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Evaluation of Nano- and Mesoscale Structural Features in Composite Materials through Hierarchical Decomposition of the Radial Distribution Function

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Evaluation of Nano- and Mesoscale Structural Features in Composite Materials through Hierarchical Decomposition of the Radial Distribution Function

Supplementary Information Document

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Supplementaty Information

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I. Derivation of the radial distribution function (RDF) between two parallel discs.

The interaction between atoms arranged in adjacent planes of a single crystallite can be modeled by the interaction of two two-dimensional discs, in which the atomic density is distributed uniformly over each disc. For circular discs, the interaction between one pair of discs, $g^*_{\text{meso,1-pair}}(r)$, can be analytically evaluated following the four step procedure described below. The planes defining these two discs are assumed to be parallel. The discs have centers located on a common normal vector. The inputs to this process are the radius of plane 1, $r_{p,1}$, the radius of plane 2, $r_{p,2}$, and the separation between center points, d_p.

A general, four-step procedure is employed to generate the mesoscale, single-pair RDF, $g^*_{\text{meso,1-pair}}(r)$. This same procedure is applied to the crystalline-crystalline intracrystallite interplanar component and the crystalline-crystalline intercrystallite component. In the first step, a joint probability distribution is formulated in terms of the independent coordinates over which the RDF is to be averaged. These coordinates correspond to the 2D or 3D mesoscale objects. Since the coordinates are independent, the joint probability distribution is the product of the single variable probability distributions. In the second step, the argument *r* of $g^*_{\text{meso,1-pair}}(r)$ is defined as a function of the independent coordinates in the system. In the third step, integration over all the independent variables is performed, which generates a cumulative distribution function in the single variable of interest, *r*. In the fourth and final step, the cumulative distribution is differentiated with respect to *r* in order to obtain the probability distribution function, which is directly related to the component RDF, $g(r)$. Once $g^*_{\text{meso,1-pair}}(r)$ is known, it is convoluted with $g^*_{\text{meso}}(r)$ to obtain the component RDF. The component, $g^*_{CC,\text{intraC,interP}}(r)$, is described below.

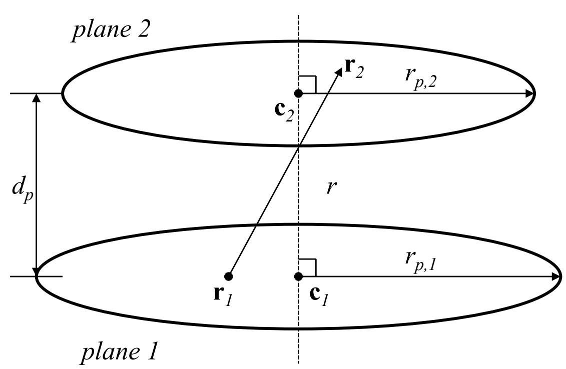

Figure S.1. A schematic of two parallel, circular planes arranged in three-dimensional space.

Step 1. Formulate a joint probability distribution in terms of the independent coordinates

We work this problem in cylindrical coordinates. We define point $\mathbf{r}_1$ in plane 1 in terms of r_1 and θ_1. The normalized single-variable distributions are given by

$$f_{r_1}(r_1) = \begin{cases} \dfrac{2r_1}{r_{p,1}^2} & \text{for } 0 \le r_1 \le r_{p,1} \\ 0 & \text{otherwise} \end{cases} \tag{S.1}$$

$$f_{\theta_1}(\theta_1) = \begin{cases} \dfrac{1}{2\pi} & \text{for } 0 \le \theta_1 \le 2\pi \\ 0 & \text{otherwise} \end{cases} \tag{S.2}$$

Similarly, we can completely define point $\mathbf{r}_2$ in plane 2 in terms of r_2 and θ_2. The normalized single-variable distributions are analogously given by

$$f_{r_2}(r_2) = \begin{cases} \dfrac{2r_2}{r_{p,2}^2} & \text{for } 0 \le r_2 \le r_{p,2} \\ 0 & \text{otherwise} \end{cases} \tag{S.3}$$

$$f_{\theta_2}(\theta_2) = \begin{cases} \dfrac{1}{2\pi} & \text{for } 0 \le \theta_2 \le 2\pi \\ 0 & \text{otherwise} \end{cases} \tag{S.4}$$

Since these coordinates are independent of each, their joint distribution is the product of their individual distributions

$$f_{r_1,\theta_1,r_2,\theta_2}(r_1,\theta_1,r_2,\theta_2) = f_{r_1}(r_1) f_{\theta_1}(\theta_1) f_{r_2}(r_2) f_{\theta_2}(\theta_2) = \frac{2r_1}{r_{p,1}^2}\frac{1}{2\pi}\frac{2r_2}{r_{p,2}^2}\frac{1}{2\pi} = \frac{r_1 r_2}{\pi^2 r_{p,1}^2 r_{p,2}^2} \tag{S.5}$$

Step 2. Define the function of the random variable of interest.

The function of interest is $r = |\mathbf{r}_2 - \mathbf{r}_1|$, which is given as:

$$r = \sqrt{(r_1\cos\theta_1 - r_2\cos\theta_2)^2 + (r_1\sin\theta_1 - r_2\sin\theta_2)^2 + d_p^2} \tag{S.6}$$

Step 3. Integrate over the independent variables to form a cumulative distribution function in r

The cumulative distribution function is then

$$F_r(r) = P(R \le r) = \int_0^{2\pi}\int_0^{r_{p,2}}\int_0^{2\pi}\int_0^{r_{p,1}} f_{r_1,\theta_1,r_2,\theta_2}(r_1,\theta_1,r_2,\theta_2)\,dr_2\,d\theta_2\,dr_1\,d\theta_1 \tag{S.7}$$

$$F_r(r) = P(R \le r) = \int_0^{2\pi}\int_0^{r_{p,2}}\int_0^{2\pi}\int_0^{r_{p,1}} \frac{r_1\, r_2}{\pi^2 r_{p,1}^2 r_{p,2}^2} dr_2 d\theta_2 dr_1 d\theta_1 \tag{S.8}$$

It is useful to split this integral up into two parts,

$$F_r(r) = P(R \le r) = \frac{1}{\pi^2 r_{p,1}^2 r_{p,2}^2}\int_0^{2\pi}\int_0^{r_{p,1}} I(r) r_1 dr_1 d\theta_1 \tag{S.9}$$

where the interior integral is defined as

$$I(r) = \int_0^{2\pi}\int_0^{r_{p,2}} r_2\, dr_2 d\theta_2 \tag{S.10}$$

This interior integral describes the area of plane 2 contained within a radius r, centered at $\mathbf{r}_1$. This two-dimension integral has four cases, dependent upon the magnitude of r, described below. The projection of the intersection of a sphere of radius r onto plane 2 results in a circle of radius, r_x, on plane 2, where r_x, is defined by the Pythagorean theorem

$$r^2 = d_p^2 + r_x^2 \tag{S.11}$$

Case 1. $r < d_p$

In this case the planes are separated by a distance greater than r. Therefore, there is no contribution from the surrounding medium at any value of $\mathbf{r}_2$ to the integral.

$$I_1(r) = 0 \tag{S.12}$$

Case 2. ($d_p \le r$ and $r_x < r_{p,2} - r_1$) or $d_p \le r < \sqrt{d_p^2 + (r_{p,2} - r_1)^2}$

For some values of r, the projected circle of radius r_x, may be entirely enclosed within the disc of radius, $r_{p,2}$. In this case, the area is given by

$$I_2(r) = 4\pi r_x^2 \tag{S.13}$$

Case 3. ($r_{p,2} - r_1 \le r_x < r_{p,2}$) or $\sqrt{d_p^2 + (r_{p,2} - r_1)^2} \le r < \sqrt{d_p^2 + r_{p,2}^2}$

For some values of r, there is partial overlap between the projected circle of radius r_x and the disc of radius $r_{p,2}$. In this case, the area is given by

$$I_3(r) = A_{over}(r_{p,2}, r_x(r), r_1) \tag{S.14}$$

Case 4. $r_{p,2} \le r_x$ or $\sqrt{d_p^2 + r_{p,2}^2} \le r$)

For large values of r, the projected circle of radius r_x, entirely encloses the disc of radius, $r_{p,2}$. In this case, the area is given by

$$I_4(r) = 4\pi r_{p,2}^2 \tag{S.15}$$

Required for Case 3, the overlapping area for two circles, one of radius $r_{p,2}$ and the other of radius r_x with centers separated by distance r_1 is

$$\begin{aligned} A_{over}(r_{p,2}, r_x, r_1) &= r_{p,2}^{\ 2} \cos^{-1}\left(\frac{r_1^{\ 2} + r_{p,2}^{\ 2} - r_x^{\ 2}}{2 r_1 r_{p,2}}\right) + r_x^{\ 2} \cos^{-1}\left(\frac{r_1^{\ 2} + r_x^{\ 2} - r_{p,2}^{\ 2}}{2 r_1 r_x}\right) \\ &- \frac{1}{2}\sqrt{(r_1 + r_x + r_{p,2})(r_1 - r_x + r_{p,2})(r_1 + r_x - r_{p,2})(-r_1 + r_x + r_{p,2})} \end{aligned} \tag{S.16}$$

For all four cases, the integrand is not a function of θ_1, therefore, that integration is trivial, resulting in

$$F_r(r) = P(R \le r) = \frac{2}{\pi r_{p,1}^2 r_{p,2}^2} \int_0^{r_{p,2}} I(r) r_1 dr_1 \tag{S.17}$$

Further manipulation yields the cumulative distribution function

$$F_r(r) = \frac{2}{\pi r_{p,1}^2 r_{p,2}^2} \int_0^{r_{p,1}} I_1(r) r_1 dr_1 \qquad \text{for } r < d_p \tag{S.18}$$

$$F_r(r) = \frac{2}{\pi r_{p,1}^2 r_{p,2}^2} \left[\int_0^{r_{p,1}-r_x} I_2(r) r_1 dr_1 + \int_{r_{p,1}-r_x}^{r_{p,1}} I_3(r) r_1 dr_1 \right] \qquad \text{for } d_p \le r < \sqrt{d_p^2 + r_{p,2}^2} \tag{S.19}$$

$$F_r(r) = \frac{2}{\pi r_{p,1}^2 r_{p,2}^2} \left[\int_0^{r_x-r_{p,1}} I_4(r) r_1 dr_1 + \int_{r_x-r_{p,1}}^{r_{p,1}} I_3(r) r_1 dr_1 \right] \qquad \text{for } \sqrt{d_p^2 + r_{p,2}^2} \le r < \sqrt{d_p^2 + 4 r_{p,2}^2} \tag{S.20}$$

$$F_r(r) = \frac{2}{\pi r_{p,1}^2 r_{p,2}^2} \int_0^{r_{p,1}} I_4(r) r_1 dr_1 \qquad \text{for } \sqrt{d_p^2 + 4 r_{p,2}^2} \le r \tag{S.21}$$

Further manipulation yields the cumulative distribution function

$$F_r(r) = 0 \quad \text{for } r < d_p \tag{S.22}$$

See Appendix SI.I. for $d_p \le r < \sqrt{d_p^2 + r_{p,2}^2}$ (S.23)

See Appendix SI.I. for $\sqrt{d_p^2 + r_{p,2}^2} \le r < \sqrt{d_p^2 + 4r_{p,2}^2}$ (S.24)

$$F_r(r) = 1 \quad \text{for } \sqrt{d_p^2 + 4r_{p,2}^2} \le r \tag{S.25}$$

Where the analytical expressions have no compact form, the results are given in Matlab codes in the appendices.

Step 4. Differentiate with respect to r

The definition of the cumulative probability distribution function is

$$F_r(r) = P(R \le r) \equiv \int_{-\infty}^{\infty} f(r')dr' \tag{S.26}$$

where $f(r')$ is the probability distribution function. Therefore

$$f(r) = \frac{dF_r(r)}{dr} \tag{S.27}$$

The derivatives of equations (22) through (25)were evaluated analytically.

$$f_r(r) = 0 \quad \text{for } r < d_p \tag{S.28}$$

See Appendix SI.I. for $d_p \le r < \sqrt{d_p^2 + r_{p,2}^2}$ (S.29)

See Appendix SI.I. for $\sqrt{d_p^2 + r_{p,2}^2} \le r < \sqrt{d_p^2 + 4r_{p,2}^2}$ (S.30)

$$f_r(r) = 0 \quad \text{for } \sqrt{d_p^2 + 4r_{p,2}^2} \le r \tag{S.31}$$

The radial distribution function is related to this differential as follows.

$$g^*_{\text{meso, 1-pair}}(r; r_{p,1}, r_{p,2}, d_p) = \frac{f(r)}{4\pi r^2} \tag{S.32}$$

This distribution provides the RDF for one pair of discs. In this model a crystallite is made up of a series of parallel discs, spaced at intervals of d_p, each with its own radius. The distribution $g^*_{\text{meso}}(z)$ described the arrangement of discs along the z-axis, normal to the planes.

$$g^*_{\text{meso}}(z) = \sum_{i=1}^{N_p} \delta(z - z_i) \tag{S.33}$$

where N_p is the number of planes in a crystallite and z_i is the axial position of each. The RDF for this component is given by the convolution of equation (S.32) and (S.33),

$$\begin{aligned} \rho_{CC,\text{intraC,interP}}(r) &= \int_{z_1+\varepsilon}^{\infty} \int_{0}^{\infty} g^*_{\text{meso, 1-pair}}\left(r; r_{p,1}, r_{p,2}, d_p\right) g^*_{\text{meso}}(z_1) g^*_{\text{meso}}(z_2) dz_1 dz_2 \\ &= \sum_{i=1}^{N_p} \sum_{j=i+1}^{N_p} g^*_{\text{meso, 1-pair}}\left(r; r_{p,i}, r_{p,j}, d = \left|z_j - z_i\right|\right) \end{aligned} \tag{S.34}$$

The epsilon is included in the integral limit to avoid self-interactions of a disc. The intraplanar contributions to the RDF were already accounted for explicitly in another component of the hierarchical decomposition. Since there are on the order of 10 planes in a nanocrystallite, this sum can be evaluated explicitly. The radius of each plane is chosen based on each plane being a slice through a spherical nanoparticle at a different axial position.

This distribution as derived contains no thermal noise and has units of volume rather than atomic density. It is essentially a $T = 0$ distribution. The addition of thermal noise is performed by convoluting the RDF with a Gaussian at each point.

$$\rho_{CC,\text{intraC,interP}}(r) = \int_{\sigma}^{\infty} \rho^{T=0}_{CC,\text{intraC,interP}}(r') f_g\left(r - r'; \mu_g = r', \sigma_g = \sigma_{T,\text{inter}}\right) dr' \tag{S.35}$$

where $\sigma_{T,\text{inter}}$ is a common standard deviation to account for thermal noise in intermolecular interactions.

Finally, this RDF is scaled to provide $g^*_{CC,\text{intraC,interP}}(r)$. The scaling parameter is the two-dimensional density of atoms in the planes.

$$g^*_{CC,\text{intraC,interP}}(r) = \frac{\rho_{CC,\text{intraC,interP}}(r)}{\rho_{tot}} \tag{S.36}$$

A code generating the RDF of equation (S.32) for a single pair of planes is provide below in Appendix SI.I. A simple main program used to set sample parameter values is given in SI.I.A. The function itself is given in SI.I.B. This code was used to generate the following plots for a single pair of planes with the radius of plane 1, $r_{p,1} = 7.0$, the radius of plane 2, $r_{p,2} = 10.0$, and the separation between center points, $d_p = 3.4$..

