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Random jammed packings of hard discs and spheres

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Abstract. A method for transforming low-density configurations of rods, discs or spheres to rigidly jammed packings is described. In D dimensions, it repeats a cycle in which each particle is moved towards to the centre of the cage of the $D+1$ neighbouring particles that most closely contain it. Low-density fluid configurations of discs and spheres form rigidly jammed amorphous packings with densities below the normal glass transition density. The glassy structures contain large pores and many mobile rattler particles.

1. Introduction

The canonical partition function $Q(N, V, T)$, for N particles in a volume V at temperature T, can be expressed as a sum of parts:

$$Q(N, V, T) = \sum_k q_k(N, V, T) \tag{1}$$

which may be non–trivial when a suitable prescription [1–6] is given for assigning the states within Q to the individual q_k. For systems with continuous potentials the usual prescription [4–6] consists of collecting into q_k all of those configurations that map to the same inherent structure, k, when the system is instantaneously cooled. For hard discs, Stillinger, DiMarzio and Kornegay [1] proposed subdividing Q with the following recipe: starting with any low-density configuration, with periodic boundaries, the discs are uniformly expanded and allowed to push each other apart until they reach a rigidly jammed state, which is the inherent structure to which the initial configuration belongs. All configurations that compress to the same structure, without distinction between states that differ only by the interchange of identical particles, belong to that inherent structure and may be given the same label k. In two and three dimensions the number of distinct inherent structures is $\exp(\alpha N)$ where N is the number of particles and α is of order unity [4–6].

Despite much clever work on the packing of discs and spheres, recently reviewed by Meakin and Skjeltorp [7], who give many references, direct evidence about the distribution of the densities of their inherent structures is lacking. Indirect evidence [8, 9], from attempts to interpret the thermodynamic properties of fluids and glasses of discs and spheres in terms of equation (1), shows that a broad distribution of inherent structures is needed to explain the large change in heat capacity at the glass transition. In particular, it was suggested [8, 9] that the most numerous inherent structures have densities near or below the glass transition density of the fluids, but that these are not observed in the usual molecular dynamics experiments because the fluids relax quickly to denser and more stable structures.

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This paper shows that the low-density glasses exist. They can be made by compressing fluid configurations to jammed states in which the average disc makes 3.05 ± 0.1 contacts or an average sphere makes 4.2 ± 0.1 contacts. A remarkable feature of these packings is that about 6% of the discs or 4% of the spheres are free to move within large pores in a rigidly jammed framework.

A specific prediction that the present work was designed to test is that a fluid of discs or spheres, equilibrated at packing fraction y, samples glasses, or inherent structures, with a limiting density $y_0(y)$ that increases with y. If the number of glasses with limiting density y_0 follows a normal distribution about the most probable value, y_m, then a few plausible assumptions lead to the prediction [8, 9]

$$y_0 = \frac{y_m + y + \sqrt{(y_m - y)^2 + 2C/\gamma}}{2}. \tag{2}$$

The constant γ characterizes the width of the distribution and C is a measured property of the glasses. For hard disks and spheres, the constants in equation (2) were chosen to fit the pressure and entropy of the fluids and glasses [8, 9], so it is of interest to see whether they agree with measured values of $y_0(y)$. Equation (2) can be tested by compressing fluid configurations, equilibrated at density y, to their limiting density $y_0(y)$, taking care not to allow the configuration to escape from its inherent structure during the compression.

2. Methods

Three different methods were examined. The first is due to Mason [11], who notes that it was suggested by Bernal [12]. It starts with a random array of points, or a fluid configuration, then repeatedly locates the closest pair and increases their separation, by moving them apart along the line of their centres. If the moves are small enough this method might approximate the procedure proposed by Stillinger, DiMarzio and Kornegay [1]. The diameter of the discs or spheres, σ, is defined, at any instant, as the separation between the closest two points. The density, or packing fraction, is then $y = (N/A)(\pi/4)\sigma^2$ for discs, where A is the area, or $y = (N/V)(\pi/6)\sigma^3$ for spheres, where V is the volume. Mason found, for hard discs, that the density quickly increased to $y \approx 0.83$ and thereafter increased slowly, due to crystallization. For hard spheres, variations on Mason's method [13–15] and other methods [8, 14–17] yield limiting densities y_0 near 0.648. Most attempts to make random packings of hard discs have produced crystals [7, 11, 16, 17].

