

CHAPTER 1

THE NORMAL-COORDINATE METHOD FOR POLYMER CHAINS IN DILUTE SOLUTION*

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I. Introduction

The method of normal coordinate analysis is the newest, and perhaps the most powerful, of the mathematical tools that have been applied to the theory of high polymers. It was introduced only a few years ago by Bueche¹ and Rouse, Jr.,² working independently. However, normal coordinate analysis has had a long history in other branches of mathematical physics.^{2a}

Perhaps the genesis of the method goes back to Sir Isaac Newton's theory of sound. At that time the theory of differential equations was not yet developed—in fact calculus itself had only just been invented—and Newton was forced to use an artifice to describe the propagation of sound through an elastic medium such as air. His artifice consisted of representing the continuous medium by a chain of weights connected by springs. The sound wave was assumed to propagate down this chain, and in this way the problem of the modes in which such a chain could vibrate came to the fore.

A fairly complete discussion of this problem was accomplished a few years later by two Swiss mathematicians, John and Daniel Bernoulli, in a

* This chapter is the manuscript of a lecture delivered before a joint meeting of the Society of Rheology and the Division of High Polymer Physics of the American Physical Society in New York in February 1956. Although it is not intended to be a comprehensive review of the subject, the Editor has wished to include it because of the special interest of the subject.

¹ F. Bueche, *J. Chem. Phys.* **22**, 603 (1954).

² P. E. Rouse, Jr., *J. Chem. Phys.* **21**, 1272 (1953).

^{2a} L. Brillouin, in his book "Wave Propagation in Periodic Structures" (McGraw-Hill, New York, 1946; Dover, New York, 1953) gives an interesting historical account from which the next few paragraphs are drawn.

correspondence beginning about 1727. They explicitly discussed the normal vibrations, i.e., the ones which would perpetuate themselves down the chain without change of type, and they worked this problem out in quite complete detail. Since that time the analysis of complex systems of masses and springs, and sometimes including damping forces in addition, has usually been reduced by means of a normal-coordinate analysis.

On the other hand, the dynamical theory of the specific heat of solid substances, which was founded by Debye and by Born and von Karman in the early part of this century, is essentially a theory of the normal vibrations of the crystal lattice. Likewise, the normal coordinate theory has been very important—in fact, absolutely necessary—in discussing the design of electrical filter apparatus for communications equipment.

Despite the fact that this problem is well known to almost any student of advanced physics, until very recently it remained unused in the field of high polymers. The mathematical theory of high polymer chains probably dates from the pioneering work of Meyer, Mark, and Guth over twenty years ago. Since that time it has been recognized that the model of a chain of weights connected by springs is a fair representation of the actual high polymer chain. Now such a chain is, of course, very similar to the chain which was discussed by Newton in 1686. There is one difference however, and this difference, which is much more serious in appearance than in actuality, undoubtedly kept people from applying the method of normal coordinates to high polymer chains. The difference lies in the fact that the typical high polymer chain is represented by a freely coiling chain with the universal joints joining the springs, whereas the chains which are discussed in the problems of classical physics are chains arranged in a definite linear framework in space. Now we shall see shortly that if one assumes that the springs of the high polymer chain have zero equilibrium length—and this, in fact, is just the assumption that one wants to make—then it makes no difference whether the chain is coiling or whether it is rigid. The state of each spring is described by the vector distance between its ends. Likewise, since it is a Hooke's law spring, the force between its ends is proportional to this length vector, and both the force and the length vectors project upon the coordinate axes in the same way. Therefore, the projection of each spring upon each coordinate axis acts just as if it were an identical spring laid out along this axis. The chain as a whole can be represented as three identical chains, but in each case stretched out along one of the three coordinate axes. These chains, of course, are each of the classical type.

II. The Elastic Dumbbell

Now let us study the particulars of our model more closely. By way of introduction, let us first take a very simple model, one that consists of only

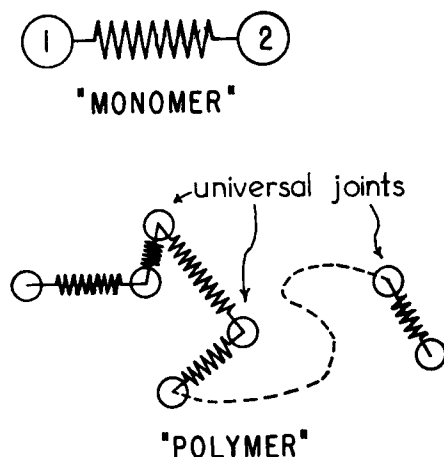


FIG. 1. Two idealized molecular models, whose motions can be given exact mathematical treatment.

one spring and two beads. This is the object depicted at the top of Fig. 1, labeled there "monomer." We assume that the springs have zero equilibrium length. This does not mean, of course, that the molecule which this object represents will have zero length, because thermal motion generally keeps this spring expanded to some extent. At first, however, let us consider the equations of motion neglecting thermal agitation.

