The shape of fibrous molecules in solution.

By Werner Kuhn (Karlsruhe).

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The views about the probable shape of fibrous molecules in solution that have been presented to date vary considerably and this question has reached a very interesting stage due to recent investigations into viscosity and birefringence of flow in brine with stretched, spherical, rigid, or deformed particles. On the basis of these considerations one can predict, for instance, how the viscosity has to behave in dependence on the molecular weight¹) as soon as one makes certain assumptions about the geometrical shape of the single particle. The decision if the assumptions were right has then to be made by comparison with the experience.

In this way one can say with certainty that the concept of molecules of highly polymerized materials like caoutchouc or cellulose being stretched rigid threads as has been represented by Staudinger until recently²), can be excluded. In fact, they can be excluded based on measurements about the viscosity of the brine of these compounds that have been published by Staudinger himself. Staudinger namely discovered for chain-molecules that in the region where the molecular weight can still be determined thermodynamically, the specific viscosity $\eta_{sp} = \frac{\eta}{\eta_0} - 1$ of equilibrated solutions increases proportional to the molecular weight of the dissolved compound. If the particles would be rigid and straight as Staudinger assumes then $\frac{1}{c}\eta_{sp}$ would be proportional to the square of the molecular weight.

The observation of $\frac{1}{c}\eta_{sp} \sim$ M therefore excludes the assumption of straight, rigid particles, and for the solution to the problem one should not be looking for in the modification of the theory of the viscosity of suspensions of rigid straight rods but in the modification of the assumptions about the shape of the particles.

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¹) W. Kuhn, Kolloid-Z. **52**, 269 (1933)

²) Compare e.g. H. Staudinger, Naturwiss. **22**, 65, 84 (1934).

An attempt in this direction shall be undertaken by the following considerations[3]). We shall make well defined assumptions about the statistic behavior of thread-like particles and based on these assumptions their average shape and their influence on the viscosity shall be determined. Even if the solution will not be satisfactory in every aspect, at least it represents a second case, the “arbitrary” coiled thread-like particle, compared to the first considered case of the rigid elongated rods.

An approach after which chain-molecules in solution are not completely straight but more or less bent has been attempted by W. Haller[4]) some time ago. The straight molecule is considered the actual stable molecule after these considerations and it is being asked about the bending it will undergo through the thermic forces in the solution. Even if I consider this question interesting, I still think that the treatment of the case of “randomly” coiled particles probably corresponds more to the real conditions. Besides the almost elongated shape, countless other shapes will be possible having approximately the same energy and of which the shape randomly deviates from the elongated form and which are caused namely by the angled conformation and the free or partly free rotatability. We want to know the shape one can expect on average under such conditions. It is a statistic question and it shall be treated following a statistic method. The approach will be valid quite universally for the case of free rotatability being practically present as well as being practically absent.

Statistic determination of the shape of “randomly” coiled thread-like particles

If a chain-like structure is given with similar or alternating bondings and I put the starting point at the origin and the bonding 1 → 2 into the direction of the z-axis then already bonding 2 → 3 will not point into the z-direction anymore because of the valence angle (fig.1); the angle formed by bonding 3 → 4 and the z-axis can already have quite different values and it is foreseeable that after a number of steps forward on the chain the direction of propagation leading from chain link s to (s+1) cannot be predicted anymore

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[3]) On the occasion of a discussion at the IXth International Congress of Pure and Applied Chemistry in Madrid it turned out that H. Mark at the same time presented similar considerations to which I already would like to point in this paper.

[4]) W. Haller, Kolloid-Z. **56**, 257 (1931); **61**, 26 (1932).

based on the direction of 1 → 2. If the whole chain consists of Z links I therefore can divide it into $\frac{Z}{s} = N$ - segments characterized in that way that the direction of propagation in one single segment does not depend anymore on the direction of the previous segment, e.g. that the direction of the transition 2s → 3s does not depend on the direction s → 2s. As consequence of this "random" line-up of the single segments a structure of a complicated cluster will be created of which the properties will be investigated now.

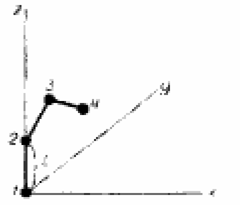

Fig.1

On average each of the N segments will have a length A and one can imagine the progression in the chain in the following way: I advance for a length A and after each step I determine say by throwing dice in what direction the next step shall be executed.

It depends on the size of the valence angle, the perfection of the rotatability and on the average distance of the single chain links (distance 1 → 2 in fig.1) how big the quantity s and how big the corresponding distance A will be in a given case. We will name the distance 1 → 2 *l*. In the case of perfect rotatability and a known specific valence angle we will be able to present a relation between A, *l*, s and valence angle by combination of a thought by H. Eyring (eq. 15a).

Treatment of the one-dimensional problem.

To simplify the task even further we first want to deal with the change that the z-coordinate experiences on average at each of the above described steps instead of searching for the propagation in the three-dimensional space. If every step has the absolute length A then the propagation in the z-direction equals $A_x = A\cos\vartheta$, independent on φ (fig. 2).

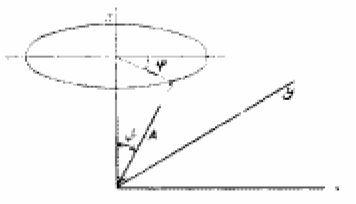

Fig. 2.

If all angles ϑ and φ appear equally frequent then on average

$$\overline{A_z^{\,2}} = \frac{A^2}{4\pi} \int_{\varphi=0}^{\pi} \int_{\vartheta=0}^{\pi} \cos^2 \vartheta \sin \vartheta \sin \varphi \mathrm{d} \vartheta \mathrm{d} \varphi$$

$$\overline{A_z} = \pm A \cdot \frac{1}{\sqrt{3}} = \pm b\,.$$

Therefore, on average we advance at every step by the distance b in either the positive or negative z-direction[5]). If we want to determine the value of the z-coordinate of the endpoint of our chain (link nr. N) by a probability consideration then we have to draw N-times a lot between the numbers 1 and –1. If +1 is drawn N_1-times and –1 N_2-times then [where

$$N_1 + N_2 = N\,] \tag{1}$$

the z-coordinate of the endpoint of the chain is

$$z_N = \frac{A}{\sqrt{3}} (N_1 - N_2) = b(N_1 - N_2) \tag{2}$$

The probability that the z-coordinate of the endpoint of our chain is –7b, for instance, equals the probability that the result for drawing the lot N-times is N_1-N_2 = -7, independent on the order in which the result N_1, N_2 is obtained.