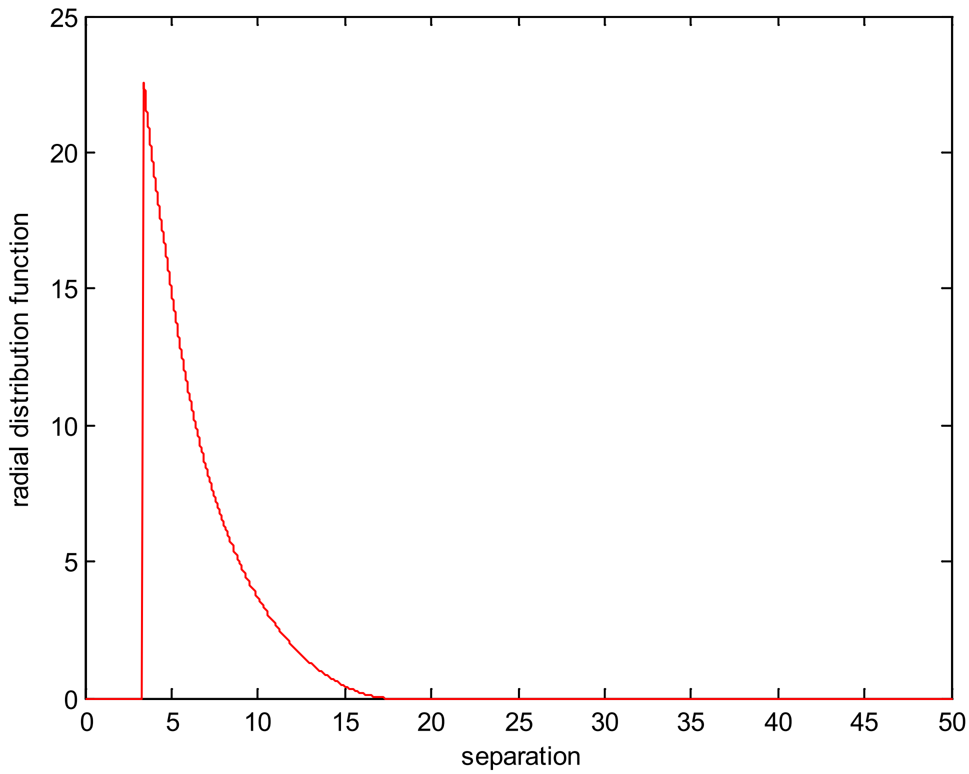

Figure S.2. The RDF for a pair of planes with $r_{p,1} = 7.0$ and $r_{p,2} = 10.0$ separated by $d_p = 3.4$. This RDF, as generated by the code, INCLUDES the factor of $\frac{1.0}{4.0\pi r^2}$.

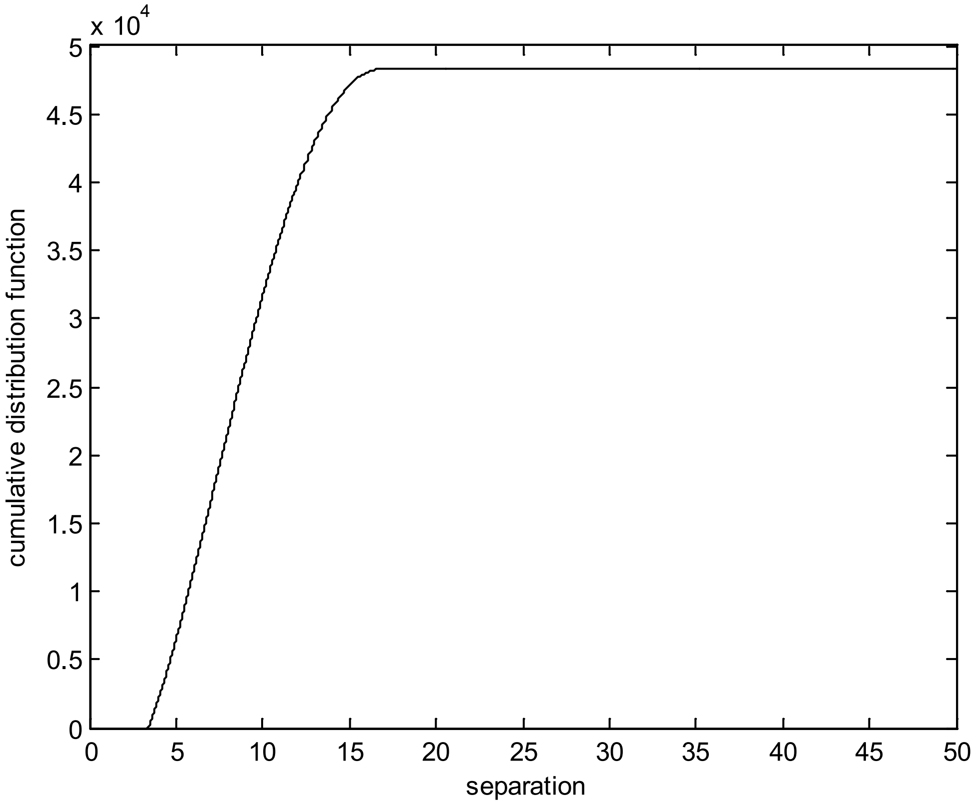

Figure S.3. The cumulative RDF for a pair of planes with $r_{p,1} = 7.0$ and $r_{p,2} = 10.0$ separated by $d_p = 3.4$. In these units, the final plateau of the cumulative distribution occurs at a value of $Area_1 \cdot Area_2 = \pi^2 r_{p,1}^2 r_{p,2}^2$.

II. Derivation of the radial distribution function (RDF) between two spheres.

The interaction between atoms located in two crystallites can be modeled by the interaction of two three-dimensional spheres, in which the atomic density is distributed uniformly over each sphere. The interaction between one pair of spheres, $g^*_{\text{meso,1-pair}}(r)$, can be analytically evaluated following the four step procedure described above. The planes defining these two discs are assumed to be parallel. The discs have centers located on a common normal vector. The inputs to this process are the radius of particle 1, $r_{p,1}$, the radius of particle 2, $r_{p,2}$, and the separation between center points, d. The same four-step procedure is employed to generate the mesoscale, single-pair RDF, $g^*_{\text{meso,1-pair}}(r)$.

Step 1. Formulate a joint probability distribution in terms of the independent coordinates

We can completely define point $\mathbf{r}_1$ inside our sphere in terms of three-dimensional spherical coordinates, r_1, θ_1 and ϕ_1. The normalized single-variable distributions for r_1, θ_1 and ϕ_1 are given by

$$f_{r_1}(r_1) = \begin{cases} \dfrac{3r_1^2}{r_p^3} & \text{for } 0 \le r_1 \le r_p \\ 0 & \text{otherwise} \end{cases} \tag{T.1}$$

$$f_{\theta_1}(\theta_1) = \begin{cases} \dfrac{\sin\theta_1}{2} & \text{for } 0 \le \theta_1 \le \pi \\ 0 & \text{otherwise} \end{cases} \tag{T.2}$$

$$f_{\phi_1}(\phi_1) = \begin{cases} \dfrac{1}{2\pi} & \text{for } 0 \le \phi_1 \le 2\pi \\ 0 & \text{otherwise} \end{cases} \tag{T.3}$$

Similarly, we can completely define point $\mathbf{r}_2$ outside our sphere in terms of three-dimensional spherical coordinates, r_2, θ_2 and ϕ_2. The normalized single-variable distributions for r_2, θ_2 and ϕ_2 are given by

$$f_{r_2}(r_2) = \begin{cases} \dfrac{3r_2^2}{r_{cut}^3 - r_p^3} & \text{for } r_p < r_1 \le r_{cut} \\ 0 & \text{otherwise} \end{cases} \tag{T.4}$$

$$f_{\theta_2}(\theta_2) = \begin{cases} \dfrac{\sin\theta_2}{2} & \text{for } 0 \le \theta_2 \le \pi \\ 0 & \text{otherwise} \end{cases} \tag{T.5}$$

$$f_{\phi_2}(\phi_2) = \begin{cases} \frac{1}{2\pi} & for\, 0 \le \phi_2 \le 2\pi \\ 0 & otherwise \end{cases} \quad \text{(T.6)}$$

Since these six coordinates are independent of each, their joint distribution is the product of their individual distributions

$$f_{r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2}(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) = f_{r_1}(r_1)f_{\theta_1}(\theta_1)f_{\phi_1}(\phi_1)f_{r_2}(r_2)f_{\theta_2}(\theta_2)f_{\phi_2}(\phi_2)$$
$$= \frac{3r_1^2}{r_p^3}\frac{\sin\theta_1}{2}\frac{1}{2\pi}\frac{3r_2^2}{r_{cut}^3 - r_p^3}\frac{\sin\theta_2}{2}\frac{1}{2\pi} = \frac{9r_1^2r_2^2\sin\theta_1\sin\theta_2}{16\pi^2r_p^3(r_{cut}^3 - r_p^3)} \quad \text{(T.7)}$$

Step 2. Define the function of the random variable of interest.

We are interested in the probability distribution function of a function of the independent random variables. The function of interest is $r = |\mathbf{r}_2 - \mathbf{r}_1|$,

$$r = \sqrt{(r_{2,x} - r_{1,x})^2 + (r_{2,y} - r_{1,y})^2 + (r_{2,z} - r_{1,z})^2} \quad \text{(T.8)}$$

$$r = \sqrt{\begin{matrix}(r_2\cos\theta_2\cos\phi_2 - r_1\cos\theta_1\cos\phi_1)^2 + \\ (r_2\sin\theta_2\cos\phi_2 - r_1\sin\theta_1\cos\phi_1)^2 + (r_2\sin\phi_2 - r_1\sin\phi_1)^2\end{matrix}} \quad \text{(T.9)}$$

Step 3. Integrate over the independent variables to form a cumulative distribution function in r

The cumulative distribution function is then

$$F_r(r) = P(R \le r) = \int_{r_1}\int_{\theta_1}\int_{\phi_1}\int_{r_2}\int_{\theta_2}\int_{\phi_2} r(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2) f_{r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2}(r_1,\theta_1,\phi_1,r_2,\theta_2,\phi_2)\, d\phi_2 d\theta_2 dr_2 d\phi_1 d\theta_1 dr_1 \quad \text{(T.10)}$$

$$F_r(r) = P(R \le r) = \frac{9}{16\pi^2 r_p^3(r_{cut}^3 - r_p^3)}\int_{r_1}\int_{\theta_1}\int_{\phi_1}\int_{r_2}\int_{\theta_2}\int_{\phi_2} r r_1^2 r_2^2 \sin\theta_1 \sin\theta_2 d\phi_2 d\theta_2 dr_2 d\phi_1 d\theta_1 dr_1 \quad \text{(T.11)}$$

This integral is performed over the geometric constraints of the six variables. It is useful to split this integral up into two parts,

$$F_r(r) = P(R \le r) = \frac{9}{16\pi^2 r_p^3(r_{cut}^3 - r_p^3)}\int_{r_1}\int_{\theta_1}\int_{\phi_1} I(r) r_1^2 \sin\theta_1 d\phi_1 d\theta_1 dr_1 \quad \text{(T.12)}$$

where the interior integral is defined as

$$I(r) = \int_{r_2}\int_{\theta_2}\int_{\phi_2} r r_2^2 \sin\theta_2 d\phi_2 d\theta_2 dr_2 \quad \text{(T.13)}$$

This interior integral captures the volume of the second particle contained within a radius *r*, centered at $\mathbf{r}_1$.

This three dimension integral has three cases, described below.

Case 1. No overlap

In this case, no portion of the second particle is enclosed within a sphere of radius *r*., centered at $\mathbf{r}_1$. Therefore, the value of the interior integral (T.13) is

$$I_1(r) = 0 \tag{T.14}$$

Case 2. Complete enclosure of second particle

In this case, the entire particle is enclosed within a sphere of radius *r*., centered at $\mathbf{r}_1$. Therefore, the value of the interior integral (T.13) is

$$I_2(r) = \frac{4\pi}{3} r_p^3 \tag{T.15}$$

Case 3. Partial Overlap

In this intermediate case, there is an overlap between the second particle and the sphere of radius *r*., centered at $\mathbf{r}_1$. A general formula for the volume of overlap between two spheres of radius *r* and *R* separated by a distance, *d*, is given by

$$V_{over} = \frac{\pi(R + r - d)^2 (d^2 + 2dr - 3r^2 + 2dR + 6rR - 3R^2)}{12d} \tag{T.16}$$

Thus the functional form of the interior integral in (T.13) is known.

At this point, we identified that the exterior integral would be more readily evaluated if expressed in bipolar coordinates,[1] r_b, *s*, and *t*, in which

$$r_b = r_{12} \tag{T.17}$$

$$s = r_{13} \tag{T.18}$$

$$t = r_{23} \tag{T.19}$$

where the point 1 corresponds to $\mathbf{r}_1$, point 2 corresponds to the center of particle 2 and, and point 3 is a radial distance, *r*, from $\mathbf{r}_1$.

In this new coordinate system, the expression for partial overlap given in (T.16) becomes $R = r$, $r = r_{p,2}$ and $d = t$,

$$V_{over} = \frac{\pi(r + r_{p2} - t)^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2}r - 3r^2)}{12t} \tag{T.20}$$

In this case, the cumulative probability distribution has the form

$$F(R \le r) = \int_0^{2\pi} \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} V_{cc}(t, r_{p2}, r) \frac{st}{r_b} dt ds d\theta_1 \tag{T.21}$$

The analytical form of the integral was determined. It took various forms depending upon the values of $r_{p,1}$, $r_{p,2}$, d and r, which changed the limits of integration for s and t. The various cases are summarized below. The cases are initially distinguished by bounds on the arguments of the RDF, r. Each case gives rise to different limits of integration on s and t.

- **Case I. ($r \le r_b - r_{p1} - r_{p2}$)** (no overlap)
- **Case II ($r_b - r_{p1} - r_{p2} < r \le r_b - r_{p2}$).**
  - **Case II. A** (overlap of some points in sphere 1 with sphere 2)
  - **Case II. B** (no overlap of some points in sphere 1 with sphere 2)
- **Case II*($r_b - r_{p2} < r < r_b - r_{p2} + r_{p1}$)**
  - **Case II*. A** (overlap of some points in sphere 1 with sphere 2)
  - **Case II* B** (no overlap by some points in sphere 1 with sphere 2)
- **Case III ($r_b - r_{p2} + r_{p1} \le r \le r_b + r_{p2}$)**
  - **Case III. A** (overlap by some points in sphere 1 with sphere 2)
  - **Case III. B** (total encapsulation by some points in sphere 1)
- **Case III* ($r_b + r_{p2} < r < r_b + r_{p1} + r_{p2}$)**
  - **Case III* A** (Overlap of some points in sphere 1 over sphere 2)
  - **Case III* B** (Case where there is total encapsulation of some points in sphere 1 over sphere 2)
- **Case IV ($r \ge r_b + r_{p1} + r_{p2}$)**

Case I. ($r \le r_b - r_{p1} - r_{p2}$) (no overlap)

In this case there is no overlap between any point in sphere 1 and any point in sphere 2.

Therefore;

$$F(R \le r) = \int_0^{2\pi} \int_{r_{p1\min}}^{r_{p1\max}} \int_{r_b - r_{p1\max}}^{t_{\max}(r_b, r, s)} V_{cc}(t, r_{p2}, r) \frac{st}{r_b} dt ds d\theta_1 = 0 \tag{T.22}$$

Case II ($r_b - r_{p1} - r_{p2} < r \le r_b - r_{p2}$).

This is divided into two subcases:

A) When there is some overlap between points in sphere 1 and sphere 2.