We will suppose that this monomer object, which might also be called an elastic dumbbell, is extended in a viscous liquid which impedes its motion. There are then three types of forces and reactions that we have to consider: the force due to the extension of the spring, the force caused by the viscosity of the liquid when one of the beads moves through it, and the inertial reaction caused by the masses of the beads. On the molecular scale the inertial reactions tend to be very much smaller than the other two forces, and for this reason we shall neglect them completely.

We shall assume that the viscous drag on the motion of one of the beads can be represented simply by a force proportional to the velocity of the bead and in the reverse direction. With this very reasonable assumption we get the two following equations of motion for beads one and two:

$$\begin{aligned} \rho \dot{x}_1 &= F_{x1} = -g(x_1 - x_2), \\ \rho \dot{x}_2 &= F_{x2} = -g(x_2 - x_1). \end{aligned} \quad (1)$$

(The dot represents a derivative with respect to time.)

The left-hand side of these equations represents the viscous drag with a resistance coefficient ρ . The velocities of the beads in the x -direction are

\dot{x}_1 and \dot{x}_2 , respectively. These must be equal to the forces on the beads F_{x1} and F_{x2} which are, in turn, equal to the forces exerted by the springs; the latter are given by the right-hand side of the equation, with g the force constant and x_1 and x_2 the x -coordinates of the two beads.

Now this set of simultaneous differential equations can be solved easily by adding and subtracting the two equations to produce two new equations. In this process two quantities naturally make their appearance. These quantities are ξ_0 and ξ_1 as given below.

$$\begin{aligned}\xi_0 &= \frac{x_1 + x_2}{\sqrt{2}} \\ \xi_1 &= \frac{x_1 - x_2}{\sqrt{2}}\end{aligned}\tag{2}$$

The first is, except for a normalization factor, the mean coordinate of the elastic dumbbell. The other is, except for the same factor, the length of the dumbbell. By adding the two equations, we get the following differential equation for ξ_0 , which is easily solved to get a result that ξ_0 is a constant:

$$\dot{\xi}_0 = 0; \quad \xi_0 = \text{constant}.\tag{3}$$

In other words, the center of mass of the dumbbell does not move, as of course it should not, since there is no force acting on the center of mass. By subtracting the two equations we get the following for ξ_1 , and this again has the simple solution given below:

$$\dot{\xi}_1 = -(2g/\rho)\xi_1; \quad \xi_1 = \xi_1' \exp [(-2g/\rho)t]\tag{4}$$

The quantity ξ_1 , therefore, decreases exponentially from its initial value ξ_1' toward 0. The two quantities ξ_0 and ξ_1 , which so markedly simplify the original set of equations, are the normal coordinates of this system.

We are now in a position to be more realistic about our model and introduce thermal agitation or Brownian motion. At the same time, with no increase in complication, we may put our model in a flowing liquid, one that is undergoing shear as a liquid would, for example, in conventional viscometer. Consider the situation in Fig. 2, in which our dumbbell molecule is shown with arrows representing the flow of liquid. The liquid is flowing in the x -direction with a velocity gradient in the z -direction. (For simplicity, we ignore the y -axis.) The equations of motion amplified by the addition of the Brownian motion and the shear-rate terms are the following:

$$\begin{aligned}\rho\dot{x}_1 &= F_{x1} = -kT \frac{\partial \ln \psi}{\partial x_1} - g(x_1 - x_2) + Kz_1, \\ \rho\dot{x}_2 &= F_{x2} = -kT \frac{\partial \ln \psi}{\partial x_2} - g(x_2 - x_1) + Kz_2.\end{aligned}\tag{5}$$

Kz_1 and Kz_2 are the shear-rate terms, K being the rate of shear. The partial derivative terms account for the Brownian motion. These require some explanation. It would seem, at first sight, impossible to introduce Brownian motion, which is a random agitation, into our equations which, up to now, at least, have been completely determined. This is, indeed, only possible if we average over the motions of the large number of identical particles, and it is in this sense that our equation must now be interpreted. The \dot{x}_1 and \dot{x}_2 now become the average motions of particles 1 and 2 in an ensemble of a large number of identical molecules. Under these conditions, we know how to handle the problem of Brownian motion. Brownian motion simply causes diffusion in the ordinary sense, and diffusion obeys Fick's Law; i.e., there is a current which flows from regions of high concentration to regions of low concentration, the strength of the current being proportional to the gradient of the concentration multiplied by kT . This is the origin of the first terms on the right of equations (5). The function ψ is the concentration generalized so that it includes both the concentration of particles 1 and particles 2. This function ψ is commonly called the distribution function of the system.