If N is large then the described procedure is correct. The fact that the steps A are in reality not equal and that the absolute values A_z are all the more unequal does not represent an objection as one can easily calculate the mean in another order than described above.

Because the probability of the results +1 or –1 shall be the same for every drawing the probability of the result N_1, N_2 is

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[5]) With this consideration it is not excluded that the same point in space is occupied by several different links of the chain; the volume of the single chain links is neglected. This is of importance as we will introduce a correction for this later.

$$W_{N_1,N_2} = \left(\frac{1}{2}\right)^N \frac{N!}{N_1! \cdot N_2!} = \left(\frac{1}{2}\right)^N \frac{N!}{N_1! \cdot (N-N_1)!}. \tag{3}$$

It will be the largest for

$$\frac{\mathrm{d} \ln W_{N_1,N-N_1}}{\mathrm{d}N_1} = 0.$$

It follows after the Stirling formula

$$\ln W_{N_1,N-N_1} = N[\ln N_1 - 1] + (N-N_1)[\ln(N-N_1) - 1]$$

and from

$$\frac{\mathrm{d} \ln W_{N_1,N-N_1}}{\mathrm{d}N_1} = 0:$$

$$N_1 = N - N_1;\, N_1 = \frac{N}{2} = N_2 \tag{4}$$

Therefore the most probable shape of the chain-molecule corresponds to the case $N_1 = N_2$, i.e. to the case that start point and end point of the chain coincide. This is very similar to Maxwell's law of velocity where the most probable velocity is zero. Similarly, we are not only interested in the most probable N_1-value but especially also in those N_1-values which are close to the most probable one. For that reason we develop the function (3) in the environment of $N_1 = \frac{1}{2}N$. We look for the probability that $N_1 = \frac{1}{2}N + \alpha$, thus N_2 equals $\frac{1}{2}N - \alpha$. By inserting into (3) we get

$$W_{\frac{N}{2}+\alpha,\frac{N}{2}-\alpha} = W_\alpha = \left(\frac{1}{2}\right)^N \frac{N!}{\left(\frac{N}{2}+\alpha\right)!\left(\frac{N}{2}-\alpha\right)!}$$

which by evaluation on the basis of the Stirling formula becomes

$$\ln W_\alpha \cong -\frac{2a^2}{N}.$$

It thus becomes

$$W_\alpha = \mathrm{const} \cdot e^{-\frac{2a^2}{N}} \tag{5}$$

To determine the constant in (5) (for that the precision of the Stirling formula is not sufficient) we use the fact that $\int_{-\frac{1}{2}N}^{+\frac{1}{2}N} W_\alpha \mathrm{d}\alpha = 1$ because the probability that N_1 falls between 0 and +N and therefore α falls between $-\frac{N}{2}$ and $+\frac{N}{2}$ has to be 1. If we assume a large N then the limits can be set to -∞ and +∞ without changing the absolute value of the integral noticeably. Then it comes:

$$\mathrm{const}\int_{-\infty}^{+\infty} e^{-\frac{2\alpha^2}{N}}\mathrm{d}\alpha = 1 = \mathrm{const}\sqrt{\frac{\mathrm{N}}{2}}\int_{-\infty}^{+\infty} e^{-x^2}\mathrm{d}x = \mathrm{const}\sqrt{\frac{\mathrm{N}}{2}}\sqrt{\pi};\,\mathrm{const} = \sqrt{\frac{2}{\mathrm{N}}}\frac{1}{\sqrt{\pi}}$$

and (5) becomes

$$W_\alpha = \sqrt{\frac{2}{\mathrm{N}}}\frac{1}{\sqrt{\pi}}e^{-\frac{2\alpha^2}{N}}\,. \tag{6}$$

The probability that the endpoint of the chain is shifted in the positive z-direction relative to the starting point by an absolute value that lies between $2b\cdot a$ and $2b\cdot(a+\mathrm{d}a)$ results from the equation (6) as

$$W_\alpha \mathrm{d}\alpha = \sqrt{\frac{2}{\mathrm{N}}}\frac{1}{\sqrt{\pi}}e^{-\frac{2\alpha^2}{N}}\mathrm{d}\alpha \tag{7}$$

because the relation

$$z = 2ba\frac{2A}{\sqrt{3}}\alpha;\quad \alpha = \frac{\mathrm{z}}{2\mathrm{b}} \tag{8}$$

applies to the z-coordinate of the endpoint of our chain. By inserting this relation into (7) we obtain as probability for the endpoint of the chain lying between z and z +dz:

$$W_z \mathrm{d}z = \frac{1}{b}\frac{1}{\sqrt{2\mathrm{N}}}\frac{1}{\sqrt{\pi}}e^{-\frac{z^2}{2Nb^2}}\mathrm{d}z\,. \tag{9}$$

Treatment of the three-dimensional problem.

To return to the spatial problem, i.e. to the question where in the space to look for the endpoint of the chain if the starting point is put at the origin of the coordinate system, we realize that relations analog to (9) also exist for the x- and for the y-coordinate.

Furthermore, we realize that the probability of the chain-endpoint having a z-coordinate which falls between z and z + dz as well as a x-coordinate that falls x and x + dx and a y-coordinate that falls between y and y + dy is equal to the product of the corresponding single probabilities. One then has

$$W_x \cdot W_y \cdot W_z \cdot \mathrm{d}x \cdot \mathrm{d}y \cdot \mathrm{d}z = \left(\frac{1}{\sqrt{2Nb}} \frac{1}{\sqrt{\pi}} \right)^3 e^{-\frac{x^2+y^2+z^2}{2b^2N}} \cdot \mathrm{d}x \cdot \mathrm{d}y \cdot \mathrm{d}z \qquad (10)$$

Thus, the probability for the chain endpoint to fall within equally large volume elements, which have the same distance $r = \sqrt{x^2 + y^2 + z^2}$ from the origin of coordinates, is equal. The probability for the chain endpoint to have a distance from the origin between r and r + dr follows therefore from (10) by integrating over the volume elements that fulfill the condition above. One obtains:

$$W_r \mathrm{d}r = \left(\frac{1}{b\sqrt{2\pi \mathrm{N}}} \frac{1}{\sqrt{\pi}} \right)^3 e^{-\frac{r^2}{2b^2N}} 4\pi r^2 \mathrm{d}r = \left(\frac{1}{b\sqrt{2\mathrm{N}}} \right)^3 \sqrt{\frac{2}{\pi}} e^{-\frac{r^2}{2b^2N}} r^2 \mathrm{d}r \qquad (11)$$

One is easily convinced that - as it has to be - $\int_0^\infty W_r \mathrm{d}r = 1$. After all, $W_r$dr is the probability of the endpoint of the chain to have a distance between r and r + dr from the origin.

