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Rumpled graphite basal plane as a model heterogeneous carbon surface

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A new model is suggested for the heterogeneous surfaces of nongraphitized carbon adsorbents. It may be called the rumpled graphite basal plane (RGBP). The atomic structure of RGBP can be obtained by squeezing a graphite basal plane in a molecular dynamics computer simulation under a random distribution of initial atomic velocities. The empirical Tersoff potential describes the carbon-carbon interactions. The degree of squeezing is chosen to reproduce the main features of the x-ray interference function of nongraphitized carbon blacks. Grand canonical ensemble Monte Carlo simulation of the isotherms of adsorption of N₂ on RGBP reproduce experimental isotherms on these carbon blacks reasonably well, especially in the BET region of relative pressures. © 1995 American Institute of Physics.

I. INTRODUCTION

The graphite basal plane (GBP) is the most widely used model of a surface in physical adsorption. Of the systems which have been modeled and tested against experiment, simple molecules interacting with GBP form the largest group.¹ The reason for that is that one can produce graphite with adequate surface area for experimental use which is chemically pure and stable and which presents surfaces that are almost entirely made up of large nearly perfect pieces of exposed GBP. However, this specially prepared graphite or graphitized carbon black differs qualitatively in its adsorption properties from most of the carbons used industrially.

For example, carbon blacks are widely used for reinforcement of elastomers, the protection of plastics from ultraviolet degradation and as a filler in paints and inks.² In distinction to graphitized carbon black whose surface is energetically homogeneous (all adsorption sites are identical), the surfaces of nongraphitized carbon blacks are heterogeneous (adsorption sites are broadly distributed in energy) and moreover that heterogeneity is very important for some applications (e.g., reinforcement of elastomers³). The same is true for active carbons.

X-ray patterns of nongraphitized carbon blacks and activated carbons contain mainly two-dimensional (asymmetric) (*hk*) reflections of GBP as diffuse peaks. There are also diffuse peaks corresponding to the (symmetric) (001) reflections of the graphite structure (see Ref. 4 and references therein). The shape and position of (*hk*) reflections roughly correspond to reflections from a disc cut of GBP.⁵ The diameter of that disc L_a is an important parameter characterizing carbon black structure.⁴ The "turbostratic" model assumes that several such discs are placed parallel to each other in a stack of height L_c (another parameter characterizing carbon black structure), stacking being random in translation parallel to the layers and random in rotation about the normal to the layers.⁵ Analysis of x-ray data using the turbostratic model gives important quantitative parameters L_a and L_c character-

izing industrial carbons but this model is not the unique possibility to explain the x-ray patterns. In particular, in Ref. 5, an assumption has been made that a basic element of the carbon black atomic structure might be not a disc cut out of GBP but a much larger imperfect graphitic layer.

The latter assumption has been confirmed in the electron microscopy investigations of carbon blacks.⁴ A model that follows from those studies was called paracrystalline,^{4,5} i.e., parallel distorted continuous graphitic layers but no discrete three-dimensional groupings forming crystallites. The model was supported for all types of commercial carbon blacks by high resolution phase contrast images.⁴ Finally, the recent scanning tunneling microscopy (STM) studies visually showed the presence of highly organized atomic patterns on the surfaces of a number of commercial carbon blacks.⁶

All these structural studies provide important guidelines for the development of a comprehensive model of the carbon black and activated carbon surfaces. Such a model should take into account the results of structural and adsorption studies of the surfaces of carbons. The latter are important for two reasons. First, adsorption and closely related adhesion properties are of primary interest for the major application of industrial carbons. Second, adsorption characteristics obtained in a computer simulation strongly depend on the atomic structure of a model surface and their deviation from experimental values may serve as a merit function for comparison of models. In particular, one of the main adsorption characteristics of heterogeneous surfaces is the distribution of adsorption sites in energy.⁷ For graphitized carbon black that distribution is rather narrow but for nongraphitized carbon blacks it is broad.³ The above mentioned models provided by structural studies are too qualitative to explain the specific shapes of these energy distributions obtained from adsorption studies. For example, as mentioned in Ref. 3, if high-energy adsorption sites are provided by edges and defects of GBP as seems to be implied by the turbostratic or paracrystalline models, one would expect the energy distribution function to have several peaks instead of one broad distribution.

