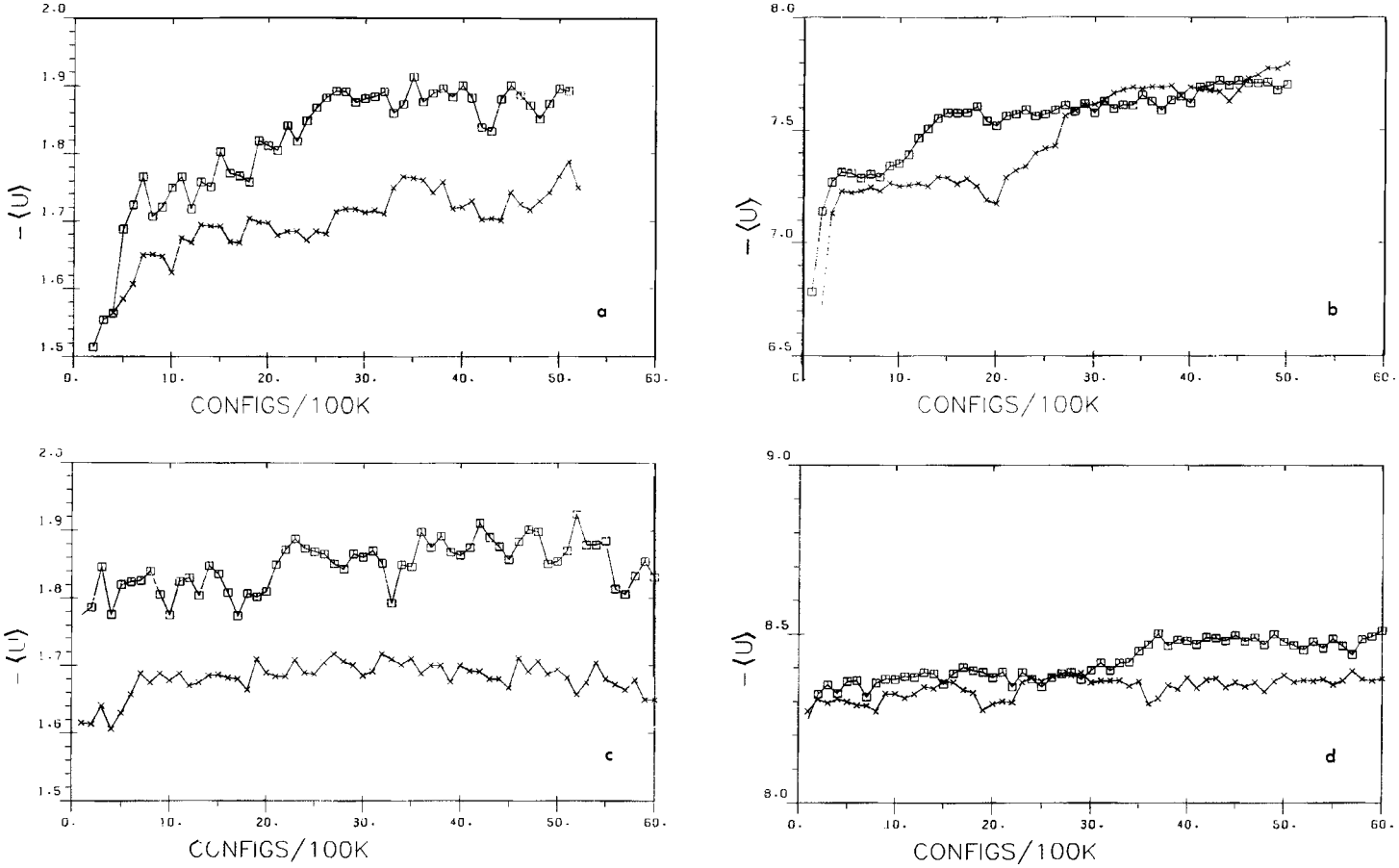

Figure 1 Mean potential energy (in units of 10^{-18}) versus number of configurations. × = Normal MC; □ = Modified MC. (a) $\varepsilon^* = 3$, start IC. (b) $\varepsilon^* = 8$, start C. (c) $\varepsilon^* = 3$, start C. (d) $\varepsilon^* = 8$, start IC. $N = 120$.

