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## Energy of Cohesion, Compressibility, and the Potential Energy Functions of the Graphite System

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The lattice summations of the potential energy of importance in the graphite system have been computed by direct summation assuming a Lennard-Jones 6-12 potential between carbon atoms. From these summations, potential energy curves were constructed for interactions between a carbon atom and a graphite monolayer, between a carbon atom and a graphite surface, between a graphite monolayer and a semi-infinite graphite crystal and between two graphite semi-infinite crystals. Using these curves, the equilibrium distance between two isolated physically interacting carbon atoms was found to be  $2.70 a$ , where  $a$  is the carbon-carbon distance in a graphite sheet. The distance between a surface plane and the rest of the crystal was found to be 1.7% greater than the interlayer spacing. Theoretical values of the energy of cohesion and the compressibility were calculated from the potential curve for the interaction between two semi-infinite crystals. They were  $\Delta E_c = -330$  ergs/cm<sup>2</sup> and  $\beta = 3.18 \times 10^{-12}$  cm<sup>2</sup>/dyne, respectively. These compared favorably with the experimental values of  $\Delta E_c = -260$  ergs/cm<sup>2</sup> and  $\beta = 2.97 \times 10^{-2}$  cm<sup>2</sup>/dyne.

**P**HYSICAL properties of solids such as energy of cohesion and compressibility can be computed from appropriate summations of the potential energy interactions of the atoms in the crystal. Graphite is a particularly suitable subject for such computations because of its crystal structure. The large spacing between graphite layers greatly simplifies the calculations and makes it necessary to consider only the interlayer cohesion. Also, the same set of lattice summations can be used in calculating the compressibility and the energy of cohesion. Furthermore, experimental values of both compressibility and energy of cohesion are available so that the results of the calculations can be compared to experiment.

Several studies have been made involving the summation of the potential energy function of carbon over the graphite lattice. Barrer,<sup>1</sup> and Crowell and Young<sup>2</sup> have used these summations to compute heats of adsorption on a graphite surface. Kraus<sup>3</sup> computed the energy of adhesion of carbon tetrachloride to graphite assuming that each graphite layer could be treated as having a uniform density and then summing over the layers. Brennan<sup>4</sup> obtained a value for the interlayer binding energy of graphite from a quantum mechanical calculation of the repulsive energy between layers. He also assumed that each layer could be treated as a continuum but that summation over the layers was necessary.

It is the purpose of this work to evaluate the lattice sums on which all studies of the type mentioned above must be based, to determine the potential energy functions important in the graphite system, and to apply these results to a calculation of the energy of cohesion and compressibility of graphite.

### POTENTIAL ENERGY FUNCTIONS IN TERMS OF LATTICE SUMMATIONS

It will be assumed that the potential energy between two physically interacting carbon atoms in graphite is given by the Lennard-Jones expression

$$\varphi = A \left[ \frac{1}{2} \frac{1}{r_0^6} - \frac{1}{r^6} \right], \quad (1)$$

where  $r$  is the distance between carbon atoms and  $A$  and  $r_0$  are constants. For the purposes of this paper it is convenient to measure distance in terms of  $a$ , the bond distance between carbon atoms in a graphite sheet. Then, letting  $y = r/a$ , Eq. (1) becomes

$$\varphi = \frac{A}{a^6} \left[ \frac{1}{2} \frac{1}{(y_0)^6} - \frac{1}{y^6} \right]. \quad (2)$$

In the graphite structure, two types of equilibrium position are possible for a carbon atom above a graphite sheet: one in which the atom is above the center of a hexagon, and the other in which the atom is above the corner of a hexagon, i.e., another atom. In forming lattice sums, therefore, two types of summation are necessary.

In the following discussion, an atom located above the center of a hexagon of a graphite sheet will be called an  $h$  atom and an atom located above the corner of a hexagon will be called a  $c$  atom.

