A model for the retention of particles in evolving fibre networks

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Abstract
A model is presented for the entrapment of a distribution of particles by a distribution of pores. The fraction of particles retained and their distribution of sizes can be calculated for evolving and static porous structures. For evolving structures the change in distribution and fractional retention through the structure can be calculated. Also, the variance in these parameters between zones in the plane of the sheet can be calculated. The agreement between the theory and experimental data is good. The theory has relevance to the retention of fillers and fines in the papermaking process and to more general problems of stochastic porous media.

INTRODUCTION
The pore radius distribution in paper is known to be approximately lognormal with standard deviation proportional to the mean [1, 2, 3, 4]. This is in agreement with the theory for pore radius distribution in random networks [2]. More recently the pore radius distribution has been derived for non-random fibrous networks [5] and has been shown to be well approximated by the gamma distribution which has a probability density function given by equation (1),

\[ f(R) = \frac{\beta^k}{\Gamma(k)} R^{k-1}e^{-\beta R}, \]  

(1)
with mean, $\bar{R} = \frac{k}{b}$ and variance $\text{Var}(R) = \frac{k}{b^2}$.

It was also shown in [5] that distribution characterising parameters, $k$ and $b$ are linearly dependent on each other for changes in grammage and flocculation for a given furnish and single ply forming. Also, presumably as a consequence of the Central Limit Theorem in statistics, fibre length distributions and particle size distributions for pigments are often described by the lognormal distribution (equation (2)):

$$g(r) = \frac{1}{\sqrt{2\pi} r \sigma} e^{-\frac{\ln(r) - \mu}{2\sigma^2}}$$  \hspace{1cm} (2)$$

where $r$ has mean, $\bar{r} = e^{\mu + \frac{\sigma^2}{2}}$ and variance $\text{Var}(r) = e^{2\mu + \sigma^2} (e^{\sigma^2} - 1)$.

The $z$-directional distribution of filler is found to be concentrated towards the wireside in handsheets and towards the topside in machine made papers [6, 7]. Radvan [8] states that in the laboratory former the sheet acts as a filter whereas, on the forming table of a paper machine drainage is faster and discontinuous, causing filler in the initially formed layers to be washed out. Here we model only the entrapment of particles by the sheet acting as a filter; washout of particles will be addressed in a future article. Studies of the source and retained particle size distribution have been made by Williams [9] who found that the retention of filler on paper machines increased with particle size resulting in fractionation of the pigment in the forming process. The effect is illustrated by comparing the retention of mineral with the same mean particle size, though with different distributions.

**THEORY**

**Mechanical entrapment**

The probability that a randomly chosen particle meets a pore of radius not greater than $r$ is:

$$F(r) = \epsilon \int_0^r R^2 f(R) dR$$  \hspace{1cm} (3)$$

since $\epsilon$ is the fractional area of all pores and the likelihood of hitting a particular pore is proportional to its area.

Now, suppose that a total mass, $M$ of particles arrive with mass-weighted probability density function, $g(r)$, independently and randomly scattered over the network. The arriving mass in the radius range $r$ to $r + dr$ is $M g(r) dr$ and the retained mass
in this range is $F(r) M g(r) \, dr$. We observe that the net mass fraction retained is:

$$
\rho_{\text{mech}} = \int_0^\infty F(r) g(r) \, dr \tag{4}
$$

and of order $\varepsilon$ in size.

The probability density function of retained particles is

$$
G(r) = \frac{F(r) g(r)}{\rho_{\text{mech}}} \tag{5}
$$

and hence, the frequency distribution of radii of the fractional mass retained is given by $\rho_{\text{mech}} G(r)$.

We use the variables $k(t)$ and $b(t)$ to characterise the evolution of the inter-fibre pore radius distribution on the forming table and calculate the distribution of radii of retained particles and the change of this distribution through the $z$-direction of the sheet. From the data of Ng et al. [10] and that of Bancroft [11] the empirical relationship between $k$ and $b$ for changes in mean grammage, $\bar{\beta}$ has been taken as:

$$
b = \begin{cases} 
-0.33 & + & 0.40\, k & \text{for machine made papers with} \\
30 \, g \, m^{-2} \leq \bar{\beta} \leq 50 \, g \, m^{-2} \\
0.13 & + & 0.12 \, k & \text{for hand sheets with} \\
5 \, g \, m^{-2} \leq \bar{\beta} \leq 25 \, g \, m^{-2}
\end{cases} \tag{6}
$$

This experimental relationship between $k$ and $b$ is significant since it seems to infer that possible paper structures are more limited than might be expected, there being infinitely many gamma distributions with a given mean. For the purpose of this study it is sufficient to state that the relationships given above have been found to give good agreement with experimental measures of pore size distribution in hand sheets and machine-made papers.

