Viscosity of Entangling Polydisperse Polymers

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(Received 4 May 1967)

This paper presents a theory of viscosity in steady shearing flow for bulk polymers and concentrated polymer solutions. The basis for the theory is the supposition that intermolecular chain entanglements control the magnitude of the viscosity and that the decrease in viscosity with increasing shear rate is caused by shear-induced changes in the network of entanglements. It was found possible to represent the effect of entanglements by an additional term in the segmental friction coefficient, and to incorporate the effects of polymer concentration, molecular weight distribution, and shear rate in the final result. At low shear rates ($\gamma < 0$) the viscosity reduces to $\eta_0 = (\text{const}) (\phi L)^{1.45}$ for highly entangled chains, where $\phi$ is the volume fraction of polymer and $L$ is an average chain length slightly greater than the weight average. The form of the viscosity-shear rate master curve was found to depend on the chain-length distribution of the polymer. Departures from Newtonian behavior occur at lower shear rates the broader the distribution, but at sufficiently high shear rates the behavior becomes similar for all distributions. The master curve for monodisperse polymers was in good agreement with measurements on solutions of narrow distribution polystyrene. The limiting power-law exponent in $\eta = k \gamma^n$ was found to be $9/11$ rather than $4$ as given by an earlier theory. The master curve calculated for most-probable distributions ($M_w/M_n = 2$) agreed moderately well with the empirical master curve of Bueche and Harding and with data on solutions of unfractionated polystyrene.

INTRODUCTION

Amorphous polymers and their concentrated solutions are non-Newtonian in steady shearing flows: viscosity coefficients depend on the rate of deformation, and the systems show certain elastic properties and memory effects in flow not present in ordinary fluids. Two types of molecular theories have been advanced to explain these properties in concentrated polymer systems. One is based on the hypothesis of a parallel or equivalence between the stresses experienced by long-chain molecules immersed in a fluid undergoing infinitesimal oscillatory deformation and in a fluid undergoing a steady shearing deformation. The other is based on the properties of a network composed of physically entangled molecules and the changes induced in this network by flow.

Rouse\textsuperscript{4} had suggested a rather realistic model for a flexible polymer chain undergoing random thermal motions and responding to flow fields imposed on the surrounding viscous medium. His approach and subsequent modifications to account for hydrodynamic interaction between the segmental motions\textsuperscript{3,5} have been quite successful in predicting dynamic viscosity and elastic compliance as functions of frequency under suitable experimental conditions.\textsuperscript{4} Yet when these same methods are applied to steady shearing flow they yield a viscosity coefficient which is completely independent of shear rate. In this respect the model (or perhaps only the method for handling the hydrodynamic interaction) gives wrong answers for steady shear even when the chains do not interact, since the intrinsic viscosity is known to depend on shear rate. An explanation of the shear dependence in dilute solution, incomplete flexibility of the chains characterized by an internal viscosity coefficient, has been suggested by Cerf\textsuperscript{4} and re-examined recently by Peterlin.\textsuperscript{8} Such considerations may be relevant to the shear dependence of viscosity in some concentrated systems also, although they are neglected in the present study.

With the equivalence hypothesis\textsuperscript{5} a shear-rate dependence is imposed upon the Rouse model automatically, since the viscosity-vs-shear-rate curve is simply the dynamic viscosity-vs-frequency curve with frequency replaced by the shear rate multiplied by a constant. The shape of the resulting theoretical curve of viscosity vs shear rate does not agree with experiments on concentrated systems.\textsuperscript{8} Nevertheless the theory introduces a molecular relaxation time which can be calculated from the properties of the system at low shear rates, and it predicts that the viscosity should first begin to decrease with increasing shear rate in the range where the product of this relaxation time and the shear rate is of the order of unity. This prediction has been borne out remarkably well in bulk polymers and concentrated solutions.\textsuperscript{9-11}

The time constant can be expressed either as the Rouse or Bueche relaxation time. In each case it is also the maximum relaxation time in the corresponding relaxation time distribution of the chains:

$$\tau_r = (6/\pi^4) (\eta_0 M/cRT) \quad \text{Rouse relaxation time, (1a)}$$

$$\tau_n = (12/\pi^4) (\eta_0 M/cRT) \quad \text{Bueche relaxation time, (1b)}$$

\textsuperscript{7} F. Bueche and S. W. Harding, J. Polymer Sci. \textbf{32}, 177 (1958).
where \( \eta_0 \) is viscosity of the system at zero shear rate, \( M \) is the polymer molecular weight, \( c \) is the polymer concentration (weight per volume), \( R \) is the gas constant, and \( T \) is the absolute temperature. The above forms apply to monodisperse bulk polymers and concentrated solutions for cases in which \( \eta_0 \) is much greater than the viscosity of the pure solvent. For convenience and to avoid ambiguities only the Rouse relaxation time will be used in later discussions.

The equivalence hypothesis has also been used to predict relationships between elastic and viscous behavior in oscillatory and steady-flow experiments without appealing to any specific molecular picture.\(^{12}\) Parallels in behavior\(^{9,13-15}\) and in many cases superposability are indeed observed under some conditions in many systems. However such observations as are presently available do not alone prove or disprove the hypothesis. According to second-order viscoelasticity theory the two types of experiments must yield the same information at sufficiently low shear rates and frequencies. If, through the relaxation-time distribution of the molecules, the same relaxation-time parameter controls both the frequency and shear rate dependencies, then departures from low frequency and low shear-rate behavior should begin to appear within the same range of frequency and shear-rate values. It might then be somewhat difficult to distinguish between the curves from dynamic and steady-flow experiments, even if the mechanisms of energy storage and dissipation were entirely different in the two cases.