Let  $S_{1,h^m}(x) = \sum_i (1/y_i^m)$  be the summation of  $1/y^m$  terms where  $x$  is the distance between an atom above the center of a hexagon and the graphite sheet and  $y_i$  is the distance between the atom above the graphite sheet and the  $i$ th atom in the graphite sheet.

The potential energy function between an  $h$  atom and a graphite monolayer sheet is given in terms of the above summation as

$$\varphi_{1,h}(x) = -\frac{A}{a^6} \left[ \frac{1}{2} (y_0)^6 S_{1,h^{12}}(x) - S_{1,h^6}(x) \right]. \quad (3)$$

<sup>1</sup> R. M. Barrer, Proc. Roy. Soc. (London) A161, 476 (1937).

<sup>2</sup> A. D. Crowell and D. M. Young, Trans. Faraday Soc. 49, 1080 (1953).

<sup>3</sup> G. Kraus, Progress Report No. 2, University of Cincinnati, Army Air Force Contract AF33(616) 231, 1953.

<sup>4</sup> R. O. Brennan, J. Chem. Phys. 20, 40 (1952).

TABLE I. The lattice sums for the graphite system.

$x$	$S_{1,h^6}(x)$	$S_{1,c^6}(x)$	$S_{\infty,h^6}(x)$	$S_{\infty,c^6}(x)$	$S_{\infty,\infty^6}(x)$	$S_{1,h^{12}}(x)$	$S_{1,c^{12}}(x)$	$S_{\infty,\infty^{12}}(x)$
0.5	3.19216	65.78386	3.212517	65.80415	69.06384	1.57397	4096.79209	4098.366
1.0	0.83067	1.519795	0.8417850	1.53019	2.399910	0.094182	1.048563	1.142745
1.5	0.220744	0.2483125	0.22740	0.254972	0.499582	0.0052127	0.0106040	0.0158167
2.0	0.074605	0.076071	0.078876	0.080342	0.170715	0.00041437	0.00050398	0.00091835
2.5	0.030890	0.030987	0.033780	0.033877	0.075836	$0.490619 \times 10^{-4}$	$0.515632 \times 10^{-4}$	0.000100625
3.0	0.014923	0.014928742	0.016963	0.0169687	0.039992	$0.81281 \times 10^{-5}$	$0.822298 \times 10^{-5}$	$0.1635108 \times 10^{-4}$
3.5	0.0080577	0.00805629	0.0095477	0.0100917	0.0242800	$0.17505 \times 10^{-5}$	$0.175493 \times 10^{-5}$	$0.350543 \times 10^{-5}$
4.0	0.0047235	0.00472194	0.0058429	0.0058429	0.015158	$0.4611 \times 10^{-6}$	$0.46133 \times 10^{-6}$	$0.92243 \times 10^{-6}$
5.0	0.0019348	0.00193324	0.0026111	0.0026111	0.0074934	$0.495 \times 10^{-7}$	$0.44496 \times 10^{-7}$	$0.93996 \times 10^{-7}$

The potential energy between an  $h$  atom and a semi-infinite graphite lattice is obtained by summing Eq. (3) over all the graphite layers in the semi-infinite crystal. The result is

$$\varphi_{\infty,h}(x) = \frac{A}{a^6} \left[ \frac{1}{2} (y_0)^6 S_{\infty,h^{12}}(x) - S_{\infty,h^6}(x) \right], \quad (4)$$

where

$$S_{\infty,h^{12}}(x) = \sum_{i=0}^{\infty} [S_{1,h^{12}}(x+2il) + S_{1,c^{12}}(x+[2i+1]l)] \quad (5)$$

and

$$S_{\infty,h^6}(x) = \sum_{i=0}^{\infty} [S_{1,h^6}(x+2il) + S_{1,c^6}(x+[2i+1]l)]. \quad (6)$$

$l$  is the distance between monolayer planes in the graphite lattice.

An analogous set of equations hold for interactions involving a  $c$  atom identical in form to Eqs. (3), (4), (5), and (6) except that the subscripts  $c$  and  $h$  are interchanged.

