Quantification of the atomic surfaces and volumes of a metal cluster based on the molecular surface model

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Abstract

The atomic volume and surface are important geometric quantities for calculating various macroscopic physical quantities from atomistic models. This paper proposes a new analytical method to calculate the atomic volumes and surfaces of a metal cluster. This method adopts metallic radii to describe atom sizes and constructs the overall volume/surface by the molecular surface (MS) model. It divides cluster atoms into two types: interior atoms and boundary atoms. For an interior atom, the method defines a variational Voronoi cell as its volume. For a boundary atom, the method defines the intersection of the overall cluster volume and its variational Voronoi cell as its volume. The atomic surfaces are calculated along with the volume calculations. Compared with other methods, the new method considers the effect of atom sizes and does not rely on the size and location of the simulation box. Therefore, the new method can accurately calculate the overall volume of a metal cluster of arbitrary shape and the individual atomic volumes. This method provides computational support for multiscale coupled calculations from the microscale to macroscale.

1. Introduction

Molecular dynamics (MD) is a powerful and widely used research tool that helps researchers study material properties at the atomic scale. The result of a molecular dynamics simulation is the trajectory of a group of atoms. According to multiscale theory, many physical quantities can be calculated from the trajectory [1–5]. The atomic volume and surface area are two geometric quantities. They play an important role in calculating the physical quantities. For example, to calculate the first Piola-Kirchhoff stress and Green-Lagrange strain distribution within an atomic cluster, the intermediate quantities need to be divided by atomic volumes [2–4]. However, the individual atomic volume is not well defined or not easy to compute in the MD simulations [6–10].

Lee and Richards presented the three-dimensional shape representation models of solvent accessible surface (SA) and molecular surface (MS) for proteins [12]. The molecular volume obtained from the MS model is named the solvent excluded volume. In the special case of the point-sized solvent, these two types of molecular surfaces coincide, referred to as the van der Waals surface (VW). These surface models are shown in figure 1. These models are widely used to study protein structures and their correlation with physicochemical parameters [11–13]. The solvent accessible surface is determined by simulating a probe sphere rolling on the surface of a molecule. The path traced out by the center of the probe forms the solvent accessible surface. Connolly [13], Richards [14], and Eisenhaber [15] developed the surface calculation methods for the SA model by using a finite set of points distributed on the spheres. McConkey introduced an analytic algorithm to quantify the atomic surface and volume for a protein [16]. McConkey defined an individual atom volume as the intersection between an atom sphere and its Voronoi cell. Based on McConkey’s work, Cazals et al. gave a derivation proof of the
calculation formulae of the individual atom surface and volume, and they implemented a robust computational program and performed a detailed numerical analysis [17]. The molecular surface is defined as the inward faces of a probe sphere rolling on the protein surface. For the MS model, Connolly developed an analytical molecular surface and volume calculation method [18, 19]. Connolly computed the solvent excluded volume accurately. This method has higher precision, so it is particularly useful for comparing three-dimensional structures of a macromolecule in slightly differing conformations. The VM model is the special case of the other models when the probe radius is zero. Many calculation methods for the VM model involved discretization steps [13, 20]. These steps require the generation of many points, either in a grid or at random. A good final precision usually requires a large computing time. Based on the Connolly’s analytical method [18, 19], Petitjean developed a fast analytical calculation method for the van der Waals surface and volume [21]. That method considers high-order overlaps between spheres. In brief, the surface area and volume computational methods based on SA, MS, and VW models can be broadly divided into two types: approximation methods [13–15, 17, 20, 22–31] and analytic methods [16, 18, 19, 21, 32–36]. Most approximation methods involve certain discretizations, such as polyhedral (generally triangular) decompositions or the representation of a surface with many dots. The widely used software PyMOL [37] and VMD (Visual Molecular Dynamics) [38] adopted approximation methods to generate the surface representation of a protein.

The SA, MS, and VW models were originally designed for protein molecules without regard to metallic materials. To compute individual metallic atom volumes, the easiest method might be to assume they were $a^3/4$ in fcc and $a^3/2$ in bcc metals, where $a$ is lattice constant. However, this assumption is valid only if the lattice structure in the cluster remains perfect and is not affected by external forces. If the cluster is deformed by external forces (the lattice structure in the cluster is changed), there is a significant error between the assumed atomic volume and the actual atomic volume, which leads to some mechanical quantities not being calculated correctly in the subsequent multiscale calculations, such as stress, elastic modulus. One ordinary method to compute individual atom volumes for a metal cluster is computing the Voronoi tessellation and defining Voronoi cells as atomic volumes [3, 4, 6, 7]. However, this method simply treats atoms as points without considering the effect of atom sizes, and it does not work for boundary atoms because the Voronoi cells of boundary atoms may be unbounded. One remedy for this problem is to define the intersection of Voronoi cells with the simulation box as atomic volumes, software LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) adopted that method [6–10, 39]. But that method introduces a new problem that the atomic volumes are closely dependent on the simulation box size and location. Stukowski [40, 41] proposed a geometric model to characterize the surface and volume of a metal cluster. First, Stukowski performed Delaunay triangulation to a metal cluster and obtained a set of tetrahedrons. Then, to identify the details of the cluster surface and the holes or small gaps in the cluster, Stukowski introduced the concept of probe sphere. Stukowski chose the size of a probe sphere, compared the probe sphere with the circumscribed sphere of each tetrahedron in the space, and then deleted the tetrahedrons whose circumscribed sphere radius was larger than the probe sphere. The remaining tetrahedrons were the metal cluster volume, and the outer faces of these tetrahedrons formed the cluster surface. However, this model also treats atoms as points without considering the atom size effect, and it can only calculate the overall volume/surface of a metal cluster, not the individual volume/surface for each atom.