B) When there is no overlap between any points in sphere 1 and sphere 2

Case II. A (overlap of some points in sphere 1 with sphere 2)

$$F(R \le r) = \int_0^{2\pi}\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}} V_{cc}(t, r_{p2}, r)\frac{st}{r_b}\, dtdsd\theta_1 \tag{T.23}$$

$$F(R \le r) = 2\pi \int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}} V_{cc}(t, r_{p2}, r)\frac{st}{r_b}\, dtds \tag{T.24}$$

$$F(R \le r) = 2\pi \int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}} \frac{\pi(r + r_{p2} - t)^2(t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2}r - 3r^2)}{12t}\frac{st}{r_b}\, dtds \tag{T.25}$$

$$F(R \le r) = \frac{\pi^2}{6r_b}\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}} (r + r_{p2} - t)^2(t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2}r - 3r^2)sdtds \tag{T.26}$$

The challenge is defining the limits to these integrals.

$$t_{\max} = \sqrt{x^2 + y^2}$$

where

$$y = \frac{a}{2} = \frac{1}{2d}\sqrt{(-d + r - R)(-d - r + R)(-d + r + R)(d + r + R)} \text{ (in variables of T.16)}$$

$$y = \frac{1}{2(r_b - r_{p2})}\sqrt{(-(r_b - r_{p2}) + r - s)(-(r_b - r_{p2}) - r + s)(-(r_b - r_{p2}) + r + s)((r_b - r_{p2}) + r + s)}$$

$$y = \frac{1}{2(r_b - r_{p2})}\sqrt{(-r_b + r_{p2} + r - s)(-r_b + r_{p2} - r + s)(-r_b + r_{p2} + r + s)(r_b - r_{p2} + r + s)}$$

$$y = \frac{1}{2(-r_{p2} + r_b)}\sqrt{(r_{p2} - r_b + r - s)(r_{p2} - r_b - r + s)(r_{p2} - r_b + r + s)(-r_{p2} + r_b + r + s)}$$

$$y^2 = \frac{(r_{p2} - r_b + r - s)(r_{p2} - r_b - r + s)(r_{p2} - r_b + r + s)(-r_{p2} + r_b + r + s)}{4(r_{p2} - r_b)^2}$$

$$x = x' + r_{p2}$$

$$x' = \frac{d^2 + r^2 - R^2}{2d} \text{ (in variables of T.16)}$$

$$x' = \frac{(r_b - r_{p2})^2 + r^2 - s^2}{2(r_b - r_{p2})}$$

$$x = \frac{(r_b - r_{p2})^2 + r^2 - s^2}{2(r_b - r_{p2})} + r_{p2}$$

$$x = \frac{r_{p2}{}^2 - r_b{}^2 - r^2 + s^2}{2(r_{p2} - r_b)}$$

$$x^2 = \frac{(r_{p2}{}^2 - r_b{}^2 - r^2 + s^2)^2}{4(r_{p2} - r_b)^2}$$

$$t_{\max} = \sqrt{\frac{(r_{p2}{}^2 - r_b{}^2 - r^2 + s^2)^2}{4(r_{p2} - r_b)^2} + \frac{(r_{p2} - r_b + r - s)(r_{p2} - r_b - r + s)(r_{p2} - r_b + r + s)(-r_{p2} + r_b + r + s)}{4(r_{p2} - r_b)^2}}$$

$$t_{\max} = \sqrt{\frac{1}{4(r_{p2} - r_b)^2}((r_{p2}{}^2 - r_b{}^2 - r^2 + s^2)^2 + (r_{p2} - r_b + r - s)(r_{p2} - r_b - r + s)(r_{p2} - r_b + r + s)(-r_{p2} + r_b + r + s))}$$

$$t_{\max} = \frac{1}{2(r_{p2} - r_b)}\sqrt{(r_{p2}{}^2 - r_b{}^2 - r^2 + s^2)^2 + (r_{p2} - r_b + r - s)(r_{p2} - r_b - r + s)(r_{p2} - r_b + r + s)(-r_{p2} + r_b + r + s)}$$

$$t_{\max} = \frac{1}{2(r_{p2} - r_b)}\sqrt{4r_{p2}{}^3 r_b - 8r_{p2}{}^2 r_b{}^2 + 4r_{p2}{}^2 s^2 + 4r_{p2} r_b{}^3 - 4r_{p2} r_b r^2 - 4r_{p2} r_b s^2 + 4r_b{}^2 r^2)}$$

$$t_{\max} = \frac{1}{2(r_{p2} - r_b)} 2\sqrt{(r_{p2} - r_b)(r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2)}$$

$$t_{\max} = \frac{\sqrt{(r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2)}}{\sqrt{(r_{p2} - r_b)}}$$

$$t_{\max} = \sqrt{\frac{(r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2)}{(r_{p2} - r_b)}}$$

$$t_{\max} = \left(\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b}\right)^{1/2} \tag{T.27}$$

$$t_{\min} = r_b - s \tag{T.28}$$

$$s_{\min} = r_b - r_{p2} - r \tag{T.29}$$

$$s_{\max} = r_{p1} \tag{T.30}$$

Now that we have defined the limits of the integration, the integral becomes

$$F(R \le r) = \frac{\pi^2}{6r_b} \int_{r_b - r_{p2} - r}^{r_{p1}} \int_{r_b - s}^{\left(\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b}\right)^{1/2}} (r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2} r - 3r^2) s\,dt\,ds \tag{T.31}$$

The inner indefinite integral (t-integral) is evaluated as:

$$\int (r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2} r - 3r^2) dt$$
$$= -3r^4 t + 4r^3 t^2 + 6r^2 r_{p2}{}^2 t - 2r^2 t^3 - 3r_{p2}{}^4 t + 4r_{p2}{}^3 t^2 - 2r_{p2}{}^2 t^3 + \frac{t^5}{5}$$

$$= -3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2) t + 4(r^3 + r_{p2}{}^3) t^2 - 2(r_{p2}{}^2 + r^2) t^3 + \frac{t^5}{5}$$

Upper t-limit

$$\int^{\left(\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b}\right)^{1/2}} (r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2} r - 3r^2) dt$$

$$= -3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)\left(\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b}\right)^{1/2} + 4(r^3 + r_{p2}{}^3)\left(\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b}\right)$$
$$- 2(r_{p2}{}^2 + r^2)\left(\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b}\right)^{3/2} + \frac{1}{5}\left(\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b}\right)^{5/2}$$

(7)

Lower t-limit

$$\int_{r_b - s} (r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2}r - 3r^2) dt$$

$$= -3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)(r_b - s) + 4(r^3 + r_{p2}{}^3)(r_b - s)^2 - 2(r_{p2}{}^2 + r^2)(r_b - s)^3 + \frac{(r_b - s)^5}{5}$$

Upper limit – Lower limit

$$\begin{aligned}
&= -3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{1/2} - (r_b - s)) \\
&+ 4(r^3 + r_{p2}{}^3)((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b}) - (r_b - s)^2) \\
&- 2(r_{p2}{}^2 + r^2)((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{3/2} - (r_b - s)^3) \\
&+ \frac{1}{5}((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{5/2} - (r_b - s)^5)
\end{aligned} \qquad (T.32)$$

Equation (T.32) contains 4 terms. So it is easier to divide the s-integral (outer integral) into 4 terms, where:

$$\begin{aligned}
&term1 = -3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{1/2} - (r_b - s)) \\
&term2 = 4r_b(r^3 + r_{p2}{}^3)(\frac{(r_{p2} - r_b + r + s)(r_{p2} - r_b - r + s)}{r_{p2} - r_b}) \\
&term3 = -2(r_{p2}{}^2 + r^2)((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{3/2} - (r_b - s)^3) \\
&term4 = \frac{1}{5}((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{5/2} - (r_b - s)^5)
\end{aligned} \qquad (T.33)$$

The s-integral is now expressed as:

$$\int_{r_b - r_{p2} - r}^{r_{p1}} (term1 + term2 + term3 + term4) s ds \tag{T.34}$$

We start with evaluating the s-integral for **term 1**;

$$\int_{r_b - r_{p2} - r}^{r_{p1}} (-3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{1/2} - (r_b - s))) s ds$$

$$\int_{r_b - r_{p2} - r}^{r_{p1}} -3s(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{1/2} - (r_b - s)) ds$$

$$= -3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2) \int_{r_b - r_{p2} - r}^{r_{p1}} s((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{1/2} - (r_b - s)) ds \tag{T.35}$$

The indefinite integral is evaluated as:

$$\int s((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{1/2} - (r_b - s)) ds = \frac{1}{3}(-\frac{r_b r^2}{r_{p2}} + r_{p2} r_b - r_b{}^2 + s^2)(\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{1/2}$$
$$-\frac{1}{2} r_b s^2 + \frac{1}{3} s^3$$

Therefore the s-integral for term 1

$$= -3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2) \int_{r_b - r_{p2} - r}^{r_{p1}} s((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{1/2} - (r_b - s)) ds$$

becomes

$$= -3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)\{Eqn14(r_{p1}) - Eqn14(r_b - r_{p2} - r)\} \tag{T.36}$$

The s-integral for **term 2** is given as

$$\int_{r_b - r_{p2} - r}^{r_{p1}} 4r_b(r^3 + r_{p2}{}^3)(\frac{(r_{p2} - r_b + r + s)(r_{p2} - r_b - r + s)}{r_{p2} - r_b}) s ds$$

Simplified as:

$$\frac{4r_b(r^3+r_{p2}{}^3)}{r_{p2}-r_b}\int_{r_b-r_{p2}-r}^{r_{p1}}(r_{p2}-r_b+r+s)(r_{p2}-r_b-r+s)sds$$

The indefinite integral is evaluated as

$$\int(r_{p2}-r_b+r+s)(r_{p2}-r_b-r+s)sds = 0.5r_{p2}{}^2s^2 - r_{p2}r_bs^2 + 0.5r_b{}^2s^2 - 0.5r^2s^2 + \frac{2}{3}s^3r_{p2} - \frac{2}{3}r_bs^3 + \frac{1}{4}s^4$$

$$\int_{r_b-r_{p2}-r}^{r_{p1}}(r_{p2}-r_b+r+s)(r_{p2}-r_b-r+s)sds = Eqn18(r_{p1}) - Eqn18(r_b-r_{p2}-r)$$

Therefore, the s-integral for term 2 can be expressed as:

$$\frac{4r_b(r^3+r_{p2}{}^3)}{r_{p2}-r_b}\int_{r_b-r_{p2}-r}^{r_{p1}}(r_{p2}-r_b+r+s)(r_{p2}-r_b-r+s)sds =$$

$$= \frac{4r_b(r^3+r_{p2}{}^3)}{r_{p2}-r_b}\{Eqn18(r_{p1}) - Eqn18(r_b-r_{p2}-r)\} \qquad \text{(T.37)}$$

The s-integral for **term 3** is evaluated thus:

$$\int_{r_b-r_{p2}-r}^{r_{p1}}(-2(r_{p2}{}^2+r^2)((\frac{r_{p2}{}^2r_b - r_{p2}r_b{}^2 + r_{p2}s^2 - r_br^2}{r_{p2}-r_b})^{3/2} - (r_b-s)^3))sds$$

$$-2(r_{p2}{}^2+r^2)\int_{r_b-r_{p2}-r}^{r_{p1}}((\frac{r_{p2}{}^2r_b - r_{p2}r_b{}^2 + r_{p2}s^2 - r_br^2}{r_{p2}-r_b})^{3/2} - (r_b-s)^3)sds$$

The indefinite integral in (21) is evaluated thus;

$$\int((\frac{r_{p2}{}^2r_b - r_{p2}r_b{}^2 + r_{p2}s^2 - r_br^2}{r_{p2}-r_b})^{3/2} - (r_b-s)^3)sds$$

$$= \frac{(r_{p2}-r_b)}{5r_{p2}}(\frac{r_{p2}{}^2r_b - r_{p2}r_b{}^2 + r_{p2}s^2 - r_br^2}{r_{p2}-r_b})^{5/2} - 0.5r_b{}^3s^2 + r_b{}^2s^3 - 0.75r_bs^4 + 0.2s^5$$

$$\int_{r_b-r_{p2}-r}^{r_{p1}}((\frac{r_{p2}{}^2r_b - r_{p2}r_b{}^2 + r_{p2}s^2 - r_br^2}{r_{p2}-r_b})^{3/2} - (r_b-s)^3)sds = Eqn22(r_{p1}) - Eqn22(r_b-r_{p2}-r)$$

Therefore the s-integral of term 3

$$-2({r_{p2}}^2+r^2)\int_{r_b-r_{p2}-r}^{r_{p1}}((\frac{{r_{p2}}^2r_b-r_{p2}{r_b}^2+r_{p2}s^2-r_br^2}{r_{p2}-r_b})^{3/2}-(r_b-s)^3)sds$$

is expressed as

$$=-2({r_{p2}}^2+r^2)\{Eqn22(r_{p1})-Eqn22(r_b-r_{p2}-r)\} \qquad \text{(T.38)}$$

The s-integral of **term 4** is evaluated below:

$$\int_{r_b-r_{p2}-r}^{r_{p1}}(\frac{1}{5}((\frac{{r_{p2}}^2r_b-r_{p2}{r_b}^2+r_{p2}s^2-r_br^2}{r_{p2}-r_b})^{5/2}-(r_b-s)^5))sds$$

$$\frac{1}{5}\int_{r_b-r_{p2}-r}^{r_{p1}}((\frac{{r_{p2}}^2r_b-r_{p2}{r_b}^2+r_{p2}s^2-r_br^2}{r_{p2}-r_b})^{5/2}-(r_b-s)^5)sds$$

The indefinite integral in (24) can be evaluated as:

$$\int((\frac{{r_{p2}}^2r_b-r_{p2}{r_b}^2+r_{p2}s^2-r_br^2}{r_{p2}-r_b})^{5/2}-(r_b-s)^5)sds$$

$$=\frac{(r_{p2}-r_b)}{7r_{p2}}(\frac{{r_{p2}}^2r_b-r_{p2}{r_b}^2+r_{p2}s^2-r_br^2}{r_{p2}-r_b})^{3.5}-\frac{1}{2}{r_b}^5s^2+\frac{5}{3}{r_b}^4s^3-\frac{5}{2}{r_b}^3s^4+2{r_b}^2s^5-\frac{5}{6}r_bs^6+\frac{1}{7}s^7$$

Therefore,

$$\int_{r_b-r_{p2}-r}^{r_{p1}}((\frac{{r_{p2}}^2r_b-r_{p2}{r_b}^2+r_{p2}s^2-r_br^2}{r_{p2}-r_b})^{5/2}-(r_b-s)^5)sds=Eqn25(r_{p1})-Eqn25(r_b-r_{p2}-r)$$

The s-integral of term 4 is then expressed as:

$$\frac{1}{5}\int_{r_b-r_{p2}-r}^{r_{p1}}((\frac{{r_{p2}}^2r_b-r_{p2}{r_b}^2+r_{p2}s^2-r_br^2}{r_{p2}-r_b})^{5/2}-(r_b-s)^5)sds=\frac{1}{5}\{Eqn25(r_{p1})-Eqn25(r_b-r_{p2}-r)\} \qquad \text{(T.39)}$$

We are done evaluating the s-integral for each terms. Hence we have an expression for

$$\int_{r_b-r_{p2}-r}^{r_{p1}}(term1+term2+term3+term4)sds \tag{T.40}$$

We have

$$F(R\le r)=\frac{\pi^2}{6r_b}\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}}(r+r_{p2}-\mathrm{t})^2(t^2+2tr_{p2}-3r_{p2}{}^2+2tr+6r_{p2}r-3r^2)sdtds$$

We have been able to evaluate the double integral in (5) in four terms. What is left to be done is incorporating the factor $\frac{\pi^2}{6r_b}$

$$F(R\le r)=\frac{\pi^2}{6r_b}\{T.36+T.37+T.38+T.39\} \tag{T.41}$$

Case II. B

At some points, there is no overlap in sphere 1 with sphere 2.

$$F(R\le r)=\int_0^{2\pi}\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}}V_{cc}(t,r_{p2},r)\frac{st}{r_b}dtdsd\theta_1=0 \tag{T.42}$$

Case II*(r_b-r_{p2} < r < r_b -r_{p2}+r_{p1})

This is similar to that of case II. The only difference is that this considers the case where the length of 'r' is relatively longer, because the value of theta is greater than π/2. We divided this case also into two sub-cases.

A) When there is some overlap between points in sphere 1 and sphere 2.

B) When there is no overlap between any points in sphere 1 and sphere 2

Case II*. A (overlap of some points in sphere 1 with sphere 2)

$$F(R\le r)=\int_0^{2\pi}\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}}V_{cc}(t,r_{p2},r)\frac{st}{r_b}dtdsd\theta_1$$

$$F(R \le r) = 2\pi \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} V_{cc}(t, r_{p2}, r) \frac{st}{r_b} dtds$$

$$F(R \le r) = 2\pi \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} \frac{\pi(r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2}r - 3r^2)}{12t} \frac{st}{r_b} dtds$$

$$F(R \le r) = \frac{\pi^2}{6r_b} \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} (r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2}r - 3r^2) sdtds \tag{T.43}$$

The only difference from case II A is in the s-limits

$$t_{\min} = r_b - s$$

$$t_{\max} = \left(\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b}\right)^{1/2}$$

$$s_{\min} = 0$$

$$s_{\max} = r_{p1}$$

The integral can be rewritten as:

$$F(R \le r) = \frac{\pi^2}{6r_b} \int_0^{r_{p1}} \int_{r_b - s}^{\left(\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b}\right)^{1/2}} (r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2}r - 3r^2) sdtds \tag{T.44}$$

Since the inner t-integral has already been evaluated in case II A, we revert to the t-integral evaluated for 4 terms and rewrite the s-integral to take in the new s-limits

$$\int_0^{r_{p1}} (term1 + term2 + term3 + term4) sds \tag{T.45}$$

The s-integral for term1 is then evaluated on the platform of the mathematical evaluations done in case II A;

$$\int_0^{r_{p1}} (-3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)\left(\left(\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b}\right)^{1/2} - (r_b - s)\right)) sds$$

Likewise, for term 2

$$\int_0^{r_{p1}} 4r_b(r^3 + r_{p2}{}^3)(\frac{(r_{p2} - r_b + r + s)(r_{p2} - r_b - r + s)}{r_{p2} - r_b})sds$$

Likewise, for term 3

$$\int_0^{r_{p1}} (-2(r_{p2}{}^2 + r^2)((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{3/2} - (r_b - s)^3))sds$$

And lastly, for term 4

$$\int_0^{r_{p1}} (\frac{1}{5}((\frac{r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 - r_b r^2}{r_{p2} - r_b})^{5/2} - (r_b - s)^5))sds$$

The particular analytical form of these integrals is provided in the code below.

