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# An estimation of the tube radius in the entanglement effect of concentrated polymer solutions

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**Abstract.** An analysis is made of the tube radius in the entanglement problem of concentrated polymer solutions. The tube radius  $a$  is defined as the mean distance between nearest segments belonging to different chains. For a moderately concentrated system of sufficiently long chains,  $a$  is found to be inversely proportional to the segment density  $\rho$ . By use of this result, several problems in the entanglement effect are discussed.

## 1. Introduction

One of the attractive approaches in the problem of the entanglement effect of polymerized materials is the tube model introduced by Edwards (1967) in the discussion of rubber elasticity of highly entangled polymer chains. The tube model was also employed by de Gennes (1971) to predict the molecular weight dependence of the self-diffusion constant and the relaxation time of a chain trapped inside a fixed network. Furthermore, the tube model was shown to explain the characteristic feature of the viscoelastic properties of concentrated polymer solutions (Doi 1974).

In the tube model, each chain is assumed to be confined in a certain tube-like region due to the topological restriction that chains cannot pass through each other. The tube represents the averaged repulsive force exerted by other chains. Thus the many body problem of a whole chain system is reduced to the problem of a single chain inside the tube, and the concentration of chains is taken into account through tube radius. Hence the estimation of the tube radius is an important problem in the theory of the tube model. However, the estimation is not as easy as it may seem at first sight.

Edwards (1967) and de Gennes (1974) have estimated the tube radius  $a$  from different approaches, but they reached the same result:

$$a \propto (\rho b)^{-1/2} \quad (1)$$

where  $b$  is the bond length and  $\rho$  is the segment density defined by  $\rho = cN$ ,  $c$  and  $N$  being the polymer density and the degree of polymerization of the chain respectively. However, equation (1) suffers a difficulty if the chains are assumed to be continuous Gaussian chains described by the Wiener measure. This may be understood from the following consideration: let us consider an ideal Gaussian chain system without excluded volume effect. The tube radius should be defined for this system. The whole system is specified by a set of functions  $R_a(s)$ , where  $R_a(s)$  denotes the position of the  $s$ th segment of the  $a$ th chain. Although there is some uncertainty in the definition of the tube radius,

$a$  should be given by the average of a certain functional  $A[\mathbf{R}_a(s)]$  representing the appropriate intermolecular separation:

$$a = \mathcal{N} \int \prod_a \delta \mathbf{R}_a(s) A[\mathbf{R}_a(s)] \exp \left[ -\frac{3}{2b^2} \sum_a \int_0^N \left( \frac{d\mathbf{R}_a}{ds} \right)^2 ds \right] \quad (2)$$

where  $\mathcal{N}$  is a suitable normalization constant. From the dimensional analysis,  $A[\mathbf{R}_a(s)]$  must be a homogeneous function of first order. Then if we introduce the scaled variables  $\tilde{\mathbf{R}}_a(\tilde{s}) = \mathbf{R}_a(s)/b\sqrt{N}$  and  $\tilde{s} = s/N$ , equation (2) is rewritten as

$$a = \mathcal{N} \int \prod_a \delta \tilde{\mathbf{R}}_a(\tilde{s}) b\sqrt{N} A[\tilde{\mathbf{R}}_a(\tilde{s})] \exp \left[ -\frac{3}{2} \int_0^1 \sum_a \left( \frac{d\tilde{\mathbf{R}}_a}{d\tilde{s}} \right)^2 d\tilde{s} \right]. \quad (3)$$

Since the statistical weight for  $\tilde{\mathbf{R}}_a(\tilde{s})$  involves no other parameters than the scaled dimensionless concentration  $c(b\sqrt{N})^3$ , the functional integral over  $\tilde{\mathbf{R}}_a(\tilde{s})$  yields a function including  $c(b\sqrt{N})^3$  only. Hence  $a$  must have the following form:

$$a = (b\sqrt{N})f(c(b\sqrt{N})^3). \quad (4)$$

Equation (1) does not have this form.

The essential point of the above argument is equivalent to the following requirement: if the tube radius is much larger than the bond length, its average should not depend on the choice of the component statistical segment and should be invariant under the transformation:

$$N \rightarrow N/m; \quad b \rightarrow b\sqrt{m}; \quad \rho \rightarrow \rho/m. \quad (5)$$

The meaning of this transformation is that if we combine  $m$  segments into one and regard this as a new component segment, the number of segments decreases from  $N$  to  $N/m$  but at the same time the segment length increases from  $b$  to  $b\sqrt{m}$ . The invariance of  $a$  for this transformation may be intuitively understood from figure 1, where the full line represents the original flexible chain and the broken line shows the new chain. This change does not affect the statistical nature of the system as far as we are concerned with the characteristic lengths much longer than the original segment length  $b$ . Hence  $a$  should be invariant under (5) as far as  $a \gg b$ .

