Geometrical percolation of hard-core ellipsoids of revolution in the continuum

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The percolation threshold of hard prolate ellipsoids of revolution dispersed in a continuum is obtained as a function of the aspect ratio. First random close packing of ellipsoids is produced by a dropping-and-shaking protocol. Two ellipsoids are regarded as connected when they come sufficiently close. Then a given fraction of ellipsoids selected randomly is removed and percolation of remaining ellipsoids is investigated as the fraction of remaining ellipsoids is varied. It is shown that the critical volume fraction of the colored ellipsoids is a decreasing function of the aspect ratio and that the aspect ratio dependence is well fitted by the inverse of the interaction range determined by the surface area and the radius of gyration of the ellipsoid surface.

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I. INTRODUCTION

Percolation in the continuum has been studied for a long time because of its importance in practical applications [1–3]. In most studies, discrete sites are distributed randomly in a continuous space and a fixed interaction range is assumed. Two sites which are within their interaction regions are assumed to be connected, and clusters are constructed by mutually connected sites. The main interest is the condition that there exist an infinitely extending, or percolating, channel which plays an important role in determining the transport properties of the system. The guiding principle for the continuum percolation is the critical volume (area in two dimensions) fraction which is thought to approximately be a dimensional invariant. Namely, when the volume fraction occupied by the objects exceeds a critical value, then the objects form a percolating cluster.

Analyzing the standard percolation process on lattices, Scher and Zallen suggested for spherical objects that the critical volume fraction is ~15.4% in three dimensions and the critical area fraction is ~44% in two dimensions [4]. It is, however, now known that the critical volume fraction depends on the shape of objects. In fact, it has been shown that the critical volume fraction depends on the polydispersity for spherical objects [5] and on the aspect ratio for nonspherical objects [6]. Similar universal behavior was proposed by Pike and Seager [7] for interpenetrating circles and spheres. They found that the critical average number of bonds per site, or the critical bond number, is approximately a dimensional invariant. Balberg *et al.* [8] extended this idea and concluded that the total excluded volume and area are invariants for soft-core objects of a given shape. There have been several papers which treat the percolation of overlapping ellipsoidal objects, and a suggestion was made that the critical density can be correlated with the excluded volume of the objects, though the correlation is not perfect [9,10].

In modern materials sciences, dispersing foreign objects in a host material is one of the most commonly used methods to control its functionality. For example, the percolation process of carbon nanotubes dispersed in polymers has been investigated and it is found that the percolation threshold strongly depends on the aspect ratio, spatial distribution, orientation, etc. [11]. In practical applications of percolation to materials, we must take account of the geometrical constraint due to the shape of the percolating objects which excludes other objects from a certain vicinity of a given object, and therefore we have to investigate the percolation of hard-core objects. This situation is in clear contrast to applications of percolation to social phenomena such as spread of epidemics and rumor [12], where it is natural to assume that the interaction range can overlap, and the Swiss-cheese-type model [13].

In this paper, we study geometrical percolation of the suspension of hard-core ellipsoids in a continuum by Monte Carlo simulation. We consider prolate ellipsoids of revolution and obtain the critical volume fraction as a function of the aspect ratio. In Sec. II, we explain the model system and method of computer simulation. In order to produce suspension of ellipsoids in the continuum, we exploit the packing and percolation procedure [5]. We present the results of simulation in Sec. III, where the critical volume fraction is determined by the finite-size scaling method. In Sec. IV, we analyze theoretically the critical volume fraction on the basis of various properties of the ellipsoid and show that the critical volume fraction is best correlated with the interaction range determined by the surface area and the radius of gyration of the surface at least for the aspect ratio studied here. Section V is devoted to a discussion.

II. MODEL AND PACKING-AND-PERCOLATION PROCEDURE

We are interested in a system where hard-core objects are dispersed in a continuum with a given volume fraction. We consider two objects are connected when they touch each other. (In practical calculations, we assume two objects are connected when they come close within a certain distance.) The questions are if there exists a channel of mutually connected objects which spans the entire system—i.e., a percolation channel—and what the critical volume fraction of the objects is above which there exists always an infinitely ex-

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tending channel and how the critical volume fraction depends on the shape of objects.

