

# Random Close Packing and the Hard Sphere Percus-Yevick

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The Percus-Yevick theory for monodisperse hard spheres gives very good results for the pressure and structure factor of the system in a whole range of densities that lie within the gas and liquid phases. However, the equation seems to lead to a very unacceptable result beyond that region. Namely, the Percus-Yevick theory predicts a smooth behavior of the pressure that diverges only when the volume fraction  $\eta$  approaches unity. Thus, within the theory there seems to be no indication for the termination of the liquid phase and the transition to a solid or to a glass. In the present article we study the Percus-Yevick hard sphere radial distribution function,  $g_2(r)$ , for various spatial dimensions. We find that beyond a certain critical volume fraction  $\eta_c$  the pair distribution function,  $g_2(r)$ , which should be positive definite, becomes negative at some distances. Furthermore, the critical values we find are consistent with volume fractions where onsets of random close packing (or maximally random jammed states) are reported in the literature for various dimensions. This work has important implications for other systems for which a Percus-Yevick theory exists.

The hard sphere model provides a canonical minimalistic model that captures the main ingredient in the description of simple liquids, namely the strong short-range repulsion between atoms in the liquid. As in other systems in equilibrium statistical physics, the model is used to obtain macroscopic observables from the microscopic description of the system. In the case of the hard sphere model the goals are the equation of state, the liquid structure factor and a description of the solidification of the liquid in terms of the average particle density,  $\bar{\rho}$  and  $R$ , the radius of the hard sphere interaction. A wide arsenal of methods has been applied over the years to the hard sphere problem with considerable success. Monte-Carlo and Molecular Dynamics simulations have been applied to that model as early as the fifties of the last century<sup>1-3</sup> and extended much later. For example, the hard sphere system is one of the first systems to be simulated on the Small Web Computing (SWC) platform in recent years<sup>4</sup>. These important numerical efforts resulted in obtaining the phase diagram of the system, including crystallization and a super dense rotation invariant phase in the three dimensions<sup>5-8</sup>. The most trusted analytic tool applied successfully to the hard sphere problem is the virial expansion, which is based in turn on the cluster expansion<sup>9-17</sup>.

The other two interesting analytic approaches are the Hyper-Netted-Chain (HNC) approximation<sup>18</sup> and the Percus-Yevick (PY) equation<sup>19</sup> for the structure factor of the hard sphere system. The most appealing, to our mind, is the PY equation and that is for a number of reasons. First the equation has been given exact analytic solutions in odd dimensions  $d \leq 7$ <sup>20-27</sup> (where  $d$  is the dimension of the system). In fact, an exact analytic solution can be obtained in principle for any odd

dimension but it involves solving a polynomial equation of degree  $d - 3$ . Thus, the highest dimension for which a strict analytic solution in closed form exists is 7, due to the Abel-Ruffini theorem. However, thanks to the existence of this developed analytic structure it is possible to obtain semi-analytic results for higher odd dimensions with a simple numerical computation<sup>27,28</sup>. More recently, a systematic analytic method of solution, based on the virial expansion for the PY equation, has been obtained for general dimensions including the even ones<sup>29,30</sup>.

The PY equation is usually seen as a certain diagrammatic approximation or closure scheme of the full problem<sup>14</sup>. It was shown, however, that the PY equation for the hard sphere system can be given a very simple and intuitive meaning. Consider the particle number density,

$$\rho(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i), \quad (1)$$

where  $\mathbf{r}_i$  is the location of particle  $i$  which is one of  $N$  identical particles enclosed in a cubic container of linear size  $L$  and periodic boundary conditions. The pair distribution function,

$$g_2(\mathbf{r}) = \frac{1}{\bar{\rho}^2} \langle \rho(\mathbf{0})\rho(\mathbf{r}) - \bar{\rho}\delta(\mathbf{r}) \rangle \quad (2)$$

yields the  $d$  dimensional distribution to find a particle at  $\mathbf{r}$  given the existence of another particle at  $\mathbf{0}$ . The hard sphere system is then viewed as an ideal gas with a pair distribution function which is constrained to vanish for  $|\mathbf{r}| < R$  (where  $R$  the radius of the hard sphere interaction). To see how it works we have to transform from particle coordinates to collective coordinates<sup>31,32</sup> as described shortly in the following for the benefit of the readers. The natural collective coordinates are the Fourier components of the density,

$$\rho_{\mathbf{q}} = \frac{1}{\sqrt{N}} \int d\mathbf{r} \rho(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}}, \quad (3)$$

