

# FINE PORE STRUCTURE—CRYSTALLITE SIZE RELATIONSHIPS IN CARBONS\*

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The relationship between crystallite size and volume of micropores was investigated for a wide range of experimental carbons and graphites. The average amounts of fine pores in the materials ranged from 4 per cent for a commercial graphite to 30 per cent for a resin carbon.

Using a sink-float method, each carbon was fractionated according to liquid-displacement density. All of the materials proved to be mixtures of carbons which spanned considerable ranges in micropore content. X-ray diffraction measurements on a number of density fractions showed that the fine-pore content increased regularly with decreasing crystallite size. The results indicated that the fine pores are voids between adjoining crystallites, with an average separation between crystallites of 3 to 8 Å, depending on the type of carbon or graphite. Thus, the amount of fine-pore volume depends upon the total surface area of the crystallites.

## INTRODUCTION

It has been known for some time that the densities of synthetic carbons, as determined by liquid or gas displacement, are less than the densities obtained from X-ray diffraction measurements. This discrepancy has been interpreted as evidence of micropores which are inaccessible to the liquid or gas, either because they are too small to admit the gas or liquid molecules or because they are sealed off from the outside.

Dresel and Roberts<sup>1</sup> showed that the apparent density of a graphite powder to helium usually increased with increased fineness of the powder. Although the helium atom should penetrate pores as small as 5 Å, grinding to a particle size of 70 microns produced significant increases in helium densities. Dresel and Roberts concluded that grinding unblocks some of the pores, allowing helium to enter pores which were completely inaccessible before grinding.

An alternative explanation of the results

of Dresel and Roberts may be that the fine pores actually are accessible to helium, but that the time required for complete penetration depends on the particle size of the sample. Rossman and Smith<sup>2</sup> showed that, even with a fine powder, complete penetration of the micropores may require a long time. They measured helium-density drift on an acetylene black for periods of several weeks and found that the density was still increasing after 800 hr. Thus, the increases in helium density noted by Dresel and Roberts may indicate differences in completeness of penetration rather than in the actual number of accessible pores.

Franklin<sup>3</sup> found that her "nongraphitizing" carbons had low apparent densities to organic liquids. On the basis of low-angle X-ray scattering measurements, she deduced that these carbons contained a large volume of pores with diameters of the order of a few tens of Å. Pores of this size would be

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<sup>1</sup> E. M. Dresel, and L. E. J. Roberts, "Closed Pores in Synthetic Graphite", *Nature* **171**, 170 (1953).

<sup>2</sup> R. P. Rossman, and W. R. Smith, "Density of Carbon Black by Helium Density", *Ind. Eng. Chem.* **35**, 972 (1943).

<sup>3</sup> R. W. Franklin, "Crystallite Growth in Graphitizing and Non-Graphitizing Carbons", *Proc. Roy. Soc.* **209A**, 196 (1951).

truly inaccessible to the organic liquids, but they might be filled by helium if given enough time to reach equilibrium.

In the present investigation, the micropore volumes of several carbons were measured by helium gas displacement and by the sink-float technique in an organic liquid. Correlation of these data with X-ray diffraction measurements of crystallite size provided further insight into the nature of the micropores and their geometrical relationship to the crystallites. The sink-float results gave conclusive evidence of the inhomogeneity of synthetic carbons.

#### MATERIALS AND EXPERIMENTAL METHODS

##### *Carbons and Graphites Studied*

Included in this investigation were a commercial graphite, Grade CSF\*, and five carbons fabricated in the laboratory. The laboratory carbons were derived from a coal-tar pitch, a petroleum asphalt, a carbon black, a phenol-formaldehyde resin, and from a sugar.

The coal-tar pitch and the petroleum asphalt were coked in a rotating metal drum under partially oxidizing conditions. The phenolformaldehyde resin was polymerized and then carbonized at 1100°C. Cane sugar was carbonized by reaction with concentrated hydrofluoric acid.

In each case, the resulting carbon was calcined at 1400°C, mixed with an appropriate binder, and formed into test specimens by cold molding. The specimens were gas baked, and then heated to a graphitizing temperature of 2570°C in a carbon-resistor tube furnace.

The thermal expansions of the carbons were measured up to 400°C using an interferometer. Crystallite sizes and  $c_0$  lattice parameters were measured by X-ray diffraction using the techniques described by Austin and Hedden<sup>4</sup>. Table I gives the

X-ray parameters and thermal expansions of the six carbons after heating to 2570°C.