The equivalence approach appears to ignore the question of chain entanglements altogether, in spite of strong evidence for their contribution to the zero-shear viscosity. Apart from this, there is another reason from questioning the validity of the equivalence approach. Without some additional hypothesis it seems to lead directly to a linear theory of steady-flow properties by implying that the local properties of the system (e.g., the relaxation-time distribution) are the same whether the system is at rest or undergoing a steady shearing flow. Recent experiments\(^{16,17}\) in which dynamic viscosity and elastic modulus were measured on polymer solutions at several superimposed shear rates suggest this is not generally true. At sufficiently large shear rates the dynamic behavior was found to change in a manner which implied a decrease in the longest relaxation times of the system. A continuum model for viscoelastic behavior which contained a shear-rate dependent relaxation-time distribution was able to correlate this nonlinear behavior in a very natural way however.\(^{18}\)

Alternative explanations of non-Newtonian behavior have been suggested for polymer systems where intermolecular chain entanglements are important.\(^{19,20}\) Viscosity changes are attributed to changes induced by the steady shearing flow in the degree of chain entanglement, which is consistent with the changes in local properties that are observed experimentally. In one recent theory for monodisperse systems,\(^{19}\) the Rouse relaxation-time parameter governs the location of the shear rate where the viscosity begins to decrease. The Rouse relaxation time appears not only as the parameter in the relaxation-time distribution of individual random-coil chains but also in any derived properties which depend mainly on the longer relaxation times in the system. Examples of such properties are the disturbance in mean segment distribution caused by a shearing flow field,\(^{21}\) the relaxation rate from a perturbed to an equilibrium distribution of end-to-end distances,\(^{22}\) and the correlation function for the end-to-end vector.\(^{23}\) Consequently, the characteristic time for passing molecules to entangle was taken to be of the order of magnitude of the Rouse parameter, since it was assumed that a complete reorganization of chain configuration would be necessary to form the couple.

Inherent in the theory is the supposition that the viscosity which appears in the characteristic time for entanglement formation is not invariably the zero shear viscosity as it would be in a linear system, but rather the viscosity at the existing shear rate. The result, after application to a simple model of the detailed processes involved and calculation of the viscosity from the rate of energy dissipation, is an implicit expression for viscosity as a function of shear rate in monodisperse systems:

\[
\frac{\eta}{\eta_0} = \frac{2}{\pi} \left[ \cot^{-1}\theta + \frac{\theta(1-\theta^2)}{(1+\theta^2)^2} \right],
\]

where

\[
\theta = \frac{1}{2}(\dot{\gamma}\tau) = \left(\frac{\eta}{\eta_0}\right) \left(\frac{5}{3}\dot{\gamma} \tau_0\right),
\]

and \( \dot{\gamma} \) is the shear rate, \( \eta \) is the viscosity at the existing shear rate, \( \tau \) is the entanglement formation time at the existing shear rate, \( \tau = (\eta/\eta_0) \tau_0 \) is the entanglement formation time, reduced to \( \dot{\gamma} = 0 \), \( \tau_0 \) is the entanglement formation time at \( \dot{\gamma} = 0 \), and \( C \) is a universal constant of order unity.

The shape of the \( \log(\eta/\eta_0) \) vs \( \log(\tau_0\dot{\gamma}) \) curve given by solving Eqs. (2) and (3) is quite similar to ex-

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Experimental results on narrow distribution polymers.\textsuperscript{34,35} The width of the transition region between Newtonian and approximate power-law behavior is about the same, and the predicted form in the high shear-rate region, $\eta \propto |\gamma|^{-3/4}$, is not far from the observed behavior. The use of the shear-dependent viscosity in the relaxation time exerts a very strong influence on the form of the master curve, and it appears that the results are not overly sensitive to the simplification of details used in arriving at Eqs. (2) and (3). It seemed worthwhile therefore to refine the theory in order to include systems with a distribution of chain lengths. Molecular weight distribution is known to influence the shape of the master curve\textsuperscript{36,37} and yet the only method presently available for handling the effect of distribution is the plausible but rather arbitrary mixing rule suggested by Petiolas and Menefee.\textsuperscript{38} The envisioned generalization to polydisperse systems, if successful, would be useful in extending the range of samples for which the present theories could be tested and compared.

In order to treat polydisperse systems, it is necessary to review and re-establish the segmental friction coefficient in the entanglement region. A natural consequence of the theory is that this coefficient depends on the rate of deformation, a factor which was neglected in the original treatment. Consequently even the earlier results for monodisperse systems must be revised slightly; the power-law behavior becomes $\eta \propto |\gamma|^{-3/4}$, for example. However, the final equations are in principal general enough to handle concentration effects, polydispersity, and even forms for the relaxation-time different than the Rouse expression.

**THEORY**

We select for examination one random-coil molecule in a fluid composed of a collection of random-coil molecules with or without the presence of a small-molecule solvent. The centers of gravity of the random-coil molecules are distributed randomly through the fluid, and their spheres of influence overlap so extensively that the number of segments per unit volume is uniform. The system is deformed uniformly and continuously such that the velocity of the fluid is parallel to the $x$ axis with magnitude $|v_x| = \gamma \lambda$ as shown in Fig. 1.

The origin of the reference coordinate system is located at the center of gravity of the molecule being observed. In the usual way we associate with each segment of the chain a segmental friction coefficient $\xi_0$, defined such that the drag force exerted by the medium on that segment is $F_d = \xi_0 v_{rel}$, where $v_{rel}$ is the difference between the average velocity of the fluid at the location of the segment if that segment itself were not present, and the average velocity of the segment. Following Bueche\textsuperscript{39} we consider a solution which is sufficiently concentrated that the flow lines are undistorted and unaffected by the location of individual molecules. Thus the velocity in the $x$ direction of the fluid at the $i$th segment of the molecule at the origin is $\gamma_0 z_i$, where $z_i$ is the $z$ coordinate of the $i$th segment.

