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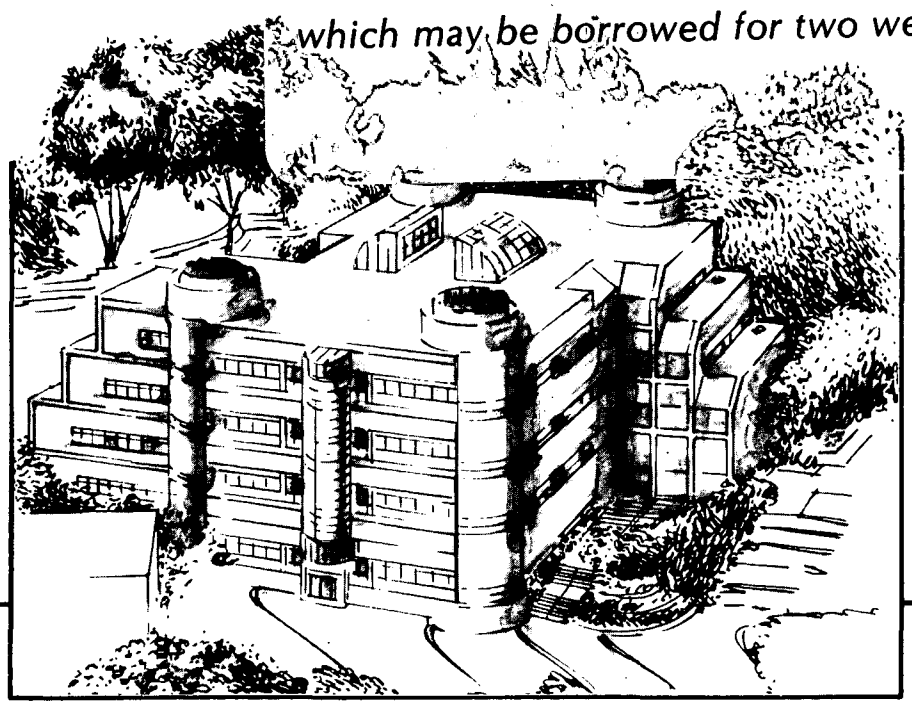

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Rotational Diffusivity of Rod-Like Molecules in Amorphous Polymeric Matrices

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In this note, scaling laws for rotational diffusivity of dilute monodisperse rigid-rod molecules (guest rods) in semi-concentrated and concentrated amorphous polymer solutions (host molecules) are derived. The coil-like matrix molecules are modeled as a collection of flexibly connected rigid sub-units. This allows an analogy with the Doi-Edwards theory for monodisperse rigid-rods in semidilute solutions to be used in the analysis. Very strong dependencies are predicted for the rotational diffusivity of the rods on host polymer volume fraction, coil length and rod length. In semi-concentrated polymer solutions the coils dramatically hinder the rotational freedom of the rods for $r^2 \gtrsim \phi_p^{-1}$, r being the rods' aspect ratio and ϕ_p the polymer volume fraction.

For dilute solutions of rod-like molecules in Newtonian solvents, Kirkwood and Auer (1) have shown that the rotational diffusion constant D_{ro} scales roughly with L^{-3}, where L is the length of the rods (the subscript "o" stands for infinite dilution). Doi and Edwards (2) have considered the case of semi-dilute rigid-rod solutions where a dependence as strong as L^{-9} is found for D_r. The diffusivity scales with c^{-2} where c is the rod number concentration. Recently Marrucci and Grizzuti (3) extended the theory to polydisperse systems.

The problem we shall consider here is different in that it is relevant to the practical preparation and processing of thermodynamically unstable systems known as "molecular composites" (4). These blends, consisting of liquid crystal polymers in amorphous polymeric matrices, hold much promise as light weight, high performance structural materials. The kinetics of phase separation of these systems is dominated by the tendency of the rigid rods to aggregate and to form liquid crystalline domains. Aggregation requires the simultaneous occurrence of translational and rotational diffusion. Since the

latter process is expected to be kinetically controlling, we attempt to establish scaling laws for the rotational diffusivity of the rigid-rod molecules in amorphous polymers. Such knowledge is also essential in understanding the rheological properties of molecular composites. Analysis of diffusion of an isolated rod in an amorphous polymer matrix is not new, as it was first considered by de Gennes (5) for the case in which the amorphous polymer is in the molten state. De Gennes assumed the elemental diffusion step to be of the order of the average distance between entanglements formed by the matrix. This resulted in a dependence of D_r on $(N_e L^{-5})$, N_e being the number of monomeric segments between entanglements. Because only molten systems are treated, the analysis did not address the dependence of D_r on polymer concentration. The L^{-5} dependency of D_r disagrees with results of the present calculation in which different exponents are found.