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for  $\mathbf{q} \neq 0$  and with components  $\mathbf{q}_\ell = \frac{2\pi n_\ell}{L}$ , where  $n_\ell$  is an integer. The ideal gas Fokker-Planck equation for the distribution of the  $N$  free particles is translated into a functional Fokker-Planck equation for the probability to obtain a given configuration of the density,  $P_{eq}^I\{\rho\}$ <sup>32</sup>, which reads at equilibrium,

$$\left[ \sum_{\mathbf{k}, \ell} \mathbf{k} \cdot \ell \frac{\partial}{\partial \rho_{\mathbf{k}}} \rho_{\mathbf{k}+\ell} \frac{\partial}{\partial \rho_\ell} - \sqrt{N} \sum_{\mathbf{k}} \mathbf{k}^2 \frac{\partial}{\partial \rho_{\mathbf{k}}} \rho_{\mathbf{k}} \right] P_{eq}^I\{\rho\} = 0. \quad (4)$$

We note that  $\rho_0 = \sqrt{N}$  is not a dynamical variable. Approximating this equation by keeping only the bilinear part in the operators  $\rho_{\mathbf{k}}$  and  $\frac{\partial}{\partial \rho_{\mathbf{k}}}$  for  $\mathbf{k} \neq 0$  (this scheme is also known as the Random-Phase-Approximation) we obtain the ideal gas equation

$$\sum_{\mathbf{k}} \mathbf{k}^2 \frac{\partial}{\partial \rho_{\mathbf{k}}} \left[ \frac{\partial}{\partial \rho_{-\mathbf{k}}} + \rho_{\mathbf{k}} \right] P_{eq}^I\{\rho\} = 0. \quad (5)$$

This allows for a solution with the following equilibrium distribution,

$$P_{eq}^I\{\rho\} \propto \exp \left[ -\frac{1}{2} \sum_{\mathbf{k}} \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \right], \quad (6)$$

leading to a structure factor  $S^I(k) = \langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle = 1$  (where  $k = |\mathbf{k}|$ ), which is the exact result in the case of an ideal gas. (This does not imply that higher order correlations obtained in the above approximation are exact.) To make the pair distribution function vanish within the hard sphere range we introduce into eq. (5) a Lagrange multiplier function  $\lambda_k$ , which is a Fourier transform of a yet unknown function  $\lambda(r)$ , that vanishes outside the hard sphere interaction range. The last requirement reflects the fact that the pair distribution function is constrained only within that range

$$\sum_{\mathbf{k}} \mathbf{k}^2 \frac{\partial}{\partial \rho_{\mathbf{k}}} \left[ \frac{\partial}{\partial \rho_{-\mathbf{k}}} + \rho_{\mathbf{k}} + \lambda_k \rho_{\mathbf{k}} \right] P_{eq}^I\{\rho\} = 0. \quad (7)$$

Thus, the term  $\rho_{\mathbf{k}}$  in the square brackets on the left hand side of eq. (5) is replaced by  $(1 + \lambda_k) \rho_{\mathbf{k}}$ . This results in the following structure factor

$$S^{HS}(k) = \frac{1}{1 + \lambda_k}, \quad (8)$$

where  $\lambda_k$  has to obey two conditions,

$$\lambda(r) = \int d\mathbf{k} \lambda_k e^{i\mathbf{k} \cdot \mathbf{r}} = 0 \text{ for } r > R, \quad (9)$$

and

$$g_2(r) = 1 + \frac{1}{N} \sum_{\mathbf{k} \neq 0} (S^{HS}(k) - 1) e^{i\mathbf{k} \cdot \mathbf{r}} = 0 \text{ for } r < R. \quad (10)$$

