Nature of Residual Liquid Holdup in Packed Beds of Spherical Particles

Werner van der Merwe, Chandra Maree, and Willie Nicol*

Department of Chemical Engineering, University of Pretoria, Pretoria, South Africa

The theoretical prediction of the residual liquid holdup in beds packed with nonporous spherical particles is tested by microscopic imaging of a bed of glass spheres wetted by water. The commonly used Young−Laplace equation accurately predicts the meniscus shapes of the pendular rings (Saez, A. E.; Carbonell, R. G. *J. Colloid Interface Sci.* **1990**, *140*, 408). The ring sizes are measured directly, and the minimum internal energy (Mao et al. *Chem. Eng. Sci.* **1993**, *48*, 2697) and critical percolation (Kramer, G. J. *Chem. Eng. Sci.* **1998**, *53*, 2985) boundary conditions proposed in the literature are shown to overpredict the average ring size. The summation of ring volumes over the bed yields a residual holdup smaller than that obtained through weighing. It is concluded that additional liquid is trapped through capillary action at locations where two or more particles are in close proximity. Photographic evidence of the existence of such liquid "globules" is presented.

1. Introduction

Residual liquid holdup (RLH) is an important parameter used in the characterization of trickle flow hydrodynamics that has been used in a number of hydrodynamic models.[1−8] It is defined as the volume of liquid (as a fraction of the total bed volume) that is retained in a packed bed after complete prewetting and subsequent drainage. A number of residual liquid holdup correlations have been proposed.[1,9−16] The most recent of these[9,16,17] assume that the liquid is present as pendular structures at the contact points between packing particles. The shape of the meniscus of liquid trapped at the contact point between two vertically aligned nonporous spheres has been shown to be the solution of the two-dimensional Young−Laplace equation and to depend on the following factors:[18] (i) the Bond number (or alternatively the Eotvos or capillary number), which is the ratio of gravitational to capillary forces within the pendular ring; (ii) the gas−liquid−solid contact angle; and (iii) the dimensionless datum pressure.

Several correlations of residual holdup as a function of Bond number are shown in Figure 1. As indicated, there is a gravity-dominant regime at high Bond numbers ($Bo > 5$) and a capillary-dominant regime at Bond numbers smaller than approximately 2. The latter covers most practical packing sizes.[12] (For very small packing sizes, little draining occurs because capillary forces completely dominate over gravity and the RLH can be expected to be higher.)

In the capillary regime, residual liquid holdup values are usually approximately 5%, although the considerable amount of available experimental data show a large amount of scatter[17] and values exceeding 10% have been reported.[13,17]

The residual holdup can be predicted theoretically following the treatment of Mao et al.[17] Although the meniscus shape for vertically aligned touching spheres is fully determined by the Young−Laplace equation, the location of the liquid−gas−solid contact point is needed as a boundary condition. In their work, Mao et al. proposed the use of a thermodynamic criterion to obtain the maximum stable pendular ring volume. Because this result holds only for vertically aligned spheres, a correction factor is used to account for smaller pendular rings at other-than-vertical alignment. The value of the correction factor is based on the findings of Turner and Hewitt,[19] who studied the variation of the pendular ring mass with elevation angle for large-diameter spheres ($Bo > 5$). Because this falls into the gravity-dominant regime, the validity of using this factor is questionable.

Reddy, Rao, and Rao[6] speculatively extrapolated Turner and Hewitt's results according to the geometric characteristics of pendular rings. They also proposed that the gas−liquid and liquid−solid interfacial areas can be deduced from the pendular ring geometry. The authors identified the need for experimental verification of their results.

Kramer[9] proposed the use of a critical percolation criterion, which results in smaller pendular rings compared to those obtained through the thermodynamic criterion.

In this study, we use microscopic imaging of a packed bed of 3-mm glass spheres wetted by water ($Bo = 0.3$) to quantify the sizes of pendular rings at various elevation angles within the capillary-dominated regime. We also investigate the assumption that nearly all of the residual liquid is held in pendular rings at particle−particle contact points.

2. Theory

2.1. Hydrostatics of the Meniscus. Consider the liquid held in a pendular ring at the contact point between two vertically aligned touching spheres (Figure 2). Under the assumptions of negligible surface tension gradients and negligible gas density, the momentum balance across the gas−liquid interface reduces to the Young−Laplace equation.[18]

* To whom correspondence should be addressed. E-mail: willie.nicol@up.ac.za.

