Eigenvalues and the Intrinsic Viscosity of Short Gaussian Chains

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Exact eigenvalues which are central to the Gaussian chain theory for dilute solutions of linear polymers have been determined for short chains. This is done for a number of chain segments N ranging from 1 to 15 and taking into account the effects of hydrodynamic interaction between segments. Using these exact eigenvalues, the molecular weight dependence of the steady flow intrinsic viscosity $[\eta]$ *is determined together with the terminal relaxation time* τ_1 *which is derivable from* $[\eta]$*. These theoretical results are compared with similar results obtained using approximate eigenvalues* λ_p *for N large and small eigenvalue index p. It is found that while the character of the dependence of the* λ_p, $[\eta]$ *and* τ_1 *on N is similar for both exact and approximate results, the numerical factors may differ significantly. Comparison of these results for* $[\eta]$ *with measured values for polystyrene over a wide range of molecular weights gives good agreement with the exact theoretical results and some indication of the inexactness of the approximate results for N large. The* τ_1 *derived from* $[\eta]$ *are compared with values obtained independently from oscillatory flow birefringence measurements.*

THE Gaussian chain theory is widely used as a mathematical model of a linear polymer molecule and forms the basis for theoretical description of a number of macroscopic properties of the polymer in dilute solutions[1-7]. The several treatments include taking into account the hydrodynamic forces on the subchains as well as hydrodynamic interaction between subchain elements or segments, Brownian motion, and internal viscosity. This work has generally been carried under the assumption that the number of segments is large. Recent work with oscillatory flow birefringence by Thurston and Schrag[8] has shown that the number of segments N remains finite in the description of the frequency response of birefringence by means of N relaxation processes. More recently a direct proportion between N and molecular weight M has been demonstrated[9]. The influence of a finite N on the theoretical predictions of oscillatory flow birefringence, acoustic birefringence, oscillatory flow viscosity[10], flow birefringence extinction angle[11], and steady flow intrinsic viscosity[12] has been determined. Comparison with measurements has been carried out[13] for polystyrene solutions.

The eigenvalues which are central to the Gaussian chain theory have been determined exactly only for the case of no hydrodynamic interaction between chain segments, the free draining condition[2]. For cases involving hydrodynamic interaction it has been necessary to assume that the number of segments N is large and that the index p which characterizes the N eigenvalues λ_p is small compared to $N^{14,15}$. The influence of these approxi-

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mations on the theoretical results has not been determined. In the present work exact values of the λ_p are determined for N in the range from 1 to 15 for all values of p while taking into consideration effects of hydrodynamic interaction. The exact eigenvalues are compared with the approximate values together with the molecular weight dependence of the steady flow intrinsic viscosity $[\eta]$ obtained using these values. In addition, the eigenvalues are used to obtain the terminal relaxation time of the chain τ_1 from $[\eta]$. The new theoretical results for the molecular weight dependence of $[\eta]$ are compared with measurements on polystyrene in Aroclor 1248 and the τ_1 derived therefrom is compared with that from frequency response of oscillatory flow birefringence to provide an independent check of the character of the chain theory.

THEORY

The Gaussian chain model as used here consists of N statistical segments joining $N+1$ beads numbered from $i=0$ to $i=N$. The entire model is assumed to be suspended in a viscous solvent of viscosity η_s which can interact with the chain through the beads only. Using the formalism of Cerf[6], the equation of motion in terms of the x components of the bead coordinates is written in matrix form as

$$-(3kT/b^2)\,\mathbf{A}\vec{\mathbf{x}} - \mathbf{Q}^{-1T}\,\Phi\,\mathbf{Q}^{-1}\,(\dot{\vec{\mathbf{x}}} - \dot{\vec{\mathbf{x}}}_\Omega) - \mathrm{f}\,(\dot{\vec{\mathbf{x}}} - \dot{\vec{\mathbf{x}}}_l) - kT\,\nabla_x \ln\psi = 0 \qquad (1)$$

where inertial effects are neglected. In the above equation, k is Boltzmann's constant, T is the absolute temperature, b is the end-to-end length of the statistical segment and $\mathbf{A}$ is the coordinate matrix given by

$$\mathbf{A} = \begin{pmatrix} 1 & -1 & 0 & \cdots & 0 & 0 \\ -1 & 2 & -1 & & 0 & 0 \\ 0 & -1 & 2 & & 0 & 0 \\ \vdots & & & \ddots & & \vdots \\ 0 & 0 & 0 & & 2 & -1 \\ 0 & 0 & 0 & \cdots & -1 & 1 \end{pmatrix} \qquad (2)$$

$\vec{\mathbf{x}}$ is the column vector whose components are the x components of each of the $N+1$ beads and $\dot{\vec{\mathbf{x}}}$ has as components the x components of the velocity of each bead. $\dot{\vec{\mathbf{x}}}_\Omega$ refers to the x components of the velocity of rotation of the molecule due to the velocity of the solvent, and $\dot{\vec{\mathbf{x}}}_l$ refers to the x components of the solvent velocity at the site of each bead if the bead were absent from that point. f is the segmental friction factor, ψ is the distribution function of the location of the beads, and Φ is the diagonal matrix of internal viscosity. $\mathbf{Q}$ is the transformation matrix to normal coordinates which allows the equation of motion to be written in diagonal form.