The broad distribution of adsorption sites in energy may be explained if one assumes that the atomic structure of a

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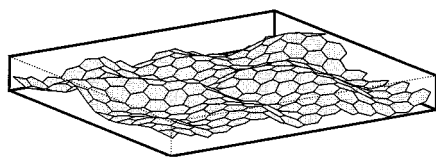


FIG. 1. Rumbled graphite basal plane (RGBP). The dimensions of a box are: $35.5 \times 32.4 \times 4.0 \text{ \AA}^3$.

surface is highly irregular—amorphous. This hypothesis makes it possible to explain the basic adsorption properties of heterogeneous surfaces of oxides.^{8–10} It also works well for heterogeneous carbon surfaces.¹¹ Actually that hypothesis implies that even if the adsorbent is crystalline, its surface is covered by a thin amorphous layer.⁸ However, electron microscopy studies of carbon blacks suggest the reverse model: the interior part of a carbon black particle is more amorphous than its surface.⁴ In this connection, another model of heterogeneous surfaces of carbons is considered in the present paper. It may be called “a rumbled graphite basal plane” (RGBP) and can be visualized with the help of Fig. 1.

The algorithm of the computer simulation of RGBP is discussed in the next section as well as a comparison of its scattering pattern (interference function) with that of turbostratic model which in turn represents the generalized experimental data for real carbon blacks. The computer simulation of the isotherm of adsorption of N_2 on RGBP is considered in Section III. The conclusion contains some remarks on the future development of the RGBP model.

II. COMPUTER SIMULATION OF RGBP

The atomic structure of RGBP may be obtained in the following way. An initial atomic structure is a rectangular piece of GBP with periodic boundary conditions in x - and y -directions. It may be constructed by replication of an enlarged orthogonal unit cell containing one hexagon of carbon atoms (4 atoms and 2 images) with the vertexes of the unit cell at the centers of neighboring hexagons. Two atoms and two of their images are on the parallel edges of the unit cell going through the opposite sides of a hexagon in the y -direction. The length of this edge of the unit cell is 3 times the side of a hexagon ($3 \times 1.42 \text{ \AA}$). The simulation rectangle consisted of 15 unit cells in x -direction, 8 in y -directions. Thus the rectangle had dimensions $q_x = 36.89 \text{ \AA}$, $q_y = 34.08 \text{ \AA}$, and contained 480 carbon atoms. There were no limitations in the z -direction.

The forces between carbon atoms were calculated by analytical differentiation of the Tersoff potential¹²:

$$u(r_{ij}) = f_C(r_{ij})[f_R(r_{ij}) + b_{ij}f_A(r_{ij})]. \quad (1)$$

Here

$$f_R(r) = A \exp(-\lambda_1 r); \quad f_A(r) = -B \exp(-\lambda_2 r)$$

are repulsion and attraction components of the Morse type potential; $f_C(r)$ is a truncation function and b_{ij} is the bond order. The peculiarity of the Tersoff potential consists in that b_{ij} is a complex empirical expression which depends on co-

ordinations of i - and j -atoms.¹² This makes a potential of Eq. (1) that appears as a pairwise potential actually a many body potential. When, say, i -atom changes its position, not only the energies of ij -bonds Eq. (1) change their values but also energies of those kl -bonds for which i -atom is a neighbor of k - or l -atoms. In this case the i -atom influences the energy of a kl -bond through its bond order.

The original expression for b_{ij} in Ref. 12 was not symmetric with respect to permutation of indexes but there was a remark there that “for aesthetic reasons” it can be replaced by the symmetrized function $\bar{b}_{ij} = (b_{ij} + b_{ji})/2$. This symmetrization was adopted in the present paper to escape dependence of the bond energy on the direction of a bond, violation of the Newton third law, etc.

Parameters $A, B, \lambda_1, \lambda_2$ and 7 other parameters which determine $f_C(r)$ and b_{ij} in Eq. (1) were taken from Ref. 13. These were empirically fitted in such a way that potential of Eq. (1) reproduced the cohesive energy and lattice constants of graphite, diamond, a number of other carbon polytypes some of which do not exist in nature but were calculated quantum mechanically as well as energy of vacancy formation in diamond.¹³ Probably, these parameters correspond to nonsymmetrized bond orders but for symmetric atomic structures from which those parameters were mainly determined symmetrization does not influence their values.