We begin by considering a dilute rod dispersion in a mixture of flexible coils and small solvent molecules. Rod-rod interaction is non-existent because of their dilute loading. However, rod-coil hard body interactions may be appreciable. If the coils form an entangled network and the rod length is greater than the average distance between adjacent polymeric sub-units the rotational freedom of the rods is strongly reduced. Figure 1 illustrates this concept schematically. Shown with a test rod are the flexible coils represented as a set of flexibly connected rigid sub-units, each of length L^*. The rod can freely oscillate within these confinements. Translational diffusion is similarly allowed in the direction of the rod axis. In particular, if the rod diameter is smaller than the mesh size of the network, this motion occurs essentially as it would in a dilute solution of rods in a small molecular weight solvent with a translational diffusion constant $D_{t//o}$ given by:

$$D_{t//o} \sim \frac{T \ln\left(\frac{L}{d}\right)}{\eta_s L} \tag{1}$$

where η_s is the solvent viscosity, d the diameter of the rod and T the product of the absolute temperature and the Boltzman constant. Long range rotation, however, is hampered by the topological constraints imposed by the entangling coils. Doi and Edwards have shown that if A and τ are the relevant length and time scales for rotation, then the rotational diffusivity behaves as:

$$D_r \sim \left(\frac{A}{L}\right)^2 \frac{1}{\tau} \tag{2}$$

For a monodisperse system of rods, τ is the time required by a molecule to translationally diffuse over a distance of the order of its own length. This motion is characterized by $D_{t//o}$, giving (for $L/d \gg 1$):

$$\tau \sim \frac{L^2}{D_{t//o}} \sim \frac{\eta_s L^3}{T \ln\left(\frac{L}{d}\right)} \tag{3}$$

Doi and Edwards also calculated the average elemental diffusion step A (2). This quantity was shown to be the average minimum distance between adjacent rods. It was obtained by expanding an imaginary cylindrical envelope around a test rod until just one neighboring rod was touched. For an isotropic rod orientation distribution, A is given by:

$$A \sim \frac{1}{L^2 c_r} \tag{4}$$

where c_r is the concentration of the rods (number of rods/volume). Subsequently, by extending the theory to account for polydispersity, Marrucci and Grizzuti (3) demonstrated that in order for a test rod to accomplish an elementary rotation two simultaneous processes must occur, namely, translational diffusion of the test rod itself over a distance of the order of its

own length, and translation diffusion of adjacent rods over a distance of the order of their own lengths. In polydisperse systems these processes are not equivalent, and the fastest one dictates the predicted rotational diffusivity. This concept equally applies to a dispersion of dilute, monodisperse rods in a semi-dilute solution of coils. In this case, while the translational diffusion time of the rods, τ_r, is still given by Eq. 3, the relevant diffusion time of the coils becomes their reptation time. As shown by de Gennes (6), in a semi-dilute solution of good solvents the coils can be topologically described as a connected sequence of smaller units referred to as "blobs". Due to thermodynamic constraints these blobs are impenetrable to each other. In this highly entangled system, the size of each blob is then the same as the average dimension of the mesh of the network. This characteristic dimension ξ, referred to as the correlation length, scales with the polymer volume fraction ϕ_p and hard core diameter d_p as follows:

$$\xi \sim d_p \, \phi_p^{-3/4} \tag{5}$$

In a good solvent the blobs behave as swollen coils, and the average number of monomeric units in each blob is :

$$g \sim \left(\frac{\xi}{d_p}\right)^{5/3} \sim \phi_p^{-5/4} \tag{6}$$

In translational diffusion the sequence of connected sub-units topologically behaves as a "snake". The length of the entire strand of blobs, L_s, scales as:

$$L_s \sim L_p \, \phi_p^{1/2} \tag{7}$$

where L_p is the total curvilinear contour length of the polymer backbone. Note that each polymer molecule, viewed as a sequence of blobs, behaves as a random coil with a mean square end-to-end distance, R_s, given by:

$$R_s^2 (\phi_p) \sim \frac{N}{g} \xi^2 \sim N d_p^2 \phi_p^{-1/4} \tag{8}$$

where N is the total number of backbone units in each polymer molecule.