The distribution function ψ must satisfy the equation of continuity

$$\partial\psi/\partial t = -\operatorname{div}\psi(\vec{\dot{\mathbf{x}}}+\vec{\dot{\mathbf{y}}}+\vec{\dot{\mathbf{z}}}) \tag{3}$$

which can be written in the form

$$\frac{\partial\psi}{\partial t} = \sum_{x,y,z} \nabla_x^T\psi \left[-\vec{\dot{\mathbf{x}}}_l^0 + \frac{kT}{\mathrm{f}}\mathbf{H}\nabla_x \ln\psi + \frac{3kT}{\mathrm{f}b^2}\mathbf{HA}\vec{\mathbf{x}} + \mathrm{f}^{-1}\mathbf{HQ}^{-1T}\,\mathbf{\Phi}\,\mathbf{Q}^{-1}(\vec{\dot{\mathbf{x}}}-\vec{\dot{\mathbf{x}}}_\Omega) \right. \tag{4}$$

where **H** is written in terms of the hydrodynamic interaction tensor **T** as

$$\mathbf{H} = \mathrm{f}\mathbf{T} + \mathbf{1} \tag{5}$$

where **1** is the identity matrix. Since the exact location of each bead is unknown, the average values of **T** are used and are given by

$$\begin{aligned} \langle T_{jk}\rangle &= \frac{1}{6\pi\eta_s}\left\langle\frac{1}{R_{jk}}\right\rangle, \quad j\neq k \\ &= 0 \qquad\qquad\quad, \quad j=k \end{aligned} \tag{6}$$

where R_{jk} is the magnitude of the vector connecting the jth and kth beads.

The determination of the average in equation (6) depends on the interpretation that is made of the nature of the statistical segments. If all N segments are taken to be of fixed length b, then the problem is to find the distribution function of the displacement vector after a three-dimensional random walk of $|j-k|$ steps, each step being the same fixed length. If, however, the length of the statistical segments is assumed to be distributed in a Gaussian manner with a root mean square length of b, the problem still reduces to a random walk, but one with steps having a Gaussian distribution of length. Since it was found that the eigenvalues calculated using the fixed segment length concept of the model do not predict properly the experimentally observed relation between intrinsic viscosity and molecular weight, the details of that development are not given here. The distribution function for the displacement vector for a three-dimensional random walk of $Z=|j-k|$ steps is given by Chandrasekhar[16] as

$$W_z(\vec{\mathbf{R}}) = \frac{1}{(2\pi Zb^2/3)^{3/2}}\exp(-3R^2/2Zb^2) \tag{7}$$

where b is interpreted as the root mean square segment length. Using equation (7) to compute $\langle 1/R_{jk}\rangle$, where $|j-k| = Z$, yields

$$\left\langle\frac{1}{R_{jk}}\right\rangle = \left(\frac{6}{\pi}\right)^{1/2}\frac{1}{|j-k|^{1/2}b} \tag{8}$$

This is the same expression used by Kirkwood and Riseman[5], although they developed the expression for use with monomer units with hindered rotation, making the expression inaccurate for small values of $|j-k|$. In the present case, however, the use of the expression is exact for any value of $|j-k|$.

Using equation (6), **T** can be written as

$$\mathbf{T}=\frac{h^*}{\mathrm{f}}\left(\frac{\pi}{3}\right)^{1/2}\begin{pmatrix} 0 & b\left\langle\frac{1}{R_{01}}\right\rangle & \ldots b\left\langle\frac{1}{R_{0N}}\right\rangle \\ b\left\langle\frac{1}{R_{10}}\right\rangle & 0 & b\left\langle\frac{1}{R_{1N}}\right\rangle \\ \vdots & & \vdots \\ b\left\langle\frac{1}{R_{N0}}\right\rangle & b\left\langle\frac{1}{R_{N1}}\right\rangle & \ldots 0 \end{pmatrix} \tag{9}$$

or

$$\langle T_{jk}\rangle=\frac{h^*}{\mathrm{f}}\left(\frac{\pi}{3}\right)^{1/2} b\left\langle\frac{1}{R_{jk}}\right\rangle \tag{10}$$

where h^* is given by Thurston and Peterlin[10] as

$$h^*=[\mathrm{f}/(12\pi^3)^{1/2}\eta_s b] \tag{11}$$

Thus, using equations (5), (8), (9) and (10), the elements of **H** are given by

$$\begin{aligned} H_{jk}&=h^*\left(\frac{2}{|j-k|}\right)^{1/2}, \quad j\neq k \\ &=1 \qquad\qquad\qquad\quad, \quad j=k \end{aligned} \tag{12}$$

The matrices in equation (4) are diagonalized by transforming to a set of normal coordinates according to

$$\begin{aligned} \vec{\mathbf{u}}&=\mathbf{Q}^{-1}\vec{\mathbf{x}} \\ \vec{\mathbf{v}}&=\mathbf{Q}^{-1}\vec{\mathbf{y}} \\ \vec{\mathbf{w}}&=\mathbf{Q}^{-1}\vec{\mathbf{z}} \end{aligned} \tag{13}$$

where $\vec{\mathbf{u}}$, $\vec{\mathbf{v}}$ and $\vec{\mathbf{w}}$ are the normal coordinates and the columns of **Q** are the eigenvectors[17] of the product **HA**. The eigenvalue equation from which the eigenvectors $\vec{\alpha}_p$ and eigenvalues λ_p are obtained is

$$\mathbf{HA}\vec{\alpha}_p=\lambda_p\vec{\alpha}_p \tag{14}$$

The components of $\vec{\alpha}_p$ are used to form the pth column of **Q** and therefore

$$\mathbf{Q}^{-1}\mathbf{HAQ}=\mathbf{\Lambda} \tag{15}$$

where $\mathbf{\Lambda}$ is the diagonal matrix whose diagonal elements are the eigenvalues λ_p of the matrix **HA**.