The use of (11) allows us to answer any question with regard to the frequency of given distances in dependence on the chain length (number of chain links).

Statistic probability of ring-shaped constellations.

We ask e.g. for the probability of the chain endpoint to lie within a small distance B from the chain origin. In the exponent of (11) then is $\frac{r^2}{b^2N} < \frac{B^2}{b^2N} << 1$ since N shall be a large number. The exponent of (11) then can be regarded as small and the quantity $e^{-\frac{r^2}{2b^2N}} \cong 1$. One has then:

$$(C)_{r=0} = \left(\frac{W_r \mathrm{d}r}{4\pi r^2 \mathrm{d}r} \right)_{r \to 0} = \left(\frac{1}{b\sqrt{2\pi}} \frac{1}{\sqrt{N}} \right)^3 \qquad (11a)$$

This quantity indicates how often per cm^3 the end of a chain consisting of N segments can be found on average in a volume element that is very close to the beginning of the molecule. The information $(C)_{r=0} = 10^{20}$ e.g. would mean that the probability for finding the end of the molecule at a distance of maximal $2 \cdot 10^{-8}$ away from the start of the molecule is equal to $10^{20} \cdot \frac{4\pi}{3} \cdot 2^3 \cdot 10^{-24} = 3.4 \cdot 10^{-3}$, i.e. that about one in 300 molecules would fulfill this condition. In any case, the number of thread-like molecules having a ring-shaped constellation can be expected to be proportional to $(C)_{r=0}$. The probability of two reactive groups (e.g. one a NH_2 and the other a Cl group), where one sits at the start and the other at the end of the chain, to find each other and react with each other should be proportional to this quantity. It could be taken from relation (11a) that this probability for a chain molecule of "random" shape is expected to be proportional to $N^{-\frac{3}{2}}$. Perhaps one could gain some insight if this is true or to what extend parallel layers of chain molecules or their parts create special conditions by compariing to ring-forming reaction rates of long chains[6]). It seems that one has to conclude to some extend from viscosity data that there are special conditions present. The discussion of the absolute reaction rate of ring-forming reactions also points to the presence of special conditions:

As will be shown later, one approximately gets for paraffin hydrocarbons with the carbon number Z = 20: $Nb^2 = 30 \cdot 10^{-16}$ and thus $(C)_{r=0} = 3.85 \cdot 10^{20}\ \text{cm}^{-3}$. This means: the end of the molecule would be present in the volume elements surrounding the start of the molecule at a concentration of 3.85 particles per cm^3 or $\frac{1000}{2.06 \cdot 10^{23}} \cdot 3.85 \cdot 10^{20} = 0.6\ \text{mol/l}$. If the chain molecules that are capable of forming a ring would have a concentration of 0.6 mol/l then we would find around one end of a molecule the other end of the same molecule and one end of another molecule with same probability. The probability of the ring formation should thus be comparable to the probability that a group sitting at the start of a molecule 1 reacts with a group sitting at the end of another molecule. (Rate of ring-formation comparable to the rate of polymerization.) It follows from the results which were obtained from the investigation of the ring formation of carbon chains with

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[6]) K.Ziegler, H. Eberle, and H.Ohlinger, Liebigs Ann. Chem. 504, 94 (1933)

large link numbers by H. Ziegler[6]) that the rate of ring formation is much smaller than it would have been expected after the considerations just presented. This can probably attributed to the fact that the ends of the molecule are not sufficiently lively because parts of the chain hinder the diffusion of the rest of the chain at least temporarily by sticking together. One could also describe this in that way that the end of the molecule inside the coil diffuses slower and, so to speak, is exposed to a higher viscosity than in free solution. In any case, these considerations show that the existing experiments about ring formation are not sufficient to secure a "randomly" coiled shape of the dissolved thread-like molecules in solution and that these experiments rather support than contradict a partly coiled, partly straight shape of those molecules.

Mean values; influence of the valence angle

Besides calculating the probability of the appearance of certain distances, (11) also allows the calculation of any mean value of which the investigation will lead to an interesting addition to the previous consideration. Because of (11) on has for instance

$$\bar{r} = \frac{2}{3}\sqrt{\frac{6}{\pi}}\sqrt{N} \cdot A = 2\sqrt{2}\frac{\sqrt{N}}{\sqrt{\pi}} b \tag{12}$$

$$\overline{r^2} = NA^2 = 3Nb^2 \tag{13}$$

The latter expression now permits a combination with the result of a calculation carried out by H. Eyring[7]): Eyring assumes that every C-C bond encloses an angle that deviates from 180° (straight propagation) by a value β and that there exists a free rotatability around each single bond. He presents a general formula for the square distance of the first C-atom to the C-atom (Z+1) in dependence on all existing angles, and by forming mean values he obtains

$$\overline{r^2} = l^2\left[Z + 2(Z-1)\cos\beta + 2(Z-2)\cos^2\beta - \ldots.. + 2\cos^{(Z-1)}\beta\right] \tag{14}$$

Here one assumes that all conceivable angles owing to the rotatability are taken into consideration with equal weight. Later we will see that the assumption is not completely permissible because based on this assumption one single point in space would possibly be occupied by several atoms of the chain molecule (e.g. by the fifth, eleventh, nineteenth,

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[7]) H. Eyring, Phys. Rev. 39, 746 (1932)

and twenty fifth) which is physically not allowed. Thus, the space filling caused by the chain itself is neglected which quite corresponds to the approach carried out so far during our statistic consideration.

As everybody knows, the tetrahedron angle in the case of carbon chains is 110°, i.e. $\beta = 180 - 110 = 70^{\circ}$; $\cos\beta = 0.333\ldots$. For large values of Z it generally is instead of (14):

$$\overline{r^2} = l^2 Z \frac{1+\cos\beta}{1-\cos\beta}. \tag{15}$$

By comparison with (13) we thus have:

$$\overline{r^2} = NA^2 = 3Nb^2 = Zl^2 \frac{1+\cos\beta}{1-\cos\beta}. \tag{16}$$

$$A^2 = sl^2 \frac{1+\cos\beta}{1-\cos\beta}. \tag{15a}$$

We tie to this the interesting remark that our case N = Z, A = l (chain of Z-links, every chain link of length *l*, complete rotatability and not fixed, statistically variable valence angle) corresponds exactly to the case $Z, l, \beta = \frac{\pi}{2}$ (chain of Z-links, every chain link of length *l*, valence angle fixed at 90°). We namely have in both cases:

$$\overline{r^2} = Zl^2. \tag{16a}$$

The resulting shape of the of chain molecule consisting of Z links therefore is the same no matter if one fixes the valence angle at 90° with free rotatability or if the angle, also with free rotatability, can statistically adopt any value between 0 and π.