The potential energy function for interaction between a graphite monolayer sheet and a semi-infinite graphite crystal  $\varphi_{\infty,s}(x)$  is therefore given by

$$\varphi_{\infty,s}(x) = \frac{1}{2\sigma} [\varphi_{\infty,c}(x) + \varphi_{\infty,h}(x)], \quad (7)$$

where  $\sigma$  is the area occupied by a carbon atom in a monolayer sheet so that  $1/2\sigma$  is the number of atoms of each type per square centimeter in the monolayer and  $\varphi_{\infty,s}$  is given per  $\text{cm}^2$  of surface.

Finally, the potential energy function for interaction between two semi-infinite graphite crystals is obtained by adding Eq. (4) and its analog for a  $c$  atom (i.e., with interchanged subscripts) multiplying by the

number of atoms of each type ( $h$  and  $c$ ) per  $\text{cm}^2$  of graphite monolayer, and summing over all the layers of the second semi-infinite crystal. The result is

$$\varphi_{\infty,\infty}(x) = \frac{A}{2\sigma a^6} \left[ \frac{1}{2} (y_0)^6 S_{\infty,\infty^{12}}(x) - S_{\infty,\infty^6}(x) \right] \quad (8)$$

where

$$S_{\infty,\infty^{12}}(x) = \sum_{i=0}^{\infty} [S_{\infty,h^{12}}(x+il) + S_{\infty,c^{12}}(x+il)] \quad (9)$$

and

$$S_{\infty,\infty^6}(x) = \sum_{i=0}^{\infty} [S_{\infty,h^6}(x+il) + S_{\infty,c^6}(x+il)]. \quad (10)$$

EVALUATION OF THE LATTICE SUMMATIONS

The sums  $S_{1,h^6}$  and  $S_{1,c^6}$ , were computed by direct summation for all atoms within a distance of  $30a$  from the atom above the graphite plane for values of  $x$  ranging from 0.5 to 5. The contribution of the remaining atoms in the plane was obtained by integration and affected only the sixth decimal place of the summations. The sums  $S_{1,h^{12}}$  and  $S_{1,c^{12}}$  were computed by direct summation for all atoms within a distance of  $10a$  from the atom above the plane. The contribution of the remaining atoms in this case amounted to only  $10^{-12}$  and was therefore neglected.

The sums  $S_{\infty,h^6}$ ,  $S_{\infty,c^6}$ , and  $S_{\infty,\infty^6}$  were obtained by carrying the summation over the sheets from  $i=0$  to 30.

Because of the rapid fall of  $1/y^{12}$  with distance it was found necessary to use only summations over adjacent layers to obtain  $S_{\infty,h^{12}}$ ,  $S_{\infty,c^{12}}$ , and  $S_{\infty,\infty^{12}}$ .

In the application of Eqs. (6), and (7) to the calculation of the other sums,  $S_{1,h^6}$  and  $S_{1,c^6}$  were needed at values of  $x$  for which direct summations had not been carried out. For values of  $x$  below 3.5, values of the lattice sums were calculated from Newton's interpolation formula. The interpolation was applied to  $\log S_{1,h^6}$  and  $\log S_{1,c^6}$  rather than to  $S_{1,h^6}$  and  $S_{1,c^6}$  because the log plots of these functions are nearly linear and can therefore be interpolated more accurately than the functions themselves. For values of  $x$  greater than 3.5,  $S_{1,h^6}$  and  $S_{1,c^6}$  were computed by integration over the graphite plane assuming a continuous, uniform density.

For  $x$  greater than 12 it was sufficient to compute  $S_{\infty,h^6}$  and  $S_{\infty,c^6}$  for use in Eq. (9) by integration assum-

TABLE II. Crowell's values of the lattice summations.