Equation 7 allows us to calculate the coil reptation time τ_p:

$$\tau_p \sim \frac{L_s^3 \eta_s}{T} \sim \frac{L_p^3 \eta_s}{T} \phi_p^{3/2} \left(f(\phi_p, T)\right)^{-1} \tag{9}$$

where f (ϕ_p,T) is an exponential pre-factor which acounts for the probability that a hole large enough is created in the network to allow the diffusion of a blob through the mesh. This factor is ignored by de Gennes. Here, we note in particular, that $f(\phi_p,T)$ must be of the order unity for very small ϕ_p (dilute solutions) and must approach a Fujita-Doolittle type functionality when $\phi_p \simeq 1$. If this is the case, then for $\phi_p = 1$ Eq. 9 gives the correct scaling law for the reptation time of the coils in a melt. This makes Eq. 9 applicable to the entire semidilute range up to the concentrated limit $(\phi_p = 1)$.

We now calculate the rotational diffusivity of a rod of length L in a semi-dilute polymer solution. Each coil will be topologically represented as a sequence of N^* flexibly connected rods each at length L^*. Following Doi and Edwards (2) we assume the rotational diffusivity D_r to be given by:

$$D_r \sim \left(\frac{A}{L}\right)^2 \frac{1}{\tau} \tag{10}$$

where τ is the relevant microscopic translational diffusion time. In particular we propose the following criterion to determine τ:

$$\tau \sim \tau_r \quad \text{if} \quad \tau_r < \tau_p \tag{11}$$

$$\tau \sim \tau_p \quad \text{if} \quad \tau_r > \tau_p \tag{12}$$

or equivalently, from Eqs. 3 and 9:

$$\tau \sim \frac{L^3 \eta_s}{T \ln(\frac{L}{d})} \quad \text{if} \quad L^3 < L_s^3 \tag{13}$$

$$\tau \sim \frac{L_s^3 \eta_s}{T f(\phi_p, T)} \quad \text{if} \quad L^3 > L_s^3 \tag{14}$$

Note that an inequality of the type $L^3 \lessgtr L_s^3$ is much less restrictive than a statment such as $L \lessgtr L_s$. Note also that L_s is a function of the polymer volume fraction and molecular weight and that a transition of relevant time scales can be expected by changing the host composition.

Similar to the analysis by Doi and Edwards, the average elementary diffusion step, A, is

$$A \sim \frac{1}{L L^* N^* c_p} \tag{15}$$

where L is the length of the test rod, and c_p the polymer concentration (molecules/volume). In Eq.15 the product ($N^* c_p$) represents the number of polymeric sub-units (L^*) per unit volume. In order to calculate L^* and N^* the following limiting cases must be considered:

(a) The blobs can be readily penetrated by the rods.

(b) The blobs are inpenetrable.

In case (a) the rod-like equivalent sub-unit of the coils is the blob

itself. Therefore N^* represents the number of blobs per coil and L^* is comparable in magnitude to ξ. We have then:

$$L^* N^* \sim L_s \sim L_p \phi_p^{1/2} \tag{16}$$

and

$$\frac{A}{L} \sim \frac{1}{L^2 c_p L_p \phi_p^{1/2}} \tag{17}$$

which in terms of polymer volume fraction, ϕ_p, and hard-core diameter, d_p, becomes:

$$\frac{A}{L} \sim \frac{d_p^2}{L^2 \phi_p^{3/2}} \qquad \text{(case a)} \tag{18}$$

In case (b), the test rod is much more constrained. The local segmental concentration of the coil-like polymer is of the same order of magnitude of the monomer concentration ($N^* \cdot c_p$), and L^* is given by the length of a monomeric segment of the polymer. Hence,

$$L^* N^* \sim L_p \tag{19}$$

Hence:

$$\frac{A}{L} \sim \frac{1}{L^2 c_p L_p} \tag{20}$$

In terms of ϕ_p and d_p Eq. 20 becomes:

$$\frac{A}{L} \sim \frac{d_p^2}{L^2 \phi_p} \qquad \text{(case b)} \tag{21}$$

A slightly different derivation of Eq. 21 is given in Appendix A. It is important to note that in the final forms (Eqs. 18 and 21) the undetermined quantities N^* and L^* disappear.

