Mechanisms of dissipation in wet granular matter

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(Dated: February 5, 2008)

The impact dynamics between wet surfaces, which dominates the mechanical properties of wet granular matter, is studied both experimentally and theoretically. It is shown that the hysteretic formation and rupture of liquid capillary bridges between adjacent grains accounts reasonably well for most relevant cases of wet granular matter. The various dissipation mechanisms are discussed with particular emphasis on their relevance. Variations of the rupture energy loss with the impact energy are quantified and discussed.

PACS numbers: 47.57.Gc; 68.08.Bc; 83.80.Fg

The interest in granular materials among the soft-matter community has been strongly increasing in recent years. It has been widely recognized that many concepts which are well established for colloidal systems and glasses apply as well to granular systems, and vice versa. Furthermore, both colloidal and granular matter play a certain role as models for other systems which are too complex to be tractable. In particular, granular systems are of great interest in the context of dynamical systems far from thermal equilibrium.

The term ‘soft matter’ applies particularly well to wet granulates, which can be shaped to stable structures but yield to rather small shear stress, and vice versa. The plasticity stands out against dry granulates, such as the sand in an hour glass, which runs through the orifice like a fluid. The reason for this difference is that in the wet system, small liquid capillary bridges form between adjacent grains, exerting an attractive force upon them by means of the surface tension of the liquid. It is clear that these only form when the liquid wets the material the grains consist of, which is well fulfilled for most sands. When a wet granulate is being sheared, or otherwise mechanically agitated, the repeated formation and rupture of the many liquid objects inside gives rise to considerable dissipation, which is then experienced as a noticeable resistance to the external drive imposed on the material. In order to understand the mechanical properties of wet granular matter, it is thus indispensable to understand the dissipation processes connected to the liquid capillary bridges in detail.

As it is well known, there is some intrinsic dissipation also in dry granular matter, which is responsible for the fact that even the perfectly dry granulate in the hourglass behaves distinctly different from a regular fluid. Some fraction of the kinetic energy of the grains is transferred at each impact to the microscopic degrees of freedom on atomic scale. The ‘heat bath’ represented by the random center-of-mass motion of the grains, which easily corresponds to Giga- or even Tera-Kelvins when converted to temperature using Boltzmann’s constant, is thus intimately coupled to the room-temperature heat bath of the atoms. Some of the most striking features of granular motion owe to this intrinsic non-equilibrium character. One usually quantifies these effects by means of the so-called restitution coefficient, ε, which is defined as the ratio of the momenta before and after the impact, \( p_f = \varepsilon p_i \). It is found that this ratio is fairly independent of the initial kinetic energy of the grains in a wide range, although for large energies it tends to be somewhat smaller. The most important aspect of this dissipation mechanism is that the energy lost in the impacts, \( \Delta E_{dry} \), scales with the impact energy, \( E \), according to

\[
\Delta E_{dry} = (1 - \varepsilon^2) E
\]

where \( \varepsilon \) is approximately constant. There is thus no specific energy scale set by this process.

On the contrary, the liquid capillary bridges which are present in a wet granulate do provide their own energy scale. This is due to their characteristic dynamics of bridge formation and rupture. When two wet grains approach each other, the liquid adsorbed on their surface will not react until they come into contact. At this point, liquid is rapidly dragged to the area of contact due to the interfacial forces, and a capillary bridge forms. When the grains withdraw from each other after the impact, the bridge remains intact for quite some distance, exerting an attractive force upon the grains. This is illustrated in Fig. 1 for the idealized case of spherical grains. The angle \( \theta \) is the contact angle the liquid makes with the grain material, and characterizes its wetting properties. For complete wetting, we have \( \theta = 0 \). At a certain critical separation of the grain surfaces, which depends upon the liquid volume of the capillary bridge, the latter ruptures and distributes its liquid content back onto the grain surfaces. If \( V = V/R^3 \) is the normalized liquid volume of a bridge between spherical grains of radius \( R \), and \( \tilde{s} = s/R \) is the normalized separation of the grain surfaces, rupture occurs at

\[
\tilde{s}_c = \left(1 + \frac{\theta}{2}\right)
\left(V^{1/3} + 0.1\tilde{V}^{2/3}\right)
\]

in good approximation.
A typical force-vs-distance curve is shown schematically in Fig. 1b. The force is normalized with respect to the contact force, 2πγRcosθ.

