



Three-Particle Distribution Functions in the Hard-Sphere Model

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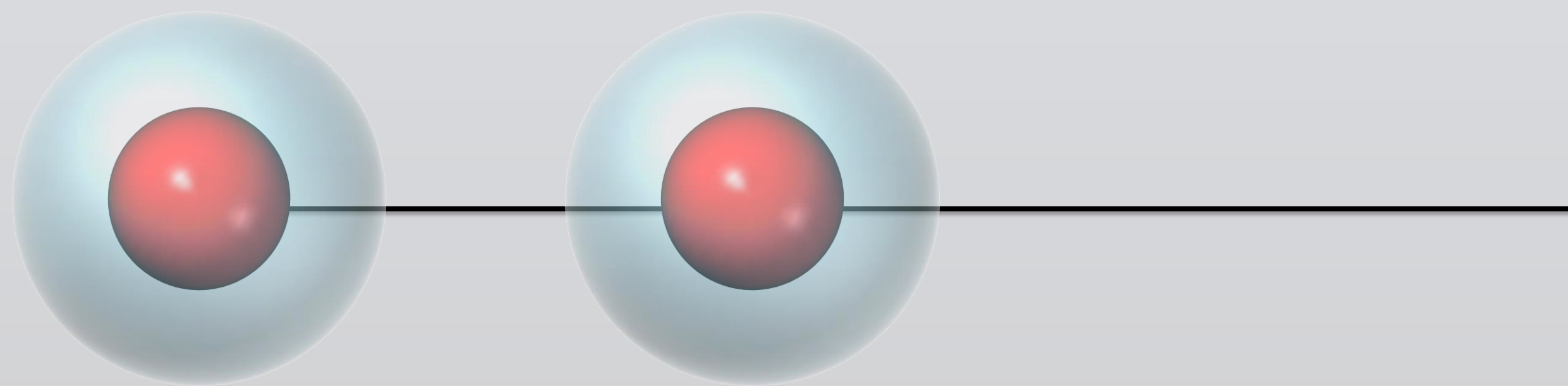
Introduction

Complex fluids, such as colloidal suspensions, bio-fluids, liquid foods, and personal care products, are all around us and play important roles in our lives. To better understand the structure of these fluids, scientists have developed a variety of approaches. Several of those approaches start with a hard-sphere model, in which each particle is a sphere and the particles interact only by bouncing off one another. Our approach is based on Shinomoto's model, to which it is particularly convenient to add features (such as making the particles elliptical, or mixing two sizes of particles together).

Methods

Calculation of $g_2(r_{12})$

We begin with a geometric model of hard colliding spheres. The model is based on a kinetic theory approach developed by Shinomoto [Phys. Lett A, 89, 19 (1982)]. In the figure below, the red spheres are the particles and the white spheres, whose radii are two times the particle radius, are the excluded volumes that surround each particle. The reason there is an excluded volume is that the center of two particles can never be closer than two times the radius. Therefore the center of another particle will never be found inside the white sphere.



The red arrows show the pressure on the second particle due to other particles colliding with it. Where the excluded volume of the first particle and second particle overlap, there is no pressure on the second particle. The result is a net force on the second particle toward the first particle.

Integrating the pressure over the surface allows us to calculate the force on the second particle:

$$F(r_{12}) = 2 \int_{\alpha}^{\pi} \rho \cos \theta (\sigma \sin \theta d\theta)$$

where ρ is density of the fluid and σ is the radius of excluded region. Initially, we assume the density is uniform ($g_2=1$). After finding the force, we can obtain the potential energy by calculating the work done to bring a particle in from infinitely far away:

$$\Phi(r_{12}) = - \int_{\infty}^r F(r') dr'$$

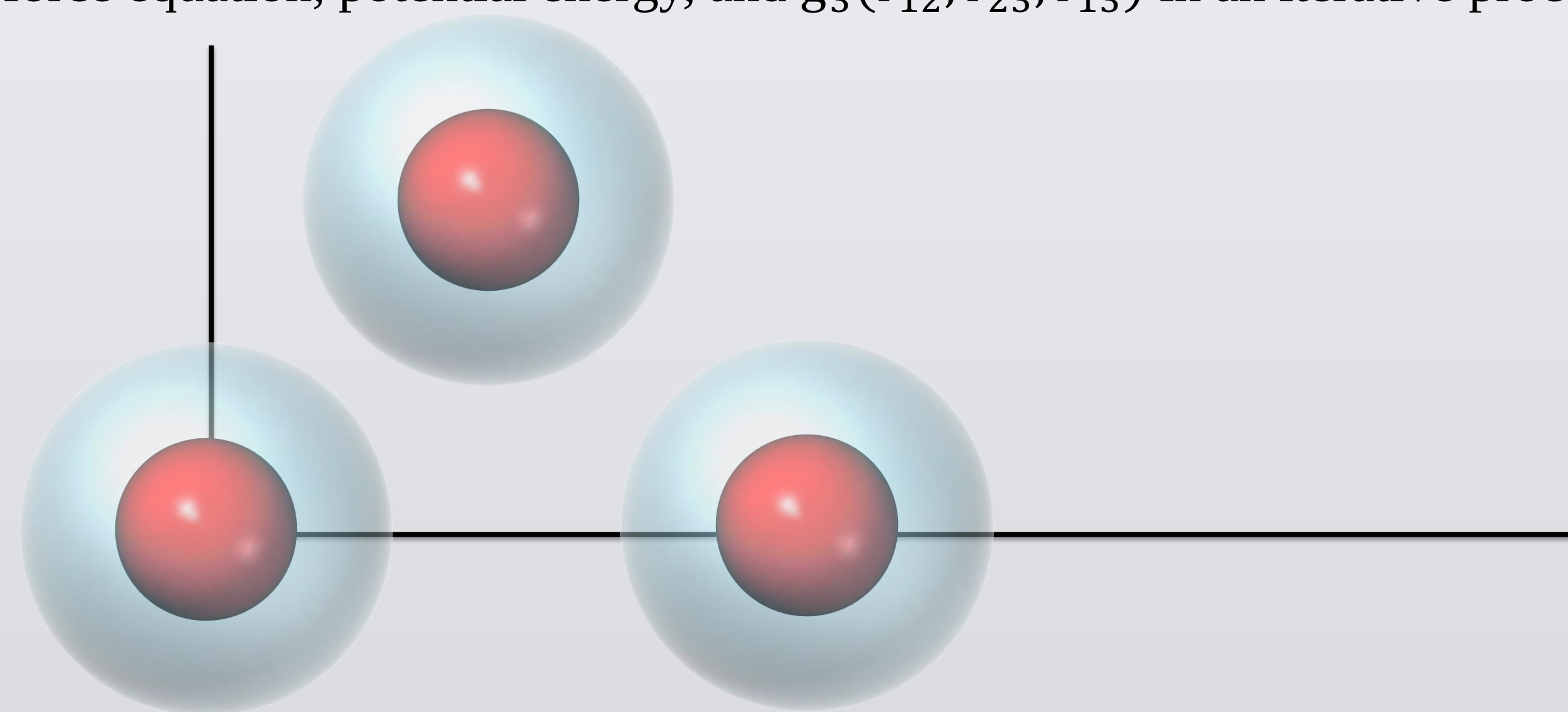
From the potential energy, the probability of finding a second particle at distance r from the first particle may be calculated using the Boltzmann factor.

$$g_2(r_{12}) = \exp\left[-\frac{\Phi(r_{12})}{kT}\right]$$

Using this spatial structure, we can improve the density(ρ) in the force equation. This leads to an improved potential energy and improved $g_2(r_{12})$. We developed a FORTRAN program to carry out these calculations. By iterating the three-step process outlined above many times, we are able to obtain a self controlled two-particle correlation function.

Calculation of $g_3(r_{12}, r_{23}, r_{13})$

Basically the calculations are the same as for $g_2(r_{12})$, but the details are more complicated. We calculate the total force on a third particle by integrating the pressure over the excluded volume surface of the third particle. The potential energy is found using the same process as in the $g_2(r_{12})$ case. Again, we will be able to calculate the probability of finding particle by Boltzmann factor, and using the spatial structure, we will be able to improve the density(ρ) in the force equation, potential energy, and $g_3(r_{12}, r_{23}, r_{13})$ in an iterative process.

