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Flocculation of cellulose fibres: new comparison of crowding factor with percolation and effective-medium theories

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Abstract New comparisons of percolation and effective-medium theories on one hand, and predictions from the crowding factor on the other hand, are described for calculating critical concentrations in suspensions of cellulose fibres. The connectivity threshold from percolation theory appears to correspond to the "gel crowding factor", which occurs at crowding factor (N) of $N = 16$ rather the criterion for fibre collisions, $N = 1$, postulated in earlier work. The rigidity threshold from percolation theory corresponds to the onset of coherent fibre flocs having mechanical network strength, which occurs at about $N = 60$. The latter value exceeds the gel crowding factor value by a factor of 3.75. In comparison, percolation theory predicts that flocculation occurs at a rigidity concentration four times higher than the connectivity threshold. These ratios are in good agreement.

Keywords Cellulose · Fibres · Flocculation · Papermaking · Percolation · Crowding factor

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Introduction

Flocculation of cellulose fibres is a topic of key industrial importance for papermakers. Flocculation of paper fibres is the result of complex interaction between surface moieties of cellulose and flocculants, fillers and electrolytes, but also originates from simple, geometric, fibre entanglement. The latter effect is expected to be the main one controlling flocculation, and is directly related to aspect ratio and concentration of fibres in aqueous suspensions. At constant composition, physico-chemical interactions seem to be only minor effects. It is the aim of this short article to demonstrate the strength of theories based on geometrical factors, either rigorous or empirical, for predicting the behaviour of suspended cellulose fibres.

In recent work, Celzard et al. (2008a) compared the crowding factor with Percolation Theory (PT) and Effective-Medium Theory (EMT) as means of describing flocculation. They concluded that although the crowding factor was a useful practical approach, well-established PT and EMT approaches offered a more rigorous basis for characterizing the suspensions, and in some cases, a more accurate prediction of transition points. The present paper extends these comparisons to recent findings of a "gel crowding factor" for suspensions of fibres having lengths and diameters of typically 1 mm and a few tens of microns, respectively, that can form clusters due to concentration effects only. The use of the "gel crowding factor" that is reported here is shown to be much more suitable for comparing the theories with each other.

Background

As described by Celzard et al. (2005a), PT and EMT have been well developed for some time and are highly efficient for predicting transitions in fibrous networks. It is not the aim of this work to describe these two theories; however, the following may be usefully recalled. PT deals with the transition from a non-connected to connected state often encountered in disordered mixtures. It is based on the onset of an infinite cluster at a critical fraction of one component, i.e., the so-called percolation threshold, and accurately describes the sharp change of a given property in the neighbourhood of the transition (Stauffer 1985). The threshold may be derived from geometrical arguments, especially from the concept of excluded volume, which is the volume around which other similarly shaped objects are not allowed to penetrate (Celzard et al. 1996). In this context, fibres are described by identical, capped, cylinders, of fixed aspect ratio.

Effective medium theory, while much older than PT [historical developments of EMT are reviewed in Landauer (1978)], is also very powerful and suitable for many different systems. Unlike PT, EMT deals with systems in which the ratio of the relevant intrinsic properties of the mixed phases is finite and sometimes low, hence no percolation threshold may occur. Nevertheless, in a number of cases, EMT equations may reduce to that of PT and derive correct values for the percolation threshold. Using EMT, fibres are described by elongated ellipsoids, all having the same aspect ratio but a very wide range of sizes.

Despite the different way the fibres were modelled by one or other theory, similar values of network connectivity threshold could be obtained (Celzard et al. 2008a). They may be written as a function of the aspect ratio A of the fibres (Celzard et al. 2000, 1996; Landau and Lifshitz 1980):

$$\Phi_{c_{\mathrm{EMT}}} = \frac{9L_c(1-L_c)}{2+L_c(15-9L_c)}$$
$$\text{where } L_c = \frac{A^2}{2(1-A^2)^{3/2}}\left[\ln\frac{1+\sqrt{1-A^2}}{1-\sqrt{1-A^2}} - 2\sqrt{1-A^2}\right] \tag{1}$$

$$1-\exp\left\{-\frac{1.4\times\left[\frac{\pi}{4}(A-1)+\frac{\pi}{6}\right]}{\frac{4\pi}{3}+2\pi(A-1)+\frac{\pi}{2}(A-1)^2}\right\} \leq \Phi_{c_{\mathrm{PT}}} \leq 1-\exp\left\{-\frac{2.8\times\left[\frac{\pi}{4}(A-1)+\frac{\pi}{6}\right]}{\frac{4\pi}{3}+2\pi(A-1)+\frac{\pi}{2}(A-1)^2}\right\}. \tag{2}$$

From these data, and based on mechanics of inter-particle contacts, it could be predicted that flocculation occurred at a higher critical point; such rigidity threshold was shown to be four times the value of the connectivity one (Celzard et al. 2001, 2008a and references therein):

$$\Phi_{r_{\mathrm{EMT}}} = 4\Phi_{c_{\mathrm{EMT}}}; \qquad \Phi_{r_{\mathrm{PT}}} = 4\Phi_{c_{\mathrm{PT}}} \tag{3}$$