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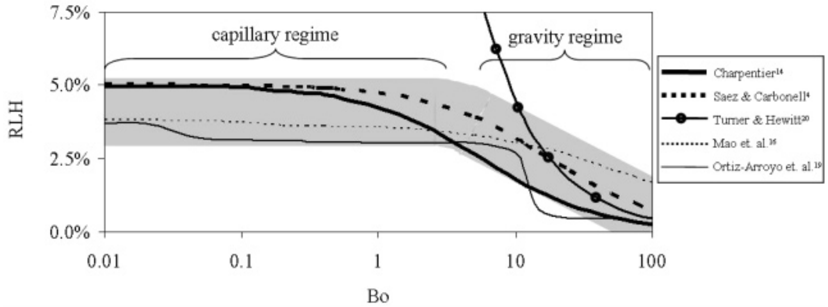

Figure 1. Residual liquid holdup correlations indicating gravity and capillary regimes (glass−air−water system).

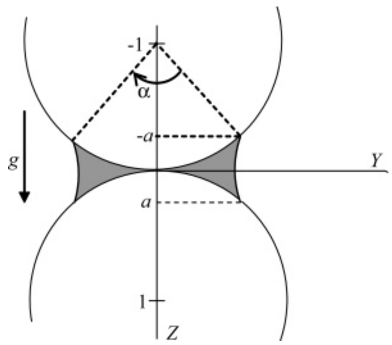

Figure 2. Geometry of a pendular ring between vertically aligned spheres.

The variables have been normalized with the sphere radius. If it is recognized that the meniscus shape is symmetrical about the Z axis, this equation reduces to[17]

$$Y'' = \frac{1 + Y'2}{Y} - (1 + Y'^2)^{3/2}(BoZ - C) \qquad (1)$$

Here, primes denote differentiation with respect to Z. Pertinent boundary conditions are[17] as follows

$$Y|_{Z=a} = Y|_{Z=-a} = \sqrt{1 - (1 - a)^2} \qquad (2)$$

$$\theta = |\tan^{-1} Y' - \tan^{-1} S'| \quad \text{at } Z = -a, a \qquad (3)$$

$$S(Z) = \begin{cases} \sqrt{1 - (1 + Z)^2} & -2 \le Z \le 0 \\ \sqrt{1 - (1 - Z)^2} & 0 \le Z \le 2 \end{cases} \qquad (4)$$

Here, a is the positive Z value of the triple point and can also be expressed as a wetting angle (α)[9] as in Figure 2, where $\alpha = 2 \cos^{-1}(1 - a)$.

Given values of the Bond number, the contact angle, and the location of the triple point (a), solution of the problem proceeds as suggested by Mao et al.[17]

2.2. Stability Criteria. The procedure described above results in the meniscus shape associated with the choice of a. A solution can be obtained for every arbitrary choice of a, and such a solution will satisfy the hydrostatic balance (eq 1). It is clear that an additional criterion for ring stability is required.

Mao et al.[17] proposed a thermodynamic criterion involving a minimization of the relative internal energy. The expression for the internal energy is

$$\Delta E = \sigma(A_{GL} - A_{LS} \cos \theta) \qquad (5)$$

where

$$A_{GL} = 2\pi \int_{-a}^{a} Y \, dZ \quad \text{and} \quad A_{LS} = 4a\pi$$

Kramer[9] presented an argument for fixing the limits of α based on the assumption that the pendular rings are at critical percolation (i.e., drainage stops as soon as a percolating path downward ceases to exist). The lower limit is set by envisioning three touching spheres in an equilateral arrangement. For wetting angles smaller than 60°, the rings are separated, and liquid ceases to drain. Because closer contact arrangements do not exist, this is taken as the lower limit for α. The upper limit is set by a body-centered-cubic array, where the rings will touch one another (and liquid will drain away) for wetting angles above 70°. This is taken as the upper limit. The author suggested using $\alpha \approx 65° \pm 2°$.

The wetting angles of Mao et al. and Kramer differ appreciably, and neither researcher reported extensive experimental verification.