to a saving of ~25%. Far more important, however, is the big saving with respect to the second stage of equilibration, that which takes $-\langle U \rangle \times 10^{18}$ from ~7.3 to ~7.6. This stage, which probably involves in the normal procedure the surmounting of the adsorbent potential barrier, is reached in ~1600 K moves with the modified method as against ~2600 K for the normal method, a saving of ~38%. During the first 1000 K moves of both runs the difference between the methods is not great, and this may be interpreted as being because during this period the main changes are in *local* equilibration and do not require many movements across potential barriers. A longer run (> 15 M moves) using the normal method gave values of -7.70×10^{18}

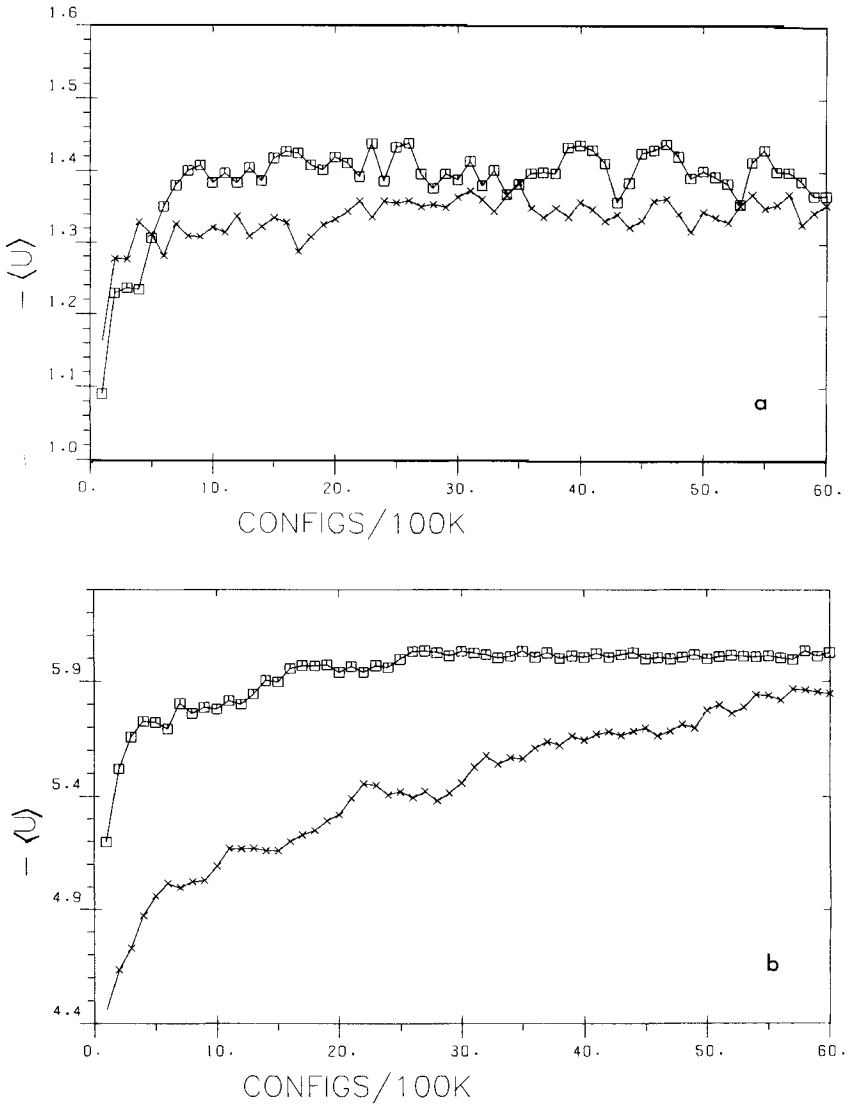

Figure 2 As Figure 1 but $N = 96$. (a) $\varepsilon^* = 3$, start IC. (b) $\varepsilon^* = 8$, start C.

and 0.320 for $\langle U \rangle$ and $\langle R \rangle$, respectively, in good agreement with the values found by the modified method in the run of ordinary length (Figures 1b and 4b).

