Statistical geometry of particle packings. I. Algorithm for exact determination of connectivity, volume, and surface areas of void space in monodisperse and polydisperse sphere packings

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Packings of spheres serve as useful models of the geometry of many physical systems; in particular, the description of the *void* region in such packings (the region not occupied by the spheres) is crucial in many studies. The void region is, in general, composed of disconnected *cavities*. We present an algorithm for decomposing void space into cavities and determining the exact volumes and surface areas of such cavities in three-dimensional packings of monodisperse and polydisperse spheres. [S1063-651X(97)10711-5]

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I. INTRODUCTION

Geometry plays an important role in determining the physical properties of many systems composed of large numbers of particles. In continuum systems, the study of geometry in a large number of cases involves the analysis of configurations of spheres, which may or may not intersect each other. In many cases, the representation of structure in terms of assemblies of spheres is dictated by the inherent properties of the component particles, as in the case of monatomic liquids [1–3], colloidal suspensions [4], etc. In other cases, such as the modeling of porous media [5], powders [6], etc. arrangements of spheres serve as useful and reasonable models that facilitate theoretical analysis.

In many problems, the *void* region (the region that lies outside an appropriately defined *occupied* space associated with the spheres; see discussion below) and the interface between the void and occupied regions are of specific interest. An important example is the hard sphere system. It has been shown [7,8] that the thermodynamics of a system composed of hard spheres is determined entirely by the volume and surface area of the *available space*, which is defined as the set of all allowed positions for the center of an additional hard sphere; the occupied space in this case is the union of spheres around each hard sphere center, whose radius equals the diameter of the hard spheres. Note that unlike the hard spheres themselves, the relevant *exclusion spheres* can overlap with each other. Another interesting example is the estimation of the solvation free energy of proteins, which depends on the accessible surface area [9].

A detailed analysis of various particle and void correlation functions has been pursued in recent years, as a useful approach to quantifying the morphology and properties of inhomogeneous media [10–12]. The *nearest neighbor* void distribution functions [11] for a given configuration of sphere centers may be related to the volume fraction and surface areas of the void region, by defining exclusion spheres of variable radius around sphere centers.

The above remarks serve to illustrate the usefulness of knowing the volumes and surface areas of the void region in packings of spheres. They also indicate that the general problem of interest is the calculation of these quantities in configurations of overlapping spheres. In such configurations, the void space is in general composed of disconnected regions, or *cavities*.

Some of the void quantities mentioned above can be calculated straightforwardly using standard Monte Carlo sampling methods. However, such estimation becomes highly unsatisfactory on account of statistical uncertainty when the volume fraction of the void region is small [13], e.g., for high densities in the hard sphere system. Hence it is desirable to have a method that permits an exact decomposition of void space into cavities and the calculation of the volume and surface areas associated with such cavities. While such methods have previously been developed for two dimensions [13–15], no exact method has been available for three-dimensional systems. Further, no method has been available for such calculation in polydisperse packings in either two- or three-dimensional systems.

In this paper, we present a method for calculating the volumes and surface areas of cavities in arbitrary monodisperse and polydisperse sphere packings. In the companion part II [16], we use the algorithm to study the statistical geometry of *inherent structures* [17] in a system composed of atoms interacting with the Lennard-Jones potential.

The paper is organized as follows. In Sec. II we state the problem considered and outline the algorithm, for the monodisperse case. In Sec. III we discuss the network mapping that allows the identification of cavities. In Sec. IV we describe the identification of polyhedra that enclose the cavity volumes. In Sec. V we discuss the calculation of cavity volumes and surface areas within such enclosing polyhedra. Some caveats that pertain to periodic arrangements of spheres are discussed in Sec. VI. The generalization to the polydisperse case is detailed in Sec. VII. Section VIII contains a summary and concluding remarks.

II. OUTLINE OF THE ALGORITHM

We consider a configuration of points (referred to as *atoms* in what follows) in a three-dimensional volume. We

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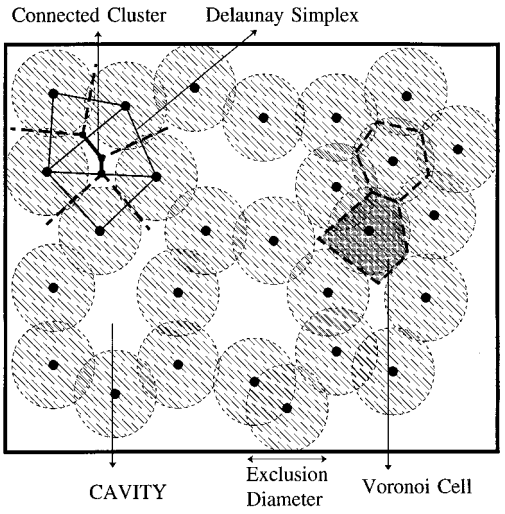

FIG. 1. A random configuration of points with exclusion disks as shown. The union of shaded areas around each disk is the ''occupied space.'' The void region is composed of disconnected cavities. Also shown are examples of Voronoi cells, Delaunay simplices, and a connected cluster of Voronoi vertices corresponding to a cavity.

assume that this volume is subjected to periodic boundary conditions, though this feature is not explicitly dealt with below. Defining an ''exclusion sphere'' around each atom, we can divide the system volume into the occupied region (union of all exclusion spheres) and the void region (complement of the occupied region). In the monodisperse case, the exclusion spheres are of the same size for each atom, while they differ from atom to atom in the polydisperse case. The void region is composed of subsets which are mutually disconnected, which we refer to as ''cavities.'' Thus a path exists *in the void* between any two points that belong to the same cavity, while no such path exists between two points belonging to two different cavities.