2.3. Mapping to a Randomly Packed Bed. The volume of a single meniscus between vertically aligned spheres can now be calculated from[14]

$$v = d^3 \int_{-a}^{a} \frac{\pi}{8}(Y^2 - S^2) \, dZ \qquad (6)$$

In the Mao et al.[17] correlation, the mean volume of a set of *randomly inclined* pendular rings was determined by an averaging procedure based on the findings of Turner and Hewitt.[19] They studied the mass of water held between two glass spheres at different elevation angles and found the average ring to have a mass of approximately 30% of the maximum ring mass (which was found at vertical alignment). Unfortunately, the result holds only for large-diameter spheres, where gravity plays a significant role in distorting the meniscus shape ($Bo > 5$). Turner and Hewitt warned that their result cannot be extrapolated to small-diameter spheres. Nevertheless, Mao et al.[17] multiplied the volume by a factor (f) to account for smaller rings at other-than-vertical alignments.

Kramer[9] used a smaller wetting angle of 65°, a contact angle of zero, and no correction factor.

The number of contact points per particle can be readily expressed in terms of the overall bed porosity using available correlations.[15,20,21] Because the number of particles per unit bed volume can be estimated as $6(1 - \epsilon)/\pi d^3$, the residual liquid holdup (RLH) is given by

$$\text{RLH} = \frac{6(1 - \epsilon)\dfrac{N_{CP}}{2}}{\pi d^3} f v \qquad (7)$$

Stein's[15] empirical correlation for the number of contact points per sphere as a function of porosity is

$$N_{CP} = 22(1 - \epsilon)^2 \qquad (8)$$

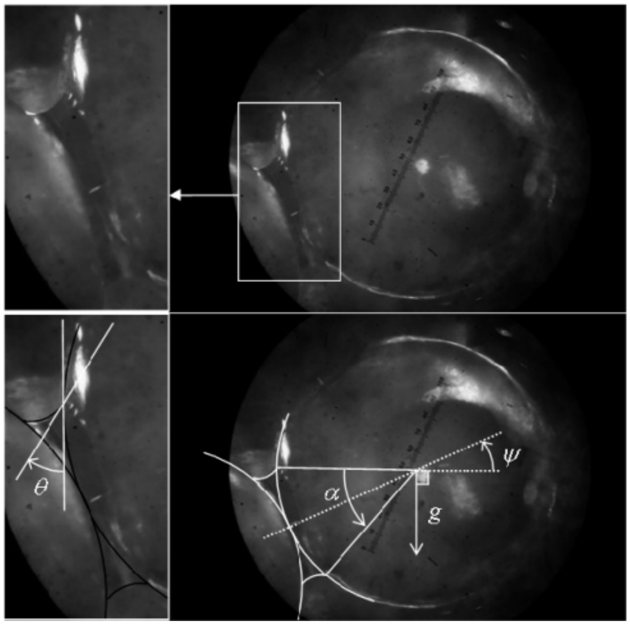

Figure 3. Measurement of wetting, contact, and elevation angles.

3. Experimental Section

3.1. Measuring Wetting, Contact, and Elevation Angles. In this study, we investigated the characteristics of residual liquid holdup inside randomly packed beds of 3-mm glass spheres. All spheres were thoroughly rinsed with water prior to use. Water was exclusively used as the wetting phase, with air as the gaseous phase. The surface tension of the water was measured in capillary rise experiments and found to be 0.067 N/m. The air−water−glass system at ambient conditions was chosen because of its generality in the literature. The Bond number for this system is equal to 0.3, indicating that capillary forces dominate over gravitational forces. Gravity can be neglected for $Bo < 0.5$.[18]

The bed was thoroughly prewetted by flooding of the entire column with water. The water was allowed to drain for at least 10 min, after which the weight remained constant. The packed bed was then digitally photographed through a microscope. Enlargement of 50 times was achieved. Two sets of microscopic photographs were taken. In the first, the bed was photographed through the opening at the top of the column. In the second, the bed interior was photographed from the side though the glass wall. Pendular rings a few particle diameters into the bed could be seen. The influence of the curvature of the glass wall was deemed to be negligible after evaluation of the shape of the spheres in the photos (which would deviate from circular if the distortion were significant).

Both sets of photographs yielded images in which the pendular rings and their wetting angles could be clearly discerned. Contact angles were more difficult to ascertain because the slope of the meniscus at the triple point was not distinguishable in all of the photographs. Angles of elevation (relative to the horizontal; see Figure 3) were measured from the side-on images. All angles were measured by construction in the MS−Visio environment. An example of a typical analysis is shown in Figure 3. The number of angles measured is reported in Table 1.