For a high concentration of chains,  $a$  becomes comparable with  $b$  and the above argument cannot apply to this case. In that case, Edwards' estimation of  $a$  seems to

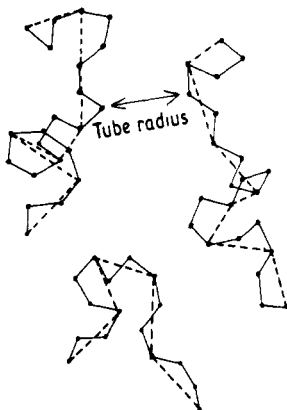


Figure 1. Illustration of the transformation (5). The case of  $m = 3$  is shown.

be plausible and equation (1) may be recovered. However, for a moderately concentrated system another expression for  $a$ , satisfying equation (4), seems to be needed, which is attempted in this paper.

As is mentioned previously, there is no definite definition for the tube radius. Here we employ a simple definition. We define the tube radius as the distance between a given segment and its nearest segment of other chains. If such a definition is adopted, the mean tube radius is calculated exactly for the ideal Gaussian chain system. The calculation method was hinted at by the theory of Ogston (1958) for the evaluation of the mean void radius in a random network of rigid rods.

## 2. Calculation of the mean tube radius

To calculate the mean tube radius previously defined, we consider a sphere of radius  $r$ , centred on some fixed segment. We first find the probability  $P(r)$  that there is no chain touching this sphere except for the chain to which the pertinent segment belongs. This probability  $P(r)$  obeys the equation

$$\frac{dP(r)}{dr} = -\lambda(r)P(r) \tag{6}$$

where  $\lambda(r) dr$  is the probability of finding a chain which touches the sphere of radius  $r + dr$  but does not touch that of radius  $r$ . If  $n(r)$  is the mean number of chains touching the sphere of radius  $r$ , then  $\lambda(r) dr$  is equal to  $n(r + dr) - n(r)$ . Hence

$$\lambda(r) = \frac{dn(r)}{dr}. \tag{7}$$

To calculate  $n(r)$ , we imagine an ensemble of random walks whose starting points are placed randomly in the three-dimensional space with concentration  $c$ . Then  $n(r)$  is evaluated as the sum of the mean number  $n_1(r)$  of starting points inside the sphere and the mean number  $n_2(r)$  of random walks which start from outside the sphere and touch the sphere in the interval of making  $N$  steps. The former is simply equal to  $4\pi cr^3/3$ . The latter is immediately obtained from the result of the previous paper (Doi 1975, to be referred to as I). Equation (23) in I indicates the mean number of chains of unit concentration, touching the sphere of radius  $a$ , starting from outside the sphere. Hence  $n_2(r)$  is  $c$  times the expression (23) in I with  $a$  replaced by  $r$ . Thus we have

$$n(r) = c\left(\frac{4}{3}\pi r^3 + 4\sqrt{\left(\frac{2}{3}\pi\right)r^2 b\sqrt{N} + \frac{2}{3}\pi r b^2 N}\right). \tag{8}$$

From equations (6) and (7) we have

$$P(r) = \exp(-n(r)). \tag{9}$$

Now we can easily obtain the probability  $Q(r) dr$  that the nearest segments of other chains lie in the distance between  $r$  and  $r + dr$ . This is equal to the probability that no chains touch the sphere of radius  $r$  and at least one chain touches the spherical shell between  $r$  and  $r + dr$ . Hence

$$Q(r) dr = P(r)\lambda(r) dr. \tag{10}$$

The function  $Q(r)$  indicates the distribution of the tube radius of our definition. Therefore the mean tube radius  $a$  is

$$a = \int_0^\infty dr Q(r)r = l \int_0^\infty dx \exp[-(\frac{4}{3}\pi x^3 + 8x^2\sigma\sqrt{\pi} + 4\pi x\sigma^2)](4\pi x^2 + 16x\sigma\sqrt{\pi} + 4\pi\sigma^2)x. \tag{11}$$

Here  $l = c^{-1/3}$  is the mean distance between the centre of mass of chains and  $\sigma = (Nb^2/6)^{1/2}/l$  is the ratio of the mean radius of gyration of the chain to  $l$ . It can be readily checked that equation (11) satisfies the requirement (4).