Using the results of Burgers's treatment[18] of the intrinsic viscosity of particles in solution and using the normal coordinate form of the diffusion equation to compute the necessary space averages, Cerf[6] obtains the expression

$$[\eta]=\frac{N_a b^2 \mathrm{f}}{6M\eta_s} \sum_{p=1}^{N} \frac{1}{\lambda_p} \tag{16}$$

for the limiting case of zero velocity gradient and small internal viscosity, where N_a is Avogadro's number. Aside from the above restrictions, equation (16) is free from any simplifying assumptions about the size of N, the number of statistical segments.

EIGENVALUE CALCULATIONS

In order to obtain theoretical values for the intrinsic viscosity from equation (16), the eigenvalues λ_p of the matrix **HA** must be computed satisfying equation (13). For the free-draining case of no hydrodynamic interaction, i.e. $h^*=0$, the free-draining eigenvalues are then simply the eigenvalues of the matrix **A** and are exactly given by

$$\lambda_{p,\text{free}}=4 \sin^2 [p\pi/2(N+1)] \tag{17}$$

For the case of $h^* \neq 0$, the eigenvalues are not as easily obtained. Previous expressions for values of λ_p as a function of N and h^* were developed using the simplifying assumption that N was large and $p \ll N$. An example of this type of expression and the one used for the approximate eigenvalue calculations in this paper is a modification of one given by Pyun and Fixman[13]. When cast in the form using the segmental hydrodynamic interaction factor h^*, the λ_p are given by

$$\lambda_p \simeq 4 \sin^2 [p\pi/2(N+1)]+4h^* N^{-3/2}[I_1(p)+I_2(p)] \tag{18}$$

where $[I_1(p)+I_2(p)]$ is as given by Pyun and Fixman.

For the case of low values of N, a precise solution of equation (14) is possible using numerical methods. Equation (14) can be written as

$$(\mathbf{HA}-\lambda_p\mathbf{1})\vec{\alpha}_p=0 \tag{19}$$

which has a non-trivial solution only if

$$\det(\mathbf{HA}-\lambda_p\mathbf{1})=0 \tag{20}$$

Denoting the product **HA** by **P**, equation (20) may be written in determinant form as

$$\begin{vmatrix} P_{00}-\lambda & P_{01} & P_{02} \; . \; . \; . & P_{0N} \\ P_{10} & P_{11}-\lambda & P_{12} & P_{1N} \\ P_{20} & P_{21} & P_{22}-\lambda & P_{2N} \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ \cdot & & & \cdot \\ P_{N0} & P_{N1} & P_{N2} \; . \; . \; . & P_{NN}-\lambda \end{vmatrix} = 0 \qquad (21)$$

This gives a polynomial in λ of order $N+1$ and yields $N+1$ roots. Since

$$\begin{aligned} \det \mathbf{A} &= 0 \\ \det \mathbf{P} &= 0 \end{aligned} \qquad (22)$$

and hence one of the roots of λ must be zero. This root is labelled λ_0 and is not used further.

A set of relaxation times τ_p occurs in mathematical solutions involving oscillatory flow and is associated with the rate of stress dissipation in the polymer after a given strain. These relaxation times are related to the eigenvalues λ_p by the expression

$$\tau_p = b^2 f / 6kT\lambda_p \qquad (23)$$

Thus λ_0 corresponds to an infinite value of τ_0 for which the chain moves as a rigid body. The N remaining eigenvalues are labelled λ_1 to λ_N inclusive in increasing order. Thus λ_1, the smallest non-zero eigenvalue, corresponds to the longest or terminal relaxation time τ_1.

For the cases of $N=1$ and $N=2$ closed form solutions of equation (21) have been obtained. Substitution of equations (2) and (12) into (20) for $N=1$ yields the determinant to be solved,

$$\begin{vmatrix} (1-\sqrt{2h^*})-\lambda & -(1-\sqrt{2h^*}) \\ -(1-\sqrt{2h^*}) & (1-\sqrt{2h^*})-\lambda \end{vmatrix} = 0 \qquad (24)$$

The roots are

$$\begin{aligned} \lambda_0 &= 0 \\ \lambda_1 &= 2\,(1-\sqrt{2h^*}) \end{aligned} \qquad (25)$$

For $N=2$, the determinant to be solved is

$$\begin{vmatrix} (1-\sqrt{2h^*})-\lambda & -1+2\sqrt{2h^*}-h^* & (h^*-\sqrt{2h^*}) \\ -(1-\sqrt{2h^*}) & 2\,(1-\sqrt{2h^*})-\lambda & -(1-\sqrt{2h^*}) \\ (h^*-\sqrt{2h^*}) & -1+2\sqrt{2h^*}-h^* & (1-\sqrt{2h^*})-\lambda \end{vmatrix} = 0 \qquad (26)$$

and the roots are

$$\lambda_0 = 0$$

$$\lambda_1 = 1 - h^*$$

$$\lambda_2 = 3 + (1 - 4\sqrt{2})\, h^* \qquad (27)$$

Thus the eigenvalues are given in closed form for $N = 1$ and 2 by (25) and (27) for all values of h^*.

A programme was written for an IBM 7040 to calculate the roots of equation (21). Several library programmes are also available in many computing systems which calculate eigenvalues of a real matrix. The programme used to calculate the eigenvalues presented in this paper uses the Newton–Raphson method to approximate the roots of the polynomial in equation (21).