In this paper, we investigate the percolation of suspended hard-core ellipsoids of revolution. It is a very time-consuming process to put the objects one by one up to a certain volume fraction because no overlap of two objects is allowed. Furthermore, if one tries to place one object without overlapping other objects, some correlation in the distribution might be introduced unintentionally. In order to avoid this difficulty and to mimic dispersing the objects randomly in a continuum with the same density, we exploit the packing and percolation procedure [5]. In this procedure, we first produce a dense packing of the objects in the continuum, where there is a percolating channel of the objects. Then, we select an object randomly from the packed structure and remove it to reduce the volume fraction of the objects. This process is repeated until the volume fraction becomes far below the critical value at which the percolating channel ceases to exist. We emphasize that this procedure is exactly the same as the site percolation process on lattices, where circles or spheres with radii of half of the lattice constant are inscribed about the lattice sites and a connection between randomly selected objects is observed. In the present study, we focus on prolate ellipsoids of revolution

$$\frac{x^2}{a^2}+\frac{y^2}{b^2}+\frac{z^2}{b^2}=1, \tag{1}$$

where the aspect ratio $\alpha \equiv \frac{a}{b} \geq 1$ is a parameter and $ab^2 \equiv \ell_0^3$ is fixed to keep the volume of the ellipsoid constant. Here, ℓ_0 is taken as the unit of length.

III. RESULTS

We prepared an $L \times L \times 4L/3$ cubic box with the long edge in the vertical direction and first produced random dense packing of ellipsoids of a given aspect ratio using MACRO PAC of Intelligensys Ltd (North Yorkshire, U.K.), where we used the dropping and shaking processes to enhance the packing fraction. This software uses an algorithm identical to one introduced by Soppe [14]. An ellipsoid in a random direction is introduced far above the simulation cell and is dropped to the bottom until its center reaches the bottom of the cell or it touches other ellipsoids settled earlier. Then, using the Monte Carlo method, its position is lowered with other orientations until it is settled. Note that the structure produced by this procedure is not the maximally random jammed structure [15]. Figure 1(a) shows an example of the random structure we obtained for $\alpha=5$. We imposed periodic boundary conditions on the horizontal directions and the soft boundary at the bottom where an ellipsoid can settle at its position if the center of gravity of the ellipsoid is within the simulation box. The top of the simulation box was assumed to be free boundary. Setting the observation box to $L \times L \times L$, ignoring $L/15$ from the bottom and $4L/15$ from the top, we obtained the packing fraction ϕ as a function of the aspect ratio which is shown in Fig. 2. When the aspect ratio α is increased from unity, the packing fraction increases initially and then decreases as α is increased further. This behavior agrees with observations in the literature [16,17].