In figure 2,  $a/l$  is plotted against  $\sigma$ . The asymptotic form of  $a/l$  is

$$a/l = \begin{cases} (3/4\pi)^{1/3}\Gamma(\frac{4}{3}) - (2/\sqrt{\pi})\sigma & (\sigma \ll 1) \\ 1/4\pi\sigma^2 & (\sigma \gg 1). \end{cases} \tag{12a}$$

$$\tag{12b}$$

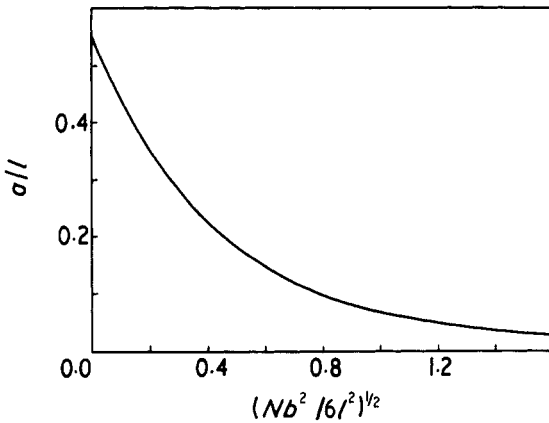


Figure 2. The molecular weight dependence of the tube radius  $a$ .

The first term in equation (12a) is just the same as the mean distance between the nearest points distributed randomly in space with concentration  $c$  (Chandrasekhar 1943). This is natural because the chain can be regarded as points when the molecular dimension  $b\sqrt{N}$  is much smaller than the intermolecular separation  $l$ . On the other hand, the result for the long-chain case is more interesting. Equation (12b) shows that  $a$  is proportional to  $l^3/Nb^2$  or to  $\rho^{-1}$ . This conclusion seems non-trivial.

The specific  $\rho^{-1}$  dependence of  $a$  is closely related to the scaling property of Gaussian chains discussed previously. In fact if we assume that  $a$  is determined by the segment density  $\rho = cN$  only, not separately by  $c$  and  $N$ , then from the general requirement (4), we must have  $a \propto \rho^{-1}$ .

Here it may be worthwhile to examine the applicability of the above result. As is discussed in the introductory section, the continuous Gaussian chain model, on which the above calculation is based, is appropriate as far as  $a \gg b$ . Then the  $\rho^{-1}$  dependence will be observed under the following condition :

$$l/\sigma^2 \gg b \quad \text{and} \quad \sigma \gg 1 \tag{13}$$

or equivalently

$$\rho b^3 \ll 1 \quad \text{and} \quad \rho b^3 \sqrt{N} \gg 1. \tag{14}$$

These conditions are satisfied only when  $N \gg 1$ . If we tentatively set the conditions as  $a > 10b$  and  $\sigma > 1$ , then  $N$  must be larger than  $10^5$ , a very large degree of polymerization. Hence the simple relation  $a \propto \rho^{-1}$  may not be observed for the usual synthetic polymers. If  $N$  is not very large, the actual situation will be as follows: for relatively low concentration,  $a$  is given by equation (11). In this case  $a$  is not a function of  $\rho$  only. For high concentration,  $a$  becomes comparable with  $b$  and the relation of Edwards and de Gennes will be recovered. However, this does not mean that use of equation (1) is justified in their theories because their theories are based upon the continuous Gaussian chain models. From the purely theoretical point of view, it is preferable to use equation (11) (or other estimation of  $a$  satisfying (4)) to be consistent in the theory.

### 3. Application to related problems

In this section, we should like to discuss two related problems of the tube model on the basis of the above result. The first is the rubber elasticity of a highly-entangled polymer chain system.

In the pioneering work of Edwards (1967), the rigidity modulus  $E$  of this system has been predicted to be proportional to  $\rho^{3/2}$ . Recently de Gennes (1974) has made a comment on this result, showing that Edwards' prediction does not satisfy the requirement that the rigidity modulus of an entangled chain system should be smaller than that of a cross-linked chain system, in which case  $E \propto \rho^2$ . He concluded that this difficulty arises from the soft harmonic potential derived from the pre-averaged tube restriction. However, his requirement can be satisfied without improving the tube potential if we employ the above obtained relation  $a \propto \rho^{-1}$  assuming  $\sigma \gg 1$ .

As was clarified by de Gennes, the rigidity modulus is given by

$$E \simeq k_B T \rho \epsilon_0 \quad (15)$$

where  $\epsilon_0$  is the lowest eigenvalue for the diffusion equation in a tube and  $k_B T$  is the Boltzmann constant multiplied by temperature. If we assume a harmonic potential, we have  $\epsilon_0 \propto b/a$  (Edwards and Freed 1969), and use of the above relation yields  $E \propto \rho^2$ . As was shown by de Gennes, use of the hard repulsive potential for the tube leads to  $\epsilon_0 \propto b^2/a^2$ , and this yields another dependence of  $E$  on  $\rho$ .

