Effect of particle shape on the random packing density of amorphous solids

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The packing density of a particulate solid strongly depends on the shape of the particles that are jammed at random close packing (RCP). To investigate the effect of particle shape on the RCP density of an amorphous solid, we studied jammed packings of binary mixtures of a-thermal or granular spherocylinders by means of mechanical contraction computer simulations. We showed that the packing density of a jammed solid can be optimized by using slightly elongated particles. Starting from the Bernal random sphere packing, the RCP density first raises to a maximum for nearly spherical rod-like particles and only beyond this maximum it monotonically decreases with the particle aspect ratio. We demonstrated that the density maximum appears not only for monodisperse systems but it is a universal feature of mixtures of randomly packed non-spherical particles. The position of the density maximum is also universal – the optimal packing is found when one of the components in the binary mixture has the unique particle aspect ratio 0.5, irrespectively of the mixture composition. In the limit of large particle size disparity in a bidisperse jammed system, we revealed a universal scaling for the total packing density as a function of the aspect ratio of one component, regardless of the shape of the second component.

1 Introduction The properties of amorphous materials such as powders, reinforced polymer composites, granular matter and glasses are determined by random packing of the particles [1–12]. When the particles are jammed at random close packing (RCP) the material becomes solid [13]. The corresponding jamming transition strongly depends on the size distribution and shape of the particles in the mixture. The RCP density of equally-sized spheres was found to be around 0.64 [14]. This Bernal sphere packing is scale-invariant and was observed in various experiments and computer simulation studies [15, 16]. Jamming of monodisperse non-spherical particles is more complicated due the additional rotational degrees of freedom of the particles. The RCP of rod-like particles exhibits an intriguing non-monotonic dependence of the packing density on the particle elongation [17, 18]. Nearly spherical rods pack denser than spheres, forming a packing density maximum at the particle aspect ratio 0.5. Further particle elongation results in expected decrease in packing volume fraction because of the growth of the orientationally averaged excluded volume. In our previous studies we discovered that the density maximum is also present in randomly packed rod–sphere mixtures, hinting at universality in optimal packing of non-spherical particles and their mixtures [19, 20]. The obtained density maximum may provide a new route to design amorphous solids with optimal particle packing by introducing non-spherical particles of different sizes and shapes. It is therefore a fundamentally interesting and practically important question whether this maximum can be observed and finely tuned in more complex polydisperse systems of non-spheres.
Here, we investigate random packing of jammed solids made of a binary mixture of spherocylinders with different aspect ratios. We perform mechanical contraction method (MCM) computer simulations of athermal spherocylinders upon isostatic compaction for a specific mixture composition. The chosen binary systems of spherocylinders allow us to study the random packing of pure spheres, pure rods and rod–sphere mixtures as limiting cases. The effect of the shape of either component in a rod–rod mixture on the random packing density is distinguished for both slightly and moderately elongated rods. We reveal the presence of a density maximum for nearly spherical spherocylinders in the rod–rod mixtures. The location of the maxima is universal and it coincides with its position for pure rods and rod–sphere mixtures for the rod aspect ratio 0.5. The rod–rod binary systems that contain moderately elongated rods exhibit a universal scaling in the limit of large size disparity of the two components in the mixture. In particular, the total packing fraction depends only on the aspect ratio of the bigger rods and not on the shape of the small ones.

2 Simulation method

We perform the MCM computer simulations to create a jammed random packing of granular particles [17, 19]. The MCM algorithm is extended to particles of different sizes and shapes and their mixtures. We consider the RCP of bidisperse mixtures of hard frictionless rods (spherocylinders) that contain \( N = 5000 \) particles in total. Initially, a dilute random arrangement of non-overlapping particles is prepared in a cubic simulation box with periodic boundary conditions. Then, the particulate system is quenched by an iterative process of its isotropic contraction. When the particles start overlapping, the overlap is removed by moving (translating and rotating) the particles within the box. The final state is an amorphous jammed structure at RCP with a reproducible packing density and neither crystalline nor liquid crystalline order (see Fig. 1). The absence of any long-range order is clearly seen from visual inspection of the obtained packing structures, which can also be indicated by essentially zero values of both bond-orientational and nematic order parameters for all studied jammed packings (not shown here).