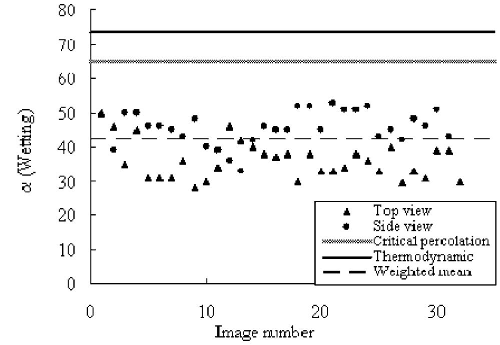

Figure 4. Wetting angle for top- and side-view images.

Table 1. Number of Measurements in Each Set of Experiments

	top view	side view
α (wetting angle)	33	31
θ (contact angle)	16	19
ψ (elevation angle)	–	31

3.2. Measuring Residual Liquid Holdup. The residual liquid holdup was measured by the difference in weight between a dry bed (9252 g, which includes the weight of the support structure) and a prewetted and drained bed (9334 g on average). The balance employed has a resolution of 0.1 g. The column was 58 mm in diameter, and the bed height was 900 mm. The supporting grid was a steel wire mesh. An end effect was evident in that a 7-mm portion of the bed above the grid remained saturated in liquid indefinitely. This corresponds to approximately 7 g of liquid. The measured weights were duly adjusted. The porosity was measured after every repacking and found to be approximately constant at 36.5%. Ten measurements were made.

In a separate evaluation, the rate of drainage was controlled through a valve at the column exit. The setting was varied from marginally open to fully open. For these extremes the liquid level dropped to the sieve in 35.9 and 1.4 min, respectively, indicating vastly different draining rates.

4. Results

4.1. Wetting and Contact Angles. Wetting angle measurements are shown in Figure 4 for both side-on and top-view experiments. Because the ring volume is a nonlinear function of wetting angle, the volume of each ring is computed, and the mean of these is taken as the average ring volume. This corresponds to an average wetting angle of 42.4°, which is indicated in Figure 4.

Minimization of the internal energy (eq 5) yields a wetting angle of 73.7° for our conditions ($Bo = 0.3$, $\theta = 32.4°$). This is indicated in Figure 4 along with Kramer's[9] suggested wetting angle of 65°.

From Figure 4, it is seen that the top-view wetting angles were generally smaller than the side-view angles. The weighted mean, however, was based on all of the data.

The measured contact angles were found to be approximately constant with a mean of 32.4° and with values ranging between 29° and 35° (RSD = 6%). Considering the difficulty in measuring these angles, the results compare well with the value of 31.7° widely reported in the literature.

4.2. Angle of Elevation and Its Effect on the Wetting Angle. From the side-on images, the angle of

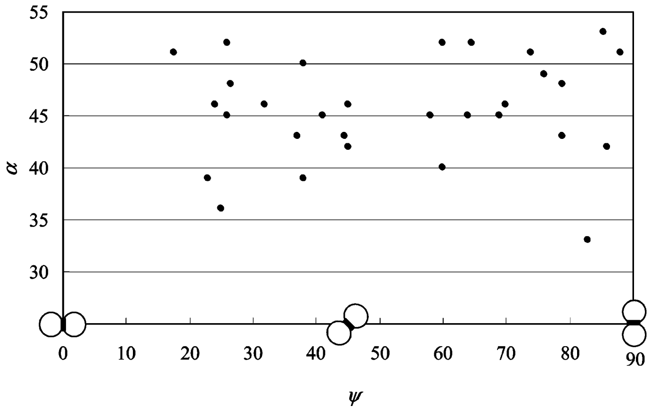

Figure 5. Wetting angle vs elevation angle.

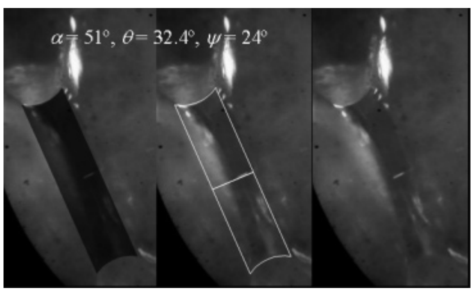

Figure 6. Comparison between modeled and experimental pendular ring shapes.

