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EVALUATION OF A MODEL POTENTIAL FUNCTION FOR Ar GRAPHITE INTERACTION USING COMPUTER SIMULATION

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The transition from a liquid-like to a solid-like state for Ar on graphite at 77 K, although well characterized experimentally, is difficult to reproduce in simulation. We review briefly the possible second order contributions to and influence on an *a priori* potential function, which may account for this difficulty. These include: anisotropy effects, three body terms and induced interactions. In view of the overall complexity of such a potential function, we propose a 2-parameter model in which the surface barrier height and adsorbate intermolecular interactions can be varied. It is found that a unique combination of parameters can bring simulation and experiment into much closer agreement than achieved hitherto.

KEY WORDS: Argon, graphite, potential functions.

INTRODUCTION

The adsorption of argon on graphite at temperatures around the normal boiling point of liquid nitrogen has been extensively studied experimentally [1–5] and using computer simulation [6–9]. Evidence from adsorption isotherms [4, 5] and from heat curves [4] supported by calorimetric measurements indicates that there is a characteristic liquid–solid transition at near monolayer coverage. The general features of this transition are readily reproduced in simulation with a variety of potential models, provided that the third dimension, normal to the surface, is included [7]. A precise representation of experimental behaviour is more difficult to achieve, suggesting that the system is well suited as a testing ground for the second order features which play a part in the subtle balance between adsorbate–adsorbate and adsorbate–adsorbent potentials. The improvement of model potential functions through a comparison of simulation and experiment in this system has a number of motivations: it should help to gain an insight into which features of the potential function are the most significant, both in this relatively elementary system, and in more complicated ones; secondly adsorption experiments at liquid nitrogen temperature are routinely used in the characterisation of microporous carbon solids where the adsorbent is ill-defined, here simulation, using reliable potential functions can be of use in interpreting experimental data. In addition, the relative size of the Ar atoms and the site spacing on the surface of graphite is such that a fairly small system (~200 particles) is able to accommodate the alternative possibilities of both commensurate and incommensurate adsorbates simultaneously. It should be noted however that the overwhelming weight of experimental evidence is in favour of the incommensurate structure.

POTENTIAL FUNCTIONS

The potential in this system can be represented in a straightforward way by writing the pair interactions (Ar–Ar and Ar–C) as 12–6 effective potentials, and summing the latter over all the sites in the graphite layers to give $u^{(1)}$, the adsorbent potential. The summations can be accurately represented by a Fourier expansion in which only the first two terms; a ‘continuum’ term, $u_0^{(1)}(z)$ and a first order correction, accounting for periodicity, are retained [10]

$$u^{(1)}(\mathbf{r}) = u_0^{(1)}(z) + u_1^{(1)}(z) f_1(x, y, \lambda) \quad (1)$$

In the modified form used in previous work [7]; λ is a parameter which controls the height of the barriers between sites

$$f_1(x, y, \lambda) = 6\lambda + (1 + \lambda) f_1(x, y) \quad (2)$$

where

$$f_1(x, y) = -2[\cos 2\pi s_1 + \cos 2\pi s_2 + \cos 2\pi(s_1 + s_2)]$$

with

$$\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} = \begin{pmatrix} 1 & 2/\sqrt{3} \\ 0 & -1/\sqrt{3} \end{pmatrix} \begin{pmatrix} x/a \\ y/b \end{pmatrix}$$

here \mathbf{s} is the vector which locates a position on the 2D graphite unit cell of side length a . The familiar results deriving from the standard 12–6 potentials [10] are obtained by setting $\lambda = 0$. Higher values of λ increase the corrugation of the potential function in the plane of the adsorbent by making the sites more repulsive; the overall barrier between sites is increased by a factor $(1 + \lambda)$ and the surface becomes more attractive.

