The effect of paper formation and grammage on its pore size distribution

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Abstract

The pore size distribution in paper, measured by fluid permeation perpendicular to the plane of the sheet, is known to be approximately lognormal with standard deviation proportional to the mean. Also, this corresponds quite well to the polygonal size distribution arising from a random array of lines in a plane, which may be approximated using the negative exponential distribution for inter-crossing distances in random networks. We use the gamma distribution to generalize to the distribution of inter-crossing distances in flocculated networks and so obtain a family of pore size distributions indexed by the degree of flocculation in the network. This new analytic work helps understand the hitherto unexplained observation that the standard deviation of pore size increases with the mean for manifestly non-random papers, when measured by laminar flow. A comparison with data from the literature is provided. Coefficients of variation of free-fibre-length and pore radius both increase with flocculation but decrease with increasing grammage.

Introduction

The pore size distribution of paper was derived for random papers by Corte and Lloyd [1]. This derivation and subsequent measurements showed the pore size distribution to be well approximated by the lognormal distribution with standard deviation proportional to the mean for papers made from the same furnish at similar densities and formation [1, 2]. These results were confirmed by the measurements of Bliesner [3].

The porosity and organisation of pore space in paper affects its performance in various applications. The entrapment of particles with a distribution of sizes in a filtering operation and the absorption of polar and non-polar

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fluids, such as water, coating colours and printing inks will be dependent on the pore size distribution. The effect was demonstrated by Ollson and Pihl [4] who studied the capillary rise of viscous oils in strips of newsprint cut at various angles to the machine direction. They observed that the rise was greatest in the machine direction and decayed monotonically as the angle was increased. The importance of this result is that it is the organisation of the pore space which determines the process of capillary penetration, which implies corresponding effects in printing and coating. Another important influence of the pore size distribution is in that of the evolving pad during the forming process. Such effects have been identified in batch forming processes [5] and their statistical characterisation will be the subject of a forthcoming article.

The term 'pore' may be applied to many classes of void space; as discussed in detail by Scheidegger [6]. It is not neccesary to repeat that discussion here, as for the purpose of this study we shall limit our classification of pores to inter-fibre void space.

In a planar network of random lines, the mean number of sides per polygon is four, so Corte and Lloyd calculated the pore size distribution as the product of two negative exponential distributions, which are known to give a good approximation to the free-fibre-lengths in a random network [7]. Here we repeat this analysis using the gamma distribution as a generalisation of free-fibre-length distributions for random and flocculated networks. We use the computer algebra package Mathematica [8] for the calculus and graphics; the code for our calculations is available from the authors [9].

Fibre length distributions

Whilst the free-fibre-length distribution can be derived analytically for the random case, for real, or flocculated paper it cannot. In a flocculated sheet dense regions will consist of several small free-fibre-lengths; conversely, sparse regions will consist of fewer, larger inter-crossing distances. Thus we might expect a distribution with a positive skew and a variance greater than that in a random network. Few measurements of free-fibre-length distributions in commercial papers are available. However, the simulations of Scharcanski and Dodson [10] suggest that inter-crossing distances in flocculated networks may be approximated by a family of gamma distributions. This carries the implication that we could back-calculate, from formation measurements, estimates of free-fibre-length distributions. The importance of free-fibre-length distributions arises from their controlling influence on the evolution of local density variations and on the potential for development of relative bonded area.

The gamma distribution has a probability density function given by equation (1):

$$f(x) = \frac{b^k}{\Gamma(k)} x^{k-1} e^{-bx}, \tag{1}$$

with mean, $\bar{x} = \frac{k}{b}$ and variance $Var(x) = \frac{k}{b^2}$. The negative exponential distribution is a gamma distribution with $k = 1$. Thus, k and b are the parameters which represent the state of flocculation: $k = 1$ and $b_{rand} = \frac{1}{\bar{x}}$ for random; $k \neq 1$ for non-random networks. For flocculated networks we expect $\frac{k}{b^2} > \frac{1}{{b_{rand}}^2}$ and to increase with flocculation; for disperse networks we expect $b^2 \gg k$ such that $\frac{k}{b^2} < \frac{1}{{b_{rand}}^2}$ and to decrease with increasing uniformity.[1]

We shall see that the same two parameters k and b which characterise the free-fibre-length distribution, characterise also the pore size distribution and are themselves controlled by grammage and formation.