In the interests of retaining a simple picture for later calculations, we consider that all segments in the chain remain fixed in space in the local coordinate system, rather than undergoing an average rotating motion as pictured by Bueche. The effect should be harmless since we are only interested in how the energy dissipation depends on chain length, and the final result for power dissipation merely differs from that of Bueche by a multiplying constant. Thus $|v_{rel}| = \gamma \lambda |z_i|$, and the power dissipated by the drag forces exerted on the molecule by the fluid is

$$\sum_i \xi_0 |v_{rel}| i^2 = \gamma_0^2 \sum_i z_i^2 = \gamma_0^2 \gamma^2 n \langle \delta^2 \rangle = \gamma_0^2 \gamma^2 n \langle R^2 \rangle / 18,$$

where $n$ is the number of segments in the chain and $\langle R^2 \rangle$ is the mean square end-to-end distance of the chain. Thus we arrive at the well-known result, that the power dissipated per random-coil chain is proportional to the square of the chain length (since $\langle R^2 \rangle$ is directly proportional to $n$) when the friction coefficient is independent of chain length:

$$\dot{\epsilon}_v = (\text{const}) \gamma^2 \xi_0 n^2. \quad (4)$$

The viscosity is given by $\dot{E}_v / \gamma^2$ where $\dot{E}_v$ is the rate of energy dissipation per unit volume. Thus, since the number of chains per unit volume $\nu$ is inversely proportional to chain length, the result

$$\eta = (\text{const}) \gamma \xi_0 n \quad (5)$$

is obtained. Likewise, if a distribution of chain lengths is present, and $\gamma_0$ is still independent of chain length,

\begin{figure}[h]
\centering
\includegraphics[width=0.3\textwidth]{molecule.png}
\caption{Molecule at the origin of coordinates and imposed velocity profile.}
\end{figure}

\footnotesize
\textsuperscript{35} R. A. Stratton, J. Colloid Interface Sci. 22, 517 (1966).
it follows immediately that for any distribution
\[ \eta = \text{(const)} \xi_0 n_w, \quad (6) \]
where \( n_w \) is the weight-average degree of polymerization.

In most polymers with degrees of polymerization greater than a few hundred, the viscosity is found to depend on \( n^{0.4} \) rather than \( n^1 \). It is assumed that the process of power dissipation is not changed in any fundamental way, only that the friction coefficient becomes a function of molecular weight: \( \xi = \text{(const)} \xi_0 n^{1.8-3.0} \). A number of analyses\(^{29-32}\) based on considerations of the effect of physical entanglement of chains larger than some critical chain length, have been presented to explain the observed chain length dependence, and yield \( \xi = \text{(const)} \xi_0 n^{1.8-3.0} \). However, all were deduced specifically for monodisperse systems, and it is not easy to see how to generalize them to polydisperse systems. The following analysis has similarities to the earlier methods, but has the advantage that it allows the straightforward inclusion of concentration, shear rate, and polydispersity effects. Moreover, it leads rather naturally to a form for the friction coefficient, \( \xi = \text{(const)} \xi_0 n^{1.8-3.0} \), which is close to the observed result.

We return to the system pictured in Fig. 1, and separate the friction coefficient into an ordinary segmental term, applying in the absence of entanglements, and a second term measuring their contribution as additional forces operating on the molecule. This isolation of entanglement effects can be thought of in the following way. Suppose each molecule were a collection of unconnected particles distributed in space and individually undergoing the same thermal motions as they would if joined. Let a velocity gradient be imposed upon a collection of such molecules and examine the motions, drag forces and power dissipation per molecule. The molecules can pass freely through one another and the properties are controlled by the magnitude of the segmental friction coefficient \( \xi_0 \) alone, as it applies to each particle or repeating unit in each molecule. Now join the particles in each molecule to form linear chains and perform the same experiment. Any additional motions, drag forces, and power dissipation brought about by this change are to be attributed to the mutual restraints upon relaxation imposed by chain connectivity, i.e., intermolecular chain entanglements.

If the average number of intermolecular couples \( J(n) \) for a chain is proportional to its chain length \( n \) (at \( v = 0 \)), then the average number of repeating units between entanglement junctions \( n_c \) is a function of concentration only, and, for a given kind of polymer, independent of chain length.\(^{32}\) We assume and later show that an entanglement friction coefficient \( \xi_e \) can be defined, such that the average drag force imposed on one molecule by another coupled to it is equal to \( \xi_e v_{\text{chain}} \), where \( v_{\text{chain}} \) is now the relative velocity of the centers of gravity of the two molecules.

If such a friction coefficient can be defined then there seems to be no fundamental reason against extending the earlier procedure to the calculation of viscosity in concentrated entangling systems. The suspending medium or continuum for each chain is simply composed of segments from other polymer chains as well as solvent molecules, and the entanglement friction coefficient becomes a communal property, a property of the continuum. The total rate of energy dissipation \( \dot{\varepsilon}_e(n) \) by the molecule at the origin can then be expressed formally by the equation
\[ \dot{\varepsilon}_e(n) = \sum_i \xi_0 \left| v_{\text{rel},i} \right| \dot{s}_i^2 + \sum_j \xi_e \left| v_{\text{chain}} \right| \dot{s}_j^2, \quad (7) \]
where \( \left( v_{\text{rel},i} \right) \) is the velocity of the fluid at the \( i \)th repeating unit of the chain at the origin, and \( \left( v_{\text{chain}} \right) \) is the velocity of the center of gravity of the molecule coupled with the molecule at the origin through its \( j \)th entanglement junction. Since in both cases \( \left| v \right| = \dot{s} \), the equation for zero rate of deformation becomes:
\[ \dot{\varepsilon}_e(n) = \dot{s}^2 \left[ \sum_i \xi_0 \dot{s}_i^2 + \sum_j \xi_e \dot{s}_j^2 \right]. \quad (8) \]
If the flow does not affect the distribution of \( s \) coordinates in the molecule, the effect of shear rate on \( \dot{\varepsilon}_e(n) \) will be accounted for by whatever changes are produced in \( \xi_e \) and \( J \). The viscosity of the system is
\[ \eta = 1/\dot{\varepsilon}_e \sum v \left[ \dot{\varepsilon}_e(n) \right], \quad (9) \]
where summation over all \( v \) chains in the unit volume is intended.

