Transition behaviour from de Gennes-type motion to Rouse's of a polymer chain in fixed network

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Abstract. De Gennes' theory on the Brownian motion of a polymer chain in the presence of fixed obstacles is generalized so as to take into account the concentration of obstacles. The molecular weight dependences of the characteristic relaxation time and the self-diffusion constant of the chain are found to change continuously from de Gennes-type to Rouse's as the concentration of obstacles decreases.

1. Introduction

In the problem of entanglement effect in polymeric chain systems, an illuminating theory has been proposed by de Gennes (1971). He discussed a Brownian motion of a chain trapped inside a fixed three-dimensional network such as a polymeric gel. He presented an idea of tube restriction to express the topological constraint that the chain cannot intersect other chains constituting the network. The idea of the tube restriction had already been proposed by Edwards (1967b) in the discussion of rubber elasticity of highly-entangled chain systems, but not applied to the dynamic problems such as the viscoelastic properties.

A two-dimensional version of the system considered by de Gennes is illustrated in figure 1. Here circles denote the obstacles, eg, chains penetrating the plane perpendicularly. The chain can move freely between the obstacles, but cannot cross any of them. The only allowed motion of the chain is thus the 'reptative' motion inside a certain tube composed of obstacles.

De Gennes described this motion by the migration process of 'defects', which express the stored length of the chain, along the tube axis. As a result he showed that many characteristic features in the dynamic properties of the chain are quite different from those in the free space: the self-diffusion constant D_G of the chain is proportional to N^{-2} (N denoting the degree of polymerization), and the longest relaxation time τ of the time correlation function of the end-to-end vector is to N^3. One should recall that in the free space, these quantities are proportional to N^{-1} and N^2, respectively as predicted by the Rouse theory.

In spite of some specific assumptions such as the defects, de Gennes' theory seems to be quite general and to describe correctly the molecular weight dependence of these quantities. However, it must be noted that his theory holds only in the case of a high density of obstacles. When the mean distance between the obstacles is comparable with the mean end-to-end distance, the concept of the tube restriction becomes meaningless.
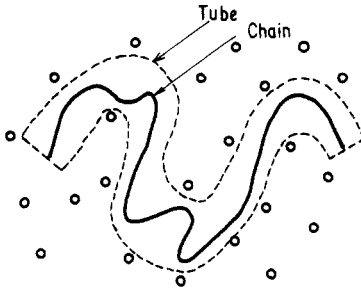
Figure 1.

Therefore de Gennes' theory will break down at some point as the concentration of obstacles or the chain length decreases, and a transition behaviour will be observed in the molecular weight dependence of D_G and τ. Unfortunately, his theory does not take into account the concentration of obstacles and hence cannot predict the range of applicability of his theory.

A computer experiment has been worked out by Doi (1973) to examine this transition behaviour. A chain is placed on a two-dimensional plane and obstacles are set up regularly at the lattice points of the square lattice with lattice constant d. The diffusion constant and the longest relaxation time were observed as functions of N and d. A diffusive transition behaviour was observed in the N dependence of these quantities.

In this paper, a theory is developed to describe this transition behaviour from de Gennes-type motion to Rouse's. We shall first modify de Gennes' theory so as to take into account explicitly the mean length $\langle L \rangle$ of the tube enveloping the chain. Then $\langle L \rangle$ is determined as a function of the chain length and the concentration of obstacles. The transition behaviour in the molecular weight dependence of D_G and τ is explained in terms of the change in N dependence of $\langle L \rangle$ as the concentration of obstacles decreases.

Although the present theory is an extension of de Gennes' theory to the case of lower concentration of obstacles, our results conform to the Rouse theory in the limit of infinite dilution of obstacles. The transition behaviour observed by the computer experiment will be shown to be well reproduced by this interpolation formula.

2. Generalization of de Gennes' theory

In this section we shall derive de Gennes' results in a generalized manner so as to take into account the concentration of obstacles.

Consider a chain confined inside a tube of radius a. The central axis of the tube is denoted by $R(s)$, where s is the curvilinear length along the tube axis measured from some origin. Here it should be remarked that in general the tube axis cannot be identified by a single parameter s, because the chain ends can penetrate the wall of the tube and can go into another tube. However, this is not important in our theory because the following discussion is concerned only with the shape of the initial tube in which the chain is trapped at time $t = 0$. In that case $R(s)$ can be determined uniquely.