But also the cases of other given fixed angles are accessible to a approach with this consideration. With the help of (16) we can introduce the quantity $Z{\cdot}l^2$ into the distribution function (11) instead of Nb^2 and we then get:

$$W_r = 3\sqrt{\frac{6}{\pi}} \frac{r^2}{\left(l^2 Z \frac{1+\cos\beta}{1-\cos\beta}\right)^{\frac{3}{2}}} e^{-\frac{3}{2}\frac{r^2}{l^2 Z \frac{1+\cos\beta}{1-\cos\beta}}} \tag{17}$$

and instead (13):

$$W_r = \frac{2}{3}\sqrt{\frac{6}{\pi}} \sqrt{Z} l \sqrt{\frac{1+\cos\beta}{1-\cos\beta}}. \tag{18}$$

If the value valid for C-C bonds (0.333) is introduced for cos β, it comes $\frac{1+\cos\beta}{1-\cos\beta}=2$ and we have:

$$W_r = \frac{3}{2}\sqrt{\frac{3}{\pi}}\frac{r^2}{\left(l^2 Z\right)^{\frac{3}{2}}}e^{-\frac{3}{4}\frac{r^2}{l^2 Z}} \tag{19}$$

$$\bar{r} = \frac{4}{3}\sqrt{\frac{3}{\pi}}\sqrt{Z}l \tag{20}$$

$$\overline{r^2} = 2l^2 Z\,. \tag{21}$$

Relation (17) is of great importance because it gives the probability to find the end point of a chain of Z links within a distance of r to r + dr from the start point only as a function of the link number Z, the length of the single chain segment *l* (fig. 1), and the valence angle β (β equals π minus valence angle). In the case of $\beta \neq \frac{\pi}{2}$ we were initially forced to divide the chain of Z links into N segments of s chain links to provide the statistic consideration with a sufficient basis. Preliminarily, we had set the length of these segments consisting of s links to A equal $\sqrt{3}b$. From (15b) we now see the necessary connection between A, s, l, and β. Additionally, one realizes that (because of N·s = Z) relation (17) always results from introduction of (15a) in (11) no matter how large s had been chosen if only A is calculated from s, l, and β with (15a). In particular s, the number of links that I have to advance in order to be able to consider the direction of the propagation as independent on the original one, could be set to 1 in equation (15a) if the corresponding distance is set to $l\sqrt{\frac{1+\cos\beta}{1-\cos\beta}}$ instead of l.

This means that for the calculation of the spatial mass distribution in chain molecules for which exists free rotatability around every C-C bond and for which every bond connects to the previous one with the valence angle π- β, besides complete rotatability one can pretend that the angles of consecutive bonds can assume arbitrary values with equal probability if one generally replaces the real C-C distance l by the value $l\sqrt{\frac{1+\cos\beta}{1-\cos\beta}}$.

The condition which is important for the quantitative aspect of this calculation is the relation (14) given by Eyring and the resulting relation (15) for large Z values, respectively, as should be emphasized once more. Without this relation it only would have been possible to give an approximate value for the quantity A following (15a) which has to be inserted into the preceding equations. However, the form of these relations and the existence of a quantity A persist beyond the range of validity of relation (15) especially if a free rotatability is only partly present. In addition, (11) differs from (15) in that the former relation (in contrast to the second) allows a statement of the relative frequency of the presence of the different conformations that are possible due to the free rotatability. This can be of importance for kinetic considerations as has already been mentioned in an example.

Mean mass distribution in the "random" coil; space filling effect.

We will consider another problem that is a part of this discussion, which is the question how one should imagine the mean mass distribution in a big coiled chain molecule. Therefore we return to equation (19), however one also could use the more general relation (17) or (11). Z is assumed to be a big number (e.g. bigger than 10). The beginning of the chain molecule shall always lie in the origin of the coordinate system. We consider many such systems next to each other and ask what position the chain link i will assume on average. The probability for its distance from the origin to lie between r and r + dr is based on (19)

$$W_r \mathrm{d}r = \frac{3}{2}\frac{\sqrt{3}}{\sqrt{\pi}}\frac{1}{\left(l^2 i\right)^{\frac{3}{2}}} \mathrm{e}^{-\frac{3}{4}\frac{r^2}{l^2 i}} r^2 \mathrm{d}r \tag{22}$$

The contribution of chain link i to the mass density $(\rho)_r$ at the distance r is therefore with m_0 being the mass of a single chain link:

$$\left(\rho_i\right)_r = \frac{\frac{3}{2}\frac{\sqrt{3}}{\sqrt{\pi}}\frac{1}{\left(l^2 i\right)^{\frac{3}{2}}} \mathrm{e}^{-\frac{3}{4}\frac{r^2}{l^2 i}} r^2 \mathrm{d}r}{4\pi r^2 \mathrm{d}r}$$

Together, the chain links with numbers between i and i + di will create a mean density of

$$(\mathrm{d}\rho)_r = m_0 \frac{3}{8\pi}\sqrt{\frac{3}{\pi}}\frac{1}{\left(l^2 i\right)^{\frac{3}{2}}}\,\mathrm{e}^{-\frac{3}{4}\frac{r^2}{l^2 i}}\mathrm{d}i$$

at the distance r. The chain links with numbers between Z_1 and Z_2 create therefore a mean mass density of

$$(\rho)_{\mathrm{r}}^{Z_1 \to Z_2} = \int\limits_{i=Z_1}^{Z_2} m_0 \frac{1}{8}\left(\frac{3}{\pi}\right)^{\frac{3}{2}}\frac{1}{\left(l^2 i\right)^{\frac{3}{2}}}\,\mathrm{e}^{-\frac{3}{4}\frac{r^2}{l^2 i}}\mathrm{d}i$$

at the distance r. As a result

$$(\rho)_{\mathrm{r}}^{Z_1 \to Z_2} = \frac{2}{3}\left(\frac{1}{\pi}\right)\frac{3}{2}\frac{m_0}{l^2 r}\int\limits_{\sqrt{\frac{4}{3}}\frac{r}{l}\sqrt{\frac{1}{Z_2}}}^{\sqrt{\frac{4}{3}}\frac{r}{l}\sqrt{\frac{1}{Z_1}}} \mathrm{e}^{-x^2}\,\mathrm{d}x \tag{23}$$