The dependence of \( \xi_e \) on the properties of a highly entangled system can be deduced as follows. The significant additional motions induced in the system by chain connectivity are assumed to be like those illustrated in Fig. 2. Without connectivity the repeating units of any passing chain would all drift through the chain at the origin with the same average velocity \( v_{\text{chain}} \), as the center of gravity of the chain. (For convenience we deal with absolute values of the various velocities rather than with their vector forms.) With the segments connected, however, the possibility of entanglement exists. If a couple did form, it would divide the passing chain into two parts, and the center of gravity of the shorter part, called \( S \), would necessarily execute an average retrograde motion towards the entanglement junction. Since we assume that all chains are highly entangled, this particular junction being examined would cause no deviation in the average motion of the center of gravity of the passing chain, and we can consider the total effect only as a delay and later catching-up of portion \( S \). Thus we
assume that the center of gravity of the larger portion, part \( L \), of the chain continues to move with velocity \( v_{\text{chain}} \), the relative velocity of the undisturbed chain.

Such a complete separation of behavior for portions \( S \) and \( L \) obviously breaks down when the entanglement point divides the chain in two nearly equal parts. However, as will be seen, the drag force is such a strong function of chain length in entangled systems that only a very small fraction of the entanglements will be so evenly balanced that the analysis will fail. These cases we must neglect.

The segments of the passing chain at the entanglement junction move at an average local velocity \( v_e \), related to \( v_{\text{chain}} \), as is shown later. If the loop is rigidly maintained in the fluid, a retrograde velocity \( v_e \) will then be imposed on the center of gravity of part \( S \). This is an idealization, of course, since one would expect both chains in the entanglement to give way, and especially the smaller chain in the case of unequal lengths. However, there is a considerable conceptual and practical advantage to allowing all additional motions to be assumed by the passing chains alone. The result is an entanglement friction coefficient which is a property of the medium, a communal property in the sense that it can be replaced by an average contribution for the system as a whole and is independent of the chain length of any "chain at the origin" to which it might be applied. The error caused by holding one chain of the entangled pair in place should be somewhat compensated by the fact that all chains enter the averaging process to obtain the communal coefficient, so that some additional motions are eventually counted for all chains.

The drag forces and the average power expended by passing chains in drawing their shorter sections through entanglement loops formed with the chain at the origin gives the second term in Eq. (8). The power expended at a particular entanglement can be estimated as follows.

Consider a passing random-coil chain of length \( n \) and velocity \( v_{\text{chain}} \) divided instantaneously at an entanglement junction into a short section \( S \) with \( n_e \) repeating units and a long section \( L \) with \( n_l \) repeating units. For an average local velocity at the junction \( v_e \), the center of gravity of \( S \) must move toward the junction with velocity \( v_e \). The drag force would be \( \xi v_n v_e \) if \( S \) itself moved as an unconnected particle cloud. However, if \( S \) is highly entangled, the average distance traveled by the segments in \( S \) will be greater than the simple drift distance, since they must pass around and through whatever entanglement junctions lie along \( S \) between them and the particular loop being considered. For a given value of \( v_e \), the time to remove the entanglement is fixed. Thus the local coordinated velocity which determines the drag force will be greater for an entangled chain or chain section since it will be proportional to the total distance to be traveled to reach the loop. The drag force will be \( \xi v_n v_{\text{eff}} \) and the power expended will be \( \xi v_n (v_{\text{eff}})^3 \), where \( v_{\text{eff}} \) is the effective drift velocity imposed in the segments as they move between entanglements points on their path towards the junction with the chain at the origin.

If the entanglements are distributed randomly along the chain, the coordinated path covered by any segment will be the contour distance of a random walk around the entanglement junctions. Without entanglements the distance traveled by a freely jointed chain of \( n_e \) units, each with length \( l \), is approximately \( \frac{1}{2} (n_e l)^{1/2} \). However, if the chain \( S \) contains \( n_e/n_s \) entanglement points, where \( n_s \) is the average number of repeating units between entanglement points, the length of a step from one entanglement to the next is \( (n_e l)^{1/2} \). The total distance to be traveled is then \( (i + \frac{1}{2}) (n_e l)^{1/2} \) for segments with \( i \) entanglement points between them and the junction with the chain at the origin. The factor \( \frac{1}{2} \) arises because the average distance to the first entanglement point to be encountered is only \( \frac{1}{2} (n_e l)^{1/2} \). The average distance traveled is found by averaging over all segments. For large values of \( n_s/n_e \) it becomes \( \frac{1}{2} (n_e l)^{1/2} (n_s/n_e) \). The effective velocity for motions of the highly entangled chain is therefore \( v_{\text{eff}} = (n_s/n_e)^{1/2} v_e \). The instantaneous power needed to move the chain through the loop at a local velocity of \( v_e \) is finally \( \xi v_n (v_{\text{eff}})^3 = \xi v_n (n_s/n_e) n_e^2 \).