We represent the position of the nth monomer r_n by its curvilinear coordinate s_n along the tube axis, and the vector u_n perpendicular to the axis:

$$r_n = R(s_n) + u_n; \qquad u_n \cdot \frac{dR(s)}{ds}\bigg|_{s=s_n} = 0. \tag{1}$$

The stochastic motion of the chain is described by a set of Langevin equations for s_n and u_n and was discussed in a previous paper (Doi 1974). As a result it can be shown that vector u_n and the curvilinear separation $s_n - s_m$ between any two monomers n and m fluctuate rapidly. Therefore in the discussion of long time scale behaviour, these quantities may be assumed to have their mean values, ie,

$$u_n = \langle u_n \rangle = 0 \qquad \text{and} \qquad s_n - s_m = \langle s_n - s_m \rangle = \langle L \rangle (n - m)/N;$$

hence

$$s_n = (n/N - \tfrac{1}{2})\langle L \rangle + s_c \qquad \text{and} \qquad r_n = R(s_n) \tag{2}$$

where $\langle L \rangle$ is the mean value of $s_N - s_1$ and s_c is the curvilinear coordinate of the $(N/2)$th monomer called the centre monomer. We call $\langle L \rangle$ the mean tube length because it is equal to the tube length enveloping the chain. In this approximation the conformation of the chain is determined by one parameter s_c and the motion of the chain is treated as a uniform diffusion process with constant end-to-end separation $\langle L \rangle$ along the tube axis.

The probability distribution function for s_c at time t obeys the usual diffusion equation:

$$\frac{\partial f(s_c ; t)}{\partial t} = D_c \frac{\partial^2}{\partial s_c^2} f(s_c ; t). \tag{3}$$

The diffusion constant D_c is proportional to N^{-1} because the friction constant for the uniform translation along the tube axis is proportional to N.

Up to this point our discussion is essentially the same as de Gennes'. The only difference is that de Gennes has assumed $\langle L \rangle$ to be equal to Nb (b denoting the bond length), whereas we regard $\langle L \rangle$ as an adjustable parameter determined by the chain length Nb and the concentration of obstacles. This is a necessary modification if we are going to treat the case of intermediate concentration of obstacles. What we discuss in the following is how this modification affects the final results.

Let us first consider the time correlation function of the end-to-end vector P. Since the shapes of different tubes have no correlation with each other, the correlation between $P(t)$, the vector at time t, and $P(0)$ vanishes when the chain disengages from the initial tube, ie, when $|s_c(t) - s_c(0)|$ becomes greater than $\langle L \rangle /2$. Therefore the longest relaxation time of $\langle P(t) . P(0) \rangle$ can be estimated by the time during which the centre monomer diffuses to a distance $\langle L \rangle /2$ along the tube axis. From equation (3) this is estimated as

$$\tau \propto \langle L \rangle^2 / D_c \propto N \langle L \rangle^2. \tag{4}$$

When the concentration of the obstacles is sufficiently high, $\langle L \rangle$ is, presumably, proportional to N and thus $\tau \propto N^3$, which coincides with de Gennes' result.

Next we consider the diffusion constant of the chain. Since the dimension of the chain is finite, the overall diffusion constant D_G (more specifically, the diffusion constant of the centre of mass) can be evaluated from the mean square displacement of a certain monomer in a sufficiently long time interval compared to τ. Therefore we may estimate D_G from the mean square displacement of the centre monomer:

$$\langle (r_{N/2}(t) - r_{N/2}(0))^2 \rangle = 4D_G t \qquad (t \gg \tau). \tag{5}$$

Since the centre monomer is confined in the initial tube during the time interval τ, its motion is restricted by the initial tube during this time interval. Hence there is a strong memory effect in the motion of the centre monomer during τ. On the other hand, for $t \gtrsim \tau$, we may assume that the motion of the centre monomer has no correlation with that for $t \lesssim \tau$. Thus for simplicity, we may regard the Brownian motion of the centre

monomer as a random walk in which the centre monomer makes t/τ independent steps during the time interval t. The mean square displacement of each step is estimated by the mean square separation between the chain end and the centre monomer, ie, $\langle(r_N - r_{N/2})^2\rangle = Nb^2/2$. Therefore the left-hand side in equation (5) is estimated as

$$\langle(r_{N/2}(t) - r_{N/2}(0))^2\rangle = \frac{t}{\tau}\frac{Nb^2}{2} \tag{6}$$

hence we have

$$D_G \propto Nb^2/\tau \propto \langle L\rangle^{-2}. \tag{7}$$

Thus our problem is reduced to determining $\langle L\rangle$ as a function of the concentration of obstacles. This is done in the subsequent sections.

