A comparison of two theoretical analyses of the elastodynamics of poly(vinyl alcohol) hydrogels

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In two recent publications, Brillouin scattering measurements of the hypersonic velocity and attenuation in poly(vinyl alcohol) (PVA) hydrogels were analysed using two different theoretical models. These are the theories of Marqusee and Deutch for Brillouin scattering from gels and of Johnson for the elastodynamics of gels. In this work we take an overview of our previous results and also present new results particularly regarding a pair of important gel parameters. These new aspects enable us to compare critically the results obtained from the two theories and to comment on the suitability of the models to Brillouin scattering from PVA hydrogels.

(Keywords: Brillouin light scattering; hypersonic waves; poly(vinyl alcohol) hydrogels; gel theory)

INTRODUCTION

In two recent papers[1,2] experimental data for the hypersonic velocity and attenuation of longitudinal sound waves in poly(vinyl alcohol) (PVA) hydrogels have been analysed carefully with two different theoretical models for gels. In the first of these articles[1] we described experimental measurements of the dependence on gel network volume fraction ϕ of the Brillouin shift and width of PVA hydrogels. The gels were prepared by irradiating, with ^{60}Co γ-rays, aqueous solutions of PVA powder. The volume fraction ϕ was varied between about 0.1 (fully swollen) and 1.0 (fully dehydrated) by controlled evaporation of water[1]. The Brillouin spectra were analysed using the theory by Marqusee and Deutch[3] (MD) for Brillouin light scattering from longitudinal waves in gels. This theory is based on the similarity expected between the frictional properties of an entangled concentrated polymer solution[4] and those of a gel in which the polymer fibres are crosslinked. In the second paper[2] we analysed essentially the same experimental data as in ref. 1 but using the theory by D. L. Johnson[5] (DJ) for the elastodynamics of gels. This theory exploits the fact that a gel, consisting of a relatively immobile polymer network pervaded throughout by a fluid, has acoustic properties related to those of the other fluid-filled porous media as investigated by Biot[6]. The DJ model contains rather fewer approximations and restrictive assumptions than the MD model and in fact has been applied to other systems besides gels[7].

In this work we not only re-examine in a different light the results of our previous analyses but also present results of new calculations. To enable a critical comparison of the two theories, the outcomes of these calculations are cast in terms of the same two fundamental gel parameters, namely the speed of sound in the network, c_n, and the frictional damping, f. From such new aspects we are able to comment on the appropriateness or otherwise of the models to the situation in PVA hydrogels.

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SUMMARY OF THE PREDICTIONS OF THE THEORIES

Both theories give lengthy expressions, which we will not reproduce here, for the ϕ dependence of the hypersonic velocity (or equivalently the Brillouin shift) and the absorption coefficient (or Brillouin width) for longitudinal waves in gels. Although these expressions are fairly different in detail, fitting them to our experimental measurements reveals that for both models there are essentially only two important adjustable parameters. In the case of the velocity the adjustable parameter is effectively $c_n(\phi)$, the speed of sound in the network in the MD model[3]. This is related to the polymer network bulk and shear moduli, $K_b(\phi)$ and $N(\phi)$, of the DJ model[5] by

$$c_n(\phi)=\left(\frac{K_b(\phi)+\frac{4}{3}N(\phi)}{\phi\rho_s}\right)^{1/2} \quad (1)$$

where ρ_s is the density of the network solid (1269 kg m^{-3} for PVA). For the absorption coefficient the adjustable parameter is effectively $f(\phi)$, the frictional damping between the network and the fluid in the MD model. This is related to the permeability of the reticular channels, $k(\phi)$, in the DJ model and the fluid viscosity η by[5]

$$f(\phi)=(1-\phi)^2\eta/k(\phi) \quad (2)$$

Since the pore fluid in PVA hydrogels is water[2] then $\eta\simeq 10^{-3}$ kg m^{-1} s^{-1}. Equations (1) and (2) provide the required links between the parameters of the MD and DJ models. In the present work we express all our results in terms of the two fundamental parameters c_n and f.