In this paper, we propose a new method for calculating the atomic surfaces and volumes of a metal cluster. This new method is mainly based on the MS model and absorbs some features of Stokowski’s model. First, this method adopts metallic radii to describe atom sizes and constructs the overall volume/surface by the MS model. The metallic radius is defined as one-half of the distance between two adjacent atoms in a metallic lattice. Then, it divides cluster atoms into two types: interior atoms and boundary atoms. For an interior atom, the method

![Diagram](image-url)
defines a variational Voronoi cell as its volume. For a boundary atom, the method defines the intersection of the overall cluster volume and its variational Voronoi cell as its volume. The atomic surfaces are calculated along with calculating the volumes. Essentially, we define all atomic volumes (both interior and boundary atoms) as the intersection of the overall cluster volume and the corresponding Voronoi cells. Our new atomic volume/surface method considers the effect of atom sizes and can calculate not only the overall volume/surface of a cluster but also the individual volume/surface for each atom. The results of the new method are physically reasonable and not dependent on the simulation box.

The structure of this paper is as follows. Section 2 reviews the MS model and surface definition equations. Section 3 gives the surface calculation method for a metal cluster and individual atoms. Section 4 gives the corresponding volume calculation method. Section 5 discusses the self-intersecting surface problem encountered in constructing a molecular surface. Section 6 discusses the probe radius selection problem. Section 7 gives three numerical examples of different shaped copper (Cu) crystals to verify the effectiveness of the volume/surface calculation method. In section 8, the conclusion is presented.

2. Review of the MS model and surface definition equations

Normally the molecular surface (MS) model adopts van der Waals radii to characterize a molecule. But in order to study metal materials by the MS model, we adopt metallic radii to characterize a metal cluster. The MS model defines a geometric description of the outer and inner boundaries of an atom cluster. The molecular surface is a smooth network of convex and reentrant faces traced by the inward-facing part of a probe sphere as it rolls over the cluster [18]. The volume obtained by the MS model is also called the solvent excluded volume [19]. It is a spatial region from which the solvent is excluded by the presence of the molecule (atom cluster). The solvent is also modeled as a hard sphere and chosen as a probe sphere. The solvent excluded volume is the van der Waals volume plus the interstitial volume. The interstitial consists of packing defects between atoms that are too small to admit a probe sphere. The MS model can characterize defect structures in a metal cluster if an appropriate probe sphere is selected. This means that the MS model is suitable for describing the occupied volume of a metal cluster. Another advantage of the MS model is that the surface it generates is smooth, which facilitates subsequent multiscale calculations of physical and chemical properties for a metal cluster.

To illustrate the MS model more intuitively, figure 2 shows the generated surfaces of alpha iron (α-Fe), copper (Cu), and magnesium (Mg) unit cells based on the MS model. The figure shows the relationship between the overall surface and its individual components, convex faces, saddle faces, concave faces. Every complete cluster surface is composed of these three components. The variables in the table 1 are used to characterize these components [18, 19].

The MS model variables are given in table 1 [18, 19]. A torus between atoms i and j is generated as a probe sphere rolls around the pair of atoms. The torus has an axis \( \mathbf{u}_{ij} \), center \( \mathbf{t}_{ij} \), and radius \( r_{ij} \). The circle of contact between atom i and the probe sphere has a center \( c_{ij} \), radius \( r_{ij} \), and signed displacement \( d \) from the center of atom i to center \( c_{ij} \). A tetrahedron is generated when the probe is simultaneously tangent to three atoms i, j, and k. Its vertices are the centers of the probe and atoms i, j, and k, and the base triangle connects the three atom centers. \( P_{ij} \) is the center of the probe and is at a height \( h_{ij} \) above a base point \( b_{ij} \) lying on the base triangle. \( \psi_{ij} \) is a vertex of a concave triangle, which is the contact point between the probe and atom i. Concave triangles meet convex faces at those vertices. \( \beta_{ij} \) and \( \alpha_{ij} \) are the interior angles of a concave triangle and convex face.
respectively. \( \varphi \) is the angle of a saddle face wrapping around the torus axis. \( \theta_i \) is the saddle width angle of a saddle face bordering a convex edge on atom \( i \). These variables will be explained in detail later in the calculations of cluster/atom surface area and volume.

3. Surface area calculations

3.1. Metal cluster surface area

Based on the MS model, we can generate an outer surface for a metal cluster, which makes the concept of metal cluster volume meaningful. The surface of a metal cluster consists of three types of faces: concave, saddle, and convex faces, as shown in figure 2. The surface area of a metal cluster is

\[
A_C = \sum C^- + \sum s A_i + \sum C^+,
\]

where \( A_C^- \) is a concave face area, \( A_i \) is a saddle face area, and \( A_C^+ \) is a convex face area [18]. The face areas of those three types can be calculated by using the radii and angles presented in table 1.

Figure 3(a) shows a concave face, it is a spherical triangle, and its boundaries are three concave arcs. The area of a concave face is

\[
A_C^- = \frac{r_p^2}{2} \left( \sum \beta_v - \pi \right), \quad v \in \{i, j, k\},
\]

where \( r_p \) is the probe radius and \( \beta_v \) is a concave triangle angle [18].

