Acta Cryst. (1980). A**36**, 194–197

The Fragile Lattice Packings of Spheres in Three-Dimensional Space

BY K. L. FIELDS

Department of Mathematics, Rider College, Lawrenceville, NJ 08648, *USA*

(*Received* 14 *May* 1979; *accepted* 24 *August* 1979)

Abstract

The close-packed-sphere model is often used to explain the frequent occurrence of face-centered cubic lattice structures. Recently, it has been found that in body-centered cubic and body-centered tetragonal lattices the volume of the interstitial void is maximized. In this paper all of the three-dimensional lattice packings of spheres with this property are determined: there are, in addition to the two just mentioned, only the simple cubic and simple hexagonal lattices. A quantitative measure of the relative instability of these packings is also given.

Introduction

A *lattice in* $\mathbf{R}^n$ is a set of points of the form $m_1\boldsymbol{\alpha}_1 + \ldots + m_n\boldsymbol{\alpha}_n$, where $m_1, \ldots, m_n$ run over the integers and $\boldsymbol{\alpha}_1, \ldots, \boldsymbol{\alpha}_n$ is a fixed set of n vectors which span $\mathbf{R}^n$; we say that the lattice is *generated* by $\boldsymbol{\alpha}_1, \ldots, \boldsymbol{\alpha}_n$. If we place the centers of hard spheres with equal radii at each lattice point, we have a *lattice packing of spheres*. The spheres cannot overlap, so our lattice limits their common radius in some fashion; but we always choose spheres of maximum possible radius, so that each sphere touches its 'nearest neighbors'. We are interested in the *density* of such a packing: if we take a large but finite portion of space, we are interested in the fraction of the volume which is occupied by the spheres.

If $\boldsymbol{\alpha}_1, \ldots, \boldsymbol{\alpha}_n$ generate the lattice L, let G be the $(n \times n)$ matrix whose jth column is $\boldsymbol{\alpha}_j$. Then any lattice point equals $G\mathbf{m}$ for some column matrix $\mathbf{m}$ with integer entries. So, if A is an $(n \times n)$ matrix with integer entries and determinant ± 1, then the columns of GA also generate L. If $\mathbf{O}$ is an orthogonal transformation (*i.e.* a product of rotations and reflections), then $\mathbf{O}\boldsymbol{\alpha}_1, \ldots, \mathbf{O}\boldsymbol{\alpha}_n$ generate a lattice L' obtained by rotating and reflecting the points of L; both L and L' clearly determine lattice packings of spheres of equal density.

The *quadratic form of the lattice* L is $\sum b_{ij}x_ix_j$, where $B = (b_{ij})$ is the positive definite symmetric matrix G^tG. Conversely, if $XPX^t = \sum p_{ij}x_ix_j$ is a positive definite quadratic form, then we can write $P = H^tH$ for some $(n \times n)$ matrix H; hence XPX^t is the quadratic form of the lattice $\mathscr{L}$ generated by the columns of H. $\mathscr{L}$ is not unique: any lattice which is an orthogonal transformation of $\mathscr{L}$ has the same quadratic form (since $H^t\mathbf{O}^t\mathbf{O}H = H^tH$).

Example. The body-centered cubic lattice is generated by (2,0,0), (0,2,0), (1,1,1); its quadratic form is therefore

$$(X_1\,X_2\,X_3)\begin{pmatrix}2 & 0 & 0\\ 0 & 2 & 0\\ 1 & 1 & 1\end{pmatrix}\begin{pmatrix}2 & 0 & 1\\ 0 & 2 & 1\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}X_1\\ X_2\\ X_3\end{pmatrix}$$
$$= 4X_1^2 + 4X_2^2 + 3X_3^2 + 4X_1X_3 + 4X_2X_3.$$

Observe that since the columns of G and GA (A integral, $\det A = \pm 1$) both generate the same lattice L, both XBX^t ($=XG^tGX^t$) and XA^tBAX^t ($=XA^tG^tGAX^t$) are quadratic forms of L. Two such quadratic forms are called 'integrally equivalent'. Finally, if $\boldsymbol{\alpha}_1, \ldots, \boldsymbol{\alpha}_n$ generate L then, for any non-zero c, $c\boldsymbol{\alpha}_1, \ldots, c\boldsymbol{\alpha}_n$ generate a lattice cL whose points are of the form $c\boldsymbol{\beta}$ where $\boldsymbol{\beta}$ is a point of L. The lattice packing determined by cL has the same density as that determined by L; the quadratic form of cL is c^2B.