In the case of the speed of sound, both theories describe the predicted behaviour of sound wave propagation in essentially two extremes: that of small frictional damping f and that of strong friction. In the DJ model these extremes are introduced via Biot's high- and low-frequency limits[6]: $v\gg v_c$ and $v\ll v_c$. The crossover from the

latter extreme to the former occurs when the viscous skin depth, $\delta=(\eta/\pi\rho_f\nu)^{1/2}$, of waves of frequency ν exceeds the average width, r, of the reticular channels through which must flow the fluid of density ρ_f (10^{-3} kg m^{-3} for PVA hydrogel). This defines the crossover frequency[2,5]

$$\nu_c=\eta/\pi\rho_f r^2 \tag{3}$$

The geometry of the real reticular channels is not known, but is probably very convolute. In order to fix things we may use the formula for the permeability of cylindrical tubes of radius r[5,6]

$$k(\phi)=(1-\phi)r^2(\phi)/8 \tag{4}$$

provided it is realized that $r(\phi)$ is then only an effective radius which, because of tortuosity, is likely to be somewhat smaller than the true characteristic pore size. Hence from equations (2), (3) and (4) the frictional parameter f of the MD model is related to the crossover frequency ν_c of the DJ model by

$$f(\phi)=8\pi\rho_f(1-\phi)\nu_c(\phi) \tag{5}$$

Thus we obtain the result that the high- (low-) frequency limit in the DJ model is equivalent to the low- (high-) frictional-damping limit in the MD model.

In the high-frequency (small f) limit both theories predict the existence of two longitudinal waves—a 'slow' and a 'fast' wave[5]—which are related to the unperturbed waves in the fluid and the network. In the opposite extreme of low frequency (large f) both theories predict the observation of a single 'fast' longitudinal wave which describes the response of the averaged elastic medium. In both theoretical studies the latter limit is preferred for describing the situation in a gel[3,5], although expressions are given for the velocity in both limits[3,5,7]. Our own Brillouin scattering measurements show the existence of only a single wave in the PVA hydrogel system[1], implying that the low-frequency limit is indeed the most appropriate. However, this is by no means conclusive proof of the correct choice of frequency limit because there are circumstances in which a slow wave may be unobservable even at high frequencies[2,7]. As we have pointed out[2], unlike the situation for ultrasonic measurements on gels where the frequency is indeed fairly low, Brillouin scattering experiments are performed at quite high frequencies and so there is some doubt about which limit of the theories, if any, is truly applicable. This is primarily because the pore size r is not known *a priori* for a PVA hydrogel and so the crossover frequency ν_c cannot be predetermined. This point is raised again later.

In the case of the absorption coefficient, both theoretical studies include the effects of damping due to intrinsic attenuation in the fluid and that due to the relative motion of the fluid against the network but neglect the attenuation within the fibres of the polymeric framework itself. Marqusee and Deutch (MD) consider specifically the case of Brillouin light scattering in gels and give expressions for the absorption coefficient in both the small and large f limits[3]. However, the Johnson (DJ) model is aimed more at ultrasonic studies of gels and an expression is given for the absorption coefficient in only the large f limit[5].

In the MD model there is a further adjustable parameter λ, where $0\leqslant\lambda<1$, which is intended to describe the degree of coupling between the elastic waves in the fluid and network[3]. Maximum coupling occurs for $\lambda\rightarrow1$ and minimum coupling for $\lambda\rightarrow0$. However, Johnson[5] has pointed out that the equations of motion of the MD model are equivalent to his own in the approximation that the gel parameters are replaced by their values at low ϕ (dilute concentrations) and that the network fibres are incompressible. From this comparison Johnson has noted that λ is not then a truly free parameter.

RESULTS OF ANALYSIS USING THE TWO THEORIES

The MD model

In our first paper[1] experimental measurements on a PVA hydrogel as a function of ϕ were analysed within the framework of the MD model. We used the expressions appropriate to the case of strong friction f and obtained two sets of results for the two extremes of coupling, $\lambda\rightarrow0$ and $\lambda\rightarrow1$. The general behaviour of the results for $c_n^{MD}(\phi,\lambda=0)$, $c_n^{MD}(\phi,\lambda=1)$, $f^{MD}(\phi,\lambda=0)$ and $f^{MD}(\phi,\lambda=1)$ is displayed as the broken curves in *Figures 1* and *2*. We were not able to provide any physical basis for this behaviour. Furthermore, since there was no obvious way of determining $\lambda(\phi)$ independently, then within the context of the MD model the 'actual' dependences for c_n^{MD} and f^{MD} may vary anywhere within the areas bounded by the respective curves. To compound this rather unsatisfactory situation further, it was found that the values for f^{MD} were too small to meet the requirement that it be 'strong'. This latter fact suggests that, contrary to theoretical guidance, the opposite extreme of small f (or high frequency) may be more appropriate for our measurements on the PVA hydrogel system. Although this possibility was investigated more carefully in the second of our studies[2], we have recently carried out a similar analysis using the MD model in the small f limit. The values thus obtained for c_n lie fairly close to those already plotted in *Figure 1*. However, the corresponding values taken by f are roughly an order of magnitude