##### *Apparent Density Measurements*

###### *By Helium Displacement*

The apparent densities of the carbons to gaseous helium were determined by the conventional displacement method, in which a measured quantity of helium is expanded into a sample tube of known volume containing a known sample weight. The helium fills the space around the sample, the space between the particles, and all accessible pores within the particles. The apparent density is found by dividing the sample weight by the apparent volume occupied by the sample.

These determinations were made on minus 200-mesh powder samples weighing 5 to 10 g. The apparatus was not suitable for observing helium-density "drift" and the values reported are the initial densities obtained after waiting  $\frac{1}{2}$  hr to reach a steady pressure. The density values were reproducible to within  $\pm 0.005$  g per cm<sup>3</sup>.

###### *By Sink-Float Method*

To determine the apparent densities to liquids, a sink-float technique was chosen because it promised to give more information than could be obtained by displacement methods. Synthetic carbons were known to be inhomogeneous with regard to crystallite size, and the sink-float method made it possible to determine the degree of inhomogeneity within each carbon. By diluting a light liquid with a heavier one, powder samples were separated into density fractions. The density distributions of the graphites were determined from the weights of the fractions and the densities at which they floated.

Separations were first made by using a bromoform - benzene - carbon tetrachloride mixture, like that described by Franklin<sup>3</sup>. Later work was done with bromoform and

\* National Carbon Company.

<sup>4</sup> A. E. Austin, and W. A. Hedden, "Graphitization Processes in Cokes and Carbon Blacks", Ind. Eng. Chem. **46**, 1520 (1954).

TABLE I  
Raw Materials and Properties of Carbons

Sample Designation	Raw Materials		Mean Coefficient of Thermal Expansion† (25 to 400°C) 10 <sup>-6</sup> per °C	X-Ray Parameters, Å		
	Filler	Binder		Crystallite $L_A$	Size $L_C$	$c_0$ Lattice parameter
CSF	Delayed petroleum coke	Coal-tar pitch	4.80	>1000	450	6.69
42	Laboratory coke from soft coal-tar pitch*	Soft coal-tar pitch	6.66	165	115	6.75
188	Sterling S carbon black	Phenolic resin	4.60	120	92	6.80
36	Laboratory coke from petroleum asphalt*	Petroleum asphalt	3.96	80	58	6.82
46	Laboratory coke from phenolic resin	Phenolic resin	3.31	60	30	6.94
39	Coke from HF reduction of cane sugar	Phenolic resin	3.12	80	39	6.90

\* Coked under partially oxidizing conditions.

† Measured in the direction of greatest preferred orientation of the  $c$ -axis.

benzene only. <sup>7</sup>Franklin<sup>5</sup> reported that benzene wet low-rank coals, and gave apparent liquid densities somewhat lower than helium-displacement densities. It is not known whether bromoform completely wets graphite. However, Firth<sup>6</sup> reports the use of chloroform in measuring the apparent density of sugar and coconut-shell charcoals. Bromoform is closely related to chloroform chemically and should behave similarly when used for density determinations.

Sink-float samples were prepared by crushing rod samples in a steel mortar. About 500 mg of only the 100- to 200-micron portion of the sample was used for the determinations. The time required to reach equilibrium (sink or float) in the liquids made the use of finer grains impractical.

The granular samples were placed in a beaker within a vacuum jar. A flask containing a 50-50 mixture, by volume, of bromoform and benzene was connected to the vacuum jar by a rubber hose. The jar and flask were evacuated simultaneously

with a mechanical pump. The pressure was reduced to approximately 200 microns of mercury, and pumping continued for  $\frac{1}{2}$  hr. At this pressure, a portion of the organic liquids vaporized and the sample was refluxed in their vapor. After  $\frac{1}{2}$  hr, the remaining liquid was poured into the beaker containing the sample. The pump was shut off, and the sample was transferred to the sink-float apparatus.

The apparatus is shown in Figure 1. It consists essentially of two glass cells connected by a glass tube. A fine screen is fused into the glass connecting tube to separate the cells. Cell A is fitted with an overflow tube for collecting the fractions. The apparatus was immersed in a constant-temperature bath maintained at  $30 \pm 0.5^\circ\text{C}$ . The density of the liquid in Cell B was measured by using a Westphal balance with a special plummet calibrated at  $30^\circ\text{C}$ . The maximum error in measuring the absolute density with this plummet was 0.24 per cent.

