

## Computer simulation studies of the heats of adsorption of simple gases

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**Abstract** - Computer simulation calculations of the heats of adsorption of two gases on the basal plane of graphite are reviewed. The role of molecular orientation in determining the heats for nitrogen on the perfect surface at 75 K is discussed. Also, the adsorption of Kr on a simple model of a heterogeneous surface has been simulated. The coverage dependence of these heats is shown together with the separate contributions of the Kr-solid and Kr-Kr interactions.

Computer simulation of the thermodynamic and dynamical properties of adsorbed layers is now a widely used technique. The amount of interesting results is rather large and this paper will be restricted to a discussion of some results obtained for the heat of adsorption of some simple gases adsorbed on carbon black. It will be shown that the simulation technique can yield new and helpful physical understanding of the data produced both in these and in real experiments.

At the outset, we note that simulations produce integral heats of adsorption rather than the differential heats measured in most real experiments. Nevertheless, the two are closely related and the interpretations of one are valid for the other. In classical statistical mechanics, the integral heat of adsorption is equal to  $RT$  minus the average potential energy of the adsorbed molecules, and since the computer is very good at calculating this average potential energy, one readily obtains such results.

The work presented here is based primarily on molecular dynamics simulations<sup>[1]</sup> in which a sample of several hundred molecules on the surface of a solid is assumed to obey the laws of classical physics. These are quite simple: basically, that the force on a molecule divided by its mass is equal to its acceleration and, if the molecule is not spherical, that its angular acceleration is equal to the torque divided by the moment of inertia. One starts with an arbitrary set of coordinates and velocities for the molecules and allows the computer to solve the equations of motion. After an initial period, it is found that the system is obeying the laws of statistical mechanics with a temperature proportional to the average kinetic energy of the molecules. We then begin to collect data for use in thermodynamic and dynamical average properties.

The point of this very brief discussion is that the force and torque on a molecule plays a central role. To calculate these, one must model the energy of interaction of the adsorbed molecule with its neighbors and with the solid. Figure 1 illustrates how we do this for nitrogen and carbon black and shows that in this regard, we and others follow very closely in the

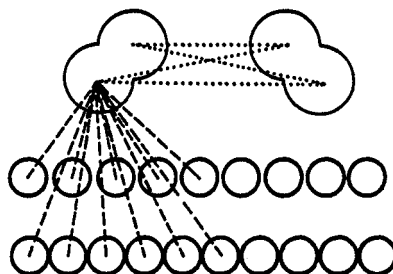


Fig. 1. A schematic representation of the site-site model for intermolecular interactions in a diatomic molecule-solid system. The small circles indicate sites in the solid, and the dashed lines indicate terms in the site-solid potential. In addition, the site-site energies between diatomics are shown by dotted lines.

models developed and utilized so well by Professor Kiselev and his group.<sup>[2]</sup> His basic idea was to compute the total energy by summing relatively simple functions over the atoms of the solid to get the adsorbate-solid energy (indicated by dotted lines in Figure 1) and over other adsorbate atoms to get the adsorbate-adsorbate energies (indicated by dashed lines). In this respect also, the parameters shown in Table I are close to those given by Kiselev many years ago. They are adjusted slightly to give good agreement with

Table I Parameters for the atom-atom interactions

	$\epsilon/k$ (K)	$\sigma$ (Å)
N-N*	35.4	3.32
N-C	31.9	3.36
Kr-Kr	145	3.60
Kr-C	75	3.42

\*Electrostatic quadrupolar interactions are also included using  $Q = 3.9 \cdot 10^{-36} \text{ C cm}^2$

experiment in the limit of zero coverage and then used in the computer work to provide information at higher coverage. Molecule-solid interaction curves are shown in Figure 2 for nitrogen interacting with graphitized carbon black as a function of distance from the surface.<sup>[3]</sup> In particular, we see that the orientation of this molecule relative to the surface will be a significant factor in its thermodynamic and dynamic behavior. The lowest curve shown is for a molecule parallel to the surface and the next curves are for a series of tilt angles approaching vertical (where  $\beta$  equals zero). They show that molecules vertical to the surface are rather improbable. Also, good agreement between the heats calculated from this model of the interaction and experiment at zero coverage is found. Energy curves for krypton are similar to those for nitrogen except of course that molecular orientation is no longer relevant.

Figure 3 shows simulation results for the heat of adsorption of nitrogen on graphitized carbon black at 78 K at coverages less than 1.5 layers.<sup>[4]</sup> The smooth rise at submonolayer coverages is normal for adsorption on a perfect homogeneous surface and is ascribed to mutual interaction between neighboring nitrogens. What is unusual is the average molecule-solid energy which slowly decreases with increasing coverage. The computer is capable of giving us the reason for this behavior, as can be seen in Figure 4 where the