As expected, the average reduced rotational mean free path A/L, is a strong function of the rod length and surrounding polymer concentration. From Eqs.10, 18 and 21 we finally obtain:

$$Dr \sim \frac{d_p^{\,4}}{L^4\ \phi_p^3\ \tau} \qquad \text{(case a)} \tag{22}$$

$$Dr \sim \frac{d_p^{\,4}}{L^4\ \phi_p^{\,2}\ \tau} \qquad \text{(case b)} \tag{23}$$

where τ is given by either Eq.13 or Eq.14 depending on the system. Indeed, in the two cases discussed previously, D_r will scale as:

$$D_r \sim \frac{d_p^{\,4}\ T\ \ln\left(\frac{L}{d}\right)}{L^7\ \eta_s\ \phi_p^3} \qquad \text{if } L^3 \ll L_s^{\,3} \qquad \text{(case a)} \tag{24}$$

$$D_r \sim \frac{d_p^{\,4}\ T}{L^4\ L_p^{\,3}\ \eta_s\ \phi_p^{\,9/2}\ f(\phi_p,T)} \qquad \text{if } L^3 \gg L_s^{\,3} \tag{25}$$

$$D_r \sim \frac{d_p^{\,4}\ T\ \ln\left(\frac{L}{d}\right)}{L^7\ \eta_s\ \phi_p^{\,2}} \qquad \text{if } L^3 \ll L_s^{\,3} \qquad \text{(case b)} \tag{26}$$

$$D_r \sim \frac{d_p^{\,4}\ T}{L^4\ L_p^{\,3}\ \eta_s\ \phi_p^{\,7/2}\ f(\phi_p,T)} \qquad \text{if } L^3 \gg L_s^{\,3} \tag{27}$$

Equations 24 to 27 are valid as long as $A/L \ll 1$. If we assume that $d_p \sim d$ and case b prevails, the condition $A/L \ll 1$ can be expressed in terms of the rod aspect ratio $r = L/d$ and polymer volume fraction as follows:

$$r^2 \phi_p \gg 1 \tag{28}$$

In a semi-dilute polymer solution, Eq.28 poses severe limitations on the range of rod aspect ratios for which rotational motion is not hindered. For example, if $\phi_p = 10^{-3}$ (a typical semi-dilute range polymer volume fraction) Eq.28 predicts hindrance for $r > 30$. Furthermore if $L_p/d_p = 10^4$, and $r = 30$ we get from Eqs. 13 and 7:

$$(L/d)^3 \sim 3 \times 10^4 \ll (L_s/d_p)^3 \sim 3 \times 10^7 \tag{30}$$

and a corresponding rotational diffusivity (assuming $\eta_s = 0.01$ P and $d = 5$ Å):

$$D_r \sim 10^6 \ \text{sec}^{-1} \ \text{rad}^2 \tag{31}$$

which is comparable in magnitude to the infinite dilution rotational diffusivity D_{ro}. This prediction is, however, totally altered when $\phi_p = 10^{-1}$. This gives (Eq.26):

$$D_r \sim 500 \ \text{sec}^{-1} \ \text{rad}^2 \tag{32}$$

and a corresponding orientation relaxation time, t:

$$t = (6 \ D_r)^{-1} \sim 10^{-4} \ \text{sec.} \tag{33}$$

which is of the same order of magnitude of the infinite dilution relaxation time of a rod 4000 Å long (Note that the rod considered here is only 150 Å). It must be pointed out that these estimates, although reasonable, are approximate in nature, since important numerical prefactors are ignored in the derived scaling relationships.

Experimental verification of the rotational diffusivity scaling laws and extension of the theory to account for higher rod concentration and polydispersity are the current goals of our research.

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Figure Captions

Fig. 1 A rigid rod molecule in a semidilute solution of an amorphous polymer. The coils are schematically represented as flexibly connected rigid sub-units, each of length L^*. Long range rotation of the test rod can be accomplished by either a translational motion of the rod itself (parallel to its own axis) or reptation of the surrounding coils. The rotational diffusivity of the rigid rod is determined by the faster of the two processes, whose relative importance depends on a number of system parameters including rod length, host polymer molecular weight and concentration.