The parameter h^* cannot become large without limit, as a simple argument can show. Considering two beads which are nearest neighbours along the chain, the force exerted on one bead by the solvent due to the motion of the second cannot be greater than the force exerted on the fluid by the second. Employing the methods of Burgers[18], the result is obtained that $h^* \leqslant 0{\cdot}471$, for the case of motion along the line joining the two beads. In equation (25), h^* is mathematically limited to values less than 0·707, or negative eigenvalues will result. In making the computer calculations, a value of $h^* = 0{\cdot}5$ allowed the computation of only the first few eigenvalues for each value of N.

Eigenvalues calculated from equation (20) and using the values for $\langle 1/R_{jk} \rangle$ given by equation (8) are listed in increasing order in *Table 1* for values of N from 1 to 15 and for h^* values of 0·01, 0·1, 0·3 and 0·4. The value in the fourth digit beyond the decimal is uncertain. *Figure 1* is a plot of these exact values of λ_p versus N for $h^* = 0{\cdot}1$. As an aid in comparison, the approximate eigenvalues are indicated for the same h^* value for $N = 20$ to $N = 100$. For each value of N, the approximate eigenvalues are larger than those calculated exactly, and the apparent asymptotic value for λ_N is greater for the approximate set than for the exact set. The exact and approximate results come into agreement as $h^* = 0$, while the disagreement increases with increasing h^*.

In order to examine the dependence of the steady flow intrinsic viscosity $[\eta]$ upon the molecular weight M, equation (16) has been cast into the form[12]

$$[\eta] = \phi N^{1/2} b^3 / N_a m_s \qquad (28)$$

where m_s is the segment mass and $\phi N^{1/2}$ is given by

$$\phi N^{1/2} = \frac{N_a \pi^{3/2}}{3^{1/2}} \frac{h^*}{N} \sum_{p=1}^{N} \frac{1}{\lambda_p} \qquad (29)$$

According to the basic inclusions of the theory N is directly proportional to M. Also, from (28) $\phi N^{1/2}$ differs from $[\eta]$ by the factor $b^3/N_a m_s$, this factor being constant for different molecular weight samples of the same polymer in the same solvent. Thus plots of $\phi N^{1/2}$ versus N should exhibit the same character as curves of $[\eta]$ versus M. *Figure 2* shows plots of $\phi N^{1/2}$ versus N computed using both the exact and approximate eigenvalues, for values of h^*=0·01, 0·03, 0·1, 0·15, 0·2, 0·3 and 0·4. The curves for h^*=0·05, 0·15 and 0·2 using the exact eigenvalues were obtained by geometrical interpolation from the other curves.

Although the $\phi N^{1/2}$ curves calculated from the exact and the approximate eigenvalues might be expected to converge to a common curve for large values of N, *Figure 2* indicates that this convergence, if it occurs, is quite slow. Overlaying *Figure 2* with experimentally determined $[\eta]$ versus M plots on the same scale can provide an indication of whether the two sets of curves do converge to a common value.

Table 1. Exact eigenvalues λ_p of equation (20) for various hydrodynamic interaction conditions h^*, and for number of chain segments N from 1 to 15

h^* = 0·01							
N = 1							
1·9717							
N = 2							
0·9899	2·9534						
N = 3							
0·5822	1·9740	3·3589					
N = 4							
0·3809	1·3675	2·5799	3·5583				
N = 5							
0·2681	0·9920	1·9745	2·9540	3·6697			
N = 6							
0·1988	0·7488	1·5380	2·4108	3·1956	3·7380		
N = 7							
0·1532	0·5838	1·2255	1·9748	2·7245	3·3592	3·7828	
N = 8							
0·1217	0·4673	0·9925	1·6342	2·3153	2·9542	3·4744	3·8137
N = 9							
0·0990	0·3822	0·8196	1·3684	1·9750	2·5805	3·1259	3·5584
3·8359							
N = 10							
0·0821	0·3183	0·6873	1·1593	1·6959	2·2540	2·7887	3·2571
3·6214	3·8524						
N = 11							
0·0693	0·2691	0·5842	0·9928	1·4672	1·9752	2·4823	2·9543
3·3593	3·6698	3·8650					
N = 12							
0·0592	0·2305	0·5023	0·8588	1·2790	1·7388	2·2115	2·6698
3·0874	3·4402	3·7078	3·8748				
N = 13							
0·0512	0·1996	0·4364	0·7495	1·1231	1·5386	1·9752	2·4113
2·8250	3·1958	3·5053	3·7381	3·8826			
N = 14							
0·0447	0·1746	0·3826	0·6594	0·9930	1·3687	1·7703	2·1802
2·5806	2·9543	3·2851	3·5584	3·7627	3·8888		
N = 15							
0·0394	0·1539	0·3380	0·5844	0·8835	1·2239	1·5925	1·9753
2·3576	2·7248	3·0630	3·3593	3·6023	3·7828	3·8940	