A non-freezing equimolar mixture of hard discs with diameters in the ratio 1.4:1 forms glasses with limiting density $y_0 = 0.851$ and the glass transition occurs near $y = 0.78$ [9]. This mixture was studied using Mason's [11] method. Starting from fluid configurations of $N = 400$ discs, with periodic boundaries, previously equilibrated in a molecular dynamics experiment, the distance between the centres of the closest pair was increased by 1%, 0.1% or 0.01% in each move. The density converged to values $y \approx 0.83$. 2×10^8 moves were required for convergence when the separation was increased by only 0.01%. The final density was not significantly affected by the size of the moves. When the starting density, y, is above 0.7, the limiting densities obtained by Mason's method are within 1% of values predicted [9] by equation (2) but when the starting density is lower the method yields limiting densities about 5% higher than predicted. Similar results were obtained for spheres [15].

In Mason's method, the closest pair is separated without regard for consequent overlaps with other particles. As discs separate they make new overlaps which push them back together, so there is an inessential 'vibrational' component of the particle trajectories and

this may allow the system to escape from its inherent structure. Results from the other methods described below seem to confirm that this occurs, by showing that the same low-density fluid configurations can be compressed to jammed states with limiting densities that are 10% lower than those found by Mason's method. However, Mason's method is not always wrong: for a tetravalent network model [10] it gave limiting densities in good agreement with independently measured values.

The following methods are based on the idea that, to prevent the system escaping from its inherent structure, a particle should remain trapped in the cage of its near neighbours during the compression. In D dimensions, the method repeats a cycle in which each particle is moved towards to the centre of the cage of the $D+1$ neighbouring particles that most closely contain it.

A one-dimensional system of rods of length σ on a line of length L, with periodic boundaries, provides a simple illustration of the method. This model has just one inherent structure, the perfect crystal, with density $y_0 = N\sigma/L = 1$. Each rod is contained between the nearest rod on either side and, in each cycle, the method moves every rod to the point midway between its containing pair, using their positions after the previous cycle. Then σ is increased until the closest pair touch and the cycle is repeated. The rods quickly expand to cover the whole line. For example, starting at $y = 0$ with five random points, $y = 0.99$ after 40 cycles and 0.999 999 after 80 cycles. If the rod positions are updated in sequence, from left to right, and a rod is placed midway between the current positions (rather than the old ones) of its containing pair, then $y = 0.999\,999$ after 20 cycles.

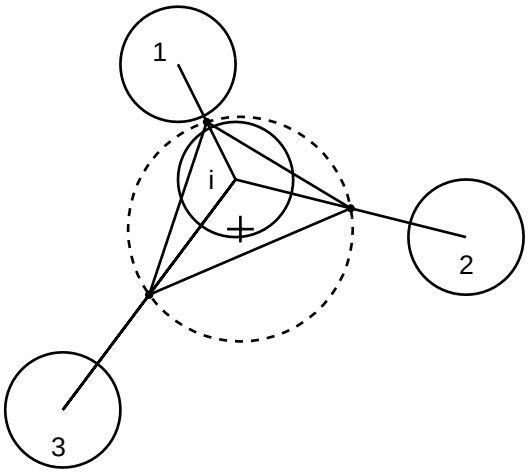

Figure 1. The geometrical construction used to find the new position of disc i in the second method. For each set of three neighbours of i the vertices of the triangle shown are midway between i and a neighbour. The new position of disc i, marked by a cross, is the circumcentre of the triangle that encloses the centre of i and has the smallest circumradius.