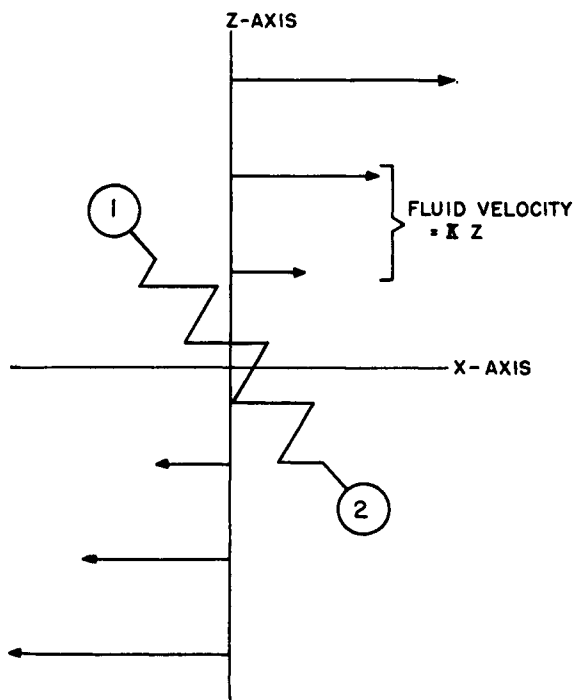


FIG. 2. A model molecule in two-dimensional shearing flow

These new, and more complicated, equations of motion still can be simplified by means of the normal-coordinate transformation. The results of the transformation are the following:

$$\begin{aligned}\rho\dot{\xi}_0 &= -kT \frac{\partial \ln \psi}{\partial \xi_0} \\ \rho\dot{\xi}_1 &= -kT \frac{\partial \ln \psi}{\partial \xi_1} - 2g\xi_1 + K\xi_1 \\ \zeta_1 &= \frac{z_1 - z_2}{\sqrt{2}}\end{aligned}\tag{6}$$

Once again ξ_0 occurs in one equation only with itself, and ξ_1 occurs only with itself and with ζ_1 . This mixing of ξ_1 and ζ_1 turns out to be harmless.

The divergence of the rates of flow of the particles is set equal to the rate of accumulation of the particles at a given point to give a second-order differential equation of the familiar type encountered in diffusion theory. From this the unknown function ψ can be determined. It would take us too far afield to give the details of the solution of this equation, since the interested reader may find it in the original literature. It is worth noting, however, that the equation for the problem in hand, the elastic dumbbell molecule in a shearing fluid, can be solved exactly without recourse to approximation. (This was first accomplished, I believe, by J. J. Hermans.³)

Quantities of particular interest are the mean square extensions of the molecules along the coordinate axes. These are proportional to the mean squares of the normal coordinates ξ_1 and ζ_1 , and expressions for them as calculated from the differential equation are given below.

$$\langle \xi_1^2 \rangle_{av} = (kT/2g)(1 + K\rho/g)\tag{7}$$

$$\langle \zeta_1^2 \rangle_{av} = kT/2g\tag{8}$$

$$\langle \xi_1\zeta_1 \rangle_{av} = kT K\rho/2g^2 = 2kT K\tau/g\tag{9}$$

$$\tau = \rho/2g\tag{10}$$

We see that, as we predicted originally, the mean square extension of this elastic dumbbell is not zero. It is, in fact, proportional to the temperature and inversely proportional to the strength of the spring. Furthermore, the mean square extension along the x -axis increases with rate of shear. At the same time the average of the cross product term $\xi_1\zeta_1$, which is zero when the rate of shear is zero, increases proportionately to the rate of shear. The net result is that the molecule extends along a diagonal line inclined somewhat to the x -axis.

³ J. J. Hermans, *Rec. trav. chim.* **63**, 219 (1944).

A further important quantity is the relaxation time τ . If we return to equation (4), which describes the relaxation of the molecule in the simple case where Brownian motion is neglected, we see that the coefficient of time in the exponential has the dimensions of reciprocal time, and this is, in fact, the reciprocal of the relaxation time of this simple model; i.e., it is the reciprocal of the time needed for the dumbbell to relax to a length which is $1/e$ of the initial value. This same quantity, the relaxation time, which is equal to $\rho/2g$, appears in our equations where Brownian motions have been considered. In fact, the variable that appears in the mean square extension is just the product of the rate of shear and the relaxation time. In other words, the rate of shear is essentially measured in units of the relaxation time.