The crowding factor, N, was derived for wood pulp fibres as an extension of Mason's early criterion for occasional fibre collisions [$N = 1$, (Mason 1954)]. According to its authors, the crowding factor is "defined as the number of fibres in a spherical volume of diameter equal to the length of a fibre" (Kerekes and Schell 1992); N depends on both the concentration of the fibres and their squared aspect ratio. The crowding number encompasses the wide range of behaviour of interest in papermaking, from $N = 1$ for occasional fibre collisions to $N = 60$ which represents 3-point contact. At $N = 60$, coherent flocs form having mechanical strength created by elastic bending forces (Kerekes and Schell 1992; Soszynski and Kerekes 1988). The rigidity threshold based on crowding factor (CF) thus reads:

$$\Phi_{r_{\mathrm{CF}}} = \frac{N}{(2/3)A^2} = \frac{90}{A^2}. \tag{4}$$

The crowding factor, being based on number of fibres rather than volume of fibres, is particularly useful for pulp fibres. Prior to papermaking, pulp fibres are typically subjected to mechanical processing which may affect their diameters to an unknown degree.

New comparison

In their recent work, Celzard et al. (2008a) compared PT, EMT, and crowding factor for predicting connectivity and flocculation thresholds. For that purpose, the system of suspended fibres was assumed to undergo a transition from non-connected to connected but "floppy" state at $N = 1$. They also compared the threshold at which fibres form a rigid network to $N = 60$. They found that although the rigidity threshold was well represented by $N = 60$, the connectivity threshold was not well represented by $N = 1$. The crowding factor was thus suggested to be, despite its empirical nature, a good tool for predicting flocculation only, whereas connectivity was poorly accounted for. The superiority of PT and EMT was hence demonstrated.

These conclusions should be modified. The criterion $N = 1$ represents one fibre in the volume swept out by the length of a single fibre, a value corresponding to occasional collisions among fibres. However, this level is smaller than that required for "connectivity", which, intuitively, should be at least 2 contacts per fibre. A number of approaches are available to characterize this higher level of contact in the behaviour of rod-like particles in flowing systems (Kerekes 2006). Of relevance to this paper is the observation of Keep and Pecora (1985) that restraint of rotation in a fibre suspension begins in the range $10 < N < 25$. Even more pertinent, Martinez et al. (2001, 2003) identified a "gel crowding factor" at $N = 16$ at which fibre suspension behaviour changes from essentially dilute behaviour to behaviour in which fibres interact significantly, but do not become immobilized as they do at $N = 60$. Thus, $N = 16$ would seem to be a more appropriate criterion of connectivity than $N = 1$. The "gel" indeed represents an incipient continuous phase, for which connectivity exists but mechanical strength has not yet developed. In other words, the connectivity threshold would read:

$$\Phi_{\mathrm{CCF}} = \frac{N}{(2/3)A^2} = \frac{24}{A^2}. \tag{5}$$

Moreover, such a critical value of the crowding factor is consistent with the finding that, in suspensions of increasing concentrations, rigidity occurs at a concentration theoretically four times that at which the connectivity first appeared (Celzard et al. 2001, 2005b, 2008b). In the present case, $16 \times 4 = 64$ approximates this criterion very well. Comparisons of the connectivity and rigidity (i.e., flocculation) thresholds calculated for $N = 16$ and $N = 60$, respectively, with those derived from PT and EMT are shown in Figs. 1 and 2. As is evident, the agreement is reasonably good.

Concerning the connectivity threshold, the agreement between prediction from the crowding factor and PT and EMT is the best for volume concentrations lower than 7 and 2%, respectively (see Fig. 1a). In other words, the critical concentration such that an infinite cluster of cellulose fibres is formed is best predicted, whatever the method, when the aspect ratio of the fibres is higher than 20 (see Fig. 1b).

Concerning the flocculation threshold, the crowding factor leads to results close to those of PT and EMT for volume concentrations lower than 30 and 10%, respectively (see Fig. 2a). The corresponding aspect ratios for which the agreement between the different methods is the highest are, again, higher than 20 (see Fig. 2b). Kerekes and Schell (1992) found that coherent flocs of mechanical strength did not form at aspect ratios less than 20 for any value of N tested in their experiments. Moreover, their expression linking crowding factor to number of contacts per fibre is not valid for the small aspect ratios and numbers of contacts per fibre likely in this range (Kerekes and Schell 1992). Thus, these results are to be expected.

