The number of capillary bridges in a wet granular medium

Dimitrios Geromichalos, Mika M. Kohonen, Mario Scheel, and Stephan Herminghaus

Applied Physics Lab., Ulm University, Ulm, D-89069, Germany
(Dated: January 20, 2022)

We observed the appearance of capillary bridges in a granular medium consisting of glass beads after adding small amounts of liquid. We found the initial bridge formation depending on the bead roughness. Furthermore we obtained a statistics for the average number of bridges for randomly packed beads in dependence of the liquid content and were able to find an explanation therefore based on recent models and former experimental data.

PACS numbers: 05.65.+b,45.70.-n,45.70.Mg

If one adds a wetting liquid to a granulate, there occur capillary bridges which exert forces on the particles. These forces are the main reason for the strongly changed mechanical properties of wet granular matter compared to the dry case [1, 2, 5, 6, 7, 8]. Despite the notable advance in the comprehension of the dynamical properties of dry granular materials [9, 10], the physical mechanisms, which are the cause for the character of wet systems, remain mostly unknown.

Since the formation of the liquid bridges depends apparently strongly on the microscopic geometry of a granulate, an adequate description of the packing is essential. The random close packing of beads, which is the simplest random packing and which occured in our experiments presented in this paper, is an interesting and challenging topic in itself and has been much studied in the past [11, 12, 13]. It was the goal of our experiments to show how the formation of capillary bridges, which are essential for the mechanics of a wet granular matter [1, 5, 6, 7, 14], depends on the geometrical particle distribution, which was subject of earlier studies [12, 13].

In order to observe and count the single bridges we used an index matching technique [15]. At this we put glass beads with diameters of 375 \( \mu m \) or 555 \( \mu m \), which had a refraction index of 1.51, into a mixture of toluene and diiodomethane with the same refractive index, so that the granular matter became quite transparent and we were able to zoom with the microscope through the glass bead layers and observe the bridges. In order to achieve this index matching the volume share of the toluene was 88.1\% and of the diiodomethane 11.9\%, respectively. This liquid mixture took over the role of "air" in a "normal" wet granular matter. As the wetting liquid, i.e. as liquid which forms the capillary bridges, we added small amounts of water with fluorescein.

The granular matter was put into a cuvette (0.95 \( \times \) 0.95 \( \times \) 4cm, filling height: 2.5 – 3cm) and was shaken in small horizontal circles with an amplitude of 5mm and with a frequency of roughly 30Hz for some minutes, until the "wetting liquid", clearly visible due to fluorescein, appeared homogeneously distributed. The diameter of the glass beads used was 375\( \mu m \) and 555\( \mu m \). In order to prevent crystallization, the small beads were chosen to be slightly polydisperse: the spread in bead size was 10\% for the glass beads with a diameter of 375\( \mu m \) and 1\% [21] for the glass beads with a diameter of 555\( \mu m \). After shaking, the volume fraction of the glass was 0.57, i.e. we found the granulate packed less densely as it would be the case for the loose random packing of 0.60 for the dry case [11]. We could also reach a random dense packing of 0.62, which is the other extreme of the random packing of glass beads and is similar to a volume fraction of the glass of 0.64 \( \approx \) \( \rho_{dp} \) [11], by tapping the sample several times.

After adding very small amounts of liquid, there was no formation of capillary bridges. The reason for this behavior is that the liquid was first trapped on the surface, as it can be seen in Fig. 1a. Only at a water content of 0.07\%, bridges on almost every bead contact were formed (see below). Fig. 1b illustrates the case for fully formed bridges.

It is well known that bridges need a certain amount of liquid content \( W \) to form properly, since the liquid is at first bound on the bead surfaces due to the roughness [3, 4, 17]. The connection between the roughness amplitude \( \delta \) and the saturation bridge volume [22] is given by \( W_0 \approx 2R\delta^2 \), where \( R \) is the bead radius, and \( W_0 \) the volume of a bridge at the water content of saturation \( W_0 \) [3]. Our measurements [18] suggest that the relationship between the water content \( W \) and the volume of a single bridge \( w \) is generally given by \( w = \alpha r^3 W \), where \( \alpha \approx 0.25 \) [5].