The expected retention by mechanical entrapment of lognormally distributed particles with mean radius, $\bar{r} = 5 \, \mu m$ and variance, $Var(r) = 5 \, \mu m^2$ is shown in Figure 1 for increasing grammage as described by equation (6) for machine made paper. The same figure also shows the change in fractional retention as fibre is deposited. The range of $k$ used represents a grammage range of 30 $g \, m^{-2}$ to 60 $g \, m^{-2}$. 
Effect of surface charge

Equation (3) holds for entrapment of particles by pores of radius less than or equal to the particle radius. Clearly, some physical chemical effects, such as pH, zeta-potential, surface chemistry, for example, will influence the way small particles aggregate and how they interact with the matrix of fibrous cellulose. No molecular model is available to represent such influences but presumably the net effect is that either the small particles are more easily trapped in the network or not. Crudely, this means that either they have a larger effective radius than their geometric radius, or not. Modelling particles as spheres, the available surface either to carry a charge or for chemical reaction is proportional to the square of its radius. Hence, a particle may be captured by a pore of radius \( r + a r^2 \) where \( a \) is a parameter accounting for the surface charge density and has units of reciprocal length. The probability that a randomly chosen particle meets a pore of radius not greater than \( r + a r^2 \) is:

\[
H(r) = \frac{\epsilon \int_{0}^{r+a r^2} R^2 f(R) \cdot dR}{\int_{0}^{\infty} R^2 f(R) \cdot dR}. \tag{7}
\]

The net mass fraction retained is

\[
\rho = \int_{0}^{\infty} H(r) g(r) \cdot dr, \tag{8}
\]
and the frequency distribution of the radii of the fractional mass retained is \( \rho H(r) \). Thus when \( a = 0 \), \( H(r) = F(r) \) and \( \rho = \rho_{\text{mech}} \).

The fractional retention of particles with radii in a given range, \( r_1 \leq r \leq r_2 \) is given by:

\[
\rho_r = \frac{\int_{r_1}^{r_2} H(r) g(r) \, dr}{\int_{r_1}^{r_2} g(r) \, dr}
\]  

(9)

The absolute value of \( a \) is of little intrinsic importance; what is significant is whether, under a change of a physical chemical parameter \( x \), the relative rate of change of \( a \), \( \frac{1}{a} \frac{da}{dx} \) is detectable. If it is, then it indicates the scale of the effect and points the way to a physical model.

**VALIDATION OF THE THEORY**

Data is presented by Bown [12] for the entrapment of minerals by laboratory hand-sheets. Full experimental details are not provided though sufficient information on sample preparation and data is presented to allow testing of the model. The pulp used was a bleached sulphite pulp beaten to 300 ml CSF. Electrochemical forces were eliminated by treating the pulp and fillers with a dispersant; retention in a dynamic drainage jar was negligible. Particle size data is reported in terms of the parameter, \( d_{50} \), where 50% of particles have diameter above or below this value.

The experimentally observed effect of grammage on the retention of clay is shown in Figure 2. The filler was close cut by multiple centrifuging to give steep particle size distributions about \( d_{50} \); pore size distributions for the filled and unfilled papers were not measured. The prediction of the model has been calculated by numerically integrating equation (9) for 0.5 \( \mu m \) intervals of particle radius, \( r \); values of \( k \) and \( b \) were calculated from the data of Bancroft [11] for machine made papers from 100 % bleached Kraft Pine furnish at grammages of 40 \( g \, m^{-2} \), 50 \( g \, m^{-2} \) and 60 \( g \, m^{-2} \). The prediction of the model is shown in Figure 3 for \( a = 0.1 \); agreement with experimental data is good. The pore size distribution for the experimental sheet was unknown and whilst different absolute values would be obtained for a different pore size distribution, the observed trend would be the same; additionally, choice of parameter \( a \) is entirely arbitrary. The modelled response is typical of a cumulative frequency distribution and, though experimental data is unavailable above 15 \( \mu m \) to show the predicted plateau, the initial low gradient at low \( r \) is consistent with a cumulative distribution.
Figure 2: Effect of grammage on retention of close cut clay samples by handsheets. Data is shown for 20 g m$^{-2}$, 40 g m$^{-2}$ and 60 g m$^{-2}$. Mineral samples were close cut using multiple centrifuging.