| Variable name                        | Value                                                                 |
|--------------------------------------|----------------------------------------------------------------------|
| Atomic coordinate                   | \( a_i, a_j, a_k, \ldots \) (input)                                 |
| Metallic radii                      | \( r_p, r_v, r_c, \ldots \) (input)                                 |
| Probe radius                         | \( r_p \) (input)                                                   |
| Interatomic distance                 | \( d_{ij} = |a_i - a_j| \)                                           |
| Torus axis unit vector               | \( u_p^i = (a_i - a_j)/d_{ij} \)                                    |
| Torus center                         | \( t_{ij} = \frac{1}{2}(a_i + a_j) + \frac{1}{2}(a_i - a_j) \times \left[(r_i + r_p)^2 - (r_i + r_p)^2/d_{ij}^2 \right] \) |
| Torus radius                         | \( r_p = \frac{1}{2}(r_i + r_j + 2r_p)^2 - d_{ij}^2/2 \) |
| Base triangle angle                  | \( \omega_{jk} = \arccos(u_{jk} \cdot u_{ik}) \)                      |
| Base plane normal vector             | \( u_{jk} = u_i \times u_k / \sin \omega_{jk} \)                      |
| Torus-basepoint unit vector          | \( u_{jk} = u_{jk} \times u_{ij} \)                                 |
| Base point                           | \( b_{jk} = t_{jk} + u_{jk}(u_{jk} \cdot (t_{jk} - t_{ij})) / \sin \omega_{jk} \) |
| Probe height                         | \( h_{jk} = [(r_i + r_p)^2 - |b_{jk} - a_j|^2]/2 \)                   |
| Probe position                       | \( p_{jk} = b_{jk} \pm h_{jk} u_{jk} \)                             |
| Vertex                               | \( \psi_{jk} = (r_s p_{jk} + r_{jk} a_i)/(r_i + r_p) \)                 |
| Contact circle center               | \( c_{ij} = (r_s t_{ij} + r_{jk} a_i)/(r_i + r_p) \)                  |
| Contact circle radius               | \( t_e = r_s n_i / (r_i + r_p) \)                                   |
| Contact circle displacement          | \( d_{ei} = u_{jk} \cdot (c_{ij} - a_j) \)                           |
| Concave arc plane normal vector      | \( n_{jk} = (p_{jk} - t_{ij}) \times u_{jk} / r_i \)                  |
| Concave triangle angle               | \( \beta_v = \arccos(n_{jk} \cdot n_{ik}) \)                         |
| Convex face angle                    | \( \alpha_v = \pi - \beta_v \)                                     |
| Saddle wrap angle                    | \( \varphi_v = \arccos(n_{jk} \cdot n_{ik}) \) when \( n_{jk} \times n_{ik} \cdot u_{ij} \geq 0 \); \( = -\arccos(n_{jk} \cdot n_{ik}) + 2\pi \) when \( n_{jk} \times n_{ik} \cdot u_{ij} < 0 \) |
| Saddle width angle                   | \( \theta_i = \arctan(d_{i} / r_i) \)                                |
| Euler characteristic                 | \( \chi = 2 - \) number of cycles                                   |

Table 1. Surface definition equations [18, 19]. Reprinted with permission from [19]. Copyright (1985) American Chemical Society.
Figure 3 shows two saddle faces. A saddle face is part of a torus surface, and its boundaries are convex and concave arcs. The area of a saddle face is

\[ A_s = \varphi \left( r_i r_{ij} (\theta_{ij} + \theta_{ji}) - r_i^2 (\sin \theta_{ij} + \sin \theta_{ji}) \right), \]

where \( \varphi \) is a saddle wrap angle, \( r_i \) is a torus radius, and \( \theta_{ij} \) and \( \theta_{ji} \) are saddle width angles [18].

Figure 3(c) shows two convex faces, and their boundaries are cycles of convex arcs. Convex faces are generated for each partially or wholly accessible atom. Interior atoms generate no surface. The area of a convex face is

\[ A_c = r_i^2 \left[ 2\pi \chi + \sum_s \phi_s \sin \theta_s - \sum_v (\pi - \alpha_v) \right], \]

where \( r_i \) is an atom radius and \( \alpha_v \) is a convex angle [18]. Figure 3(d) shows the relationship between \( \alpha_v \) and \( \beta_v \) at vertex \( v \).

3.2. Atomic surface areas of a metal cluster

Here, the atomic surface refers to the surface of an atom occupied volume. There are two types of atoms in a cluster: boundary atoms and interior atoms. Here, the variational Voronoi tessellation is defined. Based on that tessellation and MS model, we can define the individual atomic surfaces for both boundary atoms and interior atoms.

3.2.1. The surface area of an interior atom

As mentioned above, the normal Voronoi cell is not suitable as the occupied volume of an interior atom. We define a variational Voronoi cell of atom \( i \) using a new distance instead of the Euclidean distance.
where the faces of the variational Voronoi cell are planes perpendicular to the lines between atom $i$ and its adjacent atoms, and the planes pass through the torus centers $t_{ij}$ on the lines.

Figure 4 shows Voronoi tessellations of a cluster, all interior Voronoi cells are colored. Atom $i$ is located in the center, its radius is smaller than other atoms, and the radii of other atoms are the same. Figure 4(a) shows the normal Voronoi tessellation using the Euclidean distance, all interior Voronoi cells are the same size. Figure 4(b) shows the variational Voronoi tessellation using distance equations (5), (6), the Voronoi cell of atom $i$ is smaller than other interior Voronoi cells. This means that variational Voronoi cells can reflect the effect of atom sizes. From the perspective of atomic physics, the larger the atom is, the larger the region it affects. Therefore, the variational Voronoi cell is more suitable as the interior atom occupied volume than the normal cell.

The faces of a variational Voronoi cell are polygons. The surface area of a cell is the sum of those polygonal areas that can be calculated using the vertices of the cell. There are two ways to describe a variational Voronoi cell: one is by a set of inequalities, and the other is by vertex coordinates. Equations (5) and (6) describe a variational Voronoi cell by a set of inequalities. Through the primal–dual methods [42, 43], the inequalities can be transformed into a set of vertices of the Voronoi cell.