A two-dimensional illustration is shown in Fig. 1, displaying an arbitrary configuration of points with finite exclusion radii. The exclusion disks of distinct points overlap in this illustration, as in the general case to which our method applies. It is apparent from Fig. 1 that for a configuration of overlapping exclusion disks or spheres (the general case that we consider [18]) the void region may be composed of disconnected subsets. We refer to such subsets as *cavities*. Given a configuration of atoms (i.e., the three-dimensional coordinates of all centers) the separation of space into occupied and void regions may be varied continuously by changing the exclusion radius. In this case, the calculated void volumes and surface areas as a function of the exclusion radius yield *nearest neighbor* distribution functions that permit precise quantification of the system's geometry [11].

Given the configuration of atoms, the initial step in the algorithm is the generation of the corresponding Voronoi and Delaunay tessellations (for an efficient method to obtain these tessellations see, e.g., [19]). Both Voronoi and Delaunay tessellations tile space (i.e., divide it into nonoverlapping regions) and are *dual* to each other. The Voronoi tessellation divides space into regions VP_i which are closer to a given particle center i than to any other. Thus a point $\mathbf{x}$ belongs to VP_i if and only if

$$d(\mathbf{x},\mathbf{x}_i) < d(\mathbf{x},\mathbf{x}_j) \quad \forall j \neq i, \tag{1}$$

where $\mathbf{x}_i, \mathbf{x}_j$ are the positions of particle centers i and j, and $d(\mathbf{x},\mathbf{x}_i)$ is the distance between $\mathbf{x}$ and $\mathbf{x}_i$. Each Voronoi cell is a convex polyhedron. The faces of the Voronoi cell are equidistant from two particle centers. In random configurations of atoms an edge is defined by the intersection of three faces and hence is equidistant from three atoms. A Voronoi vertex is equidistant from four particle centers. As a Voronoi vertex is equidistant from (or, equally far from) the surrounding atoms, it is the point that is locally farthest from atom centers. Similarly, the edges connecting the Voronoi vertices define paths between vertices that lie farthest from surrounding atoms. These observations will be used below in the network mapping of void space. Joining pairs of particle centers whose Voronoi polyhedra share a face, one obtains a *dual* tessellation of space into simplical regions, the Delaunay simplices (Fig. 1 shows the two-dimensional illustration).

The following steps (which are justified with details in the sections mentioned) then yield the volumes and surface areas of individual cavities.

(1) *Identifying the cavities (Sec. III):* The set of Voronoi vertices and Voronoi edges that belong to the void is identified. Each set of vertices which is connected by edges in the void belong to the same cavity. Thus the cavities are identified by obtaining the percolation clusters of edges that are in the void.

(2) *Identification of polyhedra enclosing the cavities (Sec. IV):* The union of Delaunay simplices corresponding to (or *dual* to) the Voronoi vertices in a cavity encloses the cavity volume. The polyhedron defined by the union of such Delaunay simplices provides an upper bound on the cavity volume. Further, in order to calculate the volume of a given cavity exactly, we need inspect only these simplices.

(3) *Determination of cavity volume and surface area within a Delaunay simplex (Sec. V):* Each Delaunay simplex is divided into 24 subsimplices, each of which has as its vertices (a) an atom (total of 4), (b) the midpoint of a Delaunay edge (three per atom), (c) the intersection point of a Voronoi edge with the plane of a Delaunay face (two per atom per Delaunay edge), and (d) the Voronoi vertex. The volumes assigned to these 24 subsimplices can be positive or negative based on criteria described in Sec. V. Each subsimplex is *nominally* treated as forming a subset of the Voronoi polyhedron of the atom which forms one of its vertices. With such an assignment, the cavity volume and the surface area contained within each subsimplex (which can be positive or negative according to criteria defined in Sec. V) are calculated by considering the exclusion sphere of just the vertex atom. Summing in turn the cavity volumes and surface areas (with appropriate signs) within each subsimplex that belongs to a Delaunay simplex, and within each Delaunay simplex belonging to a cavity, we obtain the total cavity volume and surface area for a given cavity. The validity of the procedure is demonstrated in Sec. V.

III. IDENTIFYING THE CAVITIES

The first step in the algorithm is to establish a ''percolation problem'' or network mapping of void space in order to determine the location of the cavities. Considering the Voronoi tessellation of a configuration of spheres, Kerstein [20] (see also [21,22]) showed that a network mapping could be defined for identifying the cavities present in the configuration. We reproduce Kerstein's results below for the sake of completeness.

Lemma 1. (Kerstein): A given point in the interior or on the boundary of a Voronoi polyhedron is connected to a vertex by a path which is never closer to the polyhedron center than is the given point.

Theorem I (Kerstein): Every point in the void is connected to some vertex by a path contained in the void.

Theorem II (Kerstein): If two vertices are connected by the void, then they are connected within the void by edges of the Voronoi tessellation of the centers.

Theorem III (Kerstein): An edge of the tessellation is contained within the void if and only if its point of closest approach to the plane of the adjacent centers (i.e., the centers of the three Voronoi polyhedra sharing the edge) is in the void.

Thus, in order to determine the connectivity of the void space, we consider the network formed by Voronoi vertices and the edges that connect them. Then, each vertex is labeled (''occupied'' or not) according to whether it lies outside the exclusion radii of atoms that surround it. The edges are then examined to determine whether they lie in the void or not, and are labeled accordingly. We can then use standard cluster finding methods to determine connected vertices. Clusters of Voronoi vertices that are in the void, which are connected by edges that also lie in the void, then define each disconnected region of the void, i.e., the cavities. The number of vertices in a cluster affords a zeroth order estimate of cavity size.

IV. IDENTIFICATION OF POLYHEDRA ENCLOSING THE CAVITIES

Theorem I shows that any point in the void belonging to a given Voronoi polyhedron is connected to *some* vertex of that polyhedron. The following lemma makes this statement more specific.