The fractional retention of clay, talc and calcium carbonate by 60 g m$^{-2}$ handsheets is shown in Figure 4. The modelled response for increasing surface charge is shown in Figure 5. Values of $\rho_r$ were calculated using $k$ and $b$ values from the data of Bancroft [11] for 60 g m$^{-2}$ sheets. The source particle radii were lognormally distributed with mean, $\bar{r} = 2.5 \mu m$ and variance, $Var(r) = 1 \mu m^2$, though for a given pore size distribution, the value of $\rho_r$ is extremely insensitive to the source particle radius distribution.

The effect of fibre grammage and retention aids on the retention of clay is shown in Figure 6. The clays used were Superfill ($d_{50} = 6 \mu m$) and Grade C ($d_{50} = 2 \mu m$); retention aid was added at 0.015 mass % with 1 mass % alum on fibre. The modelled effect of increasing $a$ from 0.5 to 1 is represented by the dashed lines in Figure 6 for lognormally distributed particle radii with $\bar{d} = 6 \mu m$ and $Var(d) = 1 \mu m^2$. The values of $k$ and $b$ used to describe the pore size distribution were taken from the data of Blesner [4] for unbeaten pulps over a similar grammage range to that used by Bown [12]. However, as the retention data is for beaten pulps we would expect a narrower pore size distribution with smaller mean and hence higher retention. Calculations of retention for lognormally distributed particle radii with $\bar{d} = 2 \mu m$ and $Var(d) = 1 \mu m^2$
Figure 3: **Modelled retention of small particles.** Data is shown for 40g m$^{-2}$, 50g m$^{-2}$ and 60g m$^{-2}$; Particle radii lognormally distributed with $\bar{r} = 2.5\mu m$ and $Var(r) = 1\mu m$; parameter $\alpha = 0.1$

![Graph showing modelled retention of small particles.](image)

Figure 4: **Percentage retention of close cut mineral samples by 60 g m$^{-2}$ handsheets.** Data is shown for clay, talc and calcium carbonate.

![Graph showing percentage retention of minerals.](image)
Figure 5: Modelled percentage retention of particles by 60 g m\(^{-2}\) handsheets. Data is shown for increasing surface charge denoted by parameter \(a\).

gave retentions below 2% for \(a \leq 1\), though the shape of the curves and the change with increasing \(a\) was in agreement with the experimental data.

The predicted distribution of retained and transferred particle radii is shown in Figure 7 for retention of lognormally distributed particle radii with mean, \(\bar{r} = 5\mu m\) and variance, \(Var(r) = 5\mu m^2\) by a 60 g m\(^{-2}\) sheet using values of \(k\) and \(b\) from the data of Bancroft [11]. The figure shows the particle size distribution introduced to the system and the split of retained and transferred particles for \(a = 0\) and \(a = 0.1\). The fractional retention of particles is 0.162 for \(a = 0\) and 0.331 for \(a = 0.1\). Work is continuing to investigate the effect of white water recirculation by including some or all of the transferred particles in the source distribution. This work will provide an insight into the evolution of a steady-state particle size distribution in the feedstock, white water and the sheet.

**DISTRIBUTION OF FILLER IN THE PLANE**

The effect of grammage on the retention of particles has been demonstrated above (see Figures 2,3,4,5). The expected distribution of mass in a sheet is, by the Central Limit Theorem, Gaussian [13]. Also, for Bancroft’s data, the relationship \(k = 0.164 + 0.021\beta\)
Figure 6: **Effect of retention aids and fibre grammage on retention.** Data is shown for Superfill ($d_{50} = 6\mu m$) and Grade C ($d_{50} = 2\mu m$); predicted retentions are represented by dashed lines.