The initial velocities were chosen randomly. Each velocity component was uniformly distributed in a range $[-v_{\max}, v_{\max}]$ with the average kinetic energy corresponding to 2000 K. After that the above mentioned fragment of the GBP was subjected to the molecular dynamics evolution with the velocity version of the Verlet algorithm.¹⁴ A time step was 0.26 fs. At each time step, the x - and y -coordinates of all atoms as well as periods q_x and q_y were rescaled (squeezed) by the factor $(1-\alpha)$ with $\alpha = 2 \times 10^{-5}$. The squeezing made GBP buckle and transfigured it into the RGBP.

The resulting RGBP is presented in Fig. 1. The picture in Fig. 1 may be considered as a realization of a random surface which depends on the initial velocities of carbon atoms chosen at random. Another choice of initial velocities gives another realization of the RGBP pattern. To obtain that realization one just need to shift an initial number in a quasirandom number generator used to ascribe initial velocities.

The other parameters which determine the shape of RGBP are the number of time steps and α . Both of them determine the degree of squeezing. The latter parameter determines the velocity of squeezing. The larger is that velocity the greater will be the potential energy of RGBP due to the incomplete relaxation. The initial potential energy (cohesive energy of GBP) is -7.345 eV per atom. Squeezing with the above mentioned value of α increases that energy to about -7.2 eV . With $\alpha = 4 \times 10^{-5}$ that energy is about -7.1 eV . In both cases the number of time steps was 800. For the surface in Fig. 1 the degree of squeezing is 1.6% ($\alpha = 2 \times 10^{-5}$ and 800 time steps). If the squeezing is stopped and molecular dynamics simulation continues the potential energy begins to decrease but the total energy is constant up to 0.01%. The condition of conservation of energy determines the length of the time step.

The interference function of RGBP: The condition which

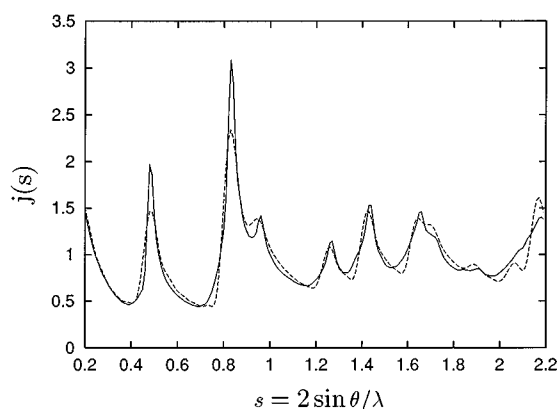


FIG. 2. Interference functions $j(s)$ [see Eq. (2)]. Solid line—RGBP; dashed line—the pattern from Fig. 3.

determines the degree of squeezing may be obtained from the comparison of the interference function of RGBP with experimental data for carbon blacks. The interference function is a relation⁵

$$j(s) = 1 + \frac{1}{N} \sum_{i,j} \frac{\sin 2\pi s r_{ij}}{2\pi s r_{ij}}. \quad (2)$$

Here r_{ij} is the distance between i - and j -atoms ($i \neq j$) and $s = 2 \sin \theta / \lambda$ where λ is the wavelength of radiation and 2θ is the angle between an incident and scattered beam. $j(s)$ gives an amplitude of a wave scattered from an arbitrary system of scattering centers, scattering factor of each center being 1, averaged over all orientation of that system with respect to an incident beam. The plot of $j(s)$ for RGBP of Fig. 1 is presented in Fig. 2.