To measure the sink-float density, the graphite sample was placed in Cell A. The density of the bath was raised slowly by adding equal volumes of bromoform to each cell until a few particles started to float. After a wait of  $\frac{1}{2}$  hr to permit inter-cell

<sup>5</sup> R. C. Franklin, "A Study of the Fine Structure of Carbonaceous Solids by Measurement of True and Apparent Density", Trans. Faraday Soc. **45**, Part I, 274 (1949).

<sup>6</sup> J. B. Firth, "Determination of the Density of Charcoals by Displacement of Liquids", Trans. Faraday Soc. **19**, 444 (1923-4).

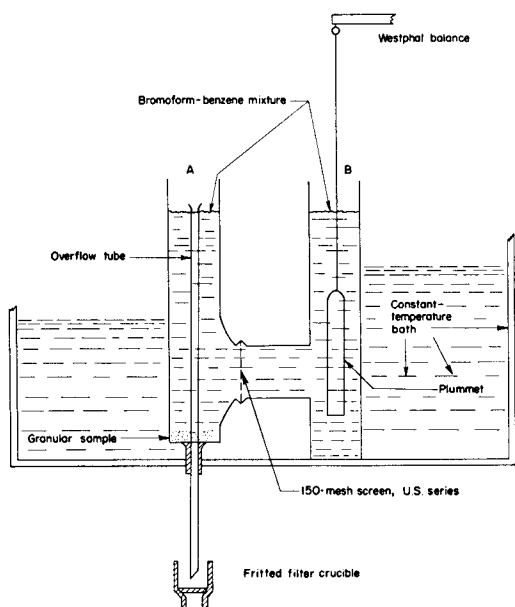


FIG. 1. Sink-float apparatus

mixing of bromoform and benzene, the liquid level was raised above the overflow tube by immersing a glass bulb in Cell B. Thus, the graphite layer at the surface of Cell A was directed into the overflow tube for collection in a fritted-glass filter crucible. Particles clinging to the overflow tube were washed down with benzene.

This operation was repeated at density intervals of about 0.020 g per cm<sup>3</sup> until the entire sample had floated. The fractions were washed several times with benzene, heated to constant weight at 100°C, and weighed. Then, a plot of cumulative weight per cent floated versus density of the liquid was made. The density at which 50 per cent of the sample had floated was taken as the apparent density.

By adding the bromoform equally to both sides, the waiting period of  $\frac{1}{2}$  hr produced density equality in the two cells to within 0.001 g per cm<sup>3</sup>. The reproducibility of the apparent density measurements is estimated to be  $\pm 0.005$  g per cm<sup>3</sup>.

## RESULTS AND DISCUSSION

The apparent densities and micropore volumes of the six carbons are shown in Table II. Micropore volume was calculated from the difference between the X-ray density and the apparent density, where the X-ray density was assumed to vary inversely with the  $c_0$  lattice parameter.

Agreement between the apparent densities measured by the two methods was only fair. Some segregation may have occurred in preparing samples for sink-float measurements, as only the 100- to 200-micron particles were used, with finer particles discarded. Thus, the micropore volumes

TABLE II  
Apparent Densities and Micropore Volumes of Carbons

Sample Designation	X-Ray Density, g per cm <sup>3</sup>	Apparent Density, g per cm <sup>3</sup>		Micropore Volume, per cent*	
		By helium displacement	By sink-float	By helium displacement	By sink-float
CSF	2.25	2.168	2.177	3.6	3.4
42	2.24	2.047	2.107	8.3	5.8
188	2.22	1.796	1.812	19.1	18.2
36	2.22	1.702	1.769	23.2	20.4
46	2.18	1.625	1.551	25.5	28.8
39	2.19	1.604	1.557	26.6	29.0

$$* \text{ Per cent} = 100 \left\{ 1 - \frac{\rho_{\text{apparent}}}{\rho_{\text{X-ray}}} \right\}$$

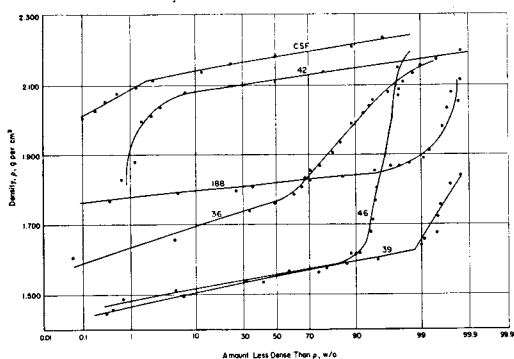


FIG. 2. Sink-float density distributions for carbons.