Lemma 2: If any point in a Delaunay simplex belongs to the void, the corresponding Voronoi vertex belongs to the void.

This lemma can easily be seen to hold by considering the definitions of the Voronoi construction. However, we demonstrate it by dividing the Delaunay simplex into subsimplices, whose construction will be useful later. The details of this construction are illustrated in Fig. 2.

Consider the sphere around the Voronoi vertex (V) with radius equal to the distance of the vertex and the atoms (A_1,A_2,A_3,A_4) comprising the Delaunay simplex. By definition, the atoms lie on the surface of this sphere, and further, no other atom lies inside the sphere. The Delaunay simplex is contained in this sphere. For each face of the Delaunay simplex ($A_iA_jA_k$), define a simplex ($AAAV$ simplex) with A_i, A_j, A_k, and V as the four corners. Any point in the Delaunay simplex is inside one (or more) of the four

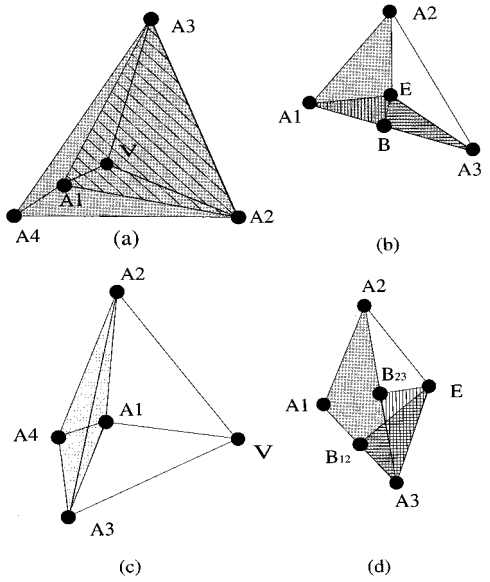

FIG. 2. Subdivision of a three-dimensional Delaunay simplex. (a) $AAAV$ simplices when the Voronoi vertex V is inside the Delaunay simplex. The shaded volume is the subsimplex $A1A2A3V$. (b) Subdivision of a Delaunay simplex face for defining $AAEV$, $ABEV$ subsimplices, when the intersection of the Voronoi edge (E) lies within the Delaunay face ($A1A2A3$). With the Voronoi vertex V (out of the plane) as the fourth vertex, $A1$, $A2$, and E define an $AAEV$ subsimplex, while $A1$, B, and E define an $ABEV$ subsimplex. (c) $AAAV$ simplices when the Voronoi vertex V is outside the Delaunay simplex. Subsimplex $A1A2A3V$ lies entirely outside the Delaunay simplex, and further, overlaps with, e.g., $A1A2A4V$. (d) Subdivision of a Delaunay simplex face for defining $AAEV$, $ABEV$ subsimplices, when the intersection of the Voronoi edge (E) lies outside the Delaunay face ($A1A2A3$). In this case, $AAEV$, $ABEV$ subsimplices may lie entirely outside the Delaunay simplex, and also overlap with each other (e.g., $A3B23EV$ and $A3B12EV$).

such simplices. Consider next the line perpendicular to a Delaunay face which is equidistant from the three atoms in the face. This line passes through the Voronoi vertex and further contains the edge in the Voronoi construction that is dual to the Delaunay face in question. Let the intersection of this point with the plane of the Delaunay face be E_{ijk}. Define simplices ($AAEV$ simplices) with two atoms in the face, the point E_{ijk}, and the Voronoi vertex as the four corners. Any point in an $AAAV$ simplex is inside one of the corresponding $AAEV$ simplices. Finally, for each $AAEV$ simplex $A_iA_jE_{ijk}V$, with B_{ij} as the bisector of A_iA_j, define two simplices ($ABEV$ simplex) $A_iB_{ij}E_{ijk}V$ and $A_jB_{ij}E_{ijk}V$. Any point in an $AAEV$ simplex is inside one $ABEV$ simplex. Thus any point in the Delaunay simplex is inside an $ABEV$ simplex.

Assume now that some point in the Delaunay simplex (the *initial point*) is in the void. This point is inside some $ABEV$ simplex. The edges AB, BE, and EV of the $ABEV$ simplex are mutually orthogonal, as can be deduced from their definitions. Define a coordinate system with A as the origin and AB,BE,EV defining the x,y,z axes (the coordinate system may be either right or left handed, but the handedness is not relevant here). By construction, V has the highest value of each coordinate among points in the $ABEV$

simplex, including the initial point. Thus the vertex is farther from atom A than the initial point. Since the vertex is equidistant from each atom of the Delaunay simplex and further, no other atom is closer to it than these atoms, the Voronoi vertex V is in the void.

Next we show that in order to calculate the volume of a cavity we need only inspect the Delaunay tetrahedra corresponding to the vertices that belong to the cavity or cluster.

Theorem IV: Given a set of Voronoi vertices and edges that belong to a cavity or cluster, the union of Delaunay simplices corresponding to the vertices in the cluster completely encloses the cavity.

Let us assume the contrary. Let us assume that a Delaunay simplex whose Voronoi vertex does not belong to the cavity contains a point (the initial point I) that belongs to the cavity.

From Lemma 2, the Voronoi vertex is in the void. Consider now the line IV joining the initial point I and the vertex V. Clearly, every point on IV lies outside the exclusion zones of the four atoms in the Delaunay simplex. Next, extrapolate IV to the surface of the circumsphere around the vertex, passing through the vertices of the Delaunay simplex. The intersection point (S) defines the closest possible position of a fifth atom to any point on the line segment IV. Further, the point on line segment IV closest to S is the initial point I. Since the initial point by our assumption is in the void (and hence outside the exclusion zone of the fifth atom), so are all points on the line joining the initial point and the vertex. This implies that the initial point and the vertex belong to the same cavity, in contradiction with our assumption. The theorem is thus proved.

