Liquid-induced transitions in granular media

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We investigate the effect of interstitial liquid on the physical properties of granular media by measuring the angle of repose as a function of the liquid content. The resultant adhesive forces lead to three distinct regimes in the observed behavior as the liquid content is increased: a granular regime in which the grains move individually, a correlated regime in which the grains move in correlated clusters, and a plastic regime in which the grains flow coherently. We discuss these regimes in terms of two proposed theories describing the effects of liquid on the physical properties of granular media. [S1063-651X(99)12311-0]

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Dry granular media are collections of small solid grains which interact primarily through two forces: elastic repulsion and friction. These forces lead to a wide variety of novel interesting dynamic and static physical behavior [1] which have been the subject of much recent interest [2]. The presence of a thin layer of liquid on the grains, however, adds a third interaction to the problem—an attractive force, comparable in magnitude to the other two, which adds a new dimension and complexity to the underlying physics [3–5]. Despite the technological ramifications (many industrial applications involve humid environments or liquid-coated grains), systematic experimental studies of the physical properties of wet granular materials have only been performed in the last two years [6–8].

A granular property which is strongly affected by the addition of liquid is the angle of repose (Θ_R), the characteristic angle exhibited by a granular slope after an avalanche. Recent experiments [6] demonstrated that even a nanometer-scale coating of liquid on millimeter-size grains can result in large changes in Θ_R. The experimental data could be fit by a theory based on the stability of grains on the top surface [3], but an alternative theory [4] based on bulk stability arguments was also proposed by Halsey and Levine. An important difference between these two models is that the former predicts Θ_R to depend only on the local surface properties, while the latter predicts that Θ_R should depend on the bulk properties of the grain pile as a whole—such as the size of the system in which Θ_R is being measured. We have performed detailed measurements of Θ_R as a function of liquid content and sample size to test these theories, and we find that the physical behavior of wet granular media is richer than anticipated by either approach. In particular, we observe three distinct characteristic regimes depending on the liquid content. We also find that the two aforementioned theories can each qualitatively describe the behavior, but in different regimes.

Our experiments consist of a series of measurements of Θ_R performed by the draining crater method [9] which is depicted in Fig. 1. In this method a cylinder of diameter d_c is filled to some height, $h_0 \gg (d_c/2)\tan(\Theta_R)$, with grains of a known quantity and packing fraction. A circular aperture is then opened in the bottom of the cylinder which allows the grains to drain from the cylinder—first forming an annular crater, and then draining in flow down the surface of the crater until static stability is reached. We then determine Θ_R (the average slope of the stable crater surface) by weighing the grains which have drained.

In order to compare the experiment to the two theories mentioned above, we made measurements of Θ_R using three different cylinders with $d_c = 10.3$, 15.6, and 20.4 cm. Our granular medium consisted of spherical glass beads of average diameter 0.90 ± 0.05 mm [10] with surface roughness ~ 1 μm. The draining aperture was sufficiently large (diameter of 2.5 cm) that the medium drained in every case [11]. To minimize the effects of evaporation, we used vacuum pump oil [12] as a wetting liquid with an uncertainty of $<3\%$ in the added liquid content. We cite the nominal average oil film thickness (δ_{liq}) as the average thickness of the liquid, assuming that the spheres are perfectly smooth, uniform in size, and that the liquid is uniformly distributed on the grains. Note that our values of δ_{liq} are thus overestimates of the actual layer thickness, since we do not account for the surface roughness. The range of liquid content studied was $0 \leqslant \delta_{\mathrm{liq}} \leqslant 275$ nm, which is equivalent to the liquid filling of $\leqslant 0.27\%$ of the interstitial volume between the grains [13].

We mixed the 5 kg granular samples for more than 30 min before measuring in order to guarantee that the liquid was well distributed among the grains, and we found that the results did not depend on the amount of further mixing. Our data also did not depend on the delay time (typically less than 1 min) between pouring the mixed sample into the cylinder and the beginning of the draining process, even when the delay was extended up to 10 min. The time period (usually less than 10 min) between the end of the mixing and the beginning of the experiment was also found not to affect the data, even for times up to 100 min. This indicates that the flow of the liquid to the contact points was unimportant to the measurements, although on a longer timescale (2–3 d) some aging was observable for the highest oil contents. The procedure for filling the cylinder was strictly controlled so that the packing fraction in the samples was 0.633 ± 0.010