As it has been mentioned above, the carbon blacks are characterized by a parameter L_a equal to a diameter of a disc cut out of GBP which gives an interference function $j(s)$ close to the experimental value of the real carbon black. For commercial carbon blacks $L_a = 15$ – 25 Å (see Table 1 in Ref. 4). Thus, instead of comparing $j(s)$ of RGBP with a real experimental interference function we compare it with $j_L(s)$ —an interference function of a group of atoms of GBP contained inside the circle of diameter L_a . A picture of such a group is presented in Fig. 3. Generally, $j_L(s)$ depends on the position of the center of the circle in the GBP but for a relatively large values of L_a (as in Fig. 3) that dependence is weak. In Fig. 4, the cumulative deviation of $j(s)$ from $j_L(s)$ $\int |j(s) - j_L(s)| ds$ vs L_a is presented. This is not a smooth curve because the number of atoms contained in the area of GBP bounded by a circle of diameter L_a changes discontinuously with continuous change of L_a which gives a discontinuous dependence of $j_L(s)$ vs L_a . Nevertheless, that dependence has a shallow minimum in Fig. 4 and the minimal value of L_a is in the range of above mentioned parameters for commercial carbon blacks.

The interference function $j_L(s)$ for the minimum value of L_a from Fig. 4 is presented in Fig. 2 as a dashed line. It deviates from $j(s)$ for RGBP but an interference function of a real carbon black also deviates from $j_L(s)$ (cf., e.g., Fig. 8

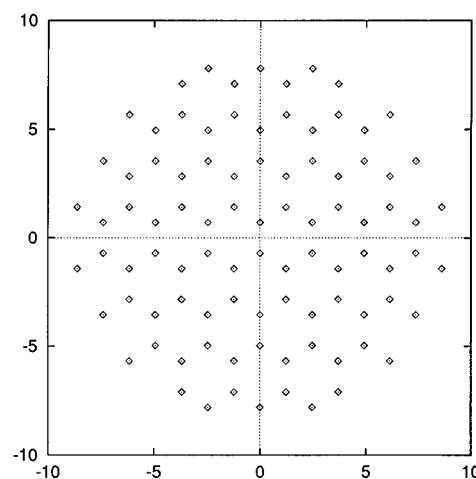


FIG. 3. A pattern of the graphite basal plane (disc) confined inside the circle of the diameter L_a corresponding to the position of a minimum in Fig. 4.

of Ref. 5). Thus a comparison of $j(s)$ with $j_L(s)$ makes it possible at least to evaluate the degree of squeezing which brings the RGBP model into agreement with the x-ray scattering studies of carbon blacks.

III. COMPUTER SIMULATION OF NITROGEN ADSORPTION ON RGBP

Adsorption of N_2 on GBP has been studied by the grand canonical Monte Carlo method in Ref. 15. The adsorbate interactions with graphite were calculated in the pair wise atom–atom (N/C) approximation. The simulated isotherm of adsorption was very close to the experimental one, except for the small deviations in the region of the second layer which were ascribed to the many body interactions that were not properly taken into account in the computer simulation.

The simulation of the present work employed the same interatomic potentials for adsorbate/adsorbent and adsorbate/adsorbate interactions, the same algorithm, and the same programs as in Ref. 15. The only difference consisted in the arrangement of C-atoms. In the present case the exposed

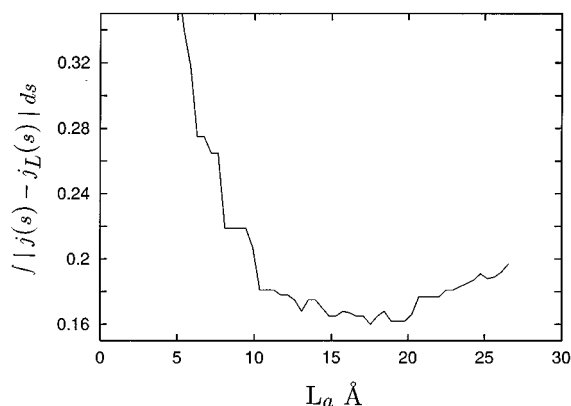


FIG. 4. Deviation of the interference function of the RGBP $j(s)$ from that of a disc (cf. Fig. 3) $j_L(s)$ vs the diameter of the disc L_a .