Summary

If we do not distinguish between lattices which are either orthogonal transforms or scalar multiples of each other, and if we do not distinguish between positive-definite quadratic forms which are integrally equivalent or are scalar multiples of each other, then to every lattice there corresponds a quadratic form, and *vice versa*. Generally speaking, it is easier to talk about quadratic forms than about lattices.

A *minimum vector* of the quadratic form XBX^t is a vector $\mathbf{m} = (m_1, \ldots, m_n)$ with integer coordinates such that $\mathbf{m}B\mathbf{m}^t \le \boldsymbol{\gamma}B\boldsymbol{\gamma}^t$ for any non-zero integral vector $\boldsymbol{\gamma}$. If $B = G^tG$ determines the lattice L generated by $\boldsymbol{\alpha}_1, \ldots, \boldsymbol{\alpha}_n$, then this means that a sphere placed at the point $m_1\boldsymbol{\alpha}_1 + \ldots + m_n\boldsymbol{\alpha}_n$ is a nearest neighbor of the sphere at the origin; the length of this vector, $(\mathbf{m}B\mathbf{m}^t)^{1/2}$, is twice the radius of the packed spheres. Let us now slightly alter the coefficients of B to $B + (\varepsilon_{ij}) = B_1$, where $\varepsilon_{ij} = \varepsilon_{ji}$. Suppose that B and B_1 have the same minimum value $\mathbf{m}B\mathbf{m}^t$ and minimum vectors $\mathbf{m} = \mathbf{m}_1, \ldots, \mathbf{m}_r$. Then the lattice packing determined by B_1 admits the same sized spheres, with each sphere

0567-7394/80/020194-04$01.00

touching the same neighbors, as in the lattice packing determined by B. Clearly, these conditions hold if and only if $\mathbf{m}_\lambda(\varepsilon_{ij})\,\mathbf{m}_\lambda^t = 0$ for $\lambda = 1, \ldots, r$.

If any small change in the coefficients of the quadratic form B yields a form B_1 whose lattice provides a less dense packing of spheres, then we call the lattice L (and its quadratic form B) *stable*. In three dimensions there is only one stable form: it corresponds to the face-centered cubic lattice. It is a classical result that if B is stable, then there are enough minimum vectors $\mathbf{m}_1, \ldots, \mathbf{m}_r$ to ensure that if $\mathbf{m}_\lambda(\varepsilon_{ij})\,\mathbf{m}_\lambda^t = 0$ for $\lambda = 1, \ldots, r$, then $(\varepsilon_{ij}) = 0$. Such quadratic forms are called *perfect*. Linear algebra tells us that $r \geq n(n+1)/2$. In a stable packing, therefore, each sphere is surrounded by at least $n(n+1)/2$ pairs of nearest neighbors; moreover, a stable packing really is 'stable' – one cannot perturb the spheres of such a lattice packing in any direction without breaking bonds.

In 1908 Voronoi established an algebraic characterization of stable quadratic forms: B is stable if and only if B is perfect and $B^{-1} = \sum \rho_i \mathbf{m}_i^t \mathbf{m}_i$ for some positive numbers ρ_i. The quadratic forms $X\mathbf{m}_i^t\mathbf{m}_i X^t$, $i = 1, \ldots, r$ are called the *minimum forms* of B. A clear account of this theorem (and all of the above) can be found in Lekkerkerker (1969).

A *fragile* lattice packing of spheres is one which locally *minimizes* the density of the volume of the packed spheres: any perturbation of the lattice which does not alter the distance (or 'break any bonds') between a sphere and its nearest neighbors results in a denser configuration (Fields, 1979*a*). Alternatively, these packings locally *maximize* the volume of the 'interstitial void' between the spheres.

Examples of such packings are provided by

(A) the *simple cubic* lattice with quadratic form

$$x^2 + y^2 + z^2;$$

(B) the *body-centered cubic* lattice with quadratic form

$$4x^2 + 4y^2 + 3z^2 + 4xz + 4yz;$$

(C) the *hexagonal* (or 'trigonal prismatic') lattice with quadratic form

$$x^2 + y^2 + z^2 + xy;$$

(D) the *body-centered tetragonal* lattice with quadratic form

$$2x^2 + 2y^2 + 2z^2 + xy + 2xz + 2yz.$$

We will show here that *these are the only fragile lattices in* $\mathbf{R}^3$. The two main ingredients of our proof will be (1) the algebraic characterization of fragile forms as those which are *not* perfect and whose adjoints are linear combinations of minimum forms (Fields, 1979*a*); and (2) the result of Korkine & Zolotareff (1877) that *any three linearly independent minimum vectors of a positive-definite quadratic form in three variables must generate the entire integer lattice.*

