# Granulation and suspension rheology: a unified treatment (Supplementary Information) 

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## S0: Granulation in industrial systems

Many industrial operations require the incorporation of powders into liquids. Often liquid is progressively added to dry powder, thus starting at high solid volume fraction and necessarily going through a granulation stage. Further addition of liquid results in an 'overwet' state in which granules no longer form, i.e. a suspension with high solids loading.

Two good examples of this are the production of molten chocolate ${ }^{\square}$ and the preparation of concrete ${ }^{[2]}$. Comparison of Fig. 1 (main), Fig. S1 and Fig. 2 in reference ${ }^{[2]}$ reveals a striking similar-
ity in phenomenology for these chemically disparate systems, suggesting a ubiquitous underlying physical mechanism.


Figure S1: Reproduced from ${ }^{[1]}$. All images are 40 mm wide.

Importantly, in the concrete and spheriglass/water/glycerol system used in this work, the transition from granules to flowing suspension at fixed processing conditions is realised by progressively increasing the proportion of liquid, thus decreasing $\phi$. In the model chocolate system however, the volume fraction remains constant and instead the jamming point, $\phi_{\mathrm{J}}$, is increased as agglomerates in the system are gradually broken up by mechanical action. As shown in this work, it is the sign and magnitude of $\phi-\phi_{\mathrm{J}}$ which determines whether a system a system will form granules or suspension and engineering either parameter can achieve the desired effect.

## S1: Model system details

Potter Spheriglass 5000 (A-Type) are uncoated soda-lime glass particles, largely spherical in shape (see Fig. S2). Scanning electron microscopy (S2a) shows that the particles are highly polydisperse and there exists a non-spherical proportion. Static light scattering measurements (Beckman Coulter LS 13 320) gives a volume-weighted mean diameter of $7.2 \mu \mathrm{~m}$. The full distribution of sizes is shown in S 2 b . The polydispersity is defined as the full-width half maximum size range of the
main peak, divided by the mean, giving a value of $147 \%$. Detailed particle shape analysis by imaging deposits of highly diluted suspensions deposited on microscope slides enables a quantitative analysis of circular and non-circular particle projections.


Figure S2: (a) SEM image of Spheriglass 5000. The particles are largely spherical, with some irregularly shaped shards. Scale bar $=10 \mu \mathrm{~m}$ (b) Volume-weighted distribution of particle diameters with a mean of $7.2 \mu \mathrm{~m}$. (c) Shape analysis shows that $\approx 45 \%$ of the particles (by area) have a circularity $C>0.90$, with $\approx 75 \%$ with $C>0.50$.

We quantify circularity, $C$, as:

$$
C=\frac{4 \pi A}{P^{2}}
$$

where $A$ and $P$ are the particle area and perimeter respectively. Using this imaging technique we are able to analyse $\sim 6 \times 10^{4}$ individual particles. We find that $\approx 75 \%$ (by area) of the particles have $C>0.50$, with $\approx 45 \%$ of the particles have $C>0.90$. These non-spherical particles will have an effect on the geometric packing of the system and will hence affect both $\phi_{\mathrm{rcp}}$ and $\phi_{\mathrm{m}}$.

In aqueous conditions, Spheriglass surface chemistry is dominated by silanol groups, rendering the surface hydrophilic. These groups dissociate to form surface charge, such that a repulsive inter-particle potential is generated.

In order to calculate volume fractions, we convert mass fractions using the densities of the materials. The glycerol-water mixture has a density of $1.243(2) \mathrm{g} \mathrm{cm}^{-3}$, measured using an Anton Paar DMA 4500 density meter at $19^{\circ} \mathrm{C}$. The density of Spheriglass is $2.64(5) \mathrm{g} \mathrm{cm}^{-3}$, measured by pynometry in a volumetric flask using a 0.885 m NaOH solution. The Spheriglass was dried in a vacuum oven at $120^{\circ} \mathrm{C}$ to remove any adsorbed moisture from the atmosphere.

