

## The Closest Packing of Equal Spheres on a Spherical Surface

BY A. L. MACKAY AND J. L. FINNEY

*Department of Crystallography, Birkbeck College, University of London, Malet Street, London WC1E7HX, England*

AND K. GOTOH

*Department of Chemical Process Engineering, University of Hokkaido, Sapporo, Japan*

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A table is given of putative solutions to the Fejes problem: to find the maximum value of the smallest angular distance between any two of  $N$  points movable on the surface of a sphere. Values of  $N$  run without omission up to 27 with six sporadic cases thereafter. Some applications of this system as a model are discussed.

The question of the arrangements of  $N$  equal spheres on a spherical surface is of relevance to the theory of coordination polyhedra. We will examine here only the Fejes problem (Fejes Toth, 1952), which is to find the maximum value  $\delta$  of the smallest angular distance between any two of  $N$  points movable on the surface of a sphere. This purely geometrical ('hard-sphere') problem is basic to the further considerations of the Thomson problem (where the points repel each other according to the inverse square law) and others involving energetic considerations.

The Fejes problem has been reviewed by Whyte (1952) and by Coxeter (1962) but the improvement in computing facilities, particularly the advent of the pocket calculator with stored program, has made further results available.

The Fejes problem as formulated above is equivalent to finding the densest packing of  $N$  hard spheres of unit radius on the surface of a sphere of radius  $R$  where  $R = \csc(\delta/2) - 1$ . Of interest also is the fraction  $p$  of the surface of the sphere included within circles of radius  $(\delta/2)$  on its surface. This superficial packing fraction is  $p = (N/2) [1 - \cos(\delta/2)]$ . For a sphere of infinite radius (hexagonal close-packing)  $p = \pi/(2\sqrt{3}) = 0.90690$ .

The close packing of equal spheres on a cylindrical surface (Erickson, 1973) is essentially regular and is readily systematized, but packing on a spherical surface (or on ellipsoidal or hyperbolic surfaces) is much less tractable. Packing on, for example, ellipsoidal surfaces arises in considering the arrangement of coat protein molecules on the surfaces of bacteria (Nabarro & Harris, 1971). Since, on a convex surface a ring of six circles in contact would leave a central circle free to 'rattle', the regular hexagonal close packing of circles (the obvious solution for  $N = \infty$ ) is excluded. Even though  $N$  may be large, and the surface packing approximately close-packed, there must be twelve dislocations (or their equivalents) where five, and not six, triangles meet at a point. Suppose that there are  $V_5$  such vertices and  $V_6$  vertices where six triangles

meet, then from the Euler relation  $F + V = E + 2$ , since all faces are triangular and two faces share an edge,  $E = \frac{3}{2}F$ .  $V = V_5 + V_6$  and  $F = (5V_5 + 6V_6)/3$  so that we obtain  $V_5 = 12$ . Physically, it is only necessary to postulate that these twelve dislocations are as far from each other as possible and the icosahedral tessellations result.

We include a table (Table 1) of what we, at present, believe to be the closest packings found. Some of the configurations have been collected from the literature (Habicht & Van der Waerden, 1951; Schütte & Van der Waerden, 1951; Whyte, 1952; Coxeter, 1962; Goldberg, 1965; Pirl, 1969), while the new values have been calculated using iterative procedures on a pocket calculator, and a simple building program on a digital computer. The problem of actually proving that a particular configuration is an absolute maximum of  $\delta$  is difficult, although it has been achieved in a few cases. We take the empirical view of accepting the values listed as maxima until they are bettered. It is unlikely that more efficient packings exist close to the given configurations, but we cannot say whether these are accessible through cooperative movements of the spheres. Our system is thus a simplified case of the energy-minimization problem (*e.g.*, protein folding, nucleation) with a small number of variables, and could be used as a test model for techniques designed to overcome the problems of false minima, and the location of, and passage over, saddle points.

For example, in each case in Table 1, every circle is fixed in position by three or more contacts, not all in the same semi-circle. No single circle may move but the condition for recognizing a maximum density packing is not obvious. In the cuboctahedral coordination ( $N = 12$  and  $\delta = 60^\circ$ ) each circle is restrained by four contacts from moving but, in fact, by a cooperative movement involving all twelve circles, the centres can move until they are  $63.4^\circ$  apart, when they each then make five contacts (Mackay, 1962). We are really dealing with paths in  $(2N - 3)$  dimensional configuration space and more elaborate methods are necessary

for distinguishing maxima, minima, and saddle points. Finding the normal vibration spectrum (Hoare & Pal, 1972) will give information only on the local volume in configuration space in the neighbourhood of a given geometrical arrangement. Full molecular dynamic or Monte Carlo procedures are, as in three-dimensional space, in danger of 'locking in' to a false minimum, and require some 'softening' of the hard sphere as a temporary measure. For example, the sphere size could be temporarily reduced during the configurational space exploration to mimic thermalization procedures [such as used by Levitt & Warschel (1975) in simulating the folding of pancreatic trypsin inhibitor]. Such procedures, however, cannot guarantee the finding of the ultimate minimum.