It turns out that these two conditions are in fact the hard sphere PY equation. In classical liquid theory a quantity termed direct correlation function is used extensively and is traditionally denoted by  $c(r)$ . In our language, the Lagrange multiplier function  $\lambda(r)$  is simply  $-\bar{\rho}c(r)$  (see supplemental material for more details on the notation used here). Also, within this framework the PY equation is just the lowest order theory in the Self-Consistent Expansion of the full model defined by

$$\left[ \sum_{\mathbf{k}, \ell} \mathbf{k} \cdot \ell \frac{\partial}{\partial \rho_{\mathbf{k}}} \rho_{\mathbf{k}+\ell} \frac{\partial}{\partial \rho_\ell} - \sqrt{N} \sum_{\mathbf{k}} \mathbf{k}^2 \frac{\partial}{\partial \rho_{\mathbf{k}}} (1 + \lambda_k) \rho_{\mathbf{k}} \right] P_{eq}^{HS}\{\rho\} = 0. \quad (11)$$

Note that this equation includes terms tri-linear in the operators  $\rho_{\mathbf{k}}$  and  $\frac{\partial}{\partial \rho_{\mathbf{k}}}$  in addition to the bi-linear terms considered previously. Eq. (11) belongs thus to a wide family of stochastic nonlinear systems, described by a functional Fokker-Planck equation that have been treated successfully by the Self-Consistent Expansion (SCE)<sup>33–39</sup>. Thus, the PY equation is not the last word, as it can be systematically improved. The interesting thing is that in spite of its simplicity the equation of state it produces is in very good agreement with simulations<sup>14</sup>. In fact, since the PY is only an approximation it produces two very good but different equations of state, depending on the route of derivation. When a proper weighted average of the two is constructed the really excellent Carnahan–Starling (CS) equation of state<sup>40</sup> is obtained

$$P_{CS} = \bar{\rho} k_B T \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \quad (12)$$

where  $P_{CS}$  is the pressure,  $T$  is the absolute temperature and the volume fraction  $\eta$  is given (in three dimensions) by

$$\eta = \frac{\pi R^3}{6} \bar{\rho}, \quad (13)$$

with similar expressions in other dimensions (see the supplemental material). Recall that  $R$  is the range of the hard sphere interaction, namely the diameter, and not the radius of a single sphere.

Since the CS equation of state holds for volume fractions below crystallization, the fact that it holds also above crystallization seems to be irrelevant. The reason is that the PY approximation assumes invariance under rotation and the emergence of a crystalline structure is just due to the fact that the free energy associated with the solid is lower than the one associated with the rotation invariant phase. It is interesting to note, however, that the hard sphere system possesses a metastable super dense rotation invariant phase. Actually, the pressure in

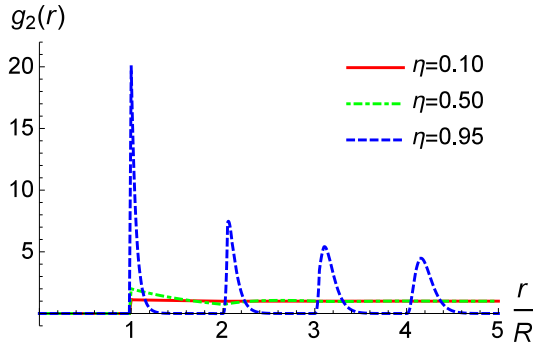


FIG. 1. The one dimensional pair distribution functions for low, intermediate and high volume fractions.

that phase is well described by the CS equation of state up to  $\eta = 0.57$ . This super dense branch should, however, have terminated at random close packing, where the pressure is expected to diverge. Furthermore, that branch as predicted by PY continues into non-physical volume fractions, even above the crystalline close packing. The main trouble with PY is therefore that there seems to be no intrinsic indication within the PY theory that something goes wrong at higher volume fractions. The message of the present article is that, contrary to the above statements, an intrinsic indication for the failure of the theory at a certain density does exist in PY.