3. Definition of the mean tube length

Conceptually, the tube represents the smeared effect of obstacles. However, it is not easy to give a clear definition of the tube. As an example, let us compare the two cases shown in figure 2. In case (a), the portion A–B–C should be included in the tube length, but in case (b), it must be excluded. To distinguish these two cases, introduction of some topological invariants, such as discussed by Edwards (1967a, 1968), will be necessary. However, if such definition of the tube is employed, the statistical calculation of the mean tube length becomes very difficult.
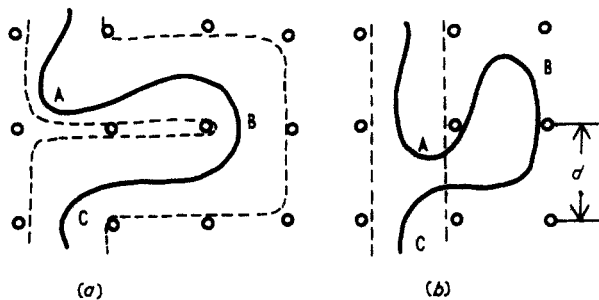

(a)   (b)

Figure 2.

Here we employ a simple definition of the tube length. Instead of considering obstacles, we imagine a set of spheres whose centres are continuously located along the chain. The radius of the sphere a is determined by the concentration of the obstacles. The tube is defined as the region occupied by these spheres (see figure 3). We shall calculate the mean volume of this region and dividing it by πa^2, the cross section of the tube, we estimate the mean tube length.

The above definition of the tube, of course, does not take into account the difference between the two cases (a) and (b) shown in figure 2. Nevertheless, we expect that it reflects the essential aspect of the concentration dependence of the mean tube length. This may be understood if we compare the two cases illustrated in figure 3. In the high concentration case (a), $\langle L\rangle$ will be proportional to N, on the other hand in the low
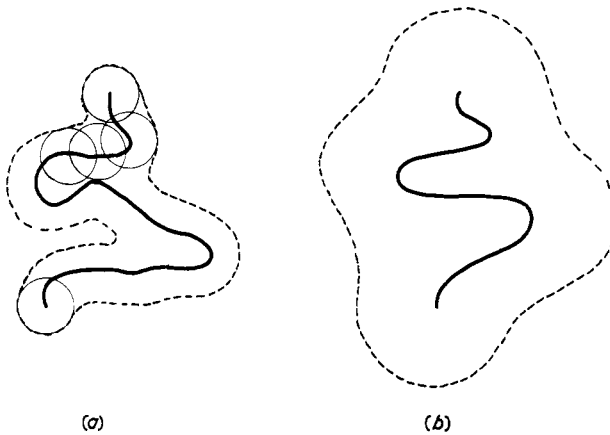
(a)   (b)

Figure 3.

concentration case (b), $\langle L \rangle$ will be proportional to the mean end-to-end distance, ie, $\langle L \rangle \propto \sqrt{N}$.

It should be stressed that the mean tube length defined above, or the mean tube volume, can be calculated exactly. Apart from our pertinent interest, a similar problem may arise in other fields of polymer science. For example, in polyelectrolyte theory, counterions are considered to be condensed in some potential trough around the polymer chain (Osawa 1971). The volume of the potential trough is just the same as our tube volume. To the author's knowledge, such a calculation has not yet been carried out. Therefore the following section is devoted for this purpose.

4. Mean tube volume

Consider a Gaussian chain starting from some fixed point R. The position of the nth monomer is denoted by $r(n)$. We regard n as a continuous parameter and assume a Wiener measure for the functional probability of finding a conformation $r(n)$:

$$\mathscr{P}[r(n)] = \mathscr{N} \exp\left[- \int_0^N dn \frac{3}{2b^2} \left(\frac{dr}{dn} \right)^2 \right] \delta(r(0) - R). \tag{8}$$

For a given conformation of the tube, we introduce a function $E(r_0 ; R, [r(n)])$, which takes unity when a point r_0 is inside the tube and zero otherwise, ie,

$$E(r_0 ; R, [r(n)]) = \begin{cases} 1 & \text{if there exists } n \text{ such that } |r_0 - r(n)| \leqslant a \\ 0 & \text{otherwise.} \end{cases} \tag{9}$$

Then the volume of the tube is given by

$$V(R, [r(n)]) = \int d^3 r_0 E(r_0 ; R, [r(n)]) \tag{10}$$

and the mean volume is

$$\langle V \rangle = \int d^3 r_0 \langle E(r_0 ; R, [r(n)]) \rangle. \tag{11}$$

The average in equation (11) should be taken over the distribution function (8):

$$\bar{E}(r_0, R) \equiv \langle E(r_0; R, [r(n)]) \rangle = \int \delta r(n) \mathscr{P}[r(n)] E(r_0; R, [r(n)]).$$ (12)

It is possible to calculate directly the functional integral (12) following the method of Edwards and Freed (1969). However, an analogy with the Brownian motion problem offers a simple way to reach the result.