Values obtained by direct summation	$S_{\infty,c^6}$	$S_{\infty,h^6}$ by approximation method	$S_{\infty,h^6}$ (This work)	$S_{\infty,c^6}$ (This work)
1.5	0.2540	0.246	0.2274	0.2550
2.0	0.07773	0.07971	0.0799	0.07888
2.5	0.03330	0.03343	0.0336	0.03378
3.0	0.01620	0.01666	0.0170	0.01696
3.5	0.009283	0.00959	0.00955	0.01009

ing a continuous, uniform, three-dimensional density. The errors introduced by these procedures were negligible.

The results of these calculations are listed in Table I.

An approximate method of obtaining lattice sums for graphite has been given by Crowell.<sup>5</sup> He evaluated the lattice sums of  $1/y^6$  for the interaction between an atom and a semi-infinite graphite lattice by the approximate method and compared them to the results of direct summation for several positions of the atom above the graphite surface. His results lead to the values of  $S_{\infty, h^6}$  and  $S_{\infty, e^6}$  given in Table II. A comparison of Tables I and II shows that Crowell's values differ somewhat from those presented in this work. In every case Crowell's values are lower than the corresponding summations obtained in this study. The source of this discrepancy is not immediately evident and can be revealed only by a step-by-step comparison of the two

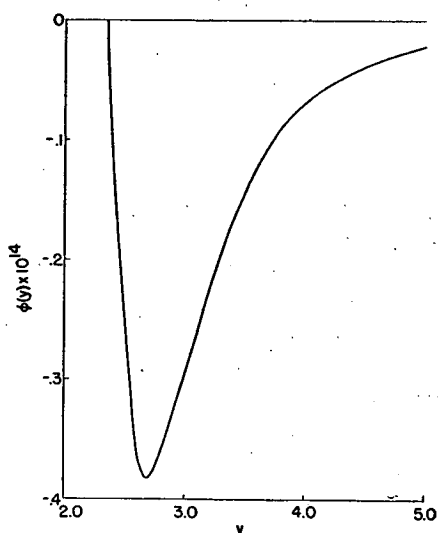


FIG. 1. The potential energy function for interaction between two carbon atoms.

sets of calculation. The fact that Crowell summed over only the nearest 100 carbon atoms can account in part for his lower results but probably not completely.

The lattice sums obtained by the approximate method agree equally well with both sets of direct summations.

POTENTIAL ENERGY FUNCTIONS

Before the lattice sums can be applied to the calculation of measurable quantities, the values of  $A$  and  $y_0$  in Eq. (2) must be known. Kraus<sup>3</sup> has computed a value of  $A = 24.3 \times 10^{-60}$  erg cm<sup>6</sup> by Kirkwood's formula using constants given by Barrer,<sup>1</sup> and  $y_0$  may be obtained from the condition that at equilibrium,

$$\left(\frac{\partial \varphi_{\infty, \infty}}{\partial x}\right)_{\text{eq.}} = 0.$$

<sup>5</sup> A. D. Crowell, J. Chem. Phys. 22, 1397 (1954).

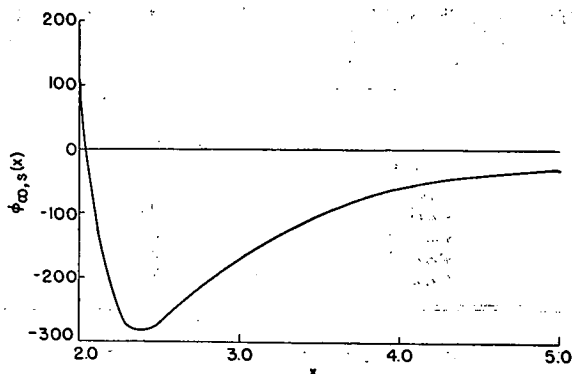


FIG. 2. The potential energy function for interaction between a graphite sheet and a semi-infinite crystal.