There are two ways to express closed pore volume. The above method calculates the closed pore volume as a percentage of the total volume occupied by the solid. The second method calculates the closed pore volume as a percentage of the total pore volume. Carbon volume, i.e., entire sample volume, is used in the first method. The second method uses the apparent density of the sample. The two methods are related by the equation:  $\text{Closed Pore Volume (\%)} = \frac{\text{Apparent Density}}{\text{X-ray Density}} \times 100$ .

obtained from helium-displacement densities may be more representative of the samples as a whole.

Each of the carbons covered a considerable range of sink-float density, with Carbon 36 having the widest density range. This is shown in Figure 2, where apparent density,  $\rho$ , is plotted versus the percentage of the sample less dense than  $\rho$ . The plots are on probability coordinates, so that a Gaussian distribution would be represented by a straight line. Four of the samples show this Gaussian behavior throughout most of the range, although significant deviations involving 10 per cent or less of the material in the sample do occur. Carbon 36 does not show a linear plot in Figure 2; there is a marked change in slope at a density of about 1.75 g per cm<sup>3</sup>. The sample contained two kinds of populations in roughly equal amounts, the denser population being characterized by a wider range of densities than the less dense one.

#### *Micropore Volume—Crystallite Size Relationships*

Comparison of Tables I and II shows a general increase in micropore volume with decreasing crystallite size. This suggests that the micropores are coextensive with the crystallite surfaces and are the result of small separations between adjoining crystallites. This assumption seems even more likely in view of X-ray diffraction results obtained on sink-float fractions of two of the carbons.

Several equidensity fractions of Carbons 36 and 46 were separated in the sink-float apparatus, and their average crystallite sizes and X-ray densities were determined. Sink-float densities were used to calculate micropore volume because the samples were too small for helium-displacement measurements. The results are shown in Table III. Micropore volume decreased with increasing crystallite size, as noted for the unseparated graphites.

TABLE III  
*Micropore Volume and Crystallite Size for Density Fractions*

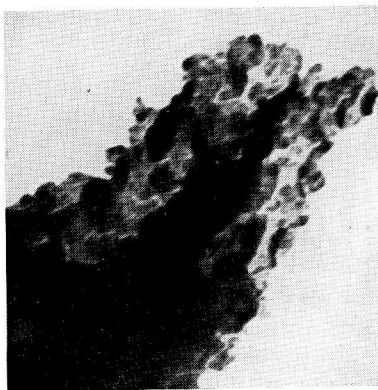
Sink-Float Density, g per cm <sup>3</sup>		Micropore Volume, per cent*	Crystallite Dimensions, Å	
Range	Average		L <sub>A</sub>	L <sub>C</sub>
Carbon 36				
1.54-1.68	1.61	26	52	30
1.69-1.76	1.72	21	86	42
1.76-1.83	1.80	18	79	56
1.83-1.91	1.87	15	110	65
1.91-1.98	1.95	12	142	93
1.98-2.06	2.02	8	194	94
Carbon 46				
1.42-1.48	1.45	33	41	24
1.48-1.52	1.50	31	65	31
1.52-1.54	1.53	30	71	32
1.54-1.57	1.56	28	64	34
1.57-1.59	1.58	27	52	35
1.59-1.61	1.60	26	54	36

\* X-ray densities varied from 2.16 to 2.20 g per cm<sup>3</sup> for 36 and from 2.16 to 2.18 g per cm<sup>3</sup> for 46.

#### *Electron Microscope Observations*

The electron microscope was used to confirm directly the existence of inter-crystallite pores. Attempts to prepare sufficiently fine powder samples by wet grinding in a ball mill were not very successful. Therefore, samples were prepared by burning small holes in thin slices. A thin graphite section was heated at about 400°C with a fine stream of oxygen directed at the top surface until a hole just broke through the lower surface. The edges of the resulting pinholes were a few hundred Å in thickness. Photographs of the edges were taken at 50,000 diameters. The technique is somewhat analogous to etching in that pores and cracks are magnified.