Equation (8) indicates that function $r(n)$ can be regarded as a trajectory of a Brownian particle starting from R at 'time' $n = 0$. Then the average $\bar{E}(r_0, R)$ can be regarded as the probability that the Brownian particle goes into the spherical region $|r - r_0| \leqslant a$ at least once during the time interval N. This probability is equal to the adsorption probability of the Brownian particle on the complete absorption surface of the sphere.

Let us introduce a Green function $G(r, R, n)$, the probability of finding the Brownian particle starting from R, at point r and time n. It obeys the diffusion equation

$$\frac{\partial G}{\partial n} - \frac{b^2}{6} \nabla^2 G = \delta(r - R)\delta(n)$$ (13)

together with the sink boundary condition

$$G(r, R, n) = 0 \qquad \text{at } |r - r_0| = a.$$ (14)

Since the diffusion constant of the Brownian particle is equal to $b^2/6$, the adsorption probability is expressed as

$$\bar{E}(r_0, R) = \int_0^N dn \int dS \cdot \frac{b^2}{6} \nabla G$$ (15)

where dS is a surface element vector of the sphere $|r - r_0| = a$, directing outward.

Let us note that $\bar{E}(r_0, R)$ is a function of $r_0 - R$. Therefore we may put the centre of the sphere r_0 at the origin and replace the integral over r_0 in equation (11) by that over the starting point:

$$\langle V \rangle = \int d^3R \bar{E}(0, R).$$ (16)

We consider a function $W(r, n)$ defined by

$$W(r, n) = \int d^3R G(r, R, n).$$ (17)

By use of $W(r, n), \langle V \rangle$ is expressed as

$$\langle V \rangle = \int_0^N dn \int dS \cdot \left(\frac{b^2}{6}\right) \nabla W(r, n).$$ (18)

From equations (13), (14) and (17), $W(r, n)$ satisfies the equation

$$\frac{\partial W}{\partial n} - \frac{b^2}{6} \nabla^2 W = 0$$ (19)

together with the conditions

$$W(r, n) = 1 \qquad \text{at } n = 0$$
$$W(r, n) = 0 \qquad \text{at the surface } |r| = a.$$ (20)

This set of equations is a familiar one in the diffusion problem (Crank 1956). Hence we can immediately write down the solution as

$$W(r, n) = 1 - \frac{a}{r} + \frac{a}{r} \operatorname{erf}\left(\left(\frac{3(r-a)^2}{2b^2 n}\right)^{1/2}\right) \tag{21}$$

where

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \mathrm{d}y \exp(-y^2). \tag{22}$$

Thus the mean volume is obtained as

$$\langle V \rangle = \int_0^N \mathrm{d}n 4\pi a^2 \left(\frac{b^2}{6}\right) \frac{\partial W}{\partial r}\bigg|_{r=a} = \frac{2\pi}{3} ab^2 N + 4\sqrt{\left(\frac{2\pi}{3}\right)} a^2 b \sqrt{N}. \tag{23}$$

One must note that in deriving (23) we have taken into account only those particles starting outside the sphere, ie, $|R| > a$. If on the other hand $|R| < a$, $E(0, R)$ is identically unity and this adds a term of the volume of the sphere $4\pi a^3/3$ to $\langle V \rangle$. However, in evaluating the mean tube length of the pertinent entanglement problem, such a term should be suppressed because it represents the volume of the two half-spheres attached to the chain ends. (Moreover the term $4\pi a^3/3$ gives an unphysical tube length when $a \gg \sqrt{(Nb)}$.) Hence we obtain the mean tube length as

$$\langle L \rangle = \langle V \rangle / \pi a^2 = 4 \sqrt{\left(\frac{2}{3\pi}\right)} b \sqrt{N} + \frac{2b^2}{3a} N. \tag{24}$$

This equation indicates that the N dependence of the mean tube length changes following the tube radius, a, in such a way as

$$L \propto \begin{cases} N & \text{for } a \ll \sqrt{(Nb^2)} \\ \sqrt{N} & \text{for } a \gtrsim \sqrt{(Nb^2)}. \end{cases} \tag{25}$$

Such behaviour is what we have expected in the foregoing section.