Pore size distributions

We shall consider the product of two independent identical gamma distributions $f(x)$ and $f(y)$ such that $xy = a$ where a is the area of a rectangular pore. The probability density of a will be given by:

$$p(a) = \int_0^\infty \frac{1}{x} f(x) f(\frac{a}{x}).dx, \tag{2}$$

Evaluation of the integrals in equation (2) gives us,

$$p(a) = \frac{2\, a^{k-1}\, b^{2\,k}\, K_0(z)}{\Gamma(k)^2}, \quad \text{where } z = 2b\sqrt{a} \tag{3}$$

and $K_0(z)$ is the zeroth order modified Bessel function of the second kind. The distribution given by equation (3) has mean, $\bar{a} = \frac{k^2}{b^2}$ and variance $Var(a) = \frac{k^2\,(1+2\,k)}{b^4}$.

Following Corte and Lloyd, we define an equivalent pore radius r which is given by $a = \pi r^2$. The probability of finding an equivalent pore radius $r_1 \leq r \leq r_2$, is given by:

$$\int_{\pi {r_1}^2}^{\pi {r_2}^2} p(a).da = \int_{r_1}^{r_2} p(\pi r^2)\, 2\pi r.dr\ . \tag{4}$$

So the probability density function for equivalent pore radii is:

$$q(r) = 2\,\pi r\, p(\pi r^2)\ , \tag{5}$$

which gives us:

$$q(r) = \frac{4\, b^{2\,k}\, \pi^k\, r^{2\,k-1}\, K_0(z)}{\Gamma(k)^2}, \quad \text{where } z = 2br\sqrt{\pi}, \tag{6}$$

[1] This makes precise the comment on page 176 in [7]

and $\int_0^\infty q(r).dr = 1$. The mean and variance of $q(r)$ are given by:

$$\bar{r} = \frac{\Gamma(k+\frac{1}{2})^2}{b\sqrt{\pi}\,\Gamma(k)^2} \tag{7}$$

and

$$Var(r) = \frac{k^2\,\Gamma(k)^4 - \Gamma(k+\frac{1}{2})^4}{b^2\,\pi\,\Gamma(k)^4} = \bar{r}^2\left(\frac{k^2\,\Gamma(k)^4}{\Gamma(k+\frac{1}{2})^4} - 1\right). \tag{8}$$

For a random network, $k = 1$ and the distribution of pore radii has mean, $\bar{r} = \frac{\sqrt{\pi}}{4\,b}$, and variance, $Var(r) = \frac{1}{b^2}\left(\frac{1}{\pi} - \frac{\pi}{16}\right)$ in agreement with Corte and Lloyd [1].

The derivation of pore size distribution for random networks allows a relatively simple determination of the relationship between the mean pore size and the standard deviation. This relationship is linear in the theoretical case, and approximately linear for experimental measurements [1, 2, 3]. A property of the gamma distribution, and of the new distribution $q(r)$, is that a given value of the mean may be associated with an infinite number of variances. The new distribution is therefore not easily characterised but a plot is given in Figure (1) to show how the standard deviation, $sd(r)$ depends on the mean, $\bar{r}$ over the range $10\mu m \leq \frac{k}{b} \leq 20\mu m$. It is expected that changes in grammage and flocculation, and hence in $\bar{x}$, will map a trajectory in this space.

Comparison with experimental data

Here we compare our distribution with the results of Bliesner, for changing grammage; and those of Corte and Lloyd for various formations. Both sets of results are for measurements made under laminar flow conditions and, as the pore size distribution had been shown to be approximately lognormal, neither article published the raw data but characterised the distributions by the mean and standard deviation.

Figure (2) shows Bliesner's lognormal distribution and the new distribution for handsheets made at grammages from 52 $g\,m^{-2}$ to 148 $g\,m^{-2}$. The hydraulic radii reported by Bliesner have been multiplied by 2 to convert to equivalent radii[2]. The agreement between the new distribution and the lognormal distribution fitted by Bliesner is clear.