Micrographs of Carbons 36 and 42 are shown in Figure 3. In the photograph of 36, pores are seen clearly between the crystallites. The pores are much wider than the 5 Å

Carbon 42. 50,000  $\times$ FIG. 3. Electron micrographs of experimental carbons  
Carbon 36. 50,000  $\times$ 

indicated by the density measurements. No doubt, preferential burning widened the pores considerably during preparation of the sample. In Carbon 42, the individual crystallites are not so clearly defined, and those pores which are visible cannot be definitely associated with the boundaries of single crystallites. The nearly uniform density of the field indicates that the crystallites are more closely packed than in Carbon 36. Several needle-shaped regions are shown. These probably are large clusters of crystallites which are highly oriented with

their basal planes parallel to the long axes of the needles.

#### *Calculation of Intercrystalline Void Spacings*

Having assumed that the micropores are coextensive with the crystallites, the data on micropore volume and crystallite size may be used to estimate the average void spacing between crystallites. A method for doing this will be given next and will serve to define "void-spacing" as used in this paper.

The fractional volume of micropores,  $p$ , is determined from initial helium-displacement

densities or from apparent liquid densities. Thus, it is based on the combined volume of crystallites and micropores. If the fractional volume of micropores per unit of crystallite volume is denoted by  $p'$ , then:

$$p' = p(\rho_i/\rho_0) \quad (1)$$

where  $\rho_i$  is the theoretical or X-ray density and  $\rho_0$  is the helium or sink-float density. The volume,  $\Delta V$ , of a thin envelope surrounding a crystallite is found by multiplying the surface area,  $s$ , of the crystallite by the thickness of the envelope. If  $\delta$  is the void spacing, the thickness of the envelope is  $\delta/2$ . Thus:

$$\Delta V = (\delta/2)s, \quad (2)$$

or

$$(\Delta V/V) = (\delta/2)(s/V). \quad (3)$$

For either a rectangular parallelepiped with sides  $L_A$ ,  $L_A$ , and  $L_C$  or a right circular cylinder of length  $L_C$  and diameter  $L_A$ ,

$$(s/2V) = (1/L_C) + (2/L_A). \quad (4)$$

In this model, which assumes identical crystallites and uniform spacings,  $(\Delta V/V) = p$ , and Equations (3) and (4) give

$$\delta = (p\rho_i/\rho_0)[(1/L_C) + (2/L_A)]^{-1} \quad (5)$$

$$[p\rho_i L_A L_C / \rho_0 (L_A + 2L_C)]$$

Values of  $\delta$  calculated from Equation (5) are shown in Table IV. It should be remembered that the spacing between the

surfaces in adjoining crystallites will be 3.35 to 3.5 Å greater than  $\delta$  if the spacing is defined in terms of the center-to-center distance between corresponding atoms.

The calculated values for  $\delta$  are in agreement with the observations that the micropores are closed to liquids and relatively inaccessible to helium gas. These values of  $\delta$  may be compared with the results obtained from helium-displacement density measurements on carbon blacks. For Carbolac 1, Grade 6 rubber black, and Shawinigan acetylene black, Rossman and Smith<sup>2</sup> found characteristic pore spacings of 0.1, 0.8, and 6 Å, respectively. Measurements of helium-displacement-density drift corroborated these calculations. The first two blacks showed no density drift while the acetylene black continued to absorb helium, even after several weeks of immersion.

#### *Relationship of Micropore Structure to Thermal Expansion*

Reference to Table I shows that the experimental carbons had a wide variation in thermal expansion. Those with the smallest expansions were 36, 39, and 46, which had large micropore volumes. In attempting to explain the wide variation in thermal expansion and, moreover, the fact that all polycrystalline graphites have much smaller expansions than that calculated for a single crystal, two points come to mind.

First, it is known that, in a highly anisotropic material such as graphite, thermal expansion will cause very large internal stresses. The nonlinear stress-strain curves and permanent sets which have been observed indicate that some plastic deformation can take place. This deformation may permit crystallite expansion into the pores and contribute to low bulk expansion.

The second effect to be considered is the one described by Mrozowski<sup>7</sup> in terms of purely geometrical considerations, with no

TABLE IV

*Calculated Void Spacings for Carbons*

Sample Designation	Micropore Volume, $p$ , per cent (by helium displacement)	Void Spacing, $\delta$ , Å
CSF	3.6	8.3
42	8.3	2.6
188	19.1	8.3
36	23.2	7.2
46	25.5	5.1
39	26.6	7.2

<sup>7</sup> S. Mrozowski, This volume, page 31.

