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A multiplanar model for the pore radius distribution in isotropic near-planar stochastic fibre networks

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A model is presented for the pore radius distribution in isotropic near-planar stochastic fibre networks. At a given areal density, the mean pore radius of two-dimensional random networks is shown to decrease with increasing fibre width and to increase with increasing fibre linear density.

For structures with a structural component in the third dimension the standard deviation of pore radii is shown to be proportional to the mean for changes in areal density and porosity in agreement with data reported in the literature. At a given porosity, near-planar networks exhibit an increase in mean pore radius with increasing fibre width and linear density.

1. Introduction

There have been many studies of the structure of web or sheet-like stochastic fibrous networks such as filter media, paper and non-woven fabrics; a recent review of these is given by Sampson [1]. The maximum dimension of such materials perpendicular to their plane is typically only a fraction of a fibre length; they are classified as 'near-planar' networks since a characteristic of their structure is that it is essentially layered with fibre axes oriented within only a few degrees of the network plane [2].

Many workers have considered the statistical geometry of two-dimensional random fibre networks; such structures have fibre centres positioned according to a point Poisson process in two dimensions and the major axes of fibres have a uniform distribution of orientations. Miles [3] showed that the expected number of sides per polygon was four and this was subsequently verified in a simulation study [4]. Building on the work of Miles, Corte and Lloyd [5] derived the probability density of pore radii in a random network of *lines*. For such networks, Corte and Lloyd [5] showed that the standard deviation of pore radii is proportional to the mean pore radius such that the coefficient of variation of pore radii is $\sqrt{16-\pi^2}/\pi$.

Commercially formed fibre networks exhibit departures from randomness due to interactions between fibres and hydrodynamic effects during manufacture. We term the mass per unit area of a fibre network its *areal density*; the distribution of local averages of areal density is known analytically for the random case [6] and at scales around the length of a fibre, industrially formed networks always exhibit a broader distribution than that determined for a random network of the same fibres [1, 7]. The pore radius distribution for such 'clumped' networks was derived by Dodson and Sampson and shown to be well approximated by a gamma distribution [8]. Note also that the gamma distribution has been used to describe the pore radius distribution in fibrous filters [9–11] and nonwoven fabrics [12].

Recent experimental studies of the structure of paper, arguably the most widely used near-planar stochastic fibre network, have demonstrated the suitability of the gamma distribution to describe its pore radius distribution [13–15]. For fibres of similar width, networks with a range of areal densities and degrees of fibre clumping exhibited proportionality between the standard deviation of pore radii and the mean pore radius. The gradient of such plots represents the coefficient of variation of pore radii and for the data presented in [13–15] this was always less than that given by Corte and Lloyd [5] for two-dimensional random networks. This observation is interesting because the coefficient of variation of local areal density of these networks was greater than that calculated for a random network. Accordingly we see that the structure of the void space is apparently more uniform than a random network whilst its complement, the distribution of mass, is less uniform. This discrepancy probably arises from the fact that the pore radius distribution is calculated indirectly as that of a system of parallel capillaries exhibiting the same flow characteristics as the sample being tested, whereas the mass distribution is measured more-or-less directly using calibrated β-radiography.

Here we consider first the statistical geometry of two-dimensional random fibre networks and derive their mean pore radius extending the work of Corte and Lloyd to incorporate the influence of fibre width. Since real fibre networks have an appreciable structural component in the third dimension, we consider the superposition of two-dimensional networks to form multiplanar structures. The probability density of pore radii in such structures is derived and used to predict the influence of fibre geometries and network characteristics on the pore radius distribution.

2. Two dimensions

Kallmes and Corte [16] considered a two-dimensional random network of fibres with aspect ratio A, and defined this as a network where less than 1% of the area is covered by more than two fibres. The expected number of crossings per fibre in such a network is given by Kallmes and Corte [16] as

$$\bar{n}_{\text{cross}} = \frac{2\bar{c}A}{\pi} \tag{1}$$

where $\bar{c}$ is the expected number of fibres covering a point or the mean *coverage* of a layer and is given by the ratio of the mean areal density of the layer to that of the fibres.