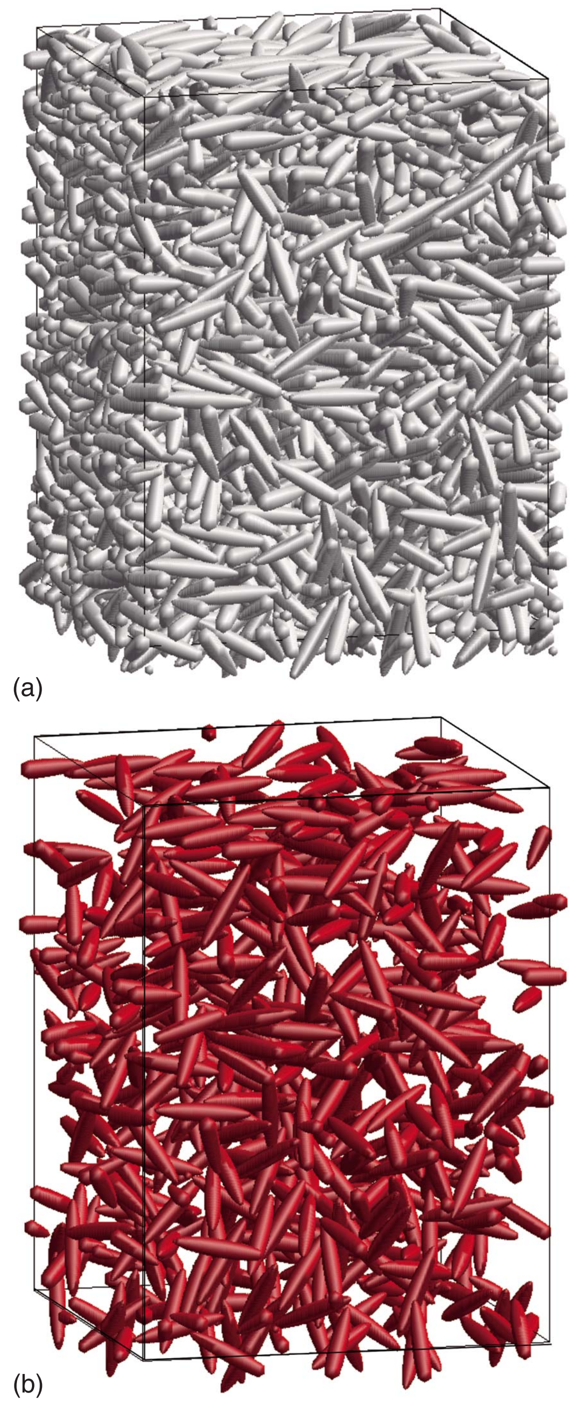

FIG. 1. (Color online) (a) Random dense packing of ellipsoids generated by MACRO PAC for $\alpha=5$. (b) Ellipsoids randomly selected are removed and the connectivity of the remaining ellipsoids is investigated. The fraction of the remaining ellipsoids is $p=0.2$. The box shows the simulation cell $L \times L \times \frac{4L}{3}$. The observation cell is $L \times L \times L$, where $\frac{L}{15}$ from the bottom and $\frac{4L}{15}$ from the top are ignored.

In order to investigate the percolation process, we first connect two ellipsoids whose distance is sufficiently small. In order to compensate for the fact that the structure is not the maximally random jammed one, we assumed that the

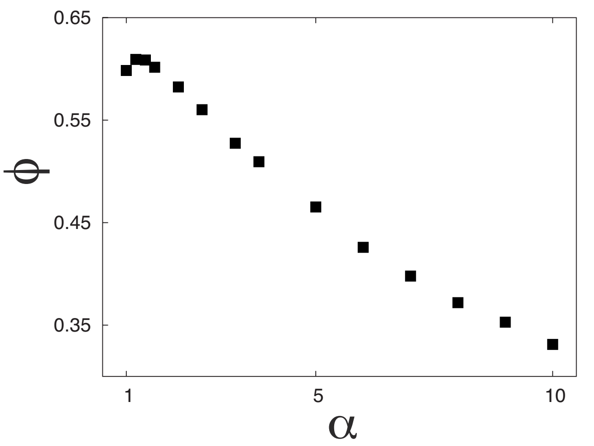

FIG. 2. Dependence of the packing fraction on the aspect ratio.

interaction range is a similar ellipsoid whose three axes are 5% longer than the core ellipsoid and that two ellipsoids whose interaction ranges overlap are connected. This relaxed condition may make the critical percolation concentration smaller, but the effect is less than a few percent.

Next, we selected randomly ellipsoids of a given fraction $1-p$ and removed them. Figure 1(b) shows a typical configuration of the ellipsoids remaining in the cell.

The percolation was judged by the existence of a percolating channel which connects the bottom and top of the observation box. We made 10 000 observations for $L=10$, 5000 observations for $L=15$, and 2000 observations for $L=25$. For systems with a given volume fraction, we obtained the fraction of tries (percolation probability) which kept a percolation channel. Figures 3(a) and 3(b) show the packing fraction dependence of the percolation probability $R(f)$. Here the packing fraction f is the volume fraction occupied by the remaining ellipsoids.

We analyzed the percolation probability shown in Fig. 3 by the finite-size scaling method, assuming

$$R(f) = R[L^{1/\nu}(f - f_C)]. \tag{2}$$

Here, we assumed $\nu=0.9$ as the ordinary percolation process in three dimensions. We estimated the critical value appropriately from the crossings of $R(f)$ for different L and replotted the percolation probability in a scaled form, which is shown in Fig. 4. Excellent collapsing of the data supports the validity of the values chosen for f_C and ν.

Figure 5 shows the aspect ratio dependence of the critical volume fraction. It is interesting to note that since the critical volume fraction is a decreasing function of the aspect ratio, the system can be transformed from the nonpercolated to percolated state by increasing the aspect ratio of the ellipsoids even if the volume fraction occupied by the ellipsoids is kept constant.

IV. ANALYSIS

For the percolation process of overlapping ellipsoids, there have been significant efforts to correlate the critical volume fraction to basic properties of the ellipsoids [9,10].