Figure 1 outlines the same principle for hard discs of equal size. The three discs that most closely contain a particular disc are located as follows: for each neighbour, k, of disc i, the midpoint P_{ik} of the line joining the centres of discs i and k is located. Each set of three neighbours define a triangle with vertices P_{ik}, $k = 1$, 2 and 3. The triangle that encloses i, in the sense that the centre of i is within the triangle, and which has the smallest circumradius of all such triangles, is the one that most closely contains it, and the new position of disc i is the circumcentre of this triangle. In each cycle, the new positions of all

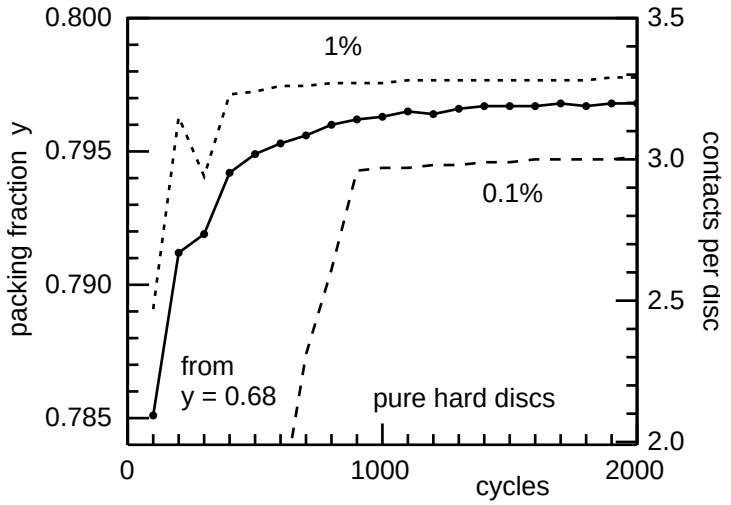

Figure 2. The variation of the density, y (solid line), and the number of contacts (dashed lines), with the number of moves, obtained using the second method. The results shown are for $N = 1600$ monodisperse hard discs started from an equilibrated fluid configuration at density $y = 0.68$ (the fluid freezes at $y = 0.69$). Contacts are defined as pairs of discs for which $r_{ij} < 1.01\sigma$ (1%) or $r_{ij} < 1.001\sigma$ (0.1%). The number of contacts with 0.1% tolerance was invariably 3.05 ± 0.1 in the jammed states, even though many of the discs are rattlers and make no contacts. (6 ± 1)% of the discs make no contacts at 1% tolerance.

of the discs are calculated, on the basis of the positions at the end of the last cycle, before any disc is moved, then all of the discs are moved simultaneously. This avoids making an arbitrary choice of the sequence in which the particles are moved [11]. The method is very efficient: 400 random points on a plane compress to a limiting density $y_0 \approx 0.755 \pm 0.005$ in about 1000 cycles; this takes 40 seconds on a desktop computer. Figure 2 shows how the density and the number of near contacts vary with the number of cycles.

For mixtures in which the diameters, σ_i, of the discs or spheres differ, the method is the same except that the points P_{ik} are located a distance $r_{ik}\sigma_i/(\sigma_i + \sigma_k)$ from the centre of disc i. For spheres, four points P_{ik} contain i and the new position is the circumcentre of the containing tetrahedron with the smallest circumradius.

For $N = 1600$ or 10 000 discs, or 4000 spheres, different fluid starting configurations, equilibrated at the same density y, compress to the same limiting densities $y_0(y)$, with a standard deviation of about 0.2%. The standard deviation increases to 1% when $N = 400$ and to 3% when $N \approx 32$, but the average values of $y_0(y)$ are the same to within 1%.

A third method was developed to check the results of the previous one. For hard discs of the same size the third method is the same, in principle, as one described by Hinrichsen *et al* [19, 20] and by Meakin and Skjeltorp [7]. Hinrichsen *et al* [19, 20] construct the Dirichlet polygon, which bounds the space closest to each disc, and then move each disc to the point, within its polygon, that is as far from any side as possible. At this point the disc is equidistant from the three closest sides of the Dirichlet polygon. The construction shown in figure 3 accomplishes the same end. It makes the triangle of the perpendicular bisectors of the lines joining i to three neighbours, finds the containing triangle with the smallest inscribed circle and moves disc i to the centre of that inscribed circle. Comparing figures 1 and 3 shows that, for the configuration shown, the new position of particle i is practically the same, so it is not surprising that the two methods yield the same results to