For fibres of mean length $\bar{\lambda}$ (m) and width ω (m) we have $A = \bar{\lambda}/\omega$ and the expected free fibre length between crossings is,

$$\bar{g} = \frac{\bar{\lambda}}{\bar{n}_{\text{cross}}} - \omega \quad \text{for } \bar{n}_{\text{cross}} \gg 1 \tag{2}$$

$$= \left(\frac{\pi}{2\bar{c}} - 1\right)\omega. \tag{3}$$

In many thermoplastic bonded polymer networks, small beads of adhesive polymer are often observed at crossings; we expect that these will effectively widen fibres at such crossings thereby slightly reducing the mean free fibre length between crossings. Such effects are likely to be small and will not be considered further here.

Now, Corte and Lloyd [5] give the mean pore radius of a two-dimensional random fibre network as

$$\bar{r} = \frac{\sqrt{\pi}}{4}\bar{g}. \tag{4}$$

and substitution of Equation 3 in 4 yields,

$$\bar{r} = \frac{\sqrt{\pi}}{4}\left(\frac{\pi}{2\bar{c}} - 1\right)\omega. \tag{5}$$

We consider fibres in terms of their width since many natural fibres do not have circular cross-section and are prone to collapse upon subjection to mechanical action. For fibres of circular cross section, the width is equivalent to the diameter. The mean coverage, $\bar{c}$ is dependent on fibre width such that

$$\bar{c} = \frac{\bar{\beta}_{2D}\omega}{\delta} \tag{6}$$

where $\bar{\beta}_{2D}$ is the areal density of a layer and δ is linear density of fibres (gm^{-1}).

Substitution of Equation 6 in 5 and rearranging yields

$$\bar{r} = \frac{\pi^{\frac{3}{2}}\delta}{8\bar{\beta}_{2D}} - \frac{\sqrt{\pi}\omega}{4} \tag{7}$$

Equation 7 gives for the first time the influence of fibre width on the mean pore radius in two-dimensional random fibre networks. As such it allows us to quantify the effect of transverse fibre collapse on the mean pore radius in a thin network. In an industrial context, such collapse is common in the processing of natural fibres prior to the manufacture of paper and during papermaking pressing and drying operations. Assuming the linear density and mean network areal density to be constant, then the effect of increasing fibre width by $\Delta\omega$ is to reduce the mean pore radius of a two-dimensional structure by $\sqrt{\pi}\Delta\omega/4 \approx 0.44\Delta\omega$.

The surface representing the mean pore radius in units of fibre width for a two-dimensional network of mean areal density 1.5 gm^{-2} is plotted for the range of fibre widths and linear densities typical of wood pulp fibres in Fig. 1. For fibres of circular cross section of diameter ω, the linear density is given by,

$$\delta = \frac{\pi\omega^2}{4}\rho \tag{8}$$

where ρ is the density of the fibre. Substitution of Equation 8 into Equation 7 yields

$$\bar{r} = \frac{\pi^{\frac{5}{2}}\rho\omega^2}{32\bar{\beta}_{2D}} - \frac{\sqrt{\pi}\omega}{4} \tag{9}$$

such that when ω has units of μm, β_{2D} has units of gm^{-2} and ρ is entered as a specific gravity, $\bar{r}$ has units of μm. Equation 9 is suitable for calculation of the mean pore radius in thin networks of, for example, glass, metal, carbon and synthetic polymer fibres of known density and diameter.

Typically we expect the porosity of near-planar stochastic networks such as fibrous filters to be approximately uniform in the z-direction. The main exception to this occurs when there are significant quantities of fibre fragments of small aspect ratio that result from fibre processing operations or when non-fibrous

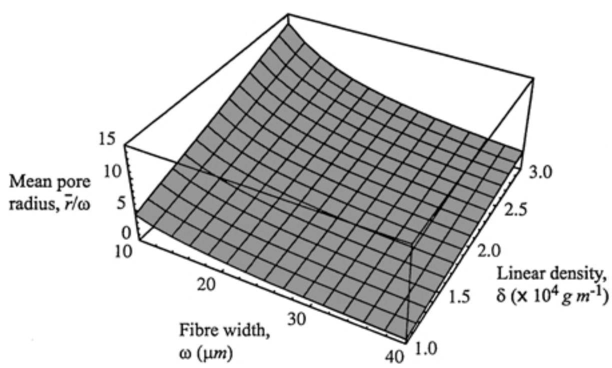

Figure 1 Mean pore radius in a layer in units of fibre width as a function of fibre width and linear density. Surface generated for a layer of areal density 1.5 gm^{-2}.