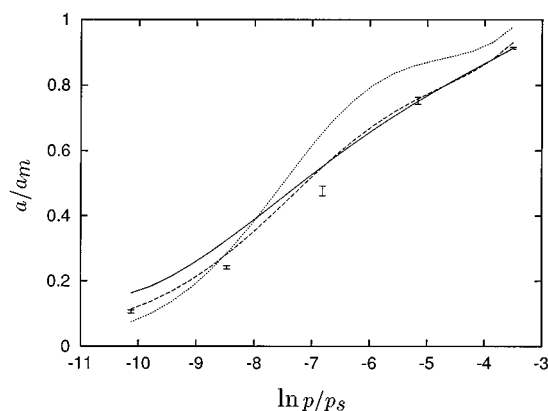


FIG. 5. Isotherms of adsorption of N_2 at 77.4 K on heterogeneous carbon surfaces in the submonolayer region. Solid line—experimental standard isotherm from Ref. 16; experimental isotherms from Ref. 17 corresponding to $E_0=9.0\text{--}10$ kJ/mol (dotted line) and $E_0=10.5\text{--}12$ kJ/mol (dashed line); symbols—computer simulation on RGBP.

surface was the RGBP. It is well known from the study of adsorption on graphite that the external GBP gives rise to about 90 % of the adsorption energy. One may assume that the same is true for RGBP. The carbon atoms below external RGBP also make some contribution to the adsorption potential but it is relatively small. To evaluate it, we arbitrarily assumed that the carbon atoms below the external surface are arranged on identical RGBPs shifted downwards parallel to each other as GBPs in graphite (and with the same distances between the parallel layers).

Simulated isotherms of adsorption for N_2 on RGBP were compared to the experimental isotherms taken from Refs. 16 and 17 where a standard isotherm of adsorption for the carbon adsorbents was presented similar to that for oxides.¹⁸ In Ref. 16, isotherms for N_2 at 77 K for 28 different carbon blacks and mesoporous carbon adsorbents were considered. Seventeen of them were chosen which represented, in their opinion, isotherms of adsorption on a free surface (without the distortion due to adsorption in micropores). The standard isotherm was an average of those isotherms. In Ref. 17, a more differentiated approach to adsorption of N_2 on heterogeneous carbon surfaces was adopted: all carbon adsorbents were divided into 4 groups according to the value of the energetic constant of the Dubinin–Radushkevich equation and a standard isotherm has been found separately for each of these groups.

A. Submonolayer region

The simulated isotherm of adsorption in the submonolayer region is presented in Fig. 5. Adsorption is presented as a fraction of a monolayer capacity a_m determined by the BET-method (see below).

Each point in Fig. 5 is an arithmetic average over 5 points representing adsorption at the same temperature and pressure on 5 different surfaces. One of those surfaces is depicted in Fig. 1, the others have the same average characteristics since they were obtained under the identical conditions of computer simulation but their specific shapes depend

on the random distributions of initial velocities, as has been described above. Since the surface in Fig. 1 has a relatively small area (a monolayer capacity of about 80 N_2 molecules), it cannot represent the RGBP as a whole but rather a small patch of that heterogeneous surface (though, due to the periodic boundary conditions, Fig. 1 represents an infinite surface). To study adsorption properties of RGBP one has either to simulate adsorption on a surface much larger than that in Fig. 1 or to repeat simulation several times on the surfaces which represent different and independent patches of RGBP. In the present paper we have chosen the latter way. The advantage of this approach is that it makes an independent and reliable evaluation of the computer simulation errors possible. The error (standard deviation) of adsorption on one sample of a surface is a standard output of a Monte Carlo program. However, this is not the entire error. It does not include, e.g., the scatter of adsorption values on different surfaces due to peculiarities of their shapes along with other possible factors of a Monte Carlo algorithm which are difficult to evaluate (e.g., nonergodicity). The evaluation of the standard deviation of the adsorption isotherm by the scatter of its values on different samples of RGBP includes all those errors and is in the sense the most reliable. (See discussion of those methods of error evaluation in Ref. 9.) The error bars in Fig. 5 were obtained as a statistical evaluation of the standard deviation of the average value of 5 independent values of adsorption at the same temperature and pressure on 5 different samples of RGBP simulated at different distributions of initial velocities (see above).