## S2: Granulation equipment

The granulation equipment used in this work consists of a high-torque overhead mixer (Ika Eurostar Power Control-Visc), driving an aluminium impeller with three equi-spaced blades (see Fig. S3). Powders and liquid were mixed inside a cylindrical glass dish with liquid added at $15 \mathrm{~mL} \mathrm{~min}^{-1}$ using a syringe pump (New Era Pump Systems Inc. NE-1000) via tubing with an internal diameter $\approx 1 \mathrm{~mm}$ through a hole in the perspex lid. Clamps were used to hold the lid down and avoid movement of the dish relative to the axis of rotation of the impeller.

High-speed photography was used to measure the average drop diameter upon exiting the tubing, and was determined to be $4.57(7) \mathrm{mm}$.

Two different sizes of mixer and dish were used in this work. Details are given in Table S1,


Figure S3: (a) The high-shear mixing apparatus used in this work: (1) Overhead mixer, (2) syringe containing the glycerol-water mixture, (3) syringe pump used to control the addition of liquid, (4) mixing dish and blade. (b) Schematic of the high-shear mixing blade, dimensions are detailed in Table S1
with reference to Fig. $\mathrm{S3b}$. For high-stress sample preparation, the total mixing time was fixed at 3 minutes following liquid addition. At 1000 rpm , this gives a total of 3000 revolutions, at which point the size distribution had stopped changing, as determined by eye. For low-stress measurements, the samples were mixed for 30 minutes, at which point the size distribution had stopped changing. At 50 rpm , this gives a total of 1500 revolutions; continuing mixing to 3000 revolutions to match the high-shear value gave no appreciable change in size distribution.

## S3: $\phi_{\mathrm{J}}$ as a function of stress

In the main text (Fig. 2) we obtained $\phi_{\mathrm{m}}$ and $\phi_{\mathrm{rcp}}$ by fitting Eq. 1 to the high- and low-stress viscosities respectively. These give us the two limiting volume fractions which define flow or

|  | Large | Small |
| :---: | :---: | :---: |
| $r(\mathrm{~mm})$ | 54.4 | 36.4 |
| $L(\mathrm{~mm})$ | 17.8 | 11.6 |
| $\theta\left({ }^{\circ}\right)$ | 120 | 120 |
| $\omega\left(^{\circ}\right)$ | 45 | 45 |
| Dish diameter $(\mathrm{mm})$ | 110.7 | 75.4 |
| Dish height $(\mathrm{mm})$ | 60.9 | 40.9 |
| $V_{\text {tot }}\left(\mathrm{cm}^{3}\right)$ | 586.1 | 182.6 |
| $V_{\text {fill }}\left(\mathrm{cm}^{3}\right)$ | 75 | 45 |
| Radial distance to hole $(\mathrm{mm})$ | 34.1 | 18.4 |

Table S1: High-shear mixer dimensions; see Fig. S3b for symbol definition.
granulation in the phase diagram (Fig. 3, main text), but to complete the boundary, we need to know how $\phi_{\mathrm{J}}$ varies for all stresses.

In order to find $\phi_{\mathbf{J}}(\sigma)$ we perform the same analysis used to obtain $\phi_{\mathrm{m}}$ and $\phi_{\mathrm{rcp}}$ for each of the intermediate stresses, denoted by the different colours in S4a. We then fit Eq. 1 (main text) to the relative viscosity as a function of volume fraction for each of these stresses, S 4 b . In these fits we fix $\lambda=1.72$, the average value calculated for $\phi_{\mathrm{m}}$ and $\phi_{\mathrm{rcp}}$.