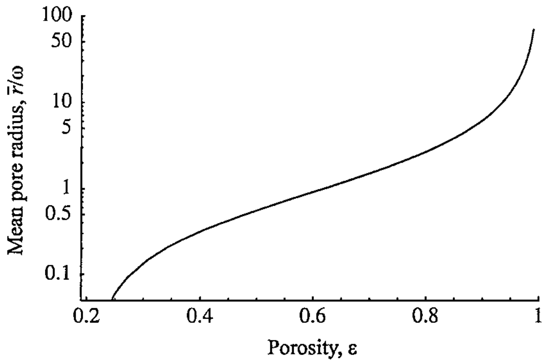

Figure 2 Mean pore radius in a layer in units of fibre width as a function of porosity.

additives such as minerals are added as in the manufacture of some paper grades. For networks formed from synthetic or glass fibres, such as those used in fibre reinforced composites and for nonwoven fabrics and glass fibre filters, these small particles are largely absent. Accordingly, we define the mean areal density of a two-dimensional network to be that where the fractional open area is equal to the porosity of a near-planar network. For a random network of fibres, the fractional open area is given by the Poisson probability that the coverage is zero such that,

$$P(0) = \varepsilon = e^{-\bar{c}} \tag{10}$$

$$\varepsilon = e^{-\frac{\omega \bar{\beta}_{2D}}{\delta}}, \tag{11}$$

and hence,

$$\bar{\beta}_{2D} = -\frac{\delta}{\omega}\log(\varepsilon). \tag{12}$$

Substitution of Equation 12 in 7 yields

$$\bar{r} = -\frac{\sqrt{\pi}}{4}\left(1 + \frac{\pi}{2\log(\varepsilon)}\right)\omega \quad \text{for } e^{-\pi/2} \le \varepsilon < 1 \tag{13}$$

the lower limit of the applicable range of ε being approximately 0.2. The mean pore radius as given by Equation 13 is plotted in units of fibre width in Fig. 2. Noting that the function is very sensitive as $\varepsilon \to 1$, we observe that for ε greater than 0.993, the mean pore radius is more than 100 fibre widths. Since the aspect ratio of most natural fibres is of order 50 to 200, then we may consider Equation 13 to be yielding estimates of the mean pore radius of the right order of magnitude.

3. Multiplanar structures

Consider a layered structure of circular voids with gamma distributed radii. The probability density function and cumulative distribution function for pore radii in a single layer are given by,

$$f(r) = \frac{b^k}{\Gamma(k)} r^{k-1} e^{-br}, \tag{14}$$

$$g(r) = 1 - \frac{\Gamma(k, br)}{\Gamma(k)}, \tag{15}$$

where $\Gamma(a, z)$ is the incomplete gamma function. The distribution given by Equations 14 and 15 has mean, $\bar{r} = k/b$; variance, $\sigma^2(r) = k/b^2$ and coefficient of variation, $CV(r) = 1/\sqrt{k}$.

A second layer with an independent and identical distribution of pore radii is placed over the first layer such that the centres of pairs of voids in the two layers are aligned. For such a structure, we assign to each pair of pores the radius of the smaller pore such that we consider effectively the radii of pore bottlenecks. The probability density of radii of pore bottlenecks is given by,

$$\begin{aligned} f(r, 2) &= 2(1 - g(r)) f(r), \\ &= 2\frac{\Gamma(k, br)}{\Gamma(k)} f(r). \end{aligned} \tag{16}$$

The cumulative distribution function for two layers is

$$g(r, 2) = 1 - \frac{\Gamma(k, br)^2}{\Gamma(k)^2}, \tag{17}$$

Applying the same notation, the addition of further layers gives us

$$f(r, 3) = 3(1 - g(r, 2)) f(r) = 3\left(\frac{\Gamma(k, br)}{\Gamma(k)}\right)^2 f(r)$$

$$g(r, 3) = 1 - \frac{\Gamma(k, br)^3}{\Gamma(k)^3},$$

$$f(r, 4) = 4(1 - g(r, 3)) f(r) = 4\left(\frac{\Gamma(k, br)}{\Gamma(k)}\right)^3 f(r),$$

$$g(r, 4) = 1 - \frac{\Gamma(k, br)^4}{\Gamma(k)^4},$$

etc. So, for a structure composed of n layers we have the general expressions for the probability density and cumulative distribution functions of pore radii respectively:

$$f(r, n) = n\left(\frac{\Gamma(k, br)}{\Gamma(k)}\right)^{n-1} f(r), \tag{18}$$

$$g(r, n) = 1 - \left(\frac{\Gamma(k, br)}{\Gamma(k)}\right)^n. \tag{19}$$

4. Tortuosity

Now, the void structure of stochastic fibre networks is highly interconnected and tortuous. The tortuosity, τ of a given path through a stochastic porous medium is given by the reciprocal of the porosity [17], i.e., $\tau = 1/\varepsilon$. We account for tortuosity by considering the void structure to be isotropic in three-dimensions. As the path through a network becomes more tortuous, so the probability of bottlenecks increases; accordingly, the number of layers is weighted to increase the probability of bottlenecks such that $n \mapsto n/\varepsilon$. So, accounting for tortuosity, the probability density and cumulative distribution functions of pore radii are given by,

$$f(r, n, \varepsilon) = \frac{n}{\varepsilon}\left(\frac{\Gamma(k, br)}{\Gamma(k)}\right)^{\frac{n}{\varepsilon}-1} f(r) \qquad (20)$$

$$g(r, n, \varepsilon) = 1 - \left(\frac{\Gamma(k, br)}{\Gamma(k)}\right)^{\frac{n}{\varepsilon}}, \qquad (21)$$

respectively. The mean and variance of pore radii for a structure consisting of n layers are determined by,

$$\overline{r_n} = \int_0^\infty r f(r, n, \varepsilon) \,.\, \mathrm{d}r$$

$$\sigma^2(r_n) = \int_0^\infty r^2 f(r, n, \varepsilon) \,.\, \mathrm{d}r - \overline{r_n}^2$$

respectively, where the integrals must be determined by numerical methods.

An analytic solution is possible for the special case where $k = 1$, when the probability density of pore radii in a single layer is negative exponential. This persists to multiplanar structures such that

$$f(r, n, \varepsilon) = \frac{bn}{\varepsilon} \mathrm{e}^{-\frac{bn}{\varepsilon}}, \qquad (22)$$

and the mean and standard deviation of pore radii are equal and given by $\varepsilon/(bn)$. Note that when $k = 1$ parameter b is given by the reciprocal of the mean pore radius in a two-dimensional structure. Accordingly, for negative exponential pore radii, the mean pore radius of a multiplanar structure is given by that of a two-dimensional network multiplied by the factor ε/n.

5. Outputs

We illustrate the application of the model by considering the pore size distribution of multiplanar structures formed from fibres of width 30 μm and linear density 1.8×10^{-4} gm^{-1}, these values being typical of a softwood fibre. For small changes in the coefficient of variation of pore radii in one layer we assume that the mean pore radius is the same as that determined by Equation 7 for random networks.

The effect of changing areal density is modelled by increasing the number of layers in the network from 1 to 50 for structures formed from layers with porosity 0.7 such that the areal density of a layer, as given by Equation 12 was 2.14 gm^{-2}. Computations have been carried out for such structures with coefficient of variation of pore radii in a single layer, $CV(r, 1) = 0.6, \sqrt{16 - \pi^2}/\pi$ and 0.9 such that we consider the random case, i.e., $CV(r, 1) = \sqrt{16 - \pi^2}/\pi \approx 0.788$, and structures that are more and less uniform. The coefficient of variation of pore radii defines parameter k for our calculations and, given k we compute b such that $k/b = \bar{r}$ as given by Equation 7. Results are shown in Fig. 3 where the broken line represents the theoretical relationship given by Corte and Lloyd [5] for two-dimensional random networks. We observe that the standard deviation of pore radii is proportional to the mean with an intercept close to the origin and this agrees

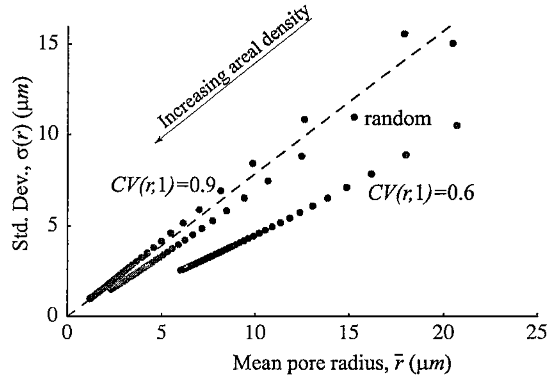

Figure 3 Standard deviation of pore radii plotted against mean pore radius for changes in mean areal density.

with experimental observation [13, 18]. The gradient of this proportionality is sensitive to the uniformity of a single layer.