Consider the pair distribution function  $g_2(\mathbf{r})$  defined above in eq. (2).  $g_2(\mathbf{r})$  is obtained, within the PY approximation, in the following way. The exact solution in odd  $d$  dimensions provides the so-called direct correlation function  $c_d(r) \equiv -\lambda_d(r)/\bar{\rho}$ , for  $r < R$ . As it happens, those are polynomials of degree  $d$  in  $r$  with coefficients that are functions of the volume fraction  $\eta$ . Since for  $r > R$ , the direct correlation vanishes, obtaining the corresponding Fourier transform  $\lambda_q$ 's is a straightforward analytic calculation. The last step in order to obtain  $g_2(r)$  is to use eq. (8) for the structure factor and finally use eq. (10) to obtain  $g_2(r)$  in the limit of infinite volume by numerical integration.

We begin with the one-dimensional case. In Fig. 1 we present the pair distribution function for three different volume fractions in one dimension. Of particular interest is the high volume fraction graph. The apparent peaks are related to the short range order in the system but it is clear enough that nothing spectacular happens as the peaks are broadened and reduced in height as a function of the distance.

We continue with Fig. 2, where we present the corresponding pair distribution function in three dimensions. The low volume fraction graph shows no interesting features, but the intermediate and high density graphs show clearly a short range order, which is manifested by the oscillations of the pair distribution function. The alert reader may have already detected a serious problem in the  $\eta = 0.65$  case. The pair distribution function,  $g_2(r)$  as defined by eq. (2), is by definition non-negative, while

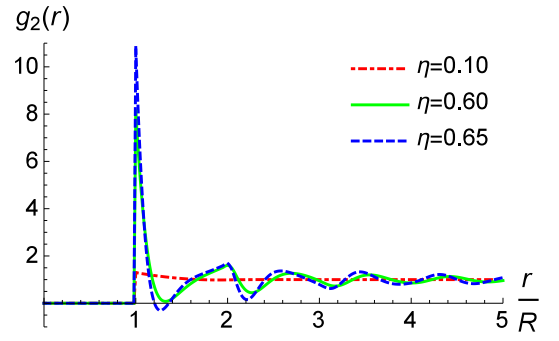


FIG. 2. The three dimensional pair distribution functions for low, intermediate and high volume fractions.

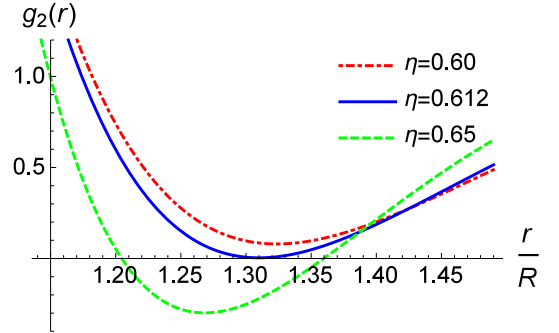


FIG. 3. The three dimensional PY pair distribution function: a zoom-in on the region where it becomes negative.

in Fig. 2 the pair distribution function is negative in a certain region of  $r$  for  $\eta = 0.65$ . The first explication that comes to mind is that this is an artifact of the approximate numerical integration needed to obtain the pair distribution function. A careful evaluation of the error in the numerical procedure, proves that this is not the case. This is also supported by increasing the precision of the integration, which does not produce any perceivable effect, and we find that the lowest volume fraction for which a negative part appears is  $\eta_c(d=3) \simeq 0.612$  as can be seen in Fig. 3.

The inevitable conclusion thus is that the PY approximation breaks down intrinsically at high enough volume fraction. Namely, in contrast to the reasoning based on the continuity of the equation of state across physically impossible densities that was discussed above, the PY calculation itself indicates that something must go wrong, by giving negative values to a function that is non-negative definite. These are obviously good news since it sets an internal limit,  $\eta_c$ , on the applicability of the fluid equation of state (or rotationally invariant case) at high volume fractions.