It has been demonstrated in earlier work [6, 7] that the $\lambda = 0$ potential does not satisfactorily account for the experimental observations. An alternative approach would be to construct an *a priori* potential; whilst this is not yet feasible, it is useful to consider what would be required in such an endeavour. Here a brief review is given of the factors involved in constructing a potential from first principles. A fuller review has been given elsewhere [11].

It is convenient to analyse a putative *a priori* potential into two body and three-body components, deriving from the usual perturbation expansion, and repulsive components which, in principle might be obtained from SCF calculations.

Repulsive terms

These include overlap and exchange repulsion; for rare gas interactions it has been shown that both types of contribution can be accounted for using only two parameters [12]. In the case of adsorption on graphite, anisotropy is an additional factor which may be very significant [13]. To date a rather arbitrary treatment of this property has been made [14, 15]; in particular its effect on surface barriers is unknown, but likely to be important.

Two body terms

The dipole–dipole dispersion term is well understood, and may be evaluated in terms

of the (anisotropic) polarizability of the carbon in graphite [16] and the polarizability of Ar; anisotropy raises the barriers to mobility on the surface by a factor of *ca* 2, compared to those for an isotropic adsorbent. Higher order (dipole–quadrupole, quadrupole–quadrupole etc.) terms are also likely to be important in the vicinity of the equilibrium separation, but nothing is known about effects on barrier heights.

Three body terms

Because of the heterogeneity of an adsorbent–adsorbate system, there are three groups of dispersion energy terms which need to be considered:

(i) (Ar, Ar, Ar). The triple dipole term is given by the well known Axilrod-Teller-Muto expression; higher order terms are also well understood [17], and very nearly cancel out in a uniform fluid. The new feature here is that for the 2D monolayer alone, many contributions from out of plane triplets will be absent. This has the effect of greatly reducing the importance of 3-body effects in the adsorbate and consequently the ‘true 2-body + many body’ energy of a monolayer is quite different from that calculated using effective potentials. Much of the ‘missing’ energy will be restored from the other two triplet terms (Ar, Ar, C): the adsorbent energy term, and (Ar, C, C): the substrate mediated term. However differences in the polarizability and the anisotropy of the adsorbent both need to be taken into account.

(ii) (Ar, Ar, C). Only the dipole–dipole energy terms have been studied in detail [18, 19]; the effect on surface corrugation of the potential is negligible. It is well established that the pair interaction between adsorbate molecules is weakened by substrate mediation, however anisotropy in the substrate diminishes the effect by about 15% for a graphite adsorbent.

(iii) (Ar, C, C). Graphite anisotropy is a major factor in determining the importance of this term, to both the holding potential and to the surface corrugation. Although there is a rather complicated distance dependence, to a first approximation the triple dipole term makes no contribution to the holding of a graphite surface, whilst the corrugation is somewhat reduced. These effects are the opposite to those found for an isotropic substrate [20].

It is difficult to obtain quantitative estimates of all these effects even for a relatively well understood system. However insight into the importance of the many body terms can be gained by calculating a monolayer lattice energy (MLE) for Ar self adsorbed on an Ar substrate [21] where it is found that effective potentials result in a more attractive energy than true potentials. If the Ar substrate is replaced by a graphite substrate, and the above factors relating to the effect of anisotropy and triplet interactions are taken into account, the difference between the ‘effective’ and ‘true’ MLE vanishes to within the accuracy of the available estimates. This suggests that it may be inappropriate to correct effective adsorbate–adsorbate potentials by an additional substrate mediated (McLachlan) dispersion energy in rare gas systems. Indeed it would seem more probable that the effective potential is already too repulsive.

Induced Interactions

A further term may arise due to the electrostatic charge separation in graphite. For the purpose of estimating this we replace the usual π -electron plus carbon core picture of graphite by an array of quadrupoles, normal to the graphite surface each with a

positive charge at its centre located on the C-atoms and two negative half charges above and below the C-atoms. The quadrupole length is taken to be equal to the graphite plane separation.