Figure 7: **Retention and transfer of particles.** The effect of $a$ on the particle size distribution of retained ($R$) and transferred ($T$) particles is shown. The source distribution of particles is denoted by $g(r)$. 
is found to hold with $r^2 = 0.812$ for grammages in the range $40 \, g \, m^{-2}$ to $60 \, g \, m^{-2}$. The distribution of fractional retained mass by zones of mean grammage, $50 \, g \, m^{-2}$ and coefficient of variation of local grammage, 7% was calculated by randomly selecting 1000 values of grammage from a normal distribution with this mean and variance; each grammage having associated values of $k$ and $b$. Retention was calculated for these zones for $0 \leq a \leq 1$. The retention of particles with lognormally distributed radii with mean, $\bar{r} = 2.5 \, \mu m$ and variance, $Var(r) = 1 \, \mu m$ is shown in Figure 8 and for particles with mean, $\bar{r} = 5 \, \mu m$ and variance, $Var(r) = 2 \, \mu m$ in Figure 9. As the variance and hence coefficient of variation of local grammage are dependent on zone size, different papers may exhibit the same variance at different scales. Definition of the size and shape of zones is therefore not required in the model. A coefficient of variation of local grammage of 7% is typical of commercial papers at the 1 mm scale. Interestingly the histograms in Figures 8 and 9 exhibit a negative skew despite the base structure of fibres having a normal distribution; also, the extent of skew increases with increasing $a$. The histogram for $a = 0$ is not shown as the fractional retention was below 4% for all zones.

The mean, variance and coefficient of variation of fractional retention are show in Figure 10 for the two particle size distributions. As expected, the variance exhibits a maximum as fractional retention increases and the coefficient of variation decreases monotonically for $\rho H(r) > 0$. It should be noted that if all or no particles are retained by the sheet, then the variance and hence the coefficient of variation are zero.

**DISCUSSION AND CONCLUSIONS**

A model has been presented for the entrapment of particles by an evolving network of fibres. The theory gives good agreement with experimental data. The between zones variance of particle retention has been calculated and has relevance to the uniformity of optical properties and of ink transfer in printing processes. Also, a distribution of filler is associated with a distribution of bonding and will affect mechanical properties of the sheet. Work is continuing to characterise the effect of particle washout in regions of high shear close to the forming fabric. Also, the effect of recirculation of transferred particles is under investigation; this work has relevance to evolution of steady state conditions on the machine and hence in the product. Experimental work is also underway to obtain pore size distributions and associated retained and transferred particle size distributions for machine made papers under a range of forming conditions and chemistries. This will allow determination of the effects of quantifiable physical
Figure 8: **Effect of retention aids on distribution of fractional retention for**
\( \bar{r} = 2.5 \mu m, \ Var(r) = 1 \mu m^2. \) Increase in charge modelled by increase in parameter \( a \) results in increased skew of the distribution.

Figure 9: **Effect of retention aids on distribution of fractional retention for**
\( \bar{r} = 5 \mu m, \ Var(r) = 2 \mu m^2. \) Increase in charge modelled by increase in parameter \( a \) results in increased skew of the distribution.
Figure 10: **Effect of retention aids on mean, variance and coefficient of variation of fractional retention.** *Top left:* mean; *top right:* variance; *bottom:* coefficient of variation.

chemical characteristics of the system on the charge parameter $a$ providing more rigorous testing of the model.

**NOMENCLATURE**

- $a$ : charge parameter
- $b$ : variable characterising gamma distribution
- $\beta$ : local grammage
- $d$ : particle diameter
- $\epsilon$ : porosity
- $k$ : variable characterising gamma distribution
- $M$ : total mass of particles in system
- $\mu$ : mean of log $r$
- $r$ : particle radius
- $R$ : pore radius
- $\rho$ : retained net particle mass fraction
- $\rho_{\text{mech}}$ : mechanically retained net mass fraction

$$\mu m^{-1}$$

$$g m^{-2}$$

$$\mu m^{-1}$$

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REFERENCES

$\rho_r$ fractional particle retention in a given range \{ \}

$\sigma$ standard deviation of log $r$ \{ \}

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References


REFERENCES