At this point it is natural to ask whether this  $\eta_c$  has any physical meaning beyond being an intrinsic upper bound on the theory? The first thing to check is whether it happens in higher dimensions as well. We have obtained the pair distribution function for dimensions  $3 < d \leq$

9. For the odd dimensions we used the exact solution, with a numerical solution of the appropriate polynomial equation when required, as well as a numerical Fourier transform to obtain the radial distribution function - see refs.<sup>27,28</sup> and the supplemental material for more details. It turns out that similar to three dimensions, for all odd dimensions in the range  $5 \leq d \leq 9$ , the radial distribution function becomes negative at some range of  $r/R$ . and above some critical value of the volume fraction,  $\eta_c(d)$ . The results are summarized in Table I below, as well as graphically in Fig. 5 (red circles).

For even dimensions we use the method and results reported in previous work<sup>29,30</sup>, which provides the pair distribution function as a power series in the volume fraction  $\eta$  as

$$g_2(r) = 1 + \sum_{n \geq 1} \eta^n g_2^{(n)}(r). \quad (14)$$

In practice, the expansion functions  $g_2^{(n)}(r)$  up to  $n = 13$  for  $d = 4, 6$  and  $8$  are available numerically from ref.<sup>30</sup>. These series work very well for small volume fractions. However, in the current work we are interested in fairly high volume fractions, and in particular in identifying the lowest volume fraction for which  $g_2(r)$  develops a negative part. Note that generically  $g_2(r)$  is a decreasing function, exhibiting oscillations that become more and more pronounced as the density rises. Based on this observation (and on the odd dimensional cases discussed above) the first negative part should appear at the first minimum of  $g_2(r)$  which is obtained in the interval  $1 < r/R < 2$ . The technical difficulty we encounter is that the radius of convergence of the series (14) is not large, and scales as  $2^{-d}$  as the dimension grows (see ref.<sup>30</sup> for a more complete discussion). In particular, for the densities that are of interest the series does not converge, and we need to use some method to re-sum it or analytically-continue it. One such popular method is the Padé approximation<sup>41</sup>. We look at various Padé approximants of  $g_2(r)$ , which are composed of a polynomial of order  $N$  in  $\eta$  divided by a polynomial of order  $M$  in  $\eta$ , of the general form

$$g_2(r) \simeq \frac{\sum_{n=0}^N \eta^n u_n(r)}{\sum_{n=0}^M \eta^n d_n(r)} \quad (15)$$

such that the ratio recovers the series  $g_2(r) = \sum_{n \geq 0} \eta^n g_2^{(n)}(r)$  up to order  $(N + M)$  in  $\eta$ . Since there are in principle many ways to choose  $N$  and  $M$ , we mapped all the options up to order  $N + M = 13$  and looked at the density for which the first zero crossing occurs. We considered only the Padé approximants for which no spurious pole appears inside the interval  $1 < r/R < 2$ , i.e. no spontaneous divergence appears where we expect no real physical divergence to occur (this is a well-known artifact

TABLE I. A summary of the values  $\eta_c(d)$  for dimensions in the range  $3 \leq d \leq 9$ .

d	3	4	5	6	7	8	9
$\eta_c(d)$	0.613	0.467	0.367	0.230	0.207	0.087	0.112

of the Padé method). The various results in  $d = 4$  are presented in Fig. 4, and lead to the following estimate of the largest volume fraction  $\eta_c(d = 4) \simeq 0.467 \pm 0.013$ . A similar analysis has been performed for  $d = 6$  and  $8$  and the results are summarized in Table I, as well as graphically in Fig. 5 (blue squares).

The next question to consider is whether the appearance of  $\eta_c(d)$  carries more physical meaning than the obvious one, namely the inadequacy of the PY equation at high volume fraction. If indeed it carries any physical meaning it must be related to the termination of the super dense, rotation invariant, metastable phase. The volume fraction at that termination point should be identified with that of the Random Close Packing (RCP), or Maximal Random Jammed (MRJ), density. Thus, in the following, we compare our critical volume fractions  $\eta_c(d)$  with available RCP or MRJ volume fractions reported in the literature. Consider first the three dimensional case where a lot of data exists. The critical volume fraction we obtain in three dimensions is  $\eta_c(3) = 0.613$ . The values of RCP volume fraction in three dimensions, obtained by numerous authors<sup>42-46</sup> are spread between 0.6<sup>45</sup> and 0.68<sup>46</sup> depending on the method of derivation. Torquato, Truskett and Debenedetti question the validity of the concept of RCP altogether and introduce instead the concept of MRJ<sup>47</sup>. The MRJ volume fraction is about 0.64 well within the range of RCP volume fractions obtained by others. Skoge et al.<sup>48</sup> give the MRJ volume fraction in 4-6 dimensions and suggest also a fit for that as a function of dimension for  $3 \leq d \leq 6$ ,