The relaxation time that we have been talking about is associated with the normal coordinate *one*. There is another relaxation time associated with normal coordinate *zero*; however, this relaxation time happens to be infinite. In general, there will be one relaxation time associated with each normal coordinate, since the original differential equation separates into as many new equations as there are normal coordinates. Later, when we take more complicated models, we will find that there will be many relaxation times of importance.

III. The Elastic Chain

We can polymerize the simple model of the elastic dumbbell into a long chain, as shown in the second half of Fig. 1. This chain is a rather realistic model of a real polymer chain.

To justify this statement, I should point out that the distribution function for the end-to-end length of one of our hypothetical springs is, in fact, of the same mathematical form as the distribution function of the end-to-end length of a chain of rigid bonds joined by freely rotating joints. This form is the Gaussian distribution function, usually taken as a starting point in any investigation of the theory of a polymer chain.

The chain containing many units has, of course, many internal coordinates, and these can be transformed into many normal coordinates. A few of the simplest of these are shown in Fig. 3. As before, there is a normal coordinate which simply represents a translation of the center of mass of the molecule. The next least complicated coordinate is one in which the ends of the molecule move in opposite directions while the center stands still, and this is analogous to the coordinate ξ_1 that we had before.

Then there are more complicated coordinates to which we had no analogy before; these have two, three, or more nodes, and they can be visualized as being related to the normal vibrations of the stretched string studied by students in elementary physics classes. As in the simple case that we have

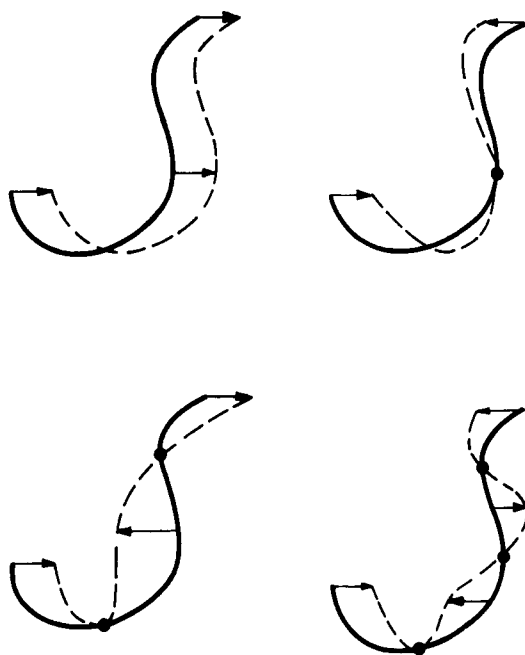


FIG. 3. Schematic representation of the first four normal modes of a chain molecule.

already discussed, however, the use of these coordinates allows the complicated differential equation of the whole chain to be separated into a non-interacting set of equations, each one of which is quite simple and can be easily solved.

There is another complication that should be mentioned at this point. A molecule suspended in a liquid and exerting forces on the liquid causes the liquid to flow, and these currents in the liquid influence the motions of other parts of the same molecule. The situation is shown in Fig. 4, where a particular bead shown at the center of the figure is acted on by a force which drags it toward the right. It, in turn, sets up currents in the liquid around it which are indicated by the curved arrows on the left-hand side of the picture. Unfortunately, an exact description of this situation makes the equations of motion too complicated to be solved. However, if we approximate the curvilinear flow field, which is shown in the left side of the figure, by a rectilinear flow field, shown on the right side of the figure, the equations become simple enough to be solved with hardly any more difficulty than would have been encountered if this flow complication had been neglected completely. The replacement of the curvilinear flow field by an approx-

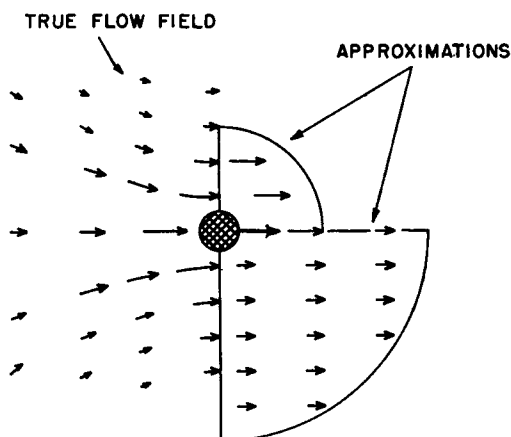


FIG. 4. Replacement of the exact flow field (left) around a moving bead by approximate rectilinear flow fields valid for limited regions (right).

appropriate rectilinear flow field is essentially the approximation that Kirkwood and Riseman made in their theory of intrinsic viscosity. (See below.)