If the distance r for which the mass density should be determined is considerably smaller than $\sqrt{l^2 Z_1}$, i.e. considerably smaller than the mean distance at which the link Z_1 can be found with the highest probability, then $\int\limits_{x_2}^{x_1} e^{-x^2}\mathrm{d}x$ must be replaced by $\left[x_1 - x_2\right]$ and instead of (23) it comes:

$$(\rho)_{\mathrm{r}}^{Z_1 \to Z_2} = \frac{1}{4}\left(\frac{1}{\pi}\right)^{\frac{3}{2}}\frac{m_0}{l^3}\left(\frac{1}{\sqrt{Z_1}} - \frac{1}{\sqrt{Z_2}}\right). \tag{24}$$

The conditions for the validity of equation (24) are especially true for the centre of the coil (r = 0). The corresponding equation could already have been obtained from (11a). We thus have especially:

$$(\rho)_{\mathrm{r}}^{Z_1 \to Z_2} = \frac{1}{4}\left(\frac{1}{\pi}\right)^{\frac{3}{2}}\frac{m_0}{l^3}\left(\sqrt{\frac{1}{Z_1}} - \sqrt{\frac{1}{Z_2}}\right). \tag{25}$$

Now $\frac{m_0}{l^3}$ is the density that the substance would assume if the mass m_0 of each chain link was contained per one cube of border length l (= distance between two chain links). For chains of paraffin hydrocarbons $\frac{m_0}{l^3}$ is approximately the density the substance would have at densest packing. For chains like polystyrene or highly polymeric sugars which have a similar l (length of the single chain link) but larger m_0 (presence of phenyl groups or O-atoms, as side appendage to each chain link so to speak), $\frac{m_0}{l^3}$ is larger than the density which the substance would assume in the solvent free state. If we then set $Z_1 \approx 4, Z_2 \approx 50 \text{ or } 60$ one recognizes corresponding to (25) that the mass density in the centre of the coil created by the 4th to 50th chain link can easily amount to 15 to 50 % of the pure solvent-free substance depending on the substance we deal with, e.g. with pure paraffin hydrocarbon chains or with chains to which side chains like O-atoms or other groups are attached.

This remark is important because it shows that the conditions under which relation (25) and its preceding relations, namely (11), were calculated need a correction. It namely is clear that the probability for the link Z being at a point where another chain link is situated has to be zero, and it already became obvious that the "occupied" areas cannot be neglected in relation to the whole available space.

Approach for the correction of the space filling effect.

One can try to take this situation into account in the following manner: It holds after (16) for the distance between the starting point of the molecule and the chain link Z at neglect of the space filling and for statistically variable valence angles[8])

$$\overline{r^2 z} = l^2 Z \tag{16a}$$

The value of $\overline{r_Z}$ has to be increased related to this value because of the space filling which will manifest itself by *l* being a function of Z and not a constant as the space filling effect depends on the total size of the chain molecule. E.g. we set

$$l = l_0 Z^{\varepsilon} \tag{26}$$

where *ε* would probably mean a rather small exponent. We then would have

$$\sqrt{\overline{r^2 Z}} = l_0 \sqrt{Z} \cdot Z^{\varepsilon}\,. \tag{27}$$

l (in 26) would mean the "effective distance" of two consecutive chain links which is decisive for the coil dimensions, *l₀* the actual distance of the same. Still another factor could possibly enter into *l₀* which takes into account the "thickness" of the chain links.

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[8]) *l* would have been replaced by $l \cdot \sqrt{\frac{1+\cos\beta}{1-\cos\beta}}$ at a given fixed angle *β*.

The consideration of the space filling in the form of approach (26) could partly be justified by the fact that the fixation of the angle β between two consecutive bondings (at free rotatability) could be traced back to the case of non-fixed angles β by introducing a corrected “effective distance” for the distance of consecutive chain links.

The approach (26, 27) would possess the peculiarity that the distance $\sqrt{\overline{r^2Z}}$ becomes independent on how the molecular dimensions are determined, i.e. either directly after formula (16a and 26) or if the chain is imagined cut into N segments of s chain links and the formulas are used first for the determination of the dimensions of each piece of s links and then for the combination of these pieces to the complete structure:
After (27) it is for one piece of s links:

$$\overline{r_s} = l_0\sqrt{s}s^{\varepsilon} .$$

$\overline{r_S}$ instead of l_0 has to be used to combine N of these pieces to the complete structure. Taking into account $Z = s \cdot N$ leads to

$$\overline{r_Z}N = r_S\sqrt{N} \cdot N^{\varepsilon} = l_0\sqrt{s}s^{\varepsilon}\sqrt{N} \cdot N^{\varepsilon} = l_0\sqrt{Z} \cdot Z^{\varepsilon} ,$$

thus, as claimed, relation (27)
The approach (26, 27) would comprise the assumption that in the beginning the first s chain links deliver a partial coil which is expanded to some extend because of the space filling and that these partial coils give again rise to space filling effects when “randomly” combined so that the complete coil consisting of the partial coils is expanded again even in a quantitative analog manner. One can also describe this as if the pores left in the partial coils cannot filled up with parts of the other partial coils. All those assumptions are, of cause, arbitrary although quite plausible, and could be replaced by other assumptions. They will play a role during the discussion of the viscosity law.
If due to space filling the distance between start and end of a chain consisting of five links would increase by 20 % compared to the “disordered” coil (neglect of space filling) then the quantity ε in (26, 27) would result from $5^{\varepsilon} = 1.2$ from what would follow:

$$\varepsilon = \frac{\log 1.2}{\log 5} = 0.113 . \qquad (28)$$

Inequality of longitudinal and diagonal dimensions of the "random" coil.

Before an analysis of these relations with regard to viscosity questions is carried out, the picture of the statistically coiled molecule shall be completed in another direction. Up to now the approach could give the impression that the outer shape which the chain molecule assumes at "disordered" coiling would be a sphere. This is by no means the case. We will rather see that the most probable form would be a bent ellipsoid (about the shape of a bean).