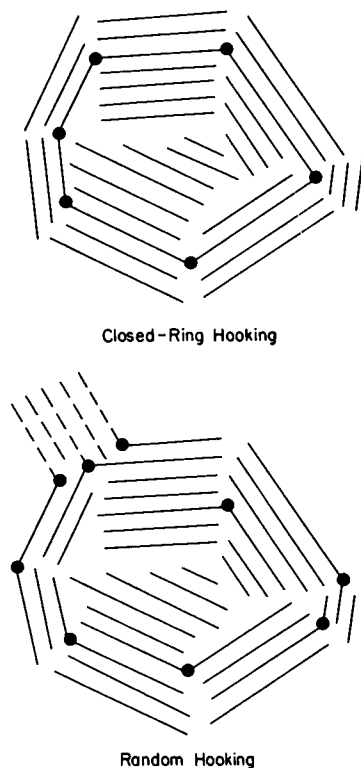


Fig. 4. Possible ring structures in carbons

question of plastic deformation involved. According to this model, the bulk expansion may be less than the crystallite expansion by virtue of crystallites (or stacks of crystallites) being hooked together to form rings. Examples of this type of bonding are shown in Figure 4, which is taken directly from the paper by Mrozowski.

The first diagram in Figure 4 shows a highly idealized structure which represents the limiting case. All crystallites are bonded at the peripheries to form fully closed rings. This type of structure would show an expansion in any direction equal to  $\alpha_a$ , the expansion of a single crystal in the  $a$ -direction.

The second diagram shows a more likely structure which Mrozowski calls "random hooking". In this case, the crystallites do not form completely closed rings and the expansion in the plane of the paper would

be the resultant of  $\alpha_a$  plus some contribution from  $\alpha_c$ , the single crystal expansion in the  $c$ -direction. In actual materials, the system of cross linking is tridimensional and the contribution from  $\alpha_c$  will be felt in all three directions. This contribution will be greatest in graphites whose crystallites are well oriented on a microscopic scale and will be least in those which have a predominance of ring structures.

Without saying it specifically, Mrozowski implies that the contribution from  $\alpha_c$  can be small only if intercrystalline pores are available to absorb the crystallite expansion in the  $c$ -direction. This is an important point. It suggests that, in addition to purely geometrical considerations, the relative amount of micropore volume and the ease with which crystallites can expand into the micropores may be important in determining the bulk thermal expansion.

That thermal expansion and micropore volume are related is shown in Figure 5, where the expansion coefficient is plotted against micropore volume,  $p$ . The correlation is very good except for CSF graphite. This may be an indication that, in carbons with large crystallites and small micropore volumes, the ease with which crystals can deform into the voids is more important than the actual amount of micropore volume. More data on well-graphitized carbons are needed to determine the relative importance

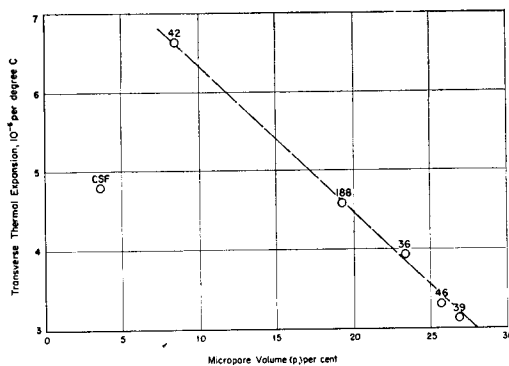


FIG. 5. Variation of thermal expansion with micropore volume.

of these factors. Investigation of the relationships between thermal expansion and stress-strain characteristics would be particularly helpful.

#### CONCLUDING REMARKS

Using data on the average crystallite sizes and micropore volumes of six carbons differing widely in crystallite size, the average spacing between adjoining crystallites was calculated to be from 3 to 8 Å. This agrees with the observations that the micropores are inaccessible to liquids and relatively inaccessible to helium gas, and is strong evidence that the micropores are located between adjoining crystallites. Measurements of helium density drift might be used to check this point.

One can only speculate on the structural details which might cause these inter-crystalline pores. In addition to purely

geometrical stacking considerations, crystallites may be held apart by clumps of disordered carbon. Other irregularities, such as steps or otherwise incomplete planes at the surfaces, may prevent the close approach of crystallites that would be possible with perfectly plane surfaces. In general, then, the average spacing between crystallites will be a secondary indication of structural perfection, in addition to the  $c_0$  lattice parameter and crystallite size.

The relationship shown here between micropore volume and thermal expansion suggests that a better understanding of some of the other properties of carbons, particularly electrical and mechanical, might result from further study of micropore structure. In this connection, the demonstrated inhomogeneity of carbons with regard to crystal and micropore structure may be very important.