Maximizing space efficiency without order, analytically

Explicit Analytical Solution for Random Close Paking in $d = 2$ and $d = 3$
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Recommended with a Commentary by Christos Likos, University of Vienna, Faculty of Physics

People who wish to pack a layer of equally-sized, nonoverlapping discs of diameter σ in a way that uses the least amount of the plane, end up intuitively (or after a few trial-and-error attempts) placing them on the vertices of a hexagonal (triangular) lattice. Intuition turns out to be correct in this case, as it has been mathematically proven by Lagrange that the resulting packing fraction $\phi_{\text{hex}}^{\text{CP}} = \pi\sqrt{3}/6$ is indeed the highest that can be achieved by any two-dimensional spatial arrangement of the circles. The three-dimensional extension of the problem is more challenging: the Kepler conjecture that another ordered assembly, the fcc crystal with close packing fraction $\phi_{\text{fcc}}^{\text{CP}} = \pi\sqrt{2}/6$, is optimal has been proven by Hales only recently [1]. It is natural, then, to ask whether there is a similar highest packing fraction for amorphous, non-crystalline arrangements of hard spheres, a quantity known as random close packing ϕ_{RCP}, which has puzzled researchers time and again since its introduction by Bernal [2, 3, 4]. The most frequently quoted value is $\phi_{\text{RCP}} \cong 0.64$, which plays also a prominent role in important theoretical insights on the RCP-transition. It has been conjectured to correspond to the state in which the rate of disappearance of accessible states diverges [5] and it has also been interpreted as the point in which a dynamical phase transition in biased random organization takes place, which is associated with hyperuniformity of the interparticle correlations [6]. In a recent paper [7], Alessio Zaccone offers a beautiful, analytical answer to this question, bringing together ideas from liquid-state theory, jamming, and rigidity theory.

First of all, the bad news: the sought-for quantity is not well-defined. Even if one puts aside complications related to *real* spheres and effects of friction on their surfaces [8, 9], the intuitively spontaneous definition of ϕ_{RCP} as "the largest possible density an amorphous assembly of *ideal*, nonovelapping spheres can attain" is problematic because it is not specified how amorphous an amorphous assembly can be. Local crystalline arrangements can increase the overall packing fraction and the question arises how much order can be tolerated in an amorphous state before it disqualifies being called *disordered*. Here, Zaccone adopts a procedure that is based on states that are disordered by construction: he employs structural information encoded in the radial distribution function (RDF) $g(r)$ of a hypothetical, uniform, ergodic fluid of hard spheres. An analytical, albeit approximate, solution for the direct correlation function $c(r)$ of the hard sphere fluid exists: the celebrated Percus-Yevick (PY) solution, which leads to the determination of $g(r)$ through the Ornstein-Zernike relation [10]. The RDF is an expression of the ratio of the probability density, over that of an ideal gas, to locate a particle at distance r from any given particle: it is identically unity for a noninteracting system and it also approaches the value 1 at large interparticle separations r for any interacting one.* In Fig. 1, we show examples of the PY-$g(r)$ for the hard-sphere fluid at three different values of the packing fraction ϕ. As hard spheres are known to undergo an equilibrium crystallization at $\phi_{\text{freeze}} = 0.494$ in coexistence with a fcc-crystal that melts at $\phi_{\text{melt}} = 0.545$, the fluid in the density range shown in Fig. 1 is metastable but the PY solution knows nothing about it. In fact, the PY solution is an approximation that remains formally valid all the way up to $\phi = 1$ (a physically impossible state, as one cannot fill space with nonoverlapping spheres), where the analytic expression for $c(r)$ develops a pole. It is precisely the properties of this translationally invariant state, which contains no information about freezing, jamming, or packing, that Zaccone takes advantage of in his approach to estimate ϕ_{RCP}.