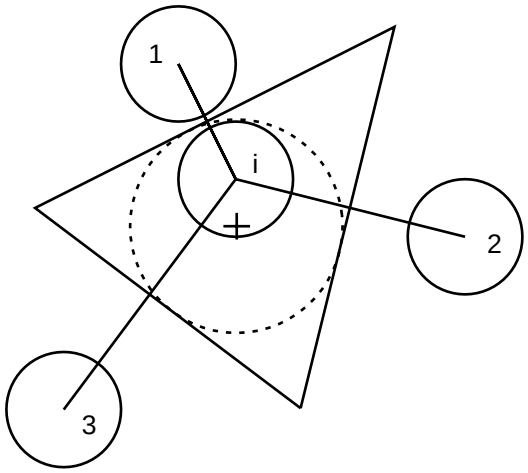

Figure 3. The construction used to find the new position of disc i in the third method. For each set of three neighbours of disc i, the sides of the triangle shown are the perpendicular bisectors of the line between i and a neighbour. The new position of i, marked by a cross, is the centre of the smallest inscribed circle of any triangle that encloses the centre of i. The cross is very close to the cross shown in figure 1.

within the scatter of the data.

A severe test of any method of making inherent structures is that the structure produced should be robust with respect to small variations in the method. Ideally, any method of finding the inherent structure should produce exactly the same structure from the same starting configuration. One way to vary the second method is to scale the size of the moves. This was done by placing the points P_{ik} at distance $fr_{ik}\sigma_i/(\sigma_i + \sigma_k)$ from the centre of i and varying the scaling factor f. Structures obtained by compressing the same fluid configuration of the $N = 400$ hard-disc mixture with $f = 0.5$, 0.8 and 1 were compared by overlaying graphics displays of the disc locations. Structures formed with different values of f were topologically the same when the starting density was greater than $y = 0.5$. The geometrical positions of a few discs often differed by a fraction of a radius, but the topology of the network constructed by joining each disc to its contacting neighbours was the same. Starting from $y = 0.2$, the structures showed more variation but there was a percolating framework containing about 60% of the discs that was topologically the same and within which local regions of 20 to 40 discs were rearranged. The local rearrangements can be traced back to a disc that passed between two of its neighbouring discs during one of the compressions. If f is increased to 1.4 the resulting jammed structure is quite different and its limiting density is about 2% higher. With $f = 2$ the moves immediately generate very close pairs and the density goes to zero. The results reported are for $f = 1$.

3. Results

Figures 4 and 5 summarize the density, $y_0(y)$, of the inherent structures to which the starting configurations at density y belong, for pure hard discs, for a non-freezing mixture of discs and for pure hard spheres. The equilibrated fluid configurations compress to inherent structures that have well defined densities and this provides a physically motivated method for defining the inherent structures in equation (1). Figures 4 and 5 also show the predictions