3 Results and discussion

The influence of the particle shape on the packing density of binary mixtures of spherocylindrical particles can be seen from Fig. 2. In Fig. 2 the total packing fraction is plotted versus the aspect ratio \( L_i/D_i \) of one component for various aspect ratios \( L_2/D_2 \) of the second component, where \( L_i \) and \( D_i \) are the length and diameter of the \( i \)-th component, respectively. For simplicity we have chosen one specific mixture composition, namely the relative volume fraction of the first component \( x_1 = \phi_1/(\phi_1 + \phi_2) = 0.5 \), where \( \phi_i \) is the volume fraction of the species (spherocylinders) \( i \). A general trend for all the packing curves is the appearance of the packing density maximum at \( L_1/D_1 = 0.5 \), irrespectively of the elongation \( L_2/D_2 \) of the second component. The density maximum is a result of the competition between the local caging and excluded volume effects. Upon particle elongation from spherical shape the packing density first raises due to a more efficient particle orientation within the cage formed by its neighbors. However, a further increase in the particle aspect ratio causes decrease in the density, which originates from the dominant effect of the excluded volume interactions. The orientationally averaged excluded volume monotonically decreases with the rod aspect ratio. The balance of these two effects results in the density maximum for slightly elongated, nearly spherical rods at \( L/D = 0.5 \).

From Fig. 2 we can conclude that the proposed mechanism of jamming of monodisperse non-spherical particles, which comprise the competing local caging and excluded volume effects, is also valid for mixtures of anisometric particles. An intriguing observation is that these two effects lead to the density maxima located at a unique rod aspect ratio 0.5 for any binary mixture, regardless of the shape of the second component. In other words, monodisperse rods as well as binary rod–sphere and rod–rod mixtures exhibit a universal optimal packing for one specific rod elongation. The absolute maximum \( \phi = 0.703 \) is found for a jammed solid made of monodisperse rods of the aspect ratio 0.5.

Another interesting observation is that the packing curves of rod–rod mixtures do not intersect at one rod aspect ratio, contrary to the mixtures of rods and spheres (Fig. 2). The combined jammed packings of rods and spheres produce the packing density that is equal to the Bernal sphere packing density at the rod aspect ratio \( L/D = 3 \) for all mixture...
The rod aspect ratio mixture by rods of that aspect ratio and obtain an amorphous observation is that one can replace spheres in a rod–sphere packing density. The practical implementation of this packing of the rods in this case produces the same Bernal packing density maxima at the rod aspect ratio 0.5. The horizontal dashed line depicts the Bernal sphere packing density of the packing density maxima at the rod aspect ratio 0.5. The mixture composition (the relative volume fraction of the first component) is $x_1 = \phi_1/(\phi_1 + \phi_s)$ = const the packing fraction $\phi$ of the larger component does not change upon addition of the small particles due to the decoupling of the length scales. Therefore, the packing fraction of the small component $\phi_s$ and the total packing fraction $\phi = \phi_1 + \phi_s$ are also the same independently of the shape of the small particles. For $L_1/D_1 \approx 10$ this approximation works very well for $L_2/D_2 = 0$, 0.1, and 0.5. For $L_2/D_2 = 1$ one can clearly see a deviation from the found universal scaling and for $L_2/D_2 = 3$ the model fails due to similar sizes of both species in the mixture.