A corollary of the above theorem is that every Delaunay simplex overlaps at most with a single cavity.

Thus the sum of volumes of Delaunay simplices corresponding to Voronoi vertices in a cavity yield the upper bound of the cavity volume. Further, we are in a position to calculate the volume of a given cavity by considering one Delaunay simplex at a time. The procedure for doing so is discussed in the next section.

V. DETERMINATION OF CAVITY VOLUME AND SURFACE AREA WITHIN A DELAUNAY SIMPLEX

The calculation of cavity volumes is done by considering one Delaunay simplex at a time from the set of Delaunay simplices enclosing the cavity. In each simplex we need to calculate the total volume (which is trivial) and subtract from it the volume that is inside the exclusion zones of the atoms. The difference is the cavity volume in that simplex. The approach is to divide the Delaunay simplex into smaller simplices in such a way that in each smaller simplex, one needs to calculate the overlap with only one exclusion zone.

Consider the $ABEV$ simplices defined in the course of proving Lemma 2. As can readily be ascertained, the sum of volumes of $ABEV$ simplices does not in the general case add up to the volume of the Delaunay simplex, since the $ABEV$ simplices can both overlap and lie partially or fully outside the Delaunay simplex. We show here that by an appropriate assignment of signs to these volumes, the sum yields the volume of the Delaunay simplex.

For any simplex (and its faces), we can define an interior and exterior surface. Consider now a face of the Delaunay simplex. The interior side is oriented towards the fourth atom that completes the simplex. Now consider an $AAAV$ simplex. The interior of the Delaunay face for this $AAAV$ simplex is the side that faces the vertex. We define the volume of an $AAAV$ simplex to be negative (specified by variable $S_V=-1$) if the interior side of a Delaunay face with respect to the $AAAV$ simplex is different from the interior side of the face with respect to the Delaunay simplex. With this definition, the volumes of $AAAV$ simplices add up to the volume of the Delaunay simplex.

To see this consider the projection (with the Voronoi vertex as the apex) of some arbitrary point in the union volume of all $AAAV$ simplices, onto a Delaunay face. If the point gets projected onto some point on the exterior surface of the Delaunay simplex, it also necessarily gets projected onto some (only one) point on the interior surface of the Delaunay simplex. Thus every volume element that is mapped to the exterior surface of the Delaunay simplex (hence contributes to the volume of an $AAAV$ simplex that is counted as negative) also gets mapped to the interior surface of the Delaunay simplex (and hence contributes to the volume of an $AAAV$ simplex which is counted as positive). On the other hand, volume elements inside the Delaunay simplex can only be mapped to the interior surface and thus are counted as positive volumes.

Next consider the area of a Delaunay face. In analogous fashion to the $AAAV$ simplex volumes, we can define the areas of 2-simplices (triangles) AAE to be positive or negative (specified by variable $S_E=\pm 1$), such that the sum of areas of AAE 2-simplices equals the area of the face AAA. The division of an $AAAV$ simplex into $AAEV$ simplices then results in the correct volume for the $AAAV$ simplex. The further division of an AAE 2-simplex into ABE 2-simplices does not lead to any sign duality, since the location of the point B is always fixed to be between two atoms.

Thus, for a given $ABEV$ simplex, if we define its volume

$$V_{ABEV}=S_V S_E|(\vec{AB}\times\vec{AE})\cdot\vec{AV}|, \tag{2}$$

the sum of these volumes yields the volume of the Delaunay simplex.

Next, we need to define how the overlap volumes of the exclusion zones are treated within this construction. We group the $ABEV$ simplices for each Delaunay simplex into four groups, according to which atom participates as a corner. We then assign each such group to the Voronoi polyhedron of the corresponding atom [e.g., $A3B12EV$ and $A3B23EV$ in Fig. 2(d) are assigned to the Voronoi polyhedron of atom $A3$]. As shown below, the volumes of subsimplices, with the sign assignments as described above, add up to the intersection volume of the Delaunay simplices in a cavity and the Voronoi cell of the appropriate atom. This means that each time an $ABEV$ simplex includes volumes outside the Voronoi polyhedron of a given atom, the fraction lying outside gets canceled by the negative volume of another $ABEV$ simplex. For each subsimplex, we define the cavity volume to be the simplex volume *minus* the overlap volume of the simplex with the exclusion sphere of the atom in question *times* $S_V S_E$.

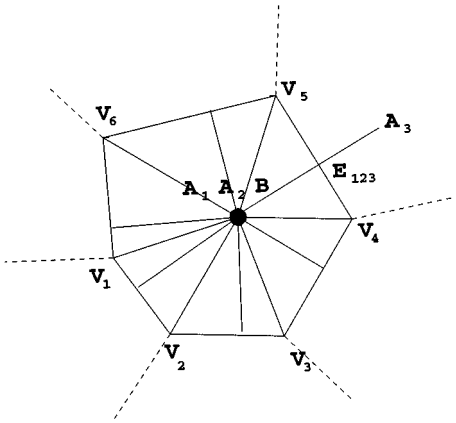

FIG. 3. Polygonal face of a Voronoi polyhedron. The figure shows a two-dimensional projection along the axis joining atoms $A1$ and $A2$ (which are thus at the same two-dimensional position in the projection). $A1$ lies below the plane of the Voronoi face, while $A2$ lies above. The projected image of the midpoint of line $A1A2$ (point B which lies in the plane of the face of the Voronoi polyhedron) coincides, in this projection, with $A1$ and $A2$. Atom $A3$ completes one face of a Delaunay simplex, which is intersected by the Voronoi edge $V4V5$ at point $E123$. The dashed lines represented edges of the Voronoi polyhedron which are out of the plane of the Voronoi face shown.