Thus we arrive at the interesting and important result that a highly entangled chain with \( n_e \) repeating units has an effective friction coefficient of approximately \( \xi (n_s^2/n_e) \) while the coefficient for a completely unentangled chain is \( \xi v_n \). From a balance of forces at the loop, the average drag force exerted by the passing chain on the chain at the origin is therefore \( 2 \xi v_n (n_s^2/n_e) v_e \) and the instantaneous power expended by the passing chain on the chain at the origin is \( 2 \xi v_n (n_s^2/n_e) (v_e) \times (v_{\text{chain}}) \). However \( v_e \) itself is simply \( v_{\text{eff}} \) but now with respect to the motion of the longer section \( L \). That is, in order that \( v_{\text{chain}} \) be maintained, the segments emerg-
ing from the loop must also move around successive entanglement loops, located randomly along $L$. As a result $v_c = (n_i/n_e)^{1/n_e}$, and for highly entangled chains:

$$F_d = 2\zeta_0 (n_e/n_e) (n_i/n_e)^{1/2} v_{\text{chain}},$$

(10)

where $F_d$ is the instantaneous drag force exerted by the passing chain on the chain at the origin. Averaging over all positions of the entanglement point on the passing chain $[n_e]$ ranging from 0 to $(n_e+n_i)/2$ gives, for a passing chain whose total length is $n$, the average effective drag force

$$F_d = 0.131\zeta_0 (n_i/n_e)^{1/2} v_{\text{chain}}.$$  

(11)

Thus the entanglement drag coefficient $\zeta_0$ for a monodisperse system has the form required earlier to derive Eq. (7) and is equal to:

$$\zeta_0 = 0.131\zeta_0 (n_i/n_e)^{1/2}.$$  

(12)

If the centers of the molecules entangled with the molecule at the origin are distributed in space according to the same function that describes the distribution of segments of the chain at the origin, then Eq. (7) can be used to calculate the average rate of energy dissipation per molecule at low shear rates. Using $J = n/n_e$,

$$\dot{\epsilon}_c(n) = (\gamma^2 \zeta_0 \langle R^2 \rangle) / 18 \left[ 1 + 0.131 (n_i/n_e)^{1/2} \right].$$

(13)

The number of polymer molecules per unit volume is $\phi V\dot{c}$, where $\phi$ is the volume fraction of polymer and $V_0$ is the volume per repeating unit. The average number of entanglement points per chain, $n_e/n_c$, can be expressed as being proportional to $\phi n/(\phi n)_e$. The quantity $(\phi n)_e$ is the product of volume fraction of polymer and the chain length at the break in the curve of viscosity versus chain length, measured at constant volume fraction of polymer. The product should be a constant for a given polymer type. At the limits of low and high entanglement densities, the zero shear viscosities of monodisperse linear random-coil molecules becomes:

$$\eta = K\phi (n_e/n_c)$$  

(14)

$$\eta = K'\phi^2 (n_e/n_c)^{1/2}$$  

(15)

where both $K$ and $K'$ are independent of $n$ and $\phi$. Experimental behavior appears to be consistent with these results.

For the case of a highly entangled polydisperse system at zero rate of deformation, an average value of $\zeta_0$ must be evaluated. Consider a system in which $P(n) dn$ is the fraction of chains in the system with repeating units in the range $n, n+dn$, and consider a molecule at the origin with $m$ repeating units. The average number of entanglement junctions is $m/n_e$. The probability that the partner in any junction selected at random has a chain length $n$ is

$$n P(n) / \int_0^\infty n P(n) dn,$$

this being the fraction of all entanglements involving chains of $n$ repeating units. The resulting drag force is given by Eq. (11). The average force exerted by an entangled molecule moving at velocity $v_{\text{chain}}$ is, therefore,

$$F_d = 0.131\zeta_0 \frac{(\int_0^\infty n^{1/2} P(n) dn) / \int_0^\infty n P(n) dn}{\int_0^\infty n^{1/2} P(n) dn / \int_0^\infty n^{1/2} P(n) dn} v_{\text{chain}}.$$  

(16)

Using the definition of weight-average chain length $\bar{n}_w$,

$$\zeta_0 = 0.131\zeta_0 \frac{\bar{n}_w}{n_e^{1/2}} \left( \frac{\int_0^\infty n^{1/2} P(n) dn / \int_0^\infty n^{1/2} P(n) dn}{\int_0^\infty n P(n) dn / \int_0^\infty n^{1/2} P(n) dn} \right).$$

(17)

Employing Eq. (8) gives

$$\dot{\epsilon}_c(m) = \frac{1}{\gamma^2} \frac{\bar{n}_w}{n_e^{1/2}} \left[ \frac{\bar{n}_w}{n_e^{1/2}} \left( \frac{\int_0^\infty n^{1/2} P(n) dn / \int_0^\infty n^{1/2} P(n) dn}{\int_0^\infty n P(n) dn / \int_0^\infty n^{1/2} P(n) dn} \right) \right],$$

(18)

where $\langle R^2 \rangle$ is the mean end–end distance of a chain with $m$ repeating units. The viscosity is given by the sum over all molecules in a unit volume:

$$\eta = \frac{1}{\gamma^2} \left[ \int_0^\infty \epsilon_c(m) P(m) dm \right] \phi \left( \int_0^\infty n P(n) dn \right)^{-1},$$

(19)

leading to the following expressions for the limits of low and high entanglement densities:

$$\eta = K\phi \bar{n}_w \quad (n_e > n_c),$$

(20)

$$\eta = K'\phi^2 \left( \frac{\bar{n}_w}{n_e^{1/2}} \right) \left( \frac{\int_0^\infty n^{1/2} P(n) dn / \int_0^\infty n^{1/2} P(n) dn}{\int_0^\infty n P(n) dn / \int_0^\infty n^{1/2} P(n) dn} \right) \quad (n_e < n_c),$$

(21)