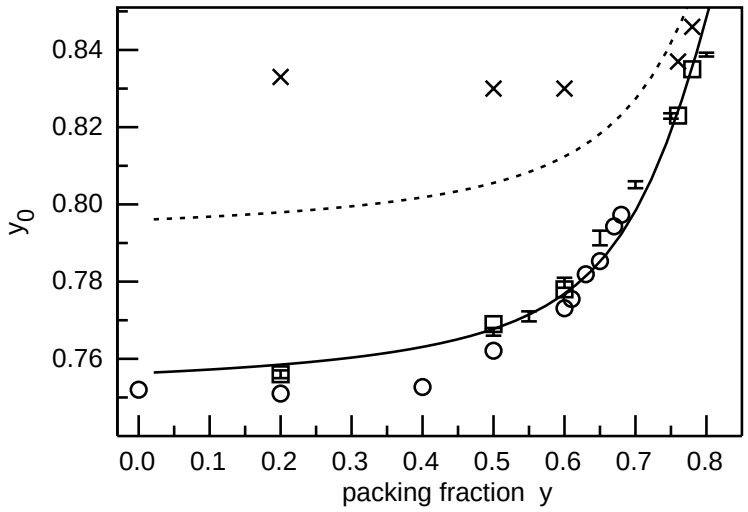

Figure 4. The limiting density of glasses, $y_0(y)$, formed by compressing equilibrated fluid configurations of hard discs from density y. Crosses show results of Mason's method applied to the equimolar mixture of $N = 400$ discs with diameters in the ratio 1.4:1. Points with error bars are from the second method applied to the same mixture with $N = 1600$. The error bars show the standard deviation in $y_0(y)$ for at least four different starting configurations at the same density y. At the highest starting density shown, the mixture is glassy. Squares show results of the third method applied to the mixture of $N = 400$ discs. Circles show results of the second method applied to $N = 400$ ($y = 0$), 1600 and 10 000 monodisperse hard discs. Values of $y_0(y)$ for monodisperse discs are systematically lower than for the mixture. The dashed line shows values predicted for the mixture by equation (2) with $y_m = 0.79$ and $2C/\gamma = 0.019$ [9] and the solid line shows the same equation with y_m adjusted to 0.75.

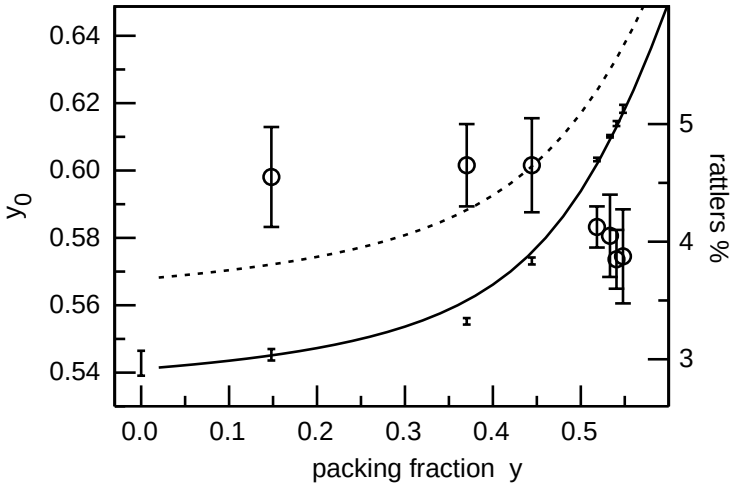

Figure 5. The limiting density of glasses, $y_0(y)$, formed by compressing equilibrated fluid configurations of $N = 4000$ monodisperse hard spheres from density y and the concentration of rattlers (identified by the symbol ○) in the jammed state. Error bars show the standard deviation for compressions from five different starting configurations equilibrated at the same y. The top of the y_0-axis is at $y_0 = 0.6487$, the random-close-packed density for spheres [14]. The dashed line shows values of $y_0(y)$ predicted by equation (2) with $y_m = 0.555$ and $2C/\gamma = 0.029$ [8] and the solid line shows the same equation with the constants adjusted to $y_m = 0.53$ and $2C/\gamma = 0.024$.

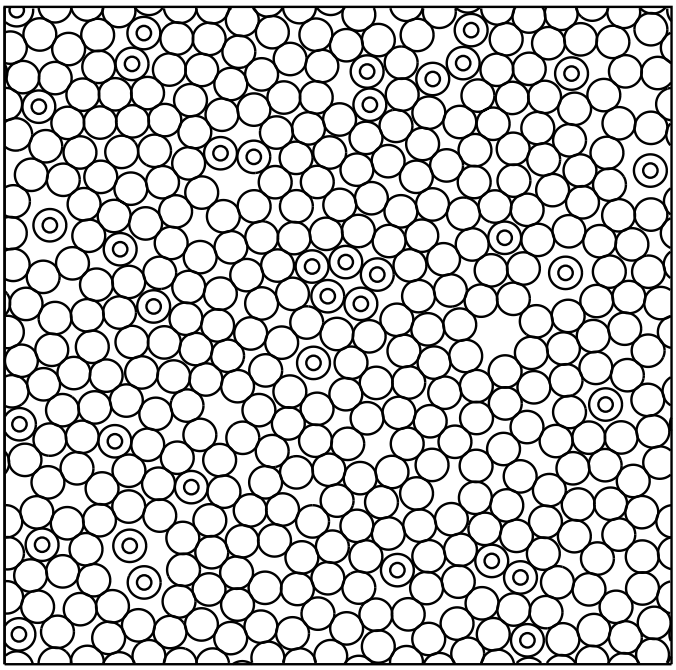

Figure 6. A configuration of 400 monodisperse hard discs made by compressing a fluid configuration from $y = 0.1$ to $y_0 = 0.7450$ using the second method. Discs that make no contacts, with $0.1\%\sigma$ tolerance, are marked with an inner circle. The linewidth is about 3% of a diameter so the appearance of contacts can be misleading.

of equation (2). The limiting densities found here are lower than the predictions but they have the same form.