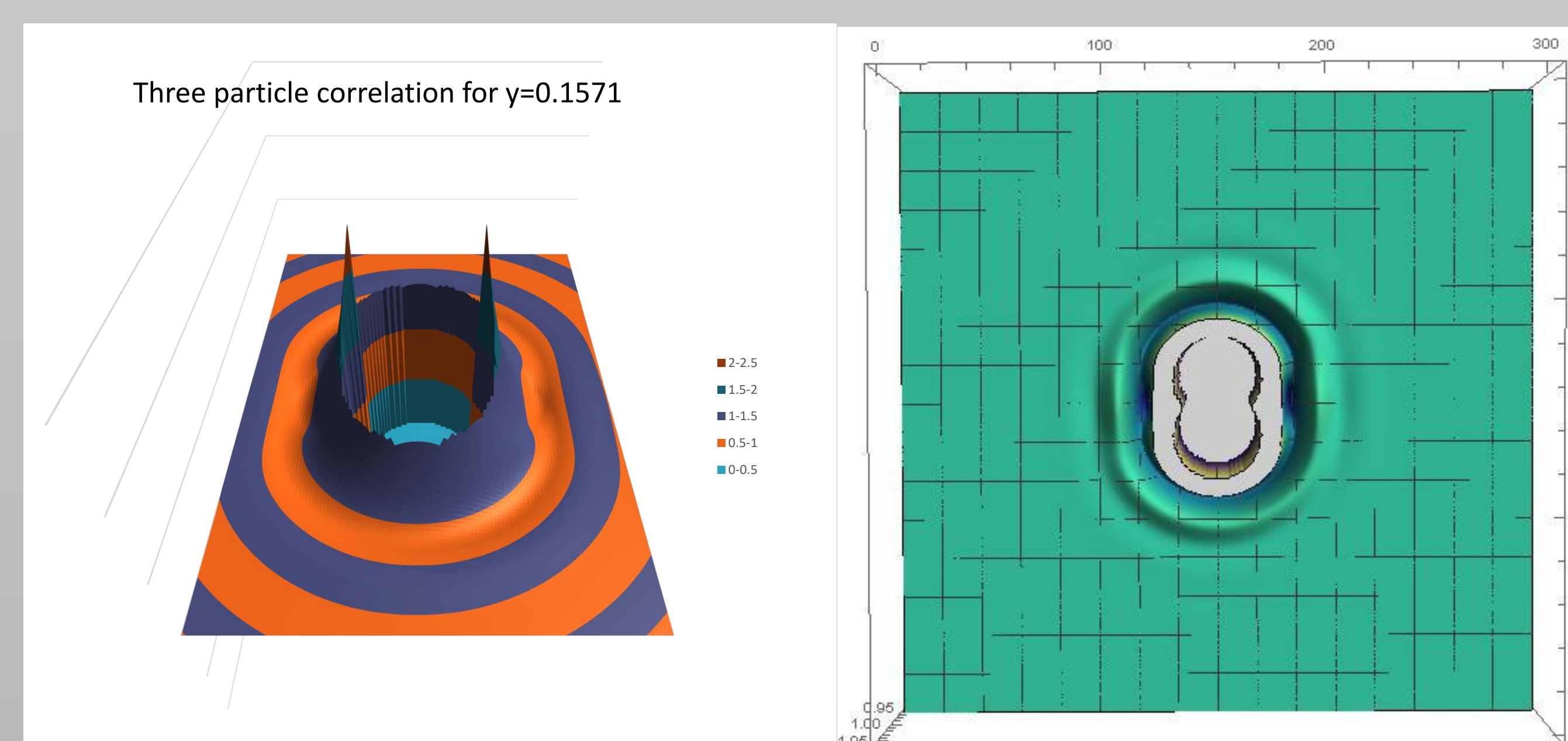


This iterative sequence of calculations will lead to the three-particle correlation function $g_3(r_{12}, r_{23}, r_{13})$. This calculation will be much more challenging than the $g_2(r_{12})$ calculation because of the increased geometric complexity of three particles and their intersecting excluded volumes.

We will develop a FORTRAN program to carry out the calculation of $g_3(r_{12}, r_{23}, r_{13})$. This will utilize some code we already have but will require new code to be written to deal with the added geometric complexity of three particles and their intersecting excluded volumes. For each possible location of the third particle in the plane, we need to describe what portions of the excluded volume spheres overlap and calculate the integral of the pressure only over the portions that do not overlap. In the calculation of g_2 , we only needed to deal with two overlapping spheres and the second particle only needed to be located along the horizontal axis, so there is considerable added complexity in finding g_3 .