Figures (3) and (4) show the new distribution plotted with the lognormal fit of Corte and Lloyd for Softwood Sulphate and Hardwood Sulphite pulps respectively. The data includes handsheets made by the lamination of five 20 $g\,m^{-2}$ layers for the Softwood and four 20 $g\,m^{-2}$ layers for the Hardwood. This was intended to approximate a random structure; however, the results of Sampson *et al.* [12] suggest that this is not necessarily the

[2]The hydraulic radius of an irregular shaped channel is the ratio of its area to perimeter, as such the radius of a circle representing an equivalent pore is twice the hydraulic radius [11]

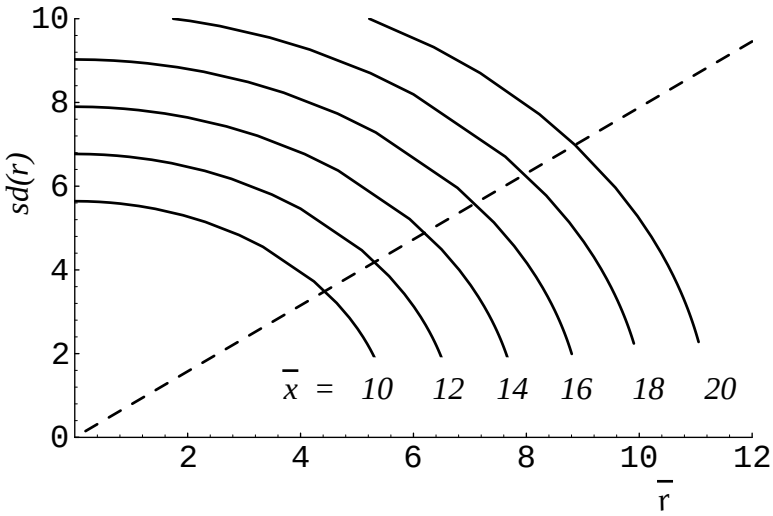

Figure 1: **Standard deviation vs mean pore radius for** $q(r)$**.** *Each mean pore radius may be associated with an infinite number of variances. The number associated with each contour curve is the mean free-fibre-length in* μm *of the source gamma distributions. The dashed line represents the random case where* $k = 1$*.*

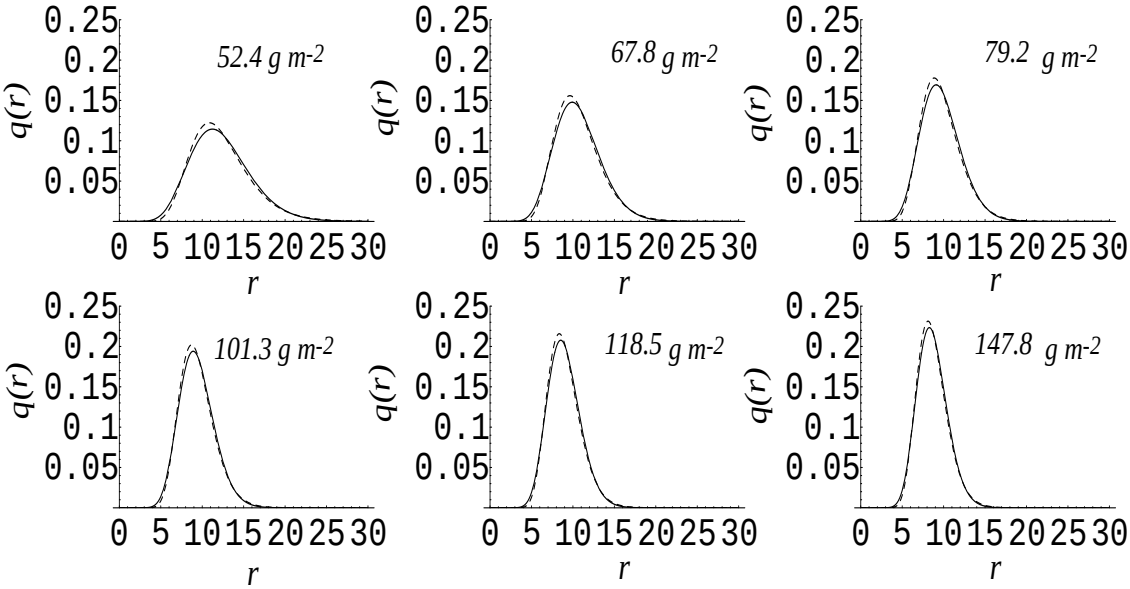

Figure 2: **Effect of grammage on pore size distribution.** *The lognormal distribution is represented by the broken line; the new distribution with the same mean and variance by the solid line. Units of* r *are* μm*. Data from Bliesner [3].*