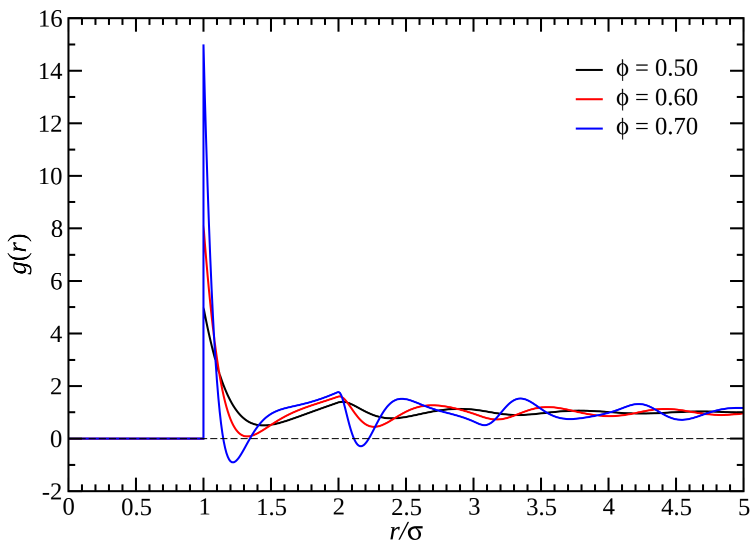

Figure 1: The Percus-Yevick solution for the radial correlation function $g(r)$ of the hard sphere fluid at three different packing fractions ϕ, as indicated in the legend. Note the appearance of unphysical regions at which $g(r) < 0$ for the highest packing fraction shown, $\phi = 0.70$. The raw data are courtesy of Vittoria Sposini.

The value of the $g(r)$ at contact, $g(\sigma^+)$, provides the pressure $P(\phi)$ of the uniform fluid as a function of its packing fraction ϕ through the relation [11]:

$$\frac{\pi\sigma^3}{6}\frac{P(\phi)}{k_{\text{B}}T} = \phi + 4\phi^2 g(\sigma^+). \quad (1)$$

*Exponentially in general and as a power-law at critical points.

The *coordination number* ζ of the fluid, i.e., the average number of particles surrounding any particle, can also be calculated with the help of $g(r)$ via:

$$\zeta = 24\phi\sigma^{-3}\int_0^{r_{\min}} r^2 g(r)\mathrm{d}r, \tag{2}$$

where $r_{\min}$ is the position at which $g(r)$ attains its first local minimum for $r > \sigma$. For dense fluids, the typical value $\zeta \approx 12$ results.

A key element of Zaccone's argument is that at the random close packing, the metastable uniform fluid reaches the state of *jamming*, i.e., particles come at fixed, closest contacts with one another, blocking relative motion and depriving the system of any further internal dynamics, save for some fraction of particles that can be rattlers [9]. This view is in agreement with earlier considerations by Rintoul and Torquato [12], who postulated the emergence of two branches of $P(\phi)$-curves out of the stable hard sphere fluid upon compression: the first follows after slow compression and traces the equilibrium transition to a crystal, diverging at $\phi_{\mathrm{fcc}} = \pi\sqrt{2}/6$. The second results out of a rapid compression, tracing amorphous, metastable fluid states and eventually diverging at ϕ_{RCP}.† Below ϕ_{freeze} there is a single, equilibrium $P(\phi)$ curve. Since the PY solution lacks thermodynamic consistency, the prediction it makes about the value of $g(\sigma^+)$ is not exact and thus the pressure obtained by this route (called 'virial' pressure P_{v}) does not coincide with the 'compressibility' pressure P_{c} resulting from the $k \to 0$ limit of the structure factor $S(k)$. This discrepancy is cured in an empirical way in the Carnahan-Starling (CS) equation of state and the associated contact value $g(\sigma^+)$, which also plays a role in Zaccone's approach.

At variance with previous approaches, Zaccone neither tries to calculate the metastable pressure branch by simulation [12, 13], nor does he attempt to determine ϕ_{RCP} by expanding the pressure around this value according to free-volume theory [5], a procedure that also requires access to highly accurate simulation data deeply into the metastable region. Instead, the approach of Ref. [7] is based entirely on the PY/CS solution as well as on considerations of jamming and mechanical stability, as explained below.

The first ingrediend of Zaccone's *analytical* approach to the problem is to consider the consequences of the fact that the pressure has to diverge at close packing, since the state is collectively jammed. Structurally, the close packing implies the existence of permanent contacts between neighbors, thus the RDF has to develop a $\delta(r-\sigma)$-peak at $\phi = \phi_{\mathrm{RCP}}$, consistently with the divergence in the pressure, as expressed by Eq. (1). An extreme example is the crystalline close packing $\phi_{\mathrm{fcc}}^{\mathrm{CP}}$, where the entire (angularly-averaged) RDF is just a superposition of δ-spikes centered at the distances r_j of the fcc-coordination shells, i.e.:

$$g_{\mathrm{fcc}}^{\mathrm{CP}}(r) = \sum_{j=0}^{\infty} \tilde{g}_j \delta(r - r_j), \tag{3}$$

†Evidently, being an equilibrium quantity, the pressure has a unique value for every value of ϕ and thus only the first curve is a true pressure. Nevertheless, a pressure can be assigned by analogy to an ensemble of metastable, 'supercooled' fluids for which crystallization is avoided for times much longer than the microcopic scales as a result of the compression protocol or of specific simulation moves that prevent crystallinity from growing.

