Hückel-type coefficients were determined and tabulated using both the McConnell and the Colpa–Bolton theories. The quantities $Q^{\pm}$ of the McConnell theory, and Q_0 and K of the Colpa–Bolton theory were tabulated to permit comparison of the electronic distributions of the various hydrocarbon-radical ions.

When one wishes to carry out calculations of various molecular parameters which depend upon molecular-orbital results, we recommended the use of the experimental values tabulated here for the energy levels for which they are available, and the values tabulated in Refs. 9 or 10 for the remaining energy levels. The use of the present values should increase the accuracy of molecular calculations which make use of tabulated Hückel coefficients.

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Rigid Disks at High Density. II

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As shown in a previous publication, the Helmholtz free energy per particle (divided by k_BT) for a rigid disk system has the following asymptotic form in the limit of the reduced density $\theta=A_0/A\to1$: $F/Nk_BT\sim 2\ln(\lambda/a)-2\ln(\theta^{-1}-1)+C+D(\theta^{-1}-1)+\cdots$, in which C and D are appropriate numerical constants, λ is the mean thermal de Broglie wavelength, a is the disk diameter, and A_0 is the close-packed value of the area, A, of a system of N particles. Moreover, a technique for estimating the value of C was developed. This technique was based upon a product representation for the partition function which considered a sequence of correlated motion of larger and larger sets of contiguous particles. An approximate value of C was previously obtained from all contributions for four or fewer correlated disks. This article extends these calculations to fifth order (contributions of all sets of five particles) with the summary result: $C=0.14384-0.013857+0.014322-0.0073211-0.004222+\cdots=0.14384-0.011078+\cdots$, in which the first number is the value of C obtained from the one-particle free-area model, and the remaining terms are the corrections from two-, three-, etc., particle correlations. These results are in slight disagreement with the estimate of C obtained by Hoover and Alder from molecular dynamics calculations, namely $C\cong0.14384-0.06\pm0.02$. The sequential approximation scheme for estimating C is applied to the tunnel model (where the exact value is known) and shows a rapid convergence. An analysis of the most compact clusters or sets also supports the fifth-order estimate of C.

I. INTRODUCTION

An earlier publication[1] described a procedure for calculating the asymptotic thermodynamic properties of rigid-disk and -sphere systems in the close-packed crystalline limit. The procedure was based upon a sequence of approximations which started with the single-particle free-volume theory and evaluated corrections from correlated motion of larger and larger sets of contiguous particles. The correlated motion of a given set of particles was formulated using the cell-cluster concept[2] but the successive approximations were based upon a product representation for the partition function.[1]

The calculations reported in Ref. 1 were for a rigid-disk system and were carried to fourth order, i.e., all contributions for four or fewer correlated disks. Despite the fact that the calculations were programmed for an electronic computer, the complexity of the five-particle figures forced us to truncate the calculations at that point. Recent improvements in the computer program for our calculations have now enabled us to extend these calculations to fifth order, and we report these results in this paper.

The sequence of approximations used in Ref. 1, while well-defined, is not unique and does not correspond to any known convergent series. It was formulated on an intuitive basis and by way of justification it was shown to yield a convergent series[1] for the case of rigid rods in one dimension. The four terms for the rigid-disk calculations did not display convincing em-

[1] F. H. Stillinger, Jr., Z. W. Salsburg, and R. K. Kornegay, J. Chem. Phys. **43**, 932 (1965).
[2] J. De Boer, Physica **20**, 655 (1954).

pirical convergence properties and for this reason we have extended the calculations to next higher order.

Because of an error in the published result for one four-particle term,[1] Hoover and Alder[3] concluded that the results reported in Ref. 1 are in disagreement with the high-density behavior of rigid disks as estimated from molecular dynamics calculations, and thus questioned the convergence properties of this sequence.

By way of further justification of the approximation scheme described in Ref. 1, we have worked out the results for the tunnel model through sixth order. These calculations are given in Sec. IV and are convincingly convergent in an empirical sense. However, the tunnel model has a strong one-dimensional character, and we do not claim that this result implies the convergence of our sequence for rigid disks.

It has also been suggested[4] that the correlated motion in a rigid-disk system is better represented by the most compact cell clusters (see Table I). To test this hypothesis the compact clusters are discussed in Sec. III, and an attempt at extrapolation to larger compact clusters is made.