From Figs. 1 and 2 it may also be concluded that, whereas the agreement between PT and EMT is excellent at low aspect ratios, the comparison is much better between EMT and prediction from the crowding factor at high aspect ratios, for which the calculated critical points tend to become identical. Such observation might be explained by the fact that EMT considers a broad distribution of fibre sizes (whereas PT only deals with strictly similar rods). Although such polydispersity does not match what is really found in suspensions of cellulose fibres, for which a distribution of aspect ratios is expected instead, EMT should better describes the real suspensions that does PT. These findings thus demonstrate the usefulness of the crowding factor for predicting one or the other critical transition point in suspensions of wood pulp fibres, for which typical aspect ratios range from 10 to 100. Moreover, according to Fig. 2, lower aspect ratios clearly lead to non-physical results, since neither connectivity nor

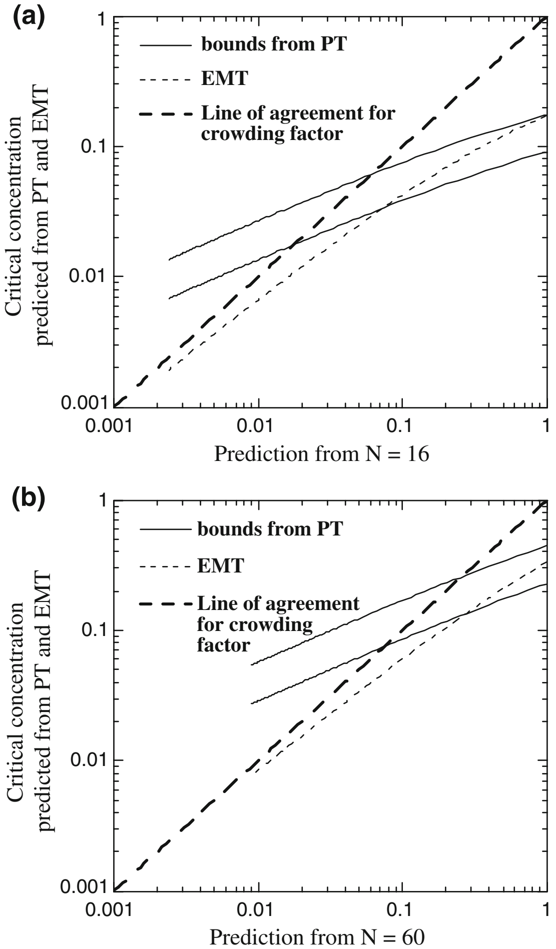

Fig. 1 Critical concentrations calculated from PT and EMT plotted as a function of those derived from the crowding factor: **a** Connectivity threshold, and **b** Rigidity (or flocculation) threshold. Both thresholds are expressed in volume fraction

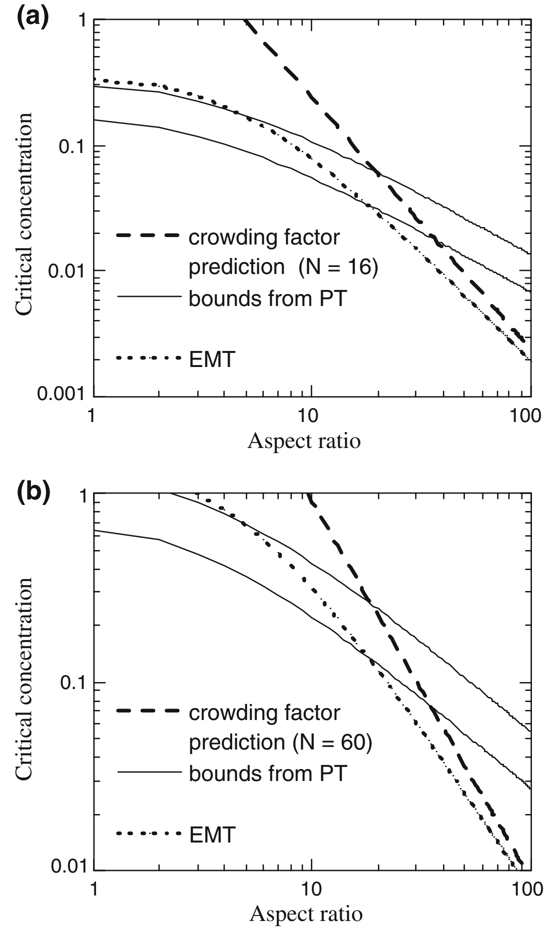

Fig. 2 Critical concentrations (volume fraction) calculated from PT, EMT and predictions from the crowding factor, plotted as a function of the aspect ratio of the fibres: **a** Connectivity threshold, and **b** Rigidity (or flocculation) threshold

flocculation would occur, even at very high concentrations. Predictions from the crowding factor are consequently valid at sufficiently high aspect ratios, provided that the suitable values for connectivity and flocculation, $N = 16$ and $N = 60$ respectively, are used.

Summary and conclusions

This paper has shown that the earlier comparison of Percolation and Effective Medium Theories with crowding factor should have used $N = 16$ instead of $N = 1$ as the criterion for connectivity. In doing so, predictions of threshold conditions for connectivity and rigidity of fibre suspensions using the crowding factor are in good agreement with ones predicted from PT and EMT. The crowding factor has some advantages for pulp fibres in that it can be calculated from mass concentrations and thereby avoid uncertainties in diameter caused by processing in papermaking. On the other hand, PT and EMT have a more rigorous basis and can be extended to account for factors beyond contacts. The empirical crowding factor, within the range of usual wood pulp fibres' diameters and aspect ratios, is thus extremely useful and much easier to use than theories derived from physics of disordered systems.

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