The number of degrees of freedom in a lattice packing

Let L be a lattice with quadratic form B whose minimum vectors are $\mathbf{m}_1, \ldots, \mathbf{m}_r$. The dimension of the subspace of symmetric matrices X which are solutions of the system of linear equations $\mathbf{m}_i(B + X)\,\mathbf{m}_i^t = \mathbf{m}_i B \mathbf{m}_i^t$, $i = 1, \ldots, r$, can be interpreted as the number of directions in which the coefficients of B can be perturbed while still preserving its minimum vectors. In $\mathbf{R}^3$, if B determines a lattice containing three independent vectors which are nearest neighbors of the origin then this dimension [written $\mathrm{df}(B)$] is either 0, 1, 2 or 3; it is a relative measure of the instability of the corresponding lattice packing, and we may intuitively regard it as the number of degrees of freedom of the spheres in the packing. If, for example, B is stable (so that L is face-centered cubic), then $\mathrm{df}(B) = 0$; more generally, if B is any stable form in $\mathbf{R}^n$ then $\mathrm{df}(B) = 0$ (*cf.* above). This dimension can be computed easily for any lattice or quadratic form. For *fragile* forms we have the following.

Proposition. If B is a fragile form in n variables, then

(1) the set of minimum vectors of B contains n linearly independent minimum vectors;

(2) $n(n-1)/2 \geq \mathrm{df}(B) \geq 1$.

Proof. Some linear combination of the minimum forms $\mathbf{m}_i^t\mathbf{m}_i$ is positive definite (Fields, 1979*a*); this implies (1). For (2), let E_i be the $n \times n$ matrix whose (i,i) entry is 1 and is zero elsewhere; and write $A * B = \sum_{i,j} a_{ij} b_{ij}$ for matrices $A = (a_{ij})$, $B = (b_{ij})$. For each $i = 1, \ldots, n$ there is some minimum vector $\mathbf{m}_k$ such that $\mathbf{m}_k^t\,\mathbf{m}_k * E_i \neq 0$; hence the solution space of $\mathbf{m}_k^t\,\mathbf{m}_k * X = 0$ (where $X = X^t$), $k = 1, \ldots, r$, has dimension at most $n(n+1)/2 - n = n(n-1)/2$. But $\mathbf{m}_k^t\,\mathbf{m}_k * X = \mathbf{m}_k X \mathbf{m}_k^t$.

In particular, a fragile form in three variables can have at most three degrees of freedom. Of the four fragile forms listed, the simple cubic has three degrees of freedom, the body-centered cubic and hexagonal forms have two degrees, and the body-centered tetragonal form has one degree of freedom.

From *Proposition* (1) and the result of Korkine & Zolotareff (1877) mentioned above, it follows that any fragile form in three variables is integrally equivalent to one for which $\mathbf{e}_1 = (1,0,0)$, $-\mathbf{e}_1$, $\mathbf{e}_2 = (0,1,0)$, $-\mathbf{e}_2$, $\mathbf{e}_3 = (0,0,1)$, $-\mathbf{e}_3$ are minimum vectors. Moreover, any other minimum vector of such a fragile form must be one of the twenty vectors $(\pm1,\pm1,0)$, $(\pm1,\pm1,\pm1)$, $(0,\pm1,\pm1)$, $(\pm1,0,\pm1)$. The minimum forms associated with $\pm\mathbf{e}_1$, $\pm\mathbf{e}_2$, $\pm\mathbf{e}_3$ are E_1, E_2, E_3 ($E_i = \mathbf{e}_i^t\mathbf{e}_i$). The minimum forms associated with the remaining ten pairs of vectors are

$$M_1 = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad M_2 = \begin{pmatrix} 1 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$M_3 = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}, \textit{etc.}$$

In what follows,

$$B = \begin{pmatrix} a & b & c \\ b & a_1 & d \\ c & d & a_2 \end{pmatrix}$$

is assumed fragile, with $\mathbf{e}_1$, $\mathbf{e}_2$, $\mathbf{e}_3$ among its minimum vectors (so that $a = a_1 = a_2$).

Lemma 1. If $\operatorname{df}(B) = 3$ then B is a multiple of

$$x^2 + y^2 + z^2.$$

Proof. B has only $\pm\mathbf{e}_1$, $\pm\mathbf{e}_2$, $\pm\mathbf{e}_3$ as minimum vectors; hence B^{-1} must be of the form

$$pE_1 + qE_2 + rE_3 = \begin{pmatrix} p & 0 & 0 \\ 0 & q & 0 \\ 0 & 0 & r \end{pmatrix},$$

and so $B = (B^{-1})^{-1}$ must also be of this form. The parenthetic remark above now implies our conclusion.