Case II* B (no overlap by some points in sphere 1 with sphere 2)

At some points, there is no overlap in sphere 1 with sphere 2.

$$F(R \le r) = \int_0^{2\pi} \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} V_{cc}(t, r_{p2}, r) \frac{st}{r_b} dt ds d\theta_1 = 0 \tag{T.46}$$

Case III (r_b-r_{p2}+r_{p1} ≤ r ≤ r_b+r_{p2})

Case III is divided into two parts:

A) When some points in sphere 1 overlaps points in sphere 2
B) When some points in sphere 1 totally encapsulates sphere 2

Case III. A (overlap by some points in sphere 1 with sphere 2)

$$F(R \le r) = \int_0^{2\pi} \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} V_{cc}(r_{p2}) \frac{st}{r_b} dt ds d\theta_1$$

$$F(R \le r) = 2\pi \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} V_{cc}(r_{p2}) \frac{st}{r_b} dt ds$$

$$F(R \le r) = 2\pi \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} \frac{\pi(r + r_{p2} - \mathrm{t})^2(t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2}r - 3r^2)}{12t} \frac{st}{r_b} dtds$$

$$F(R \le r) = \frac{\pi^2}{6r_b} \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} (r + r_{p2} - \mathrm{t})^2(t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2}r - 3r^2) sdtds$$

We define the limits of the double integral.

$s_{min} = 0$

$s_{max} = r_{p1}$

t_{min} requires a more rigorous evaluation as shown below:

$$t_{\min} = \sqrt{x^2 + y^2}$$

where; $y = a/2$ and $x = d_2 - r_{p2}$

a and d_2 are obtained from (T.16) circle-circle intersection

$$y = \frac{a}{2} = \frac{1}{2d}\sqrt{(-d + r - R)(-d - r + R)(-d + r + R)(d + r + R)} \text{ (in variables of T.16)}$$

$$y = \frac{1}{2(r_b + r_{p2})}\sqrt{(-(r_b + r_{p2}) + r - s)(-(r_b + r_{p2}) - r + s)(-(r_b + r_{p2}) + r + s)((r_b + r_{p2}) + r + s)}$$

$$y = \frac{1}{2(r_b + r_{p2})}\sqrt{(-r_b - r_{p2} + r - s)(-r_b - r_{p2} - r + s)(-r_b - r_{p2} + r + s)(r_b + r_{p2} + r + s)}$$

$$y = \frac{1}{2(r_b + r_{p2})}\sqrt{(r_{p2} + r_b - r + s)(r_{p2} + r_b + r - s)(-r_{p2} - r_b + r + s)(r_{p2} + r_b + r + s)}$$

$$y^2 = \frac{1}{4(r_b + r_{p2})^2}(r_{p2} + r_b - r + s)(r_{p2} + r_b + r - s)(-r_{p2} - r_b + r + s)(r_{p2} + r_b + r + s)$$

$$d_2 = \frac{d^2 + r^2 - R^2}{2d} \text{ (in variables of T.16)}$$

$$d_2 = \frac{(r_b + r_{p2})^2 + r^2 - s^2}{2(r_b + r_{p2})}$$

$$x = \frac{(r_b + r_{p2})^2 + r^2 - s^2}{2(r_b + r_{p2})} - r_{p2}$$

$$x^2 = (\frac{(r_b + r_{p2})^2 + r^2 - s^2}{2(r_b + r_{p2})} - r_{p2})^2$$

$$x^2 = \frac{({r_{p2}}^2 - {r_b}^2 - r^2 + s^2)^2}{4(r_{p2} + r_b)^2}$$

$$t_{\min} = \sqrt{x^2 + y^2}$$

$$t_{\min} = \sqrt{\frac{({r_{p2}}^2 - {r_b}^2 - r^2 + s^2)^2}{4(r_{p2} + r_b)^2} + \frac{1}{4(r_b + r_{p2})^2}(r_{p2} + r_b - r + s)(r_{p2} + r_b + r - s)(-r_{p2} - r_b + r + s)(r_{p2} + r_b + r + s)}$$

$$t_{\min} = \frac{1}{2(r_b + r_{p2})}\sqrt{({r_{p2}}^2 - {r_b}^2 - r^2 + s^2)^2 + (r_{p2} + r_b - r + s)(r_{p2} + r_b + r - s)(-r_{p2} - r_b + r + s)(r_{p2} + r_b + r + s)}$$

$$t_{\min} = \frac{1}{2(r_b + r_{p2})} 2\sqrt{(r_{p2} + r_b)(-{r_{p2}}^2 r_b - r_{p2}{r_b}^2 + r_{p2}s^2 + r_b r^2)}$$

$$t_{\min} = \frac{1}{(r_b + r_{p2})^{0.5}}\sqrt{(-{r_{p2}}^2 r_b - r_{p2}{r_b}^2 + r_{p2}s^2 + r_b r^2)}$$

$$t_{\min} = \sqrt{\frac{-{r_{p2}}^2 r_b - r_{p2}{r_b}^2 + r_{p2}s^2 + r_b r^2}{r_{p2} + r_b}}$$

$t_{max} = r_b + s$

The limits are summarized thus:

$s_{min} = 0$

$s_{max} = r_{p1}$

$$t_{\min} = \sqrt{\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}} \tag{T.47}$$

$t_{max} = r_b + s$

Substituting these limits (39) into (38)

$$F(R \le r) = \frac{\pi^2}{6r_b} \int_0^{r_{p1}} \int_{\left(\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2}+r_b}\right)^{1/2}}^{r_b+s} (r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2} r - 3r^2) s\,dt\,ds \tag{T.48}$$

The s-limits are the same as the previous case (Case II*A).

To evaluate (40), we start by evaluating the t-integral (inner integral)

$$\int_{\sqrt{\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2}+r_b}}}^{r_b+s} (r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2} r - 3r^2) dt$$

The indefinite integral in (41) is evaluated thus:

$$\int (r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2} r - 3r^2) dt$$
$$= -3r^4 t + 4r^3 t^2 + 6r^2 r_{p2}{}^2 t - 2r^2 t^3 - 3r_{p2}{}^4 t + 4r_{p2}{}^3 t^2 - 2r_{p2}{}^2 t^3 + \frac{t^5}{5}$$

$$= -3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)t + 4(r^3 + r_{p2}{}^3)t^2 - 2(r_{p2}{}^2 + r^2)t^3 + \frac{t^5}{5}$$

Upper limit

$$\int_0^{r_b+s} (r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2} r - 3r^2) dt$$

$$= -3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)(r_b + s) + 4(r^3 + r_{p2}{}^3)(r_b + s)^2 - 2(r_{p2}{}^2 + r^2)(r_b + s)^3 + \frac{(r_b + s)^5}{5}$$

Lower limit

$$\int_{\sqrt{\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}}}^{0} (r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2} r - 3r^2) dt$$

$$= -3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)\sqrt{\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}} + 4(r^3 + r_{p2}{}^3)(\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})$$
$$- 2(r_{p2}{}^2 + r^2)(\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{3}{2}} + \frac{1}{5}(\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{5}{2}}$$

Therefore

$$\int_{\sqrt{\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}}}^{r_b + s} (r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2} r - 3r^2) dt = upper - lower = Eqn(42) - Eqn(43)$$
$$= -3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)(r_b + s) + 4(r^3 + r_{p2}{}^3)(r_b + s)^2 - 2(r_{p2}{}^2 + r^2)(r_b + s)^3 + \frac{(r_b + s)^5}{5}$$
$$+ 3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)\sqrt{\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}} - 4(r^3 + r_{p2}{}^3)(\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})$$
$$+ 2(r_{p2}{}^2 + r^2)(\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{3}{2}} - \frac{1}{5}(\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{5}{2}}\}$$

This equation can be simplified into:

$$= 3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)(-(r_b + s) + \sqrt{\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}})$$
$$+ 4(r^3 + r_{p2}{}^3)((r_b + s)^2 - (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}))$$
$$+ 2(r_{p2}{}^2 + r^2)(-(r_b + s)^3 + \frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{3}{2}}) \qquad \text{(T.49)}$$
$$+ \frac{1}{5}((r_b + s)^5 - (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{5}{2}})$$

This has four terms, namely:

Term 1: $3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)(-(r_b + s) + (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{1}{2}})$

Term 2: $4(r^3 + r_{p2}{}^3)((r_b + s)^2 - (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}))$

Term 3: $2(r_{p2}{}^2 + r^2)(-(r_b + s)^3 + (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{3}{2}})$

Term 4: $\frac{1}{5}((r_b + s)^5 - (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{5}{2}})$

The s-integral of these four terms will be evaluated as follows:

The s-integral for term 1:

$$\int_0^{r_{p1}} 3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)(-(r_b + s) + (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{1}{2}})sds$$
$$= 3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)\int_0^{r_{p1}} (-(r_b + s) + (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{1}{2}})sds \tag{T.50}$$

The indefinite integral in (46) is evaluated as:

$$\int (-(r_b + s) + (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{1}{2}})sds$$
$$= \frac{-1}{3}(-\frac{r_b r^2}{r_{p2}} + r_{p2} r_b + r_b{}^2 - s^2)(\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{1}{2}} - \frac{1}{2} r_b s^2 - \frac{1}{3} s^3 \tag{T.51}$$

Therefore

$$\int_0^{r_{p1}} (-(r_b + s) + (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{1}{2}})sds \tag{T.52}$$

$$\int_0^{r_{p1}} 3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)(-(r_b + s) + (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{1}{2}})sds \qquad \text{(T.53)}$$

The s-integral of term 2, is evaluated as:

$$\int_0^{r_{p1}} 4(r^3 + r_{p2}{}^3)((r_b + s)^2 - (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}))sds$$

$$= 4(r^3 + r_{p2}{}^3)\int_0^{r_{p1}} ((r_b + s)^2 - (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}))sds$$

The indefinite integral is evaluated as:

$$\int ((r_b + s)^2 - (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}))sds = \frac{r_b s^2 (6r_{p2}{}^2 + 12 r_{p2} r_b + 6r_b{}^2 - 6r^2 + 8s(r_{p2} + r_b) + 3s^2)}{12(r_{p2} + r_b)}$$

(T.54)

$$\int_0^{r_{p1}} ((r_b + s)^2 - (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}))sds$$

We'll do the same for term 3. The s-integral is evaluated as:

$$\int_0^{r_{p1}} 2(r_{p2}{}^2 + r^2)(-(r_b + s)^3 + \frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{3}{2}})sds$$

$$= 2(r_{p2}{}^2 + r^2)\int_0^{r_{p1}} (-(r_b + s)^3 + (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{3}{2}})sds$$

The indefinite integral is evaluated as:

$$\int (-(r_b + s)^3 + (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{3}{2}})sds$$

$$= \frac{0.2}{r_{p2}(r_{p2} + r_b)^{\frac{3}{2}}}(-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2)^{\frac{5}{2}} - 0.5 r_b{}^3 s^2 - r_b{}^2 s^3 - 0.75 r_b s^4 - 0.2 s^5 \qquad \text{(T.55)}$$

$$\int_0^{r_{p1}} (-(r_b+s)^3 + (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2}+r_b})^{\frac{3}{2}}) s ds$$

And lastly for term 4, the s-integral is evaluated thus:

$$\int_0^{r_{p1}} \frac{1}{5}((r_b+s)^5 - (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b^2 + r_{p2} s^2 + r_b r^2}{r_{p2}+r_b})^{\frac{5}{2}}) s ds$$

which can be rewritten as:

$$\frac{1}{5}\int_0^{r_{p1}} ((r_b+s)^5 - (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b^2 + r_{p2} s^2 + r_b r^2}{r_{p2}+r_b})^{\frac{5}{2}}) s ds$$

The indefinite integral in (57) is evaluated as:

$$\int ((r_b+s)^5 - (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b^2 + r_{p2} s^2 + r_b r^2}{r_{p2}+r_b})^{\frac{5}{2}}) s ds$$

$$= \frac{(r_{p2}{}^2 r_b + r_{p2} r_b^2 - r_{p2} s^2 - r_b r^2)^3}{7 r_{p2}(r_{p2}+r_b)^2} (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b^2 + r_{p2} s^2 + r_b r^2}{r_{p2}+r_b})^{\frac{1}{2}} + \frac{r_b{}^5 s^2}{2} + \frac{5 r_b{}^4 s^3}{3} + \frac{5 r_b{}^3 s^4}{2} + 2 r_b{}^2 s^5 + \frac{5 r_b s^6}{6} + \frac{s^7}{7}$$

(T.56)

Thus

$$\int_0^{r_{p1}} ((r_b+s)^5 - (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2}+r_b})^{\frac{5}{2}}) s ds$$

We are done evaluating the s-integral (outer integral) for each term.

$$\int_0^{r_{p1}} (term1 + term2 + term3 + term4) s ds$$

$$F(R \le r) = \frac{\pi^2}{6 r_b} \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} (r + r_{p2} - t)^2 (t^2 + 2 t r_{p2} - 3 r_{p2}{}^2 + 2 t r + 6 r_{p2} r - 3 r^2) s dt ds$$

What is left to be done is incorporating the factor $\frac{\pi^2}{6 r_b}$.

$$F(R \le r) = \frac{\pi^2}{6r_b}\{T.53 + T.54 + T.55 + T.56\} \qquad \text{(T.57)}$$

Case III. B (total encapsulation by some points in sphere 1)

In this case the overlapping volume is the total volume of sphere 2; $V = \frac{4}{3}\pi r_{p2}^{3}$

$$F(R \le r) = \int_0^{2\pi}\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}} V_{cc}(r_{p2})\frac{st}{r_b}\,dtdsd\theta_1$$

$$F(R \le r) = 2\pi\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}} V_{cc}(r_{p2})\frac{st}{r_b}\,dtds$$

$$F(R \le r) = 2\pi\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}} \frac{4}{3}\pi r_{p2}^{3}\frac{st}{r_b}\,dtds$$

$$F(R \le r) = \frac{8\pi^2 r_{p2}^{3}}{3r_b}\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}} st\,dtds \qquad \text{(T.58)}$$

Let's attempt to define the limits to the double integral in (60)

$s_{\min} = r_b + r_{p2} - r$

$s_{\max} = r_{p1}$

$t_{\min} = r_b - s$

Defining tmax is a little complex, but we'll try to break it down as thus:

$t_{\max} = \sqrt{x^2 + y^2}$

Where $y = a/2$ and $x = d_2 - r_{p2}$

a and d_2 are obtained from the T.16 circle-circle intersection

$y = \frac{a}{2} = \frac{1}{2d}\sqrt{(-d+r-R)(-d-r+R)(-d+r+R)(d+r+R)}$ (in variables of T.16)

$$y = \frac{1}{2(r_b + r_{p2})}\sqrt{(-(r_b + r_{p2}) + r - s)(-(r_b + r_{p2}) - r + s)(-(r_b + r_{p2}) + r + s)((r_b + r_{p2}) + r + s)}$$

$$y = \frac{1}{2(r_b + r_{p2})}\sqrt{(-r_b - r_{p2} + r - s)(-r_b - r_{p2} - r + s)(-r_b - r_{p2} + r + s)(r_b + r_{p2} + r + s)}$$

$$y = \frac{1}{2(r_b + r_{p2})}\sqrt{(r_{p2} + r_b - r + s)(r_{p2} + r_b + r - s)(-r_{p2} - r_b + r + s)(r_{p2} + r_b + r + s)}$$

$$y^2 = \frac{1}{4(r_b + r_{p2})^2}(r_{p2} + r_b - r + s)(r_{p2} + r_b + r - s)(-r_{p2} - r_b + r + s)(r_{p2} + r_b + r + s)$$

$$d_2 = \frac{d^2 + r^2 - R^2}{2d} \text{ (in variables of T.16)}$$

$$d_2 = \frac{(r_b + r_{p2})^2 + r^2 - s^2}{2(r_b + r_{p2})}$$

$$x = \frac{(r_b + r_{p2})^2 + r^2 - s^2}{2(r_b + r_{p2})} - r_{p2}$$

$$x^2 = (\frac{(r_b + r_{p2})^2 + r^2 - s^2}{2(r_b + r_{p2})} - r_{p2})^2$$

$$x^2 = \frac{({r_{p2}}^2 - {r_b}^2 - r^2 + s^2)^2}{4(r_{p2} + r_b)^2}$$

$$t_{\max} = \sqrt{x^2 + y^2}$$

$$t_{\max} = \sqrt{\frac{({r_{p2}}^2 - {r_b}^2 - r^2 + s^2)^2}{4(r_{p2} + r_b)^2} + \frac{1}{4(r_b + r_{p2})^2}(r_{p2} + r_b - r + s)(r_{p2} + r_b + r - s)(-r_{p2} - r_b + r + s)(r_{p2} + r_b + r + s)}$$

$$t_{\max} = \frac{1}{2(r_b + r_{p2})}\sqrt{({r_{p2}}^2 - {r_b}^2 - r^2 + s^2)^2 + (r_{p2} + r_b - r + s)(r_{p2} + r_b + r - s)(-r_{p2} - r_b + r + s)(r_{p2} + r_b + r + s)}$$

$$t_{\max} = \frac{1}{2(r_b + r_{p2})}2\sqrt{(r_{p2} + r_b)(-{r_{p2}}^2 r_b - r_{p2}{r_b}^2 + r_{p2}s^2 + r_b r^2)}$$

$$t_{\max} = \frac{1}{(r_b + r_{p2})^{0.5}} \sqrt{(-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2)}$$

$$t_{\max} = \sqrt{\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}}$$

In general the limits are:

$$s_{\min} = r_b + r_{p2} - r$$

$$s_{\max} = r_{p1}$$

$$t_{\min} = r_b - s$$

$$t_{\max} = \sqrt{\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}}$$

So the integral can be written explicitly as:

$$F(R \le r) = \frac{8\pi^2 r_{p2}{}^3}{3 r_b} \int_{r_b + r_{p2} - r}^{r_{p1}} \int_{r_b - s}^{\sqrt{\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}}} t\,dt\,s\,ds \tag{T.59}$$

Evaluating the double integral

$$\int_{r_b + r_{p2} - r}^{r_{p1}} \{\int_{r_b - s}^{t_{\max}} t\,dt\} s\,ds = \frac{1}{2} \int_{r_b + r_{p2} - r}^{r_{p1}} \left(\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b} - (r_b - s)^2\right) s\,ds \tag{T.60}$$

Now that we have evaluated the inner (t-integral), we have to evaluate the s-integral

$$\int_{r_b + r_{p2} - r}^{r_{p1}} \left(\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b} - (r_b - s)^2\right) s\,ds \tag{T.61}$$

The indefinite integral is

$$\int (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b} - (r_b - s)^2) s ds$$

$$= \frac{-6r_{p2}{}^2 r_b s^2 - 12 r_{p2} r_b{}^2 s^2 - 6r_b{}^3 s^2 + 6r_b r^2 s^2 + 8r_{p2} r_b s^3 + 8r_b{}^2 s^3 - 3r_b s^4}{12(r_{p2} + r_b)} \qquad \text{(T.62)}$$

Evaluating the s-integral in applying the s-limits give;

$$\int_{r_b + r_{p2} - r}^{r_{p1}} (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b} - (r_b - s)^2) s ds$$

Case III* (r_b+r_{p2} <r < r_b+r_{p1}+r_{p2})

Case III* is similar in expression to Case III, same way Case II* is similar to Case II. The only difference is in the fact that the radius 'r' is longer in this case compared to case III. This results in the same t-limits as that of case III but different s-limit.

We have two scenarios;

A) Where some parts in sphere 1 overlaps points in sphere 2
B) Where some parts in sphere 1 totally encapsulate sphere 2

Case III* A (Overlap of some points in sphere 1 over sphere 2)

$$F(R \le r) = \int_0^{2\pi} \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} V_{cc}(r_{p2}) \frac{st}{r_b} dt ds d\theta_1$$

$$F(R \le r) = 2\pi \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} V_{cc}(r_{p2}) \frac{st}{r_b} dt ds$$

$$F(R \le r) = 2\pi \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} \frac{\pi (r + r_{p2} - \mathrm{t})^2 (t^2 + 2t r_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2} r - 3r^2)}{12t} \frac{st}{r_b} dt ds$$

$$F(R \le r) = \frac{\pi^2}{6r_b} \int_{s_{\min}}^{s_{\max}} \int_{t_{\min}}^{t_{\max}} (r + r_{p2} - \mathrm{t})^2 (t^2 + 2t r_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2} r - 3r^2) s dt ds \qquad \text{(T.63)}$$

We define the s-limits and reintroduce the t-limits of case III A

s_{min} = r-r_b-r_{p2}

s_{max} = r_{p1}

$$t_{\min} = \sqrt{\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}}$$

t_{max} = r_b + s

The integral is written explicitly as:

$$F(R \le r) = \frac{\pi^2}{6r_b} \int_{r-r_b-r_{p2}}^{r_{p1}} \int_{\sqrt{\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2}+r_b}}}^{r_b+s} (r + r_{p2} - \mathrm{t})^2 (t^2 + 2tr_{p2} - 3r_{p2}{}^2 + 2tr + 6r_{p2}r - 3r^2) sdtds \tag{T.64}$$

The inner integral (t-integral) as already been evaluated in the case of Case III A.

The evaluation of the s-integral for the terms in which the t-integral evaluations are broken down into is the only difference between Case III* A and Case III A. Therefore, we go straight to evaluating the s-integral based on the equations in case III A.

For term 1:

$$\int_{r-r_b-r_{p2}}^{r_{p1}} 3(r^4 + r_{p2}{}^4 - 2r^2 r_{p2}{}^2)(-(r_b + s) + (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{1}{2}}) sds \tag{T.65}$$

For term 2:

$$\int_{r-r_b-r_{p2}}^{r_{p1}} 4(r^3 + r_{p2}{}^3)((r_b + s)^2 - (\frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})) sds \tag{T.66}$$

We’ll do the same for term 3:

$$\int_{r-r_b-r_{p2}}^{r_{p1}} 2(r_{p2}{}^2 + r^2)(-(r_b + s)^3 + \frac{-r_{p2}{}^2 r_b - r_{p2} r_b{}^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b})^{\frac{3}{2}}) sds \tag{T.67}$$

And lastly for term 4:

$$\frac{1}{5}\int_{r-r_b-r_{p2}}^{r_{p1}}((r_b+s)^5-(\frac{-r_{p2}{}^2r_b-r_{p2}r_b{}^2+r_{p2}s^2+r_br^2}{r_{p2}+r_b})^{\frac{5}{2}})sds \qquad \text{(T.68)}$$

Now that we are done evaluating the s-integral (outer integral) for each term, the integral becom

$$F(R\le r)=\frac{\pi^2}{6r_b}\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}}(r+r_{p2}-\mathrm{t})^2(t^2+2tr_{p2}-3r_{p2}{}^2+2tr+6r_{p2}r-3r^2)sdtds$$

What is left to be done is incorporating the factor $\frac{\pi^2}{6r_b}$

$$F(R\le r)=\frac{\pi^2}{6r_b}\{T.65+T.66+T.67+T.68\} \qquad \text{(T.69)}$$

Case III* B (Case where there is total encapsulation of some points in sphere 1 over sphere 2)

$$F(R\le r)=\int_0^{2\pi}\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}}V_{cc}(r_{p2})\frac{st}{r_b}dtdsd\theta_1$$

$$F(R\le r)=2\pi\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}}V_{cc}(r_{p2})\frac{st}{r_b}dtds$$

$$F(R\le r)=2\pi\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}}\frac{4}{3}\pi r_{p2}{}^3\frac{st}{r_b}dtds$$

$$F(R\le r)=\frac{8\pi^2r_{p2}{}^3}{3r_b}\int_{s_{\min}}^{s_{\max}}\int_{t_{\min}}^{t_{\max}}stdtds \qquad \text{(T.70)}$$

As we stated earlier, the t-limits are the same as that of Case III B, the only difference is in the s-limit. The limits are explicitly stated as thus:

$s_{\min}=r-r_b-r_{p2}$

$s_{\max}=r_{p1}$

$t_{\min}=r_b-s$

$$t_{\max} = \sqrt{\frac{-r_{p2}^2 r_b - r_{p2} r_b^2 + r_{p2} s^2 + r_b r^2}{r_{p2} + r_b}}$$

The integral can be rewritten as:

$$F(R \le r) = \frac{8\pi^2 r_{p2}^3}{3r_b} \int_{r-r_b-r_{p2}}^{r_{p1}} \int_{r_b-s}^{\sqrt{\frac{-r_{p2}^2 r_b - r_{p2} r_b^2 + r_{p2} s^2 + r_b r^2}{r_{p2}+r_b}}} t\,dt\,s\,ds \qquad \text{(T.71)}$$

The evaluation of the s-integral is the only difference from that in case III B. So we build on this pedestal.

Evaluating (T.71) in this regard, we have

$$F(R \le r) = \frac{8\pi^2 r_{p2}^3}{3r_b} \int_{r-r_b-r_{p2}}^{r_{p1}} \int_{r_b-s}^{\sqrt{\frac{-r_{p2}^2 r_b - r_{p2} r_b^2 + r_{p2} s^2 + r_b r^2}{r_{p2}+r_b}}} t\,dt\,s\,ds = \frac{4\pi^2 r_{p2}^3}{3r_b}\{T.62(r_{p1}) - T.62(r - r_b - r_{p2})\} \qquad \text{(T.72)}$$

Case IV ($r \geq r_b + r_{p1} + r_{p2}$)

This case represents when all the points in sphere 1 encapsulates all the volume of sphere 2.

$$F(R \le r) = \frac{16}{9}\pi^2 r_{p1}^3 r_{p2}^3 \qquad \text{(T.73)}$$

Step 4. Differentiate with respect to r

The definition of the cumulative probability distribution function is

$$F_r(r) = P(R \le r) \equiv \int_{-\infty}^{\infty} f(r')dr' \qquad \text{(S.26)}$$

where $f(r')$ is the probability distribution function. Therefore

$$f(r) = \frac{dF_r(r)}{dr} \qquad \text{(S.27)}$$

The derivatives of the cumulative distribution function given derived in Step 3 have no compact analytical form. The result is presented in the Matlab code in the appendices below.

A code generating the RDF of equation (S.32) for a single pair of spheres is provide below in Appendix SI.II. A simple main program used to set sample parameter values is given in SI.II.A. The function itself is given in SI.II.B. This code was used to generate the following plots for a single pair of spheres with the radius of particle 1, $r_{p,1} = 7.0$, the radius of particle 2, $r_{p,2} = 7.0$, and the separation between center points, $d_p = 25.0$..

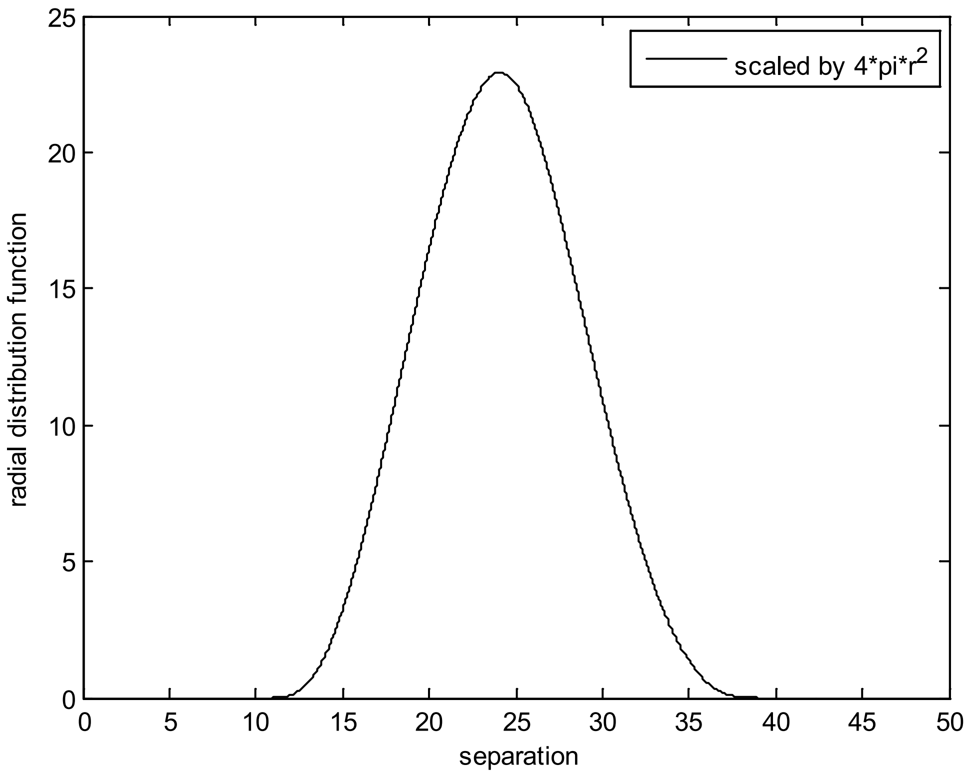

Figure S.4. The RDF for a pair of spheres with $r_{p,1} = 7.0$ and $r_{p,2} = 7.0$ separated by $d_p = 25.0$. This RDF included the factor of $\frac{1.0}{4.0\pi r^2}$, but this factor was included in the driver, NOT in the function (as is the case with the disc-disc code). (The factor was omitted in the sphere-sphere case since it is (in our application) eventually convoluted with a continuous mesoscale RDF and the factor was included later.)

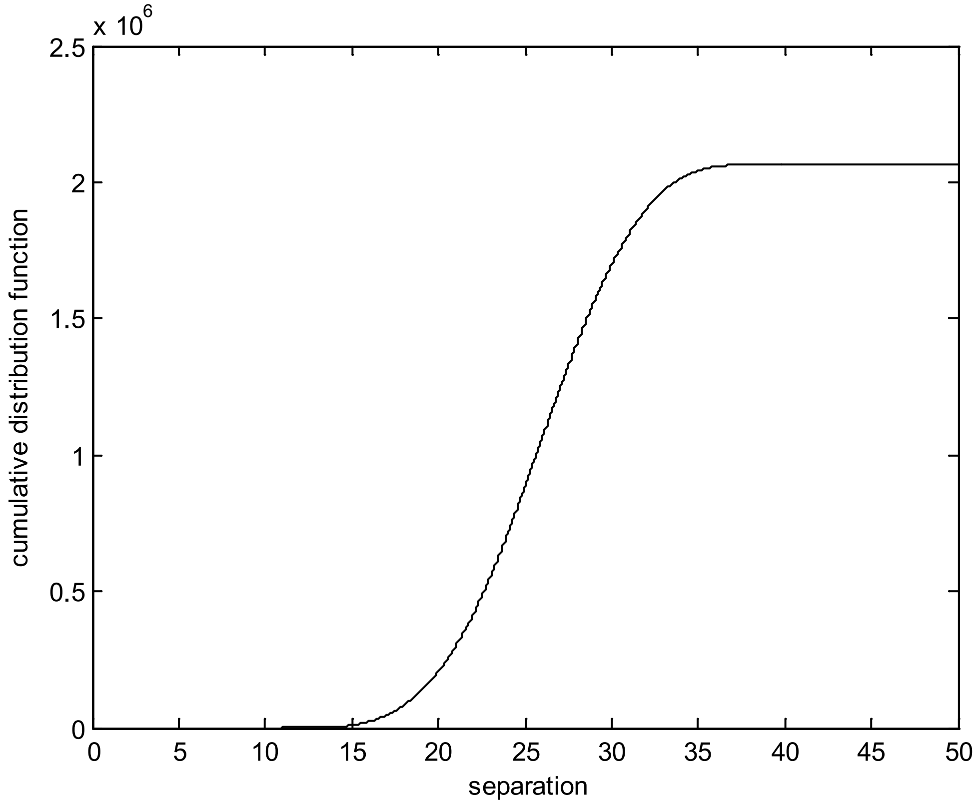

Figure S.3. The cumulative RDF for a pair of planes with $r_{p,1} = 7.0$ and $r_{p,2} = 7.0$ separated by $d_p = 25.0$. In these units, the final plateau of the cumulative distribution occurs at a value of $Volume_1 \cdot Volume_2 = \frac{16}{9}\pi^2 r_{p,1}^3 r_{p,2}^3$.