Table 1—continued

$h^* = 0{\cdot}1$

$N=1$							
1·7171							
$N=2$							
0·8999	2·5343						
$N=3$							
0·5499	1·7402	2·8613					
$N=4$							
0·3721	1·2380	2·2375	3·0207				
$N=5$							
0·2699	0·9206	1·7457	2·5402	3·1093			
$N=6$							
0·2055	0·7108	1·3855	2·1036	2·7338	3·1634		
$N=7$							
0·1624	0·5660	1·1220	1·7489	2·3576	2·8642	3·1987	
$N=8$							
0·1319	0·4620	0·9258	1·4685	2·0277	2·5422	2·9557	3·2231
$N=9$							
0·1096	0·3848	0·7768	1·2470	1·7507	2·2427	2·6796	3·0222
3·2406							
$N=10$							
0·0927	0·3260	0·6614	1·0707	1·5212	1·9791	2·4105	2·7841
3·0719	3·2535						
$N=11$							
0·0796	0·2801	0·5702	0·9288	1·3312	1·7520	2·1643	2·5432
2·8652	3·1101	3·2634					
$N=12$							
0·0692	0·2435	0·4970	0·8133	1·1735	1·5578	1·9454	2·3156
2·6497	2·9293	3·1399	3·2711				
$N=13$							
0·0608	0·2140	0·4374	0·7182	1·0416	1·3919	1·7529	2·1076
2·4401	2·7361	2·9807	3·1638	3·2773			
$N=14$							
0·0539	0·1897	0·3882	0·6391	0·9305	1·2500	1·5845	1·9206
2·2443	2·5438	2·8070	3·0226	3·1832	3·2822		
$N=15$							
0·0482	0·1694	0·3471	0·5726	0·8362	1·1282	1·4375	1·7536
2·0647	2·3603	2·6306	2·8659	3·0570	3·1991	3·2862	

$h^* = 0{\cdot}3$

$N=1$							
1·1515							
$N=2$							
0·7000	1·6029						
$N=3$							
0·4774	1·2207	1·7563					
$N=4$							
0·3514	0·9499	1·4778	1·8267				
$N=5$							
0·2724	0·7610	1·2381	1·6215	1·8642			
$N=6$							
0·2192	0·6255	1·0474	1·4217	1·7083	1·8866		
$N=7$							
0·1813	0·5252	0·8970	1·2477	1·5431	1·7648	1·9009	
$N=8$							
0·1533	0·4489	0·7775	1·1008	1·3894	1·6276	1·8034	1·9107
$N=9$							
0·1318	0·3892	0·6814	0·9774	1·2531	1·4930	1·6883	1·8309
1·9177							

Table 1 ($h^* = 0{\cdot}3$)*—continued*

$N = 10$							
0·1149	0·3417	0·6032	0·8739	1·1336	1·3690	1·5706	1·7334
1·8544	1·9228						
$N = 11$							
0·1014	0·3031	0·5385	0·7865	1·0295	1·2569	1·4585	1·6304
1·7678	1·8664	1·9267					
$N = 12$							
0·0904	0·2712	0·4846	0·7121	0·9392	1·1561	1·3548	1·5290
1·6773	1·7943	1·8783	1·9298				
$N = 13$							
0·0812	0·2446	0·4390	0·6484	0·8605	1·0664	1·2594	1·4336
1·5855	1·7148	1·8152	1·8878	1·9322			
$N = 14$							
0·0735	0·2220	0·4001	0·5934	0·7916	0·9866	1·1723	1·3443
1·4977	1·6318	1·7450	1·8320	1·8955	1·9341		
$N = 15$							
0·0670	0·2028	0·3660	0·5458	0·7309	0·9157	1·0934	1·2615
1·4146	1·5508	1·6701	1·7698	1·8456	1·9019	1·9357	

$h^* = 0{\cdot}4$

$N = 1$							
0·8686							
$N = 2$							
0·6000	1·1372						
$N = 3$							
0·4397	0·9609	1·2051					
$N = 4$							
0·3393	0·8047	1·0996	1·2307				
$N = 5$							
0·2719	0·6795	0·9851	1·1638	1·2425			
$N = 6$							
0·2244	0·5809	0·8782	1·0820	1·1971	1·2488		
$N = 7$							
0·1894	0·5028	0·7839	0·9977	1·1374	1·2164	1·2525	
$N = 8$							
0·1627	0·4404	0·7023	0·9170	1·0714	1·1716	1·2283	1·2549
$N = 9$							
0·1418	0·3896	0·6326	0·8423	1·0049	1·1194	1·1939	1·2362
1·2565							
$N = 10$							
0·1251	0·3478	0·5728	0·7748	0·9400	1·0649	1·1519	1·2093
1·2415	1·2577						
$N = 11$							
0·1114	0·3130	0·5214	0·7145	0·8786	1·0098	1·1067	1·1751
1·2201	1·2452	1·2586					
$N = 12$							
0·1001	0·2836	0·4770	0·6605	0·8218	0·9554	1·0604	1·1368
1·1921	1·2278	1·2480	1·2593				
$N = 13$							
0·09069	0·2585	0·4385	0·6124	0·7694	0·9036	1·0131	1·0976
1·1593	1·2051	1·2334	1·2502	1·2598			
$N = 14$							
0·08265	0·2369	0·4048	0·5695	0·7215	0·8547	0·9665	1·0569
1·1255	1·1767	1·2149	1·2375	1·2520	1·2602		
$N = 15$							
0·07573	0·2182	0·3751	0·5313	0·6774	0·8090	0·9214	1·0158
1·0903	1·1470	1·1905	1·2225	1·2406	1·2535	1·2605	