$$\eta_{MRJ} = \frac{c_1 + c_2 d}{2^d}, \quad (16)$$

where  $c_1 = -2.72$  and  $c_2 = 2.56$ . In contrast, the large  $d$  dependence of the random close packing volume fraction is given by Parisi and Zamponi<sup>49</sup> as

$$\eta_{RCP} \propto \frac{d \cdot \log d}{2^d}. \quad (17)$$

We compare these results to the terminal volume fraction for which the PY radial distribution function becomes first negative  $\eta_c(d)$  in Fig. 5. Note the RCP density based on eq. (17) leaves the proportionality coefficient undetermined, and we fitted it to the data in Table I for the sake of comparison. We also tried to fit our results using the functional form given by eq. (16), giving rise to the estimated values  $\hat{c}_1 = -5.397$  and  $\hat{c}_2 = 3.385$ . As can be seen, the fit based on eq. (16) (solid line) and the fit based on eq. (17) (dashed line) are very close to each other.

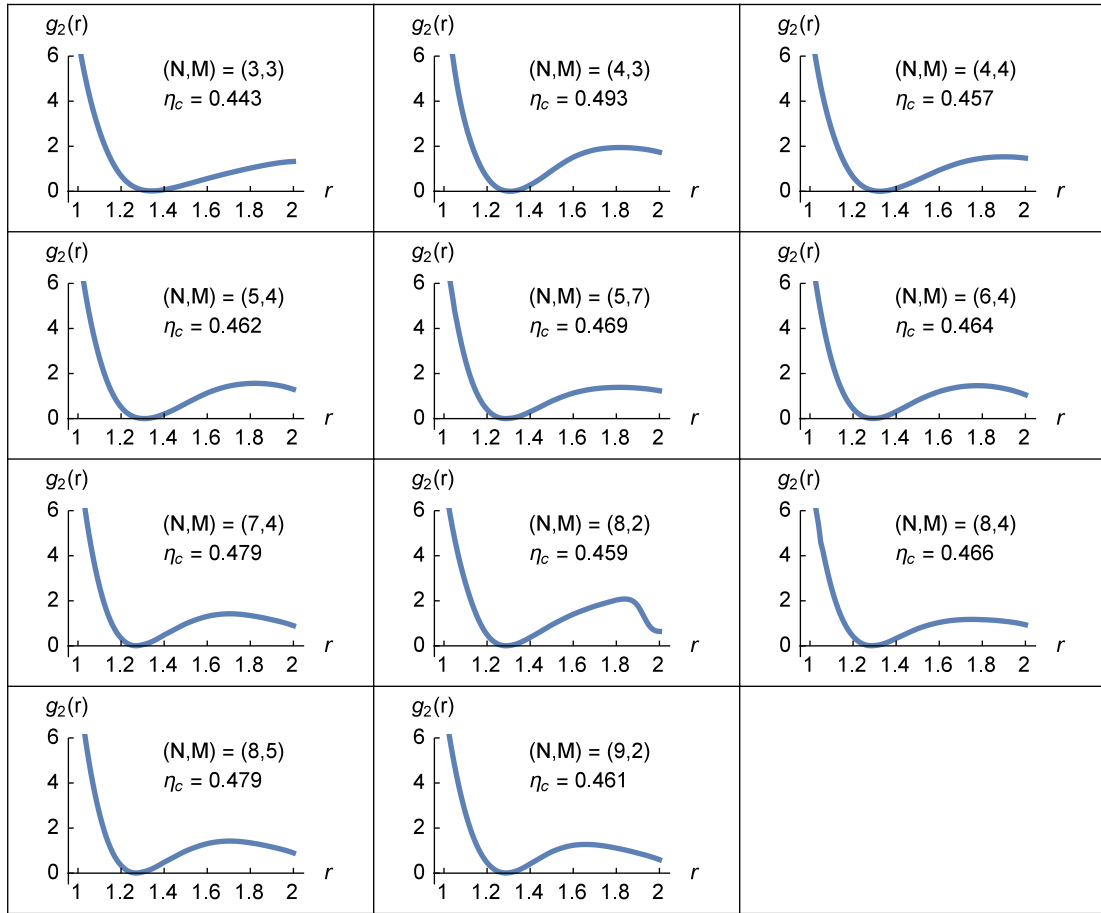


FIG. 4. The various Padé approximants of the PY pair distribution function in  $d = 4$ . In each case, the order of the approximation is indicated along with the resulting terminal density. The final estimate is based on the average of these different estimates. It results in  $\eta_c(d) \simeq 0.467 \pm 0.013$ .

The conclusion is that our hunch that the terminal volume fraction identified by the Percus-Yevick theory has a physical meaning seems to be justified in the sense that  $\eta_c(d)$  is close to and behaves as a function of dimension similarly to the theoretical predictions for MRJ/RCP. Actually, this conclusion is also supported by the one dimensional result where the PY pair distribution function remains positive for all volume fractions consistent with the fact that the real system of hard spheres never crosses to a RCP or MRJ state as the volume fraction is increased all the way up to  $\eta = 1$ , where it crystallizes.