Figures 1c and d show the corresponding charts for runs in which the simulations start from configurations similar to the final configurations. Thus, the starting configuration for run 120C, which has the same parameters as run 120A, was commensurate. Likewise, run 120D, which shares the same parameters as run 120B, was started from an incommensurate configuration. In the modified version of run 120C the value of $-\langle U \rangle$ is drifting very slowly upwards; in run 120D the corresponding drift is almost imperceptible. The modified version of run 120C gives results that are

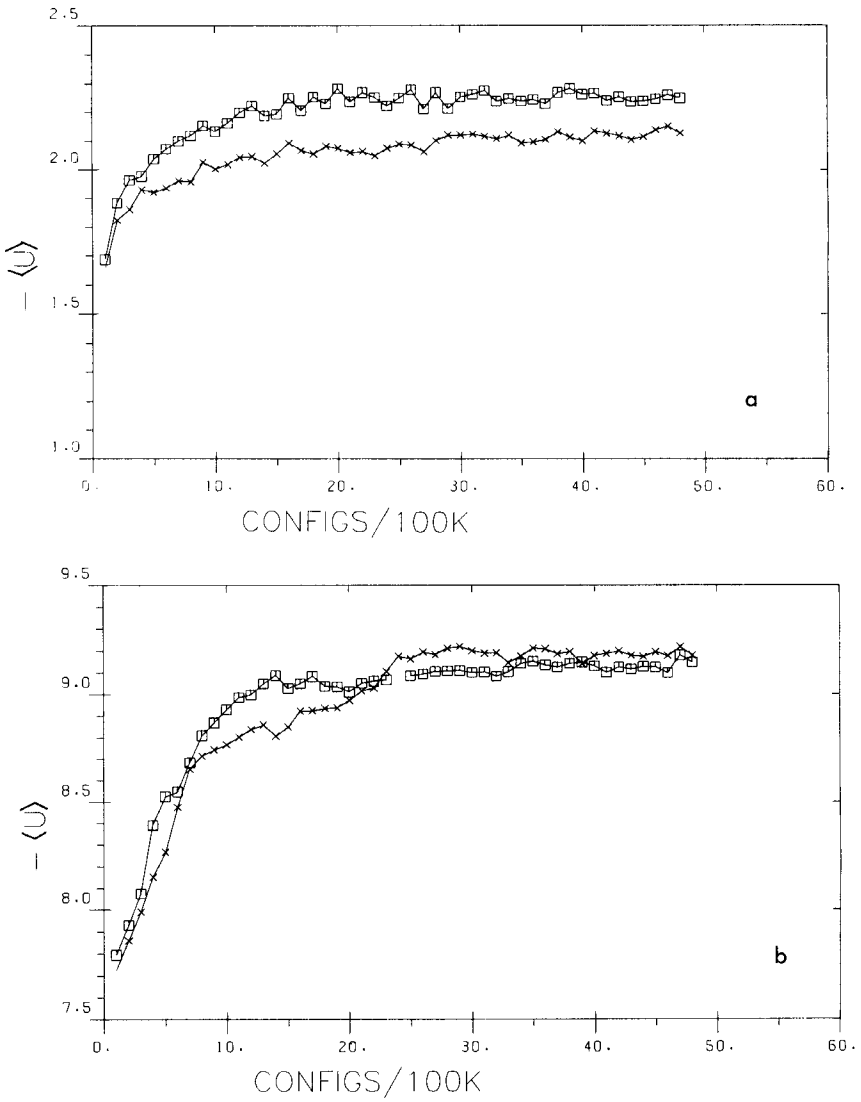

Figure 3 As Figure 1 but $N = 138$. (a) $\varepsilon^* = 3$, start IC. (b) $\varepsilon^* = 8$, start C.