3.2.2. The surface area of a boundary atom

As shown in figure 5, the surface of a boundary atom consists of six parts: partial concave faces, partial saddle faces, convex faces, interior faces, concave supplementary faces and saddle supplementary faces. The surface area of atom $i$ is

$$A_i = \sum_{c^+_{ij}} A_{c^+_{ij}} + \sum_{s_i} A_{s_i} + \sum_{c^-_{ij}} A_{c^-_{ij}} + \sum_{n_i} A_{n_i} + \sum_{l_i} A_{l_i} + \sum_{k_i} A_{k_i},$$

where $c^-_{ij}$, $s_i$, $c^+_{ij}$, $n_i$, $l_i$, and $k_i$ represent a partial concave face, partial saddle face, interior face, concave supplementary face, and saddle supplementary face, respectively.

A concave face is shared by three atoms, as shown in figure 6(a). It should be divided into three parts. Each partial concave face belongs to the corresponding atom. There is one torus between every two atoms. Three tori converge at the concave face. The middle longitudinal sections of those tori intersect at a point $c_{ijk}$ on the concave face, and they divide the concave face into three parts, $c^-_{ij}$, $c^+_{ij}$, and $c_{ijk}$, each of which corresponds to atoms $i$, $j$, and $k$, respectively. The area of a partial concave face $c^-_{ij}$ is

$$A_{c^-_{ij}} = r_p^2 \cdot (\beta_i + \gamma_i - \pi),$$

where $\beta_i$ is a concave triangle angle corresponding to atom $i$, and $\gamma_i$ is an interior angle on $c_{ijk}$.
Figure 5. The surface of a boundary atom (dark yellow, convex volume; dark green, partial concave volume or partial saddle volume; shaded, atomic interior volume).

Figure 6. The components of a boundary atom surface. (a) The vertical view of a concave face, (b) a saddle face between atoms \( i \) and \( j \), (c) two concave supplementary faces, and (d) a saddle supplementary face.
A saddle face is shared by two atoms, as shown in Figure 6(b). It should be divided into two parts. Each partial saddle face belongs to the corresponding atom. A saddle face is a part of the torus that is between atoms i and j. The middle longitudinal section of the torus divides the saddle face into two parts that belong to atoms i and j respectively, denoted as partial saddle faces $s_i$ and $s_j$. The area of $s_i$ is

$$A_{s_i} = \varphi \beta \rho (r_i \theta_{ij} - r_j \sin \theta_{ij}), \quad (9)$$

where $\varphi \beta$ is a saddle wrap angle, $r_i$ is a torus radius, and $\theta_{ij}$ and $\theta_{ji}$ are saddle width angles.

As shown in Figure 5, a convex face only relates to a single atom, its area is completely contained in that atom surface area. A convex face area is given by equation (4).

In Figure 5, interior faces are red lines of the gray region, which are inside the cluster. Essentially, an interior face is a part of the variational Voronoi partition plane between two atoms. Assuming that atom i forms a torus with atom j, the inequalities describing the shaded region of atom i are

$$\begin{align*}
\mathbf{x} \cdot \mathbf{v}_i &\leq \mathbf{t}_{ij} \cdot \mathbf{v}_j \quad \text{for all } j,
\mathbf{x} \cdot \mathbf{n}_h &\leq \mathbf{a}_i \cdot \mathbf{n}_h \quad \text{for all } T_h,
\end{align*} \quad (10)$$

where $\mathbf{x}$ is a point in the shaded region, $\mathbf{t}_{ij}$ is a torus center between $\mathbf{a}_i$ and $\mathbf{a}_j$, $\mathbf{v}_j$ is a unit direction vector from $\mathbf{a}_j$ to $\mathbf{a}_i$, $\mathbf{T}_h$ is a triangle formed by three boundary atoms (including atom i), and $\mathbf{n}_h$ is an outward unit normal vector of $\mathbf{T}_h$. The above first inequality represents the variational Voronoi cell of atom i, the second inequality represents the region towards the interior of cluster, which is separated by the triangles having atom i as a vertex. Similar to calculating the face areas of an interior-atom variational Voronoi cell above, the primal–dual methods [42, 43] can be used to convert equalities equation (10) to vertices of the shaded region. Then, interior face areas can be obtained.

For a boundary atom, each related concave face produces two supplementary faces, called concave supplementary faces. Figure 6(c) shows concave supplementary faces as shaded areas. A concave supplementary face is the intersection of a torus middle section and the region between a concave face and triangle base. In fact, it lies on an unbound face of the Voronoi cell of a boundary atom. A concave supplementary face area $A_{cs}$ is

$$A_{cs} = A_{vi} + A_{d}, \quad (11)$$

$$A_{v} = (h_{ijk}/2)\|(r_i + r_j)^2 - \|\mathbf{t}_{ij} - \mathbf{a}_i\|^2 - h_{ijk}^2/2\| - (r_j^2/2)\times$$

$$\arccos(h_{ijk}/\|(r_i + r_j)^2 - \|\mathbf{t}_{ij} - \mathbf{a}_i\|^2 \|/2), \quad (12)$$

where $A_{vi}$ and $A_{d}$ are calculated in the same way (a triangle minus a sector), and the formula of $A_{d}$ can be obtained by simply transforming equation (12).

Each saddle face produces a supplementary surface called the saddle supplementary face. A saddle supplementary face is the intersection of a saddle piece (as defined hereinafter), and the corresponding torus middle section, as shown in Figure 6(d). A saddle supplementary face area $A_{s}$ is

$$A_{s} = \frac{1}{2} \varphi \beta (r_j - r_j)^2, \quad (13)$$

cwhere $\varphi \beta$ is a saddle wrap angle and $r_j$ is a torus radius.