To summarize, in this paper we show that unlike the common lore, the Percus-Yevick theory for mono-disperse hard spheres provides an intrinsic indication for its limitation in the regime of high densities. More specifically, the positivity of the pair-correlation function  $g_2(r)$  is violated at a certain volume fraction which we denote  $\eta_c(d)$ , and thus beyond it the PY theory is no longer consistent. It turns out that this phenomenon occurs over all dimensions in the range  $3 \leq d \leq 9$ , suggesting that it should hold also beyond. A comparison of  $\eta_c(d)$  to the various results and predictions for the RCP or MRJ volume frac-

tions shows that they are close and behave similarly as a function of dimension. This supports the idea that the terminal volume fraction in the PY theory actually indicates the largest density for which a spherically invariant state (essentially a fluid state) can exist, even if the solid phase is already preferred energetically at this point.

We hope this work will motivate other researchers to check this phenomenon in many other systems described by a Percus-Yevick theory. A few examples are hard spheres experiencing more complicated interactions such as Sticky Hard Spheres<sup>50,51</sup> or Square-Well Fluids<sup>52</sup>. Other important direction are systems composed of Polydisperse or Mixture of hard spheres<sup>14,50,52-54</sup>, various charged hard sphere fluids<sup>50</sup> such as the hard sphere Yukawa fluid<sup>55</sup>, Ionic liquids<sup>14,52</sup>, polarizable fluids<sup>54</sup>, and even fluids of non-spherical shapes such as chain-like molecules<sup>50,52</sup>.

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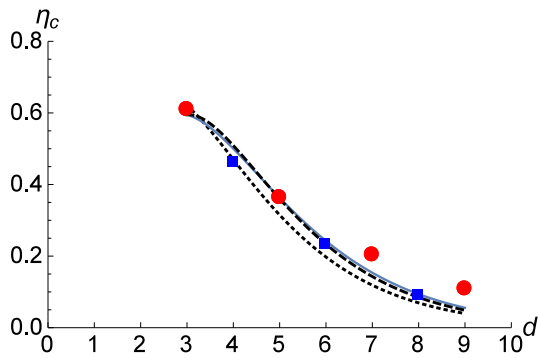


FIG. 5. A plot of  $\eta_c(d)$  for odd (red circles) and even (blue squares) dimensions in the range  $3 \leq d \leq 9$ . We also present the theoretical predictions for the MRJ density based on eq. (16) (dotted line), our fit based on Eq. (16) (solid line) and the theoretical prediction for the RCP density based on Eq. (17) (dashed line).

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