Now let us look at the results of this theory for the high polymer chain. One of the most interesting quantities is the intrinsic viscosity. Since we have a theory that includes relaxation effects, we can calculate intrinsic viscosity for a molecule suspended in oscillating shear as well as in the more usual case of steady-state shear. The results, which show the effect of the various relaxation processes quite clearly, are presented in Fig. 5, where the viscosity is plotted as a function of the frequency of the oscillating shear on a logarithmic scale. The total viscosity falls from a low-frequency plateau to another plateau at very high frequencies; the latter plateau is just the viscosity of the solvent.

To understand what is going on, one need only consider what the molecular processes are in these two extremes. At low frequency (or steady flow) the molecules are being extended by the shear rate, but at the same time they are revolving slowly in the flow gradient. The result is that the energy which is put into them is gradually dissipated by the slippage of the molecule through the fluid. Therefore, energy is lost and a true viscosity appears.

At high frequencies, on the other hand, the molecules, which are essentially springlike, are extended slightly in one phase of the motion. However, before they have a chance to dissipate the energy stored in this extension, the motion reverses itself and the energy stored in the springs is given back to the fluid. There is thus very little energy loss and the viscosity is very small. Instead, a modulus of elasticity appears which corresponds to the springlike action of the molecules. (We do not show the modulus here.)

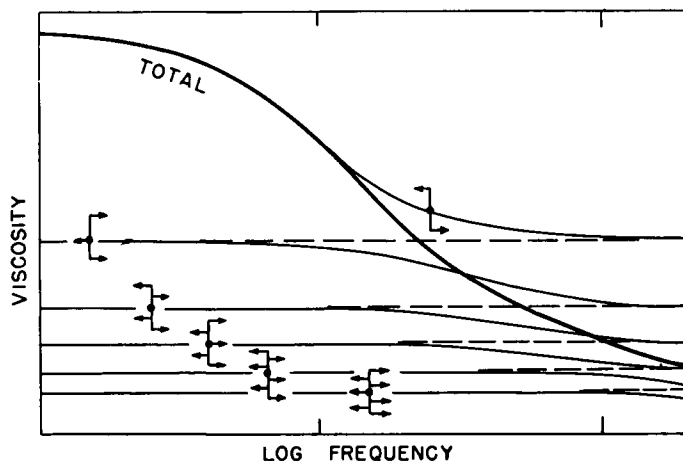


FIG. 5. The real part of the complex viscosity of an isolated chain molecule and its decomposition into contributions from the various normal modes of relaxation.

The curve of viscosity versus frequency is actually a composite curve made up of the contributions of the various relaxation processes corresponding to the various normal coordinates. These are indicated in detail in Fig. 5. About half of the total viscosity is caused by the motions of the simplest of the normal coordinates, the one in which the two ends move in opposite directions. The more complicated types of motion contribute in successively smaller portions to the total viscosity. It is also noteworthy that the relaxation times of these various normal coordinates are different, the simplest normal coordinate having a longer relaxation time than the more complicated ones.

A comparison of this theory with experiments is shown in Fig. 6 and Table I. Figure 6 shows experimental curves of viscosity versus frequency as determined by Rouse and Sittel⁴ on solutions of various samples of polystyrene in toluene. The general agreement in regard to the form of the curve is noteworthy. Furthermore, the relaxation times taken from experimental curves are quite close to those calculated theoretically. This comparison is shown in Table I.

The theory provides a formula which connects the relaxation time with the viscosity of the solution and with known numerical constants. The times calculated from this formula are shown in the next to the last column of this table with the measured experimental times in the last column. It can be seen that while the agreement is not perfect, there is a systematic difference between the theoretical and observed times amounting to about 50 %;

⁴ P. E. Rouse, Jr. and K. Sittel, *J. Appl. Phys.* **24**, 690 (1953).

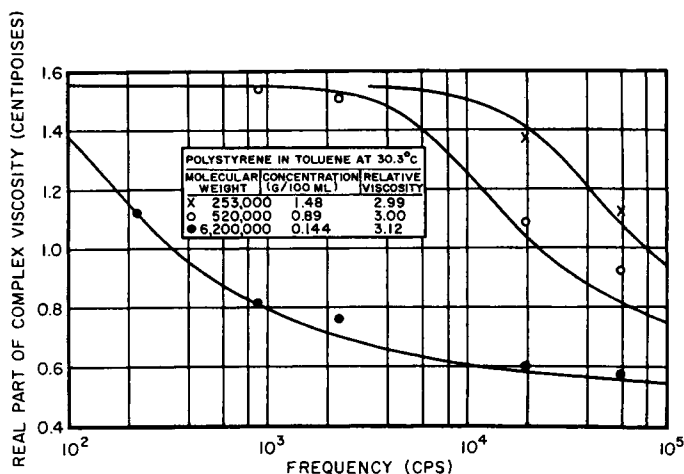


Fig. 6. Experimental viscosity versus frequency for polystyrene solutions. From Rouse and Sittel.⁴