For spherical grains, the shape of this curve is well known in the quasi-static case [22]. It corresponds to the force exerted by a rotationally symmetric minimal surface spanned between the spheres, where the liquid volume of the bridge and the contact angle are the main geometric parameters. A good approximation is

\[ F = \frac{F_0}{1 + 1.05S + 2.5S^2} \]  

where \( S = \tilde{s}/\sqrt{V} \) [22]. This is in fact the curve displayed in Fig. 1b. It terminates at \( S_c = \tilde{s}_c/\sqrt{V} \) as given by eq. (2). Using this approximation, we can evaluate the integral and obtain

\[ \Delta E_{\text{cap}} = 0.67 F_0 R \sqrt{V} \arctan (0.35 + 1.68S_c) \]  

for complete wetting (\( \theta = 0 \)). \( S_c \) is at least of order unity, such that \( \arctan(\ldots) \approx 1.1 \) or larger, and it never goes beyond 1.57. Hence a reasonable approximation is

\[ \Delta E_{\text{cap}} \approx F_0 R \sqrt{V} \]  

Given the fact that we have neglected side effects such as contact angle hysteresis, this should be as good as it gets.

The presence of a defined energy loss, which does not scale with the impact energies of the colliding grains, has dramatic consequences for the collective physical properties of the system. Most prominently, it leads to phase transitions which occur when the granular temperature is comparable to the energy loss [12, 23, 24, 25]. It is illustrative to express the fixed energy loss in terms of an energy-dependent restitution coefficient. We readily obtain

\[ \varepsilon_{\text{cap}} = \sqrt{1 - \frac{\Delta E_{\text{cap}}}{E}} \]  

where \( \Delta E_{\text{cap}} \) is constant. Obviously, \( \varepsilon \) becomes zero when \( E = \Delta E_{\text{cap}} \). As a consequence, an energy-driven phase transition occurs when the granular temperature comes close to \( \Delta E_{\text{cap}} \) [25]. This is not the case in a dry system described by a constant restitution coefficient.

If the impact dynamics is sufficiently slow as compared to the dynamics of bridge formation and rupture, we may assume that the dynamic force-vs-distance curve corresponds to the quasi-static case, as represented by eq. (4). However, when we consider dynamical processes, as they take place in a sheared or otherwise agitated wet granular material, we have to discuss the influence of this dynamics on \( \Delta E_{\text{cap}} \).

In doing so, we will also have to consider the energy loss due to viscous damping in the liquid. In reasonable approximation, the viscous force is given by [26]

\[ F_{\text{visc}} = \frac{3\pi}{2} R^2 \eta \frac{v}{s} \]  

for spherical grains, where \( \eta \) is the viscosity of the liquid and \( v \) is the relative velocity of the grains at impact. If viscous forces are dominant, the equation of motion during withdrawal reads \( F_{\text{visc}} = -m \dot{s} \), with the grain mass \( m \), and the dot indicating the derivative with respect to time. Direct integration leads to

\[ \Delta E_{\text{visc}} = mv_0 \int_\delta^{s_c} \dot{s} \, ds = \frac{1}{2} m v_0^2 \ln \frac{s_c}{\delta} \left( \frac{v}{v_0} - \ln \frac{s_c}{\delta} \right) \]  

where \( v_0 \) denotes the velocity directly after the impact and \( \delta \) is a cutoff parameter, which may be identified with the roughness of the grains [12]. \( v_0 = 9\eta/8\mu R \) is
a characteristic velocity, where $\rho$ is the density of the grain material. If $v = v_0 \ln \frac{v}{s_c}$, the grains stick together in the sense that their kinetic energy is not sufficient to supply the viscous energy required for reaching the rupture distance, $s_c$, even at zero surface tension. If $v$ is considerably larger, one obtains the known result \[\Delta E_{\text{visc}} \approx \frac{3\pi}{2} R^2 \eta v \ln \frac{s_c}{\delta} \] (10)