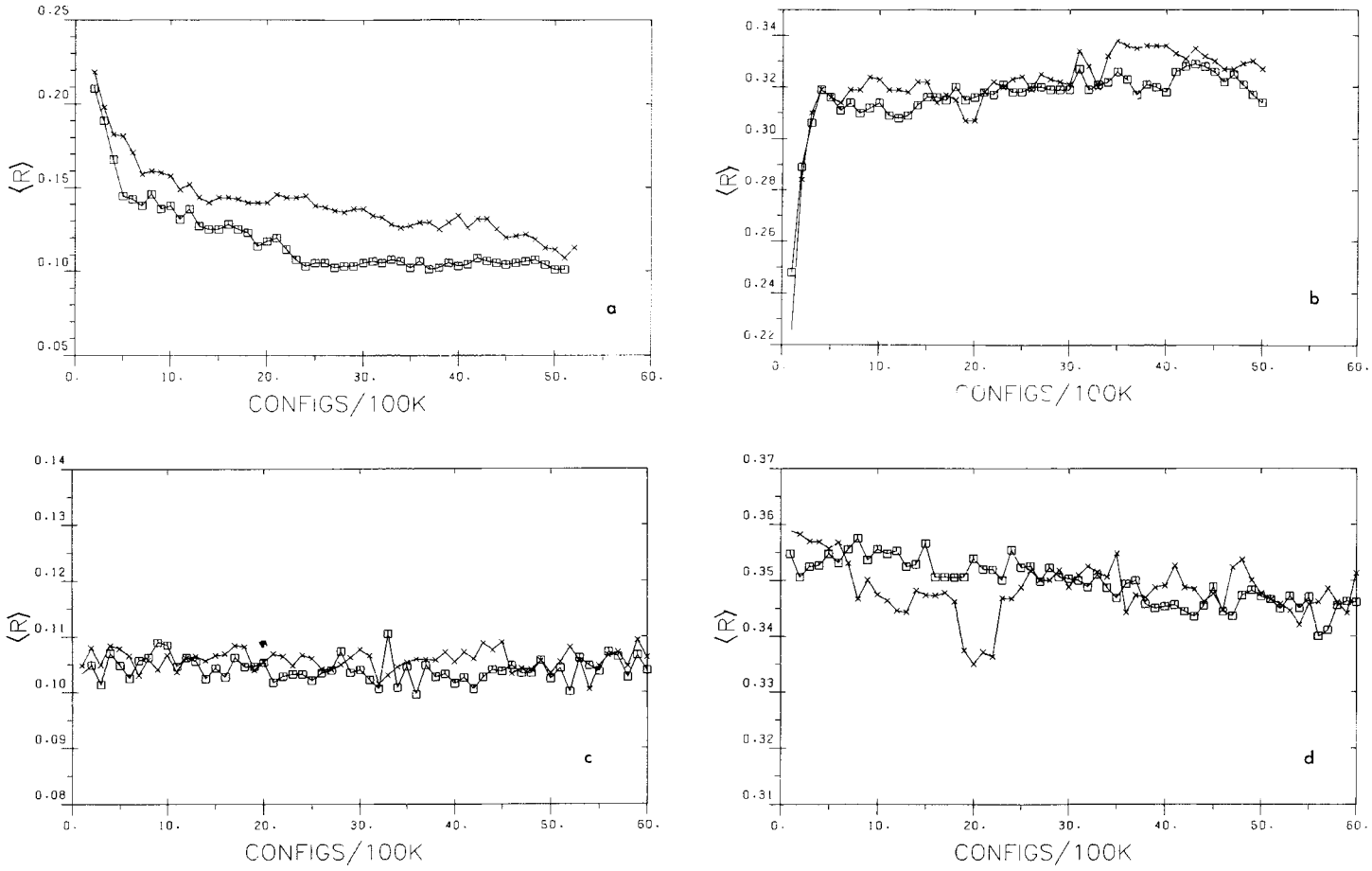

Figure 4 Mean displacement from the nearest site of the commensurate lattice ⟨R⟩ versus number of configurations. $N = 120$. a, b, c, d as for Figure 1.