The electrostatic field arising from this array is calculated by treating each quadrupole as a pair of dipoles and Fourier expanding the field due to the arrays of dipoles. The zeroth order term for the whole array is zero, but higher order periodic terms can induce multipoles in a polarizable adsorbate near to the surface. Therefore each argon atom has an induced dipole whose magnitude and orientation depends on its position on the graphite lattice. To estimate the order of magnitude of this term we consider an argon atom at a site position with other argon atoms close packed around it at equilibrium separations [25]. A nearest neighbour estimate of the energy of such a cluster is repulsive and ~ 5 K; equivalent to a small reduction in the 12-6 potential parameter ϵ_{ArAr} .

To construct an empirical potential function based on the above factors, three modifications can be considered:

(i) An increase in barrier heights which favours localisation of the adsorbate without promoting a transition to a commensurate phase [22], which is not observed experimentally.

(ii) A modification to ϵ_{ArAr} in the monolayer. Previous comparisons between simulation and experiment [6, 7, 8, 9] suggest that these should be repulsive; this can be approximately accounted for by multiplying ϵ_{ArAr} by a factor Q which is less than 1. The preceding arguments suggest that a much smaller adjustment than that attributable to the 3-body mediated dispersion energy ($\sim 15\%$, i.e. $Q = 0.85$) is required if 12-6 potentials are used for the Ar interactions. Induced interactions are not likely to significantly alter this conclusion.

(iii) Changing the corrugation of the potential in the above manner alters the net holding potential of the substrate. We therefore adjust ϵ_{gs} so as to give a Boltzmann averaged isosteric heat at zero coverage ($\beta q_{\text{st}}(\theta = 0)$) which is equal to the experimental value.

RESULTS AND DISCUSSION

Two sets of experimental data, covering the incommensurate liquid-solid transition at 77.4 K are available [3, 4]. A conflict in the interpretation of these results has been resolved, in part with the aid of computer simulation; details are given elsewhere [7]. Figure 1 shows the experimental isotherm together with results of simulations carried out with a variety of potentials having different values of λ and Q . In all cases ϵ_{gs} was adjusted, as described above to give the Boltzmann averaged value of $\beta q_{\text{st}}(\theta = 0)$ from experiment. The simulations were performed in the grand ensemble at 77.5 K. The box size was $19.5 \times 11.6 \times 5.0$ (in σ_{Ar} units) such that a close packed monolayer would contain *ca* 200 atoms and a completed commensurate monolayer (which does not in fact occur in this system) 192 atoms. Long range corrections were applied at each step of the calculation, and the corrected pressures, calculated from the corrected chemical potential, were used in plotting the results. Values of $\langle N \rangle$ from the simulation were converted into θ using $\theta = 1$ for a completed close packed monolayer. The proportion of moves:creation:destruction trials was 1:1:1 in the majority of runs. Typically *ca* 5×10^6 total trials were needed to reach convergence, although this figure could vary substantially for each individual run. Convergence was monitored