We had positioned the beginning of the chain molecule into the origin of the coordinate system during the approach that lead us to equation (11) and we then calculated the distance r_Z of the end of the molecule by statistic calculation. After (12), (13), (16), and (16a) we obtained for this distance which will be named r_l in the following (if N = Z, A = l, $3b^2 = A^2$[9])

$$r_1 = 2\sqrt{2}\sqrt{\frac{Z}{\pi}}b = \frac{2\sqrt{2}}{\sqrt{3\cdot\pi}}\sqrt{Z}l\,. \qquad (16b)$$

The direction which connects the starting point to the end point will represent a preferred direction on inspection of the shape of the single coiled molecules, and we will assign this direction to the z-direction for further considerations of the coil shape. The coordinate system (which is fixed for each coil) will be oriented in such a way that the chain begins and ends on the z-axis. The statistics for the extension of the coil into the x- and y-direction will now be much different as for the determination of r_l (where no constraint with regard to the position of the end point existed). For a chain with Z links it is easy to understand that the largest values the x- and y-coordinates can assume are to be expected for the middle of the chain. We thus find a measure for the cross section of the coil by looking for the x- and y-coordinates of the chain link number $\frac{1}{2}Z$.

We begin with the dimension in the x-direction. We will start by throwing the dice Z-times and by advancing each time by either +b or by –b in the x-direction, very similar to the determination of r_l. We now have the condition that after throwing the dice Z-times the number of positive steps (Z_1) has to equal the number of the negative steps (Z_2).

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[9]) In the case of fixed angles β the factor $\sqrt{\frac{1+\cos\beta}{1-\cos\beta}}$ would have to be attached to l.

$$Z_1 = Z_2 \tag{29}$$

But for the point we are looking for $\left(\frac{1}{2}Z\right)$, the numbers (P1 positive and P2 negative; $P_1 + P_2 = \frac{1}{2}Z$) obtained until this point will in general not be equal to each other. We are interested in the difference, thus for the quantity

$$P_1 - P_2 = 2p\,. \tag{30}$$

It follows from relation (29) that for the second "branch" of the chain (point $\frac{1}{2}Z$ to Z) P$_1$' positive and P$_2$' negative steps have to be carried out where it has to be $P_1' - P_2' = -2p$. The probability of the event $P_1 - P_2 = 2p$; $P_1' - P_2' = -2p$ is now proportional to the number of possibilities of realization of this event. We first have

$$\begin{aligned} &P_1 + P_2 = \frac{1}{2}Z = P_1' + P_2' \\ &P_1 - P_2 = -P_1' + P_2';\ P_1 = P_2' \\ &P_1' = \frac{1}{2}Z - P_1;\ \ \mathrm{P}_1 = \frac{1}{4}Z + p;\ \ \mathrm{P}_2 = \frac{1}{4}Z - p \end{aligned} \tag{31}$$

The number of possibilities to distribute P$_1$ positive signs within Z positive and negative signs is equal to $\begin{pmatrix} \frac{Z}{2} \\ P_1 \end{pmatrix}$ and analogue for P$_1$' equal to $\begin{pmatrix} \frac{Z}{2} \\ P_1' \end{pmatrix}$. The number of possibilities to induce these events simultaneously is equal to the product of these quantities, i.e.

$$W_{P_1} = \begin{pmatrix} \frac{Z}{2} \\ P_1 \end{pmatrix} \cdot \begin{pmatrix} \frac{Z}{2} \\ P_1' \end{pmatrix} = \begin{pmatrix} \frac{Z}{2} \\ P_1 \end{pmatrix} \begin{pmatrix} \frac{Z}{2} \\ \frac{Z}{2} - P_1 \end{pmatrix} = \left[\begin{pmatrix} \frac{Z}{2} \\ P_1 \end{pmatrix} \right]^2 . \tag{32}$$

Because in general it holds

$$\begin{pmatrix} \frac{Z}{2} \\ P_1 \end{pmatrix} = \frac{\left(\frac{Z}{2}\right)!}{P_1! \left(\frac{Z}{2} - P_1\right)!} \tag{33}$$

then we conclude similarly to what followed equation (3) that the most probable value of P_1 is equal to $\frac{Z}{4}$, hence the most probable x-coordinate of the chain centre is zero. To find the mean cross dimension of the chain we develop the function (32) or its logarithm, respectively, like function (3) in the environment of $P_1 = \frac{Z}{4}$ after the quantity $P_1 - \frac{Z}{4} = p$. Very similar, we find by using the Stirling formula:

$$\ln W_p = \text{const} - \frac{8p^2}{Z},$$

because

$$\text{const} \int_{-\infty}^{+\infty} e^{-\frac{8p^2}{Z}} \mathrm{d}p = 1$$

has to be constant it follows

$$\text{const} = \sqrt{\frac{8}{Z}} \frac{1}{\sqrt{\pi}}$$

and

$$W_P = \sqrt{\frac{8}{Z}} \frac{1}{\sqrt{\pi}} e^{-\frac{8p^2}{Z}}.$$

Because the x-coordinate $x = 2b \cdot p$ corresponds to a value p it follows [analogue to equation (9)]:

$$W_x \mathrm{d}x = \frac{1}{2b} \sqrt{\frac{8}{Z}} \frac{1}{\sqrt{\pi}} e^{-\frac{2x^2}{b^2 Z}} \mathrm{d}x \tag{34}$$

as probability for the chain molecule having an x-coordinate between x and x + dx.
It results analogously for the y-coordinate of the chain centre

$$W_y \mathrm{d}y = \frac{1}{2b} \sqrt{\frac{8}{Z}} \frac{1}{\sqrt{\pi}} e^{-\frac{2y^2}{b^2 Z}} \mathrm{d}y \tag{34b}$$

Combination of (34) and (34a) gives analog to equations (10) and (11) for the probability that the distance from the chain centre (point $\frac{1}{2}Z$) to the z-axis is between r_2 and $r_2 + \mathrm{d}r$

$$W_{r_2}\mathrm{dr}_2 = \frac{1}{b^2}\frac{2}{Z}e^{-\frac{2r^2}{b^2 Z}}2\mathrm{r}_2\mathrm{dr}_2 \tag{35}$$

from what comes in a known way

$$r_2 = \frac{\sqrt{\pi}}{2\sqrt{2}}\sqrt{Z}b^2 \tag{36}$$

$$r_2^{\;2} = \frac{1}{2}Zb^2\,. \tag{37}$$

It is interesting to compare this result to equation (16b) which gave the longitudinal dimension of the coil (distance between the two ends). We find:

$$\frac{\overline{r_1}}{\overline{r_2}} = \frac{8}{\pi} \approx 2.55$$

which thus means that the mean diagonal dimension of the coil is two to three times smaller than the longitudinal dimension.