Lemma 2. If $\operatorname{df}(B) = 2$ then B is equivalent to a multiple of

$$4x^2 + 4y^2 + 3z^2 + 4xz + 4yz$$

or

$$x^2 + y^2 + z^2 + xy.$$

Proof. B must have another pair of minimum vectors $\pm\mathbf{m}$ in addition to $\pm\mathbf{e}_1$, $\pm\mathbf{e}_2$, $\pm\mathbf{e}_3$ such that $\{E_1, E_2, E_3, \mathbf{m}^t\,\mathbf{m}\}$ is a basis of the space spanned by the minimum forms of B. Moreover, by using the transformations

$$T_j(\mathbf{e}_i) = \begin{cases} \mathbf{e}_i & i \neq j \\ -\mathbf{e}_i & i = j \end{cases}, \quad j = 1, 2, 3,$$

we can transform B so that the non-zero entries of $\mathbf{m}$ are all $+1$. Hence there are in effect only two cases to consider:

Case I: $\mathbf{m} = (1,1,0)$; then B^{-1} is a linear combination of E_1, E_2, E_3, and M_1 so that

$$B^{-1} = \begin{pmatrix} \alpha & \delta & 0 \\ \delta & \beta & 0 \\ 0 & 0 & \gamma \end{pmatrix}.$$

Hence, B is also decomposable and so must be equivalent to the hexagonal form.

Case II: $\mathbf{m} = (1,1,1)$; then

$$(1,1,1)\begin{pmatrix} a & b & c \\ b & a & d \\ c & d & a \end{pmatrix}\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} = a,$$

so $a + b + c + d = 0$. Moreover, B^{-1} is a linear combination of E_1, E_2, E_3 and M_3 so that

$$B^{-1} = \begin{pmatrix} \alpha & \delta & \delta \\ \delta & \beta & \delta \\ \delta & \delta & \gamma \end{pmatrix}.$$

Therefore, $\alpha\beta - \delta^2 = \alpha\gamma - \delta^2 = \beta\gamma - \delta^2$ and so $\alpha = \beta = \gamma$.

If we now compute the (i, j) cofactors of B^{-1}, we see that $b = c = d$, and therefore $b = c = d = -a/3$. But now

$$\begin{pmatrix} 3 & -1 & -1 \\ -1 & 3 & -1 \\ -1 & -1 & 3 \end{pmatrix}$$

is equivalent to the body-centered cubic form.

Lemma 2 is proved.

Lemma 3. If $\operatorname{df}(B) = 1$ then B is equivalent to a multiple of

$$2x^2 + 2y^2 + 2z^2 + xy + 2xz + 2yz.$$

Proof. B must have two other pairs of minimum vectors $\pm\mathbf{m}_1$ and $\pm\mathbf{m}_2$ in addition to $\pm\mathbf{e}_1$, $\pm\mathbf{e}_2$, $\pm\mathbf{e}_3$ such that $\{E_1, E_2, E_3, \mathbf{m}_1^t\,\mathbf{m}_1, \mathbf{m}_2^t\,\mathbf{m}_2\}$ is a basis of the space spanned by the minimum forms of B.

Case I: $\mathbf{m}_1 = (1,1,0)$, $\mathbf{m}_2 = (1,0,1)$. As above, we have

$$\begin{aligned} 2a + 2b &= a, \\ 2a + 2c &= a, \end{aligned} \tag{1}$$

so that $b = -a/2$ and $c = -a/2$. Moreover,

$$B^{-1} = \begin{pmatrix} \alpha & \delta & \eta \\ \delta & \beta & 0 \\ \eta & 0 & \gamma \end{pmatrix}.$$

Therefore, $ad - bc = 0$ and $d = a/4$ by (1). But now

$$\begin{pmatrix} 4 & -2 & -2 \\ -2 & 4 & 1 \\ -2 & 1 & 4 \end{pmatrix}$$

is equivalent to the body-centered tetragonal quadratic form.

Case II: $\mathbf{m}_1 = (1,1,1)$, $\mathbf{m}_2 = (1,1,-1)$; then,

$$\begin{aligned} a + b + c + d &= 0, \\ a + b - c - d &= 0, \end{aligned}$$

so that $a = -b$ and $c = -d$. But now

$$\begin{pmatrix} a & -a & -d \\ -a & a & d \\ -d & d & a \end{pmatrix}$$

is not positive definite, so this case cannot arise.