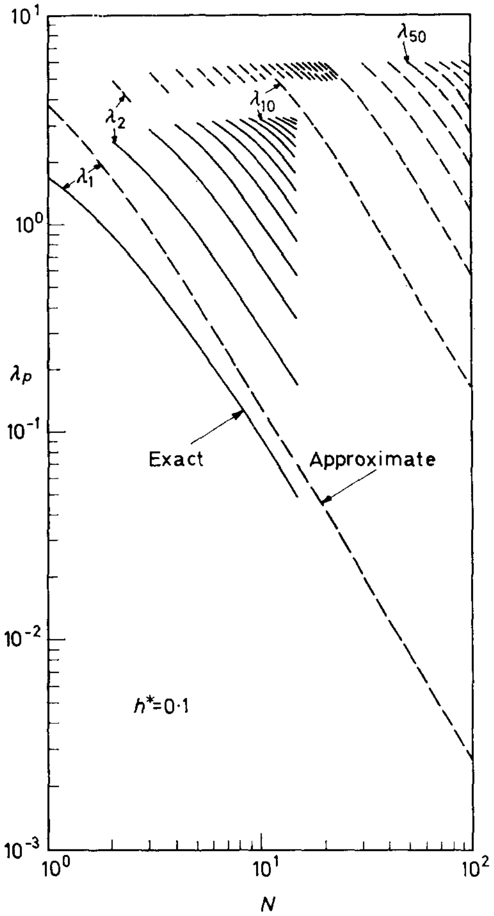

Figure 1—Exact eigenvalues λ_p (solid lines) for $N=1$ to 15 and approximate eigenvalues (dashed lines) from equation (18) for $h^*=0{\cdot}1$

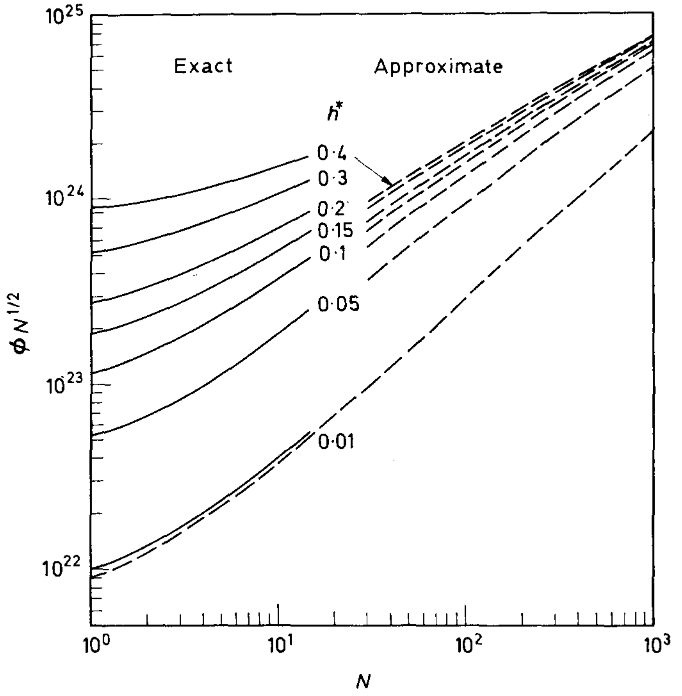

Figure 2—$\phi N^{1/2}$ versus N calculated from equation (29) using exact eigenvalues (solid lines) and approximate eigenvalues (dashed lines) for several values of h^*

Equations (16) and (23) may be combined to give an expression for τ_1 in terms of $[\eta]$. Using a form introduced elsewhere[11], τ_1 may be written as

$$\tau_1 = C(N,h^*)\,[\eta]\,M\eta_s/N_a kT \tag{30}$$

where

$$C(N,h^*) = \left[\sum_{p=1}^{N} \lambda_1/\lambda_p\right]^{-1} \tag{31}$$

Equation (30) is useful in obtaining values for τ_1 from intrinsic viscosity measurements which can then be compared with values of τ_1 obtained from independent measurements of oscillatory flow phenomena on the same polymer samples. *Figure 3* presents plots of $C(N,h^*)$ versus N using both the exact and approximate sets of eigenvalues. Again, the curves using the exact eigenvalues for values of $h^* = 0{\cdot}15$ and $h^* = 0{\cdot}2$ are geometrically interpolated. The problem of the convergence of the $C(N,h^*)$ curves computed from the exact to those obtained from approximate eigenvalues

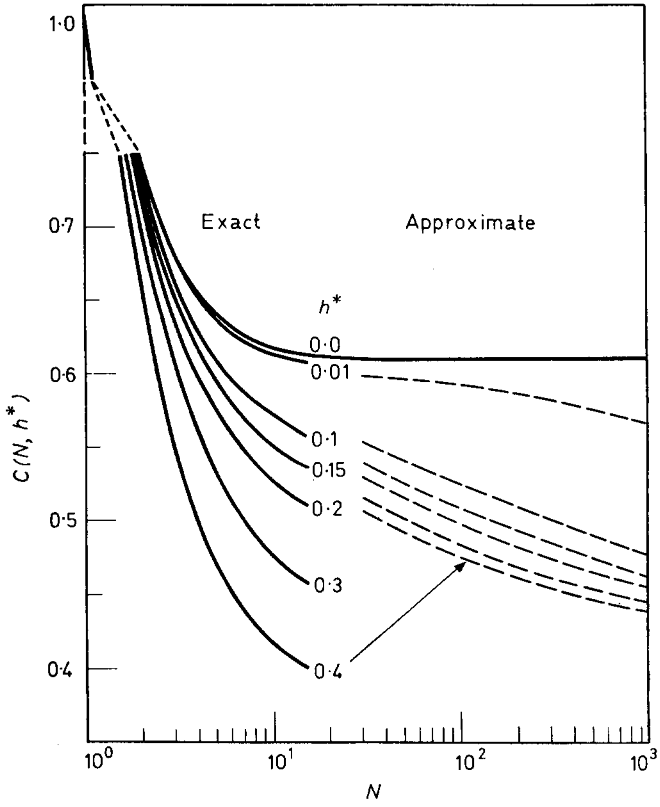

Figure 3—$C(N,h^*)$ versus N calculated from equation (31) using exact eigenvalues (solid lines) and approximate eigenvalues (dashed lines) for several values of h^*

at large values of N is even more evident here than in the case of the function $\phi N^{1/2}$. Such a convergence, if it occurs, is indeed slow and occurs for quite large values of N.