Fig. 2. Calculation of the average number of times a plane surface Σ (defined by Σ: $\{x = b;\ -\pi a \leq y \leq \pi a;\ \frac{L}{2} \leq z \leq \frac{L}{2}\}$) is crossed by a random coil of radius R. The center of mass of the coil is at a distance d from plane α to which Σ belongs as a subsection. The random coil is assumed to be made of a sequence of flexibly connected rigid sub-units, each of length L^*. A second plane, α' (parallel to α) is located at a distance L^* from α. This defines volume V (V:$\{b \leq x \leq b+L^*;\ -\pi a \leq y \leq \pi a;\ -\frac{L}{2} \leq z \leq \frac{L}{2}\}$) in which the average number of (L^*) segments is calculated by the argument presented in the Appendix.

Fig. 3 A cylinder of radius a and length L surrounded by random coils. The end-to-end distance of the coils is R and their number concentation is n_c.

Appendix A

We begin with the calculation of the average numer of times the plane surface Σ, defined by Σ: $(x = b;\ -\pi a \leq y \leq \pi a;\ -\frac{L}{2} \leq z \leq \frac{L}{2})$, is crossed by a random coil of radius R. The center of mass of the coil is at a distance d from plane α to which Σ belongs as a subsection (Fig. 2).

We first calculate the number of segments of length L^* (along the coil) which are contained in the volume

$$V: (b \leq x \leq b + L^*;\ -\pi a \leq y \leq \pi a;\ -\frac{L}{2} \leq z \leq \frac{L}{2}).$$

For a random coil the segment density distribution function, p(r), is given by:

$$p(r) = \frac{L_c}{L^* \pi \sqrt{\pi}\ R^3}\, e^{-(r^2/R^2)} \qquad \text{(A1)}$$

where r is the radial distance from the center of the coil, L_c is the total curvilinear contour length of the coil and L^* the length of a rod-like segment (L_c/L^* is then the total number of such segments of length L^* per coil). The number of rigid segments in volume V is given by:

$$N_s = \frac{L_c}{L^* \pi \sqrt{\pi} R^3} \int_{-L/2}^{L/2} dz \int_{-\pi a}^{\pi a} dy \int_{d}^{d+L^*} e^{-\frac{(x^2+y^2+z^2)}{R^2}}\, dx \qquad \text{(A2)}$$

which can be written as:

$$N_s = \frac{L_c}{L^* \sqrt{\pi}}\, \mathrm{erf}\left(\frac{L}{2R}\right)\, \mathrm{erf}\left(\frac{a\pi}{R}\right) \int_{\frac{d}{R}}^{\frac{d+L^*}{R}} e^{-t^2}\, dt \qquad \text{(A3)}$$

where erf ( ) denotes the error function. The total number of times (Ni) which the surface Σ is crossed by the random walk is obtained as:

$$Ni = \lim_{L^* \to 0} Ns \tag{A4}$$

Taking this limit we obtain:

$$Ni = \frac{L_c}{\sqrt{\pi} R} \operatorname{erf}\left(\frac{L}{2R}\right) \operatorname{erf}\left(\frac{a\pi}{R}\right) e^{-\left(d^2/R^2\right)} \tag{A5}$$

Now we let n_c be the coil concentration (number of coils/volume) and L the length of a test rod contained in a cylinder of radius a and length L (Fig. 3) and assume d (the distance of the coil centers from the cylindrical surface) to be equal to R. The total number of times, N_t, the cylinder is crossed by the surrounding coils is proportional to the number of coils near the rod and to Ni ($\equiv$ intersections/coil). i.e.:

$$N_t \simeq \underbrace{n_c \pi \left((a + R)^2 - a^2\right) L}_{\text{(Total number of coils around the cylinder)}} \quad \underbrace{Ni}_{\text{(Number of intersections per coil)}} \tag{A6}$$

or

$$N_t \simeq n_c \, 4\pi R^2 \left(1 + \frac{a}{R}\right) L \, N_i \tag{A7}$$

From Eq. A5, with d = R, we obtain:

$$N_t \simeq 4 \sqrt{\pi} \, n_c \, R \, L \, L_c \left(1 + \frac{a}{R}\right) \operatorname{erf}\left(\frac{L}{2R}\right) \operatorname{erf}\left(\frac{a\pi}{R}\right) e^{-1} \tag{A8}$$

