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Letter to Editor of "Carbohydrate Polymers" – Comments on a recent paper by Wang and Li ☆

We wish to point out that comments in the recent article by Wang and Li in this journal (Wang & Li, 2005) repeat a common misconception regarding so-called critical exponents, and the concentration dependence of gel modulus. The object of the present letter is to elucidate some of these issues.

According to the paper of Wang and Li, the concentration dependence of the modulus of a polymer gel follows directly from the critical behaviour described by percolation theory. The percolation model suggests that, in general, the behaviour of a specific property P of any critical system, in this case a gel, can be written as:

$$P \propto \left(\frac{p}{p_c} - 1\right)^{\varepsilon} \tag{1}$$

Here, for a gel, p_c represents the critical "degree of conversion" (or gel point), p is the actual conversion and ε is the "critical exponent".

This is in no way contentious; gel percolation theory is a general case of the classical Flory–Stockmayer gelation model, which, in turn, can be regarded simply as percolation on a tree-like or Bethe lattice (de Gennes, 1979; Gordon & Ross-Murphy, 1975; Stauffer, 1985; Stauffer, Coniglio, & Adam, 1982). Many properties can indeed be related back directly to the ratio p/p_c, although very close to p/p_c critical fluctuations need to be taken into account. The extent of this critical region and the real validity of the critical regime are, however, governed by precise criteria such as that of Ginzburg. While evaluation of the extent of the critical domain remains the realm of the theorist, a practical guide, quoted directly from the excellent review by Stauffer, Coniglio and Adam (Stauffer et al., 1982), is that the gel critical regime applies only *within* the region where $10^{-2} \leqslant (p/p_c) - 1 \leqslant 10^{-1}$.

Moreover, and just as importantly from the present perspective, the use of C as an appropriate scaling parameter is incorrect. In a chemical step-growth system, the basic paradigm for a gelling system, (Flory, 1953; Gordon & Ross-Murphy, 1975; Ross-Murphy, 2005) what is generally monitored is the disappearance of reactants, or equivalently, the appearance of product. It then becomes straightforward to relate p to chemical kinetics, using an appropriate kinetic order equation. However, as the present author has already suggested, this means that some degree of selectivity needs to be applied before assuming that any arbitrary measurable can be substituted for the p (and p_c) in Eq. (1) (Ross-Murphy, 2007).

This means that it is inappropriate to assert *a priori* that *any* particular property or variable can be employed. Indeed in any "chemical system" such as the physical gelation of methylcellulose, there will be some kinetic relationship between concentration and time, and the "reaction order" must be positive, if the system is to gel. It can be shown quite straightforwardly that simply substituting say polymer concentration, C, for p in Eq. (1) and assuming that a critical exponent has been obtained, is not allowed; full details are given elsewhere (Ross-Murphy, 2005, 2007).

Even if, despite these arguments, we assume C can still be substituted for p, a further factor needs to be considered, because the value of the "critical" exponent is very sensitive to the regime in which it is measured. As we have noted above, the critical regime applies only within the region where $10^{-2} \leqslant (p/p_c) - 1 \leqslant 10^{-1}$. However, clearly in the article of Li and Wang the range of (p/p_c) addressed, approximately. $0.1 > (p/p_c) - 1 > 2$, lies entirely outside the required Ginzburg region. Under these circumstances, any apparent similarity between the measured slope (exponent) and predicted "critical exponents" is illusory. Of course there is nothing novel, of itself in this assertion, indeed the paper by Gordon and Torkington, published more than 25 years ago, made almost the same point (Gordon & Torkington, 1981).

However it has clearly not been appreciated, because sadly the present author continues regularly to have sent to referee papers in which, say, a series of measurements have been made on biopolymer gels, at a range of concentrations. By plotting measured gel modulus versus scaled time or concentration the authors obtain an exponent of say ~2–3 and claim this to be a critical exponent, in conformity with the predictions of percolation theory.

This conclusion is also incorrect. Indeed it has been known for many years now that plotting $\log G$ versus $\log C$, or $\log(C/C_0)$ does not give a single exponent (or even two as in the paper of Wang and Li) but a continuous curve with limit exponents of ∞ very close to the gel point, and

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☆ Wang, Q. Q., & Li, L. (2005). Effects of molecular weight on thermoreversible gelation and gel elasticity of methylcellulose in aqueous solution. *Carbohydrate Polymers, 63*, 232–238.

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$\sim$1.5–2 at very large values of C/C_0. The arguments for this were given, for example, in the article by Clark A. H. and the present author (Clark & Ross-Murphy, 1987), and elsewhere (Clark, 1993; Kavanagh & Ross-Murphy, 1998).

Incidentally, the above comments do not alter the main contentions of the above paper (Wang & Li, 2005), with most of which this author is in agreement. Indeed it is fair to say that all the significant conclusions reached appear quite independent of these assumptions.

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