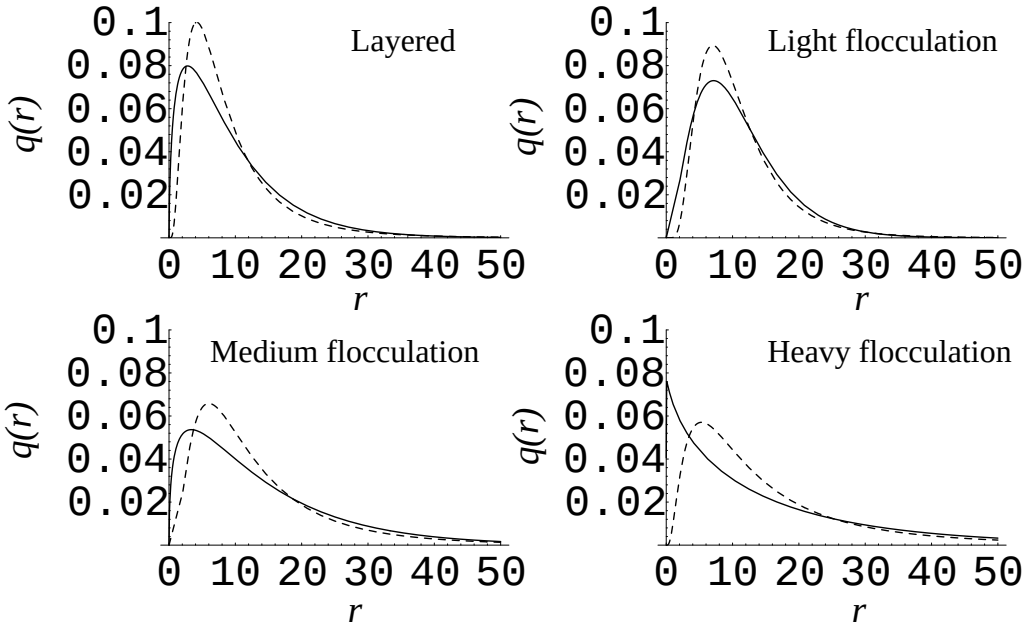

Figure 3: **Effect of formation on pore size distribution for Softwood Sulphate.** *The lognormal distribution is represented by the broken line; the new distribution with the same mean and variance by the solid line. Units of r are μm. Data from Corte and Lloyd [1].*

case. The agreement between the two distributions is not as strong as that with Bliesner's data; though the trends are similar and agreement is closest in the tail of the distribution where flow measurements are most reliable. In all cases, the new distribution was found to be approximated within $\pm 5\%$, for $2\mu m \leq r \leq 50\mu m$, by a gamma distribution with the same mean and variance.

For a given set of pore size data, $q(r)$ is characterised by parameters k and b. Referring back to the start of our derivation, these same parameters characterise also the free-fibre-length distribution in our network (see equation (1)). Figures (7) to (9) show our gamma distributions representing free-fibre-length distributions for the published data. The mean and standard deviation of pore size and free-fibre-length distribution are plotted in Figures (5) and (6) respectively. The relationship in both cases can be seen to be linear; the mean and standard deviation increasing with flocculation and decreasing with increasing grammage. Interestingly, the sheets made by the lamination of 20 $g\,m^{-2}$ layers do not fall on the straight line; presumably an effect of the discontinuous method of forming.

The relationship between k and b is shown for grammage in Figure (10) and for flocculation in Figure (11). In both cases the relationship is linear; k and b both increase with grammage and decrease with flocculation. Again, the points for the laminated handsheets do not fall on the straight line. The full data set for figures (5) to (11) are given in Tables (1) and (2); the crowding numbers, n_{crowd} in Table (2) are calculated form the data in [1].