TABLE I
RELAXATION TIMES OF POLYSTYRENE IN TOLUENE^a

$$\tau_{1\text{theor}} = 0.422 M (\eta_{sp}/C) \eta_{\text{sol}} / RT^b$$

M	$C, \text{g./ml.}$	η_{sp}/C	$\tau_{1\text{theor}}, \text{sec.}$	$\tau_{1\text{exper}}, \text{sec.}$
6,200,000	0.00144	1470	0.81×10^{-3}	1.22×10^{-3}
520,000	0.0089	225	10.3×10^{-6}	16.8×10^{-6}
253,000	0.0148	134	3.00×10^{-6}	4.8×10^{-6}

^a Reference 4.

^b Reference 6.

but this is, in fact, quite small compared with the total range of variation among polymers of different molecular weights.

The difference between the theoretical and experimental times may reflect inadequacies in the theory or may perhaps even be due to experimental complications. It will be necessary for further investigation to settle this point. However, we could point out one source of difficulty which, in fact, has considerable interest of its own.

In Fig. 7 are shown the relaxation curves for the viscosity of solutions of two polymers of the same molecular weight but of which one is a narrow fraction and the other has a broad distribution corresponding to that produced in many common types of polymerizations. It can be seen that the apparent τ_1 's of these two materials would differ considerably even though a certain average relaxation time might be the same.

Although the experiments of Rouse and Sittel were performed on frac-

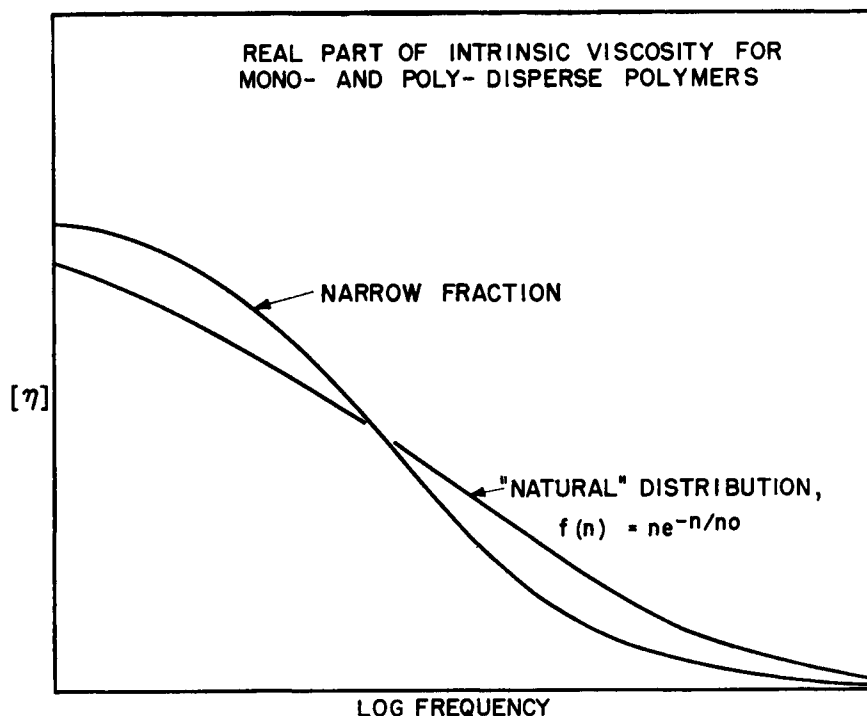


FIG. 7. Real part of the intrinsic viscosity against the logarithm of the frequency for a polymer with a uniform molecular weight and for one with a molecular weight distribution.

tionated materials, the efficiency of fractionation in general, and of the fractionation employed in this case in particular, is unknown. Therefore, we are not at all sure that the curve that they actually obtained corresponds to the narrow fraction curve of Fig. 7 or to something more like the broader curve. And in this fact lies a possible source of the discrepancy in the relaxation times. On the other hand, when we find out more about this subject we may be able to use the difference between curves of materials of different molecular weight distributions to discover something about the molecular weight distributions.

Before we leave the subject of the intrinsic viscosity, another interesting point deserves mention. Some years ago, Kirkwood and Riseman⁵ derived a much quoted relation between the intrinsic viscosity in steady flow $[\eta]_0$ and certain molecular constants, namely, the molecular weight M and

⁵ J. G. Kirkwood and J. Riseman, *J. Chem. Phys.* **16**, 565 (1948).

the root-mean-square distance between the ends of the chain L . We can easily derive a similar formula from our theory⁶ and this is given here.

$$[\eta]_0 = 2.84 \times 10^{23} L^3 / M. \quad (11)$$

The only difference between this formula and Kirkwood and Riseman's original result is in the numerical constant, which is 2.84 in our case and was originally found to be 3.6 by Kirkwood and Riseman. A subsequent revision of some details of the calculations by Kirkwood and associates⁷ reduced this constant to about 3.4, and later Auer and Gardner⁸ showed that another method of carrying out the mathematical details gave the value of 2.90. The latter is very close to our value of 2.84. The small remaining discrepancy can be attributed to some minor differences in the models which could probably be removed if someone were sufficiently interested to do so.