In the case of a densely packed system of small blobs of radius $\xi = R \ll L$, surrounding a rod of length L, and for $\frac{a}{R} \ll 1$, the following approximations

are valid:

$$\frac{a}{R} \ll 1 \begin{cases} 1 + \frac{a}{R} \sim 1 \\ \text{erf}\left(\frac{a\pi}{R}\right) \sim \frac{2a\sqrt{\pi}}{R} \end{cases} \tag{A9}$$

$$\frac{L}{R} \gg 1 \qquad \text{erf}\left(\frac{L}{2R}\right) \sim 1$$

Thus, from Eqs. (A8) and (A9) we obtain:

$$N_t \simeq \frac{8\pi}{e} n_c L_c L a \tag{A10}$$

which, in terms of polymer volume fraction, ϕ_p, and hard-core diameter, d_p, becomes:

$$N_t \simeq \frac{32}{e} \frac{\phi_p L a}{d_p^2} \tag{A11}$$

We seek the condition for which $N_t \sim 1$ ($a \sim A$ see text), hence:

$$A \sim \frac{e\, d_p^2}{32\, \phi_p L} \tag{A12}$$

and:

$$\frac{A}{L} \sim \frac{d_p^2}{\phi_p L^2} \tag{A13}$$

which corresponds to case (b) treated in the text. Note that this result is independent upon the particular choice made for function p(r) (in this case Gaussian). A different density distribution would only produce different numerical constants.