The structures of low-density packings of discs are shown in figures 6 and 7. A stable packing of discs or spheres may be defined as one that contains a percolating backbone of rigidly jammed particles. Each backbone particle must contact $D + 1$ other backbone particles, with at least one contact on any semicircle (discs) or hemisphere (spheres) of its surface. Loose particles may rattle in cages within the backbone. Counting as rattlers those that have no neighbours within 1.01 diameters, $(6 \pm 1)\%$ of the discs and $(4 \pm 1)\%$ of the spheres are rattlers. The rattler concentration is insensitive to the density, as shown in figure 5, and to the size of the system. Lubachevsky *et al* [17] reported a rattler concentration of 2.3% in a denser ($y_0 = 0.63$) packing of 8000 spheres and Jodrey and Tory [14] found that 4.9% of the spheres had fewer than four neighbours within 1.003 diameters in a packing with $y_0 = 0.645\,68$. Thus there is no indication that an 'ideal glass with no rattlers' is approached as y_0 increases towards the 'random-close-packed' density $y_0 = 0.6487$ [14].

The lowest-density jammed packings found had $y_0 = 0.753$ for $N = 1600$ discs (0.739 for $N = 400$), and $y_0 = 0.539$ for $N = 4000$ spheres (0.494 for $N = 32$) seem to be the lowest value yet reported. The high-density limit was not approached because the methods were only applied to equilibrated fluid starting configurations, below the glass transition density.

The number of rattlers scales with N, which means that the jammed states possess a significant configurational entropy, S_c, and this gives some flexibility to the interpretation of equation (1). For instance, the configuration shown in figure 6 might be counted as

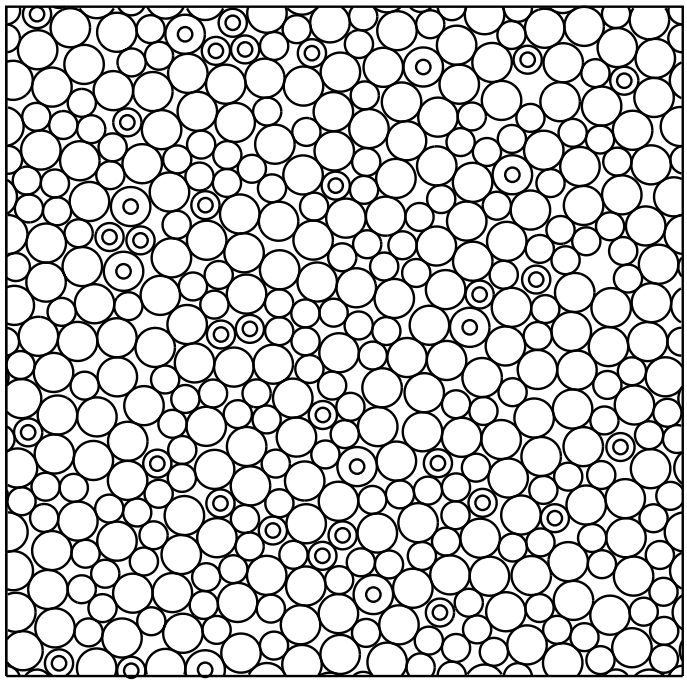

Figure 7. A jammed configuration of an equimolar mixture of $N = 400$ discs with diameters in the ratio 1.4:1. It was made by compressing the fluid from $y = 0.72$ with the second method to $y_0 = 0.8089$. Discs that make no contacts, with $0.1\%\sigma_{ij}$ tolerance, are marked with an inner circle.

$\exp(S_c/k)$ distinct inherent structures, or as one inherent structure which possesses the entropy S_c at its limiting density.