The relationship between the geometric pore size distribution and that measured by fluid permeation is complex. Not only are pores interconnected in a three dimensional network but, as sheet thickness will be greater and pore

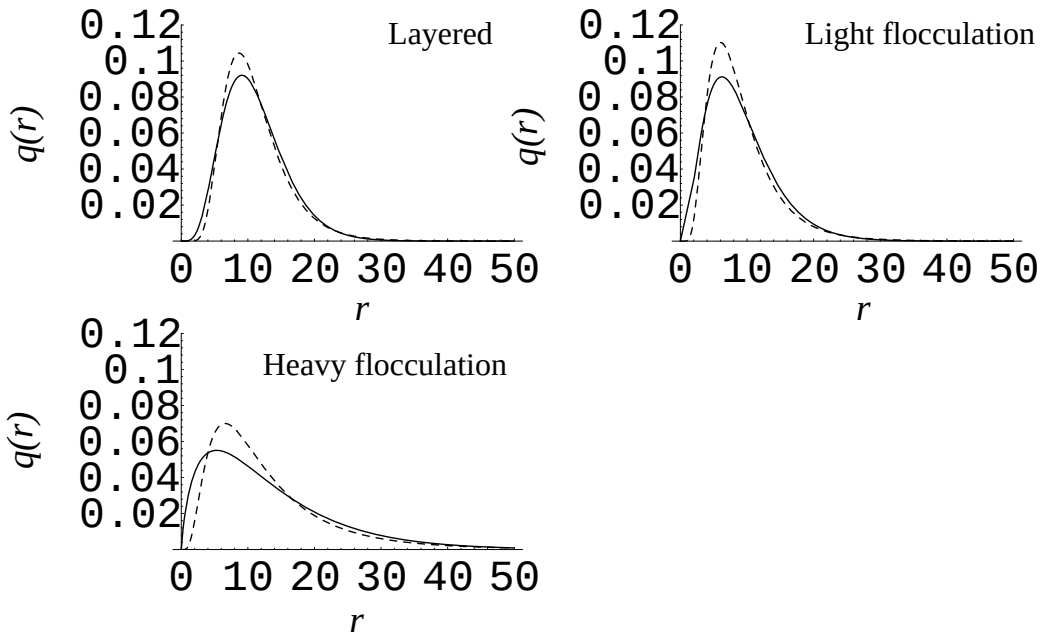

Figure 4: **Effect of formation on pore size distribution for Hardwood Sulphite.** *The lognormal distribution is represented by the broken line; the new distribution with the same mean and variance by the solid line. Units of r are μm. Data from Corte and Lloyd [1]*

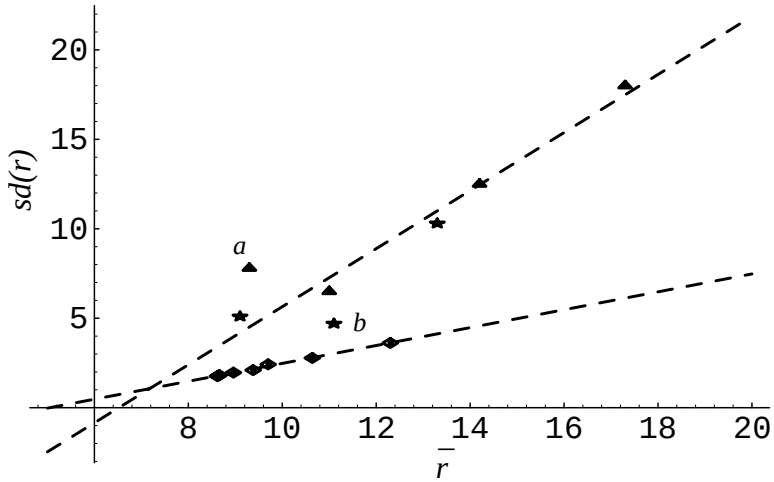

Figure 5: **Standard deviation vs mean for pore radius.** *The mean and standard deviation of pore radius decrease with increasing grammage and increase with flocculation.* **Key:** *stars - Hardwood (from [1]); triangles - Softwood (from [1]); diamonds - grammage (from [3]); points a and b are for the laminated handsheets. Units of $\bar{r}$ and $sd(r)$ are μm.*