Section II is devoted to a brief review of the general theory, and the five particle cell-cluster results are presented in Sec. III.

II. GENERAL THEORY

The sequential approximation scheme developed in Ref. 1 starts with the free-area approximation illustrated in Fig. 1. In this approximation all the particles are fixed on their nominal lattice sites except one which is allowed to move in the six-sided "free area" bounded by its nearest neighbors. The cannonical partition function Q_1 and the Helmholtz free energy F_1 for this particle can then be computed and the free energy F_N for a system of N particles is approximated by

$$F_N \cong N F_1. \tag{2.1}$$

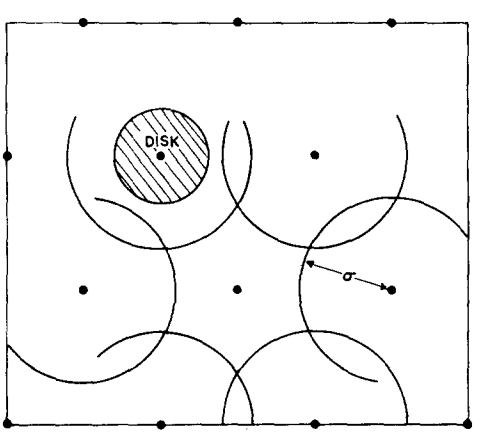

FIG. 1. The six sided "free area" for a one-particle cell cluster is illustrated. This is based upon the triangular or hexagonal lattice whose sites are given by the solid dots. A typical disk fixed at its lattice site is illustrated as well as the collision circles of all the neighboring fixed disks. The center of the free particle is confined to the central area bounded by segments of the collision circles.

[3] W. G. Hoover and B. J. Alder, J. Chem. Phys. 45, 2361 (1966).
[4] W. G. Hoover and B. J. Alder (private communication).

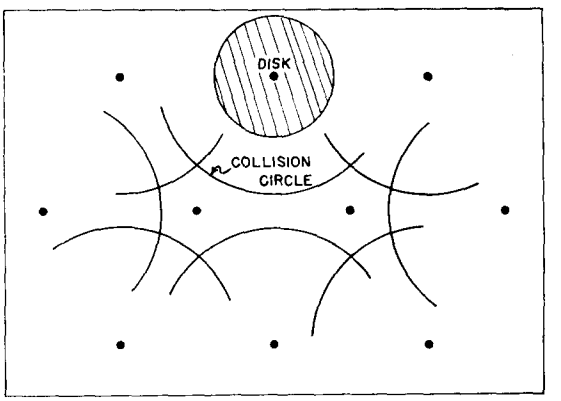

FIG. 2. An illustration of the two-particle cell-cluster. The configuration depicted here is for a relatively low-density system. At high densities one obtains two isolated regions around the two central lattice sites.

The first correction to this free-area approximation is obtained by attaching all particles on their nominal lattice sites except a nearest-neighbor pair. This pair is allowed to move in the region illustrated in Fig. 2, and the canonical partition function Q_2 and the Helmholtz free energy F_2 for this pair are then computed. A multiplicative correction factor, Y_2, for the partition function or equivalently an additive correction term for the free energy, W_2, is defined by

$$Y_2 = Q_2/(Q_1)^2, \tag{2.2a}$$

$$W_2 = F_2 - 2F_1 = -k_B T \ln Y_2. \tag{2.2b}$$

For a two-dimensional rigid disk system with N particles near close packing there are $3N$ nearest-neighbor pairs and the free energy F_N for this system is approximated by

$$F_N \cong N F_1 + 3N W_2. \tag{2.3}$$

The complete approximation scheme is based upon a product representation of the partition function. In general all sets of n disks ($n=1, 2, \cdots$) which form a connected grouping are considered. In each case all the particles are fixed on their nominal lattice sites except for the n disks under consideration. These n particles are allowed to move in the available free area and the partition function and free energy for this system are computed. For large n there will tend to be a very large number of distinct types of connected groupings or clusters. For our purpose we label each cluster with a pair of indices (n, α) denoting a cluster of n particles and type α (see Table I). The corresponding partition function and free energy for each cluster are denoted by $Q_{n,\alpha}$ and $F_{n,\alpha}$, respectively.