4. Volume calculations

4.1. Metal cluster volume

According to the MS model definition and face area equations, we can analytically calculate the MS volume. As shown in Figure 2, the MS volume of a cluster can be divided into four parts: interior polyhedron, convex pieces, saddle pieces, and concave pieces. A cluster volume is

$$V_c = V_i + \sum_i V_c^i + \sum_i V_c^s + \sum_i V_c^c, \quad (14)$$

where $V_c^i$ is the interior polyhedron volume, $V_c^s$ is a convex piece volume, $V_c^s$ is a saddle piece volume, and $V_c^c$ is a concave piece volume [19].

The interior polyhedron is inside the cluster surface, and it can be derived from the surface. For each concave triangle of the surface, a flat triangle is constructed between the centers of the three atoms that the concave triangle bridges. Those flat triangles define the interior polyhedron. As shown in Figures 7(a)(b), the interior polyhedron volume is

$$A_f = 1/2d_{ij}d_{ik} \sin \omega_{ijk}, \quad (15)$$

where $d_{ij}$ and $d_{ik}$ are distances between atoms i, j, and k.
where \( A_f \) is the area of a base triangle between the centers of atoms \( i, j \) and \( k \), \( \mathbf{u}_{ijk} \) is a triangle face normal vector, and \( z \) is a unit vector pointing along the positive z-axis [19].

A convex piece is the volume between the center of an atom and its convex face, shown in figure 7(c). A convex piece volume is

\[
V_{c^+} = \frac{1}{3} r_f A_{c^+},
\]

where \( A_{c^+} \) is a convex face area [19].

A saddle piece (shaded part in figure 6(b)) is between two atoms \( i, j \), and it can be divided into four parts. Between the center of each atom and its circle of contact with a probe sphere is a sector of cone. Between these two conical pieces is a sector of the hole inside the torus, which for ease of later computing the atom occupied volume is divided into two parts lying on each side of the plane bisecting the torus. The volume of a saddle piece is

\[
V_s = V_{si} + V_{sj} + V_{ij} + V_{ji},
\]

\[
V_{si} = (\phi_i / 6) r_i^3 \sin \theta_i \cos^2 \theta_i,
\]

\[
V_{sj} = (\phi_j / 2)[r_j^2 t_p \sin \theta_{ij} - r_p t_p^2 (\sin \theta_{ij} \cos \theta_{ij} + \theta_{ij}) + (r_p^2 / 3) \times (2 \sin \theta_{ij} \cos^2 \theta_i + 2 \sin \theta_{ij})].
\]

where \( V_s \) and \( V_j \) can be obtained by simply transforming equations (19), (20) [19].

A concave piece is the volume of a triangular pyramid minus the volume of a part of the probe sphere, shown in figure 7(d). The volume of a concave piece is

\[
V_{c^-} = \frac{1}{3} (h_{ijk} A_f - r_p A_{c^-}),
\]

where \( A_{c^-} \) is a concave face area [19].
4.2. Atomic volumes of a metal cluster
As mentioned above, there are two types of atoms in the cluster: boundary atoms and interior atoms. Different types of atoms calculate their volumes in different ways.

4.2.1. The volume of an interior atom
As with atomic surface area calculations above, the variational Voronoi cell is regarded as the interior atom occupied volume. The vertices of a variational Voronoi cell can be obtained by equations (5), (6) and the primal–dual methods [42, 43]. The volume of a variational Voronoi cell can be computed by dividing it into a set of pyramids. Each pyramid has a face of the polyhedron as its base and the center of the polyhedron as its apex.

Therefore, the Voronoi cell volume for an interior atom \( i \) is

\[
V_i = \sum_j A_{ji} d_j / 3, \tag{22}
\]

where \( A_{ji} \) is a face area of the Voronoi cell and \( d_j \) is a distance from the center of the cell to a face \( F_j \).

4.2.2. The volume of a boundary atom
The normal Voronoi cell of a boundary atom may be unbounded, thus it cannot represent the occupied volume of a boundary atom. The surface of a boundary atom we defined above encloses a bounded region, and the larger the atom is, the larger the enclosed region. This enclosed region can be regarded as the occupied volume of a boundary atom.

As shown in figure 5, the volume of a boundary atom is divided into four parts

\[
V_i = V_{ii} + \sum_s V_{i+s} + \sum_s V_{i-s} + \sum_s V_{i-s}, \tag{23}
\]

where \( V_{ii} \) is the atomic interior volume, \( V_{i+s} \) is a convex volume, \( V_{i-s} \) is a partial saddle volume, and \( V_{i-s} \) is a partial concave volume.

The atomic interior volume of a boundary atom (figure 5) is the intersection of its variational Voronoi cell and the interior polyhedron of a cluster. We obtain the inequalities of the interior part of a boundary atom by equation (10). Through the primal–dual methods [42, 43], we calculate the vertices of the interior part and further calculate its volume, denoted as \( V_{ii} \).

A convex piece is only related to an atom (figure 5). Therefore, the corresponding volume can simply be assigned to that atom. The volume formula is given by equation (17).

A partial saddle volume is a part of the volume of a saddle piece. A saddle piece (figures 5 and 6(b)) is relevant to two atoms. A saddle piece volume should be split into two parts according to a certain rule. Here, we split the saddle piece by the middle section of the torus between the two atoms. Each part volume is assigned to the corresponding atom. For a torus piece between atoms \( i \) and \( j \), a partial saddle volume for atom \( i \) is

\[
V_{ii} = V_{ij} + V_{ii}, \tag{24}
\]

where \( V_{ij} \) and \( V_{ii} \) are given by equations (19), (20).