Case III: $\mathbf{m}_1 = (1,1,1)$, $\mathbf{m}_2 = (1,1,0)$; then

$$a + b + c + d = 0, \tag{1}$$

$$b = -a/2 \tag{2}$$

and

$$B^{-1} = \begin{pmatrix} \alpha & \delta & \eta \\ \delta & \beta & \eta \\ \eta & \eta & \gamma \end{pmatrix},$$

so that

$$bd - ac = -ad + bc. \tag{3}$$

Equations (1) and (3) imply that $c = d = -a/4$. But again

$$\begin{pmatrix} 4 & -2 & -1 \\ -2 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix}$$

is equivalent to the body-centered tetragonal quadratic form.

Case IV; $\mathbf{m}_1 = (1,-1,1)$, $\mathbf{m}_2 = (1,1,0)$. As above,

$$a - b + c - d = 0,$$

$$b = -a/2,$$

$$c = -d = -3a/4.$$

But

$$\begin{pmatrix} 4 & -2 & -3 \\ -2 & 4 & 3 \\ -3 & 3 & 4 \end{pmatrix}$$

has minimum value 2 so that $\mathbf{m}_1$ and $\mathbf{m}_2$ *are not minimum vectors*; *i.e.* this case cannot arise.

In all remaining cases, either there is *no* fragile form having $\mathbf{m}_1$ and $\mathbf{m}_2$ as minimum vectors or else the form is body-centered tetragonal; the details are exactly similar to the above cases.

Lemma 3 and our classification is complete.

Post script

Our attention has been directed to Patterson (1941) and Patterson & Kasper (1959). In the latter the packing properties of the one stable and four fragile lattices are summarized. In the former, Patterson essentially considers the quadratic forms

$$\begin{pmatrix} 1 & g_1 & g_2 \\ g_1 & 1 & g_3 \\ g_2 & g_3 & 1 \end{pmatrix}$$

and, using geometric arguments, derives conditions on g_1, g_2, g_3 for there to be 3, 4, 5 or 6 pairs of minimum vectors. The associated lattices are called 'lattice close packings'. Patterson then derives conditions on g_1, g_2, g_3 to distinguish between the various possible space groups. He finds there are 15 'essentially different' lattice close packings (Patterson, 1941, Table III and Fig. 5). Patterson then concludes that the four fragile lattices (*cf.* above) provide locally minimally dense packings.

Our results may be viewed as providing *proof* of Patterson's geometric findings; they also establish that there are *no other* locally minimally-dense lattice packings. In particular, the remaining ten 'essentially different' close packings are neither stable nor fragile: in each case it is possible either to increase or to decrease the packing density without breaking any bonds by perturbing the set of generating vectors in two different ways.

Some physics

If one accepts the model of a weakly bonded monatomic metallic solid as being a lattice of positive ions in an electron sea, then one would expect such a lattice to be minimally dense (*i.e. fragile*). The simple cubic lattice would be ruled out since it is geometrically unstable, having three degrees of freedom: the three pairs of nearest neighbors of any ion can be perturbed independently. Of the three remaining fragile lattices, the body-centered cubic is singled out by the fact that its Epstein zeta function $\sum |r|^{-2s}$ is *locally minimal* (Fields, 1979*b*). In other words, repulsive energy is minimized with respect to perturbations which preserve the bonding in a body-centered cubic metallic lattice; we would therefore expect this structure to prevail among weakly bonded metals.

Our considerations cannot easily be applied to ionic solids because here the potential energy is determined by a series which is not absolutely convergent (the Madelung constant). We point out, however, that if the (two) ions have approximately equal size and polarizability, then the polarization energy of the crystal lattice is proportional to $\sum |r|^{-4}$; hence polarization energy is locally minimized in simple cubic and body-centered cubic lattices (Fields, 1979*b*).

References

FIELDS, K. L. (1979*a*). *Mathematika*. In the press.

FIELDS, K. L. (1979*b*). Submitted.

KORKINE, A. & ZOLOTAREFF, G. (1877). *Math. Ann.* **11**, 242–292.

LEKKERKERKER, C. (1969). *Geometry of Numbers*. Amsterdam: North-Holland.

PATTERSON, A. (1941). *Rev. Sci. Instrum.* **12**, 206–211.

PATTERSON, A. & KASPER, J. (1959). *International Tables for X-ray Crystallography*, Vol. II, pp. 342–354. Birmingham: Kynoch Press.