TABLE I. Catalog of the various species of connected sets of disks including five or fewer particles. The solid bonds in the graphs indicate nearest neighbors. $K_{n,\alpha}=Q_{n,\alpha}/Q_1^n$ and $Y_{n,\alpha}$ is defined in Eq. (2.4).

Cluster graph	Cluster number (n,α)	$t(n,\alpha)$	$Q_{n,\alpha}/Q_1^n = K_{n,\alpha}$	$Y_{n,\alpha}$
	1, 1	1	1.0	3.0
	2, 1	3	1.004 629 629	1.004 629 629 63
	3, 1	3	0.999 691 358	0.990 498 842 618
	3, 2	6	1.009 465 021	1.000 182 632 89
	3, 3	2	1.020 679 012	1.006 633 169 29
	4, 1	3	0.991 422 019	0.996 627 042 601
	4, 2	12	1.003 089 482	0.998 592 837 560
	4, 3	6	1.013 896 544	0.999 578 890 751
	4, 4	6		
	4, 5	2	1.017 025 830	1.002 480 901 51
	4, 6	12	1.017 260 068	1.001 390 685 90
	4, 7	3	1.043 528 929	1.005 943 266 82
	5, 1	3	0.982 233 796	0.998 995 865 125
	5, 2	12	0.994 310 219	0.999 515 662 664
	5, 3	12	1.007 228 048	0.999 737 002 065
	5, 4	12		
	5, 5	6	1.006 284 475	0.999 786 705 084
	5, 6	6		
	5, 7	6	1.018 236 824	0.999 891 297 088
	5, 8	12		
	5, 9	6		
	5, 10	6	0.996 155 016	0.999 398 855 343
	5, 11	6	1.009 424 264	1.000 241 588 93
	5, 12	12	1.021 271 803	1.000 207 056 34
	5, 13	12	1.007 229 639	0.999 805 292 092
	5, 14	12	1.020 260 873	0.999 973 336 915
	5, 15	12		
	5, 16	6	1.010 883 143	1.000 445 600 35
	5, 17	12	1.012 643 630	1.000 215 038 37
	5, 18	6	1.013 921 852	1.000 489 645 89
	5, 19	3	1.028 367 543	1.000 205 498 98
	5, 20	12	1.039 323 649	1.001 147 302 41
	5, 21	6	1.043 676 153	0.999 446 361 361
	5, 22	6	1.060 651 019	1.001 323 386 788
	6, 1	3	0.972 848 255	0.999 709 728 514

Moreover, for each cluster we define a $W_{n,\alpha}$ and a corresponding $Y_{n,\alpha}$ by means of the recursion relations

$$W_{1,1}=F_{1,1},$$

$$W_{2,1}=F_{2,1}-2W_{1,1},$$

$$W_{n,\alpha}=F_{n,\alpha}-\sum_{l=1}^{n-1}\sum_{\gamma}C_{n,\alpha}{}^{l,\gamma}W_{l,\gamma}, \qquad (2.4)$$

and

$$Y_{1,1}=Q_{1,1},$$

$$Y_{2,1}=Q_{2,1}/(Q_{1,1})^2,$$

$$\vdots$$

$$Y_{n,\alpha}=\exp[-W_{n,\alpha}/k_BT],$$

$$=Q_{n,\alpha}\prod_{l=1}^{n-1}\prod_{\gamma}(Y_{l,\gamma})^{-C_{n,\alpha}{}^{l,\gamma}}. \qquad (2.5)$$

$C_{n,\alpha}{}^{l,\gamma}$ is the number of subclusters of type (l, γ) in the cluster (n, α). As an example, consider all the distinct clusters of five or fewer particles which are catalogued in Table I. For cluster (5, 14) Eq. (2.4) has the explicit form

$$W_{5,14}=F_{5,14}-5W_{1,1}-5W_{2,1}-W_{3,1}-2W_{3,2} -W_{3,3}-W_{4,2}-W_{4,4}-W_{4,6}. \quad (2.6)$$

For a macroscopic system of N particles, Eqs. (2.4) and (2.5) can be written in the following forms which are identities for F_N and Q_N:

$$F_N=\sum_{n=1}^{N}\sum_{\alpha} Nt(n,\alpha)W_{n,\alpha}, \quad (2.7a)$$

$$Q_N=\prod_{n=1}^{N}\prod_{\alpha}(Y_{n,\alpha})^{Nt(n,\alpha)}. \quad (2.7b)$$

$Nt(n, \alpha)$ is the number of different ways the cluster (n, α) can be formed in the system of N particles.