At equilibrium  $x = l = 2.36$  and differentiation of Eq. (10) gives

$$y_0^6 = 2 \left(\frac{\partial S_{\infty, \infty^6}}{\partial x}\right)_{2.36} / \left(\frac{\partial S_{\infty, \infty^{12}}}{\partial x}\right)_{2.36} \quad (11)$$

Calculation from Eq. (11) gave  $y_0 = 2.70$ . The derivatives were obtained graphically from plots of  $\log S_{\infty, \infty^6}$  and  $\log S_{\infty, \infty^{12}}$  vs  $y$ . Several values of the lattice sums between  $x = 2$  and  $x = 3$  were calculated by Newton's interpolation formula.  $\varphi, \varphi_1, h, \varphi_1, e, \varphi_{\infty, h}, \varphi_{\infty, e}, \varphi_{\infty, s}$ , and  $\varphi_{\infty, \infty}$  were computed using the following set of constants:

$$A = 24.3 \times 10^{-60} \text{ erg cm}^6 \quad y_0 = 2.70$$

$$a = 1.42 \times 10^{-8} \text{ cm} \quad \sigma = 2.62 \times 10^{-16} \text{ cm}^2.$$

The potential energy curves for  $\varphi, \varphi_{\infty, s}$  and  $\varphi_{\infty, \infty}$  are shown in Figs. 1 to 3. The equilibrium distance for each potential function was obtained from an expanded plot in the region of the minimum. These distances, given in Table III, require some comment. The equilibrium distance of approach between two carbon atoms is 2.70. This, of course, is for a hypothetical case; namely, two isolated carbon atoms that are interacting physically and not chemically, and for which the potential energy constants are the same as those for graphite. If a carbon

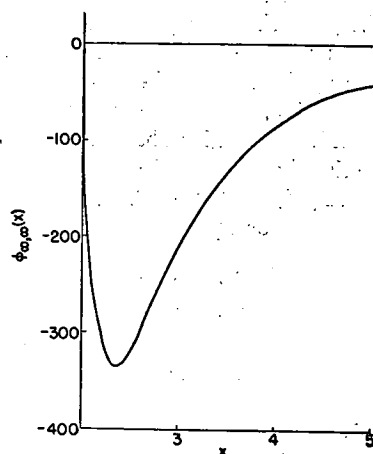


FIG. 3. The potential energy function for interaction between two semi-infinite graphite crystals.

TABLE III. The position of the minimum for the various potential energy functions—distance measured in units of the carbon—carbon distance in a graphite monolayer.

Potential function	Equilibrium distance
$\varphi(x)$	2.70
$\varphi_{1,c}(x)$	2.41
$\varphi_{1,h}(x)$	2.37
$\varphi_{\infty,c}(x)$	2.40
$\varphi_{\infty,h}(x)$	2.37
$\varphi_{\infty,s}(x)$	2.40
$\varphi_{\infty,\infty}(x)$	2.36

atom interacts with a graphite monolayer, the equilibrium distance decreases to 2.41 for a *c* position and to 2.37 for an *h* position. This is as expected because of the increased number of atoms interacting with the atom above the sheet. Similarly, one might expect a further contraction in equilibrium distance for a surface layer on a semi-infinite crystal because of the interactions between the surface atoms and those in the layers beneath them. This interaction has been found by Lennard-Jones and Dent<sup>6</sup> to result in a 5% contraction in the surface layer spacing of alkali halides. However, the large interlayer spacing characteristic of the graphite structure leads to an expansion of 1.7%. The large interlayer spacing results in a negligible contribution to the repulsive potential for all except the adjacent layers. Therefore, the repulsive potential between a plane and a semi-infinite crystal is essentially the same as the repulsive potential between two semi-infinite crystals. However, the attractive potential does not decrease as rapidly with distance so that planes at larger distances also make an appreciable contribution. Thus, the attractive potential is less for interaction between a surface plane and a semi-infinite crystal than for interaction between two semi-infinite crystals. The net result is an increase in interplanar spacing for surface layers.