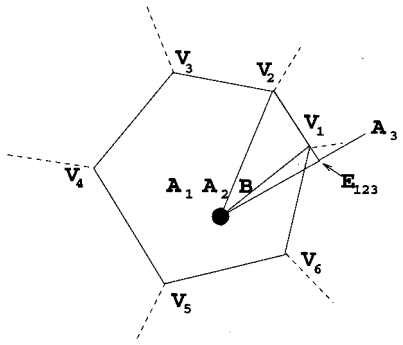

FIG. 4. Polygonal face of a Voronoi polyhedron, when a Voronoi edge $(V1V2)$ does not intersect the corresponding Delaunay simplex face $(A1A2A3)$. In this case, the BEV triangles for $V1$ and $V2$ overlap, but with $BEV1$ counted as negative, the sum of the two areas is $BV1V2$.

To demonstrate that the above prescription is valid, we first consider the *simple* case, and note the possible exceptions. Then we demonstrate that in the exceptional cases, the counting of volumes outlined above results in a meaningful answer.

Let us consider a (polygonal) face of a Voronoi polyhedron and the pyramid defined with the polygon as the base and the atom in the center of the polyhedron as the apex. In the simple case, the $ABEV$ simplices can be described as follows. Define points E between each pair of polygon vertices (which are Voronoi vertices), as shown in Fig. 3 (the location of the points E between two vertices is the ''simple'' feature). The point B (defined as the intersection point of a Delaunay edge with the corresponding Voronoi face) in the simple case is located inside the polygon. Thus triangles BEV tessellate the polygon. For each triangle, taking the atom as the fourth vertex, we obtain the $ABEV$ simplices, which, in this case, are clearly contained inside the Voronoi polyhedron. Thus our prescription works in the simple case.

The exceptions to the situation arise for two possible reasons. (i) The points E do not lie ''between'' two vertices, but on an extrapolation of the line joining two vertices. In this case, clearly, E lies outside the Voronoi polyhedron. (ii) Point B does not lie inside the polygon. In this case also, B lies outside the Voronoi polyhedron.

Consider the case when B lies inside the polygon, but one of the points E does not lie between the corresponding two vertices. This situation is illustrated in Fig. 4. Considering the face that is shared by the Delaunay simplices corresponding to the two vertices, we identify one of them $(V1)$ to be closer to the face than the other $(V2)$. If $V1$ belongs to the void, $V2$ also belongs to the void, and in this case, they both belong to the same cavity (since the edge between them also belongs to the void). $V2$ can belong to the void without $V1$ lying in the void, but we need not consider this possibility: In this case, no point in any $ABEV$ simplex (with $V=V1$) has points lying in the void. Hence we can *nominally* assign $V1$ to the same cavity as $V2$, without changing anything. Since $V1$ and $V2$ belong to the same cavity, we can define a new simplex $ABV1V2$ by combining the volumes of $ABEV1$ and $ABEV2$. Note that both $V1$ and $V2$ are on the same side of the Delaunay face they share, while their corresponding Delaunay simplices are on opposite sides. Hence $ABEV1$ has negative volume while $ABEV2$ has positive volume (in the general case, i.e., when we let the location of B vary, the two simplices have *opposite* signs). Further, the negative volume of $ABEV1$ cancels exactly the volume of $ABEV2$ that lies outside the Voronoi polyhedron (both simplices share the base ABE, with choices for the fourth vertex—$V1$ or $V2$—lying on the same line orthogonal to the base), the difference being the volume of $ABV1V2$, which lies entirely inside the Voronoi polyhedron.

Next we consider the situation when B lies outside the polygon. This case is illustrated in Fig. 5. For its analysis, we first consider the following theorem.

Theorem V: When the intersection point of a Delaunay edge and the plane of the corresponding Voronoi face lies outside the Voronoi face, all Voronoi vertices that are vertices of the Voronoi face, if in the void, belong to the same cavity.

Consider the plane of the Voronoi face. The cross section of the exclusion sphere around the atom is a circular area (see Fig. 5), whose center lies at B (the intersection point of the Delaunay edge and the plane of the corresponding Voronoi face) and whose radius is given by $(r_c^2-r_B^2)^{1/2}$, where r_c is the radius of the exclusion sphere, and r_B is the distance of B from the atom. Considering the perimeter of the Voronoi face, any vertex that lies outside a distance $(r_c^2-r_B^2)^{1/2}$ from B is connected along the perimeter to any other vertex that lies outside. Thus such vertices (a) belong to the void, and (b) belong to the same cavity.

As before, if any vertex of the polygon is not in the void, we can *nominally* include it in the cavity, since the $ABEV$ simplices corresponding to such a vertex do not contribute any volume. Now, as earlier, we can define (by combining

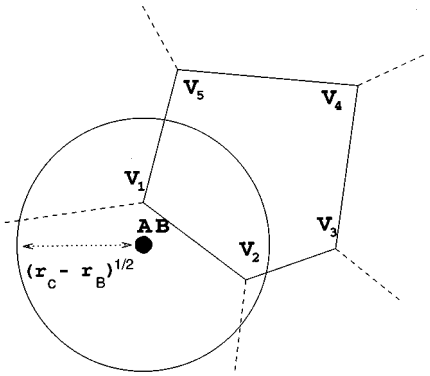

FIG. 5. Polygonal face of a Voronoi polyhedron, when the intersection point B of the Delaunay edge does not lie within the polygonal face. r_c is the exclusion radius from the position of the atom A, and r_B is the distance between the atom and point B. The radius of the circle of intersection of the exclusion sphere and the plane of the Voronoi face is thus $(r_c^2-r_B^2)^{1/2}$.