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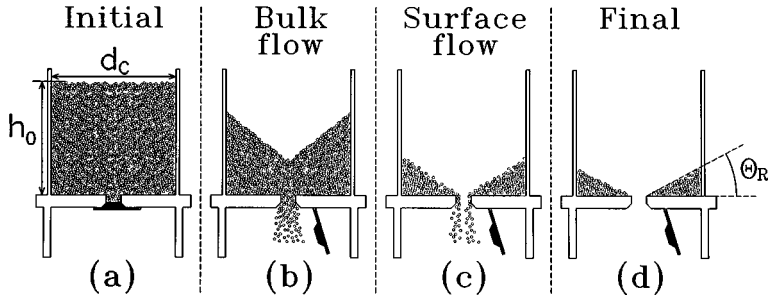

FIG. 1. A depiction of the draining crater method for measuring the angle of repose. (a) The initial filling of the container to a depth h_0. (b) The first stage of draining through ''bulk flow.'' (c) The second stage of draining through ''surface flow.'' (d) The final stable crater with slope at the angle of repose (Θ_R).

(independent of $\delta_{\rm liq}$), although we did not find Θ_R to vary beyond the experimental uncertainty if the filling procedure was changed slightly.

In Fig. 2 we show our raw data of Θ_R vs. $\delta_{\rm liq}$ which displays three regimes with different characteristic behavior in each. At the lowest liquid contents, in what we will call the *granular regime* ($\delta_{\rm liq}<20$ nm), $\Theta_R(\delta_{\rm liq})$ is linear in $\delta_{\rm liq}$ and does not depend on the container size. For larger liquid contents, in what we will call the *correlated regime* ($20 \lesssim \delta_{\rm liq} \lesssim 175$ nm), $\Theta_R(\delta_{\rm liq})$ has a clear negative curvature and decreases for larger containers. At the largest liquid contents ($\delta_{\rm liq} \gtrsim 175$ nm), which we call the *plastic regime*, $\Theta_R(\delta_{\rm liq})$ first decreases and then increases slightly with $\delta_{\rm liq}$, but still depends on d_c. The boundaries between the three regimes can be seen clearly in Fig. 3(a) where we plot the numerical derivative of Θ_R, $d(\Theta_R)/d(\delta_{\rm liq})$, which has a sharp peak at the transition at $\delta_{\rm liq} \sim 30$ nm and also a broader negative peak at $\delta_{\rm liq} \sim 200$ nm.

The dynamics of the draining process also reflect the above three regimes, and can be quantified by the time required for draining the cylinder, $\tau_{\rm drain}$, which is plotted in Fig. 3b. As shown in Fig. 1, the draining process consists of two stages; ''bulk flow,'' which lasts for time $\tau_{\rm bulk}$, and ''surface flow,'' which lasts for time $\tau_{\rm surf}$ such that $\tau_{\rm drain} = \tau_{\rm bulk} + \tau_{\rm surf}$. During bulk flow [Fig. 1(b)] the aperture is covered by the grains, and the flow rate is limited by the aperture size and the pressure on the grains over the aperture. During surface flow [Fig. 1(c)], the aperture is no longer covered by grains, and flow is along the exposed crater surface. We found by varying the initial mass of grains in the cylinder, that $\tau_{\rm bulk}$ depends only weakly on $\delta_{\rm liq}$ (less than 10% change over the full range of $\delta_{\rm liq}$). Consequently the strong $\delta_{\rm liq}$ dependence of $\tau_{\rm drain}$ can be attributed to changes in $\tau_{\rm surf}$.

In the *granular regime* the surface flow is homogeneous around the crater, and appears to involve only the top few layers of grains as in the case of dry granular media [2]. Indeed, in this regime, $\tau_{\rm drain}$ is dominated by this relatively inefficient surface flow, and the decrease in $\tau_{\rm drain}$ with increasing $\delta_{\rm liq}$ possibly corresponds to the increasing thickness of the flow layer, which decreases $\tau_{\rm surf}$. In the *correlated regime*, the surface flow becomes strongly correlated in that clumps of many attached grains fall in each avalanche. Such avalanches often nucleate at some point on the surface, and then the instability travels laterally around the crater. The final crater is typically highly anisotropic with the height at the cylinder wall varying by 5–15 mm, and the crater surface is rough with pronounced ridges and depressions. The large individual avalanches transport the grains more efficiently to the aperture, decreasing $\tau_{\rm surf}$ so that $\tau_{\rm drain}$ is determined primarily by the bulk flow rate (which is almost independent of $\delta_{\rm liq}$). In the *plastic regime*, the surface flow is reminiscent of a viscous fluid in that the medium retains a smooth crater surface and the motion is coherent, draining at the same speed on all sides of the crater. Visual observation of draining in a transparent container demonstrates, however, that flow in this regime occurs within a surface layer at the crater surface. When the draining ceases in this regime, the surface layer undergoes a slight elastic contraction analogous to the contraction of a dripping viscous fluid after a drop has fallen [14]. In this regime, the moving layer does not break loose from the surface like the avalanches of the correlated regime, but moves slowly along the surface. Thus the surface flow is apparently slowed by adhesive forces, and $\tau_{\rm surf}$ increases so that it once again determines $\tau_{\rm drain}$.