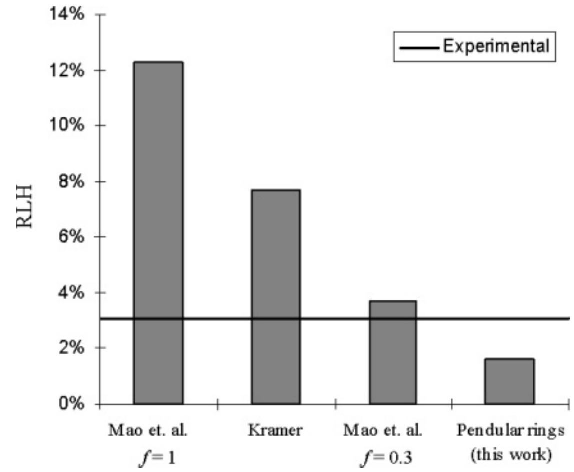

Figure 7. Comparison of residual holdup predictions and experimental value.

elevation and the wetting angle could both be measured. The results are shown in Figure 5.

This is clear evidence that, for the capillary regime, the wetting angle is not uniquely determined by the elevation angle, as is the case for the gravity regime.[19]

4.3. Meniscus Shape. The ability of eq 1 to predict the meniscus shape when the correct boundary conditions are specified is illustrated in Figure 6. The predicted pendular ring for the measured wetting, contact, and elevation angles is superimposed on the image on the left. The center image shows the modeled pendular ring's boundary. The original image is shown on the right. The meniscus shape closely resembles that of a circular arc.

4.4. Residual Liquid Holdup. Using the drain-and-weigh technique, the residual liquid holdup was measured reproducibly at 3.1% (RSD = 2.4%). This is exactly equal to the value obtained from the most recent empirical correlation[16] for the given system. The RLH was found to be constant irrespective of the draining rate, even when the draining rate was increased by a factor of 25. Any draining rate effects were therefore neglected.

The critical percolation[9] boundary condition yielded an RLH value of 7.7%. The internal energy minimization[17] procedure predicted an RLH value of 3.7% (12.3% without the correction factor).

In terms of the procedure followed herein, knowledge of the mean wetting and contact angles allows determination of the volume of liquid held in a single pendular ring via eqs 1−4 and 6. The residual liquid held in pendular rings throughout the bed can be determined from eq 7 and was found to be 1.6%. In summary, the relevant values are compared in Figure 7.

5. Discussion

From the values of the measured wetting angles (Figures 3 and 4), it is evident that the wetting angle is not uniquely determined from the choice of system parameters. It likely depends on additional factors that might include local draining kinetics, local porosity variations, and the mechanism of liquid deposition (as was found by Turner and Hewitt[19]). All wetting angles are between 28° and 53°, which are significantly smaller than the wetting angles used by both Mao et al.[17] and Kramer.[9] In the case of Mao et al., the thermodynamic criterion is seen to overpredict the size of the rings, even for vertically aligned spheres. Because the correction factor does not apply when small-diameter spheres are used, the procedure grossly overestimates the RLH. Kramer's assumption of the rings being at critical percolation cannot be validated—the liquid probably continues to drain through film flow even after the rings have become separated.

The procedure of using the weighted-average wetting angle to predict the RLH clearly underpredicts the experimental result. It is therefore concluded that the residual liquid holdup is present in forms other than pendular rings. Photographic evidence of such phenomena is presented in Figure 8, where liquid-filled areas are explicitly indicated in the images on the right.

The liquid is trapped in globules at locations where more than two particles are in close proximity. It is evident that the amount of liquid held in such globules is more than the sum of the respective pendular rings. It is difficult to ascertain the amount of liquid in each globule as no information is available on the shape of the globules in the direction perpendicular to the photographic plane. Using the present technique, the same globule could not be photographed both from the top and from the side.

The liquid trapped in globules does not drain even when a percolating path downward exists. Because we have already established that rings continue to drain after separation, both arguments for fixing the wetting angle based on critical percolation seem to fail.

This analysis indicates that 52% of the RLH is present as pendular rings, whereas the remainder is made up of globules of liquid that cannot be directly associated with particle−particle contact points.