VE line segments of adjoining vertices) triangles on the Voronoi face $BV1V2$, one of whose sides will be a Voronoi edge. For such edges whose interior side in a $BV1V2$ triangle is different from the interior side with respect to the polygonal face, S_E will be negative. Thus we see that the area of the Voronoi face, and hence the volume of the pyramid with the polygon as base, is counted correctly in our prescription.

Thus, counting the volumes of $ABEV$ simplices (and the corresponding overlap volumes with the exclusion spheres) as in Eq. (2), we obtain the proper calculation of the cavity volumes.

The practical step of calculating the overlap volume within each $ABEV$ simplex is straightforward, and is described in the Appendix. Thus the procedure outlined in Sec. II may be used for calculating cavity volumes and the distribution thereof. Note that within each $ABEV$ simplex, if one calculates, instead of the overlap volume, the area of the exclusion sphere, the summation of such area elements yields the cavity surface areas.

VI. CAVEATS FOR PERIODIC CONFIGURATIONS

When the configurations considered are periodic, the Voronoi vertices sometimes *do not* possess the property that four Voronoi edges meet at a vertex, since, due to the symmetries present in periodic configurations, one may find more than four atoms at equal distances from a Voronoi vertex. In such an event, the Delaunay tessellation of space is *degenerate*; there exist Delaunay polyhedra which may be arbitrarily broken up into Delaunay simplices in more than one way. Then, the Voronoi vertices dual to such Delaunay simplices coincide. The practical problems to be solved in such cases in order to determine cavity volumes are (i) a systematic procedure for breaking the degeneracy in defining the Voronoi or Delaunay tessellations, and (ii) accounting for the fact that the ''edges'' connecting degenerate Voronoi vertices are in fact points, which further coincide with the locations of the two Voronoi vertices in question. Both these problems are ''bookkeeping'' problems and do not affect the applicability of our algorithm. It must further be noted that the degeneracies present in regular structures are destroyed by infinitesimal perturbations away from perfect regularity.

VII. POLYDISPERSE PACKINGS

In order to generalize the algorithm for polydisperse systems, we need correspondingly to generalize the type of tessellations utilized. We consider two such generalizations below and discuss the extension of our algorithm for calculating cavity volumes and surface areas in the two cases.

A. Voronoi *S* regions

The usual Voronoi construction is not very useful in the case of polydisperse packings, since the Voronoi vertices, edges, and faces no longer retain the properties of equidistance from particles (since the particles we consider in the polydisperse case are not identical, we drop from now on the reference to ''atoms'' adopted before and henceforth refer to ''particles''). In particular, the relevant notion of equal distance from distinct particles (which we use in the conventional Voronoi construction to define the faces of the Voronoi polyhedra) is the equality of a distance measured from the ''surface'' of each given particle. Thus one must construct tessellations of space into regions that are closest, not to the centers, but to the ''surfaces'' of individual particles. Such a construction has recently been investigated by Medvedev [21]. In this construction, the notion of a Voronoi polyhedron generalizes to a Voronoi *S* region, defined to be the set of points closer to the surface of a given spherical particle than to any other surface. Unlike Voronoi polyhedra, the faces and edges of the Voronoi *S* regions are curved. In particular, the faces are pieces of rotation hyperboloids (the geometric locus of points equidistant from the surfaces of two spheres of different radii). The edges are defined by intersections of such hyperboloids. A two-dimensional example is shown in Fig. 6.

As discussed by Medvedev [21], the topology of the tessellation by Voronoi *S* regions is not in general equivalent to that of the conventional Voronoi tessellation. However, there are polydisperse systems whose topology is equivalent, and such polydisperse systems are termed by Medvedev *regular systems*. At present, no criteria have been established for determining *a priori* which polydisperse systems are regular and which are not.

The discussion that follows is restricted to polydisperse systems which are regular. Thus we assume that the network topology of Voronoi *S* vertices and edges is the same as in the conventional Voronoi tessellation.

In this circumstance, then, the cavities may be identified by vertices and edges of the *S* regions that belong to the void. In analogy to the monodisperse case, then, we can identify cavities in terms of Voronoi vertices connected via Voronoi edges.

Thus, in order to justify the generalization of the algorithm to the polydisperse case, we need only to demonstrate that (a) an appropriate set of Delaunay simplices covers the cavity volume and (b) the volumes of individual Delaunay simplices can be divided and evaluated by a procedure analogous to the monodisperse case.

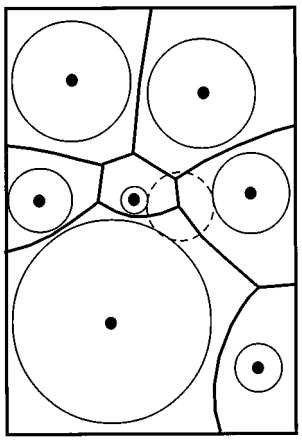

FIG. 6. Construction of Voronoi S regions. The boundaries between Voronoi S regions are segments of surfaces (curves in two dimensions) that are at equal distances from the surfaces of particles adjacent to them. The dashed circle illustrates the fact that the Voronoi vertex at the center of the circle is at equal distances from the surfaces of the three corresponding particles (figure adapted with permission from [21]).

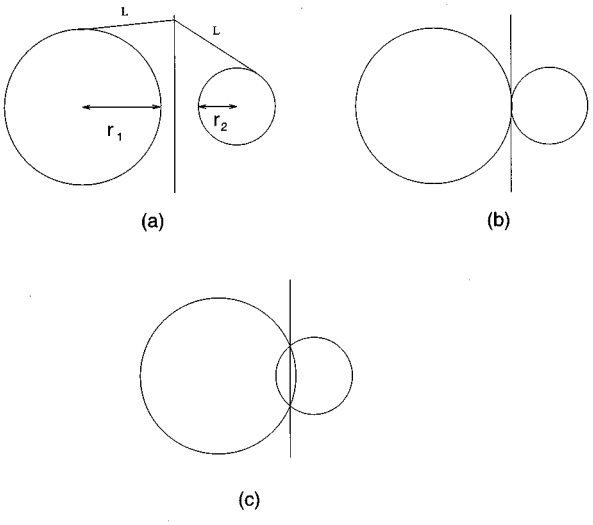

FIG. 7. Radical plane construction. Boundaries are shown for three separations of the sphere centers. (a) also illustrates the fact that the tangent distances to the two spheres are equal along the boundary.