At high coverage ($a/a_m > 0.7$), the experimental isotherms and simulated adsorption points almost coincide but at lower coverages there is some difference between them. The relatively small (comparable to the simulation errors) deviation of the simulated isotherm from the experimental curve of Ref. 17 as well as deviation between experimental isotherms from Ref. 16 and Ref. 17 reflects the differences in the energetic heterogeneity of real and simulated adsorption systems.

Energetic surface heterogeneity is the most widely used concept in the theory of adsorption on heterogeneous surfaces.⁷ It means that the local minima of the gas–solid potential function vary when passing from one adsorption site to another (see, e.g., Ref. 7, p. 186). Energetic heterogeneity of a surface is, first of all, a consequence of its structural heterogeneity.⁷ The structural heterogeneity of a surface or atomic surface roughness designates various kinds of atomic disorder on a surface. (Some authors use the concept of heterogeneity in a more general sense referring the faces of an ideal crystal as the regularly heterogeneous surface; I use here the term heterogeneity as a synonym of irregularity.) The structural heterogeneity is a more fundamental concept than energetic heterogeneity because the latter is a characteristic of an adsorption system. It depends not only on the atomic structure of the surface but also on the nature of an adsorbed molecule—its size, type, number of atoms etc. The atomic surface roughness is a basic concept which characterizes (albeit not completely) the adsorption (or adhesion, or catalytic, etc.) behavior of a heterogeneous surface. It will be called here the primary surface heterogeneity (PSH).

According to Ref. 17 the isotherms of adsorption on heterogeneous carbon surfaces approximately obey the Dubinin–Radushkevich equation at small coverages. The larger is the energetic parameter E_0 of that equation the greater is PSH of a nonporous carbon adsorbent. The dotted curve in Fig. 5 represents adsorption on the first group of carbon surfaces with the lowest PSH (the narrowest energy distribution functions). The dashed curve corresponds to the second group. The solid curve corresponds to a surface (imaginable, because it is an isotherm averaged over 17 adsorption systems) which is more heterogeneous than those from the second group of carbon surfaces. Actually what is meant here by heterogeneity is PSH that is the heterogeneity that determines the shape of the distribution of adsorption sites in energy. Surfaces with greater PSH have broader energy distribution of adsorption sites; i.e., they have more strong adsorption sites than surfaces with lower PSH. Since strong adsorption sites determine adsorption at low relative pressures, the greater PSH, the higher the adsorption at low relative pressures. Thus, one may see from Fig. 5 that PSH of RGBP is close to that of the carbon surfaces referred to as the second group in Ref. 17.

In our previous paper,¹¹ where the heterogeneous carbon surface has been modeled by an amorphous carbon atomic structure, the correspondence between simulated and experimental isotherms was closer at small coverages than for RGBP. So it well may be that the real heterogeneous surface of carbon contains areas of amorphous carbon together with relatively ordered areas like RGBP. This does not contradict the results of electron microscopy or STM studies. Actually some of the models suggested in those studies assumed presence of amorphous carbon on heterogeneous carbon surfaces (see, e.g., Fig. 3 in Ref. 4). Other defects of RGBP like irregular holes in the atomic net (see, e.g., Fig. 12 in Ref. 4) also may increase the number of stronger adsorption sites.

Whatever might be the reason of the relatively small deviation (note that there were no adjustable parameters in the simulation) of the simulated points in Fig. 5 from the dashed curve, the fact is that the experimental isotherms on various carbon adsorbents differ between themselves more than our model deviates from some of them. They deviate considerably from the dotted curve in Fig. 5 that represents adsorption on a relatively homogeneous carbon surface and the simulated isotherm is clearly closer to those on heterogeneous carbon surfaces than to the dotted curve. Nevertheless, one cannot expect a model like RGBP with fixed parameters to describe simultaneously adsorption on all heterogeneous carbon surfaces in the submonolayer region because the experimental isotherms of adsorption on those surfaces differ in that region.

B. BET region

The BET-plot of the isotherm is presented in Fig. 6 for the standard BET interval of relative pressures $0.05 < p/p_s < 0.35$ (see Ref. 18, p. 52). The error bars of simulated (“experimental”) points were obtained as explained above. The parameters of the straight line in Fig. 6 were obtained by the least-square fit with the help of the slightly modified (the modification is described in Ref. 9) subroutine FIT from Ref.