De Gennes' argument for the estimation of  $\epsilon_0$  seems very plausible if the mean tube radius  $a$  is the most probable value. However, as is suggested by equations (8) and (10), the distribution of the tube radius is a Poisson-type for  $\sigma \gg 1$  and its peak is at  $r = 0$ . Hence the employment of the harmonic potential (which has minimum at  $r = 0$ ) seems to have some physical grounds. However, at this stage, the author has no convincing answer for this problem.

Another application of the present result is the problem of the condition of the onset of the entanglement effect. This condition is related to the well known break-point in the doubly logarithmic plot of steady flow viscosity  $\eta$  against molecular weight. In I, we have discussed the fact that the characteristic molecular weight dependence predicted by the tube model breaks down around the critical degree of polymerization  $N_c$  satisfying

$$(b\sqrt{N_c})/a = \text{constant}. \quad (16)$$

Since  $a/l$  depends only on  $\sigma$  and  $b(\sqrt{N})/l$  is equal to  $\sigma\sqrt{6}$ , this condition is equivalent

to  $\sigma_c = (N_c b^2 / 6l^2)^{1/2} = \text{constant}$ , or

$$N_c \propto (\rho b^3)^{-2}. \quad (17)$$

This conclusion may be compared with Bueche's relation  $N_c \propto \rho^{-1}$  (Bueche 1962). His relation has been verified by several viscoelastic experiments for relatively concentrated polymer solutions. However, for relatively low concentration, the experimental relation  $\rho \propto N_c^{-\alpha}$  gives results scattered from  $\alpha = 0.54$  to  $0.72$  (Onogi *et al* 1966). (It is also observed that the transition becomes rather diffusive for these concentrations.) We expect equation (17) to hold for relatively dilute solutions of very long polymers. It should be stressed that though equation (17) has been derived on the basis of some ambiguous concept such as the tube length (see I) and tube radius, the result will not be altered even if the problem is attacked in a more sophisticated manner (eg Edwards and Grant 1973). This may be understood from the following argument.

We consider free-draining Rouse chains subjected to the constraints that chains cannot cross over each other. The inhibition of chain cross-over can be taken into account in such a way that if bonds (defined as a line segment connecting the nearest-neighbour frictional elements in the same chain) collide, they are repulsed. Thus the entanglement effect can be incorporated into the theory without introducing any additional parameters such as the hard-core radius of the chain. In so far as the topological restriction is imposed, this thin Gaussian chain system is expected to exhibit the characteristic feature of the entangled chain system.

In this system, there appear five independent parameters,  $N$ ,  $b$ ,  $\rho$ ,  $k_B T$  and  $\zeta$  (denoting the friction constant of a segment). From the dimensional analysis, we find that the steady flow viscosity  $\eta$  is written in the form

$$\eta = \frac{\zeta}{b} F(N, \rho b^3). \quad (18)$$

We now impose the scaling requirements on this expression. If we combine  $m$  segments into one,  $N$ ,  $b$  and  $\rho$  are transformed according to equation (5). At the same time,  $\zeta$  is transformed into  $\zeta m$  because of the free-draining condition. We require that  $\eta$  must be invariant for this transformation. This requirement restricts the functional form of  $\eta$  as

$$\eta = \frac{\zeta \sqrt{N}}{b} G(N(\rho b^3)^2). \quad (19)$$

This may be called a similarity rule for the steady flow viscosity of a free-draining Rouse chain system. The similarity rule is satisfied for the dilute solution. In fact for the dilute solution, we must have  $\eta \propto \rho$ , which yields  $\eta \propto \zeta N \rho b^2 = c \zeta N^2 b^2$ . This is just the result of the Rouse theory (Rouse 1953). In the Rouse theory, submolecules are first assumed as the fundamental relaxing unit, but his final result does not depend on the size of the submolecules. The above discussion is just the generalization of this idea. We expect that  $\eta$  should not depend on the hypothetical submolecules even in the concentrated polymer solutions. If this expectation is true, then the similarity rule (19) indicates that the change in the molecular weight dependence should appear only through  $N(\rho b^3)^2$ . Thus we get equation (17).

#### 4. Conclusion

We have calculated the mean tube radius in the entangled chain system based on a

simple definition of the tube radius. The result is consistent with the scaling requirement which should be satisfied in the continuous Gaussian chain model. The result is then applied to the rubber elasticity of a highly entangled chain system and to the steady flow viscosity of undiluted polymer solutions. It is found that in the free-draining Rouse chain system of relatively low concentration, the critical molecular weight  $M_c$  at the onset of the entanglement effect is inversely proportional to the square of the weight concentration of polymers.

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