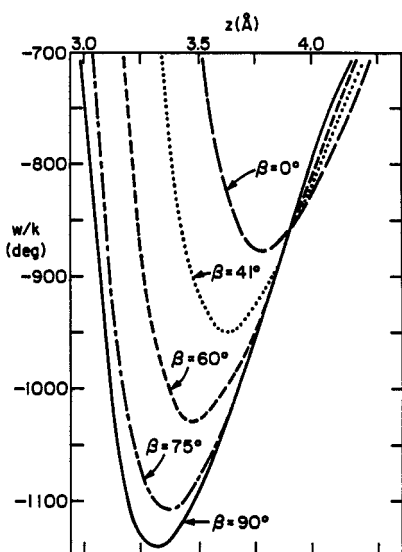


Fig. 2

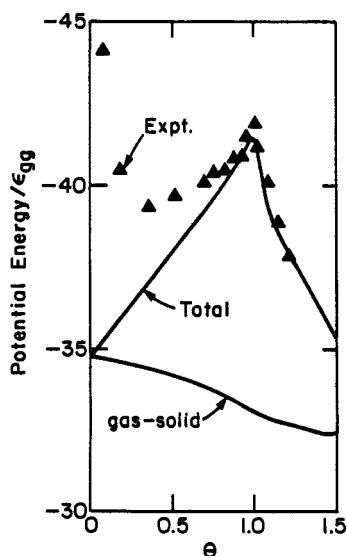


Fig. 3

Fig. 2. The interaction of a nitrogen molecule with the basal plane of graphite is shown here as a function of the center-of-mass distance from the solid surface. The different curves are for different tilt angles, with  $\beta = 90^\circ$  corresponding to an axis parallel to the surface. The curves shown here have been averaged over the surface unit cell.

Fig. 3. Simulations of the integral molar heat of adsorption minus  $RT$  are shown for nitrogen on graphitized carbon black and compared with experiment. The values of average potential energy are reduced by  $\epsilon_{gg}$ , with  $\epsilon_{gg}/k=35.4$  K. In addition to plotting the total energy, the contribution of the average molecule-solid interaction is also given. The temperature of the simulation and the experiment is 75 K.

distributions of molecular orientation relative to the surface are shown as a function of coverage. Note that  $\cos \beta$  equal to zero corresponds to molecules parallel to the surface and is the most probable orientation in all cases. However, as coverage increases, the molecules interfere with each other and begin to produce distributions with larger probabilities of vertical orientation. It is this change that gives the decrease in gas-solid energy—a decrease that does not appear in most theoretical descriptions of the energies of molecules in monolayers on perfect surfaces.

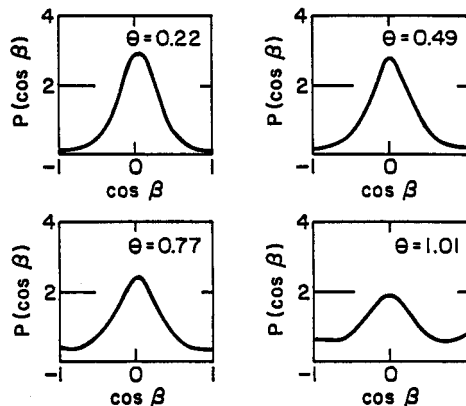


Fig. 4. Simulated curves for the distribution of tilt angles for  $N_2$  on graphitized carbon black at 75 K are shown here for various coverages. Note that the molecules are more often parallel to the surface at low coverage than at high.

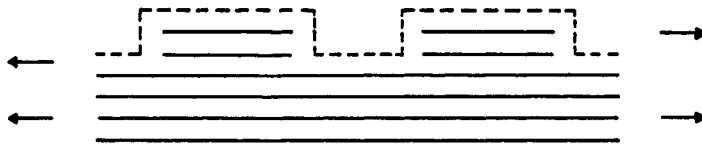


Fig. 5. A schematic representation of the model heterogeneous surface used in the simulation study discussed here. A side view of the surface profile is given which shows the steps and grooves produced by the periodic boundary conditions.

We now discuss the behavior of krypton adsorbed at 110 K on graphite with a simple model of heterogeneity that is schematically represented in Figure 5.[5] The graphite surface has been modified by adding strips of basal plane carbon atoms to produce steps and grooves on the originally flat surface. After some algebra the interaction energy of a Kr atom with such a surface can be calculated. (Note that the atomic structure of the basal plane of graphite is omitted for mathematical convenience.) The nature of the heterogeneity introduced in this way is shown in Figure 6 where the minimum Kr-solid interaction energy is plotted as a function of the Kr position relative to the steps and grooves. Deep wells are found at the bottom of the steps which would thus ordinarily be described as strong sites; the small energies at the tops of the steps are weak sites; and the remainder of the energies are close to those for the homogeneous, flat surface. On such a surface, the local properties generated by the computer are of interest. For example, the average potential energy per particle at a given position relative to the step is shown in Figure 7. This local energy for particles on the homogeneous flat surface is shown to illustrate the magnitude of the statistical fluctuations present and to show the contrast between this and the rapidly varying average energy per particle on the stepped surface, which follows closely the minimum energy curve of Figure 6. These calculations were repeated for a number of surface coverages. By calculating the potential energy per particle averaged over the entire surface, the curve of heat of adsorption versus coverage shown in Figure 8 was obtained. The points denoted  $U_{tot}$  are essentially those for an experimental measurement of the integral heat of adsorption; however, the computer allows us to evaluate the average molecule-solid interaction energy  $U_{gs}$ , which changes with coverage as the strong sites fill and adsorption proceeds on the weaker areas of the adsorbing surface. In addition, the curve of the Kr-Kr mutual interaction  $U_{LJ}$  is shown to play a large part in determining  $U_{tot}$ , which is of course the sum of  $U_{gs}$  and  $U_{LJ}$ . In fact, much of the rapid decrease in  $U_{gs}$  is compensated by the increase in lateral interaction, giving a net curve that changes relatively little with increasing coverage.