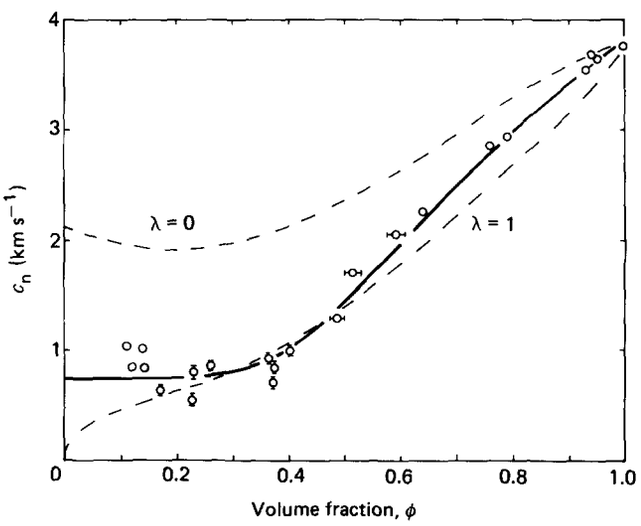

Figure 1 Behaviour of the speed of sound in the network, c_n, as a function of gel network volume fraction, as calculated from the experimental measurements using the two theories. The broken curves are the dependences obtained from the MD model in the limits $\lambda=0$ and $\lambda=1$. The bold full curve is a fit of equation (6) to the data obtained using the DJ model (○)

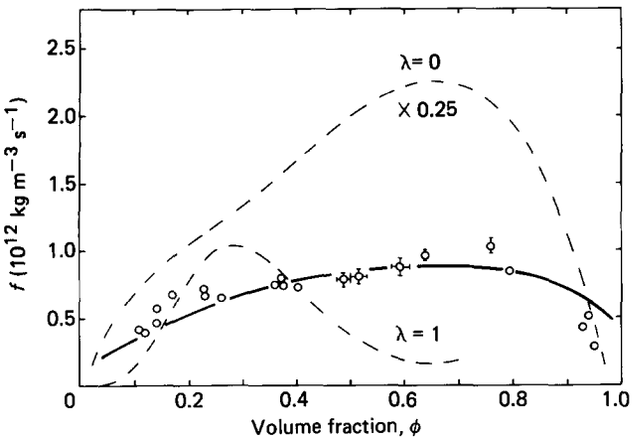

Figure 2 Behaviour of the frictional damping parameter f as a function of gel network volume fraction, as calculated from the experimental measurements using the two theories. The broken curves are the dependences obtained from the MD model in the limits $\lambda = 0$ and $\lambda = 1$. The data for $\lambda = 0$ have been reduced by factor of 0.25. The open circles (○) represent the data calculated from the DJ model. The bold full curve is derived from a fit of equation (8) to the permeability data

larger than those shown in *Figure 2*. In fact this again turns out to be inconsistent with the initial assumptions of the model, this time that f be 'small'. Therefore we may conclude that for our measurements on the PVA hydrogel system it is not possible to obtain a set of values for f consistent with either of the two suggested approximations in the MD model.