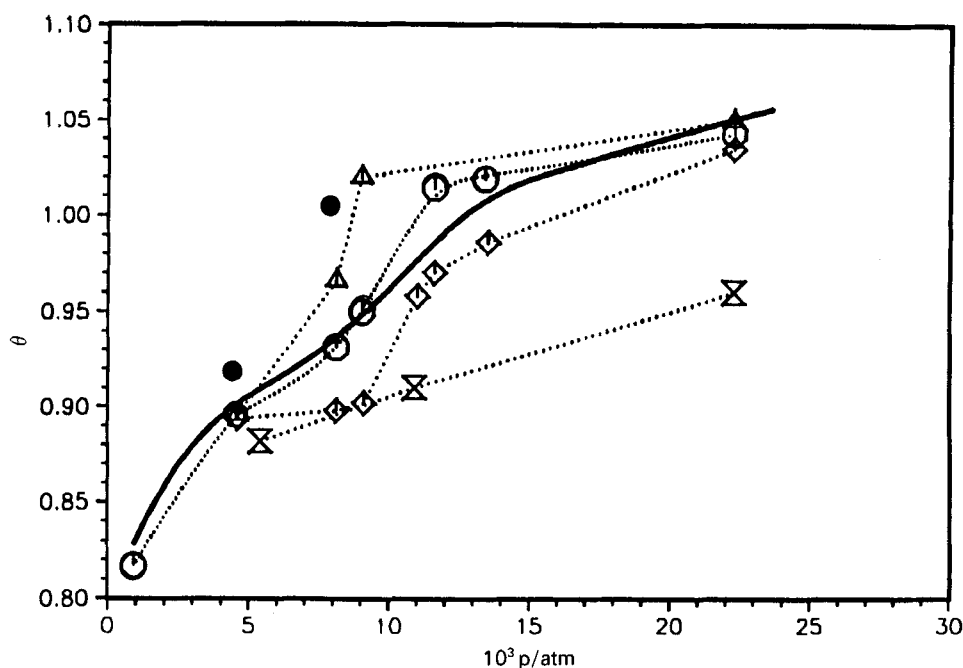


Figure 1 Adsorption isotherms for Ar adsorbed on graphite at 77.5 K. θ is the surface coverage expressed as a fraction of the close packed, incommensurate monolayer coverage. The full line is taken from experimental data [3, 4, 5]. The points are from simulations using potentials with the following parameters: Filled circles; $\lambda = 0$, $Q = 1.0$. Triangles; $\lambda = 2$, $Q = 1.0$. Double triangles; $\lambda = 0$, $Q = 0.85$. Diamonds; $\lambda = 2$, $Q = 0.92$. Open circles; $\lambda = 2$, $Q = 0.96$.

by calculating partial averages every 5×10^4 configurations, and averaging for data collection was usually made over at least 2×10^6 configurations. Starting configurations were either a close packed monolayer, or a nearby converged run; points in the transition region were approached from below and above in separate runs to check that no ergodic hindrance was occurring.

The first sets of runs were carried out with $Q = 1.0$ and different values of λ . Only two points are shown here for $\lambda = 0$ (unmodified barriers obtained using accepted effective functions for Ar-Ar interactions of $\epsilon = 120$ K, $\sigma = 0.3405$ nm) and for Ar-graphite [23]. Clearly the transition occurs at pressures well below experimental. It is reasonable to assume that the transition might be delayed to higher pressures by increasing the potential corrugation, thereby inhibiting the formation of an ordered close packed solid structure. The set of points (Δ) for $\lambda = 2$, $Q = 1.0$ indeed confirms this expectation; however the shift, even for this rather strongly corrugated potential is fairly small. It was also noted that quite strong correlations with surface sites occur [7] when the adsorbate molecules are near to the surface and still higher barriers are likely to result in the commensurate structures observed in previous work with model systems [22, 24] in contradiction to experimental observation. Furthermore, it appears unlikely, from the reported simulations, and from other preliminary results obtained with even higher λ , not reported here, that the gradual form of transition experimentally observed, would not be reproduced by modifying barrier heights in the manner adopted here. Of course this is not to say that other possible modifications, suggested

by the above discussion, e.g. changes in the form of the repulsive part of the wall potential function, would not be more successful.

The other form of modification, $Q < 1.0$, considered here has a remarkably strong influence on the transition. Three points were simulated using the potential function of Cheng and Steele ($\lambda = 0$, $Q = 0.85$). Clearly this modification pushes the transition to higher pressures than experiment and appears to spread out the range over which it occurs. It is clear that a compromise in which both λ and Q are changed can successfully reproduce observed behaviour. The best results were obtained with $\lambda = 2$ and $Q = 0.96$. It is interesting to see that changing the latter parameter to $Q = 0.92$ gives significantly less successful results.