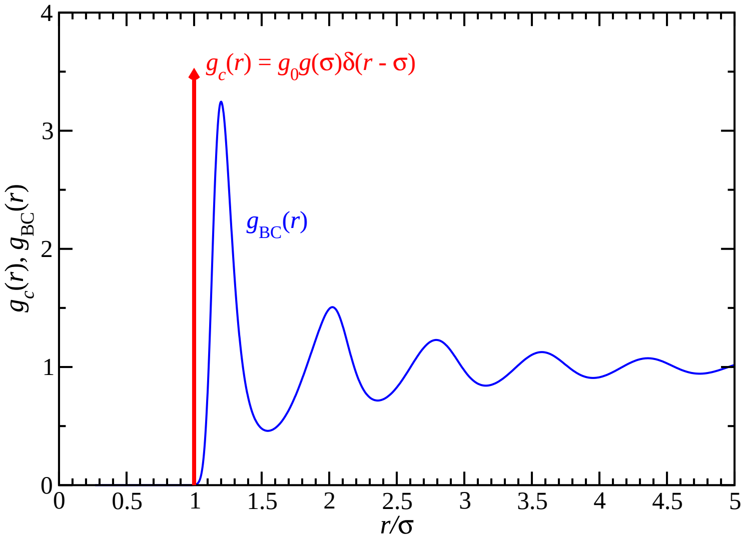

Figure 2: A schematic example of the terms appearing on the right-hand side of eq. (4). The raw data are courtesy of Vittoria Sposini.

with appropriate weight factors $\tilde{g}_j$ and $r_0 = \sigma$. The RDF of the amorphous, close-packed states, call it $g_{\rm am}^{\rm CP}(r)$, is now postulated to be a hybrid between the continuous shape of the uniform, ergodic, albeit metastable fluid and the discrete form of the closed-packed fcc-solid, namely

$$g_{\rm am}^{\rm CP}(r) \quad = \quad g_c(r) + g_{\rm BC}(r) \tag{4}$$

where $g_{\rm BC}(r)$ is the RDF from all contributions beyond contact and $g_c(r)$ contains the aforementioned δ-contribution, expressed as:

$$g_c(r) \quad = \quad g_0 g(\sigma^+)\delta(r-\sigma), \tag{5}$$

where $g(\sigma^+)$ is taken to be the contact value of the RDF of a uniform fluid, obtained from a theory that is completely agnostic over the possibilities of both crystalline ordering and jamming/random close packing.

In Fig. 2 we show a sketch of such a RDF. The appearance of a δ-contribution at contact is consistent with simulations results by Donev *et al.* [14], who have additionally established that the function $g_{\rm BC}(r)$ features a split second peak at $r = 2\sigma$ as well as kinks [6, 14]. Accordingly, the curve $g_{\rm BC}(r)$ shown in Fig. 2 is only a schematic result shown for demonstration purposes only; its precise form is irrelevant in Zaccone's calculation anyhow. One can now define a coordination number z arising from those particles in permanent contact only, by introducing a more restricted form of eq. (2) appropriate for RDF's that contain δ-contributions, namely

$$z = 24\phi\sigma^{-3}\int_0^{\sigma^+} r^2 g_{\rm am}^{\rm CP}(r){\rm d}r, \tag{6}$$

which, in conjunction with eq. (5), and given that the RDF has to vanish for $r < \sigma$, implies

$$z = 24\phi\, G_0\, g(\sigma^+), \tag{7}$$

with $G_0 \equiv g_0/\sigma$. Within the Percus-Yevick approximation, the dependence of $g(\sigma^+)$ on ϕ reads as:

$$g(\sigma^+) = \frac{1 + 0.5\phi}{(1-\phi)^2}. \tag{8}$$

Eq. (5) contains a drastic and bold assumption. The dependence the overall prefactor of the δ-function of $g_c(r)$ has on the packing fraction ϕ is assumed to be dictated by the value at contact of the RDF of a putative ergodic liquid, $g(\sigma^+)$; the additional factor g_0 plays the role of an overall normalization constant that does not depend on concentration. There is no a priori reason why this should be valid; even the meaning of such a fluid at deeply metastable densities is questionable and Zaccone is indeed very careful not to raise any such claims. The only implicit statement hidden beyond the choice expressed in eq. (5) is that the growth with density of the coordination number z in states with particles in permanent contact is following the associated increase of the contact value of $g(r)$ of (metastable) ergodic states in exactly the same way. What makes the assumption even more daring is the fact that this dependence is read off from the Percus-Yevick solution for hard spheres, for which not only is the value $g(\sigma^+)$ inaccurate at high densities but the whole $g(r)$ develops negative parts for $\phi \gtrsim 0.60$, rendering the RDF unphysical (see Fig. 1). Nevertheless, the approach, supplemented by a definition of random close packing based on a statistical view of mechanical stability, yields remarkably accurate results.

To proceed further one needs two additional ingredients: a reference state to calibrate the theory, so as to be able to fix the yet undetermined value of the constant G_0 as well as a working definition of what random close packing means. For the latter, Zaccone resorts to previous work by himself and Scossa-Romano [15], which showed that mechanical stability of elastic spheres in $d = 2$ and $d = 3$ dimensions is marginal when $z = 2d$, in agreement with Maxwell's isostaticity criterion [6]. Accordingly, it is asserted that any amorphous packing with average coordination number $z < 2d$ is not rigid and thus a packing fraction ϕ resulting in such an inequality will necessarily be below ϕ_{RCP}. As systems with $z > 2d$ are mechanically stable, the threshold $z = 2d$ is used here to *define* the random close packing in a precise, albeit statistical way.[‡] Accordingly, by setting $z = 6$ as the condition of random close packing at $d = 3$ and using eqs. (7) and (8), an implicit equation for ϕ_{RCP} is obtained:

$$\phi_{\mathrm{RCP}} \frac{1 + 0.5\phi_{\mathrm{RCP}}}{(1-\phi_{\mathrm{RCP}})^2} = \frac{1}{4G_0}, \tag{9}$$

resulting into

$$\phi_{\mathrm{RCP}} = \left(\frac{1+2G_0}{1-2G_0}\right) - \sqrt{\left(\frac{1+2G_0}{1-2G_0}\right)^2 - \frac{1}{1-2G_0}}. \tag{10}$$

[‡]Whichever value is obtained cannot exclude that there might exist particular, stable random close packings with $\phi \neq \phi_{\mathrm{RCP}}$.

To fix the constant G_0, Zaccone proceeds now to his final, bold assumption: the range of validity of the theory is also extended to jammed *ordered* states and, in particular, all the way to the extreme value $\phi_{\rm fcc}^{\rm CP} = \pi\sqrt{2}/6$ with its coordination $z = 12$. Application of the same procedure based on eqs. (7) and (8), yields the estimate of G_0 calibrated on this crystalline close-packing state as:

$$G_0 = \frac{(6-\pi\sqrt{2})^2}{\pi\sqrt{2}(12+\pi\sqrt{2})} \cong 0.033\,189\,4. \tag{11}$$

Subsitution of eq. (11) into eq. (10) now yields the result

$$\phi_{\rm RCP} = 0.658\,963. \tag{12}$$

The same approach applied *mutatis mutandis* in $d = 2$ yields

$$\phi_{\rm RCP}^{\rm (2D)} = 0.886\,44. \tag{13}$$

Both estimates in eqs. (12) and (13) above are extremely satisfying because they fall within the limits set by various (real or numerical) experiments that have determined $\phi_{\rm RCP}$ both in $d = 3$ and in $d = 2$. If the CS equation of state for hard spheres is adopted, the estimate $\phi_{\rm RCP} = 0.677\,376$ results. This is interpreted by Zaccone as the realization of a different 'protocol' for creating random packing, akin to the various numerical protocols of imposing disorder in crowded hard spheres that result in different random-close-packing outcomes.

These are beautiful findings and it is remarkable achievement that one can obtain an analytical result to such a difficult problem. The question arises, then, why exactly is this working so well? As someone with a (long) past in liquid state theory, I have learned not to trust integral equations in general far beyond the crystallization transition. Indeed, using, e.g., structure factors whose maximum exceeds the Hansen-Verlet value $S_{\rm max} \cong 3.0$ has to be done with care and liquid state data beyond the parameters set by the Mode-Coupling Theory ideal glass transition are almost never reliable. Even less reliable is the PY solution for hard spheres, for which already at $\phi \cong 0.62$ the RDF develops negative parts, an absolute no-go. And yet, here the PY solution is employed all the way to its extreme: an expression that diverges at $\phi = 1$ is used, data are calibrated at $\phi \cong 0.74$ and then the parameter G_0 extracted there is employed to yield a remarkably good value of $\phi_{\rm RCP}$. Neither the pressure of the metastable fluid branch [5] nor the RDF of the crowded amorphous states [14] bear any resemblance to their PY-counterparts. How is this all possible?