Figure 2 (online colour at: www.pss-a.com) The total packing fraction of binary rod–rod mixtures as a function of the aspect ratio of one mixture component for various aspect ratios of the spherocylinders that comprise the second component. The bottom graph represents the same packing curves, which are enlarged in the region of the packing density maximum for nearly spherical rods having the aspect ratio 0.5. The mixture composition (the relative volume fraction of the first component) is $x_1 = 0.5$ for all studied here binary mixtures. The vertical dashed line indicates the universal position of the packing density maxima at the rod aspect ratio 0.5. The horizontal dashed line depicts the Bernal sphere packing density of $\phi = 0.633$. The thick black line is the packing curve of a system of monodisperse spherocylinders. Compositions [19]. It means that the competing local caging and excluded volume effects balance each other at one unique rod aspect ratio in rod–sphere mixtures. However, if the shape of the second component in the mixture deviates from spherical, then the corresponding packing curves intersect at larger rod aspect ratios $L_1/D_1$, partly breaking the universality of the packing of moderately elongated rods.

Note that the packing curves of the rod–sphere mixture and rod–rod mixture, which contains rods of aspect ratio $L_2/D_2 = 3$, almost coincide before the intersection point (see Fig. 2). The rod aspect ratio $L/\rho = 3$ is special since the packing of the rods in this case produces the same Bernal sphere packing density. The practical implementation of this observation is that one can replace spheres in a rod–sphere mixture by rods of that aspect ratio and obtain an amorphous solid with equal packing density. Beyond the intersection point the corresponding rod–rod system packs much looser than the rod–sphere mixture.

From Fig. 2 one can see that the packing densities of the rod–sphere and rod–rod mixtures of particles with large size disparities $(L_2/D_2 = 0, 0.1, \text{and } 0.5)$ approach some master curve upon increase in rod aspect ratio $L_1/D_1$. This universal scaling can be understood on the basis of the model for random packing of particles with infinite or large size ratio [20]. When the particles are much different in size, the packing of each sub-system is independent and does not geometrically frustrate the packing of the other one. The bigger particles jam and the smaller particles pack in the interstices between the big ones. In this case, for a given relative volume fraction of the large particles $x_1 = \phi_1/(\phi_1 + \phi_s) = \text{const}$ the packing fraction $\phi$ of the larger component does not change upon addition of the small particles due to the decoupling of the length scales. Therefore, the packing fraction of the small component $\phi_s$ and the total packing fraction $\phi = \phi_1 + \phi_s$ are also the same independently of the shape of the small particles. For $L_1/D_1 \approx 10$ this approximation works very well for $L_2/D_2 = 0, 0.1, \text{and } 0.5$. For $L_2/D_2 = 1$ one can clearly see a deviation from the found universal scaling and for $L_2/D_2 = 3$ the model fails due to similar sizes of both species in the mixture.

4 Summary and conclusions We have shown that the shape of the particles has a pronounced effect on the random packing density of amorphous solids. The jammed random packings were computer-generated by using the mechanical contraction numerical simulations. The packing density of the jammed solids composed of a bidisperse mixture of non-spherical particles strongly depends on the particle asphericity and the relative amount of two components in the system. We modeled the rod-like particles as hard spherocylinders that undergo only excluded volume interactions. The spherocylindrical shape of the particles allowed us to investigate not only the packing behavior of rod–rod mixtures but also that of pure spheres, pure rods and rod–sphere mixtures as limiting cases. The jammed binary mixtures of rods showed an existence of the universal packing density maximum for the near-spherical rods. The location of the density maxima is always at one unique rod aspect ratio 0.5 of one component, irrespectively of the shape of the second species in the system. The density maxima result from the competition between the local caging and excluded volume effects, which is the jamming mechanism for both monodisperse and polydisperse non-spheres. Beyond the maximum the packing curves monotonically decrease upon the rod elongation due to the dominant excluded volume effect. Starting from moderately elongated rods this monotonic decrease obeys the universal scaling for the binary mixtures which contain particles with large size disparity. The universal scaling is explained on the basis of the model for bidisperse mixtures of particles with infinite size ratio.
References