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Note that, in contrast to the mixing rules of Fujita and Ninomiya,\textsuperscript{25} the friction coefficient is averaged separately, resulting in a viscosity which depends on the produce of averages similar to that used by Conti and Gigli,\textsuperscript{26} rather than the average of a product. Experimentally it is observed that the melt viscosities of polydisperse systems are closely correlated with $\bar{n}_w$.\textsuperscript{27} The result of this analysis implies a slightly stronger dependence on the high-molecular-weight tail. For example, with a most-probable distribution of chain lengths, $P(n) = ae^{-an}$, and the average size

$$[\bar{n}_w (\int_0^\infty n^{1/2} P(n) dn / \int_0^\infty n P(n) dn)]^{2/3}$$

lies between the weight and $z$-average size, being 23\% greater than $\bar{n}_w$. However, it might be difficult to observe the difference between this average and $\bar{n}_w$ unless comparing polymers with very different distributions. Bueche\textsuperscript{28} has made calculations based on his viscosity model which suggest that $\bar{n}_w$ is the proper correlating variable at low entanglement densities, while $\bar{n}_e$ is more correct at high entanglement densities.

**SHEAR-RATE EFFECTS**

The viscosity of a polydisperse, highly entangled system at finite rates of deformation can be expressed formally in terms of integrals involving two functions. The forms of these functions will depend upon the particular model chosen to represent the interaction between the flow field and the entanglement density. One function is the ratio $g(\gamma, n)$, the average number of entanglement junctions for a chain of length $n$ in a steady flow field of shear rate $\gamma$, divided by the number in the limit of $\gamma = 0$:

$$g(\gamma, n) = \left( \frac{n/n_w}{\bar{n}_w} \right)^{d - d_4/4d_6} \frac{(n/n_e)^{d_4/4d_6}}{\bar{n}_w^{d - d_4/4d_6}}.$$

(22)

The other function is also a ratio, $h(\gamma, n)$, the rate of energy dissipation by a chain of length $n$ in a system with shear rate $\gamma$ and some prescribed communal friction coefficient $\xi$ divided by $\gamma^2$, divided by the value of that same quantity at the same value of $\xi$ but in the limit of $\gamma = 0$:

$$h(\gamma, n) = \left( \frac{\epsilon / \gamma^2}{\bar{\xi}/\gamma^2} \right)^{d - d_4/4d_6} \frac{(\epsilon / \gamma^2)^{d_4/4d_6}}{\bar{\xi}^{d - d_4/4d_6}}.$$

(23)

Consider a chain of length $m$ at the origin. The probability that any of its entanglements selected at random couples it with a chain of length $n$ is, in terms of the earlier definition,

$$nP(n) g(\gamma, n) / \int_0^\infty n P(n) g(\gamma, n) dn.$$  

The drag force associated with that entanglement is

$$0.131 (\bar{\xi} / \gamma^2)^{4/4d_6} \frac{(\epsilon / \gamma^2)^{4/4d_6}}{\bar{\xi}^{4/4d_6}} n P(n) g(\gamma, n) P(n) dn \int_0^\infty n P(n) g(\gamma, n) dn.$$  

The communal frictional coefficient for the system is therefore a function of $\gamma$ and equal to:

$$\epsilon(\gamma, m) = \frac{0.131 \gamma^2 \bar{\xi}(\gamma, m)(R^2)_{\text{chain}}}{18 (\bar{\xi})_{\text{chain}}}.$$  

(25)

Finally, employing the earlier methods, we find that the viscosity of the system is

$$\eta = \bar{\eta} \left( \int_0^\infty m^3 h(\gamma, m) P(m) dm / \int_0^\infty m^2 P(m) dm \right),$$  

or

$$\eta = \bar{\eta} \int_0^\infty n^2 P(n) dn \int_0^\infty n^2 h(\gamma, n) P(n) dn \int_0^\infty n P(n) dn / \int_0^\infty n^2 P(n) dn \int_0^\infty n P(n) dn \int_0^\infty n^2 P(n) dn,$$

(27)

where $\bar{\eta}$ is the viscosity at $\gamma = 0$, as expressed by Eq. (21). The analysis is thus complete if suitable expressions can be found for $g(\gamma, n)$ and $h(\gamma, n)$.

\textsuperscript{25} H. Fujita and K. Ninomiya, J. Polymer Sci. 24, 233 (1957).
\textsuperscript{27} K. Ninomiya, Y. Yamanaka, J. Phys. Chem. 67, 2297 (1963).
\textsuperscript{28} F. Bueche, J. Polymer Sci. 43, 527 (1960).
and there is some average probability \( p(r) \) that the chains at any instant will be entangled. By this last statement we mean that if suddenly a relative motion were to be imposed on their centers of gravity, there is a probability \( p(r) \) that the motion would be resisted by an entanglement junction of the kind discussed earlier. However, if the chains are in relative motion at all times as in the case of a steady shearing flow, then the time required to establish this "equilibrium" probability of entanglement formation must also be considered.

Relative to a coordinate system on one molecule, the second molecule approaches from infinity, moves steadily through the regions where entanglement formation is possible past some distance of closest approach, and then on to infinity. It was suggested in the earlier paper\(^9\) that if the passing molecule remained within the entanglement region substantially longer than the time required for a complete reorganization of the chain configuration, the effective entanglement probability would be the equilibrium probability. If on the other hand the time within the entanglement region were much shorter than the configurational relaxation time, the probability would be essentially zero.