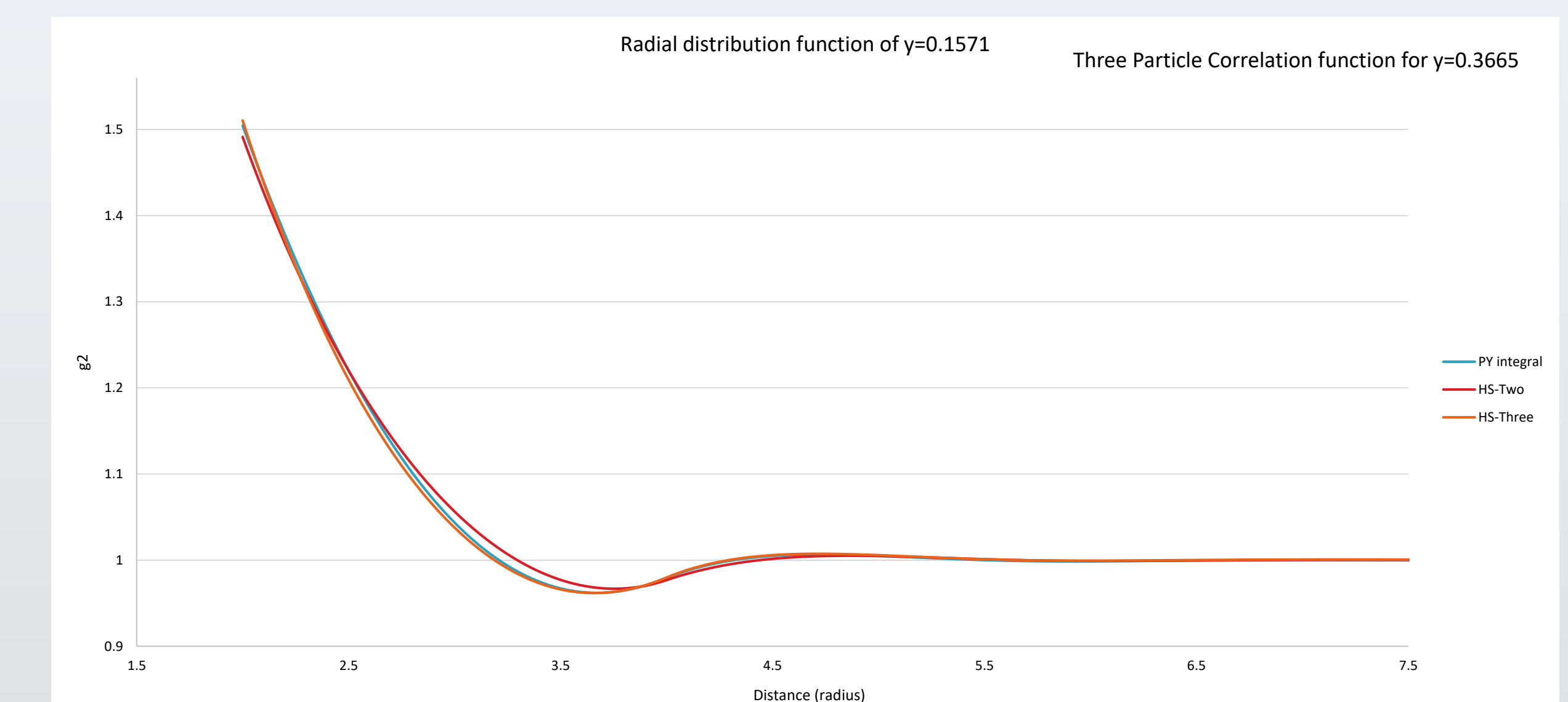
Results

To obtain g_2 , we first calculated g_3 at $y=0.1571$.



The both graph shows the three particle correlation function at low density with very small distance of r_{12} .

By the calculation from the three particle correlation, we calculated two particle correlation function for the $y=0.1571$.



Red line is the calculation without three particle correlation function, the orange line is the calculation with three particle correlation function, the blue line is result from different approach by Percus–Yevick integral.

Our g_2 by three particle correlation showed significantly improved result compared to g_2 by two particle correlation. The curve is almost identical to the calculation by Percus–Yevick integral.

Conclusion

Very few attempts have been made to calculate the three-particle correlation function (g_3) so this result is very significant contribution to knowledge of fluid structure. In addition, we have incorporated the results into our calculation of g_2 leading to improvement in our pair-correlation function result which, in turn, has enabled us to determine the structure in the fluid. Our improved model provided a better understanding of the structure of simple fluids and, because it can be easily modified with additional features, is a promising foundation upon which more complex fluid models can be built such as making the particles elliptical, or mixing two sizes of particles together.

Reference

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