First we consider Lemma 2 for the polydisperse case. As before, we consider $ABEV$ ''simplices,'' where B is now the intersection point of a Delaunay edge with a face (in general, extension of the face) of the Voronoi S region, E, the intersection of an edge (or extension) of the Voronoi S region with the corresponding Delaunay face, and V is a Voronoi vertex. Note that one face of the $ABEV$ simplex is nonplanar (the BEV face). Any point O inside the Delaunay simplex is inside some $ABEV$ simplex. Now, the conical projection O' (with the particle coordinate A as apex) of any point inside an $ABEV$ simplex maps the initial point onto the BEV face and the projected point is necessarily farther from the location of the particle. We can consider next a ''curvilinear'' projection O'' of the projected point O' with point B as base. To do so, we consider the plane formed by points A, B, and O' and its intersection with the BEV face. On this intersection curve, O'' is the farthest point away from B that is on the BEV face. O'' lies between E and V, and is farther from A than O'. Point E is the point closest to the surface of A along EV. Thus a projection of O'' along the curve EV, namely, the point V, is farther from A than O''. Thus, if any point inside a Delaunay simplex is in the void, the corresponding Voronoi vertex is in the void, since the Voronoi vertex is closer to the surfaces of the particles of the given Delaunay simplex than to any other particles.

Next we generalize Theorem IV. Consider some point i which belongs to a given cavity C. The point i is inside the Voronoi S region of some particle α, V_α. V_α is composed of overlap volumes of V_α with Delaunay simplices which have α as one of the vertices. Let i be inside one such Delaunay simplex. Since i is in the void, the corresponding vertex is in the void by Lemma 2. Further, points along the line joining i and the vertex are at increasing distances from the sphere surface and thus the vertex belongs to the cavity C. Hence, given any point in the cavity, it belongs to a Delaunay simplex whose vertex is in the cavity.

The prescription for calculating the cavity volumes remains as before, except that individual Delaunay simplices are now decomposed into $ABEV$ simplices with one face that is not planar (the BEV face). Though this complicates the calculation of volumes and intersection volumes for individual $ABEV$ simplices, the procedure outlined in Sec. V for calculating the cavity volumes remains valid.

B. Radical plane construction

Another generalization of the Voronoi construction is the *radical plane construction*. In this construction, one generalizes the usual Voronoi construction by considering a different distance measure for defining regions that are associated with each particle [23]. A significant advantage in this method is that the boundaries between regions associated with each particle remain planar. A point $\mathbf{x}$ belongs to the generalized Voronoi cell of particle i, if

$$d(\mathbf{x},\mathbf{x}_i)^2 - r_i^2 < d(\mathbf{x},\mathbf{x}_j)^2 - r_j^2 \quad \forall j \neq i, \tag{3}$$

where r_i are the radii of the particles, $\mathbf{x}_i$ the position of the particle center, and $d(\mathbf{x},\mathbf{x}_i)$ is the distance between $\mathbf{x}$ and $\mathbf{x}_i$. The radical plane construction is illustrated in Fig. 7.

It has recently been shown by van der Marck [24] that the network mapping obtained by Kerstein [20] for the monodisperse case generalizes to the polydisperse case under the radical plane construction.

The arguments presented in Secs. IV and V apply to the radical plane construction as well. To show this, we first consider Lemma 2. The construction and properties of the $AAAV$, $AAEV$, and $ABEV$ simplices is identical to that in Sec. IV. Thus, if some point in a Delaunay simplex is in the void, the corresponding vertex is in the void. Consider a point i which is in the void. Let i belong to some Voronoi cell V_α. Further, i belongs to the overlap volume of V_α with some Delaunay simplex which has α as one of the vertices. Any point in a Delaunay simplex belongs to at least one $ABEV$ simplex. Since the Voronoi vertex is in the void by Lemma 2, and is farther from particle α than i, the point i is connected to the Voronoi vertex, which consequently be-

longs to the same cavity as the initial point i. Finally, the arguments in Sec. V apply without change for the radical plane construction. The radical plane construction for the polydisperse case has the advantage that its geometry is no more complicated than that of the usual Voronoi or Delaunay construction equal sized particles.

VIII. SUMMARY

In this paper, we have presented an algorithm for the exact calculation of volumes and surface areas of cavities in monodisperse and polydisperse sphere packings in three dimensions. The method depends on the tessellation of space into Voronoi and Delaunay polyhedra. In discussing the applicability of our algorithm for the polydisperse case, we described two generalizations of the usual Voronoi or Delaunay construction to the polydisperse case, namely, the construction of Voronoi S regions and the radical plane construction. With the appropriate tessellation of space, the void space is characterized first by employing a network mapping, wherein the ''nodes'' and ''bonds'' are the vertices and edges of the Voronoi tessellation. By labeling these nodes and bonds according to whether they lie in the void or not, we obtain a preliminary description of the cavities present as percolation clusters of Voronoi vertices that are in the void, connected by edges that lie in the void space. We have presented a method for calculating the void volume and the cavity surface area for individual Delaunay simplices and have shown how the total void volumes and surface areas of cavities may be calculated by considering Delaunay simplices dual to Voronoi vertices defining the cavities.