The backbone of the low-density glass of discs, shown in figure 6, contains large pores with 9 to 12 discs on their surface. Some of these pores contain rattlers and others are empty. Larger pores have a smaller surface curvature and when three of the surface disks are nearly linear a very small displacement of one disk, such that it passes between two of its containing discs into the pore space, allows the pore to collapse inwards, unjamming the surrounding backbone. This probably explains why Mason's method produces much denser states and why low-density glasses of discs or spheres, that can be formed by rapid compression in molecular dynamics experiments [8, 9, 15, 18], are unstable and quickly relax to denser states.

The radial distribution functions for the jammed states are similar to those shown for discs by Hinrichsen *et al* [20] and for spheres by Lubachevsky *et al* [17]. They have a very sharp peak at the contact distance but no other sharp peaks and no sign of long-range order.

Figure 8 shows that the equation of state of the fluids [8, 9, 21] can be approximated by

$$pV/NkT = 1 + C_D y/(y_0(y) - y) \tag{3}$$

where C_D depends on the spatial dimension D. Equation (3) is exact for hard rods at all densities with $C_1 = 1$ and $y_0(y) = 1$. For discs and spheres, using the measured values of y_0, the value of C_D is constant to within about 10% from the ideal gas to the glass

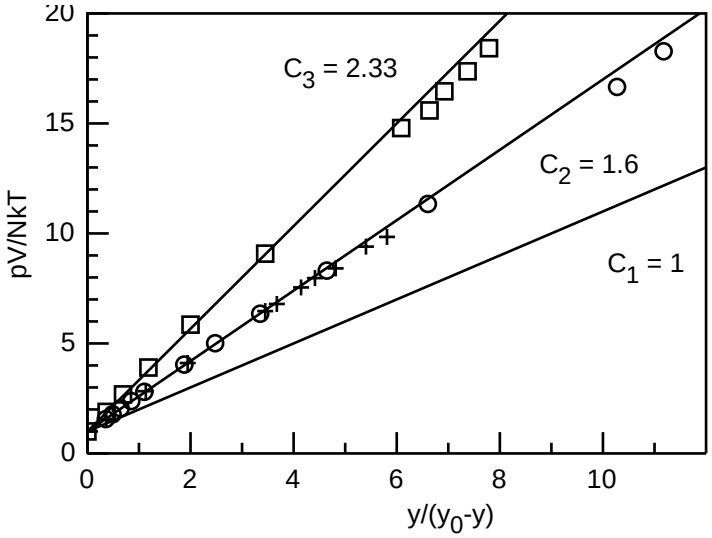

Figure 8. The pressure, pV/NkT, for hard rods, discs and spheres plotted against $y/(y_0 - y)$. C_D, where D is the spatial dimension, is the slope of the lines shown. Crosses: pure discs; circles: the disc mixture; squares: pure spheres.

transition; however, the values of C_D are lower than values obtained by fitting the pressure of glasses to equation (3). The assumption that C_D is constant [8, 9] is clearly too simple.

4. Conclusions

The main goal was to verify the existence of the low-density inherent structures of hard discs and spheres that are suggested by analyses [8, 9] of the thermodynamic properties of the fluids and glasses in terms of equation (1). These glasses have eluded detection in molecular dynamics experiments because they relax quickly to denser structures, but they need to be included in any comprehensive description of the fluids and glasses in terms of inherent structures.

The results are relevant to realistic systems because the inherent structures of hard discs or spheres are also inherent structures (potential energy minima) of soft discs or spheres [5] that interact with a repulsive potential that varies as $(\sigma/r)^n$. Each particle in the packings formed by the second or third methods is contained in a cage of its $D + 1$ neighbours, and they are equidistant from it, so any small displacement of a particle moves it closer to a neighbour and increases the potential energy.

The methods used here suggest that there may be a way to define a network of bonds connecting each particle to a few others that always contain it, in such a way that the topology of this network is invariant during the compression and is the same for all states that compress to the same inherent structure. If the appropriate rules are found, the assignment of a configuration to its inherent structure could then be made without doing the compression. The same rules could then be applied as constraints [22] in a simulation, providing a way to extend the entropy measurements on glasses to low densities, or, equivalently, to measure the q_k in equation (1).

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