Eq. (9) may as well be expressed in terms of an energy-dependent restitution coefficient as

\[\varepsilon_{\text{visc}} = 1 - \sqrt{\frac{E_0}{E}} \] (11)

where $E_0 = \frac{m}{2} [v_0 \ln(s_c/\delta)]^2$ is the impact energy below which sticking occurs. We see from eqs. (7) and (11) that there are great similarities between the capillary and the viscous effects, and both strongly differ from the scale-free energy loss encountered with the dry systems.

In order to investigate to what extent the concepts discussed above apply under realistic conditions, we have performed an experiment particularly designed to map the conditions in agitated wet granular matter as closely as possible. As model grains, we have used spherical glass beads with $R = 1$ mm. These fell freely in a closed box containing humid air onto a wet glass plate. Initial heights were about 2 cm, such that the impact velocities were on the order of a few cm/sec, which corresponds to typical granular temperatures in agitated granulates. The motion of the glass spheres was recorded with a fast CCD camera, the images were subsequently analyzed by standard image processing techniques.

Since all arguments put forward above concerning forces between two spherical grains apply as well to forces between a sphere and a flat wall, we have studied the latter because of its better experimental accessibility. We just have to keep in mind that in formulas developed for two spherical grains, the radius of the sphere must be multiplied by two. This corresponds to the well-known Derjaguin approximation, $R_{\text{eff}}^{-1} = (R_1^{-1} + R_2^{-1})/2$. Although this is not an accurate expression for the system under study \[22\], it provides a reasonable approximation since other effects, like contact angle hysteresis, give rise to larger uncertainties \[12\].

The result is shown in Fig. 2. The height of a bouncing glass sphere is plotted as a function of time (circles). On the same time scale, the total energy as obtained from the instantaneous velocity and height is indicated by the black squares. While there is some scattering in the vicinity of the impacts, mostly due to the finite delay between consecutive images, the energy is observed to be constant with high accuracy away from the impacts, allowing for an accurate determination of the energy level of each bounce.

Below the main panel, we show three consecutive closeup images in the ultimate temporal vicinity of an impact with the glass plate. The time elapsed between the images is 2.04 ms. The hysteretic character of the capillary bridge is clearly visible from its absence before the impact (left) and its persistence afterwards (right). From the difference in the energy levels of consecutive bounces, we can deduce the energy lost in the impact with the glass plate. For a quantitative analysis, we have to consider as well the energy loss due to viscous friction in the air, $\Delta E_{\text{air}}$. Using Stokes’ formula, it is straightforward to see that

\[\Delta E_{\text{air}} \approx 4\pi R \bar{\eta} g \left(\frac{2E}{m}\right)^{3/2} \] (12)

where $\bar{\eta}$ is the viscosity of air. This is valid at low Reynolds numbers. We have $Re \approx \sqrt{v/v_0} \approx \sqrt{H/15.6\mu m}$, where $H$ is the height of the bounce, such that $Re$ reaches values around 30 in our experiment. Since turbulence sets in only at much higher $Re$ \[27\], we can safely assume eq. (12) to describe our system well.

The most convenient way of analyzing the data is to
plot the energy of each bounce as a function of the energy of the previous one. Taking all dissipation mechanisms into account, we obtain

$$E_{n+1} = \varepsilon^2 E_n - \Delta E_{\text{cap}} - \Delta E_{\text{visc}} - \Delta E_{\text{air}}$$  \hspace{1cm} (13)$$

where \(n\) numbers the bounces, and the last two terms depend upon \(E_n\). The result is displayed in Fig. 3a. The full squares represent the results for \(E_{n+1}\) as obtained from the experiment, while the open circles have been corrected for \(\Delta E_{\text{air}}\) according to eq. (12), which is known without any free parameters. As one can clearly see, the correction is of minor importance, as is suggested already by the energy data from the trajectories in Fig. 2a. From eq. (10), we see that the viscous energy loss in the liquid is of order \(mv_0v\), which is readily checked to be below 3 nJ in our experiments. It is thus even smaller than the viscous dissipation in the air, and will henceforth be neglected. The experimental error of the results displayed in Fig. 3a is well below the size of the symbols.