High-Density Limit

Figure 1 illustrates the regular hexagonal lattice formed by the nominal equilibrium positions for a system of rigid disks under high compression. Let the vectors $\mathbf{R}_1{}^0, \cdots, \mathbf{R}_N{}^0$ locate these lattice sites. If we imagine the crystal to be contained within rigid boundaries, the restriction to high densities implies that disk i is confined to the vicinity of $\mathbf{R}_i{}^0$ $(i=1, \cdots, N)$ (i.e., we consider densities such that particle interchanges are impossible) and only nearest-neighbor pairs can interact. Then let $\mathbf{r}_1, \cdots, \mathbf{r}_N$ denote the respective displacements of the disks from their nominal lattice sites. The distance between nearest-neighbor particles R_{ij} may be formally expanded in powers of these displacements to give

$$R_{ij}=|\mathbf{R}_{ij}{}^0+\mathbf{r}_{ij}|=R^0+(\mathbf{R}_{ij}{}^0/R^0)\cdot\mathbf{r}_{ij}+\cdots, \quad (2.8)$$

where

$$\mathbf{r}_{ij}=\mathbf{r}_j-\mathbf{r}_i$$

and R^0 is the lattice spacing between nearest-neighbor lattice sites.

The canonical partition function Q_N and Helmholtz free energy F_N for a system of rigid disks may be expressed in the form

$$Q_N=\exp[-F_N/k_BT] =\lambda^{-2N}\int d\mathbf{r}_1\cdots\int d\mathbf{r}_N\prod_{i<j}^{(nn)}U(R_{ij}-a), \quad (2.9)$$

where $\lambda=(h^2/2\pi mk_BT)^{1/2}$ is the mean thermal de Broglie wavelength, a is the diameter of a disk and U denotes the unit step function,

$$U(x)=0 \quad (x<0)$$
$$=1 \quad (x\geq 0). \quad (2.10)$$

The product is taken over nearest-neighbor pairs only. In the high-density limit we use the leading two terms in the expansion of R_{ij} [Eq. (2.8)] to obtain

$$U(R_{ij}-a)=U[R^0-a+(\mathbf{R}_{ij}/R^0)\cdot\mathbf{r}_{ij}] =U(1+\mathbf{w}_{ij}\cdot\mathbf{t}_{ij}),$$
$$\mathbf{w}_{ij}=\mathbf{R}_{ij}/R^0,$$
$$\mathbf{t}_i=\mathbf{r}_i/(R^0-a). \quad (2.11)$$

This operation amounts to replacing exclusion circular arcs by tangent lines perpendicular to the respective interlattice vectors, $\mathbf{R}_{ij}$.

III. RESULTS

As shown in Ref. 1, our analysis leads to the following asymptotic form for the Helmholtz free energy per particle:

$$F_N/(Nk_BT)\sim 2\ln(\lambda/a)-2\ln(\theta^{-1}-1)+C+O(\theta^{-1}-1) \quad (3.1)$$

in terms of the reduced density

$$\theta=a^2/(R^0)^2.$$

In this limit we focus our attention on the additive free-energy constant C. Using the expansion given in Eq. (2.7) we find the following expansion for C:

$$C=C_{\mathrm{fv}}-\sum_{n=2}^{N}[\sum_{\alpha}t(n,\alpha)\ln Y_{n,\alpha}].$$
$$C_{\mathrm{fv}}=-\ln(\sqrt{3}/2). \quad (3.2)$$

C_{fv} is the value of C obtained from the one-particle free "volume" model. The terms in Eq. (3.2) have been ordered by the number of cluster particles n. Although we have no way of rigorously discussing the rate of convergence of this series, hopefully a few terms with small n will yield a good estimate of C. As n increases not only does the number of logically distinct cases increase rapidly but each becomes more difficult to calculate. A digital computer program was developed for the Murray Hill IBM 7094 computer to perform the integrations for all the clusters with four or fewer particles, and these results were reported in Ref. 1. In addition several five-particle clusters were analyzed. This program was subsequently modified and recoded for the Rice University Computer and applied to the five-particle clusters.