A partial concave volume is a part of the volume of a concave piece, as shown in figures 5 and 8. A concave piece is relevant to three atoms, so a concave piece volume can be divided into three parts and each part volume is assigned to the corresponding atom. A concave face corresponds to a base triangle. The middle sections of tori related to a concave face divide the concave and base triangle into three parts, respectively. For a concave piece generated by atoms \( i, j, \) and \( k \), the intersections of three middle sections on the concave face and base triangle are points \( c_{ijk} \) and \( b_{ijk} \). Therefore, the concave piece is divided into three parts by three middle sections, denoted as \( V_{c_{ij}}, V_{c_{jk}}, \) and \( V_{c_{ki}} \). A partial concave volume for atom \( i \) is

\[
V_{c_{ij}} = 1/3(h_{ijk} A_{fi} - r_p A_{c_{ij}}) \tag{25}
\]

where \( A_{c_{ij}} \) is given by equation (8).

5. Self-intersecting surface problem
A saddle face intersects itself when the torus radius is less than the probe radius, as shown in figure 9. It can also lead to two concave faces interpenetrating. Therefore, the calculation of the surface area and spatial occupied volume of affected atoms must be wrong. These problems typically occur in deep grooves [18, 44]. The precise solution to this problem will be discussed in the next paper. At present, there is an approximate solution. The surface area and occupied volume of an affected atom is taken as the average of those of the neighboring unaffected atoms within a small range.
6. Probe radius problem

The probe radius $r_p$ is artificially determined when constructing the surface area and volume of an atomic cluster. A larger radius makes the cluster surface smoother, and a smaller radius makes the surface present more details. Assuming that the radius of atom $i$ greater than $j$, if $r_p$ is relatively large, the middle longitudinal section of the torus between atoms $i$ and $j$ may directly pass through atom $j$. Obviously, we do not want that case to happen because the spherical volume of an atom itself should belong to its spatial occupied region. Therefore, the selection of $r_p$ needs to be carefully considered. In chemistry, the solvent molecule radius is often chosen as $r_p$ [16, 17, 44]. For a metal cluster, we generally choose the radius of the smallest atom in the cluster as $r_p$ because this selection can accurately characterize the metal cluster volume and ensure that the atom itself is completely located in the corresponding atom occupied region in most cases.

7. Numerical experiments

Stukowski’s [40, 41] method constructs a surface representation of the three-dimensional shape of a set of atoms. It generates a geometric description of the outer and inner boundaries of an atomistic solid in terms of a triangulated surface mesh. That geometric description of a surface is useful for quantitative measurements of the surface area and solid volume of a metal cluster. However, Stukowski’s method can only calculate the overall volume of a cluster, not the individual atomic volumes. Moreover, it treats atoms as points and does not consider the contribution of the atom sphere to the atomic volume. Based on Connolly’s method [18], Petitjean developed a fast analytical calculation method for the cluster surface and volume, which is implemented based on Monte Carlo method [21]. However, Petitjean’s method also can only calculate the overall volume of a cluster. Cazals [17] developed McConkey’s method and presented a robust algorithm for atomic volume calculation. Cazals’s method relies on the decomposition of the volume of the atom union into convex regions, namely the
restrictions of the balls to their regions in the power diagram. Cazals’s method is based on the SA model, mainly designed for the protein molecule. But for the metal cluster, that method ignores tiny spaces between atoms, which exist even when atoms are arranged closely. Therefore, the obtained atom occupied volumes in the metal cluster are inaccurate, and will affect the accuracy of subsequent multiscale calculations. LAMMPS defines the intersection of Voronoi cells with the simulation box as atomic volumes [6–10]. In a MD simulation, the simulation box shape is very important, it specifies the extent of the entire simulation system. The simulation box shape is not arbitrary, it is defined as a parallelepiped with triclinic symmetry. If the configuration is compatible with the simulation box, the calculation results of LAMMPS adopted volume method are reasonable; if not (such as cylindrical nanoparticles, cracks, and some complex configurations), LAMMPS adopted method is not working. The calculation results of LAMMPS adopted method are closely dependent on the size and location of the simulation box, which is not supposed to. Unreasonable volume calculation can lead to errors in the calculation of physical quantities in MD simulations, such as stress and strain energy density. Our method can accurately calculate the atomic volume. The calculations consider the effect of atom sizes and do not depend on the simulation box.

Here, we gave three numerical experiments of calculating atomic volumes for different shaped Cu crystals by Stukowski’s method, Petitjean’s method, Cazals’s method, LAMMPS adopted method and our method. The configurations were constructed by software Atomsk [45]. Noted that to obtain accurate atomic volumes, the prerequisite is to accurately calculate surface areas.

7.1. Nanopillar of cylindrical shape

Figure 10 is the configuration of a cylindrical Cu nanopillar with an orientation [010], black lines are the simulation box. The cylindrical nanopillar does not match the simulation box. We calculated the atomic volumes of this configuration by Stukowski’s method, Petitjean’s method, Cazals’s method, LAMMPS adopted method and our method respectively.

Figure 11(a) shows the configuration of the cross-section (100), figure 11(b) shows the results of Stukowski’s method, yellow circles are atoms, thick black lines are the generated nanopillar surface; figure 11(c) shows the results of Petitjean’s method, all the solid yellow circles together constitute the cluster occupied volume; figure 11(d) shows the results of Cazals’s method, solid yellow circles are atom occupied volumes, blue lines are the dividing lines of the Voronoi tessellation; figure 11(e) shows the results of LAMMPS adopted method, thick black lines are the simulation box; figure 11(f) shows the results of our method, red circles are probe spheres, thick black lines are the generated surface.