Appendix SI.I. Code to Evaluate Disc-Disc RDF

SI.I.A. Driver

```
%
%  gofr_discdisc_test.m
%
%  This script calls gofr_discdisc.m
%
% use:
% g = gofr_discdisc_test
%
%
%  authors: David J. Keffer & Akinola D. Oyedele
%  Dept. of Materials Science & Engineering
%  University of Tennessee
%  dkeffer@utk.edu
%  last updated:  June 1, 2017
%
clear all;
close all;
format long;
%
%  discretize radial dimension
%
rmin = 0.0;
rmax = 50.0;
dr = 0.01;
rvec = [rmin:dr:rmax];
nr = length(rvec);
%
%  test system parameters
%
%  rp1 must be less than or equal to rp2
rp1 = 7.0;
rp2 = 10.0;
dp = 3.4;
%
%  compute RDF
%
g = zeros(nr,1);
g = gofr_discdisc(dp,rp1,rp2,nr,rvec);
%
%  plot RDF
%
%
%  plot RDF
%
figure(1);
plot(rvec,g,'r-');
xlabel(' separation');
ylabel(' radial distribution function ');
%
%  check volume
%
vol1 = pi*rp1^2;
vol2 = pi*rp2^2;
volprod = vol1*vol2;
%
integral = 0.0;
cumulative = zeros(nr,1);
for i = 2:1:nr
```

```
    base = rvec(i) - rvec(i-1);
    height1 = 4.0*pi*rvec(i-1)^2*g(i-1);
    height2 = 4.0*pi*rvec(i)^2*g(i);
    area = 0.5*base*(height1 + height2);
    cumulative(i) = cumulative(i-1) + area;
    integral = integral + area;
end
%
%  plot cumulative RDF
%
figure(2);
plot(rvec,cumulative,'k-');
xlabel(' separation');
ylabel(' cumulative distribution function ');
%
%  error checking
%
diff = (integral - volprod)/volprod;
fprintf(1, ' analytical %e numerical %e error %e \n',volprod,integral,diff);
```

SI.I.B. Function

```
function g = gofr_discdisc(dp,rp1,rp2,nr,rvec)
%
%  gofr_discdisc
%
%  This code calculates the contribution to the radial distribution function
%  due to the atoms distributed uniformly over two discs of radius rp1 and rp2
%  and separated by a distance p.
%
%  The RDF is returned in units of area squared.
%  The RDF IS normalized by a factor of 1.0/(4.0*pi*r^2).
%  The value of rp1 must be less than or equal to rp2.
%
% use:
% g = gofr_discdisc(dp,rp1,rp2,nr,rvec)
%
% inputs:
% dp:  distance between particles
% rp1:  radius of particle 1
% rp2:  radius of particle 2
% nr:  number of radial points to evaluate function
% rvec:  vector of radial positions
%
% outputs:
% g:  radial distribution function
%
%  authors: David J. Keffer & Akinola D. Oyedele
%  Dept. of Materials Science & Engineering
%  University of Tennessee
%  dkeffer@utk.edu
%  last updated:  June 1, 2017
%
%


%
% input parameters
%
fvec = zeros(nr,1); % d/dr
g = zeros(nr,1); % Radial distribution function

for i = 1:1:nr
    r = rvec(i);

    if (r <= dp)  %  no contribution until r is bigger than dp
        fvec(i) = 0;

    else
       rx =  sqrt( r*r - dp*dp);
       drxdr = r/rx;
       rp1min_cond = rx-rp2;
       rp1min = abs(rp1min_cond);
       rp1max = min(rp2+rx,rp1);
       test = rp2*rp2+rx*rx-rp1min*rp1min;
       if test > 0
           result = pi/2.0;
       else
           result = -pi/2.0;
       end
       if rp1min_cond <= 0    % Encapsulated+overlap or only overlap
```

```
    if rp1min < rp1max   % Encapsulated plus overlap
        den = eqn_den(rp2,rx,rp1max);
        num = eqn_num(rp2,rx,rp1max);

        if rp1max == rp1
            drp1maxdr = 0;
        elseif rp1max == rp2 + rx
            drp1maxdr = drxdr;
        end
        %
        % Area of overlap  % Term 1
        f1_u = eqn_f1_u(rp2,rx,rp1max,drxdr,den,drp1maxdr);
        drp1mindr = (rp1min_cond/rp1min)*drxdr;
        dFdrx = -2*pi*rp2*rp2*rx*result;
        f1_l = dFdrx*drxdr;
        f1 = f1_u - f1_l;
        % Term 2
        f2_u = eqn_f2_u(rp2,rx,rp1max,drxdr,den,drp1maxdr);
        dFdrx = 2*pi*pi*rx*rp1min*rp1min;
        dFdrp1min = 2*pi*pi*rx*rx*rp1min;
        f2_l1 = dFdrx*drxdr + dFdrp1min*drp1mindr;
        dFdrx = -2*pi*rx*rp2*rp2*result;
        f2_l3 = dFdrx*drxdr;
        f2_l = f2_l1 + f2_l3;
        f2 = f2_u - f2_l;
        % Term 3
        f3 = eqn_f3(rp2,rx,rp1max,drxdr,num,drp1maxdr,result);
        %
        area_overlap = f1 +f2 +f3;
        %
        % Area of encapsulated
        dFdrx = 2*pi*pi*rx*rp1min*rp1min;
        dFdrp1min = 2*pi*pi*rx*rx*rp1min;
        drp1mindr = (rx - rp2)/(abs(rx-rp2))*drxdr;
        area_small = dFdrx*drxdr + dFdrp1min*drp1mindr;
        % Area of overlap plus encapsulated
        fvec(i) = area_overlap +area_small;

    else    % Encapsulated only
        dFdrx = 2*pi*pi*rx*rp1*rp1;
        fvec(i) = dFdrx*drxdr;
    end

else   % Encapsulates+overlap or only overlap
    if rp1min < rp1max   % Encapsulates plus overlap
        den = eqn_den(rp2,rx,rp1max);
        num = eqn_num(rp2,rx,rp1max);
        if rp1max == rp1
            drp1maxdr = 0;
        elseif rp1max == rp2 + rx
            drp1maxdr = drxdr;
        end
        %
        % Area that encapsulates % Term 1
        f1_u = eqn_f1_u(rp2,rx,rp1max,drxdr,den,drp1maxdr);
        drp1mindr = (rp1min_cond/rp1min)*drxdr;
        dFdrp1min = 2*pi*pi*rp2*rp2*rp1min;
        f1_l1 = dFdrp1min*drp1mindr;
        dFdrx = -2*pi*rp2*rp2*rx*result;
        f1_l3 = dFdrx*drxdr;
        f1_l = f1_l1 + f1_l3;
        f1 = f1_u - f1_l;
        % Term 2
```

```
                f2_u = eqn_f2_u(rp2,rx,rp1max,drxdr,den,drp1maxdr);
                dFdrx = -2*pi*rp2*rp2*rx*result;
                f2_l = dFdrx*drxdr;
                f2 = f2_u - f2_l;
                % Term 3
                f3 = eqn_f3(rp2,rx,rp1max,drxdr,num,drp1maxdr,result);
                %
                % Area of overlap
                area_overlap = f1 +f2 +f3;
                %
                % Area of overlap plus area that encapsulates
                dFdrp1min = 2*pi*pi*rp2*rp2*rp1min;
                drp1mindr = (rx - rp2)/(abs(rx-rp2))*drxdr;
                area_large = dFdrp1min*drp1mindr;
                fvec(i) = area_overlap +area_large;

            else   % Encapsulates only
                fvec(i) = 0;
            end
        end
    end
end

fac = 1.0/(4.0*pi);
for i = 2:1:nr
    fac2 = fac/(rvec(i)*rvec(i));
    g(i) = fac2*fvec(i);
end
end


function result = eqn_den(rp2,rx,rp1max)
result = (-rp2*rp2*rp2*rp2+2*rp2*rp2*(rx*rx+rp1max*rp1max)-(rx*rx-rp1max*rp1max)^2);
end


function result = eqn_num(rp2,rx,rp1max)
result =(rp2+rx-rp1max)*(rp2-rx+rp1max)*(-rp2+rx+rp1max)*(rp2+rx+rp1max);
end


function result = eqn_f1_u(rp2,rx,rp1max,drxdr,den,drp1maxdr)
dFdrx = 2*pi*rp2*rp2*rp1max*rp1max*rx/sqrt(den);
dFdrp1max_1 = 2*pi*rp2*rp2*rp1max*acos((rp2*rp2-rx*rx+rp1max*rp1max)/(2*rp2*rp1max));
dFdrp1max_2 = pi*rp2*rp2*rp1max*(rp2*rp2-rx*rx-rp1max*rp1max)/sqrt(den);
dFdrp1max = dFdrp1max_1 + dFdrp1max_2;
f1_u1 = dFdrx*drxdr + dFdrp1max*drp1maxdr;
%
dFdrx = -pi*rp2*rp2*rx*(rp2*rp2-rx*rx+rp1max*rp1max)/sqrt(den);
dFdrp1max = -pi*rp2*rp2*rp1max*(rp2*rp2+rx*rx-rp1max*rp1max)/sqrt(den);
f1_u2 = dFdrx*drxdr + dFdrp1max*drp1maxdr;
%
dFdrx_1 = -pi*rp2*rp2*rx*(-rp2*rp2+rx*rx+rp1max*rp1max)/sqrt(den);
dFdrx_2 = - 2*pi*rp2*rp2*rx*atan((rp2*rp2+rx*rx-rp1max*rp1max)/sqrt(den));
dFdrx = dFdrx_1 + dFdrx_2;
dFdrp1max = 2*pi*rp2*rp2*rx*rx*rp1max/sqrt(den);
f1_u3 = dFdrx*drxdr + dFdrp1max*drp1maxdr;
%
result =  f1_u1 + f1_u2 + f1_u3;
end


function result = eqn_f2_u(rp2,rx,rp1max,drxdr,den,drp1maxdr)
```

```
fac = 2*pi*rp1max*rx*acos((rx*rx-rp2*rp2+rp1max*rp1max)/(2*rx*rp1max));
dFdrx = rp1max*fac-(rp2*rp2+rx*rx-rp1max*rp1max)*pi*rp1max*rp1max*rx/sqrt(den);
dFdrp1max = rx*fac-(rp2*rp2-rx*rx+rp1max*rp1max)*pi*rp1max*rx*rx/sqrt(den);
f2_u1 = dFdrx*drxdr + dFdrp1max*drp1maxdr;
%
dFdrx = pi*rx*(rp2^4+rp1max^4+2*rx^4-3*rp1max^2*rx^2-2*rp2^2*rp1max^2-
3*rp2*rp2*rx*rx)/sqrt(den);
dFdrp1max = -pi*rp1max*rx*rx*(rp2*rp2+rx*rx-rp1max*rp1max)/sqrt(den);
f2_u2 = dFdrx*drxdr + dFdrp1max*drp1maxdr;
%
dFdrx_1 = -pi*rp2*rp2*rx*(-rp2*rp2+rx*rx+rp1max*rp1max)/sqrt(den);
dFdrx_2 = -2*pi*rp2*rp2*rx*atan((rp2*rp2+rx*rx-rp1max*rp1max)/sqrt(den));
dFdrx = dFdrx_1 + dFdrx_2;
dFdrp1max = 2*pi*rp2*rp2*rx*rx*rp1max/sqrt(den);
f2_u3 = dFdrx*drxdr + dFdrp1max*drp1maxdr;
%
result =  f2_u1 + f2_u2 + f2_u3;
end


function result = eqn_f3(rp2,rx,rp1max,drxdr,num,drp1maxdr,result)
% Term 3: Upper limit
dFdrx = (pi*rp2*rp2*rp1max*rp1max*rx + pi*rp2*rp2*rx*rx*rx +2*pi*(rp1max^2)*(rx^3) -
pi*rx*rp1max^4-pi*(rx^5))/sqrt(num);
dFdrp1max = (pi*rp1max*(rp2^4) + pi*rp1max*(rx^4) +pi*(rp1max^5) -
2*pi*(rp2^2)*(rp1max^3)-2*pi*(rx^2)*(rp1max^3))/sqrt(num);
f3_u1 = dFdrx*drxdr + dFdrp1max*drp1maxdr;
dFdrx = pi*rp2*rp2*rx*(-
rp2*rp2+rx*rx+rp1max*rp1max)/sqrt(num)+2*pi*rp2*rp2*rx*atan((rp2*rp2+rx*rx-
rp1max*rp1max)/(sqrt(num)));
dFdrp1max = -2*pi*rp2*rp2*rx*rx*rp1max/sqrt(num);
f3_u2 = dFdrx*drxdr + dFdrp1max*drp1maxdr;
f3_u = f3_u1 + f3_u2;
% Term 3: Lower limit
dFdrx = 2*pi*rp2*rp2*rx*result;
f3_l2 = dFdrx*drxdr;
f3_l = f3_l2;
%
result = f3_u - f3_l;
end
```

Appendix SI.II. Code to Evaluate Sphere-sphere RDF

SI.II.A. Driver

```
%
%  gofr_spheresphere_test.m
%
%  This script calls gofr_spheresphere.m
%
% use:
% g = gofr_spheresphere_test
%
%
%  authors: David J. Keffer & Akinola D. Oyedele
%  Dept. of Materials Science & Engineering
%  University of Tennessee
%  dkeffer@utk.edu
%  last updated:  June 1, 2017
%
clear all;
close all;
format long;
%
%  discretize radial dimension
%
rmin = 0.0;
rmax = 50.0;
dr = 0.01;
rvec = [rmin:dr:rmax];
nr = length(rvec);
%
%  test system parameters
%
rp1 = 7.0;
rp2 = rp1;
dp = 25.0;
%
%  compute RDF
%
g = zeros(nr,1);
g = gofr_spheresphere(dp,rp1,rp2,nr,rvec);
%
%  normalize by 4*pi*r^2
%
pi = 2.0*asin(1.0);
gnorm = zeros(nr,1);
for i = 2:1:nr
    fac = 1.0/(4.0*pi*rvec(i)^2);
    gnorm(i) = fac*g(i);
end
%
%  plot RDF
%
figure(1);
plot(rvec,gnorm,'k-');
xlabel(' separation');
ylabel(' radial distribution function ');
legend('scaled by 4*pi*r^2');
%
figure(2);
plot(rvec,g,'r-');
```

```
xlabel(' separation');
ylabel(' radial distribution function ');
legend('unscaled');

%
%  check volume
%
vol1 = 4.0/3.0*pi*rp1^3;
vol2 = 4.0/3.0*pi*rp2^3;
volprod = vol1*vol2;
%
integral = 0.0;
integralnorm = 0.0;
cumulative = zeros(nr,1);
for i = 2:1:nr
    base = rvec(i) - rvec(i-1);
    height1n = 4.0*pi*rvec(i-1)^2*gnorm(i-1);
    height2n = 4.0*pi*rvec(i)^2*gnorm(i);
    height1 = g(i-1);
    height2 = g(i);
    area = 0.5*base*(height1 + height2);
    areanorm = 0.5*base*(height1n + height2n);
    cumulative(i) = cumulative(i-1) + areanorm;
    integral = integral + area;
    integralnorm = integralnorm + areanorm;
end
%
%  plot cumulative RDF
%
figure(3);
plot(rvec,cumulative,'k-');
xlabel(' separation');
ylabel(' cumulative distribution function ');
%
%  error checking
%
diff = (integral - volprod)/volprod;
diffnorm = (integralnorm - volprod)/volprod;
fprintf(1, ' analytical %e numerical %e errors %e %e
\n',volprod,integral,diff,diffnorm);
```