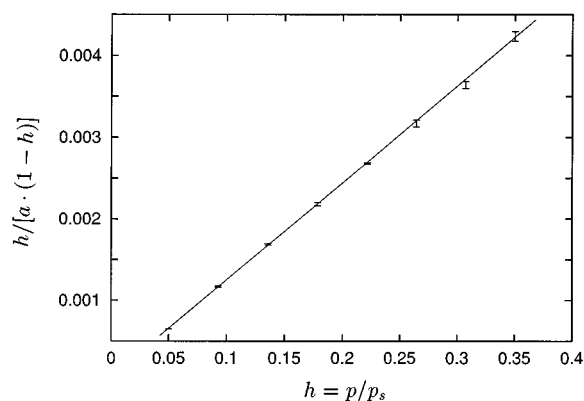


FIG. 6. The BET plot of N_2 on RGBP at 77.4 K.

19. In this way, one obtains the parameters of the BET equation along with their standard deviations: $a_m = 83.6 \pm 0.3$; $C = 194 \pm 17$. The reason why the isotherm is presented here as a BET plot is that experimental isotherms of adsorption on heterogeneous surfaces usually obey the BET equation pretty well.¹⁸ The shape of the BET isotherm is determined solely by the dimensionless parameter C . Thus the value of the C constant is a convenient measure of the deviation of a simulated isotherm from experimental data.

The standard experimental isotherm of adsorption of N_2 on carbon blacks from Ref. 16 obeys the BET equation very well with $a_m = 10.33 \mu\text{mol}/\text{m}^2$ and $C = 186.4$. These parameters have been determined by the least-squares fit of the polynomial $a-p/p_s$ from Ref. 16 in the interval $0.05 < p/p_s < 0.35$ divided into 20 points. There is no standard deviations for the smoothed (probably, by the least-squares method) standard isotherm from Ref. 16 so that standard deviations of parameters a_m and C has no clear sense in this case. However, one can obtain some notion on the possible variation of the parameter C from the fact that among the 17 carbon adsorbents from which the standard isotherm was obtained the value of C changed from 100 to 280 (see Table 1 in Ref. 16). As to the goodness-of-fit of the standard isotherm from Ref. 16 to the BET model, the maximum deviation of the points of its BET-plot from a straight line is found to be 1% (average deviation is 0.5%). For comparison, the maximum deviation from the best fit straight line of the BET-plot for the standard isotherm of adsorption of N_2 on the homogeneous surface of graphitized carbon black from Ref. 20 in the interval $0.06 < p/p_s < 0.3$ (7 points) is 10% (average deviation is 3.3%). The BET parameters of the latter isotherm are $a_m = 11.16 \mu\text{mol}/\text{m}^2$; $C = 70.1$. Again their standard deviations are not presented here because the isotherm is a smoothed curve.

The difference between the values of C for the isotherm simulated on RGBP and experimental standard isotherm on a heterogeneous carbon surface¹⁶ is statistically insignificant (less than the standard deviation for the simulated isotherm: 194 ± 17 and 186). This value of C should be compared to $C = 70$ which determines the shape of the best fit BET isotherm on a homogeneous surface of GBP. The comparison suggests the conclusion that it is the heterogeneity of the

nongraphitized carbon black surfaces that is the reason for the relatively high value of C of the standard isotherm from Ref. 16 and that the RGBP-model adequately reflects that heterogeneity.

However, this is not the kind of heterogeneity (PSH) that has been discussed in the previous subsection. That kind of structural heterogeneity which determines the energy distribution of adsorption sites (minima of adsorption potential) is not readily seen in Fig. 1. It is connected with the curvature at the bottoms of the pits and ravines. What is seen in Fig. 1 may be called the secondary surface heterogeneity (SSH). It is also a surface roughness but on about an order of magnitude larger scale of length than PSH. One might call it a geometric surface heterogeneity but this term is already employed to designate a disorder in relative positions of adsorption sites.⁷

A conclusion which may be drawn from the present results consists in the fact that while PSH determines the shape of the isotherm of adsorption in the submonolayer region, the SSH is responsible for the shape of the isotherm of adsorption in the BET region. We came to the same conclusion in our paper⁹ where we simulated the isotherm of adsorption of Ar on a model amorphous oxide with atomic structure of anions modeled by the dense random packing of hard spheres (the Bernal model). We called that model the Bernal surface (BS). The heterogeneity of the BS is mainly the PSH and the isotherm of adsorption of Ar simulated on BS does not obey the BET equation: the goodness-of-fit is pretty bad and the value of the C constant does not correspond to the experimental value. Much better results have been obtained with another model that was called the corrugated Bernal surface (CBS). The CBS had higher SSH than BS (in Ref. 9 SSH was called the geometrical heterogeneity).