Table 2 gives the detailed calculation results for the entire configuration. Stukowski’s and Petitjean’s method could only calculate the overall nanopillar volume. Cazals’s method could calculate the overall volume and individual atomic volumes. However, the obtained volumes did not include the tiny spaces between atoms. LAMMPS adopted method could calculate the overall volume and individual atomic volumes. Since the simulation box contained empty space, the overall nanopillar volume of LAMMPS adopted method was significantly larger than other methods and the range of boundary atom volumes varied widely $3.00 \leq V \leq 70.11 \text{ Å}^3$, the average was 13.36, the standard deviation was 9.55. The calculation results of LAMMPS adopted method were very affected by the simulation box, especially for the atoms near the corners of the box. Our method also could calculate the overall volume and individual atomic volumes. Due to the generated nanopillar surface by the MS model, the calculation results of our method were not affected by the simulation box size and position.
The boundary atom volumes were consistent with interior atom volumes, namely the size of a boundary atom volume was not much different from an interior atom volume. The average atomic volume was 11.75, the standard deviation was only 0.18, which was much smaller than LAMMPS adopted method. Therefore, the atomic volume definition of our method was more reasonable than other methods.

7.2. Plate with a crack

Figure 12 shows a plate with an edge crack, the plate consists of Cu atoms, and black lines represent the simulation box. We used Stukowski’s method, Petitjean’s method, Cazals’s method, LAMMPS adopted method and our method to calculate the atomic volumes for the plate. Figure 13(a) shows atoms near the edge crack, yellow circle are atoms; figure 13(b) shows the results of Stukowski’s method, thick black lines are the part of the generated plate surface; figure 13(c) shows the results of Petitjean’s method, solid yellow circles together constitute the cluster occupied volume; figure 13(d) shows the results of Cazals’s method, solid yellow circles are atom occupied volumes; figure 13(e) shows the results of LAMMPS adopted method, thick black lines are the simulation box; and (f) the results of our method (red circles are probe spheres and thick black lines are the generated surface).

Figure 11. Atomic volumes of the Cu nanopillar. (a) The configuration of the cross-section (100), (b) the results of Stukowski’s method (yellow circles are atoms and thick black lines are the generated nanopillar surface), (c) the results of Petitjean’s method (all the solid yellow circles together constitute the cluster occupied volume), (d) the results of Cazals’s method (solid yellow circles are atom occupied volumes and blue lines are the Voronoi tessellation edges), (e) the results of LAMMPS adopted method (thick black lines are the simulation box), and (f) the results of our method (red circles are probe spheres and thick black lines are the generated surface).

| Spatial volume | Stukowski’s method | Petitjean’s method | Cazals’s method | LAMMPS adopted method | Our method |
|----------------|---------------------|---------------------|-----------------|------------------------|------------|
| The nanopillar | $1.32 \times 10^5$  | $1.10 \times 10^5$  | $1.10 \times 10^5$ | $1.69 \times 10^5$  | $1.48 \times 10^5$ |
| Atoms          |         |         | 8.75 | [3.00, 70.11] | [10.67, 11.94] |
| Average        |         |         | 13.36 | 11.75 |
| Standard deviation |         |         | 9.55 | 0.18 |
| Interior atoms |         |         | 8.75 | 11.81 |
| Boundary atoms |         |         | 8.75 | [3.00, 70.11] | [10.67, 11.94] |

Table 2. Atomic volumes of the nanopillar calculated by Stukowski’s method, Petitjean’s method, Cazals’s method, LAMMPS adopted method and our method (unit: Å³)

The boundary atom volumes were consistent with interior atom volumes, namely the size of a boundary atom volume was not much different with an interior atom volume. The average atomic volume was 11.75, the standard deviation was only 0.18, which was much smaller than LAMMPS adopted method. Therefore, the atomic volume definition of our method was more reasonable than other methods.

7.2. Plate with a crack

Figure 12 shows a plate with an edge crack, the plate consists of Cu atoms, and black lines represent the simulation box. We used Stukowski’s method, Petitjean’s method, Cazals’s method, LAMMPS adopted method and our method to calculate the atomic volumes for the plate. Figure 13(a) shows atoms near the edge crack, yellow circle are atoms; figure 13(b) shows the results of Stukowski’s method, thick black lines are the part of the generated plate surface; figure 13(c) shows the results of Petitjean’s method, solid yellow circles together constitute the cluster occupied volume; figure 13(d) shows the results of Cazals’s method, blue lines are the Voronoi tessellation edges, solid yellow circles are atom occupied volumes; figure 13(e) shows the results of LAMMPS adopted method, thick black lines are the part of the simulation box; figure 13(f) shows the results of our method, thick black lines are the part of the generated plate surface.
Figure 12. A Cu plate with an edge crack (black lines are the simulation box).

Figure 13. Atomic volumes of the plate near the crack. (a) The configuration of the plate near the crack, (b) the results of Stukowski’s method (thick black lines are the generated surface), (c) the results of Petitjean’s method (all the solid yellow circles together constitute the cluster occupied volume), (d) the results of Cazals’s method (solid yellow circles are atom occupied volumes and blue lines are the Voronoi tessellation edges), (e) the results of LAMMPS adopted method (thick black lines are the simulation box), and (f) the results of our method (red circles are probe spheres and thick black lines are the generated surface).