The three data points for the largest energies lie on a straight line within errors. From the slope of this line, we obtain the restitution coefficient connected to the solid impact of the glass sphere with the bottom plate. The result is \(\varepsilon = 0.82 \pm 0.02\). Interpreting the intercept with the vertical axis as the capillary bridge energy, we obtain \(\Delta E_{\text{cap}} = 0.07 \pm 0.02 \mu\text{J}\). However, this intercept can be determined in principle for each pair of consecutive energy levels, \(E_n\). The corresponding results for \(\Delta E_{\text{cap}}\) are shown in the inset of Fig. 3a as a function of the incident energy. The deviation of the datum point at lowest energy from the straight line in the main panel transforms into a pronounced increase of \(\Delta E_{\text{cap}}\) at low energy.

From the few times at which we could capture the formation of a bridge with the camera, we could estimate the bridge volume assuming an axisymmetric shape. For the bridge at the slowest impact, we obtained \(V = 0.25 \pm 0.06\) for the dimensionless volume. Together with eq. (3) this leads to \(\Delta E_{\text{cap}} = 0.214 \pm 0.056 \mu\text{J}\), where we have assumed complete wetting (\(\theta = 0\)). This result is indicated by the shaded area in the inset of Fig. 3a and compares very favorably with the experimental value obtained at low impact energy.

The reduction of \(\Delta E_{\text{cap}}\) at larger impact energies may be understood when one considers the dynamics of formation of the bridge. There is some time needed for the liquid to rearrange from the thick wetting layer around the impact point to the thin liquid capillary bridge structure. The entire process spans several time scales, starting from the microsecond range at individual asperities of the grain roughness to ripening processes on the scale of minutes. Consequently, although the impact duration of the glass sphere with the bottom is sufficient to form a small bridge, the volume of the latter will be larger when it has more time to form. The characteristic time scale of the early stage of bridge formation can be estimated from the typical height of the bridge at contact, which is \(h/h = h/R \approx \sqrt{V/2\pi} \approx 0.2\). Knowing that viscous damping is of minor importance, we consider the dispersion relation of undamped capillary waves, \(\omega^2 = \gamma q^3/\rho_{\text{liq}}\). With \(q \approx 1/h\) we obtain the time scale \(\tau = 1/\omega \approx 3.3 \times 10^{-4} \text{ sec}\). It is straightforward to calculate the kinetic impact energy \(E_\tau\) at which the solid surfaces are closer than \(h\) for a duration equal to \(\tau\). We obtain

$$E_\tau = \frac{8\pi R^2 \gamma \rho}{3h \rho_{\text{liq}}} \approx 780n\text{J}$$  \hspace{1cm} (14)$$

which is of the same order as the transition seen in the inset of Fig. 3a.
However, the dynamics not only of bridge formation, but also of bridge rupture gives rise to variations in $\Delta E_{\text{cap}}$. If the solid surfaces withdraw rapidly, the formation of the extended neck will be impeded and the bridge is expected to pinch off at a separation which is smaller than the ‘quasi-static’ $s_c$. This reduces the upper limit of the integral in eq. (3), and thus the value of $\Delta E_{\text{cap}}$. By measuring the bridge volumes for different impacts independently, we can distinguish these two effects. This is shown in Fig. 3b, where $\Delta E_{\text{cap}}$ is plotted as a function of the bridge volume, as determined from images close to the respective impacts. The solid line represents eq. (6) and has no fitting parameters. Good agreement is found for the larger bridge volume, which corresponds to the leftmost point in the inset of Fig. 3a. At smaller volume, $\Delta E_{\text{cap}}$ is indeed reduced, but this reduction is much stronger than predicted by the solid line, which represents the quasi-equilibrium shapes.