Still another confirmation of the above point of view on the role of SSH can be drawn from our previous work¹¹ where we simulated the isotherm of adsorption of Ar on a planar amorphous carbon surface. That surface has strong PSH but its SSH was probably not so pronounced as for RGBP. Actually it was a surface of a carbon liquid. On such a surface the SSH should be suppressed by surface tension. For that surface we obtained $C=90\pm5$ while for experimental isotherm of adsorption of Ar on the untreated carbon black Spheron $C=150\pm15$.¹¹

IV. CONCLUSION

A rumbled graphite basal plane (RGBP) is a model of a heterogeneous carbon surface. As a basic element of the atomic structure of heterogeneous carbon adsorbents it can describe both the main features of their x-ray (neutron) scattering patterns and adsorption behavior of their surfaces. This is its distinctive feature as against other models of the atomic structure of active carbons and carbon blacks. For example, the well known turbostratic model has been developed to quantitatively describe the x-ray patterns of those carbon adsorbents. To my knowledge, it has never been used for computer simulation of adsorption behavior of those adsorbents. On the other hand, there are other models which

were used to describe only the adsorption behavior of carbon adsorbents. The most notorious of them is the graphite basal plane (GBP); amorphous carbon has also been used in our recent work. These do not describe the basic features of the scattering patterns of active carbons and carbon blacks. The scattering patterns and adsorption behavior are important characteristics of atomic structure of heterogeneous carbon adsorbents and a comprehensive model should take into account both of them.

I have not compared in this paper the interference function (the basic element of a scattering pattern) of the RGBP to that of a real carbon black or active carbon. Instead the basic result of the turbostratic model that the two dimensional interference function of a carbon adsorbent can be approximated by that of a disc of diameter L_a cut out of the GBP was used. This is an approximate result and it well may be that the RGBP model (with the proper choice of parameters) can describe an interference function of a real carbon adsorbent better than the turbostratic model.

As to the adsorption properties of the RGBP, I was also able to compare them with experimental data only in general terms. The reason for that is that the isotherms of adsorption on heterogeneous carbon surfaces in the submonolayer region depend considerably on the type of carbon adsorbent. I compared here simulated isotherm on RGBP with averaged experimental data. For a more detailed comparison, one needs reliable adsorption characteristics (isotherms and heats of adsorption) for a heterogeneous nonporous carbon blacks with known interference functions or other quantitative structural characteristics. However, the preliminary conclusion is that the RGBP model, probably, should be augmented by some other features such as those for an amorphous carbon surface layer.

In the BET pressure region, the comparison of the simulated isotherm of adsorption of N_2 on RGBP with experimental data is more favorable. The simulated isotherm without adjustable parameters almost coincides with experimental data. The scatter of experimental isotherms for different nonporous carbon adsorbent is not so big in this range as in the submonolayer region. This result concurs with the conclusion of our previous paper⁹ that the heterogeneity of a surface that is responsible for the shape of the isotherm of adsorption in the BET range of relative pressures is not the same as the so called energetic heterogeneity of a surface. Here the former type of heterogeneity of a surface was called the secondary structural heterogeneity (SSH) to distinguish it from the primary structural heterogeneity (PSH). It is the PSH what is usually meant by the heterogeneity of a surface but what one can readily see in Fig. 1 is actually the SSH and it is this type of the heterogeneity of a surface that determines the shape of the isotherm of adsorption in the BET pressure region.

Finally, I hope that the RGBP model might provide a good basis for computer simulations of adsorption and other properties of some carbon materials like carbon blacks, active carbons and others.

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