in excellent agreement with the corresponding results for run 120A and with those from the extended normal version of 120A; agreement for run 120D with the equivalent 120B results is less good, indicating that the present method is most advantageous when the forces opposing epitaxy are not too strong. Figures 2 and 3, which refer to corresponding runs with 96 and 138 particles, respectively, are discussed later.

Figures 4, 5 and 6 show the corresponding partial sum averages for the mean value of the distance of an adsorbed molecule from its nearest site ($\langle R \rangle$). (It is not difficult to show that for the present model a completely random arrangement of the particles would lead to $\langle R \rangle = 0.3832$.) For run 120A (Figure 4a), the modified method is

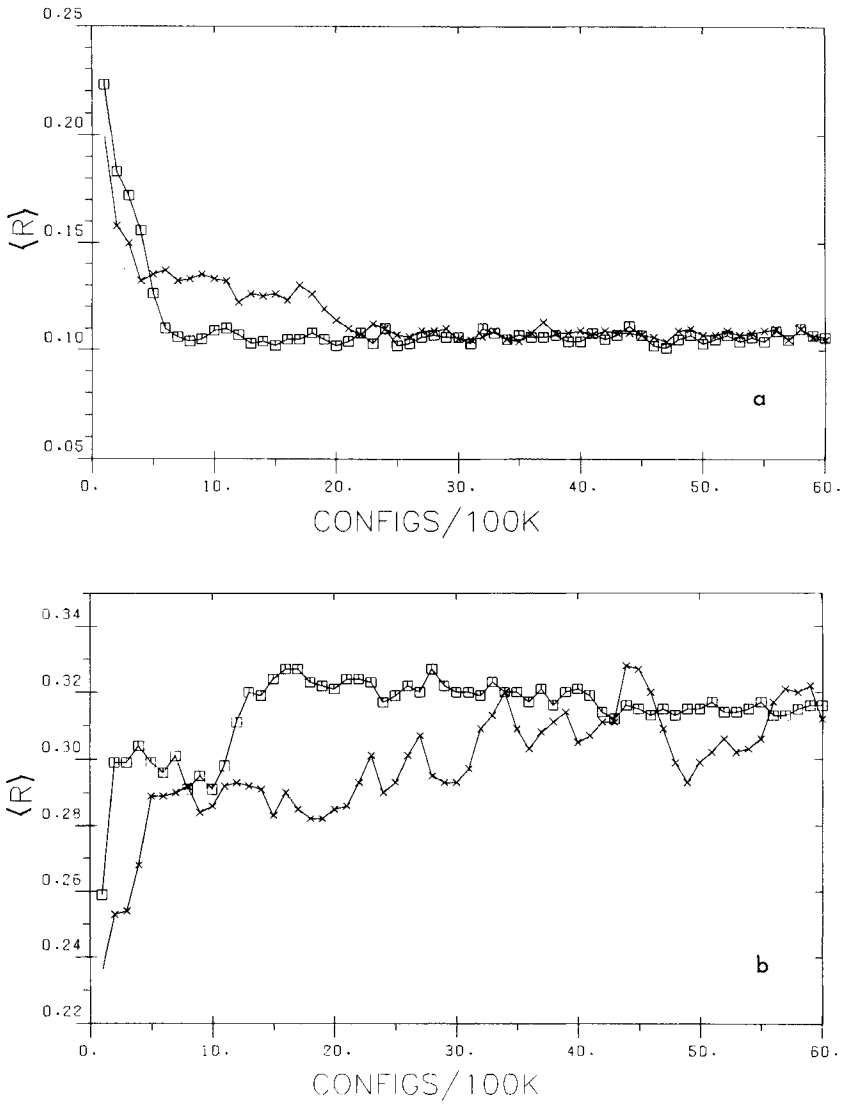

Figure 5 As Figure 4 but $N = 96$. (a) $\varepsilon^* = 3$, start IC. (b) $\varepsilon^* = 8$, start C.