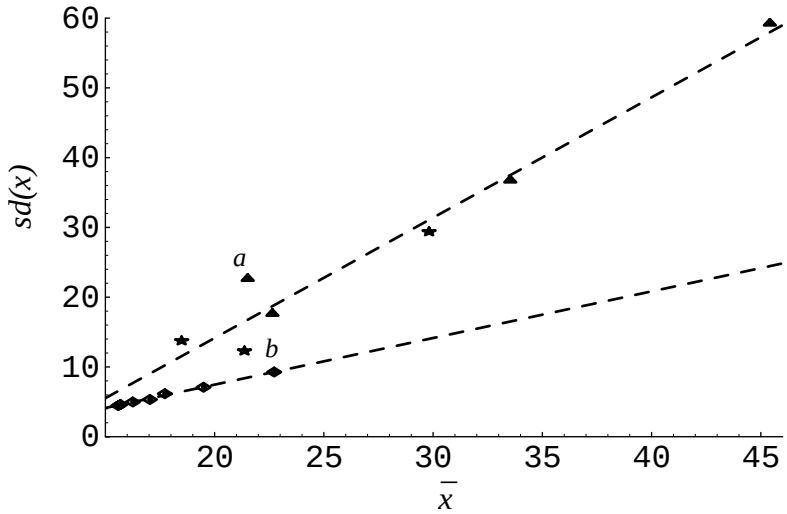

Figure 6: **Standard deviation vs mean for free-fibre-length.** *The mean and standard deviation of pore radius decrease with increasing grammage and increase with flocculation.* **Key:** *stars - Hardwood (from [1]); triangles - Softwood (from [1]); diamonds - grammage (from [3]); points a and b are for the laminated handsheets. Units of* $\bar{x}$ *and* $sd(x)$ *are* μm.

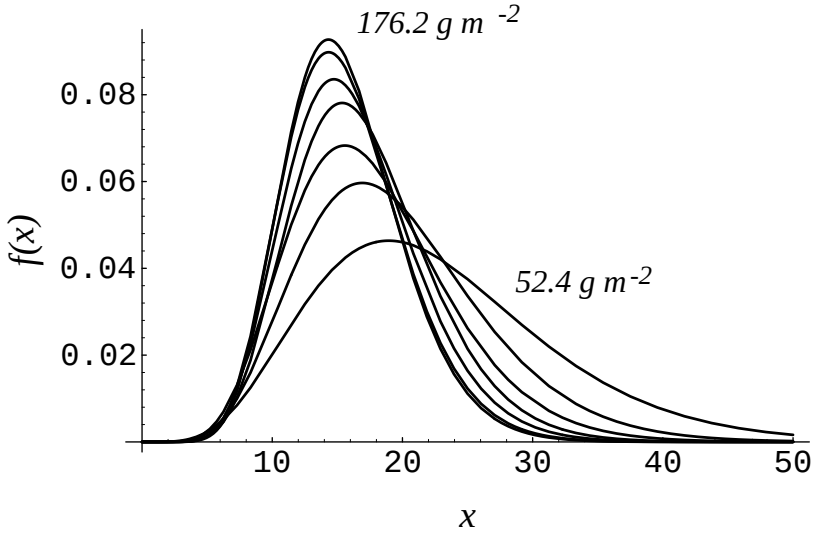

Figure 7: **Effect of grammage on gamma distribution for free-fibre-length.** *The mean and variance of free-fibre-length decrease with increasing grammage. Units of* x *are* μm. *Calculated from Bliesner's data [3].*

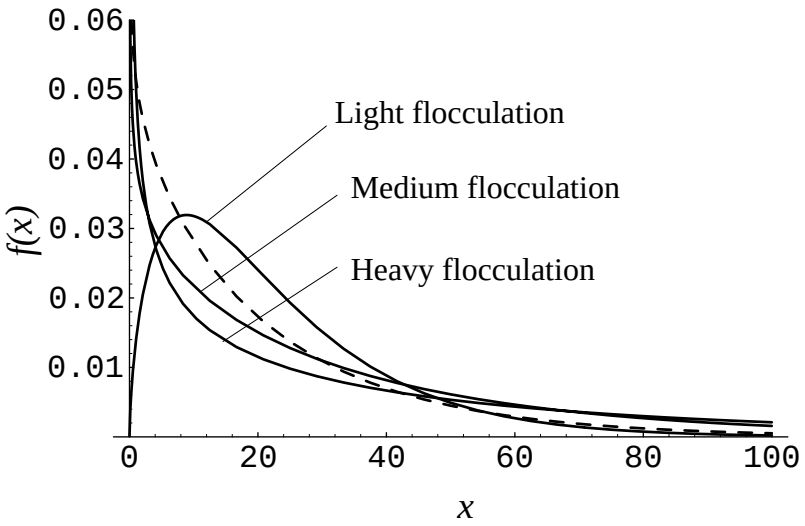

Figure 8: **Effect of flocculation on gamma distribution for free-fibre-length for Softwood Sulphate.** *The dotted line represents the layered sheet. The mean and variance of free-fibre-length increase with increasing degree of flocculation. Units of x are μm. Calculated from Corte and Lloyd's data [1].*