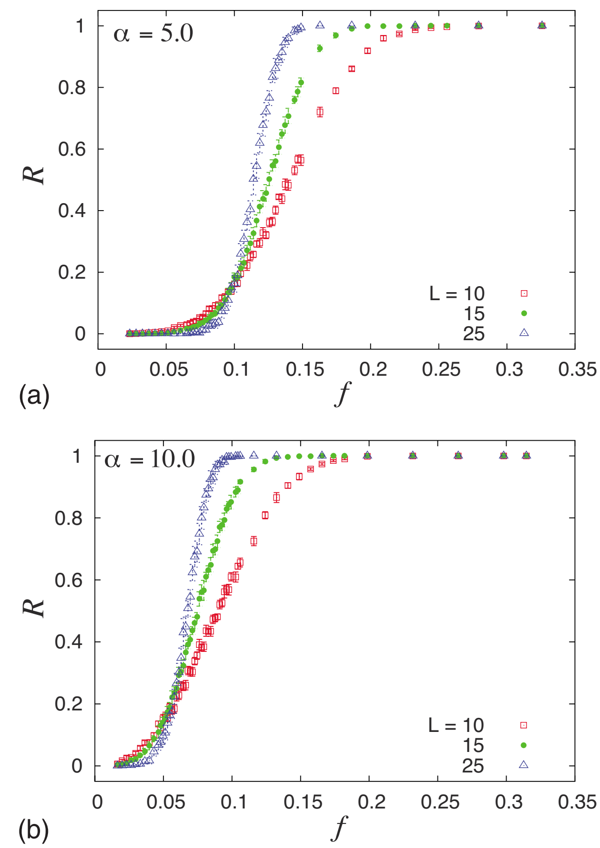

FIG. 3. (Color online) Percolation probability as a function of the packing fraction for $L=10$, 15, and 25. (a) $\alpha=5$, (b) $\alpha=10$.

Here, we analyze the correlation between the critical volume fraction and the basic properties of ellipsoids in a slightly different manner. We may assume that a given ellipsoid will have a percolating path only when there is a sufficiently large number of other ellipsoids in its vicinity. We first define the vicinity by the interaction range $V_{\text{int}}(\alpha)$ around a given ellipsoid. We expect that the number of ellipsoids in this interaction range must be larger than a critical value when a percolating channel exists. Namely, we can postulate that

$$V_{\text{int}}(\alpha) f_C(\alpha) = V_C. \tag{3}$$

When the correlation between the critical volume fraction and the interaction range is strong, the critical value V_C will not depend on α. Namely, we can test the correlation by observing if $\frac{f_C(1)}{f_C(\alpha)}$ and $\frac{V_{\text{int}}(\alpha)}{V_{\text{int}}(1)}$ coincide.

We can consider several definitions for the interaction range. Here, we test three possibilities: One is to identify it as the exclusion volume [8]

$$V_{\text{int}}(\alpha) = V_{\text{ex}}(\alpha). \tag{4}$$

It may be natural to consider that the interaction area is determined by the surface area multiplied by an effective linear dimension of the ellipsoid. Thus, we introduce the second model, which identifies $V_{\text{int}}(\alpha)$ as the area occupied by an ellipsoid itself and its vicinity determined by the surface area $A(\alpha)$ and the average radius of gyration of the surface $r_g(\alpha)$:

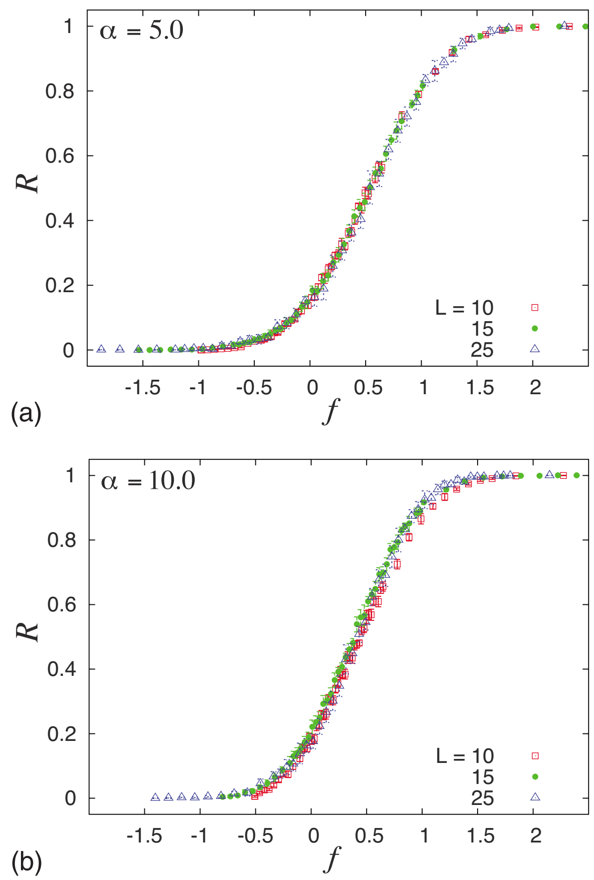

FIG. 4. (Color online) Percolation probability in the scaled form (2). (a) $\alpha=5$, (b) $\alpha=10$.