It should be mentioned that, as far as this investigation goes, all the potential models considered here would be expected to give satisfactory agreement over the whole range of relative pressure ($0 < p/p_0 < 1.0$). The experimental results considered here are high resolution data for the narrow range $2.5 \times 10^{-4} < p/p_0 < 1.25 \times 10^{-3}$.

Figure 2 shows the experimental and simulated isosteric heat curves for the best potential investigated here ($\lambda = 2.0$, $Q = 0.96$). The discrepancy between theory and simulation at $\theta = 0$ is attributed to the fact that rather strong corrugation favours adsorption at sites and the Boltzmann averaging used to adjust ϵ_{gs} does not represent the true situation well enough. The overall shape of the heat curve is well reproduced,

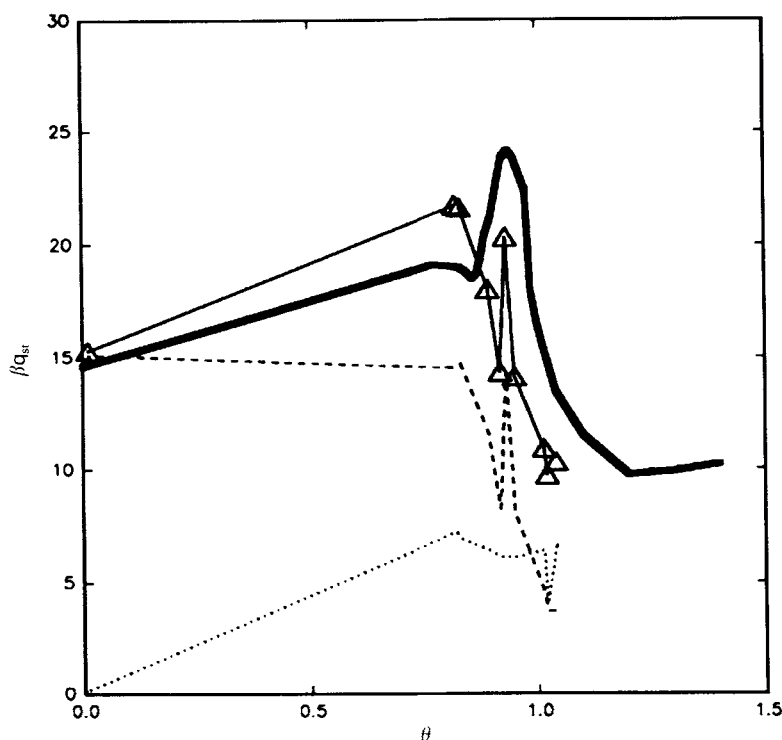


Figure 2 Isosteric heat curves. The heavy line is from experimental data [2]; the triangles are from simulation with $\lambda = 2.0$ and $Q = 0.96$. The dotted and dashed lines are the adsorbate and wall parts of the heat respectively.

and the interpretation of this curve in the light of simulation results has been discussed elsewhere [7]. It is somewhat disappointing that the very high values for the differential heat, associated with completion of the incommensurate solid are not reproduced here. The best model potential ($\lambda = 2$, $Q = 0.96$) investigated is successful in giving the observed transition on a plane surface; it can therefore be applied to simulations of Ar adsorption in graphite pores with some confidence that any occurrence of the transition in these systems will be reproduced. The poorer result for the heat curves is perhaps indicative of the need for more fundamental studies of the potential function in spite of the substantial difficulties alluded to above and elsewhere [11]. The contribution which could arise from induced many body interactions has not, to our knowledge, been considered previously. Although the effect is very small, it may have a significant role to play in a more fundamental model of the interaction given the extreme sensitivity to changes in Q noted in this work. Conversely it is interesting that a system of considerable importance to other applications should provide a particularly sensitive test for the progress of the fundamental theory of intermolecular forces.

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