Here a note should be made concerning the applicability of equation (24). Following equation (24), $\langle L \rangle$ can exceed the chain length Nb and can become infinitely large when a is very small. This inconsistency arises from the Gaussian chain assumption employed in our calculation. The Gaussian chain assumption holds only when one is concerned with the scale larger than the bond length b. Therefore equation (24) should not be applied to the case $a \lesssim b$.

5. Comparison with the Monte Carlo results

Substituting equation (24) into (4) and (7), we have

$$\tau = AN^2(1 + \tfrac{1}{2}\sqrt{(\pi/6)}\alpha \sqrt{N})^2 \tag{26}$$

$$D_G^{-1} = BN(1 + \tfrac{1}{2}\sqrt{(\pi/6)}\alpha \sqrt{N})^2 \tag{27}$$

where $\alpha = b/a$ and A and B are constants independent of N. Equations (26) and (27) indicate that when $\alpha\sqrt{N} \gg 1$, τ and D_G are proportional to N^3 and N^{-2} respectively, in accordance with de Gennes' theory, and when $\alpha\sqrt{N} \lesssim 1$, they are respectively proportional to N^2 and N^{-1}, which recovers Rouse's theory. Of course since equations (4) and (7) were derived starting from the tube model, the recovery of the Rouse theory may be a fortuitous thing. However, we expect that these equations describe the qualitative feature of the transitional behaviour from de Gennes-type motion to Rouse's.

Let us compare equations (26) and (27) with the result of the computer experiment. Here it should be remembered that the computer experiment was performed for the two-dimensional case and thus cannot be compared directly with the present theory for the three-dimensional case. The modification of the present theory to the two-dimensional case is discussed in the appendix. The resulting expression for $\langle L \rangle$ is much more complicated, but the qualitative feature is almost the same as for the three-dimensional case. In fact for relatively small values of $\alpha\sqrt{N}$, $\langle L \rangle$ is well approximated by

$$\langle L \rangle = 1 \cdot 8b\sqrt{N} + 0 \cdot 30Nb^2/a \qquad (b\sqrt{N}/a \lesssim 6 \cdot 0). \tag{28}$$

The functional form of equation (28) is just the same as (24). Hence the modification for the two-dimensional case solely changes the numerical factor before $\alpha\sqrt{N}$ in equations (26) and (27) from $\frac{1}{2}\sqrt{(\pi/6)}$ to $0 \cdot 30/1 \cdot 8 = 0 \cdot 17$.

With this in mind, let us rewrite equations (26) and (27) as

$$\tau^{1/2}/N = A'(1 + 0 \cdot 17\alpha\sqrt{N}) \tag{29}$$

$$(D_G N)^{-1/2} = B'(1 + 0 \cdot 17\alpha\sqrt{N}): \tag{30}$$

then plots of $\tau^{1/2}/N$ against $N^{1/2}$ and $(D_G N)^{-1/2}$ against $N^{1/2}$ should be straight lines. The observed data are in fact on straight lines as shown in figures 4 and 5. From this plot α is obtained and listed in table 1.

If we take the tube radius, a, to be equal to $d/2$, the half-distance between the neighbouring obstacles, α is equal to $1 \cdot 0$ and $0 \cdot 67$ for $d/b = 2$ and 3 respectively. These values compare well with the observed ones. Furthermore, since a is proportional to d,
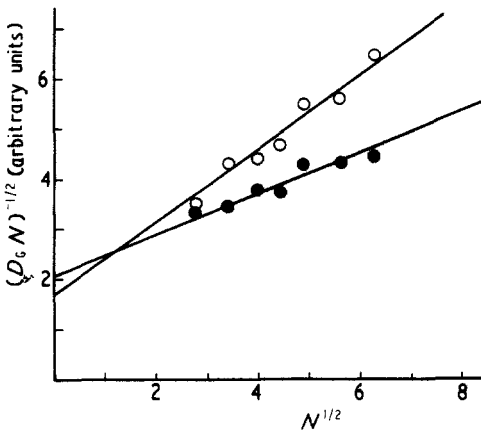