I think this result is interesting in two ways. First, it shows an unexpected dividend of the normal-coordinate method, in that it was possible to obtain a more accurate result than the original Kirkwood and Riseman one with less labor, principally as a result of the simplifications obtained by transforming from the ordinary coordinates into the normal ones.

A further matter of interest is the question of whether this value of 2.84 is in accord with experimental facts. The determination of the experimental value, which has been pursued in particular by Flory and his co-workers, is subject to some uncertainty, and over the past two years the experimental value has shown a tendency to rise. The most recent value of which I am aware⁹ is, in fact, 2.5, with an estimated error of perhaps 10%. We can say, therefore, that the theoretical and experimental values are now almost in agreement with each other.

I should now like to make a few remarks about branched molecules. The possibility of branching in polymer chains has been a rather mysterious subject until recently, and one which has been blamed for all sorts of discrepancies between accepted ideas and experimental results. In the last few years mathematical analysis of the properties to be expected in branched molecules has made it possible to begin to dispel some of this mystery.

Some time ago a calculation was made of the quantity which might be called the mean square radius of the branched molecule. This is a quantity which, in principle, is measurable by light-scattering. In practice, however,

⁶ B. H. Zimm, *J. Chem. Phys.* **24**, 269 (1956).

⁷ J. G. Kirkwood, R. W. Zwanzig, and R. J. Plock, *J. Chem. Phys.* **23**, 213 (1955).

⁸ P. L. Auer and C. S. Gardner, *J. Chem. Phys.* **23**, 1545 (1955).

⁹ S. Newman, W. R. Krigbaum, C. Laugier and P. J. Flory, *J. Polymer Sci.* **14**, 451 (1954).

TABLE II

THEORETICAL INTRINSIC VISCOSITIES AND RADII OF MOLECULES WITH ONE BRANCH POINT AND f ARMS OF EQUAL LENGTH COMPARED TO THOSE OF A LINEAR MOLECULE OF THE SAME MOLECULAR WEIGHT^a

<i>No. of arms, f</i>	<i>Mean square radius ratio</i>	<i>Viscosity ratio</i>
1 and 2	(1.000)	(1.000)
3	0.778	0.907
4	0.625	0.814
8	0.344	0.632

^a Reference 9a.

the measurement has turned out not to be very useful, probably because the result depends on the degree of polydispersity, which is usually unknown.

It has been observed experimentally that the relation between the intrinsic viscosity and the weight-average molecular weight depends upon the extent of branching. Therefore, if the theoretical relation between these quantities could be obtained, it would offer a means of determining the amount of branching. We have already seen that we were able to find this relation in the case of linear polymers. Calculation of this relation for branched polymers has turned up some rather surprising results.^{9a}

We have already seen that the intrinsic viscosity in the case of linear polymers depends upon the three-halves power of the mean square radius of the molecule. We might expect, therefore, that the same relation would hold true in the case of branched polymers; and, in fact, this hypothesis was proposed by Flory. However reasonable this hypothesis may seem on a dimensional basis, the actual calculations have not borne it out. In fact, the results given in Table II indicate that the intrinsic viscosity varies more nearly with the *square root* of the mean square radius as the number of branch points in the molecule is increased at constant molecular weight.

It is rather difficult to give a convincing explanation of this result in a few words, since the actual flow of liquid through the molecule is a rather complicated process. Nevertheless, the theoretical calculations are strikingly well confirmed by experiment.

Figure 8 shows some experimental results by Schaeffgen and Flory¹⁰ on polyamides. The straight line drawn through the circles representing the experiments on the linear molecule is an empirical relation between the viscosity and the molecular weight. The other two solid straight lines are displaced from it by the square root of the mean square radius, as suggested by our theory. It can be seen that these lines pass through the experimental

^{9a} B. H. Zimm and R. W. Kilb, *J. Polymer Sci.* in press (1958).

¹⁰ J. R. Schaeffgen and P. J. Flory, *J. Am. Chem. Soc.* **70**, 2709 (1948).