COMPARISON WITH MEASUREMENTS

The theoretical behaviour of the intrinsic viscosity at low molecular weights may be compared with experimental data by comparing the plots of $\phi N^{1/2}$ versus N with experimental plots of $[\eta]$ versus M. From equations (28) and (29), values of $[\eta]$ can be obtained from $\phi N^{1/2}$ by specifying values for h^*, b and m_s. This procedure may be carried out in reverse by making a best fit of the $\phi N^{1/2}$ versus N curves with the experimentally determined $[\eta]$ versus M curves. *Figure 4* shows a plot of intrinsic viscosity versus molecular weight obtained by Thurston and Schrag[9] for dilute solutions of polystyrene in Aroclor 1248 over a wide range of molecular weights. The measurements were made at a temperature of 25°C, at which the viscosity of the Aroclor 1248 was 2·23 poises. The dashed line through the data points shows clearly the characteristic upward curvature of the plot for low molecular weights. The solid line is the theoretical curve of $\phi N^{1/2}$ versus N for a value of $h^* = 0{\cdot}15$ and for a superposition of the theoretical and experiment curves such that $N=1$ segment at $M=3\,200$ and $\phi N^{1/2} = 10^{24}$ at $[\eta] = 43\ \mathrm{cm^3/g}$. For this particular case of $h^* = 0{\cdot}15$, the experimentally determined $[\eta]$ versus M curve approaches the $\phi N^{1/2}$ curve calculated from the approximate eigenvalues for large N. However, for higher values of h^*, the data points may not approach the $\phi N^{1/2}$ curves given by the approximate eigenvalues. Using equations (11) and (28) and the relation

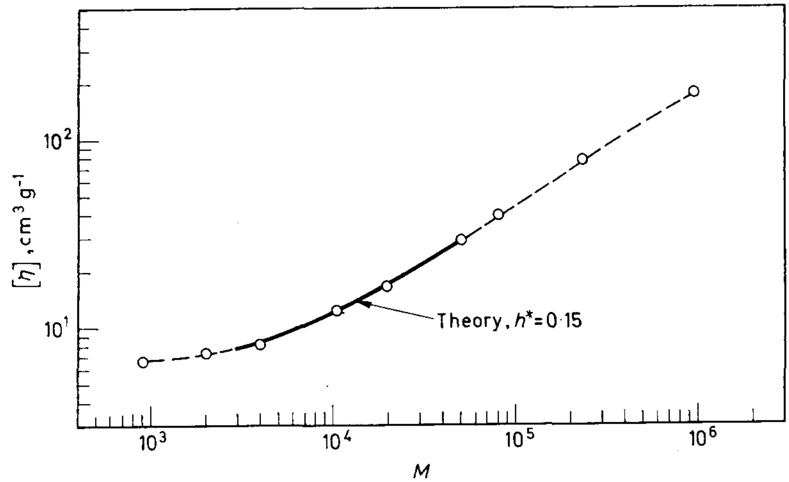

Figure 4—$[\eta]$ versus M (dashed lines) for polystyrene in Aroclor 1248 and $\phi N^{1/2}$ versus N (solid lines) for $h^* = 0{\cdot}15$

$$m_s = M/N\,N_a \tag{32}$$

the following relations are obtained: $m_s = 5{\cdot}31 \times 10^{-21}$g, $b = 5{\cdot}16 \times 10^{-7}$ cm, $f = 3{\cdot}33 \times 10^{-6}$g sec^{-1}. Since the molecular weight of the styrene monomer is 104·14, this value of m_s places about 32 monomer units in each statistical segment. These values may be used to find terminal relaxation times for the polymer chains of different molecular weights using equation (30). Appropriate values of $C(N,h^*)$ for the case $h^* = 0{\cdot}15$ may be read from *Figure 3* and substituted into equation (30) to find τ_1 at each value M. The range of these determinations is restricted to the range of N from 1 to 15 for which exact eigenvalues are known. The results of these calculations are shown by the dashed curve of *Figure 5*.