$$V_{\rm int}(\alpha)=V_0+C_1 r_g(\alpha)A(\alpha), \tag{5}$$

where C_1 is an adjustable parameter. Here, $r_g(\alpha)$ is defined by

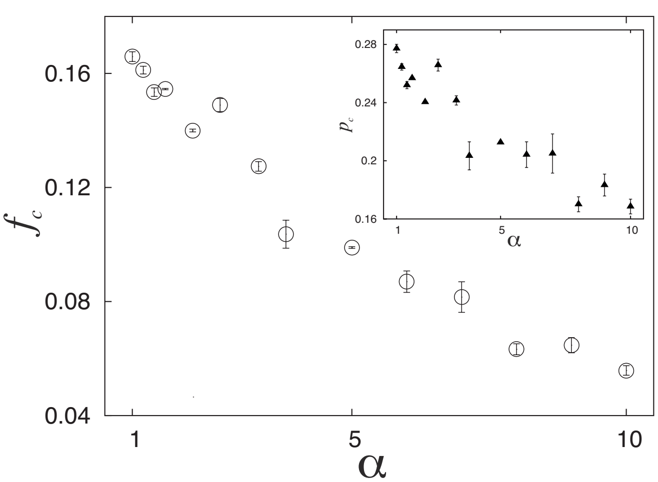

FIG. 5. The critical volume fraction $f_C(\alpha)$ is plotted against the aspect ratio α. The inset shows the critical concentration $p_C(\alpha)$ as a function of α.

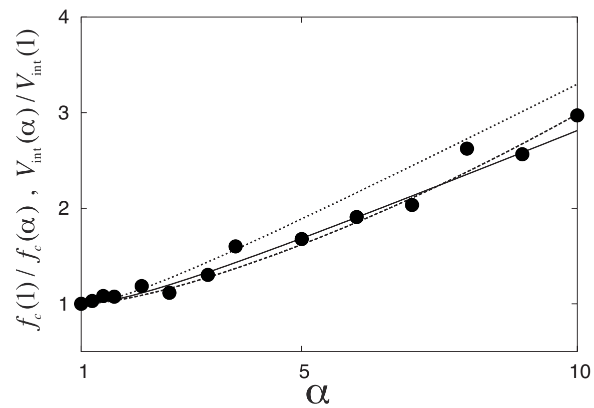

FIG. 6. Dependence of $\frac{f_C(1)}{f_C(\alpha)}$ and $\frac{V_{\rm int}(\alpha)}{V_{\rm int}(1)}$ on the aspect ratio. The solid circles show the inverse of the critical volume fraction. The curves represent three choices for the interaction range: The dotted curve is the excluded volume (4); the solid and dashed curves show Eq. (5) with $C_1=0.5$ and Eq. (7) with $C_2=0.25$, respectively.

$$[r_g(\alpha)]^2=\frac{\int_{\rm surface}(x^2+y^2+z^2)d\sigma}{\int_{\rm surface}d\sigma}, \tag{6}$$

where the origin of the coordinate is set to the center of the ellipsoid and $d\sigma$ is the surface element at (x,y,z) on the surface. This radius is a more relevant measure of the extension of an ellipsoid than the standard radius of gyration of an ellipsoid, because the contents in ellipsoids do not affect the connectivity determined by touching two ellipsoids.

The third model is to regard it as an expanded ellipsoid by a certain fraction of $r_g(\alpha)$ in all axes:

$$V_{\rm int}(\alpha)=\frac{4\pi}{3}[a+C_2 r_g(\alpha)][b+C_2 r_g(\alpha)]^2, \tag{7}$$

where C_2 is an adjustable parameter.