SI.II.B. Function

```
%
%  gofr_spheresphere
%
%  This code calculates the contribution to the radial distribution function
%  due to the atoms distributed uniformly over two spheres of radius rp1 and
rp2
%  and separated by a distance p.
%
%  The RDF is returned in units of volume squared.
%  The RDF is NOT normalized by a factor of 1.0/(4.0*pi*r^2).
%  For this version, the value of rp1 equal to rp2.
%
% use:
% g = gofr_spheresphere(dp,rp1,rp2,nr,rvec)
%
% inputs:
% dp:  distance between particles
% rp1:  radius of particle 1
% rp2:  radius of particle 2
% nr:  number of radial points to evaluate function
% rvec:  vector of radial positions
%
% outputs:
% g:  radial distribution function
%
%  authors: David J. Keffer & Akinola D. Oyedele
%  Dept. of Materials Science & Engineering
%  University of Tennessee
%  dkeffer@utk.edu
%  last updated:  June 1, 2017
%
function g = gofr_spheresphere(dp,rp1,rp2,nr,rvec)
%
% input parameters
%
fvec = zeros(nr,1); % d/dr
g = zeros(nr,1); % Radial distribution function
rb = dp;
%
%  create the volume as a function of r for this value of rp1
%
rmin = rb-rp1-rp2;
rlim1 =rb-rp2;
rlim2 = rb-rp2+rp1;
rlim3 = rb+rp2;
rmax = rb+rp1+rp2;

for i = 1:1:nr
    r = rvec(i);
    %
    if r <= rmin
        % Case I: No overlap
```

```
        fvec(i) = 0;

    elseif (r > rmin) && (r <= rlim1)
        % Case II A: Some overlap at some points in sphere 1
        fvec(i) = caseIIa(r,rp1,rp2,rb);

    elseif (r > rlim1) && (r < rlim2)
        % Case II* A: Some overlap at some points in sphere 1
        fr_II_star_A_1 = caseIIstar_A1 (r,rp2,rb);
        fr_II_star_A_2 = caseIIstar_A2 (r,rp1,rp2,rb);
        fvec(i) = fr_II_star_A_1 + fr_II_star_A_2;

    elseif (r >= rlim2) && (r <= rlim3)
        % Case III A: Some overlap at some points in sphere 1
        fr_IIIA_1 = caseIII_A1 (r,rp2,rb);
        fr_IIIA_2 = caseIII_A2 (r,rp1,rp2,rb);
        fr_IIIA = fr_IIIA_1 + fr_IIIA_2;
        %
        % Case III B: All overlap at some points in sphere 1
        fr_IIIB = caseIII_B (r,rp1,rp2,rb);
        fvec(i) = fr_IIIA + fr_IIIB;

    elseif (r > rlim3) && (r < rmax)
        % Case III* A: Some overlap at some points in sphere 1
        fr_III_star_A = caseIIIstar_A (r,rp1,rp2,rb);
        %
        % Case III* B
        fr_III_star_B_1 = 16/3*pi^2*rp2^3*(-rb-rp2+r)^2;
        fr_III_star_B_2 = caseIIIstar_B2(r,rp1,rp2,rb);
        fr_III_star_B = fr_III_star_B_1 + fr_III_star_B_2;
        fvec(i) = fr_III_star_A + fr_III_star_B;

    elseif r >= rmax
        % Case IV: All overlap at all points in sphere 1 and 2
        fvec(i) = 0;
    end
end

% fac = 1.0/(4.0*pi);
for i = 2:1:nr
    %fac2 = fac/(rvec(i)*rvec(i));
    fac2 = 1.0; % NOTE: keffer added this
    g(i) = fac2*fvec(i);
end
end


function result=caseIIa(r,rp1,rp2,rb)
Fac1 = ((rp2^2*rb-rp2*rb^2+rp2*rp1^2-rb*r^2)/(rp2-rb));
Fac2 = -168*r*rp1^5*rp2^2+84*Fac1^(5/2)*rp2*rb^2*r/(rp2-rb);
Fac3 = -5040*rp2^4*r^4-2016*rp2^7*r-6048*r^5*rp2^3-42*rp2^2*rb^5*r;
Fac4 = 420*rp2^2*Fac1^(3/2)*rb^3*r/(rp2-rb)+3486*rb*rp2^6*r;
Fac5 = -840*r^3*Fac1^(3/2)*rp2^2-840*r^3*Fac1^(3/2)*rb^2;
Fac6 = 630*r^5*Fac1^(1/2)*rb^3/(rp2-rb)+840*rp2^4*r*Fac1^(3/2);
Fac7 = -2100*rb*rp1^2*rp2^4*r+840*rp2^2*r*Fac1^(3/2)*rb^2+2016*rp2^2*r^6;
```

```
Fac8 = -10080*r^4*rp2^3*rb-210*rp2*rb^5*r^2+2100*rp2*rb^3*r^4;
Fac9 = 3486*rp2*r^6*rb-1008*rp2^6*rb^2+2016*rp2^7*rb+1008*rp2^8;
Fac10 = -1260*rb^2*r^3*rp2^3-2310*rb^2*rp2^5*r+1680*r^3*Fac1^(3/2)*rp2*rb;
Fac11 = -1260*r^5*Fac1^(1/2)*rp2*rb^2/(rp2-rb)-1680*rp2^3*r*Fac1^(3/2)*rb;
Fac12 = Fac2+Fac3+Fac4+Fac5+Fac6+Fac7+Fac8+Fac9+Fac10+Fac11;
Fac13 = 2520*rp2^3*r^3*Fac1^(1/2)*rb^2/(rp2-rb)+336*r*Fac1^(5/2)*rp2*rb;
Fac14 = -840*r^3*Fac1^(3/2)*rp2*rb^2/(rp2-rb)-5838*rp2*r^5*rb^2;
Fac15 = 11886*rp2^2*r^5*rb-420*rp2^3*rb^4*r+1260*rp2^4*rb^3*r;
Fac16 = -420*rp2^2*rb^3*r^3+12180*rb*r^4*rp2^3-210*rb*r^2*rp2^5;
Fac17 = -1260*rb^3*r^2*rp2^3-9240*rb^2*r^4*rp2^2+840*rb^2*r^2*rp2^4;
Fac18 = 840*rp2^4*r*rp1^3-840*r^3*rp1^3*rp2^2+42*rp2*r*rb^6;
Fac19 = 6048*rb^2*r^5*rp2+5040*rp2^2*r^4*rb^2-4032*r^6*rp2*rb;
Fac20 = -2016*rp2^7*rb+6048*rp2^3*r^5+2016*rb^2*r^6+2016*rp2^7*r;
Fac21 = Fac12+Fac13+Fac14+Fac15+Fac16+Fac17+Fac18+Fac19+Fac20;
Fac22 = 420*rp2*rb^4*r^3+2016*rp2^5*r*rb^2+5040*rp2^4*r^4;
Fac23 = 630*rb*rp1^4*rp2*r^2-1680*rb^2*rp1^3*rp2*r^2-12096*r^5*rp2^2*rb;
Fac24 = -2520*rb^2*rp1^2*rp2^2*r^2-2100*rb*rp1^2*rp2*r^4;
Fac25 = 1260*r^3*rb*rp1^2*rp2^2-1260*r^3*rb^2*rp1^2*rp2;
Fac26 = 840*r^3*rp1^3*rp2*rb-840*rp2^3*r*rp1^3*rb-1008*rp2^8;
Fac27 = -4032*r*rp2^6*rb+1008*rb^2*rp2^6-2016*rp2^2*r^6;
Fac28 = -840*r*rp1^3*rp2^2*rb^2+840*r*rp1^3*rp2*rb^3;
Fac29 = -420*r*rb^4*rp1^2*rp2+168*r*rp1^5*rp2*rb+630*r*rb*rp1^4*rp2^2;
Fac30 = -168*r*Fac1^(5/2)*rb^2+630*r^5*Fac1^(1/2)*rp2^2*rb/(rp2-rb);
Fac31 = -1260*rp2^4*r^3*Fac1^(1/2)*rb/(rp2-rb);
Fac32 = Fac21+Fac22+Fac23+Fac24+Fac25+Fac26+Fac27+Fac28+Fac29+Fac30+Fac31;
Fac33 = -168*r*Fac1^(5/2)*rp2^2+1680*rb*rp1^3*rp2^2*r^2;
Fac34 = 630*rp2^4*Fac1^(1/2)*rb^3*r/(rp2-rb);
Fac35 = -42*Fac1^(5/2)*rp2^2*rb*r/(rp2-rb);
Fac36 = -840*rp2^3*Fac1^(3/2)*rb^2*r/(rp2-rb)+840*rp2^2*rb^4*r^2;
Fac37 = 630*rp2^6*Fac1^(1/2)*rb*r/(rp2-rb)+1260*rb*rp1^2*rp2^3*r^2;
Fac38 = -1260*rp2^2*r^3*Fac1^(1/2)*rb^3/(rp2-rb)+2100*rb*r^3*rp2^4;
Fac39 = 420*rp2^4*Fac1^(3/2)*rb*r/(rp2-rb)+1260*rb^3*rp1^2*rp2*r^2;
Fac40 = 420*r^3*Fac1^(3/2)*rb^3/(rp2-rb)+1260*rp2^3*r*rb^2*rp1^2;
Fac41 = -630*r*rb^2*rp1^4*rp2+420*r*rb^3*rp1^2*rp2^2;
Fac42 = -42*Fac1^(5/2)*rb^3*r/(rp2-rb);
Fac43 = -1260*rp2^5*Fac1^(1/2)*rb^2*r/(rp2-rb);
Fac44 = +420*r^3*Fac1^(3/2)*rp2^2*rb/(rp2-rb);
Fac45 = Fac32+Fac33+Fac34+Fac35+Fac36+Fac37+Fac38+Fac39+Fac40+Fac41+Fac42;
Fac46 = Fac43+Fac44;
result = 1/1260*pi^2*(Fac45+Fac46)/rp2/(rp2-rb)/rb;
end


function result = caseIIstar_A1 (r,rp2,rb)
Fac0 = 6*rp2^2+(-2*r-2*rp2)*(6*rp2-6*r);
Fac1 = 2/5*(r-rb+rp2)^6-8/5*r*(r-rb+rp2)^5;
Fac2 = 4*rp2*r-2*r^2-2*rp2^2+4*rb^2;
Fac3 = 2*(r+rp2)^2*(6*rp2-6*r)-24*r*rb^2;
Fac4 = 2*(r+rp2)*(2*r+2*rp2)+2*(r+rp2)^2-12*rp2*r+6*r^2+Fac0;
Fac5 = 2/3*(r+rp2)^2+2/3*(-2*r-2*rp2)*(2*r+2*rp2)+Fac2;
Fac6 = 2*Fac4*rb+4*(r+rp2)*(6*rp2*r-3*r^2-3*rp2^2)+Fac3;
Fac7 = (r+rp2)^2*(2*r+2*rp2)+(-2*r-2*rp2)*(6*rp2*r-3*r^2-3*rp2^2);
Fac8 = (r+rp2)^2+(-2*r-2*rp2)*(2*r+2*rp2)+6*rp2*r-3*r^2-3*rp2^2;
Fac9 = 2*rb^4+2*Fac7*rb+2*(r+rp2)^2*(6*rp2*r-3*r^2-3*rp2^2)+2*Fac8*rb^2;
Fac10 = Fac1+Fac5*(r-rb+rp2)^4+1/3*Fac6*(r-rb+rp2)^3+Fac9*(r-rb+rp2)^2;
result = 1/6*pi^2*Fac10/rb;
```

```
end


function result = caseIIstar_A2 (r,rp1,rp2,rb)
Fac1 = ((rp2^2*rb-rp2*rb^2+rp2*rp1^2-rb*r^2)/(rp2-rb));
Fac2 = -1260*r^5*Fac1^(1/2)*rp2*rb^2/(rp2-rb)-1680*rp2^3*r*Fac1^(3/2)*rb;
Fac3 = -6930*rp2*rb^5*r^2+2520*rp2^3*r^3*Fac1^(1/2)*rb^2/(rp2-rb);
Fac4 = 336*r*Fac1^(5/2)*rp2*rb+1008*rp2^8;
Fac5 = 12978*rp2*r^5*rb^2-19026*rp2^2*r^5*rb-24780*rb*r^3*rp2^4;
Fac6 = 24570*rb^2*rp2^5*r+420*rp2^2*Fac1^(3/2)*rb^3*r/(rp2-rb);
Fac7 = 630*rp2^6*Fac1^(1/2)*rb*r/(rp2-rb)+420*r^3*Fac1^(3/2)*rb^3/(rp2-rb);
Fac8 = -168*r*Fac1^(5/2)*rb^2-41580*rb^3*r^2*rp2^3+68040*rb^2*r^4*rp2^2;
Fac9 = -7140*rp2^3*rb^4*r-12180*rp2^4*rb^3*r;
Fac10 = -840*r^3*Fac1^(3/2)*rp2^2+630*r^5*Fac1^(1/2)*rp2^2*rb/(rp2-rb);
Fac11 = -840*r^3*Fac1^(3/2)*rb^2+630*r^5*Fac1^(1/2)*rb^3/(rp2-rb);
Fac12 = 27720*rp2^2*rb^4*r^2-2646*rp2*r*rb^6-13986*rb*rp2^6*r;
Fac13 = 9366*rp2^2*rb^5*r-81060*rp2^2*rb^3*r^3;
Fac14 = Fac2+Fac3+Fac4+Fac5+Fac6+Fac7+Fac8+Fac9+Fac10+Fac11+Fac12+Fac13;
Fac15 = -1260*rp2^5*Fac1^(1/2)*rb^2*r/(rp2-rb)-41580*rb*r^4*rp2^3;
Fac16 = -42*Fac1^(5/2)*rb^3*r/(rp2-rb)-168*r*Fac1^(5/2)*rp2^2;
Fac17 = -1260*rp2^4*r^3*Fac1^(1/2)*rb/(rp2-rb)+1680*rb*rp1^3*rp2^2*r^2;
Fac18 = 27720*rb^2*r^2*rp2^4-6048*rb^6*rp2^2+8064*rp2^3*rb^5;
Fac19 = 3360*rp2^4*rb^4-42*Fac1^(5/2)*rp2^2*rb*r/(rp2-rb);
Fac20 = 840*rp2^4*r*rp1^3-840*r^3*rp1^3*rp2^2+1344*rp2*rb^7;
Fac21 = -840*rp2^3*Fac1^(3/2)*rb^2*r/(rp2-rb)-20160*rp2^5*rb^3;
Fac22 = -2100*rb*rp1^2*rp2^4*r-12096*r^5*rp2^2*rb-4032*r*rp2^6*rb;
Fac23 = -546*rp2*r^6*rb+1008*rb^2*rp2^6+21168*rp2^6*rb^2-4032*r^6*rp2*rb;
Fac24 = Fac14+Fac15+Fac16+Fac17+Fac18+Fac19+Fac20+Fac21+Fac22+Fac23;
Fac25 = -2016*rp2^7*rb+6048*rb^2*r^5*rp2+5040*rp2^2*r^4*rb^2;
Fac26 = 2016*rp2^5*r*rb^2+2016*rb^2*r^6+2016*rp2^7*r-31500*rp2*rb^3*r^4;
Fac27 = 2016*rp2^2*r^6+630*rb*rp1^4*rp2*r^2-1680*rb^2*rp1^3*rp2*r^2;
Fac28 = 1260*rb*rp1^2*rp2^3*r^2-2520*rb^2*rp1^2*rp2^2*r^2;
Fac29 = 1260*rb^3*rp1^2*rp2*r^2+1260*r^3*rb*rp1^2*rp2^2;
Fac30 = 1260*rp2^3*r*rb^2*rp1^2+840*r^3*rp1^3*rp2*rb+6048*rp2^3*r^5;
Fac31 = 2016*rp2^2*r^6+5040*rp2^4*r^4+2016*rp2^7*r-2100*rb*rp1^2*rp2*r^4;