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APPENDIX: VOID VOLUME IN A SUBSIMPLEX

Here we calculate the cavity volume inside an $ABEV$ subsimplex described in Secs. IV and V. Let r_V be the distance from the atom A to the Voronoi vertex V. Similarly, let r_E and r_B be the distances from A to the intersection of the Voronoi edge with the Delaunay face E and the midpoint of a Delaunay edge B, respectively. Points B, E, and V lie in a plane perpendicular to the Delaunay edge along which B lies (i.e., perpendicular to AB). Further, the line joining the Voronoi vertex V with E is perpendicular to the plane containing points A, B, and E. Thus, by choosing the appropriate coordinate system, we can describe the coordinates of B, E, and V as

$$\mathbf{B}=(x_0,0,0), \quad \mathbf{E}=(x_0,y_0,0), \quad \mathbf{V}=(x_0,y_0,z_0), \tag{A1}$$

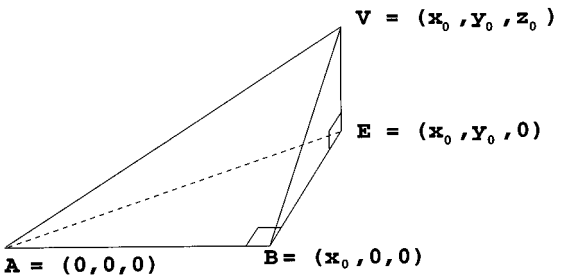

FIG. 8. $ABEV$ subsimplex, with coordinate assignments for points B, E, and V, relative to atom A.

where x_0, y_0, and z_0 are related to r_V, r_E, and r_B by

$$r_B=x_0, \quad r_E=\sqrt{x_0^2+y_0^2}, \quad r_V=\sqrt{x_0^2+y_0^2+z_0^2}. \tag{A2}$$

The geometry is illustrated in Fig. 8. In order to calculate the cavity volume, we need to calculate the overlap volume V_c of the subsimplex with the exclusion sphere of radius r_c ($<r_V$). The cavity volume is then obtained by subtracting V_c from V_t, the volume of the subsimplex, $=\frac{1}{6}(x_0y_0z_0)$. Differentiating V_c with respect to r_c yields the contribution of the given subsimplex to the cavity surface area, S_c. The calculation is straightforward and will not be elaborated here. The final expressions for V_c and S_c follow.

Case I: $r_c<x_0$.

$$V_c=\frac{r_c^3}{6}\left(2\theta-\pi/2-\arcsin\left[\frac{(z_0^2x_0^2-y_0^2r_V^2)}{r_E^2(y_0^2+z_0^2)}\right]\right), \tag{A3}$$

$$S_c=\frac{r_c^2}{2}\left(2\theta-\frac{\pi}{2}-\arcsin\left[\frac{(z_0^2x_0^2-y_0^2r_V^2)}{r_E^2(y_0^2+z_0^2)}\right]\right). \tag{A4}$$

Case II: $x_0<r_c<r_E$.

$$V_c=\frac{\theta}{2}\left(r_c^2x_0-\frac{x_0^3}{3}\right)-\frac{r_c^3}{6}\left(\frac{\pi}{2}+\arcsin\left[\frac{(z_0^2x_0^2-y_0^2r_V^2)}{r_E^2(y_0^2+z_0^2)}\right]\right), \tag{A5}$$

$$S_c=\theta x_0r_c-\frac{r_c^2}{2}\left(\frac{\pi}{2}+\arcsin\left[\frac{(z_0^2x_0^2-y_0^2r_V^2)}{r_E^2(y_0^2+z_0^2)}\right]\right). \tag{A6}$$

Case III: $r_E<r_c<r_V$.

$$\begin{aligned}V_c=&\frac{1}{2}\left(\theta-\frac{\pi}{2}+\arcsin\left[\frac{y_0}{\sqrt{r_c^2-x_0^2}}\right]\right)\left(r_c^2x_0-\frac{x_0^3}{3}\right)\\&+\frac{x_0y_0}{6}\sqrt{r_c^2-r_E^2}+\frac{r_c^3}{6}\arcsin\left[\frac{x_2^2-y_2^2-x_0^2}{r_c^2-x_0^2}\right]\\&-\frac{r_c^3}{6}\arcsin\left[\frac{(z_0^2x_0^2-y_0^2r_V^2)}{r_E^2(y_0^2+z_0^2)}\right],\end{aligned} \tag{A7}$$

$$S_c = x_0 r_c \left(\theta - \frac{\pi}{2} + \arcsin\left[\frac{y_0}{\sqrt{r_c^2 - x_0^2}} \right] \right) - \frac{1}{2} \left(r_c^2 x_0 - \frac{x_0^3}{3} \right) \frac{y_0 r_c}{(r_c^2 - x_0^2)\sqrt{r_c^2 - r_E^2}} + \frac{x_0 y_0}{6} \frac{r_c}{\sqrt{r_c^2 - r_E^2}} + \frac{r_c^2}{2} \arcsin\left[\frac{x_2^2 - y_2^2 - x_0^2}{r_c^2 - x_0^2} \right]$$
$$+ \frac{r_c^3}{3} \frac{2 r_c x_0^2 y_0^2}{r_E^2 (r_c^2 - x_0^2)} \frac{1}{\sqrt{(r_c^2 - x_0^2)^2 - (x_2^2 - y_2^2 - x_0^2)^2}} - \frac{r_c^2}{2} \arcsin\left[\frac{(z_0^2 x_0^2 - y_0^2 r_V^2)}{r_E^2 (y_0^2 + z_0^2)} \right], \tag{A8}$$

where $\theta = \arctan(z_0/y_0)$, $x_2 = r_c x_0 / r_E$, and $y_2 = r_c y_0 / r_E$.

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