If we now transform not only the longitudinal dimension of the coil into the z-axis but also the direction of the large diagonal dimension (direction of the vector r_2) into the y-axis and its perpendicular into the x-axis and name the extension of the chain in this direction r_3, we thus find for r_3 in a quite analog way to r_2:

$$W_{r_3}\mathrm{dr}_3 = \frac{4}{b\sqrt{Z}}\frac{1}{\sqrt{\pi}}e^{-\frac{4r^2}{Zb^2}}\mathrm{dr}_3 \tag{38}$$

$$r_3 = \frac{b}{2\sqrt{\pi}}\sqrt{Z} \tag{39}$$

$$\overline{r_3^{\;2}} = \frac{b^2}{8}Z \tag{40}$$

One also notices that

$$\frac{r_1}{\overline{r_3}} = 4\sqrt{2} \approx 5.7\,.$$

Thus, a very probable shape of the “random” coil would be a “bean shape” with a length:width:thickness ratio of ca.

$$1:\frac{1}{2.6}:\frac{1}{5.7} \approx 6:2.3:1$$

There will exist, of cause, many other shapes with a high probability as it is a feature of a statistic approach that actually any shape has a certain probability of realization.

Based on these considerations, the volume of the "random" coil can be set to about equal to the volume of an ellipsoid of which the axes are given by relations (12), (36), and (39). Therefore it comes

$$V = \frac{4}{3} r_1 r_2 r_3 \frac{\pi}{8} = \frac{\sqrt{\pi}}{12} b^3 Z^{\frac{3}{2}} \tag{41}$$

Utilization of viscosity measurements.

If the dissolved particles would have a length to thickness ratio of $\frac{s}{d}$ then the specific viscosity of a solution which contains per cm^3 solvent G cm^3 dissolved substance (including swelling volume) would be equal to[10])

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1 = 2.5G + \frac{G}{30}\left(\frac{s}{d}\right)^2 . \tag{44}$$

$\frac{s}{d}$ would be approximately 3 for "randomly" coiled molecules so that in (44) the second term could be neglected compared to the first one.

If m$_0$ is the molecular weight of the base substance of the chain molecule so that $Z \cdot m_0$ is the molecular weight of a chain consisting of Z links and if c gram equivalents of base substance are dissolved per liter solution then 1 cm^3 of solution obviously contains $\frac{cN_L}{1000 \cdot Z}$ single chain molecules (N_L = Loschmidt's number). The volume that is occupied by each single molecule in the case of "random coiling" is given by (41) so that for such a solution

$$G = \frac{\sqrt{\pi}}{12} \frac{cN_L}{1000 \cdot Z} b^3 Z^{\frac{3}{2}} . \tag{45}$$

The quantity $\frac{\eta_{sp}}{c}$ will in this case become equal to

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[10]) W. Kuhn, Kolloid-Z. **52**, 269 (1933), especially equation (15b); compare also R. Eisenschitz, Z. phys. Chem. Abt. A 163, 133 (1933).

$$2.5\frac{\sqrt{\pi}}{12}\frac{b^3Z^{\frac{1}{2}}}{1000}N_L, \tag{46}$$

i.e. proportional to $\sqrt{Z}$.

In the case of a completely straight chain molecule the second term in (44) would be determinant for the viscosity and it would be

$$G=\frac{d^2\pi}{4}s\cdot\frac{cN_L}{1000\cdot Z};\quad \mathrm{s}=Z\cdot l_0$$

and it would as one immediately realizes:

$$\frac{\eta_{sp}}{c}\sim \mathrm{Z}^2, \tag{47}$$

thus $\frac{\eta_{sp}}{c}$ proportional to the square of the chain length. Because the quantity $\frac{\eta_{sp}}{c}$ increases proportional to Z after Staudinger and because this quantity should increase theoretically proportional to $\sqrt{Z}$ in the case of random coils and in the case of straight sticks proportional Z^2 it obviously has to be concluded that neither the case of the "randomly" coiled molecules nor the case of the completely straight rigid molecules corresponds exactly to reality.

But it has been emphasized during the development of the "random" coil theory that the volume of the single chain links has been neglected for the derivation of expression (41) for the volume occupied by the particle. It has been shown that this effect can be considered by an approach of the from (26, 27) and it has been found that if for a 5-link chain the "expansion" of the coil due to the space filling effect would be 20%, the exponent ε in (26, 27) would have to be set equal to 0.11_3. Instead of (41) the particle volume would then be

$$V=\frac{\sqrt{\pi}}{12}b^3Z^{\frac{3}{2}}Z^{0.34},$$

resulting in:

$$\frac{\eta_{sp}}{c}\approx 2.5\frac{\sqrt{\pi}}{12}\frac{b^3}{1000}Z^{0.84}. \tag{48}$$

This correction would already bring this exponent which gives the dependency of the viscosity on the chain length from 0.5 to 0.84, i.e. quite close to 1. It also should be emphasized that the value 0.84 does not represent a preferred or especially probable value of the “theoretical” exponent, in that by other quantitative assumptions about the space filling different values of this exponent (larger or smaller) could also be obtained. (If the expansion of the 5-link coil would have been set to 25% instead of 20% the number 0.92 would have been obtained instead of 0.84.)

Birefringence of expansion and orientation for chain molecules.

About two years ago, on the occasion of considerations about the birefringence of flow which is observed in colloidal solutions I had the opportunity to notice that the birefringence of flow which is observed for highly polymer substances can be regarded qualitatively and approximately quantitatively as a stretch birefringence caused by tensile and pressure forces of the streaming solution exercised on the suspended coiled molecule. I would like to use this opportunity to come back to this explanation which in principle seems to be correct because it has been attacked be R. Signer and H. Gross in a paper about birefringence of flow in brines of highly polymeric substances that appeared some time ago[11]).

The paper contains a whole string of interesting experimental observations which already at a rough inspection are in agreement with the expectations for a more or less coiled molecule shape. For instance, a table is presented on page 185 of the mentioned paper after which polystyrenes with a molecular weight ratio of $\frac{5.6}{0.6} \approx \frac{9.3}{1}$ give a flow birefringence ratio of $\frac{88}{6.1} \approx \frac{14}{1}$. With the assumption of rod-like particles that only differ by their length (which is proportional to the molecular weight) the expected flow birefringence should be proportional to the third power of the length of the molecule[12]) and the birefringence values of both brines should have a ratio of $\frac{800}{1}$. Hence, the differences between the experimental birefringence and the birefringence to be expected for the assumption of a rod shape amount to several orders of magnitude.