If we finally return to the conversion of the energy loss into an energy-dependent restitution coefficient, we see that the variations in $\Delta E_{\text{cap}}$ will cause $\varepsilon(E)$ to decrease even stronger with decreasing impact energy than suggested by eq. (7). This stresses again the qualitative differences to the dry systems, where $\varepsilon(E)$ tends to be decreasing with increasing impact energy. When one looks at the results in the main panel of Fig. 3a, one might not anticipate that the small negative intercept with the vertical axis should be of any importance for the collective behavior of many spheres. Quite surprisingly, the dramatic mechanical differences between dry and wet sand show that this is nevertheless the case.

Acknowledgements

Inspiring discussions with Jürgen Vollmer are gratefully acknowledged.

[1] K. Sela, I. Goldhirsch, Phys. Fluids 9 (1996) 856.
[2] A. Coniglio et al., Physica A 339 (2004) 1.
[3] N. Brilliantov, T. Poeschel, Kinetic Theory of Granular Gases (Oxford Univ. Press, Oxford, UK, 2004).
[4] R.P. Behringer, K.E. Daniels, T. S. Majmudar, and M. Sperl, Fluctuations, Correlations, and Transitions in Granular Materials: Statistical Mechanics for a Non-Conventional System, in Proc. 9th Experimental Chaos Conference (Sao Jose dos Campos, Brazil, 2006).
[5] T. S. Majmudar, M. Sperl, S. Luding, and R. P. Behringer, Phys. Rev. Lett. 98 (2007) 058001.
[6] Y. Nahmad-Molinari and J. C. Ruiz-Suarez, Phys. Rev. Lett. 89 (2002) 264302.
[7] T. Aste, A. Coniglio, Europhys. Lett. 67 (2004) 165.
[8] O. Carvente and J. C. Ruiz-Suarez, Phys. Rev. Lett. 95 (2005) 018001.
[9] A. S. Keys et al., Nature Physics 3 (2007) 260.
[10] K. Feitosa and N. Menon, Phys. Rev. Lett. 92 (2004) 164301.
[11] S. Aumaitre, J. Farango, S. Fauve, and S. McNamara, Eur. Phys. J. B 42 (2004) 255.
[12] S. Herminghaus, Adv. Phys. 54 (2005) 221.
[13] see, for instance: http://www.sandworld.de
[14] D. J. Hornbaker et al., Nature 387 (1997) 765.
[15] T. Mikami, H. Kamiya, M. Horio, Chem. Eng. Sci. 53 (1998) 1927.
[16] L. Bocquet, F. Restagno, and E. Charlaix, Europhys. Lett. 14 (2004) 177.
[17] M. Scheel, D. Gromichalos, S. Herminghaus, J. Phys.: Condens. Matter 16 (2004) S4213.
[18] V. Richefeu, M. S. El Youssoufi, and F. Radjai, Phys. Rev. E 73 (2006) 051304.
[19] J. Duran, Sands, Powders, and Grains (Springer, New York 2000)
[20] G. Lian, C. Thornton, M. J. Adams, Chem. Eng. Sci. 53 (1998) 3381.
[21] S. J. R. Simons, R. J. Fairbrother, Powder Technol. 110 (2000) 44.
[22] Ch. D. Willet et al., Langmuir 16 (2000) 9396.
[23] A. Samadani, A. Kudrolli, Phys. Rev. Lett. 85 (2000) 5102.
[24] D. Geromichalos, M. Kohonen, F. Mugele, and S. Herminghaus, Phys. Rev. Lett. 90 (2003) 168702.
[25] A. Fingerle, K. Roeller, K. Huang, and S. Herminghaus, submitted to Phys. Rev. Lett.
[26] B. J. Ennis, G. Tardos, and R. Pfeffer, Powder Technol. 65 (1991) 257.
[27] A. G. Tomboulides, S. A. Orszag, J. Fluid Mech. 416 (2000) 45.
[28] L. Zitzler, S. Herminghaus, F. Mugele, Phys. Rev. B 66 (2002) 155436.
[29] M. M. Kohonen et al., Physica A 339 (2004) 7.