The effect of changing porosity has been determined for networks of fibres with the same morphology considered above. The mean areal density of single layer was determined using Equation 12 for $0.25 \leq \varepsilon \leq 0.9$ for increments of porosity of 0.05 and the number of such layers was allowed to vary such the mean areal density of the network was constant at 60 gm^{-2}. Data are shown in Fig. 4 and again we observe that the standard deviation of pore radii is proportional to the mean with intercept close to the origin.

Since the model is showing the standard deviation of pore radii to be closely bound to the mean pore radius, in what follows the effect of variables on the pore size distribution is discussed in terms of the mean pore radius only.

The influence of fibre width on the mean pore radius is shown in Fig. 5 for multiplanar networks of mean areal density 60 gm^{-2} and porosity $\varepsilon = 0.7$ formed from fibres of linear density $\delta = 2 \times 10^{-4}$ gm^{-1}. Curves are shown for layers with coefficients of variation of pore radii $CV(r, 1) = 0.6$, 0.788 and 0.9 as discussed above. As observed in Figs 3 and 4 the mean pore radii are smaller for multilayer structures formed from layers with a higher coefficient of variation of pore radii. This is to be expected since, at a given mean pore radius in a layer, a broader distribution of pore radii increases the probability of small pores and hence bottlenecks in

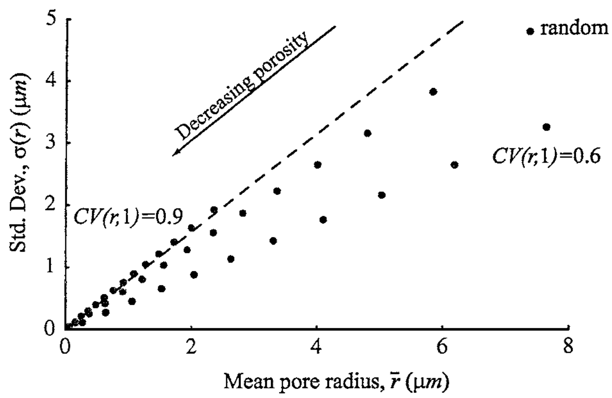

Figure 4 Standard deviation of pore radii plotted against mean pore radius for changes in porosity.

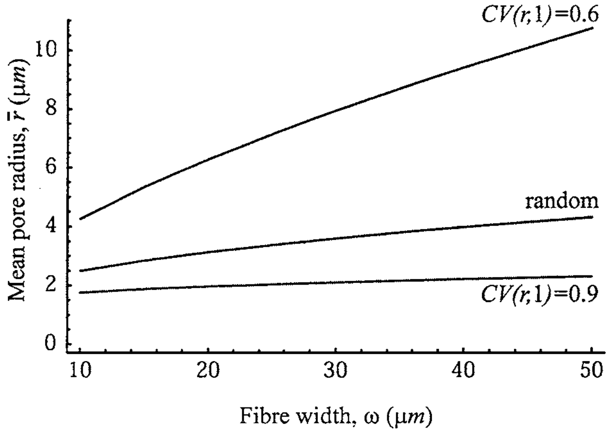

Figure 5 Mean pore radius plotted against fibre width for layers with differing levels of uniformity. Curves plotted for networks of mean areal density 60 gm^{-2} and porosity $\varepsilon = 0.7$ formed from fibres of linear density $\delta = 2 \times 10^{-4}$ gm^{-1}.

the multiplanar structure. The effect of increasing fibre width is to increase the mean pore radius, the effect being greater for more uniform layers, i.e., those with a lower coefficient of variation of pore radii.

Recall that for a two-dimensional structure, Equation 7 shows that increasing fibre width *decreases* pore radius when the areal density of a layer is constant. From Equation 12 we observe however that the areal density of a layer is inversely proportional to fibre width. Accordingly, increasing fibre width reduces the areal density of a layer and hence increases the number of layers required to form a multiplanar structure of given areal density. The net effect of these changes is an increase in mean pore radius with increasing fibre width, as shown in Fig. 5.

The influence of the linear density of fibres on the mean pore radius is shown in Fig. 6 for multiplanar networks of mean areal density 60 gm^{-2} and porosity $\varepsilon = 0.7$ formed from fibres of width $\omega = 30$ μm. Since increasing linear density reduces the number of fibres per unit area required to form a network of given areal density, we observe an increase in the mean pore radius with increasing linear density.