clearly more efficient: it yields steady partial sum averages from ~ 2.2 M configurations onwards, whereas the normal procedure, after the initial rapid fall up to 1 M configurations, shows a steady downward drift that is still not complete after 5 M configurations. For run 120B (Figure 4b), in contrast, there is little to choose between the normal and modified methods, although the former shows rather more "wandering" near 3500 K configurations.

Figures 4c and d refer to runs 120C and 120D. Here there is little to choose between the normal and modified methods. For run 120C neither method encounters any serious problems of convergence, the value of $\langle R \rangle$ being very steady (note the scale

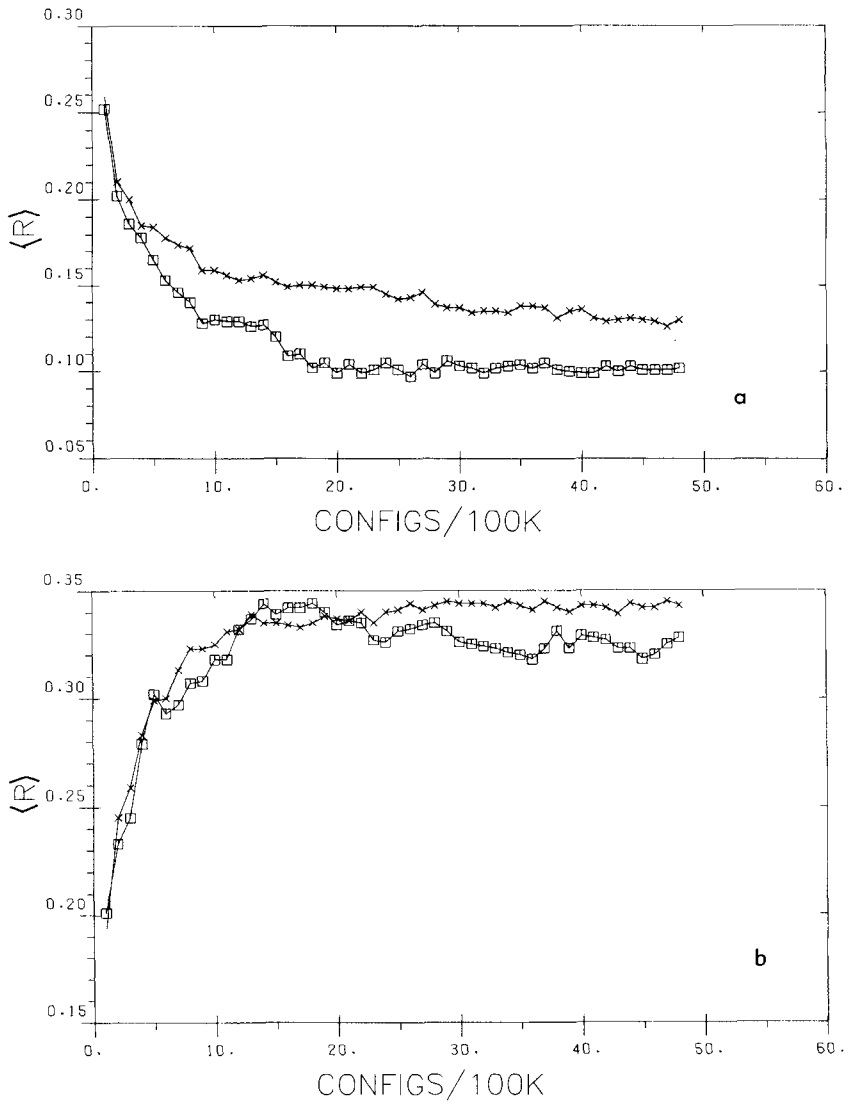

Figure 6 As Figure 5 but $N = 138$. (a) $\varepsilon^* = 3$, start IC. (b) $\varepsilon^* = 8$, start C.