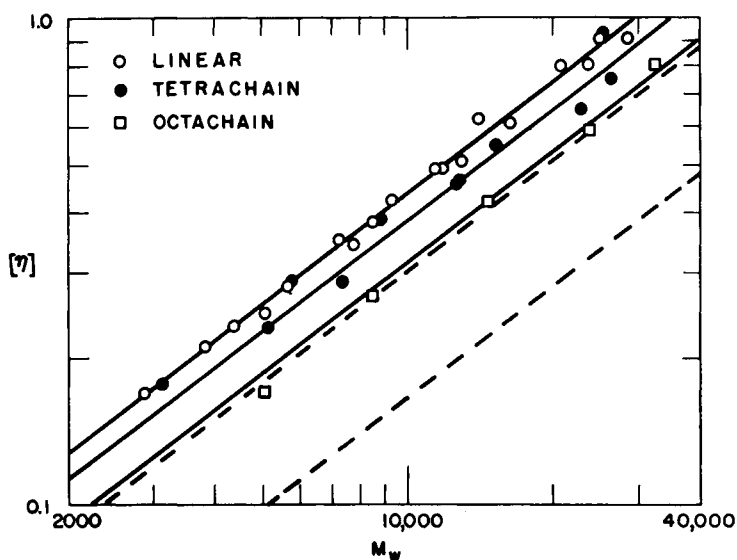


FIG. 8. Experimental results of Schaeffgen and Flory on the viscosity-molecular weight relation for linear and branched polyamides. See text.

points on the branched molecules as well as could reasonably be expected. The dotted lines which represent the hypothesis that the viscosity depends upon the cube of the root-mean-square radius obviously do not fit the experiments at all.

Another subject that can be treated by the normal mode theory is the dependence of viscosity on the rate of shear. The first theory of the intrinsic viscosity gave no dependence of viscosity on the rate of shear at all. However, it has been subsequently found that refinement of the hydrodynamic interaction approximations does introduce a change of viscosity with the rate of shear. We mentioned before that the real curvilinear flow field of a liquid around a moving bead is replaced in our theory by a rectilinear flow field. The strength of this rectilinear field is determined by the average distance between the two pairs of elements whose interaction is being considered.

In the original simple theory an average value of this distance characteristic of the molecule at rest was introduced. An obvious refinement would be to introduce the value of the distance calculated from the simple theory, a value which changes with the rate of shear, as we have seen above in the case of the simple elastic dumbbell model. When this is done, a dependence of viscosity upon the rate of shear appears which is, at least, rather like the experimental dependence; i.e., the viscosity at first decreases rather rapidly with increasing rate of shear and then levels off. Whether the dependence

is quantitatively exact has not yet been determined at the time of writing. The determination must await the results of some rather lengthy numerical computations.

We have described some of the interesting results that have been obtained by the use of normal-mode theory. All of these problems have dealt with single, isolated chains which correspond in practice to dilute solutions of polymers. Some of our most important problems however, concern concentrated solutions or solid polymers where many chains are interacting at once. Normal-mode analysis has proved very useful in this field also, particularly in the hands of Bueche,¹¹ who has applied it boldly and with considerable success to the discussion of the viscoelastic behavior of rubberlike materials. This field is less developed than dilute solution theory, however, in that the exact way in which the polymer chains couple mechanically with each other is still rather mysterious. Mention should also be made of the extensive comparisons between theory and experiment by Ferry and co-workers, which are conveniently summarized in recent reviews.¹²

Finally we ought to mention that the present interest in the relaxation properties of *dilute* polymer solutions stems from the initial work of W. O. Baker, W. P. Mason, J. H. Heiss and H. J. McSkimin of the Bell Telephone Laboratories.¹³

Nomenclature

C	Concentration, weight per unit volume	z	Vertical coordinate
		ζ	Vertical normal coordinate
F_{x1}, F_{x2}	x -components of mechanical force	η	Viscosity
		η_{sp}	Specific viscosity
L	Root-mean-square distance between the ends of a polymer chain	$[\eta]_0$	Intrinsic viscosity for steady flow
		K	Shear rate
M	Molecular weight	ξ	Horizontal normal coordinate
R	Gas constant per mole	$\dot{\xi}$	Rate of change of ξ
T	Absolute temperature	ρ	Resistance or frictional coefficient
g	Spring constant		
k	Boltzmann's constant	τ	Relaxation time
t	Time	τ_1	Longest relaxation time for a polymer chain
x	Horizontal coordinate		
\dot{x}	Rate of change of x	ψ	Distribution function

¹¹ F. Bueche, *J. App. Phys.* **26**, 738 (1955).

¹² J. D. Ferry, *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)* **16**, 85 (1955).

¹³ See, for example, W. O. Baker, W. P. Mason, and J. H. Heiss, *J. Polymer Sci.* **8**, 129 (1952); H. J. McSkimin, *J. Acoust. Soc. Am.* **24**, 355 (1952).