#### COMPARISON WITH EXPERIMENTAL DATA: ENERGY OF COHESION AND COMPRESSIBILITY

The energy of cohesion for graphite is given by the interlayer binding energy and may be calculated from the potential energy curves. If there were no difference in lattice spacing between a surface layer and interior layers, the energy of cohesion would be given by  $\varphi_{\infty,\infty}$  (2.36) i.e., the value of the interlayer potential at equilibrium. This value, however, requires a small correction because of the expansion of the surface layer spacing from 2.36 to 2.40. The energy of cohesion  $\Delta E_c$  is then given by

$$\Delta E_c = \varphi_{\infty,\infty}(2.36) - [\varphi_{\infty,s}(2.40) - \varphi_{\infty,s}(2.36)]$$

therefore  $\Delta E_c = -330$  ergs/cm<sup>2</sup>.

Brennan<sup>4</sup> has given two values of  $\Delta E_c$  based on two different wave functions. These are  $-69.5$  ergs/cm<sup>2</sup> and

$-1027$  ergs/cm<sup>2</sup> so that our results are in serious disagreement with Brennan's regardless of which wave function is chosen as correct. Recently, experimental energies of cohesion have become available<sup>7</sup> from heat of wetting data. The mean of eight such values for graphite gives  $\Delta E_c = -260$  ergs/cm<sup>2</sup> with an average deviation from the mean of about 11%. A comparison of these values is summarized in Table IV. The agreement between our value and the experimental value is quite satisfactory considering the experimental error and the possible error in the value of *A*. Furthermore, the lattice sums yield a value of  $\Delta E_c$  that is valid only at 0°K whereas the experimental value was determined at room temperature. Since the magnitude of  $\Delta E_c$  decreases as the temperature increases, the discrepancy between the experimental and theoretical values is easily accounted for.

The compressibility  $\beta$  can be computed from the relation

$$\frac{1}{\beta} = V \frac{d^2 U}{dV^2}, \quad (12)$$

where *V* is volume and *U* = energy of the crystal. If it is assumed that the total volume change on compression

TABLE IV. Comparison of various values of the energy of cohesion.

Method	Reference	$\Delta E_c$ ergs/cm <sup>2</sup>
Lattice summation	This work	-330.0
Zener's wave function	4	-69.5
Kohlrausch's wave function	4	-1027.0
Experimental (heat of wetting)	7	-260.0

is the result of changing the interlayer spacing and that the entire energy change is the change in the lattice energy  $\varphi_{\infty,\infty}$ , then Eq. (12) becomes

$$\frac{1}{\beta} = l \frac{d^2 \varphi_{\infty,\infty}}{dl^2}, \quad (13)$$

where *l* = interlayer spacing. The derivative ( $d^2 \varphi_{\infty,\infty} / dl^2$ ) was computed graphically from plots of  $\log S_{\infty,\infty}$ <sup>6</sup> and  $\log S_{\infty,\infty}$ <sup>12</sup> as a function of *x*. The result thus obtained was  $3.18 \times 10^{-12}$  cm<sup>2</sup>/dyne. This is in excellent agreement with the experimental value  $2.97 \times 10^{-12}$  cm<sup>2</sup>/dyne that Brennan<sup>5</sup> calculated by extrapolating Bridgeman's<sup>8</sup> data to zero pressure.

#### SUMMARY

The various lattice sums of importance in the graphite system were computed and used to calculate the potential energy functions for interactions between two carbon atoms, between a carbon atom and a monolayer graphite sheet, between a carbon atom and a semi-infinite crystal, and between two semi-infinite crystals.

<sup>6</sup> J. E. Lennard-Jones and B. M. Dent, Proc. Roy. Soc. (London) 121, 247 (1928).

<sup>7</sup> L. A. Girifalco, Ph.D. thesis, University of Cincinnati (1954).

<sup>8</sup> P. W. Bridgeman, Proc. Am. Acad. Arts Sci. 76, 9 (1945).

Theoretical values of the energy of cohesion and the compressibility were computed from the appropriate potential energy curves which agreed satisfactorily with the experimental values.

#### ACKNOWLEDGMENTS

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