Thus it is not surprising that, for a given value of  $N$ , there may be several stable configurations with very similar packing densities but different geometry. For example, Goldberg (1965) has examined three configurations for  $N=18$ ; namely (3,3,6,3,3) with  $\delta=47^\circ 26'$ , (1,3,3,6,4,1) with  $\delta=48^\circ 38'$ , and (1,4,4,4,4,1) with  $\delta=49^\circ 33'$ . Each of these configurations appears 'locked' and in order to pass from one packing of circles to another, the circles would have to be shrunk before they could be moved. Such configurations,

mutually inaccessible unless the circles are 'softened' or reduced in size, are relevant to the nucleation of crystals from the melt, and to the local structure of amorphous solids. In nucleation a local cluster may well be locked into a local maximum of packing density (minimum energy), but cannot crystallize as the best local arrangement is inaccessible without temporary density reductions. It has been previously suggested (Finney, 1975*a,b*; 1976; Barker, Hoare & Finney, 1975) that several different, essentially non-crystalline amorphous structures may exist, depending upon the precise nature of the intermolecular potential function, the conditions of preparation (*e.g.* rapid cooling from the melt or vapour deposition), and the nature of the boundary conditions (*e.g.* thin film or bulk materials). These geometrically dense clusters of similar density but different geometry illustrate in a simple way the possibility of such mutually inaccessible amorphous structures, and suggest what their local geometries might be.

One characteristic which emerges from the table is that all the configurations are highly symmetrical, having at least one pronounced axis of three-, four- or fivefold symmetry. Föppl's (1912) notation, which shows the numbers of equivalent circles at the same

Table 1. *The closest packings on a spherical surface*

$N$	$\delta$ degrees	$(N/2)$ [1 - cos ( $\delta/2$ )] Packing fraction	Type of packing Föppl notation	Point group	Notes
2	180	1.00000	(1,1)	$\infty/mm$	
3	120	0.75000	(3)	$\bar{6}m2$	
4	109.47122	0.84530	(1,3) or (2,2)	$\bar{4}3m$	arc cos ( $-\frac{1}{3}$ ); tetrahedral
5	90	0.73223	(1,4)	$4mm$	octahedral less one
6	90	0.87868	(1,4,1) or (3,3)	$m3m$	octahedral
7	77.86954	0.77748	(1,3,3)	$3mm$	arc cos ( $\frac{1}{2} \cot^2 40^\circ - \frac{1}{2}$ )
8	74.85849	0.82358	(4,4)	$\bar{8}2m$	arc cos [ $(\sqrt{8}-1)/7$ ]; square antiprism
9	70.52878	0.82577	(3,3,3)	$\bar{6}m2$	arc cos ( $\frac{1}{3}$ )
10	66.14682	0.81014	(2,4,4)	$mm2$	$16r^6 - 44r^4 + 34r^2 - 7 = 0$ where $r = 1/[2 \sin(\delta/2)]$
11	63.43495	0.82142	(1,5,5)	$5m$	arc tan (2); icosahedral less one
12	63.43495	0.89609	(1,5,5,1) or (3,3,3,3)	$5m3$	arc tan (2); icosahedral
13	57.13670	0.79139	(1,4,4,4)	$4mm$	
14	55.67057	0.80994	(1,4,2,2,4,1)	$\bar{4}2m$	b.c.c. distorted to $\bar{4}2m$
15	53.66	0.80738	(3,3,3,3,3)	3	estimated by van der Waerden
	> 53.61202	> 0.80596		32	calc. for more symmetrical arrangement at saddle point
16	52.24439	0.81714	(4,4,4,4)	$\bar{8}2m$	
17	51.02655	0.82887	(1,5,5,5,1)	$5/mm$	Goldberg (1965)
18	49.55159	0.82841	(1,4,4,4,4,1)	$\bar{8}2m$	Goldberg (1965)
19	> 47.42	> 0.80187	(1,3,3,6,3,3)	$3m$	Goldberg (1965)
20	47.41439	0.84388	(1,3,3,6,3,3,1)	$\bar{6}m2$	Goldberg (1965)
21	44.95599	0.79772	(1,5,5,5,5)	$5m$	
22	44.40313	0.81554	(1,5,5,5,5,1)	52	
23	43.69077	0.82580		1	Snub cube less one
24	43.69077	0.86174	(4,4,4,4,4,4)	432	Snub cube
25	41.39306	0.80668	(5,5,5,5,5)	$5/mm$	
26	41.03024	0.82446	(1,5,5,5,5,5)	$5m$	
27	40.67758	0.84167	(1,5,5,5,5,5,1)	$5/mm$	
32	37.37737	0.84362		$5m3$	T = 3 tessellation of icosahedron
33	35.42	0.78196	(3,3,(6),(9),(6),3,3)	$\bar{6}m2$	Goldberg (1963)
42	31.71747	0.79929		$5m3$	T = 4 tessellation of icosahedron; arc tan (1/ $\tau$ )
60	26.82127	0.81801		532	T = 7 less 12 points
72	24.83976	0.84248		532	T = 7 icosah.
92	21.35652	0.79657		532	T = 9 rotated
122	18.71254	0.81151		532	T = 12 rotated
$\infty$	—	0.90690		—	$\pi/(2\sqrt{3})$ ; h.c.p.

latitude in successive rings from the  $N$  pole to the  $S$  pole, is thus the most concise description. There not being strict proofs of the absoluteness of the maxima encountered, there remains, in many cases, the doubt as to whether some solutions of low symmetry may not be better. Clearly the most symmetrical figures are the most easily calculated and are unduly preferred.