The DJ model

In our more recent paper[2] the experimental data were fitted with the DJ model to obtain the network moduli $K_b(\phi)+\frac{4}{3}N(\phi)$ from the velocity measurements and the permeability $k(\phi)$ from the absorption coefficient measurements. The results for $K_b+\frac{4}{3}N$ were found to be remarkably insensitive to which extreme of frequency (or equivalently friction) of the theory was employed. Moreover, we were not able to obtain unambiguous values for the 'tortuosity parameter' α[5,7] because the calculated values of the speed of sound also proved fairly insensitive to what values were chosen for this parameter ranging from unity to infinity[2]. The results for $k(\phi)$ were obtained using only the low-frequency (large f) approximation. From the values obtained for $K_b(\phi)+\frac{4}{3}N(\phi)$ and $k(\phi)$ we can calculate from equations (1) and (2) the dependences of $c_n^{DJ}(\phi)$ and $f^{DJ}(\phi)$ in the DJ model. The results of these calculations are displayed as data points in *Figures 1* and *2*. The error bars originate, in the case of c_n^{DJ}, mainly from the uncertainty in the choice for the Poisson ratio which is not known for the PVA hydrogel system[2]. For f^{DJ} the error bars arise primarily from experimental uncertainties[1,2].

In analysing the data for $K_b+\frac{4}{3}N$ it was found[2] that the system crossed over from a 'weak frame' for $\phi \lesssim 0.3$ to a 'stiff frame' for larger ϕ. This behaviour was well described by the following phenomenological expression:

$$K_b(\phi)+\tfrac{4}{3}N(\phi)=K_0\phi+(\tfrac{3}{2}K_s-K_0)\exp[D(1-\phi^{-1})] \quad (6)$$

where $K_0 \simeq 7.6\times10^8\ \mathrm{N\,m^{-2}}$, $D \simeq 2.9$ and the bulk modulus of the solid $K_s \simeq 1.22\times10^{10}\ \mathrm{N\,m^{-2}}$. The equivalent behaviour for c_n^{DJ} from equations (1) and (6) is shown as a bold full curve in *Figure 1*. It is clear from equation (6) that for small ϕ, $K_b(\phi)+\frac{4}{3}N(\phi) \simeq K_0\phi$ and so $c_n^{DJ}(\phi) \simeq (K_0/\rho_s)^{1/2}$. This is evident from *Figure 1* in that c_n^{DJ} remains roughly constant (at $\sim 774\ \mathrm{m\,s^{-1}}$) for $\phi \lesssim 0.3$. However, for large ϕ it is possible to show from equation (6) that $K_b(\phi)+\frac{4}{3}N(\phi) \simeq \frac{3}{2}K_s\phi^D$ and so $c_n^{DJ}(\phi) \simeq \phi^{(D-1)/2}(3K_s/2\rho_s)^{1/2}$. Since $D \simeq 3$ then $c_n^{DJ}(\phi) \simeq 3800\phi$ for large ϕ. Again this limiting linear behaviour for c_n^{DJ} is evident from *Figure 1*.

The volume of the pore spaces is proportional to $(\phi^{-1}-1)$ but is also approximately proportional to r^3. With this straightforward assumption, the average pore size shrinks with increasing ϕ as

$$r=R_0(\phi^{-1}-1)^{1/3} \quad (7)$$

Thus from the crude model, equation (4), we obtain for the permeability:

$$k(\phi) \simeq \tfrac{1}{8}R_0^2(1-\phi)^{5/3}\phi^{-2/3} \quad (8)$$

The data for $k(\phi)$ were found[2] to be well described by this simple expression with $R_0 \simeq 680$ Å. The behaviour for f resulting from combining equations (2) and (8) is:

$$f^{DJ}(\phi) \simeq 8\eta\phi^{2/3}(1-\phi)^{1/3}/R_0^2 \quad (9)$$

The bold full curve in *Figure 2* shows this dependence, from which it may be seen that the qualitative features of $f(\phi)$ are well explained not only for the DJ model but also incidentally for the MD model with $\lambda = 0$. However, the values for f^{DJ} are unfortunately too small to satisfy the criterion assumed in their derivation, namely that f be 'large'. Equivalently, one can also say that the resulting crossover frequency $\nu_c(\phi)$ is too small. The calculations of ν_c from the data for $f(\phi)$ and equations (5) are shown in *Figure 3* together with the behaviour given by combining equations (3) and (7):

$$\nu_c(\phi) \simeq \eta\phi^{2/3}/[\pi R_0^2\rho_f(1-\phi)^{2/3}] \quad (10)$$

From this it may be seen that ν_c increases from about 0.02 GHz at $\phi \simeq 0.1$ to about 0.3 GHz at $\phi \simeq 0.9$. Hence the low-frequency approximation $\nu \ll \nu_c$ cannot be satisfied for our Brillouin frequencies lying between about