A simple step-function model of this behavior was then considered, in which the probability of entanglement formation with the chain at the origin was taken to be a constant inside a sphere of some radius \( R \), and equal to zero outside. Chains entering this sphere formed entanglements with probability \( p \) if their paths and velocities were such that they remained within the sphere at least a time \( \tau \). The entanglement then exerted its effect from that time onward, until the passing molecule had been outside the sphere a time \( \tau \). If the chain passes completely through the sphere in a time less than \( \tau \), the entanglement probability was zero. Finally the time \( \tau \) was taken to be of the order of the Rouse relaxation-time parameter, evaluated at the existing rate of deformation:

\[
\tau(\gamma, n) = C \tau_r(\gamma, n),
\]

where \( C \) is a constant of order unity and \( \tau_r \) is the Rouse parameter [Eq. (3)].

Equation (1) was derived from the foregoing model, and that equation for viscosity is exactly the function \( k(\gamma, n) \). Both \( g(\gamma, n) \) and \( h(\gamma, n) \) can be expressed by integrals over the entanglement sphere. With the choice of coordinate axes in Fig. 1:

\[
g(\gamma, n) = \int_{-R}^{R} \int_{-R}^{R} \frac{(R^2 - y^2 - z^2)^{1/2} \, dx \, dy}{(R^2 - y^2 - z^2)^{1/2} \, dx \, dy},
\]

\[
h(\gamma, n) = \int_{-R}^{R} \int_{-R}^{R} \frac{z^2 (R^2 - y^2 - z^2)^{1/2} \, dx \, dy}{(R^2 - y^2 - z^2)^{1/2} \, dx \, dy},
\]

where \( z = \{(R^2 - y^2)/[1 + (\gamma \tau)^2]\}^{1/2} \). Evaluation leads to the expressions

\[
g(\gamma, n) = (2/\pi) \left\{ \cot^{-2} \theta + \frac{\theta}{(1 + \theta)^2} \right\},
\]

\[
h(\gamma, n) = (2/\pi) \left\{ \cot^{-2} \theta + \frac{\theta}{(1 - \theta)^2} \right\},
\]

where \( \theta = \gamma \tau(\gamma, n) \).

It should be noted that, for any model, \( g(\gamma, n) \) and \( h(\gamma, n) \) must be even functions of \( \gamma \) because of their definitions and general symmetry requirements. Equations (29) and (30) obviously define even functions because \( \gamma \) only enters as \( \gamma^2 \). However, although power series expansions of Eq. (31) and (32) contain no first-order term in \( \theta \), they do contain terms involving \( \theta^2 \), \( \theta^4 \), and higher odd powers of \( \theta \). This peculiarity appears to arise from the mathematical discontinuity introduced by the step functions in the model and is not important from the physical viewpoint. A correct interpretation is obtained if absolute values of \( \gamma \) are used in subsequent equations.

If all chains have the same number of repeating units \( n \), the viscosity can be factored out of the relaxation time, giving \( \tau_0 = (\eta_0 - \eta_s)/(\nu k T) \). The parameter \( \tau_0 \) is thus the relaxation time at \( \gamma = 0 \), a constant of the system and the normalizing parameter for the shear rate. A communal relaxation time constant can be obtained in polydisperse systems by a similar factoring procedure, provided the fact is properly accounted for that the chains contribute differently depending upon their chain lengths and the imposed shear rate.

Consider again the behavior of a chain of length \( n \) located in the system at the origin of coordinates. If a shear rate \( \gamma \) is imposed, then, according to the considerations presented earlier, the rest of the system acts upon the chain as a continuum with a communal friction coefficient \( \xi(\gamma) \). According to the Rouse analysis, the relaxation-time parameter for \( \nu \) non-interacting identical chains per unit volume is

\[
\tau_r = (6/\pi^2) [(\eta_0 - \eta_s)/(\nu k T)],
\]

where \( \eta_0 \) is the solution viscosity and \( \eta_s \) is the viscosity of the pure solvent. Since \( (\eta_0 - \eta_s)/\nu \) is the contribution that each chain makes to the viscosity, the Rouse relaxation time of a chain imbedded in a medium characterized by \( \xi(\gamma) \) can be expressed as:

\[
\tau_r(n, \gamma) = (6/\pi^2) [(\Delta \eta(n, \gamma)/k T)],
\]

where \( \Delta \eta \) is the increment of the total viscosity of the
system contributed by that chain. From Eq. (26):
\[
\frac{\Delta \eta(\dot{\gamma}, n)}{\eta_0} = \frac{f_s(\dot{\gamma})}{f_s(0)} \left[ n^2 h(\dot{\gamma}, n) \int_0^\infty n^2 P(n) \, dn \right]
\]
(35)
or expressed in terms of the viscosity at the imposed shear rate:
\[
\Delta \eta(\dot{\gamma}, n) = \frac{\eta(\dot{\gamma})}{\nu} \left[ n^2 h(\dot{\gamma}, n) \int_0^\infty n^2 h(\dot{\gamma}, n) P(n) \, dn \right],
\]
(36)
where as before, \( \nu \) is the total number of chains per unit volume.

Substituting into Eq. (34) and considering conditions where the solvent viscosity of pure solvent is negligible compared to the solution viscosity:
\[
\tau_r(\dot{\gamma}, n) = \frac{6 \eta(\dot{\gamma})}{\pi^2 \nu kT} \left[ n^2 h(\dot{\gamma}, n) \int_0^\infty n^2 h(\dot{\gamma}, n) P(n) \, dn \right].
\]
(37)

Since
\[
\nu = c \int_0^\infty P(n) \, dn \left/ \left( m_0 \int_0^\infty n P(n) \, dn \right) \right.,
\]
where \( c \) is polymer concentration (weight per volume) and \( m_0 \) is the molecular weight of the monomer, Eq. (37) can also be expressed as
\[
\tau_r = \frac{6 \eta(\dot{\gamma}) M_w}{\pi^2 kT \eta_0} \left( \frac{n}{\eta_0} \right)^2 \times \left[ h(\dot{\gamma}, n) \int_0^\infty n^2 P(n) \, dn \int_0^\infty n^2 h(\dot{\gamma}, n) P(n) \, dn \right].
\]
(38)