In the high-density limit the evaluation of the partition functions is purely an algebraic problem, since it can be reduced to the integration of polynomials between planar boundaries. The computer programs use a nonnumerical technique to carry out these integrations analytically. For some of the simpler cases we obtained the exact value for the Y's as a rational fraction. For some of the more complicated cases we obtained values for the Y's in decimal form to ten significant figures and for the sake of minimizing computer

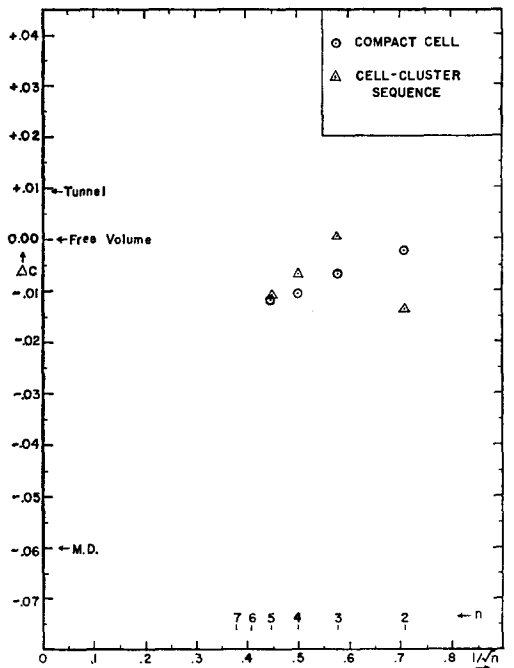

FIG. 3. $\Delta C = C - C_{fv}$ as a function of $1/(n)^{1/2}$, where n is the number of particles in the cluster. The compact cell analysis gives the value of C for that particular cell. The triangular point at n gives the value of C estimated from all cells with n or fewer particles. M.D. denotes the value of ΔC estimated from molecular dynamics calculations. The $n=1$ point corresponds to the fv theory and would be at the coordinates (1, 0) on this figure.

time did not attempt to get the exact rational fraction. The results of all the calculations to date are summarized in Table I (Ref. 5) which gives the values of $K_{n,\alpha}=Q_{n,\alpha}/Q_1^n$ and $Y_{n,\alpha}$ in decimal form.

The final numerical values of the successive terms in the C series (for $n=1, 2, 3, 4, 5$) are found to be

$$C=0.14384-0.013857+0.014322 \\ -0.0073211-0.004222+\cdots \\ =0.14384-0.011078+\cdots. \qquad (3.3)$$

The α summation for each n has already been performed. The results here include the correction to a small error in the calculation of $Q_{4,6}$ reported in Ref. 1.

A detailed examination of Table I reveals that the largest corrections in each order of n come from the correlated motion of n particles in a line and from the most compact cluster. The result of the linear cluster motion increases the free energy while the result of the compact cluster motion decreases the free energy. The contribution to C in Eq. (3.3) for each order of approximation is a subtle weighted average of these opposing contributions.

Compact Clusters

It has been suggested that an alternative and perhaps more meaningful analysis of our results[4] would be to consider only the most compact clusters and extrapolate the free energy for these clusters alone as a function of $1/n^{1/2}$ to obtain an estimate of the free energy for a system of N disks. This is illustrated in Fig. 3 where $\Delta C_n=(1/n)\ln[Q_{n,\text{compact}}/Q_1^n]$ is plotted as a function of $1/(n)^{1/2}$.

For comparison we have marked the values of ΔC_∞ predicted by the tunnel model,[6] our expansion taken to five terms, and the value obtained from extrapolating the molecular dynamics data.[3]

IV. TUNNEL MODEL FOR DISKS AT HIGH COMPRESSION

In Ref. 1 we tested the convergence of the sequential approximation scheme for a strictly one dimensional system. Since the exact high-density value of C in Eq. (3.1) is known for the 2-D tunnel model,[6] we would like to illustrate the behavior of the cell-cluster expansion applied to this model.

The tunnel model is depicted in Fig. 4 where all disks are fixed on their nominal lattice sites except those in one row. Applying the analysis of Sec. 2 to this model one obtains the following relations, since only the linear clusters contribute to the free energy for this model:

$$Y_{2,1}=Q_{2,1}/(Q_{1,1})^2 \\ \vdots \\ Y_{n,1}=Q_{n,1}Q_{n-2,1}/(Q_{n-1,1})^2 \qquad (4.1)$$

and

$$C=-\ln(\sqrt{3}/2)-\sum_{n=2}^{\infty}\ln Y_{n,1}. \qquad (4.2)$$

The results have been calculated explicitly for $n\leq 6$ and the corresponding Y's may be found in Table I.