The explicit expressions for $V_{\rm ex}(\alpha)$, $A(\alpha)$, and $r_g(\alpha)$ are summarized in the Appendix. Figure 6 shows a comparison of $\frac{f_C(1)}{f_C(\alpha)}$ with these choices for the interaction range.

It is clearly seen in Fig. 6 that the expression (5) with $C_1=0.5$ coincides perfectly well with the inverse of the critical volume fraction.

V. DISCUSSION

We have obtained the critical percolation volume fraction f_C of hard-core prolate-ellipsoids suspended in the continuum as a function of the aspect ratio α. As α is increased from $\alpha=1$, $f_C(\alpha)$ decreases even though the packing fraction $\phi(\alpha)$ increases initially. The inset of Fig. 5 shows the fraction of ellipsoids, p_C, at the percolation threshold as a function of the aspect ratio. Needless to say, the critical volume fraction is given by the product of p_C and ϕ, i.e., $f_C(\alpha)=p_C(\alpha)\phi(\alpha)$. The strong dependence of p_C near $\alpha=1$ compensates the initial rise in the packing fraction seen in Fig. 1

so that the critical volume fraction becomes a monotone decreasing function of the aspect ratio.

In view of the comparison in Fig. 6, we can conclude that the expression (5) is a good approximation for the interaction range and that $V_{\mathrm{int}}(\alpha)f_C(\alpha)$ is approximately a dimensional invariant at least for the ellipsoids studied here. It should be noted that the critical volume fraction also correlates rather well with the excluded volume at least for the aspect ratio investigated.

It is a future problem to test if these relations hold for ellipsoids of large aspect ratio and for oblate ellipsoids.

In this paper, we investigated the correlation of the critical volume fraction only to the excluded volume and the average radius of gyration of the surface, because these properties give good correlation. In Ref. [9], various functionals of ellipsoids such as the average curvature and the radius of gyration have been investigated in connection to the critical volume fraction for the percolation of overlapping ellipsoids. We did not show the correlation of those functionals to our results because the correlation is poor except for the radius of gyration defined for the entire body of the ellipsoid and the physical meaning for the correlation with the radius of gyration of the body is not clear.

In order to see if the critical bond number is a dimensional invariant [7], we also obtained the bond number per ellipsoid B_C at the percolation threshold. We found that B_C depends rather strongly on α and therefore it cannot be a dimensional invariant.

In conclusion, we would like to comment on the relaxed condition for connection that we employed. In real applications, it is known in many cases that the observed volume fraction of an object differs from the connection range due to a shell of absorbed solvent. If this is the case, the packing and connection are determined by the outer shell including the absorbed solvent though the volume fraction is measured by the core. This situation is somewhat similar to the pips inside a pomegranate studied by J. Kepler in the 16th century. Furthermore, the effect of the relaxed condition for the connection can be estimated to be about 5% and the main results presented here should not differ much even if one prepares a really jammed structure and imposes a stricter condition for touching.

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APPENDIX: SOME PROPERTIES OF A PROLATE ELLIPSOID OF REVOLUTION

Here we give a partial list of basic properties of a prolate ellipsoid of revolution. See Ref. [9] for a fuller discussion. In the following $\epsilon=\sqrt{1-(1/\alpha^2)}$ is the eccentricity.

(i) The excluded volume [18]

$$V_{\mathrm{ex}}(\alpha)=V_0\left[2+\frac{3\alpha}{2}\left\{1+\frac{1-\epsilon^2}{2\epsilon}\ln\frac{1+\epsilon}{1-\epsilon}\right\}\left\{\sqrt{1-\epsilon^2}+\frac{\sin^{-1}(\epsilon)}{\epsilon}\right\}\right]. \tag{A1}$$

(ii) The surface area

$$A(\alpha)=2\pi ab\left\{\sqrt{1-\epsilon^2}+\frac{\sin^{-1}\epsilon}{\epsilon}\right\}. \tag{A2}$$

(iii) The radius of gyration of the surface,

$$r_g(\alpha)^2=\frac{\pi a^3 b}{2\epsilon A(\alpha)}\left\{\frac{4}{\alpha^2}(\sin^{-1}\epsilon+\epsilon\sqrt{1-\epsilon^2})+\sin^{-1}\epsilon-\epsilon\sqrt{1-\epsilon^2}(1-2\epsilon^2)\right\}. \tag{A3}$$

Note that $r_g(\alpha)$ is different from the radius of gyration of the body and that it is a more appropriate measure of the extension of the ellipsoid in the present problem.

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