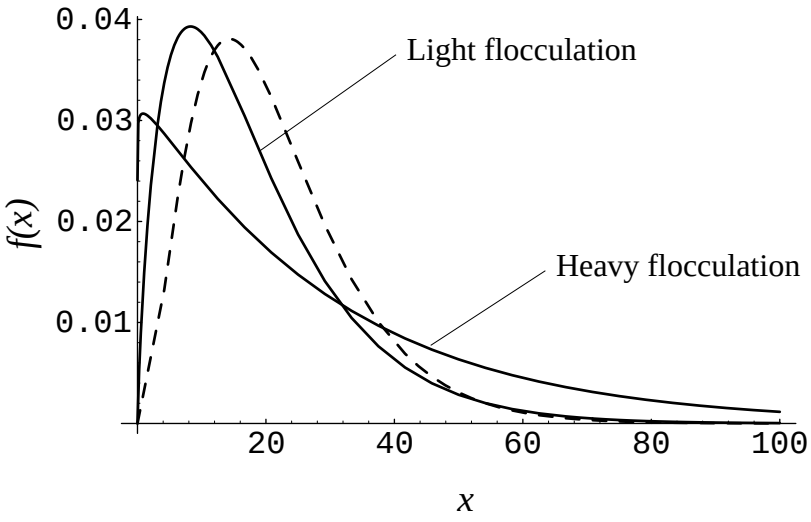

Figure 9: **Effect of flocculation on gamma distribution for free-fibre-length for Hardwood Sulphite.** *The dotted line represents the layered sheet. The mean and variance of free-fibre-length increase with increasing degree of flocculation. Units of x are μm. Calculated from Corte and Lloyd's data [1].*

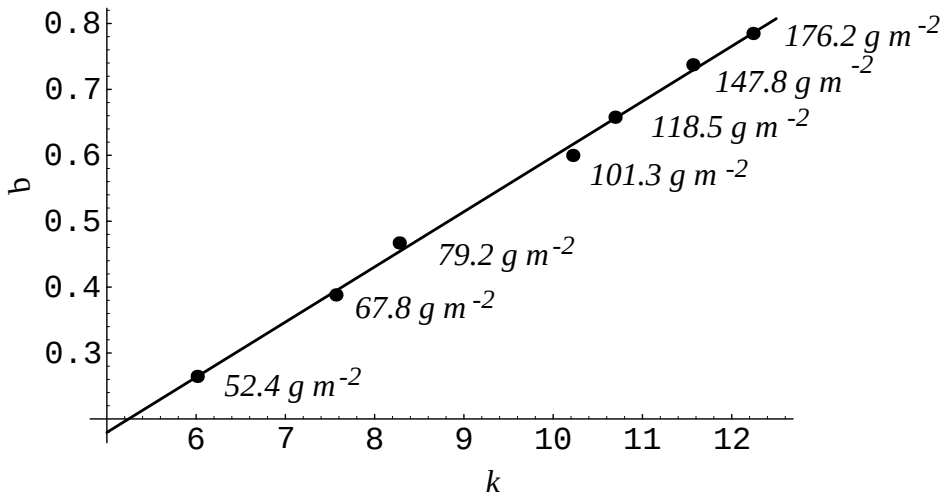

Figure 10: **Effect of grammage.** *Both k and b increase with grammage. Although the relationship is linear,* $\frac{k}{b} = \bar{x}$ *varies as the intercept is non-zero. Calculated from Bliesner's data [3], see Table (1).*