Well, to begin with, the worst of all aforementioned problems, i.e., the negative parts of the PY-RDF is immaterial for Zaccone's argument, as the only feature of this function entering his argument is its contact value $g(\sigma^+)$, and this remains nicely positive, growing monotonically with ϕ and diverging at $\phi = 1$. The crucial reason why the rest works, probably lies in the fact that the PY solution is indeed completely ignorant of any order or close packing and merely gives a statistical estimate of the degree of crowding as density grows, which is precisely what is asked for in Zaccone's approach. Indeed, one is not looking for the RDF of the real, metastable fluid, as this contact value will necessarily diverge at $\phi_{\rm RCP}$. Close-packed, ordered states become unreachable if one follows this path, therefore the calibration of the strength of the δ-function in eq. (5) would not be possible. What is needed here is some underlying, fictitious uniform state, spanning the whole density domain, which possesses a RDF that captures, in broad terms, the increased crowding upon compression. It is even immaterial whether this state truly exists: inaccuracies in the PY (or CS) $g(\sigma^+)$ are compensated by the calibration of the prefactor G_0 on some standard, ordered close-packed state. In this sense, it is instructive to attempt, in $d = 3$, a different calibration by using the bcc lattice with $z = 8$ and $\phi_{\rm bcc}^{\rm CP} = \pi\sqrt{3}/8$ [16] to determine G_0 according to eqs. (7) and (8). One may hope to improve the result since the PY solution is now applied at a lower packing value than for the fcc close packing. It is straightforward to show that we now obtain the value

$$G_0 = \frac{2(8 - \pi\sqrt{3})^2}{3\pi\sqrt{3}(16 + \pi\sqrt{3})} \cong 0.037\,406\,8. \tag{14}$$

Subsitution of eq. (14) into eq. (10) now yields the result

$$\phi_{\rm RCP} = 0.643\,320, \tag{15}$$

cf. eqs. (11) and (12), respectively. The latter value is practically coinciding with the most frequently quoted value $\phi_{\rm RCP} = 0.64$ [5, 6] but this could be just a mere numerical coincidence.

As a final remark, and extending somewhat Zaccone's considerations, let us take a closer look at the behavior of eqs. (7) and (8) and their solution at some interesting, limiting cases for G_0. Solving for $\phi(z, G_0)$, dropping for now the condition $z = 2d$ and keeping a general G_0 without reference yet to any kind of close packing, we obtain the two solutions:

$$\phi_{\mp}(z, G_0) = \left(\frac{z + 12G_0}{z - 12G_0}\right) \mp \sqrt{\left(\frac{z + 12G_0}{z - 12G_0}\right)^2 - \frac{z}{z - 12G_0}}, \tag{16}$$

where, for small values of G_0 the minus-sign solution must be chosen but for high values of G_0 the plus-sign, so that $0 \leq \phi \leq 1$. There are two limits in which the solution becomes z-independent: first, as $G_0 \to 0^+$, $\phi \to 1^-$, corresponding to the hypothetical case in which the system does not jam at any $\phi < 1$. Then, consistently with the properties of the structure of this putative system, the approach predicts a random close packing at $\phi_{\rm RCP} = 1$, which is the RCP-value of the Percus-Yevick solution. At the other extreme, we can *prescribe* to the system some very high value of G_0, roughly corresponding to a strong stickiness on the surface of the hard spheres, and then, letting $G_0 \to \infty$, eq. (16) now predicts $\phi_{\rm RCP} \to 0^+$, independently of z. This is strongly reminiscent of the 'empty liquids', i.e., hard sphere colloids endowed with very strong, patchy, associating interactions that lead to the formation of very low density arrested states with a low-coordination, network structure [17].

There are probably many other ways of thinking about the findings and the interpretation of the work discussed in this comment [7]. In any event, Zaccone's very fresh, original, and physically insightful approach to an old problem, provides us with an analytical solution to it. Moreover, it carries strong potential for extensions to anisotropic shapes and mixtures, opening up new ways and motivating us to think about and appreciate anew the power and beauty of the Percus-Yevick solution for hard bodies in d-dimensions.

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