Following this, we can then plot $\phi_{\mathrm{J}}$ as a function of stress, S 4 c . We can then fit this data using the following form:

$$
\begin{equation*}
\phi_{\mathbf{J}}(\sigma)=\left(1-\exp \left[-\left(\frac{\hat{\sigma}^{\star}}{\sigma}\right)^{\beta}\right]\right)\left(\phi_{\mathrm{rcp}}-\phi_{\mathrm{m}}\right)+\phi_{\mathrm{m}} \tag{S1}
\end{equation*}
$$

where $\beta$ is the stretch in the exponential part and $\hat{\sigma}^{\star}$ is related to the experimentally measured $\sigma^{\star}$ by a $\beta$ dependent factor. Performing this analysis gives $\hat{\sigma}^{\star}=3.57 \mathrm{~Pa}$ and $\beta=0.745$. We then use Eq. S1 and the fitted parameters to construct the $\sigma-\phi$ phase diagram (Fig. 3, main text).

## S4: Vortex mixer stress estimation

The mixing action of the vortex mixer is very different to that of the high shear mixer discussed in the main text. Most significantly, it does not have a blade with which to mechanically stir the sample, instead using the inertia of the material to set up flow and induce a mixing action.

For solid granules, the mixing action provides rapid oscillations, resulting in a complex mixing pattern involving many collisions with both other granules and the walls of the vial. Although


Figure S4: (a) Relative viscosity, $\eta_{\mathrm{r}}$, as a function of applied stress, $\sigma$ for different volume fractions, $\phi$. Points are coloured according to applied stress. Grey symbols represent data for which either the flow was unsteady (i.e. onset of discontinuous shear thickening), or the sample edge started to show signs of fracture. These grey points are not used in the determination of $\phi_{\mathrm{J}}(\sigma)$ (b) $\eta_{\mathrm{r}}$ vs $\phi$. Colours same as (a) and each fitted with Eq. 1 (main text) with $\lambda=1.72$ (c) $\phi_{\mathrm{J}}$ as a function of applied stress from fits to Eq. 1 (main text) to the data in (b).
these collisions may in fact exert stresses higher than the onset stress, the strain may not be high enough to shear thicken the samples.

Previous work has found that liquid drops which jam and solidify upon impact with solid surfaces with which the binder has a low contact angle, can relax in a few milliseconds back to a flowing state ${ }^{3}$. These droplets stick to the surface preventing further collisions, thus minimising the effect of these high stresses while vortex mixing. Since these samples often stick to the vial and are highly viscous, the rotational mixing action of vortex mixer causes centrifugal body force that applies a stress to the sample that varies with radius.

Due to the rotation of the vortex mixer, a centrifugal force is experienced by the material in


Figure S5: Schematic of a vial on the vortex mixer. The vial rotates about the center point, $c$, with angular velocity, $\omega$. The vial has a diameter $r_{1}$, and the vortex mixer has an orbital radius of $r_{2}$. The outer point of the vial follows the large black dashed ring with radius $R=r_{1}+r_{2}$, but the vial itself does not rotate, instead a point in the vial, for example the red point highlighted, follows the dashed red circle and thus experiences a range of accelerations during a single revolution of the mixer.
the rotating frame of reference. The acceleration experienced by the rotating material is normally termed the relative centrifugal force ( RCF ) and is a number that gives the acceleration in terms of $g$, the gravitational acceleration. The RCF can be calculated:

$$
\begin{equation*}
\mathrm{RCF}=\frac{R \omega^{2}}{g}, \tag{S2}
\end{equation*}
$$

where $R$ is the radial distance from the center of rotation and $\omega$ is the angular velocity. This can be re-written in terms of $N$, the number of revolutions per minute (rpm) of the vortex mixer:

$$
\begin{equation*}
\mathrm{RCF}=\left(\frac{2 \pi}{60}\right)^{2} \frac{R}{g} N^{2} \tag{S3}
\end{equation*}
$$

The vial has a radius of $r_{1}=10 \mathrm{~mm}$ and the mixer has a radial orbit of $r_{2}=2 \mathrm{~mm}$. This gives a combined centrifugal radius of $R=r_{1}+r_{2}=12 \mathrm{~mm}$. The vortex mixer is operated at a maximum rate of 425 rpm , measured using a tachometer (Lutron DT-2236), giving RCF $=2.423$.