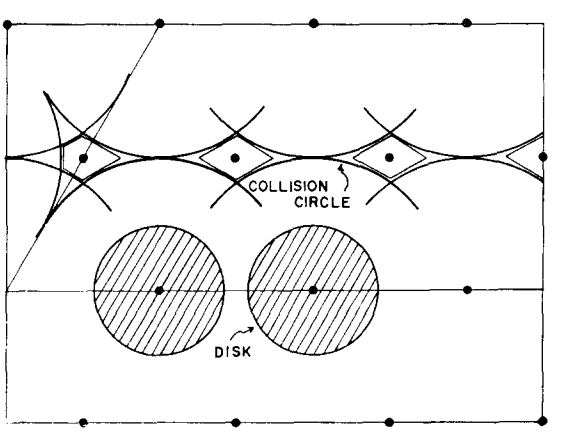

FIG. 4. Free area associated with the tunnel model at high densities. In this model we have taken the fixed-boundary conditions in which a disk is held fixed on a lattice site at each end of the row of movable particles.

[5] Note that the numbering of the five-particle clusters in Table I is slightly different from that given in Ref. 1.

[6] Z. W. Salsburg and W. G. Rudd, J. Chem. Phys. **45**, 1026 (1966).

The expansion for the additive constant C has the following form through 6th order:

$$C=0.14384-0.00462+0.00955+0.00337+0.00100+0.00029+\cdots,$$
$$=0.15343+\cdots; \quad (4.3)$$

the exact result is

$$C=0.15356\cdots. \quad (4.4)$$

This indicates a very rapid convergence. In the strictly one dimensional rigid-rod example[1] it was proven that this series behaved as $1/n^2$. The results in Eq. (4.3) indicate that the series for large n may behave as $\exp(-\gamma n)$ for the tunnel model. In the tunnel model the neighboring rows of fixed particles tend to localize the movable disks near their nominal lattice sites, and this results in the corresponding more rapid convergence of the cell-cluster series.

V. DISCUSSION

The principal question about these calculations is the significance of the low-order results. Although it may never be possible to prove convergence of the very complicated cell-cluster free-energy series, we have proceeded under the tentative assumption that useful results could be derived at least in the sense of asymptotic series. This assumption appears to be challenged by the results obtained from molecular dynamic calculations.[3]

Preliminary estimates from molecular dynamics[3] indicate a value of $\Delta C=C-C_{fv}\cong-0.06\pm0.02$.[7] One must remember that this limiting value is obtained by integrating the molecular dynamics equation of state data from the ideal gas state to the limit of a high density crystal using the thermodynamic relation

$$P=-(\partial A/\partial V)_T, \quad (5.1)$$

where P is the pressure. This involves estimating the position of the rigid disk "phase transition" in the limit $N\to\infty$. Until the details of these calculations are presented it is difficult to estimate the error that might be involved.

On the other hand the fifth-order cell-cluster results give a value of $\Delta C\cong-0.011$. If the remaining terms (sixth and higher) were to contribute -0.05 to ΔC then the behavior of the first five terms would have to be highly misleading, a situation difficult to rationalize. In fact all evidence points to a well behaved sequence of approximations. This comprises not only the one-dimensional rigid-rod analysis[1] and the tunnel-model calculation but also the application of the method to a two dimensional triangular lattice of harmonic oscillators.[8] The trend displayed by the compact clusters (see Fig. 3) also supports the estimates of the cell-cluster expansion. It seems unlikely that the cooperative motion of larger compact clusters will dramatically raise the entropy per particle (i.e., lower the value of C). On the other hand, linear cooperative motion of particles along one row lowers the entropy (i.e., raises the value of C) below that of the free-volume theory. To test these statements we plan to analyze the most compact six and seven particle cell-clusters in the near future.

ACKNOWLEDGMENTS

The authors wish to thank the Robert A. Welch Foundation and the National Science Foundation through GP-6447 for their support of this research. We also wish to thank Dr. Albert Yu for his help in preparing our computer program and the staff of the Rice Computer for their help in running our problem.

[7] The error estimate is obtained from B. J. Alder (private communication).

[8] Z. W. Salsburg and W. G. Rudd, Physica **32**, 1234 (1966).