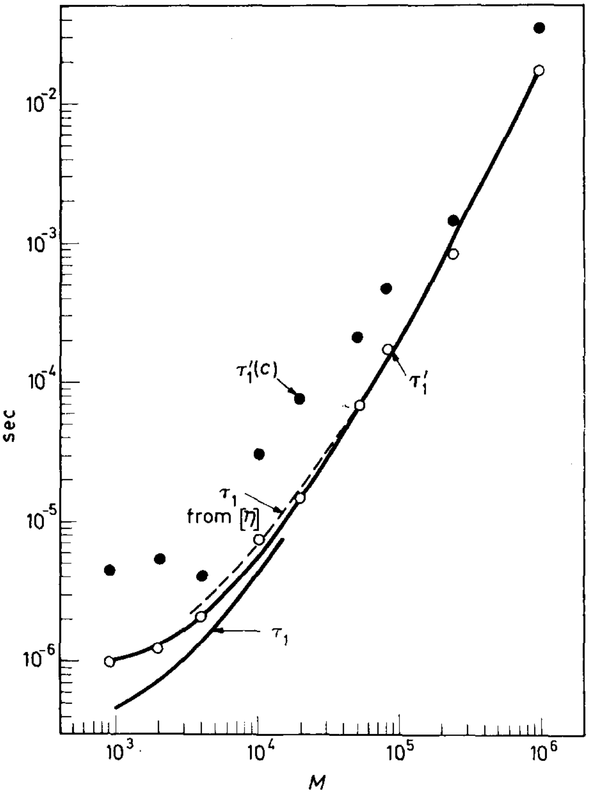

Figure 5—$\tau_1'(c)$ and τ_1' versus M for polystyrene in Aroclor 1248; τ_1 versus M computed from intrinsic viscosity measurements using equation (30) (dashed line); τ_1 versus M computed from oscillatory flow birefringence using τ_1' in equation (33) (solid line)

A comparison set of relaxation times for polystyrene in Aroclor 1248 may be determined from oscillatory flow birefringence measurements[13]. In this system having multiple relaxation times, the initial departure from low frequency response is largely determined by the longest relaxation time, τ_1'. The relaxation time τ_1' is to be distinguished from τ_1 of equation (23) in that τ_1' is dependent upon the internal viscosity of the chain. τ_1 can be derived from the τ_1' values by the expression[10, 6]

$$\tau_1' = \tau_1 \left(1 + \frac{\varphi}{\mathrm{f}} \frac{1}{N} \frac{\lambda_1}{\lambda_{1,\mathrm{free}}}\right) \tag{33}$$

where φ is the coefficient of internal viscosity. In contrast to the dilute solution conditions of the steady flow viscosity measurements, the oscillatory flow measurements are for solutions of finite concentration for which there is significant interaction between polymer molecules. By comparing a single theoretical relaxation time response curve with the low frequency ends of the experimentally measured response curves for each of the polystyrene samples shown in *Figure 4*, a set of concentration dependent relaxation times $\tau_1'(c)$ may be determined. Following the method of Thurston[13] the values for $\tau_1'(c)$ may be related to the times τ_1' for dilute solutions by the expression

$$\tau_1' = \tau_1'(c)/K(c) \tag{34}$$

where $K(c)$ is a concentration factor relating the measured and intrinsic viscosities for each molecular weight. Both the times $\tau_1'(c)$ and τ_1' are shown in *Figure 5*. In order to use equation (33), the relation between M and N and the values of h^* and φ/f must be known. Holding h^* to 0·15 and assuming the internal viscosity to be very low so that φ/f is near zero, the set of times τ_1 computed this way would lie very nearly along the τ_1' line of *Figure 5*. The effects of concentration upon the relation between M and N and the values of h^* and φ/f are not known, however, and the relaxation times observed in finite concentration oscillatory flow birefringence may differ from those calculated from steady flow viscosity measurements. Using different methods with the same samples of polystyrene at finite concentrations, it has been found[13] that approximately $\varphi/\mathrm{f} = 2{\cdot}0$, $h^* = 0{\cdot}3$ for lower molecular weights, and a segment weight is 1 000. This corresponds to approximately ten monomer units per segment. Using these values and equation (33), the values for τ_1 shown as a solid line in *Figure 5* are calculated. Here again the range of the calculation is restricted to that for which exact values of λ_1 are known. In spite of the uncertainty in concentration effects upon the parameters involved, the two sets of relaxation times, τ_1 from $[\eta]$ and τ_1 from oscillatory flow birefringence, differ by a factor of less than two at $M = 4\,000$ and by about 50 per cent at $M = 15\,000$. The comparison of these two separately determined relaxation times is considered to be a demanding test of the Gaussian chain theory, particularly since one of the τ_1s is dependent upon the internal chain viscosity while the other is not, and the two types of experimental measurements are mutually independent.

Comparisons have also been made between the theoretical function $\phi N^{1/2}$ versus N and experimentally determined values of polystyrene in benzene, decalin, dioctylphthalate and toluene taken by Meyerhoff[19] and Berry[20], and for similar data for low molecular weights of poly-γ-benzyl-L-glutamate in dichloracetic acid taken by Mitchell, Woodward and Doty[21], poly-α-methylstyrene in toluene taken by Cottam, Cowie and Bywater[22], and for polyoxyethyleneglycol in water and benzene taken by Sadron and Rempp[23]. In each of these cases the character of the molecular weight dependence curves is consistent with that of the theory. However, oscillatory flow measurements are not available to use in exacting a more demanding check between theory and experiment.

In summary, it is noted that the use of the exact eigenvalues calculated in this work permits the successful theoretical description of the experimentally determined molecular weight dependence of intrinsic viscosity at low molecular weights, using N and h^* as significant parameters. In addition, a set of terminal relaxation times is obtained from steady flow intrinsic viscosity measurements which compare favourably with those obtained from independent measurements of oscillatory flow birefringence, subject to the uncertainties of concentration effects. In order to extend the application of the exact eigenvalues over a wider range of molecular weights, more convenient methods for solving the eigenvalues for values of N greater than 15 are needed, and an analysis of the significance of the errors in the approximate eigenvalue calculations would also be useful. Additional data on other polymers from measurements under both steady and oscillatory flow conditions over a wide range of molecular weights and concentrations are needed to clarify possible effects of concentration upon the theoretical parameters and to examine the relaxation times encountered in both types of experiments.

The authors wish to acknowledge the support of the U.S. Army Research Office, Durham, during the course of this work.

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(*Received August 1968*)

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