Since each measurement of Θ_R was performed 30 times to obtain an average, we can also examine σ_Θ, the standard deviation of the measured values of Θ_R, which is plotted in Fig. 3(c). As can be seen in the figure, σ_Θ is small in the granular and plastic regimes but much larger in the correlated regime. We attribute the differences between the three regimes to the dynamic nature of the surface flow processes. In the granular and plastic regimes the surface remains

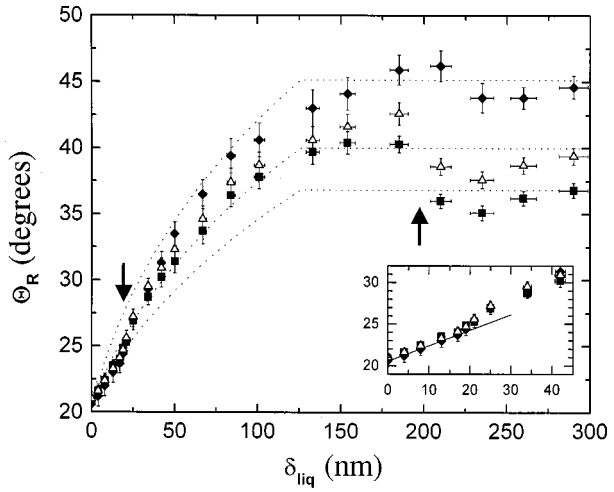

FIG. 2. The angle of repose as a function of the nominal average oil film thickness ($\delta_{\rm liq}$) with three different container diameters (◆, $d_c = 10.3$ cm; △, $d_c = 15.6$ cm; ■, $d_c = 20.4$ cm). The two vertical arrows indicate the transitions between the granular, correlated, and plastic regimes. The three dashed lines are fits [15] to the bulk theory [4] for the three different container sizes used. The inset shows an enlargement of the small $\delta_{\rm liq}$ regime.

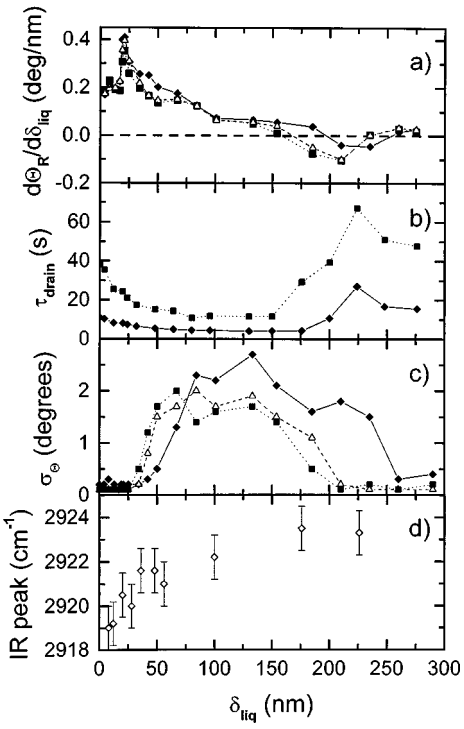

FIG. 3. Various measured properties of our system as a function of the nominal average oil film thickness, $\delta_{\rm liq}$ (◆, $d_c = 10.3$ cm; △, $d_c = 15.6$ cm; ■, $d_c = 20.4$ cm). The approximate boundaries between the granular, correlated, and plastic regimes are indicated by the shaded regions. (a) The numerical derivative, $d(\Theta_R)/d(\delta_{\rm liq})$, based on the data in Fig. 2. (b) The total time required to drain the apparatus, $\tau_{\rm drain}$, as discussed in the text. (c) The standard deviation, σ_Θ in the measured angle of repose. The much larger value in the correlated regime reflects the roughness of the surface. (d) The position of the FTIR line associated with the antisymmetric C-H stretching mode in the oil on our grains. The increase at small $\delta_{\rm liq}$ corresponds to the increase in the liquid fraction of the film.

smooth, and the flow of the grains is continuous throughout the draining process, and thus the system evolves adiabatically to its final state. By contrast, in the correlated regime the surface flow is dominated by individual avalanches, the character of which is determined by the particular arrangement of the grains at the start of a given draining process. The relatively large value of σ_Θ in the correlated region corresponds to the resulting roughness on the final surface of the crater.