Suppose we have two spherical particles of equal size, one touching the vial wall and the other approaching it in a radial direction from the center of the vial. At the point of maximum acceleration, the spheres will experience an acceleration of $\sim 2.4 g$. We can calculate the force acting between the two particles as they collide using the acceleration and the mass of the particles:

$$
\begin{equation*}
F=\frac{4}{3} \pi r^{3}\left(\rho_{\mathrm{p}}-\rho_{\mathrm{l}}\right) \times 2.4 g \tag{S4}
\end{equation*}
$$

where $\rho_{\mathrm{p}}$ and $\rho_{\mathrm{l}}$ are the particle and liquid densities respectively. We can then estimate a stress scale, by dividing this force by an interaction area:

$$
\begin{equation*}
\sigma_{\mathrm{vortex}}=\frac{F}{\pi a^{2}}=\frac{4}{3} r\left(\rho_{\mathrm{p}}-\rho_{\mathrm{l}}\right) \times 2.4 g . \tag{S5}
\end{equation*}
$$

If we suppose the particles have a radius $a=5 \mu \mathrm{~m}$ (approximately equal to the peak size of both Spheriglass samples), and use the material densities measured in section S1, we get a stress of $\simeq 0.22 \mathrm{~Pa}$. This value is below the onset stress, $\sigma^{\star} \simeq 1 \mathrm{~Pa}$, such that particle contacts remain in the hydrodynamically lubricated, frictionless state in the vortex mixer.

This value constitutes an upper bound on the stress. Since the vial orientation remains fixed throughout the vortex mixer rotation, the acceleration experienced at any point in the sample varies with mixer rotation angle. Additionally, for any point in the sample located closer to the center of the vial, the magnitude of the acceleration will decrease, since the RCF varies with $R$.

## S6: Granule structure

In order to determine the structure of granules we sliced them open and revealed a core-shell structure, Fig. S6. In order to better examine the interior structure we used scanning electron
microscopy (SEM) (Jeol JSM-6010PLUS/LV), but due to the high vacuum operation of the SEM we had to modify the liquid binder in order to avoid evaporation. In order to do this we introduced a water-soluble cross-linking monomer (Sartomer SR610) and UV initiator to the binder phase. The prepared granules were then exposed to UV light in order to set the glue.

Due to the opacity of the material, in most cases very little of the binder set, making cutting the granules without damaging the structure impossible. Thermally activating initiators were also tried, but we found that liquid evaporated from the shell, making it very friable and impossible to cut.


Figure S6: (a) Cross section of a granule prepared using low stress at $\phi=0.70$, in which the binder has been cross linked. The core-shell structure is clear and we measure the shell thickness as $\simeq 45 d$, where $d$ is the mean primary particle diameter. (b) Schematic of a core-shell granule, with total radius $R$ and core radius $r_{\mathrm{c}}$. The shell contains a very small proportion of the liquid $\left(\phi_{\mathrm{sl}}^{\text {shell }} \rightarrow 1\right)$. The core has a stress dependent packing, $\phi_{\mathrm{J}}$, and can vary between $\phi_{\mathrm{m}}$ at high stress and $\phi_{\mathrm{RCP}}$ at low stress.

In S6a we show a granule granulated at low stress at $\phi=0.70$. The shell has a thickness of
$\approx 45 d$, where $d$ is the mean primary particle diameter. A schematic of the structure is shown in S6b, with the total granule radius, $R$, the core radius, $r_{\mathrm{c}}$ and the shell thickness, $t_{\mathrm{s}}$.

We see from S6a, the core of the granule appears to be densely packed, with no dry powder or air inclusions. In order to determine how representative this is of granules in general we used Xray tomography (SkyScan 1172) to scan the entire volume of several granules. Due to the density difference between the solid and liquid phases, using this technique we are only able to see air voids which are larger than several particle sizes, hence we don't observe the core shell structure.

In Fig. S7 we show the x-z projection of a granule (a), with a number of $x-y$ slices at the marked positions (b-e). In these binarised images the white part is the glass particles and the black is air. We do see a small number of small air pockets in the granules, however these only account for $\lesssim 2 \%$ of the total granule volume and do not change the interpretation of our data.