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[11]) R. Signer und H. Gross, Z. Physik. Chem. Abt. A 165, 161 (1933)

[12]) Compare W. Kuhn, Kolloid-Z. 52, 274 (1933), especially eq. (10)

Following the considerations mentioned earlier about flow stretch birefringence, it came in the case of not very long stretched particles

$$\gamma_1 - \gamma_2 = G_0 \frac{G}{G_0} \frac{\eta q}{4} (\varepsilon_1 - \varepsilon_2).$$

$\varepsilon_1 - \varepsilon_2$ would be the mechanical birefringence of the swollen particles caused by the force of 1 Dyn per cm^2, q the flow difference, and G/G_0 the ratio of the volumes of the swollen particle to the volume of the dry substance. It has been shown of the quantity $\varepsilon_1 - \varepsilon_2$ that it stays constant between certain limits[13]). At a comparison of 1% solutions G_0 is constant and the expected flow birefringence would approximately proportional to G/G_0. Following the preceding statistic considerations G/G_0 would be proportional to the square root of the chain link number and, thus, proportional to the molecular weight at neglected space filling of the single chain links. When considering the space filling effect one would obtain proportionality to about $M^{0.8}$ to $M^{0.9}$ following (28). The numbers for which one would demand equality under this view would be $(9.3)^{0.9}$ and 14; this is a very coarse but at least fair agreement. At an earlier point of the mentioned paper of Signer and Gross the conjecture is pronounced that the high molecular weights should even be increased. Hence, a bigger number would have to be used instead of $(9.3)^{0.9}$ which would improve the agreement. By no means, however, should the birefringence rise proportionally to M^3 which one would have to demand if the hypothesis of the straight rod molecules would be correct.

In the same work by Signer and Gross the objection has been made against the determination of the particle size from flow birefringence data that the approach of the Brownian rotation movement carried out by me would not be permissible because this movement would be too lively for the small particles under consideration. It is claimed on page 183 of the mentioned paper that the Brownian movements carried out by the particles have to be slow compared to the movements inflicted by the outer forces if Stokes' law is to be applied. This objection can be rejected because it contradicts the experimental experience and the well known classic methods of particle size determination: 1. The (electrically charged) particle in colloidal suspensions of gold or

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[13]) Of cause it is a hypothesis that this constancy holds for the whole area to which these considerations relate.

selenium migrate in an electric field with a velocity that is exactly proportional to the potential. At a molecular weight of about 10^6 the particles have a mean translational velocity of a few meters per second. To my knowledge nobody yet has claimed that therefore Stokes' law could only then be applied to the particles if the velocities inflicted on the particles by external forces amount to about ten meters per second. 2. The principle of the particle size determination after Einstein and Perrin is based on the fact that the fall velocity expected in a suspension following Stokes' law superimposes undisturbedly the Brownian motion of the particles where again the distances covered due to Brownian movement amount to multiples of the distances covered due to the fall velocity. 3. Even if one reduces the particle size to molecular dimensions, Stokes' law (proportionality between translation velocity and force acting on the particle) strictly remains valid. Namely, the validity of this law has been confirmed by measuring the translational velocity (electric conductivity) that is adopted by ions in a liquid under the influence of electric fields for the smallest and the highest field strengths, also for different solvents[14]). But in my considerations the only condition to obtain the law that $\frac{\eta_{sp}}{c}$ increases proportionally to the square of the length of rod-like particles and to determine the particle length from flow birefringence consists in the approach that the frictional force that acts on the particle moving in the liquid is proportional to the particle's translational velocity. Because there can barely be any doubt about the accuracy of this assumption, I believe that the conclusions cannot be disputed from this point of view.

Completely independent on this discussion I would not like to consider on the other hand stretch-dependent flow birefringence and orientation-dependent birefringence under all circumstances as incompatible and mutually exclusive contrasts. I rather believe that on the basis of the previously described statistic considerations a transition from the pure stretch-dependent flow birefringence for highly polymeric substances to a partly orientation-dependent flow birefringence for smaller molecular substances (of the same polymer-homologues) has to be expected. Because the length dimension of the coiled

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[14]) Compare especially L. Ebert, Handbuch der Experimentalphysik (Wien-Harms), Bd. XII (Leipzig 1932).

molecule is proportional to $\sqrt{Z}$, i.e. proportional to the square root of the single steps that have to be carried to go from the start of the molecule to its end, it follows that the number of steps to be carried out in the direction of the length of the molecule has to be somewhat larger than the number of steps to be gone in the other directions. This has to entail an optical preference of the particle's length dimension, i.e. a birefringence coming from the particle itself. This birefringence will be approximately proportional to $\frac{1}{\sqrt{Z}}$ for small Z values, but it will decrease faster (at least proportional to $\frac{1}{Z}$) for larger Z values. In any case, a substantial "self-birefringence" has to be expected for small Z and an infinitely small "self-birefringence" has to expected for large Z. Because of the communicated statistic consideration a quantitative approach of this question can attempted but it requires a refinement or the same, especially also a development of additional approximations.

Apart from that, also the orientation effects caused mechanically on the particles (stretch birefringence) could depend on the chain length Z, as the stretch birefringence in general will relate to a dilation or to the coils being partly unrolled.

Summary

A statistic approach is developed concerning the shape that can be adopted by chain-like molecules which are suspended in a solution (or in the gaseous phase) due to the valence angle and the free rotatability.

With small modifications of the occurring constants the obtained relations are also valid for the case of restrained rotatability and given fixed to quite "random" valence angles.

A bent ellipsoid is a very probable outer boundary of the "randomly" coiled chain molecule of which the axes relate approximately 6:2.3:2.

A coil volume that increases proportionally to $\sqrt{Z}$ (Z number of the chain links) and, hence, a viscosity that also would increase proportionally to $\sqrt{Z}$, result if the own volume of the several parts of the chain is neglected during the construction of the coil.

But the consideration of the volume occupied by the several parts of the chain results in an expansion of the coil which explains at least partially, if not completely, the linear increase of the viscosity with increasing chain link number Z.

Experiments about the rate of the formation of rings with large link numbers also suggest a substantial expansion of the coils connected to a reduced diffusion rate of the inner coil components with respect to each other.

It is shown that the coiled chain molecules give rise to a “self birefringence” which is substantial for low molecular products and infinitely small for high molecular products.