While the experimental results clearly indicate the existence of three major regimes in wet granular media, we now must address the question of how to understand the regimes in the context of the existing theories. The characteristics of $\Theta_R(\delta_{\rm liq})$ in the granular and correlated regimes are qualitatively similar to the predictions of the surface [3] and bulk [4] theories, respectively, although neither can fully describe the entire data set. In the granular regime, the observation of smooth surface flow, the linearity of $\Theta_R(\delta_{\rm liq})$, and the independence of $\Theta_R(\delta_{\rm liq})$ on d_c are all consistent with the expectations of the surface theory. Some quantitative discrepancies persist, however, since we find $\Theta_R(\delta_{\rm liq}=0) \cong 21°$—about 10% smaller than the theoretical prediction [3]. Furthermore, this theory only applies when Θ_R is determined by the behavior of individual grains on the surface, and thus cannot account for the behavior in the correlated regime where the dynamics of correlated clumps dominate the surface flow.

In the correlated regime, the existence of bulk avalanches, the curvature of $\Theta_R(\delta_{\rm liq})$, and the decrease of Θ_R with d_c are all consistent with the bulk theory, within which one expects that Θ_R is determined by structural failure within the bulk of the material [4]. We attempted to fit the theory to the entire data set, and the best fits are shown by the lines in Fig. 2 [15]. While we find that it overestimates the changes in Θ_R due to the different d_c (especially in the granular regime where we observe no dependence of Θ_R on d_c), the theory does describe the basic qualitative features of $\Theta_R(\delta_{\rm liq})$ in the correlated and plastic regimes, with the exception of the drop in Θ_R at the transition to the plastic regime. The quantitative disagreement in these regimes may be due to the cylindrical experimental geometry, which is not incorporated into the theory. One other potential source of disagreement is that both theories predict the maximum angle of stability rather than the repose angle which we measure, but the stability of the final surfaces of the samples suggest that the differences between the two angles are not much beyond the uncertainties in the data.

While the two theories can qualitatively describe the data in the three regimes, there is an outstanding question as to the origin of the transitions between the regimes. Although the nanometer-scale films are difficult to probe directly, we performed Fourier-transform infrared (FTIR) spectroscopy [16] on the oil to determine the structural nature of the films. We find that the frequency of the absorption line associated with the antisymmetric C-H stretching mode shifts upwards for $\delta_{\rm liq} \lesssim 30$ nm and then saturates [see Fig. 3(d)]. Such a shift is consistent with the expected difference in the absorption line for molecules in solid and liquid states [17], and these data suggest that the film consists of a localized wetting layer under a delocalized liquid layer which comprises a growing fraction of the total film volumes as $\delta_{\rm liq}$ increases. We speculate that the delocalized liquid layer is covering an increasing fraction of the grain surface through continuous percolation as $\delta_{\rm liq}$ increases, and the increasing $\Theta_R(\delta_{\rm liq})$ corresponds to the increasing coverage of the grain surfaces by this layer. Assuming that the intergrain attractive force is proportional to $\delta_{\rm liq}$ in this percolative regime, the surface theory predicts that Θ_R should increase linearly with $\delta_{\rm liq}$, which is consistent with our experimental results in the granular regime. The transition to the correlated regime then corresponds to a complete coating of the grain surface with a delocalized liquid film. In this case the increase in force due to the onset of capillarity [18] would account for the peak in $d(\Theta_R)/d(\delta_{\rm liq})$ and also the onset of the bulk correlated behavior. We speculate that the transition to the plastic regime, in particular the decrease in Θ_R and the smooth nature of the flow, corresponds to the onset of lubrication effects, something which is not incorporated in the existing theories.

In summary, we observe three distinct regimes of coverage in the physical behavior of wet granular media. This complex behavior is not described by existing theories, and it suggests that the addition of liquid would have strong and nontrivial effects on other granular properties, such as size

segregation [1], pattern formation [1], sound propagation [19], and granular drag [20]. Given the richness of the physics of wet granular media and their technological importance, we expect that the present results will provide a framework for further research on the topic.

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[11] For smaller apertures, the adhesion of the grains can prevent draining [6].

[12] Duniway stockroom MPO-190, chemical formula: $(CH_2)n$ where $20 \leqslant n \leqslant 40$.

[13] The conversion between δ_{liq} and %volume saturation is $V\% = 300(\delta_{\mathrm{liq}}/R)\,\eta/(1-\eta)$, where $V\%$ is the %volume saturation, R is the average radius of the grains, and η is the packing fraction.

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[15] We fit the data to the theory of Ref. [4] by treating as free parameters their roughness parameters (l_R, χ, and d) and the surface tension (Γ). This fit reproduces most of the qualitative features of the behavior in the correlated and plastic regimes, although the necessary value of Γ ($\sim$0.09 N m) is almost three times larger than expected. The fit could not be improved by fixing the transitions between their three regimes to coincide with the three regimes we observe in the data.

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