Figure 4. Monte Carlo results for the self-diffusion constant D_G. ○: d/b = 2; ●: d/b = 3.
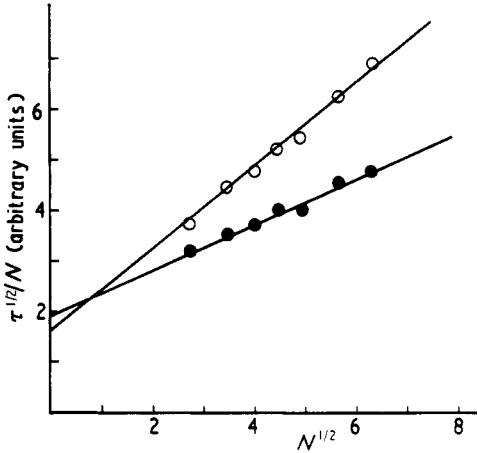
Figure 5. Monte Carlo results for the longest relaxation time τ of the time correlation function of the end-to-end vector. $\bigcirc$: $d/b = 2$; $\bullet$: $d/b = 3$.

Table 1. Values of $\alpha = b/a$ obtained from the plots of τ and D_G.

	$d/b = 2$	$d/b = 3$	Ratio
From τ	0·93	0·54	1·7
From D_G	1·0	0·56	1·8

the ratio $\alpha(d/b = 2)/\alpha(d/b = 3)$ should be $\frac{3}{2}$. The observed ratios also agree relatively well with these values as is shown in table 1.

6. Conclusions

We have generalized de Gennes' theory to the case of low concentration of obstacles by explicitly taking into account the mean length of the tube in which the chain is trapped. The result is found to conform to Rouse's theory for sufficiently low concentration of obstacles. It is shown that a diffusive transition occurs in the molecular weight dependence of the diffusion constant and the characteristic relaxation time from de Gennes' prediction to Rouse's. The theory has been shown to fit well with the data of the computer experiment.

Appendix. Tube length of the two-dimensional case

Equation (19) with (20) for the two-dimensional case has already been solved in the diffusion problem (Crank 1956). Replacing the diffusion constant by $b^2/4$, we have

$$W(r, n) = \frac{2}{\pi} \int_0^\infty \frac{du}{u} \exp\left(-\frac{b^2 u^2}{4} n \right) \frac{Y_0(ur)J_0(ua) - J_0(ur)Y_0(ua)}{J_0^2(ua) + Y_0^2(ua)}. \tag{A.1}$$

Hence the mean volume (or the area in this case) of the tube is

$$\langle V \rangle = \int_0^N dn \frac{b^2}{4} 2\pi a \frac{\partial W}{\partial r}\bigg|_{r=a}$$

$$= \frac{8a^2}{\pi} \int_0^{\xi^2/4} dy \int_0^\infty dx \frac{\exp(-yx^2)}{x(J_0^2(x) + Y_0^2(x))} \tag{A.2}$$

where $\xi = b\sqrt{(N)}/a$.

The mean tube length is now defined by $\langle L \rangle = \langle V \rangle / 2a$. We have calculated $\langle L \rangle / a$ as a function of ξ numerically. The result is shown in figure 6, where $\langle L \rangle / a\xi$ is plotted against ξ for convenience of comparison with the three-dimensional case. It is observed that $\langle L \rangle / a\xi$ is well approximated by the broken line shown in figure 6 for $\xi \lesssim 6 \cdot 0$, which leads to equation (28).
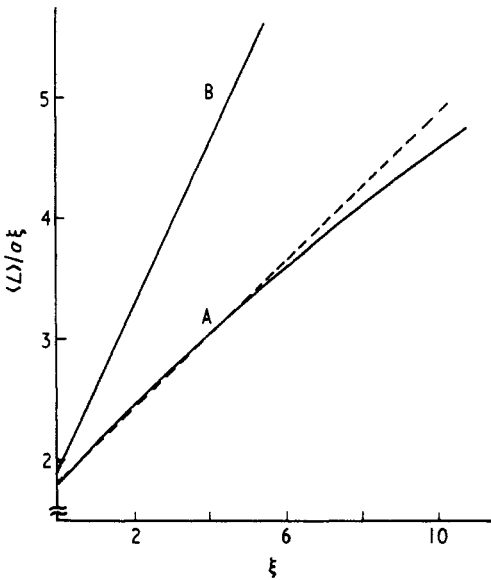

Figure 6. Mean tube length $\langle L \rangle$ is shown for the two-dimensional (curve A) and three-dimensional (curve B) cases. Here $\xi = b\sqrt{N}/a$.

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