From \( W_0 \approx 0.07\% \) we get \( \delta \approx 500nm \), which is similar to the peak-to-peak roughness we found from the inspection of the beads by atomic force microscopy.

We obtained the average number of bridges per bead by zooming with the microscope through the sample and counting the bridges. We carried this out for different liquid contents for the random loose packing which was in our case 0.57 as well as for the random dense packing of 0.62. In order to reach better statistics we counted the bridges of 40 beads for each data point for the dense packing and 20 beads for the loose packing and calculated the average bridge number \( N \). We took the standard deviation as error for \( N \). Since we counted only bridges from beads of the second to the sixth layer, an estimation of the influence of the sample boundary is necessary. Therefore we measured \( N \) for different layers \( L \). We found that

*Electronic address: Dimitrios.Geromichalos@physik.uni-ulm.de
N(L) = const for 3 ≤ L ≤ 6, whereas for L ≤ 2 small variations were observed. We believe therefore that we can exclude any effect of the sample boundary on N.

The dependence of N on the water content is shown in Fig. 2. N is equal to zero for very small W. At a water content slightly smaller than W_b it goes up very fast, then the curve becomes flatter. It can be seen further, that N(W) for the random dense packing is about 10% larger than N(W) for the random loose packing.

As it was mentioned earlier, the number of capillary bridges is influenced strongly by the microscopic geometrical properties of the granular medium. A model which deals with the number of contacts of randomly packed glass beads is the caging model [13]. According to this model one needs 4.79 =: N_{dc} bead contacts on average in order to pin a bead with other beads. We assumed that this model provides at least roughly an appropriate explanation for our experiments and have defined W_b accordingly. Consequently W_b is the water content at which a capillary bridge exists then and only then, if two beads touch, i.e. if their surface distance d is zero. The smaller non-zero values at W < W_b can be explained as follows. The water film on the beads varies in thickness at different areas of the bead surface. Therefore it is possible at certain water contents that bridge formation occurs only at a fraction of the bead contacts. On the other hand, for W > W_b there can also occur slightly "stretched" bridges between beads which do not touch, but which are close enough to each other (see below).

Our assumption that the caging model is appropriate for our case is confirmed further if we compare the measured distribution of the capillary bridges at water contents W ≈ W_b for the random loose packing to the distribution obtained by a simulation [13] based on the caging model. As it can be seen in Fig. 3, the measured curve is very similar to the simulated one. Particularly the measured curve does not exceed the value of 8, i.e. it fulfills a necessary condition for the validity of the caging model [13]. At higher water contents the histogram curve is shifted to the right, but we did never see a glass bead with more than 9 capillary bridges [23].

We will compare now our measurements concerning the dependence of the number of capillary bridges on W to the measured distance distribution of beads in a random close packing [12]. For W ≥ W_b there exists at least at every bead contact (i.e. at every point with d = 0, where d is the surface distance of the beads) a capillary bridge: N ≥ N_c. N_c is here the number of real contacts per bead. According to the caging model we have N_{dc} = 4.79. Bridges can also exist between beads which do not touch, but which are only sufficient close to each other. Due to the hysteretic nature of bridge formation [19], it is reasonable to suppose that such bridges can form only between beads which collided in the past and then moved away from each other. For sufficient strong shaking this should be statistically the case for a certain part A* of the beads, i.e.

\[ N(W) = N_c + A^* N_b(W) \]
In accordance to our own measurements \[24\], we have approximately given by the bridge rupture distance \(d\), measured \(R\) where

\[ d \approx \frac{N(W) - N_c}{A^*}. \]

Here \(N_b\) is the number of nearest neighbors, which do not touch the bead, but whose distance \(d\) is smaller than the bridge rupture distance \(d_p\). The total number of neighbors in between a distance \(d_p\) is

\[ N_t(W) = N_c + N_b(W) = N_c + \frac{N(W) - N_c}{A^*}. \]