Figure S7: (a) Transmission image of a granule in the Skyscan 1172. Binarised slices of the 3D reconstruction corresponding to location (b) A, (c) B, (d) C, (e) D. Scale bars are 1 mm . White regions correspond to the location of solid particles, with the (internal) black regions corresponding to pockets of air.

## S1 S7: Granule size

We measure the distribution of granule sizes by sieving into different mesh sizes ranging from $90 \mu \mathrm{~m}$ to 20 mm and weighing the mass contained in each. The sieving was performed by gently agitating the sieve stack by hand, rather than using a mechanical sieve shaker in order to minimise granule breakage. In the main text we create a model a single size of granule to fit the mean granule size. To further refine this model we introduced a polydispersity in granule sizes into the model in order to better represent the reality of the measured granule sizes.

We start by assuming there exists a distribution of granule radii, $R$, with a probability density function, $p(R)$, of a log-normal distribution:

$$
\begin{equation*}
p(R)=\frac{1}{R \chi \sqrt{2 \pi}} \exp \left[-\frac{(\ln R-\nu)^{2}}{2 \chi^{2}}\right] \tag{S6}
\end{equation*}
$$

where $\nu$ and $\chi$ are the mean and standard deviation of the $\log$ of the distribution respectively. The log-normal distribution has moments:

$$
\begin{align*}
m_{s} & =\int_{0}^{\infty} p(R) R^{s} \mathrm{~d} R \\
& =\exp \left[s \nu+\frac{1}{2} s^{2} \chi^{2}\right] . \tag{S7}
\end{align*}
$$

We can then write the volume of solid, $V_{\mathrm{s}}$, and volume of liquid, $V_{1}$, in the system as:

$$
\begin{align*}
& V_{\mathrm{s}}=\phi_{\mathrm{J}} \cdot \frac{4}{3} \pi \int_{0}^{\infty} p(R) R^{3} \mathrm{~d} R  \tag{S8}\\
& V_{1}=\left(1-\phi_{\mathrm{J}}\right) \cdot \frac{4}{3} \pi \int_{t_{\mathrm{s}}}^{\infty} p(R)\left(R-t_{\mathrm{s}}\right)^{3} \mathrm{~d} R \tag{S9}
\end{align*}
$$

where $\phi_{\mathrm{J}}$ is the stress-dependent internal volume fraction of the granule.

We have assumed here that all granules have radii larger than the shell thickness $t_{\mathrm{s}}$. We write the total volume fraction as an integral sum over all granule sizes:

$$
\begin{equation*}
\phi=\frac{V_{\mathrm{s}}}{V_{\mathrm{s}}+V_{1}}=\frac{\phi_{\mathrm{J}} \int_{0}^{\infty} p(R) R^{3} \mathrm{~d} R}{\phi_{\mathrm{J}} \int_{0}^{\infty} p(R) R^{3} \mathrm{~d} R+\left(1-\phi_{\mathbf{J}}\right) \int_{t_{\mathrm{s}}}^{\infty} p(R)\left(R-t_{\mathrm{s}}\right)^{3} \mathrm{~d} R} \tag{S10}
\end{equation*}
$$

We can evaluate $V_{\mathrm{s}}$ using the moments of the log-normal distribution defined in Eq. $\mathbf{S 7}$.

$$
\begin{equation*}
V_{\mathrm{s}}=\phi_{\mathrm{J}} \cdot \frac{4}{3} \pi \exp \left[3 \nu+\frac{9}{2} \chi^{2}\right] . \tag{S11}
\end{equation*}
$$

$V_{1}$ needs a little more work in order to make progress with Eq. $\mathrm{S10}$. We can start by expanding the polynomial term in Eq. $\mathrm{S9}$.