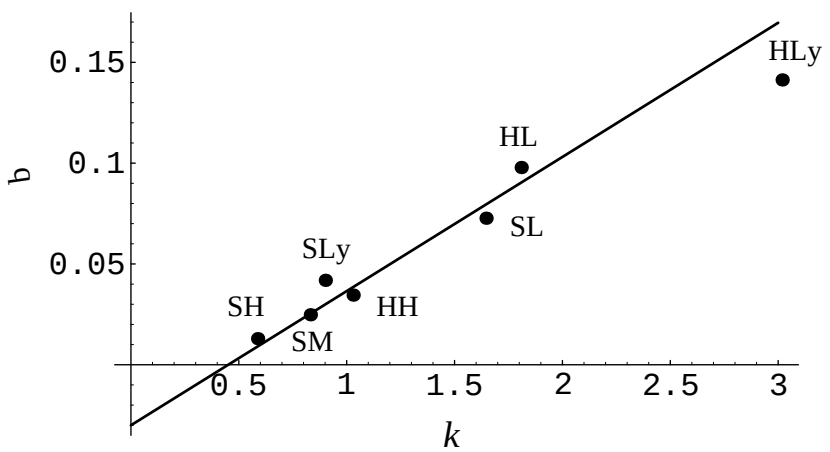

Figure 11: **Effect of flocculation.** *The points for the layered sheet fall outside the line; k and b decrease with increasing flocculation.* **Key:** *H - Hardwood, S - Softwood; Ly - layered, L - light, M - medium, and H - heavy flocculation. Calculated from Corte and Lloyd's data [1], see Table (2).*

Grammage $g\,m^{-2}$	k { }	b μm^{-1}	$\bar{x}$ μm	$sd(x)$ μm	$cv(x)$ %	$\bar{r}$ μm	$sd(r)$ μm	$cv(r)$ %
52.4	6.012	0.265	22.72	9.27	40.8	12.30	3.62	29.4
67.8	7.566	0.388	19.49	7.09	36.4	10.64	2.78	26.1
79.2	8.276	0.467	17.72	6.16	34.8	9.70	2.42	24.9
101.3	10.219	0.600	17.04	5.33	31.3	9.38	2.10	22.4
118.5	10.693	0.658	16.26	4.97	30.6	8.96	1.96	21.9
147.8	11.565	0.737	15.69	4.61	29.4	8.66	1.82	21.0
176.2	12.239	0.784	15.59	4.45	28.6	8.62	1.76	20.4

Table 1: **Reinterpretation of Bliesner's data [3].** *sd = standard deviation; cv = coefficient of variation.*

	n_{crowd} { }	k { }	b μm^{-1}	$\bar{x}$ μm	$sd(x)$ μm	$cv(x)$ %	$\bar{r}$ μm	$sd(r)$ μm	$cv(r)$ %
SW - Layered	0.2	0.901	0.042	21.51	22.66	105.3	9.3	7.8	83.9
SW - Light	1.4	1.646	0.073	22.65	17.65	77.9	11.0	6.5	59.1
SW - Medium	22.6	0.832	0.025	33.53	36.77	109.7	14.2	12.5	88.0
SW - Heavy	113.1	0.587	0.013	45.41	59.26	130.5	17.3	18.0	104.0
HW - Layered	0.1	3.019	0.141	21.37	12.30	57.6	11.1	4.7	42.3
HW - Light	0.3	1.809	0.098	18.49	13.75	74.4	9.1	5.1	56.0
HW - Heavy	24.7	1.030	0.035	29.82	29.38	98.53	13.3	10.3	77.4

Table 2: **Reinterpretation of Corte and Lloyd's data [1].** *sd = standard deviation; cv = coefficient of variation.*

size predominantly smaller in dense regions (and *vice versa* in sparse regions), the tortuosity and hence the effective capillary length will be affected by variation in local grammage. Work is continuing to characterise such effects.

It is interesting to note that the gamma distribution and our new distribution for pore size both resemble lognormal distributions. The lognormal distribution is a natural consequence of the Central Limit Theorem in statistics when a large number of independent random variables are involved in an attrition process, such as grinding of particles. Here we see a similar phenomenon in the stochastic subdivision of a plane region by fibres.

Conclusions

A new theory is given for pore size distribution in planar flocculated networks like paper. It agrees with the old theory in the random case. The pore size distribution and free-fibre-length, as represented by the gamma distribution, may be characterised by the variables k and b. These parameters are linearly dependent on each other and increase with grammage, decrease with flocculation, and control the standard deviation and the mean for the pore size distribution and the free-fibre-length distribution. The net effect is that the coefficients of variation of free-fibre-length and pore radius both increase with flocculation but decrease with increasing grammage.

Acknowledgements

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