Herewith we get

\[ N(W) = A^* N_t(W) + (1 - A^*) N_c \]

We need now to correlate the water content \(W\) to rupture distance \(d_p\). According to \[21\] this correlation is approximately given by

\[ d_p = w^+ + \frac{1}{10} \frac{w^2}{R} \]

where \(R\) is the bead radius and \(w\) the bridge volume. In accordance to our own measurements \[21\], we have \(w = \alpha R^3 W\) with \(\alpha \approx \frac{1}{4}\). Therefore

\[ d_p = R \left( (\alpha W)^+ + \frac{1}{10} (\alpha W)^2 \right). \]

Now it is possible to calculate \(N\) from the measurements of \(N_t\) \[12\], plot it over \(d_p\) and compare it with the directly measured number of capillary bridges. Before doing this we defined \(W^* := W - W_b\), i.e. the water content above \(W_b\) which is located in the bridges. The reason therefore is that the glass bead surface absorbs a certain amount of liquid \(W_b\) before bridge formation starts. Accordingly we defined \(d_p^* := d_p(W^*)\) as corresponding rupture distance.

In order to get a quantitative expression the values of \(A^*\) one has to consider the mechanism of bridge formation. A bridge between two non-touching beads can only exist if their distance is smaller than \(d_p\) if this beads touched each other in the past. Therefore one would expect \(A^* = \frac{1}{2}\) for a one-dimensional system with statistically moving particles. In a real granulate the situation is more complicated. It is possible that particles move against each other by a distance smaller than \(d_p\) without ever touching, which leads to a decrease of the value of \(A^*\).

In order to obtain an estimation for \(A^*\) we considered a single bead with radius \(R\) in the point of origin. Then we assumed other beads with radius \(R\) moving by at an impact parameter \(p^*\) which was chosen at random. It is evident that bridges can only form if \(0 \leq p^* \leq 2 R\), i.e. a bead collision is a necessary condition for bridge formation. If the moving bead moves along the x-axis, the distance between the surfaces is given by \(d = \sqrt{x^2 + p^2} - 2 R\). At a certain point of time a bridge can only exist if \(d \leq d_p^*\). A further condition for the existence of a bead is that the collision took back in the past which means that only half of the beads with \(0 \leq p^* \leq 2 R\) and \(d \leq d_p^*\) will have a bridge. The arc length of a bead which has a bridge is given by

\[ B_1(p^*) = \int_{x_1}^{x_2} \sqrt{1 + \frac{x^2}{x^2 + p^*^2}} \, dx \]

with \(x_1 = \sqrt{(2 R)^2 - p^*^2}\) and \(x_2 = \sqrt{(d_p^* + 2 R)^2 - p^*^2}\). The arc length of a (bridgeless) bead with \(2 R < p^* \leq 2 R + d_p^*\) and \(d^* \leq d_p^*\) is analogous

\[ B_1(p^*) = \int_{0}^{x_2} \sqrt{1 + \frac{x^2}{x^2 + p^*^2}} \, dx \]
With $I_1 := 2\pi p^* \int_0^{2R} B_1(p^*)dp^*$ and $I_2 := 2\pi p^* \int_{2R}^{d_p^*} B_2(p^*)dp^*$ one finally gets

$$A^*(d_p^*) = \frac{I_1}{2I_1 + I_2}$$

$A^*(d_p^*)$ can be approximated very well as follows:

$$\frac{1}{A(d_p^*/R)} \approx 1.447 \frac{d_p^*}{R^2} + 2$$

Fig. 4 shows the plots of our measured $N$ over $d_p^*$ for the beads with a diameter of 555\,$\mu$m and for the random loose packing and the random dense packing. The drawn curve represents the values of $N$ for the dense packing which were calculated from the literature values of $N_c$ [12] using $A^*$. It is clearly visible that our calculated values lie near to those of the literature for $N_c = 3.3$ for the loose and $N_c = 4.3$ for the dense packing. $N_c$ differs from the $N_c$ of the caging model [13] significantly for the loose packing, while the difference in the dense packing is quite small. Hence the assumption that $N_c$ depends directly on the packing density $\rho_p$ is self-evident. The measured $N_c(\rho_p)$ as well as the theory values are in agreement with the linear curve $N_{dc} = N_c(\rho_p) = 22(\rho_{rdp} - \rho_p)$ (see Fig. 4 (inset)). This plot displays the $N_c$ of the loose as well as the dense packing for the used beads with a diameter of 555 and 375\,$\mu$m. The point of origin corresponds to the $N_{dc}$ of the caging model for the random dense packing $\rho_{rdp}$. Concluding the value of the number of contacts according to the caging model [13] $N_{dc}$ is given by the linear extrapolation of the $N_c(\rho_p)$ obtained from our measurements: $N_{dc} = N_c(\rho_{rdp})$.

The authors thank the German Science Foundation for financial support within the Priority Program ‘Wetting and Structure Formation at Interfaces’. MMK acknowledges the Alexander von Humboldt Foundation for generous funding.

[1] T. Mikami, H. Kamiya, and M. Horio, Chem. Eng. Sci. 53, 1927 (1998).
[2] J. N. Israelachvili, Intermolecular and Surface Forces (Academic, London, GB, 1991), 2nd ed.
[3] D. J. Hornbaker, R. Albert, I. Albert, A.-L. Barabasi, and P. Schiffer, Nature 387, 765 (1997).
[4] T. C. Halsey and A. J. Levine, Phys. Rev. Lett. 80, 3141 (1998).
[5] N. Fraysse, H. Thomé, and L. Petit, Eur. Phys. J. B 11, 615 (1999).
[6] L. Boquet, E. Charlaix, S. Ciliberto, and J. Crassous, Nature 396, 24 (1998).
[7] D. Geromichalos, M. M. Kohonen, F. Mugele, and S. Herminghaus, Phys. Rev. Lett. 90, 168702 (2003).
[8] G. H. Ristow, Pattern Formation in Granular Materials (Springer, Berlin, Germany, 2000).
[9] H. M. Jaeger, S. R. Nagel, and R. P. Behringer, Rev. Mod. Phys. 68, 1259 (1996).
[10] L. P. Kadanoff, Rev. Mod. Phys. 71, 435 (1999).
[11] D. Scott, Nature 188, 908 (1960).
[12] G. Mason, Nature 217, 733 (1968).
[13] E. A. J. F. Peters, M. Kollmann, T. M. A. O. M. Barenbrug, and A. P. Philipse, Phys. Rev. E 63, 021404 (2001).
[14] C. Feng and A. B. Yu, Journal of Colloid and Interface Science 231, 136 (2000).
[15] S. J. R. Simons, J. P. K. Seville, and M. J. Adams, Sixth International Symposium on Agglomeration, Nagoya, Japan p. 117 (1993).
[16] N. Jain, D. V. Khaklar, R. M. Lueptow, and J. M. Ottino, Phys. Rev. Lett. 86, 3771 (2001).
[17] C. D. Willett, M. J. Adams, S. A. Johnson, and J. P. K. Seville, Langmuir 16, 9396 (2000).
[18] M. M. Kohonen, D. Geromichalos, and S. Herminghaus, manuscript in preparation (2003).
[19] L. Zitzler, S. Herminghaus, and F. Mugele, Phys. Rev. B 66, 155436 (2002).
[20] C. D. Willett, M. J. Adams, S. A. Johnson, and J. P. K. Seville, Langmuir 16, 9396 (2000).
[21] Although a spread of only 1\% can lead to a crystallization of the granulate, it has not always to be the case. In our experiments presented in this paper we observed no crystallization.
[22] The reason for calling $w_b$ saturation bridge volume comes from the Halsey-Levine theory. According to this modell, the force exerted by bridges with a volume $w > w_b$ does no longer increase significantly with $w$. [4]
[23] At very high liquid contents ($W \geq 3\%$) there form liquid clusters between the beads, so that the bridge concept is no longer valid.
[24] M. M. Kohonen, D. Geromichalos, and S. Herminghaus; to be published.