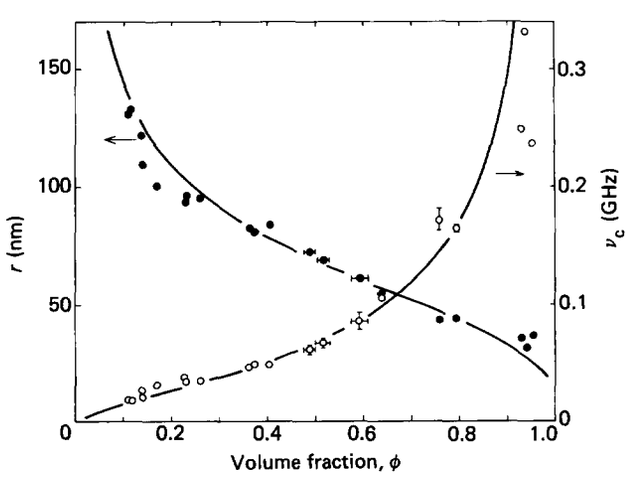

Figure 3 Behaviour of the average effective pore size r (●) and the crossover frequency ν_c (○) as functions of gel network fraction, as calculated from the DJ model. The bold full curves show the descriptions for r and ν_c given by equations (7) and (10) respectively

5 and 15 GHz[1]. This situation is very similar to that found in the analysis using the MD model and again the implication is that we should try to analyse the data using the opposite extreme of the DJ model, namely high frequencies (or small f). Although such an analysis revealed, as mentioned above, virtually no change in the values for $K_b+\frac{4}{3}N$ (and hence c_n^{DJ}) it was not possible to calculate f^{DJ} because explicit expressions for the absorption coefficient in the high-frequency limit are not available.

DISCUSSION

A feature common to both the MD and DJ models is that the results obtained for c_n are quite insensitive to which frictional (or frequency) extreme of the theories is employed. Therefore, one might tentatively conclude that the values obtained for c_n are fairly reliable within the context of the respective theories. However, the ambiguity over the choice for λ in the MD model is very unsatisfactory. This is manifest in *Figure 2* for the two limits of λ which give rise to quite different sets of values for f^{MD}, neither of which agree particularly well with f^{DJ}. Furthermore, since Johnson[5] asserts that the MD model describes gel behaviour only in the limits of small ϕ and $K_s\rightarrow\infty$, then the apparent rough agreement between c_n^{MD} and c_n^{DJ} at large ϕ in the present study should be regarded not as indicating any strong underlying agreement between the theories but merely as fortuitous. Consequently it is difficult to comment further on the results obtained using the MD model.

We demonstrated in the previous section that $K_b+\frac{4}{3}N$, as calculated using the DJ model, is at small ϕ roughly proportional to ϕ but at large ϕ rises roughly as the cube of ϕ. We are not aware of any concrete physical explanation for these limiting behaviours. However, it seems reasonable to surmise that, as ϕ increases and the network collapses from its original fully swollen state, the frame would stiffen slowly at first as ϕ^β, where the exponent $\beta\geqslant 1$. However, as the network continues to collapse and becomes increasingly congested, the number of contacts between the polymer fibres would rise quickly. One would then expect the frame to stiffen appreciably, the moduli to increase more rapidly, and to observe a larger value for β. We find that $\beta(\phi)\simeq 1$ for $0.1\lesssim\phi\lesssim 0.3$ and $\beta(\phi)\simeq 3$ for $\phi\gtrsim 0.4$. De Gennes[8] has described the behaviour of the free energy and osmotic pressure of dilute and semidilute polymer solutions as functions of ϕ. From these one may demonstrate that the bulk modulus of such systems as a function of ϕ does indeed contain both roughly linear and roughly cubic terms for small ϕ. However, the detailed ϕ dependence does not agree with our observations for PVA hydrogels, especially for large ϕ, where it would be imprudent anyway to attempt to draw any close analogies with dilute and semidilute polymer systems. Although we are as yet unable to account adequately for the observed behaviour of $c_n(\phi)$, the DJ model nevertheless provides a very satisfactory description of the hypersonic velocity without any assumptions about smallness of concentration.