Fac32 = -10080*r^4*rp2^3*rb-840*rp2^3*r*rp1^3*rb-840*r*rp1^3*rp2^2*rb^2;
Fac33 = 420*r*rb^3*rp1^2*rp2^2-420*r*rb^4*rp1^2*rp2+168*r*rp1^5*rp2*rb;
Fac34 = -630*r*rb^2*rp1^4*rp2+1680*r^3*Fac1^(3/2)*rp2*rb;
Fac35 = Fac24+Fac25+Fac26+Fac27+Fac28+Fac29+Fac30+Fac31+Fac32+Fac33+Fac34;
Fac36 = Fac35+630*r*rb*rp1^4*rp2^2+420*rp2^4*Fac1^(3/2)*rb*r/(rp2-rb);
Fac37 = 79380*rb^2*r^3*rp2^3-6930*rb*r^2*rp2^5+840*rp2^4*r*Fac1^(3/2);
Fac38 = 6048*r^5*rp2^3+420*r^3*Fac1^(3/2)*rp2^2*rb/(rp2-rb);
Fac39 = 840*r*rp1^3*rp2*rb^3-1260*rp2^2*r^3*Fac1^(1/2)*rb^3/(rp2-rb);
Fac40 = 5040*rp2^4*r^4-840*r^3*Fac1^(3/2)*rp2*rb^2/(rp2-rb)-8736*rp2^7*rb;
Fac41 = 27300*rp2*rb^4*r^3+630*rp2^4*Fac1^(1/2)*rb^3*r/(rp2-rb);
Fac42 = 84*Fac1^(5/2)*rp2*rb^2*r/(rp2-rb)-168*r*rp1^5*rp2^2+1008*rp2^8;
Fac43 = -1260*r^3*rb^2*rp1^2*rp2+840*rp2^2*r*Fac1^(3/2)*rb^2;
Fac44 = Fac36+Fac37+Fac38+Fac39+Fac40+Fac41+Fac42+Fac43;
result = 1/1260*pi^2*(Fac44)/rp2/(rp2-rb)/rb;
end


function result = caseIII_A1 (r,rp2,rb)
Fac0 = 6*rp2^2+(-2*r-2*rp2)*(6*rp2-6*r);
Fac1 = -2/5*(rb+rp2-r)^6-8/5*r*(rb+rp2-r)^5;
Fac2 = 4*rp2*r-2*r^2-2*rp2^2+4*rb^2;
```

```
Fac3 = 2*(r+rp2)^2*(6*rp2-6*r)-24*r*rb^2;
Fac4 = 2*(r+rp2)*(2*r+2*rp2)+2*(r+rp2)^2-12*rp2*r+6*r^2+Fac0;
Fac5 = 2/3*(r+rp2)^2+2/3*(-2*r-2*rp2)*(2*r+2*rp2)+Fac2;
Fac6 = 2*Fac4*rb+4*(r+rp2)*(6*rp2*r-3*r^2-3*rp2^2)+Fac3;
Fac7 = (r+rp2)^2*(2*r+2*rp2)+(-2*r-2*rp2)*(6*rp2*r-3*r^2-3*rp2^2);
Fac8 = (r+rp2)^2+(-2*r-2*rp2)*(2*r+2*rp2)+6*rp2*r-3*r^2-3*rp2^2;
Fac9 = 2*rb^4+2*Fac7*rb+2*(r+rp2)^2*(6*rp2*r-3*r^2-3*rp2^2)+2*Fac8*rb^2;
Fac10 = Fac1-Fac5*(rb+rp2-r)^4+1/3*Fac6*(rb+rp2-r)^3-Fac9*(rb+rp2-r)^2;
result = 1/6*pi^2*Fac10/rb;
end


function result = caseIII_A2 (r,rp1,rp2,rb)
Fac1 = ((-rp2^2*rb-rp2*rb^2+rp2*rp1^2+rb*r^2)/(rb+rp2));
Fac2 = 420*rp2^2*Fac1^(3/2)*rb^3*r/(rb+rp2)-6930*rp2*rb^5*r^2;
Fac3 = 840*rp2^3*Fac1^(3/2)*rb^2*r/(rb+rp2);
Fac4 = 2016*rp2^7*r-1260*rp2^4*r^3*Fac1^(1/2)*rb/(rb+rp2)+8064*rp2^3*rb^5;
Fac5 = 630*r^5*Fac1^(1/2)*rp2^2*rb/(rb+rp2)-840*rp2^4*r*Fac1^(3/2);
Fac6 = -31500*rp2*rb^3*r^4+12978*rp2*r^5*rb^2+19026*rp2^2*r^5*rb;
Fac7 = 26460*rb*r^3*rp2^4+79380*rb^2*r^3*rp2^3+1050*rb^2*rp2^5*r;
Fac8 = 1260*rp2^5*Fac1^(1/2)*rb^2*r/(rb+rp2);
Fac9 = 420*rp2^4*Fac1^(3/2)*rb*r/(rb+rp2);
Fac10 = -420*r*rb^4*rp1^2*rp2-168*r*rp1^5*rp2*rb+27300*rp2*rb^4*r^3;
Fac11 = -9366*rp2^2*rb^5*r+81060*rp2^2*rb^3*r^3-41580*rb*r^4*rp2^3;
Fac12 = -3570*rb*r^2*rp2^5-41580*rb^3*r^2*rp2^3-68040*rb^2*r^4*rp2^2;
Fac13 = -24360*rb^2*r^2*rp2^4-7140*rp2^3*rb^4*r+420*rp2^4*rb^3*r;
Fac14 = 3360*rp2^4*rb^4-2646*rp2*r*rb^6+2226*rb*rp2^6*r;
Fac15 = Fac2+Fac3+Fac4+Fac5+Fac6+Fac7+Fac8+Fac9+Fac10+Fac11+Fac12+Fac13;
Fac16 = 840*rp2^4*r*rp1^3-840*r^3*rp1^3*rp2^2+1344*rp2*rb^7;
Fac17 = -630*r*rb*rp1^4*rp2^2+1680*rb*rp1^3*rp2^2*r^2+Fac14;
Fac18 = 1680*r^3*Fac1^(3/2)*rb*rp2+1008*rp2^8*-1+6048*rb^6*rp2^2;
Fac19 = -840*rp2^2*r*Fac1^(3/2)*rb^2+6048*r^5*rp2^3;
Fac20 = -42*Fac1^(5/2)*rp2^2*rb*r/(rb+rp2);
Fac21 = 2016*r^6*-1*rb^2-2016*r*rp2^7*-1+5040*r^4*rp2^4*-1;
Fac22 = -6048*r^5*-1*rp2^3-12096*-1*rp2^2*rb*r^5-27720*rp2^2*rb^4*r^2;
Fac23 = 4032*-1*rp2*rb*r^6+840*r^3*Fac1^(3/2)*rb^2-2016*rp2^5*-1*rb^2*r;
Fac24 = -2520*rp2^3*r^3*Fac1^(1/2)*rb^2/(rb+rp2)-5040*rp2^4*r^4;
Fac25 = -1008*rp2^8+630*r^5*Fac1^(1/2)*rb^3/(rb+rp2)+630*rb*rp1^4*rp2*r^2;
Fac26 = 1680*rb^2*rp1^3*rp2*r^2+1260*rb*rp1^2*rp2^3*r^2;
Fac27 = Fac15+Fac16+Fac17+Fac18+Fac19+Fac20+Fac21+Fac22+Fac23+Fac24+Fac25;
Fac28 = 840*r^3*Fac1^(3/2)*rb^2*rp2/(rb+rp2)+420*rb*rp1^2*rp2^4*r+Fac26;
Fac29 = -2016*rp2^2*r^6+5040*r^4*-1*rb^2*rp2^2-6048*r^5*-1*rb^2*rp2;
Fac30 = -1008*rp2^6*rb^2-4032*-1*rp2^6*rb*r+10080*-1*rp2^3*rb*r^4;
Fac31 = 2016*-1*rp2^7*rb+1008*rp2^6*-1*rb^2-2016*rp2^7*rb;
Fac32 = 2520*rb^2*rp1^2*rp2^2*r^2-2100*rb*rp1^2*rp2*r^4;
Fac33 = -1260*r^3*rb*rp1^2*rp2^2-1260*r^3*rb^2*rp1^2*rp2;
Fac34 = 1260*rp2^3*r*rb^2*rp1^2-840*r^3*rp1^3*rp2*rb-168*r*rp1^5*rp2^2;
Fac35 = 840*rp2^3*r*rp1^3*rb-630*r*rb^2*rp1^4*rp2-840*r*rp1^3*rp2^2*rb^2;
Fac36 = -840*r*rp1^3*rp2*rb^3-420*r*rb^3*rp1^2*rp2^2+168*r*Fac1^(5/2)*rb^2;
Fac37 = 420*r^3*Fac1^(3/2)*rb^3/(rb+rp2)+168*r*Fac1^(5/2)*rp2^2;
Fac38 = -546*rp2*r^6*rb-1680*rp2^3*r*Fac1^(3/2)*rb+2016*r^6*-1*rp2^2;
Fac39 = -42*Fac1^(5/2)*rb^3*r/(rb+rp2)+1260*rb^3*rp1^2*rp2*r^2;
Fac40 = 840*r^3*Fac1^(3/2)*rp2^2-1260*rp2^2*r^3*Fac1^(1/2)*rb^3/(rb+rp2);
Fac41 = 1260*r^5*Fac1^(1/2)*rb^2*rp2/(rb+rp2)+336*r*Fac1^(5/2)*rb*rp2;
Fac42 = 630*rp2^6*Fac1^(1/2)*rb*r/(rb+rp2);
Fac43 = 630*rp2^4*Fac1^(1/2)*rb^3*r/(rb+rp2);
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Fac44 = 420*r^3*Fac1^(3/2)*rp2^2*rb/(rb+rp2);
Fac45 = -84*Fac1^(5/2)*rp2*rb^2*r/(rb+rp2);
Fac46 = Fac38+Fac39+Fac40+Fac41+Fac42+Fac43+Fac44+Fac45;
Fac47 = Fac27+Fac28+Fac29+Fac30+Fac31+Fac32+Fac33+Fac34+Fac35+Fac36+Fac37;
result = 1/1260*pi^2*(Fac46+Fac47)/rp2/(rb+rp2)/rb;
end


function result = caseIII_B (r,rp1,rp2,rb)
Fac1 = 8/3*pi^2*rp2^3;
Fac2 = 1/2*rp2/(rb+rp2)-1/2;
Fac3 = rp1^2-(rb+rp2-r)^2;
Fac4 = 1/2*(-rp2^2*rb-rp2*rb^2+rb*r^2)/(rb+rp2)-1/2*rb^2;
Fac5 = -Fac2*(rb+rp2-r)^3-rb*(rb+rp2-r)^2;
result = Fac1*(-Fac5+1/2*rb*r/(rb+rp2)*Fac3+1/2*Fac4*(2*rb+2*rp2-2*r))/rb;
end


function result = caseIIIstar_A (r,rp1,rp2,rb)
Fac1 = ((-rp2^2*rb-rp2*rb^2+rp2*rp1^2+rb*r^2)/(rb+rp2));
Fac2 = 1260*rp2^5*Fac1^(1/2)*rb^2*r/(rb+rp2)-210*rp2*rb^5*r^2;
Fac3 = -2016*rp2^7*r-6048*r^5*rp2^3+420*rp2^4*Fac1^(3/2)*rb*r/(rb+rp2);
Fac4 = -1260*r^3*rb*rp1^2*rp2^2+630*r^5*Fac1^(1/2)*rb^3/(rb+rp2);
Fac5 = -840*r*rp1^3*rp2^2*rb^2-630*r*rb^2*rp1^4*rp2+840*rp2^3*r*rp1^3*rb;
Fac6 = 1260*rp2^3*r*rb^2*rp1^2+168*r*Fac1^(5/2)*rb^2+2100*rp2*rb^3*r^4;
Fac7 = -840*r*rp1^3*rp2*rb^3+420*r^3*Fac1^(3/2)*rb^3/(rb+rp2);
Fac8 = 1260*r^5*Fac1^(1/2)*rb^2*rp2/(rb+rp2)+840*r^3*Fac1^(3/2)*rp2^2;
Fac9 = -840*rp2^4*r*Fac1^(3/2)-840*rp2^2*r*Fac1^(3/2)*rb^2;
Fac10 = -630*r*rb*rp1^4*rp2^2-168*r*rp1^5*rp2*rb-420*r*rb^4*rp1^2*rp2;
Fac11 = 1680*rb*rp1^3*rp2^2*r^2-42*Fac1^(5/2)*rb^3*r/(rb+rp2);
Fac12 = 2016*r^6*-1*rb^2+5040*r^4*rp2^4*-1-2016*r*rp2^7*-1+42*rp2*r*rb^6;
Fac13 = Fac2+Fac3+Fac4+Fac5+Fac6+Fac7+Fac8+Fac9+Fac10+Fac11+Fac12;
Fac14 = -1260*rp2^2*r^3*Fac1^(1/2)*rb^3/(rb+rp2)-6048*r^5*-1*rp2^3;
Fac15 = 2016*r^6*-1*rp2^2-42*Fac1^(5/2)*rp2^2*rb*r/(rb+rp2);
Fac16 = 3486*rp2*r^6*rb-2016*0*rp2^2*rb*r^6+1008*rp2^6*rb^2;
Fac17 = 2016*-1*rp2^7*rb+1008*rp2^8+2016*rp2^7*rb+420*rb*rp1^2*rp2^4*r;
Fac18 = 2016*rp2^2*r^6-2100*rb*rp1^2*rp2*r^4+1260*rb^3*rp1^2*rp2*r^2;
Fac19 = 10080*-1*rp2^3*rb*r^4-4032*-1*rp2^6*rb*r-6048*r^5*-1*rb^2*rp2;
Fac20 = -5838*rp2*r^5*rb^2+4032*-1*rp2*rb*r^6-12096*-1*rp2^2*rb*r^5;
Fac21 = -11886*rp2^2*r^5*rb-420*rb*r^3*rp2^4-1260*rb^2*r^3*rp2^3;
Fac22 = 1050*rb^2*rp2^5*r+840*rp2^4*r*rp1^3-840*r^3*rp1^3*rp2^2;
Fac23 = -1806*rb*rp2^6*r+420*rp2*rb^4*r^3+42*rp2^2*rb^5*r;
Fac24 = Fac13+Fac14+Fac15+Fac16+Fac17+Fac18+Fac19+Fac20+Fac21+Fac22+Fac23;
Fac25 = 12180*rb*r^4*rp2^3-3570*rb*r^2*rp2^5-1260*rb^3*r^2*rp2^3;
Fac26 = 9240*rb^2*r^4*rp2^2-1680*rp2^3*r*Fac1^(3/2)*rb-4200*rb^2*r^2*rp2^4;
Fac27 = 420*rp2^4*rb^3*r-168*r*rp1^5*rp2^2-2016*rp2^5*-1*rb^2*r;
Fac28 = 840*r^3*Fac1^(3/2)*rb^2*rp2/(rb+rp2)+336*r*Fac1^(5/2)*rb*rp2;
Fac29 = -2520*rp2^3*r^3*Fac1^(1/2)*rb^2/(rb+rp2)+1008*rp2^6*-1*rb^2;
Fac30 = 2520*rb^2*rp1^2*rp2^2*r^2+1260*rb*rp1^2*rp2^3*r^2+5040*rp2^4*r^4;
Fac31 = 420*rp2^2*Fac1^(3/2)*rb^3*r/(rb+rp2)+1008*rp2^8*-1;
Fac32 = 1680*rb^2*rp1^3*rp2*r^2+630*r^5*Fac1^(1/2)*rp2^2*rb/(rb+rp2);
Fac33 = Fac24+Fac25+Fac26+Fac27+Fac28+Fac29+Fac30+Fac31+Fac32;
Fac34 = Fac33+630*rp2^4*Fac1^(1/2)*rb^3*r/(rb+rp2)+168*r*Fac1^(5/2)*rp2^2;
Fac35 = -84*Fac1^(5/2)*rp2*rb^2*r/(rb+rp2)-1260*r^3*rb^2*rp1^2*rp2;
Fac36 = 1680*r^3*Fac1^(3/2)*rb*rp2+630*rp2^6*Fac1^(1/2)*rb*r/(rb+rp2);
Fac37 = -840*r^3*rp1^3*rp2*rb+5040*r^4*-1*rb^2*rp2^2-420*rp2^3*rb^4*r;
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Fac38 = 840*r^3*Fac1^(3/2)*rb^2+840*rp2^3*Fac1^(3/2)*rb^2*r/(rb+rp2);
Fac39 = 630*rb*rp1^4*rp2*r^2+420*r^3*Fac1^(3/2)*rp2^2*rb/(rb+rp2);
Fac40 = -1260*rp2^4*r^3*Fac1^(1/2)*rb/(rb+rp2)-840*rp2^2*rb^4*r^2;
Fac41 = -420*r*rb^3*rp1^2*rp2^2+420*rp2^2*rb^3*r^3;
Fac42 = Fac34+Fac35+Fac36+Fac37+Fac38+Fac39+Fac40+Fac41;
result = 1/1260*pi^2*(Fac42)/rp2/(rb+rp2)/rb;
end


function result = caseIIIstar_B2(r,rp1,rp2,rb)
Fac1 = 8/3*pi^2*rp2^3;
Fac2 = 1/2*rp2/(rb+rp2)-1/2;
Fac3 = rp1^2-(-rb-rp2+r)^2;
Fac4 = 1/2*(-rp2^2*rb-rp2*rb^2+rb*r^2)/(rb+rp2)-1/2*rb^2;
Fac5 = -Fac2*(-rb-rp2+r)^3-rb*(-rb-rp2+r)^2;
result = Fac1*(Fac5+1/2*rb*r/(rb+rp2)*Fac3+1/2*Fac4*(2*rb+2*rp2-2*r))/rb;
end
```

References

[1] Lloyd L. Lee, Molecular Thermodynamics of Nonideal Fluids, Butterworth Publishers, Stoneham MA, 1988, p. 139-143.