$$
\begin{equation*}
\left(R-t_{\mathrm{s}}\right)^{3}=R^{3}-3 R^{2} t_{\mathrm{s}}+3 R t_{\mathrm{s}}^{2}-t_{\mathrm{s}}^{3}, \tag{S12}
\end{equation*}
$$

and substituting this expansion into the definition of $V_{1}$ :
$V_{\mathrm{I}}=\left(1-\phi_{\mathrm{J}}\right) \cdot \frac{4}{3} \pi\left(\int_{t_{\mathrm{s}}}^{\infty} p(R) R^{3} \mathrm{~d} R-t_{\mathrm{s}} \int_{t_{\mathrm{s}}}^{\infty} p(R) R^{2} \mathrm{~d} R+t_{\mathrm{s}}{ }^{2} \int_{t_{\mathrm{s}}}^{\infty} p(R) R \mathrm{~d} R-t_{\mathrm{s}}{ }^{3} \int_{t_{\mathrm{s}}}^{\infty} p(R) \mathrm{d} R\right)-V_{\text {air }}$.

In order to evaluate the integrals we can make use the result for the log-normal cumulative distribution function:

$$
\begin{align*}
\int_{0}^{x} p(t) \mathrm{d} t & =\frac{1}{\chi \sqrt{2 \pi}} \int_{0}^{x} \frac{1}{t} \exp \left[-\frac{(\ln t-\nu)^{2}}{2 \chi^{2}}\right] \mathrm{d} t \\
& =\frac{1}{2}+\frac{1}{2} \operatorname{erf}\left[\frac{\ln x-\nu}{\sqrt{2} \chi}\right] \tag{S14}
\end{align*}
$$

where 'erf' is the error function. In order to evaluate integrals between the limits of $t_{\mathrm{s}}$ and $\infty$, we can subtract Eq. S14 from 1 to obtain:

$$
\begin{equation*}
\int_{t_{\mathrm{s}}}^{\infty} p(R) \mathrm{d} R=\frac{1}{2}-\frac{1}{2} \operatorname{erf}\left[\frac{\ln t_{\mathrm{s}}-\nu}{\sqrt{2} \chi}\right] \tag{S15}
\end{equation*}
$$

We can then evaluate the integrals in Eq. S13, using solutions of the following form:

$$
\begin{align*}
\int_{t_{\mathrm{s}}}^{\infty} p(R) R^{s} \mathrm{~d} t & =\int_{t_{\mathrm{s}}}^{\infty} \frac{1}{R \chi \sqrt{2 \pi}} \exp \left[-\frac{(\ln R-\nu)^{2}}{2 \chi^{2}}\right] R^{s} \mathrm{~d} R \\
& =\int_{t_{\mathrm{s}}}^{\infty} \frac{1}{R \chi \sqrt{2 \pi}} \exp \left[-\frac{(\ln R-\nu)^{2}}{2 \chi^{2}}\right] \exp [s \ln R] \mathrm{d} R \\
& =\exp \left[s \nu+\frac{1}{2} s^{2} \chi^{2}\right] \int_{t_{\mathrm{s}}}^{\infty} \frac{1}{R \chi \sqrt{2 \pi}} \exp \left[-\frac{\left(\ln R-\left(\nu+s \chi^{2}\right)\right)^{2}}{2 \chi^{2}}\right] \mathrm{d} R \\
& =\exp \left[s \nu+\frac{1}{2} s^{2} \chi^{2}\right]\left[\frac{1}{2}-\frac{1}{2} \operatorname{erf}\left[\frac{\ln t_{\mathrm{s}}-\left(\nu+s \chi^{2}\right)}{\sqrt{2} \chi}\right]\right] \tag{S16}
\end{align*}
$$

where we have used the following expansion to obtain the final form of the exponents:

$$
\begin{align*}
s \ln R-\frac{(\ln R-\nu)^{2}}{2 \chi^{2}} & =-\frac{-2 \chi^{2} s \ln R+(\ln R)^{2}-2 \ln R \nu+\nu^{2}}{2 \chi^{2}} \\
& =-\frac{1}{2 \chi^{2}}\left[(\ln R)^{2}-2\left(\nu+s \chi^{2}\right) \ln R+\left(\nu+s \chi^{2}\right)^{2}+\nu^{2}-\left(\nu+s \chi^{2}\right)^{2}\right] \\
& =-\frac{\ln R-\left(\nu+s \chi^{2}\right)^{2}}{2 \chi^{2}}-\frac{\nu^{2}+\left(\nu+s \chi^{2}\right)^{2}}{2 \chi^{2}} \\
& =-\frac{\ln R-\left(\nu+s \chi^{2}\right)^{2}}{2 \chi^{2}}+\frac{s\left(2 \nu+s \chi^{2}\right)}{2} . \tag{S17}
\end{align*}
$$

We can then use Eq. S16 to give a final form of $V_{1}$ :

$$
\begin{align*}
V_{1}=\left(1-\phi_{\mathrm{J}}\right) \cdot \frac{4}{3} \pi & \left(\exp \left[3 \nu+\frac{9}{2} \chi^{2}\right]\left[\frac{1}{2}-\frac{1}{2} \operatorname{erf}\left[\frac{\ln t_{\mathrm{s}}-\left(\nu+3 \chi^{2}\right)}{\sqrt{2} \chi}\right]\right]\right. \\
& -3 t_{\mathrm{s}} \exp \left[2 \nu+2 \chi^{2}\right]\left[\frac{1}{2}-\frac{1}{2} \operatorname{erf}\left[\frac{\ln t_{\mathrm{s}}-\left(\nu+2 \chi^{2}\right)}{\sqrt{2} \chi}\right]\right] \\
& +3 t_{\mathrm{s}}{ }^{2} \exp \left[\nu+\frac{1}{2} \chi^{2}\right]\left[\frac{1}{2}-\frac{1}{2} \operatorname{erf}\left[\frac{\ln t_{\mathrm{s}}-\left(\nu+\chi^{2}\right)}{\sqrt{2} \chi}\right]\right] \\
& \left.-t_{\mathrm{s}}{ }^{3}\left[\frac{1}{2}-\frac{1}{2} \operatorname{erf}\left[\frac{\ln t_{\mathrm{s}}-\nu}{\sqrt{2} \chi}\right]\right]\right) \tag{S18}
\end{align*}
$$

Equations $\mathrm{S11}$ and $\mathrm{S18}$ can then be substituted into Eq. S10, allowing the volume fraction to be calculated as a function of $\nu$ and $\chi$. In order to compare these fits to our measured data, we need to calculate the volume weighted mean radius, $\bar{R}$, which we can write as:

$$
\begin{equation*}
\bar{R}=\frac{\int_{0}^{\infty} p(R) R^{4} \mathrm{~d} R}{\int_{0}^{\infty} p(R) R^{3} \mathrm{~d} R} \tag{S19}
\end{equation*}
$$

This can be evaluated by comparing the integrals to the moments for the log-normal distribution given by Eq. $\mathrm{S7}$,

$$
\begin{equation*}
\bar{R}=\frac{m_{4}}{m_{3}}=\frac{\exp \left[4 \nu+8 \chi^{2}\right]}{\exp \left[3 \nu+\frac{9}{2} \chi^{2}\right]}=\exp \left[\nu+\frac{7}{2} \chi^{2}\right] . \tag{S20}
\end{equation*}
$$

We can now vary $\nu$ whilst maintaining a constant $\chi$ in order to plot parameterised forms of $\bar{R}$ as a function of $\phi$ to fit the data in S8a. Here we fix the shell thickness to $t_{\mathrm{s}}=45 d$ as measured in Sec. S6 and use a value of $\chi=0.5$ which gives a reasonable fit to the observed size distributions for $\phi=0.85$, Fig. S8b


Figure S8: (a) Polydisperse granule model (solid lines) in comparison to the monodisperse granule size model described in the main text (dotted lines). Red; low-stress mixing, black; high-stress mixing. (b) Distribution of granule sizes for $\phi=0.85$. A log-normal distribution with $\chi=0.5$ is overlayed for high- and low-stress mixing.

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