However, for PVA hydrogels the analysis of the absorption coefficient, performed in the low-frequency limit of the DJ theory, does present some problems. It suggests that the frictional damping at frequencies of our Brillouin scattering experiments is too small for this limit to apply. While this has been demonstrated to be not at all crucial for the description of the velocity in PVA hydrogels, it may well be important when obtaining $f(\phi)$ from an analysis of the absorption coefficient data. Furthermore, from the results for $k(\phi)$ mentioned above and the crude model, equation (4), we have also calculated r, the average effective pore radius. This is shown in *Figure 3* together with the behaviour predicted by equation (7). From this it may be seen that r shrinks from about 1400 Å at $\phi\simeq 0.1$ to 330 Å at $\phi\simeq 0.9$. If these can be taken as roughly indicative of the size of the reticular channels, then this also calls to question a very basic initial assumption of the Biot theory[6], namely that there must exist volumes which are large compared to the pore sizes but small compared to the wavelength of sound. The wavelength of the hypersound in our Brillouin study of PVA hydrogels is small—about 2500 Å—so, since the values we have obtained for the pore sizes are so large, then this assumption of the Biot theory is apparently not well satisfied in our case, particularly at small ϕ. However, it is conceivable that the pore sizes have been overestimated due to our (unavoidable) use of a possibly inappropriate limit of the DJ model (the low-frequency approximation).

Therefore it would be of great interest to develop the DJ model so as to obtain an expression for the absorption coefficient at high frequencies to see if different values result for v_c and consequently the pore size. Alternatively, we may use Johnson's full expressions for the complex-valued phase velocity[5] at arbitrary frequencies and attempt to solve in a self-consistent manner for f as well as for $K_b+\frac{4}{3}N$. This is an exceedingly complex task, the results of which we hope to publish in full later. However, we have made a preliminary attempt at such an analysis but find that the tortuosity parameter α takes on values martinally less than unity. Since α must necessarily be equal to or larger than unity[5], this result seems nonsensical or at best possibly an unfortunate consequence of a combination of scatter in the experimental data and computational rounding errors. It is conceivable that the proper inclusion of the attenuation within the network fibres, which both theories neglect, might remove this problem. This aspect awaits further theoretical study.

SUMMARY AND CONCLUSIONS

We have compared closely the results of analysing with two different theories for gels our Brillouin light scattering measurements of the ϕ dependence of the hypersonic velocity and absorption coefficient of longitudinal waves in PVA hydrogels. While the two sets of results for the speed of sound in the network and the frictional damping parameter obtained from these two different analyses are roughly consistent, the model of Johnson provides an overall more satisfactory description than that of Marqusee and Deutch, primarily because it makes no assumptions about smallness of concentration and has less ambiguity in its constituent parameters. Using Johnson's model we have obtained what we believe to be fairly reliable data for the framework elastic moduli, which we find increase linearly with ϕ for small ϕ but as the cube of ϕ for large ϕ. This behaviour as yet awaits a proper theoretical explanation.

The data for the frictional damping parameter are less reliable due to an ambiguity in the correct choice of the frequency limit of the theory, although this apparently does not affect the results crucially for the framework elastic moduli. It has so far not proved possible to obtain a completely consistent description of the PVA hydrogel system within the framework of the Johnson model. We are currently investigating whether such a description can be achieved using the 'full' theory with no approximations about the smallness or otherwise of the wave frequency, although preliminary studies indicate some difficulties also exist in this approach.

REFERENCES

1 Ng, S. C., Hosea, T. J. C. and Gan, L. M. *J. Phys. Lett.* 1985, **46**, L887
2 Hosea, T. J. C. and Ng, S. C. *Chem. Phys.* 1986, **103**, 345
3 Marqusee, J. A. and Deutch, J. M. *Chem. Phys.* 1981, **75**, 5239
4 de Gennes, P. G. *Macromolecules* 1976, **9**, 587
5 Johnson, D. L. *J. Chem. Phys.* 1982, **77**, 1531
6 Biot, M. A. *J. Acoust. Soc. Am.* 1956, **28**, 168, 179
7 Johnson, D. L. and Plona, T. J. *J. Acoust. Soc. Am.* 1982, **72**, 556
8 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, NY, 1979, p. 118