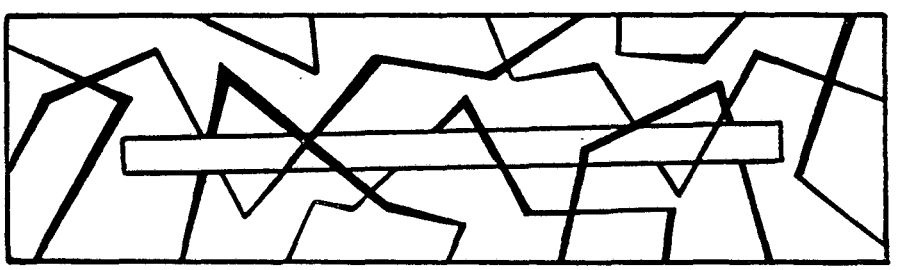

Figure 1

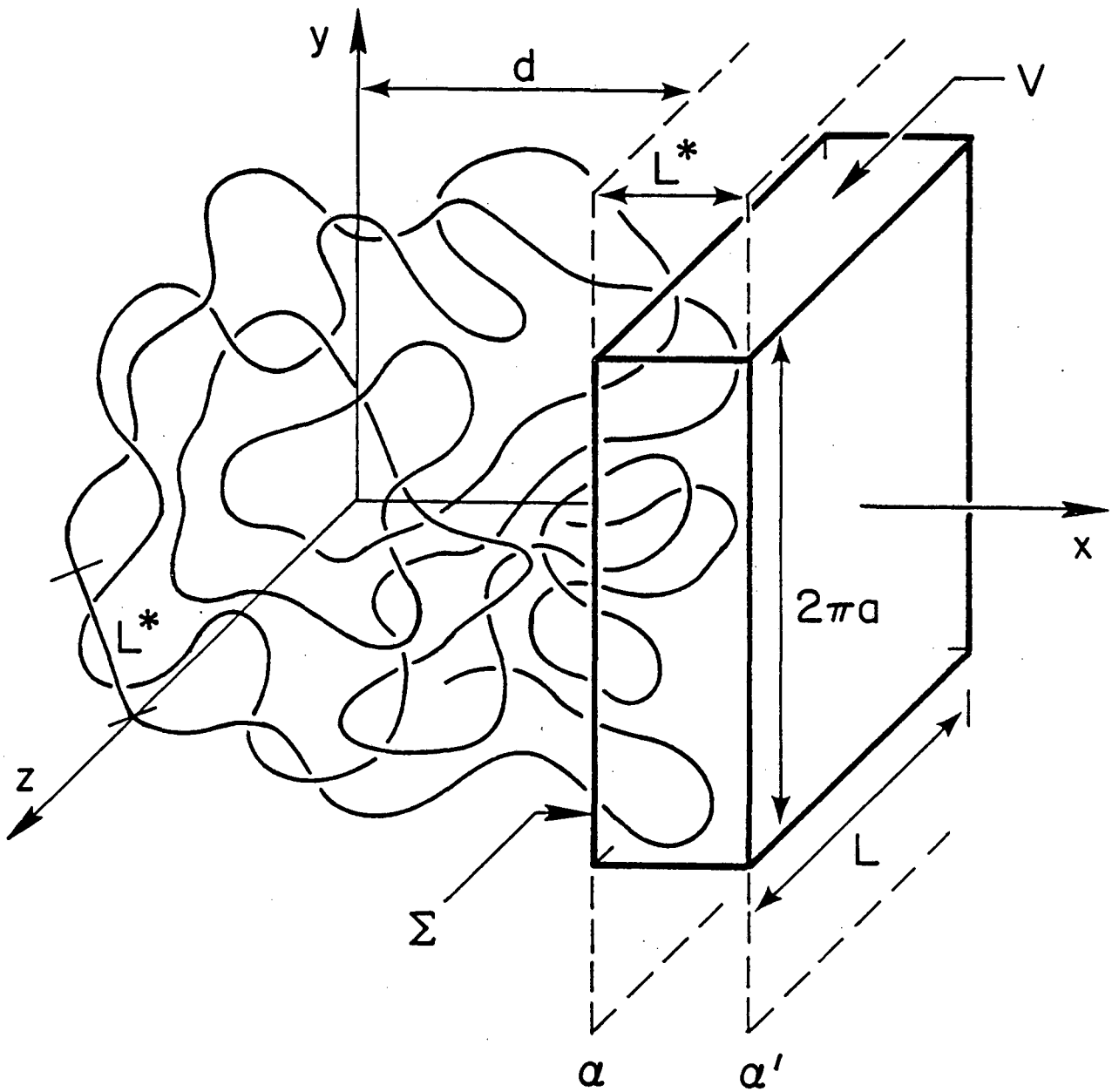

Figure 2

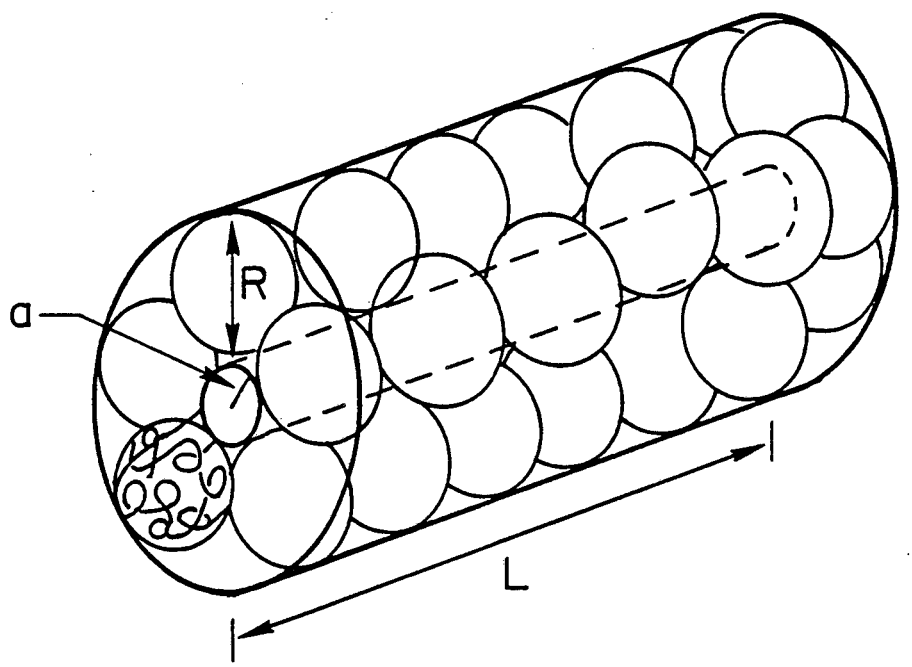

Figure 3

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