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## The Use of Structural Information in the Phase Probability of a Triple Product

By J. J. L. HEINERMAN

*Laboratorium voor Structuurchemie, Rijksuniversiteit, Padualaan 8, Utrecht, The Netherlands*

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A derivation is given of the probability distribution of the phase of a triple product  $\varphi = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3}$  with  $\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = \mathbf{0}$ , employing *a priori* structural information. This derivation is valid if normalized group scattering factors are small and certain conditions for  $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$  are fulfilled. To derive this distribution it is necessary to regard the atomic position vectors as primitive random variables, not all independent in view of the structural information. It is also shown that if no structural information is available the expression for the probability distribution of the phase of a triple product, where the atomic position vectors are regarded as the primitive random variables, is identical to the one where  $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$  are regarded as the primitive random variables. In the first case certain conditions for  $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$  must be fulfilled; in the second the atomic position vectors are subject to certain conditions.

### Introduction

Recently Main (1975) has generalized Cochran's (1955) formula for the phase probability of a triple product. In Main's formula *a priori* knowledge about the structure can be used. The kinds of information which he has considered are (a) randomly positioned atoms, (b) randomly positioned and randomly oriented atomic groups, (c) randomly positioned but correctly oriented atomic groups, (d) correctly positioned atoms.

A rigorous mathematical derivation of Main's formula, which also shows its limitations, will be given for space group  $P1$ .

### The primitive random variables

In this section we define the normalized structure factor for equal-atom structures by

$$E_{\mathbf{h}} = \frac{1}{N^{1/2}} \sum_{j=1}^N \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j), \quad (1)$$

where  $N$  is the number of atoms in the unit cell and  $\mathbf{r}_j$  is the position vector of atom  $j$ . In deriving joint probability distributions of structure factors defined

by (1), two methods can be followed. The first is to regard the structure as fixed, although unknown, and one or more reciprocal lattice vectors as the primitive random variables. The second is to regard the atomic position vectors as the primitive random variables and the reciprocal lattice vectors as fixed.

Let  $\varphi_{\mathbf{h}}$  denote the phase of  $E_{\mathbf{h}}$  and let  $P(\Phi|R_1, R_2, R_3)$  denote the conditional probability distribution of  $\varphi = \varphi_{\mathbf{h}_1} + \varphi_{\mathbf{h}_2} + \varphi_{\mathbf{h}_3}$  with  $\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = \mathbf{0}$ , given  $|E_{\mathbf{h}_1}|, |E_{\mathbf{h}_2}|$  and  $|E_{\mathbf{h}_3}|$  (equal to  $R_1, R_2$  and  $R_3$  respectively). Then  $P(\Phi|R_1, R_2, R_3)d\Phi$  is the probability that  $\varphi$  lies between  $\Phi$  and  $\Phi + d\Phi$ , given  $|E_{\mathbf{h}_1}|, |E_{\mathbf{h}_2}|$  and  $|E_{\mathbf{h}_3}|$ . If the reciprocal lattice vectors  $\mathbf{h}_1, \mathbf{h}_2$  and  $\mathbf{h}_3$  are the primitive random variables,  $P(\Phi|R_1, R_2, R_3)d\Phi$  is equal to the fraction of the triple products  $E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}$  of a fixed structure and with fixed values for  $|E_{\mathbf{h}_1}|, |E_{\mathbf{h}_2}|$  and  $|E_{\mathbf{h}_3}|$ , for which  $\Phi < \varphi < \Phi + d\Phi$ . If the atomic position vectors  $\mathbf{r}_j$  are the primitive random variables,  $P(\Phi|R_1, R_2, R_3)d\Phi$  is equal to the fraction of the triple products  $E_{\mathbf{h}_1}E_{\mathbf{h}_2}E_{\mathbf{h}_3}$ , with  $\mathbf{h}_1, \mathbf{h}_2, \mathbf{h}_3$  fixed, of all structures with  $N$  atoms in the unit cell and with fixed values for  $|E_{\mathbf{h}_1}|, |E_{\mathbf{h}_2}|$  and  $|E_{\mathbf{h}_3}|$ , for which  $\Phi < \varphi < \Phi + d\Phi$ .

It has been found that with  $\mathbf{h}_1, \mathbf{h}_2$  and  $\mathbf{h}_3$  as the primitive random variables the only information