Table 1 Overall acceptance rate and the acceptance for jump moves.

	Run 96A	*Run 96B*	*Run 138A*	*Run 138b*
Overall acceptance rate (%)	~63	~40	~60	~40
Acceptance rate for jump moves (%)	1.30	0.008	0.76	0.015

of the graph). For the 120D run, however, there is a small, though distinct, drift downwards in both versions towards the values reached in run 120B, which has the same parameters but a commensurate starting configuration.

Figures 5a, b and 6a, taken with Figures 2a, b and 3a, show that the modified method has a large advantage for runs 96A, 96B and 138A; Figure 6b, taken with Figure 3b, indicates little difference between the methods for run 138B, with possibly even a small advantage for the normal method.

The percentage success rates for all moves and for the jump moves only are given in Table 1. It will be seen that the rates for jump moves are low, so that the observed improvement in convergence is achieved in spite of this. Although the jump moves are infrequently accepted, when they are they make important changes in the configuration of the system. Also, the rate for jumps is much larger for runs with $\varepsilon = 3$ than for those with $\varepsilon = 8$. This is probably because the commensurate structures, for which the jump moves are especially appropriate, are dominant for $\varepsilon = 3$, but not for $\varepsilon = 8$. Finally, for $\varepsilon = 3$ there is a small decrease in the jump rates as the coverage of the surface is increased. This may simply be due to the reduction in the number of vacant nearest neighbour commensurate positions into which the particle could jump. That the effect observed for $\varepsilon = 8$ is the opposite direction may be associated with the fact that the adatoms are now to a large extent clustered as a result of the strong interaction between them, in spite of the potential barriers.

CONCLUSIONS

The new method has been shown to have clear advantages over the normal method with respect to speed of convergence for a potential barrier of ~ 7 kT. It is reasonable to assume that the advantage would be even more striking for larger values of barrier/kT. Clearly, at very large values of this quantity the normal method will not converge, whereas the modified method will still do so.

What are the limitations of this approach? The main restriction would appear to be the requirement to know beforehand what value the lattice parameters (a_x and a_y) should take and what the symmetry of the lattice should be. In the case of adsorption systems it is clear that the "jump" parameter of the method should be equal to or simply related to that of the lattice structure of the surface of the adsorbent, which is always known. For uniform three-dimensional systems, say the study of melting or a solid–solid transition, one would need to know beforehand the lattice parameters of the competing phases, and it may be feared that guesses for these items of information would prejudice the choice of structure eventually adopted in the simulation. The method described here could be used for a system with high internal rotational barriers, since one knows beforehand where the barrier is going to occur (at $\theta = 0$, $2\pi/3$, and $4\pi/3$). Indeed, the procedure adopted here would have the

advantage over the umbrella sampling method used by Jorgensen [6] in that it could deal with very large or even infinite barriers without additional complication, whereas the umbrella technique would then call for a very large or even infinite number of intermediate distributions.†

It can be argued that, if an incommensurate structure is one of the competing phases, the provision of a jump related to the substrate lattice would not necessarily facilitate development: a jump related to the incommensurate structure would also be needed. This argument is supported by the observation that the advantage of the modified method is greater when the system is striving to form a commensurate phase ($\varepsilon = 3$, in this work) than when its goal is an incommensurate phase ($\varepsilon = 8$ here). Nevertheless, the advantage is often large even for the latter.

With the method as used here the convergence problems arising from the substrate potential barrier can be largely obviated, leaving as a residual problem that which is present even in the absence of that barrier. These residual problems were met in studies of the simple two-dimensional liquid–gas equilibrium by simulation [1c]. However, the difficulties of the residual problem should not lead to any qualitative error. Hence, with the present technique results of good accuracy should be obtainable for the commensurate–incommensurate transition in adsorption systems.

Acknowledgement

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†Note added following an observation by a referee.