Typically the width and linear density of natural fibres are coupled such that increased linear densities are

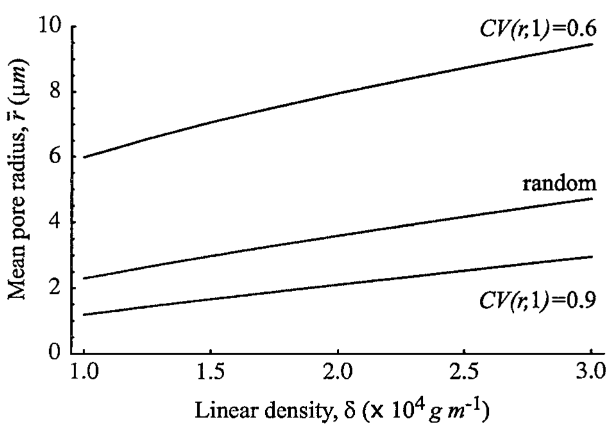

Figure 6 Mean pore radius plotted against fibre linear density for layers with differing levels of uniformity. Curves plotted for networks of mean areal density 60 gm^{-2} and porosity, $\varepsilon = 0.7$ formed from fibres of width, $\omega = 30$ μm.

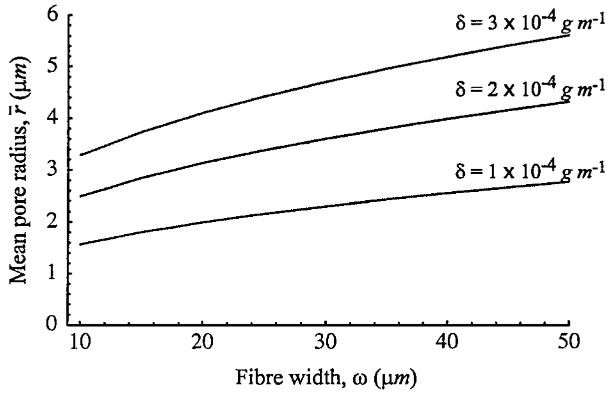

Figure 7 Mean pore radius plotted against fibre width for random layers formed from fibres of different linear density. Curves plotted for networks of mean areal density 60 gm^{-2} and porosity, $\varepsilon = 0.7$.

associated with increased width. Accordingly, the effect of linear density and width are shown together in Fig. 7 for multiplanar structures formed from random layers with mean areal density 60 gm^{-2} and porosity $\varepsilon = 0.7$. For coupled linear density and width we can expect the dependence of mean pore radius on width to be greater than shown by the curves in Fig. 7 and to map a monotonically increasing trajectory within the envelope shown.

6. Real networks

The areal density and porosity of commercially formed near-planar fibre networks such as paper and fibrous filter media are closely controlled during their manufacture to meet product specifications. Such fibre networks are typically formed by collapsing a three-dimensional fibre suspension into a near-planar structure by a continuous filtration-type process. During such processes, there is interaction between the structure that has been formed and the fibres forming subsequent layers [19]. As mentioned previously, the processing of natural fibres prior to papermaking generates a significant mass fraction of fibre fragments and it has recently been shown that these reduce the mean pore radius [15].

In accounting for tortuosity, the void structure of the network has been assumed to be isotropic in three-dimensions. We note the recent work of Huang *et al.* [20] who present measurements of void dimensions in the plane of the network and perpendicular to it demonstrating three dimensional anisotropy in the dimensional characterisation of void space. Recent theory [21], simulation studies [22] and experimental measurements [23] suggest that the pore height, i.e., the pore dimension perpendicular to the plane of the network is described well by the negative exponential distribution. This is important, since the negative exponential distribution is a special case of the gamma distribution as given by Equation 14 with $k = 1$. The pore height distribution is coupled with the mass distribution such that the relationship between the distributions of local average areal density and local average thickness is bivariate Normal [24, 25].

Future work will seek to incorporate the change in pore radius distributions with orientation to the plane of the network to allow for this anisotropy. The applicability of the model to commercially formed fibre networks will be tested against existing data characterising the porosity and pore radius distribution in real networks [13, 15, 25].

7. Conclusions

A model has been presented for the pore radius distribution in near-planar stochastic fibre networks. At a given areal density, the mean pore radius of two-dimensional random networks is shown to decrease with increasing fibre width and to increase with increasing fibre linear density. For structures formed by the superposition of such two-dimensional networks, the standard deviation of pore radii is proportional to the mean for changes in areal density and porosity; the gradient of proportionality being dependent on the uniformity of a layer. At a given porosity, such structures exhibit an increase in mean pore radius with increasing fibre width and linear density.

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