Table 3. Atomic volumes of the plate calculated by Stukowski’s method, Petitjean’s method, Cazals’s method, LAMMPS adopted method and our method (unit: Å³).

| Spatial volume     | Stukowski’s method | Petitjean’s method | Cazals’s method | LAMMPS adopted method | Our method |
|--------------------|--------------------|--------------------|-----------------|-----------------------|------------|
| The plate          | $1.05 \times 10^5$ | $9.27 \times 10^4$ | $9.27 \times 10^4$ | $1.08 \times 10^5$    | $1.24 \times 10^5$ |
| Atoms              | —                  | —                  | 8.75            | [1.54, 29.53]         | [10.40, 11.94] |
| Average            | —                  | —                  | —               | 10.17                 | 11.72      |
| Standard deviation | —                  | —                  | —               | 3.38                  | 0.16       |
| Interior atoms     | —                  | —                  | 8.75            | 11.81                 | 11.81      |
| Plate boundary atoms| —                  | —                  | 8.75            | [1.54, 6.00]          | [10.40, 11.57] |
| Crack surface atoms| —                  | —                  | 8.75            | [6.48, 29.53]         | [10.40, 11.94] |
Table 3 gives the detailed calculation results for the entire plate. Stukowski’s method and Petitjean’s method could only calculate the overall volume. Cazals’s method could calculate the overall volume and individual atomic volumes, but it did not consider the tiny spaces between atoms. LAMMPS adopted method did not consider the sizes of atoms themselves, the simulation box directly passed through plate boundary atom centers. So, the occupied volumes of plate boundary atoms were significantly smaller than interior atoms. For the crack surface atoms, the atomic volumes of LAMMPS adopted method obviously included extra space, incorrectly making those atomic volumes larger. Therefore, LAMMPS adopted method could not accurately calculate occupied volumes of plated boundary atoms and crack surface atoms. It obtained a wide range of atomic volumes, the standard deviation was as high as 3.38. Our method solved that problem by strictly following the atomic volume definition given by MS model. The plate cluster surface generated by the MS model was tightly close to boundary atoms, so the calculated atomic volumes did not include extra space or lose necessary space. The atomic volume distribution obtained was consistent, the standard deviation was only 0.16.

7.3. Complex shaped configuration
Figure 14(a) shows a dog-shaped configuration, it consists of Cu atoms and black lines represent the simulation box; The yellow spheres constitute the cluster occupied volume in the Petitjean’s and Cazals’ methods), (b) the surface generated by Stukowski’s method, and (c) the surface generated by our method.

Table 4 gives the detailed calculation results for the entire plate. Stukowski’s method and Petitjean’s method could only calculate the overall volume. Cazals’s method could calculate the overall volume and individual atomic volumes, but it did not consider the tiny spaces between atoms. LAMMPS adopted method did not consider the sizes of atoms themselves, the simulation box directly passed through plate boundary atom centers. So, the occupied volumes of plate boundary atoms were significantly smaller than interior atoms. For the crack surface atoms, the atomic volumes of LAMMPS adopted method obviously included extra space, incorrectly making those atomic volumes larger. Therefore, LAMMPS adopted method could not accurately calculate occupied volumes of plated boundary atoms and crack surface atoms. It obtained a wide range of atomic volumes, the standard deviation was as high as 3.38. Our method solved that problem by strictly following the atomic volume definition given by MS model. The plate cluster surface generated by the MS model was tightly close to boundary atoms, so the calculated atomic volumes did not include extra space or lose necessary space. The atomic volume distribution obtained was consistent, the standard deviation was only 0.16.

| Spatial volume | Stukowski’s method | Petitjean’s method | Cazals’s method | LAMMPS adopted method | Our method |
|---------------|-------------------|------------------|----------------|----------------------|------------|
| The cluster   | $2.91 \times 10^5$ | $2.44 \times 10^5$ | $2.44 \times 10^5$ | $1.31 \times 10^6$ | $3.27 \times 10^5$ |
| Atoms         | —                 | —                | 8.75           | [6.00, 18801.90]     | [8.75, 12.13] |
| Average       | —                 | —                | 47.02          | 11.73                |
| Standard deviation | —            | —                | 294.75         | 0.22                 |
| Interior atoms | —                 | —                | 11.81          | 11.81                |
| Boundary atoms | —                 | —                | 8.75           | [6.00, 18801.90]     | [8.75, 12.13] |

Table 4. Atomic volumes calculated by Stukowski’s method, Petitjean’s method, Cazals’s method, LAMMPS adopted method and our method (unit: Å³).
8. Conclusion

In multiscale research, researchers pay much attention to the calculation of macroscopic physical quantities from microscopic models. The atomic volume and surface area are important intermediate quantities to calculate macroscopic quantities. This paper proposes a multiscale calculation method for atomic volumes and surface areas of a metal cluster based on the MS model. There are two atom types in the cluster: interior atoms and boundary atoms. For an interior atom, the method defines a variational Voronoi cell as its volume. The variational Voronoi cell is affected by the atom sphere size: the larger the atom sphere, the larger the cell. For a boundary atom, the method defines the intersection of the overall cluster volume and its variational Voronoi cell as its occupied volume. The atomic surface calculations are along with the atomic volume calculations. Finally, we provided numerical examples of a Cu cylindrical nanopillar, plate with a crack, and dog-shaped cluster. We compared our method with Stukowski’s method, Petitjean’s method, Cazals’s method, LAMMPS adopted method. Our method could accurately calculate atomic volumes, even for the atoms on the cluster boundaries and defects. From the numerical results, our method was superior to other methods because it considered the effect of atom sizes and did not rely on the simulation box size and location.

In fact, there is no standard definition of metal cluster surface/volume in molecular dynamics simulations. Thus, there is no absolute way to prove that the results for cluster surfaces and volumes obtained by our method are correct. But we still think that our method is physically reasonable, because its ideas come from the MS model [18, 19] that has achieved good results in calculating protein surfaces/volumes. It fully takes into account the characteristics of metal clusters and avoids the obvious shortcomings of the existing volume calculation methods. The reasonable cluster surfaces/volumes can be used to calculate the macroscopic quantities from the microscale structures according to multiscale theory. In the future research, we plan to calculate the elastic constants, heat capacities and thermal expansions of a metal cluster by our volume calculation method and EAM potentials, then compare these results with the experimental results to further prove the effectiveness and correctness of our method from a physical perspective.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Declarations of interest

None.

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