This compensation between the two contributions to  $U_{tot}$  is perhaps the most surprising and most significant aspect of this work, especially since current theories of adsorption on heterogeneous surfaces based on Langmuir or B.E.T. type local isotherms must omit this kind of attractive lateral interaction altogether.<sup>[6]</sup> It would appear that significant error can be made by the application of such theories. Of course, the type of heterogeneity studied here is quite specific; many other models for surface imperfection, etc. can be visualized and in many cases, studied by simulation techniques.

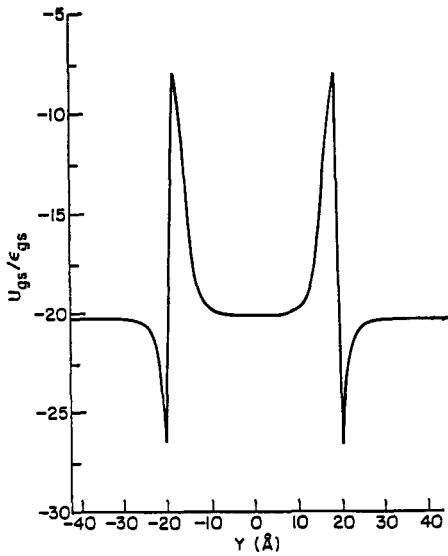


Fig. 6

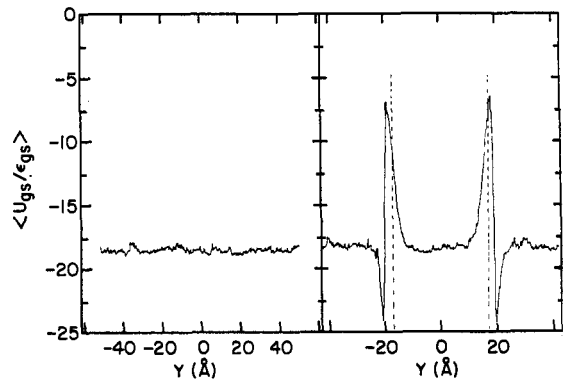


Fig. 7

Fig. 6. The minimum Kr-solid potential  $U_{gs}$  for the surface shown in Figure 5 is plotted here as a function of the Kr position relative to the groove-step structure. The reducing factor  $\epsilon_{gs}/k = 75$  K.

Fig. 7. The average potential energy densities for a simulation of Kr adsorption at 110 K and a coverage of 1 layer. These local interaction energies are plotted as a function of position for a homogeneous surface (left hand panel) and for the heterogeneous surface of Figs. 5 and 6.

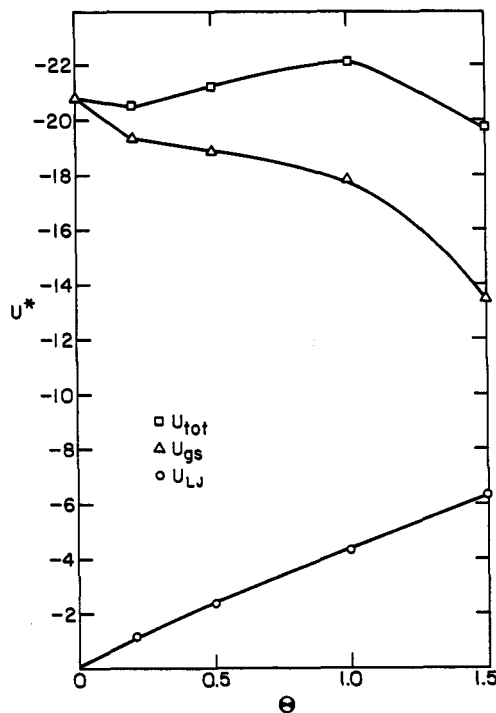


Fig. 8. The coverage dependence of the average potential energy of Kr layers adsorbed on the heterogeneous surface of Figs. 5 - 7 is shown. The total potential  $U_{tot}$ , the Kr-solid part  $U_{gs}$  and the Kr-Kr part  $U_{LJ}$  are all shown for coverages in the monolayer region. One sees that the Kr-Kr energy makes a significant contribution to the total, especially at coverages near monolayer completion.

One can also imagine that the results may be different from those discussed here, particularly in regard to the importance of lateral interactions. It is basically a question of how the strong sites (or more generally, regions of strong molecule-solid interaction) are distributed across the surface. It seems likely that such simulations could play an essential role in unraveling this difficult and (to date) unsolved problem of understanding physical adsorption of simple gases on heterogeneous surfaces.

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