Residual liquid holdup is often seen as a dead zone for mass transfer, and as a consequence, pendular ring

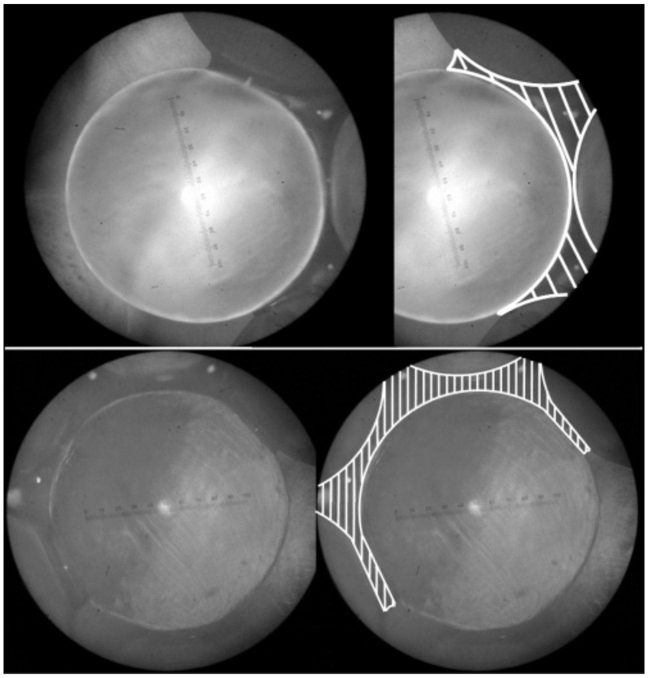

Figure 8. Demonstration of the existence of liquid globules.

geometry has been used to estimate the gas−liquid and liquid−solid interfacial areas.[6] Because a large fraction of the liquid is present in globular form, the pendular-ring-geometry-based calculations do not apply. Moreover, the globules represent relatively large volumes of liquid that have comparatively small interfacial areas. The globules will therefore influence the mass-transfer characteristics of the dead zone. Consequently, the existence of such structures should be incorporated into gas−liquid−solid transfer models that use residual liquid holdup−gas and residual liquid holdup−solid areas.

6. Conclusions

A large number of wetting, contact, and elevation angles were measured through the use of microscopic photography. Although the contact angles compared well with those previously reported in the literature, the wetting angles were found to be much smaller than those suggested by the use of a thermodynamic stability criterion or critical percolation theory. This result indicates that the thermodynamic criterion is not met in a typical bed. It also indicates that the pendular rings might continue to drain even when they become separated.

The wetting angle and pendular ring volumes were found not to be functions of the elevation angle. As such, it was shown that the result of Turner and Hewitt[19] cannot be extrapolated to small particles where capillary forces dominate over gravity.

Given experimental data on the wetting and contact angles, the Young−Laplace equation can be solved to obtain the meniscus shape. Proper integration of this shape and mapping to the entire bed yields a predicted value of the residual liquid holdup that is significantly smaller than that obtained through the recognized drain-and-weigh procedure. This is attributed to the existence of liquid globules at points in the bed where more than two particles are in close contact. Photographic evidence of these globules suggests that their volumes are larger than the sum of the volumes of the respective pendular rings.

The fact that the predicted residual holdup is only 52% of the measured value indicates that a large number of these globules exist throughout the bed. This has an important impact in terms of the gas−solid and liquid−solid mass transfer in the bed given that these regions are expected to represent significant dead zones.

Importantly, the theoretical prediction of RLH is not possible through modeling of pendular ring geometry alone.

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Nomenclature

A = interfacial area (m^2)
a = Z coordinate of the triple point
Bo = Bond number ($\rho g r^2/\sigma$), or Eotvos number ($\rho g d^2/\sigma$), or capillary number [$\kappa\rho/(g\sigma \cos\theta)$]
C = dimensionless datum pressure
d = sphere diameter (m)
E = internal energy (J)
f = correction factor
g = gravity vector (m/s^2)
N_{CP} = number of contact points per sphere
n = number of samples
RLH = residual liquid holdup
RSD = relative standard deviation

$$\left(\frac{n}{\sum x}\sqrt{\frac{n\sum x^2 - (\sum x)^2}{n(n-1)}}\right)$$

r = particle radius (m)
S = function describing sphere circumference in 2-D (normalized with respect to r)
v = volume of pendular ring (m^3)
x = sample value
Y = normalized horizontal coordinate
Z = normalized vertical coordinate

Greek Letters

α = wetting angle (deg)
ϵ = porosity
κ = bed permeability (m^3/s)
θ = contact angle (deg)
ρ = density (kg/m^3)
σ = surface tension (N/m)
ψ = elevation angle (deg)

Subscripts

GL = gas−liquid
LS = liquid−solid

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