Thus, continuing to assume that the characteristic entanglement time is proportional to the Rouse relaxation time, we can factor out the viscosity and express the argument in Eqs. (31) and (32) as
\[
\theta(\dot{\gamma}, n) = \frac{\eta}{\eta_0} \left( \frac{\dot{\gamma} \tau_0}{2} \right) \left( \frac{n}{\langle n \rangle} \right)^2 \frac{h(\dot{\gamma}, n)}{\hat{h}(\dot{\gamma})},
\]
(39)
where \( \tau_0 \) is a communal relaxation-time parameter for the polydisperse system:
\[
\tau_0 = C (6/\pi^2) (\eta_0 M_w / c kT),
\]
(40)
and \( \hat{h}(\dot{\gamma}) \) is still another communal property defined as
\[
\hat{h}(\dot{\gamma}) = \int_0^\infty n^2 h(\dot{\gamma}, n) P(n) \, dn / \int_0^\infty n^2 P(n) \, dn.
\]
(41)

Inspection of Eq. (39) shows that for monodisperse systems, \( \theta \) becomes \( (\eta / \eta_0) (\dot{\gamma} / \tau_0) \) as given earlier, while at \( \dot{\gamma} = 0 \) for any distribution of chain lengths, it becomes
\[
\theta(0, n) = (\dot{\gamma} \tau_0) \left( n / \langle n \rangle \right)^2,
\]
(42)
a result already presented elsewhere.\(^{29}\)

As given by Eqs. (38) and (39), the relaxation times of individual chains in a polydisperse system depend not only upon chain length and the magnitude of communal properties such as \( \eta_0 \) and \( \tau_0 \) but also upon the additional communal property \( \hat{h}(\dot{\gamma}) \) which depends directly on the distribution of chain lengths in the system. Furthermore \( h(\dot{\gamma}, n) \) is a function of the single variable \( \dot{\gamma} \), so the determination of \( \theta(n, \dot{\gamma}) \) and the relaxation time of any individual chain requires solution of an implicit equation for \( \theta \).

TABLE I. Viscosity master curves for various molecular weight distributions.

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<th>Z=1</th>
<th>Z=5</th>
<th>Z=10</th>
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<td>(η/η₀)</td>
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</tr>
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<td>86.9</td>
<td>78.2</td>
<td>64.8</td>
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</table>

The labor involved in solving the equation can be greatly decreased by proceeding in the following manner. Equation (39) is of the form:

\[ \theta = F(\dot{\gamma}) \left( m_h \eta_0 \right)^{1/2} h(\theta), \]  

(43)

where \( F(\dot{\gamma}) = (\eta/\eta_0)(\dot{\gamma}\tau_0) (\dot{h})^{-1} \). If a value of \( F(\dot{\gamma}) \) is chosen, \( \theta \) can be calculated by an appropriate trial-and-error technique for various values of \( \eta/\eta_0 \). These values of \( \theta \) can then be used, together with the distribution function \( P(n) \) for the sample, to evaluate the integrals in Eqs. (27) and (41). The values of \( \eta/\eta_0 \) and \( \dot{h} \) so obtained are used finally to calculate \( \dot{\gamma}\tau_0 \) from the \( F(\dot{\gamma}) \) originally chosen. This procedure can be repeated for different values of \( F(\dot{\gamma}) \), thereby generating a series of values of \( \eta/\eta_0 \) vs \( \dot{\gamma}\tau_0 \) for the chosen distribution of chain lengths.

Since \( h(\theta) = 1 \) for small \( \theta \) and approaches \( h(\theta) = (16/3\pi \theta^2) \) for large \( \theta \), the relaxation time of individual chains has the following asymptotic behavior:

**sufficiently small \( n/\eta_0 \):**

\[ \theta = \frac{1}{2}[\dot{\gamma} \tau(n, \dot{\gamma})] = \frac{(\eta/\eta_0)(\dot{\gamma}\tau_0)}{\dot{h}} \left( n/\eta_0 \right)^{1/2}. \]  

(44)

**sufficiently large \( n/\eta_0 \):**

\[ \theta = \frac{1}{2}\left[\dot{\gamma} \tau(n, \dot{\gamma})\right] = \left[\frac{(\eta/\eta_0)(\dot{\gamma}\tau_0)}{\dot{h}}\right]^{1/4} \left(\frac{16}{3\pi}\right)^{3/4} \left(\frac{n}{\eta_0}\right)^{1/2}. \]  

(45)

**DISCUSSION OF SHEAR-RATE EFFECTS**

In monodisperse systems, Eq. (27) reduces to

\[ \eta/\eta_0 = h g^{1/2}, \]  

(46)

whereas the earlier analysis\(^{19}\) gave simply \( \eta/\eta_0 = h \).

At large values of \( \eta/\eta_0 \) and \( \dot{h} \ll \dot{\gamma} \), the relaxation time of individual chains has the following asymptotic behavior:

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(45)
Fig. 5. Comparison between master curve calculated for samples with most distribution (solid line) and the experimental Bueche-Harding master curve (open circles). The experimental curve was shifted parallel to the shear-rate axis to achieve a best fit with the theoretical curve.

Fig. 6. Comparison of experimental results on solutions of unfractonated polystyrene \( (\overline{M}_n = 1 \times 10^6) \) in \( n \)-butyl benzene with calculated master curves for broad distributions. The theoretical curves were shifted parallel to the coordinate axes to achieve a best fit with the experimental results.

The parameter \( Z \) is a number controlling the distribution breadth. For \( Z = 0 \), the most-probable distribution for linear chains is produced \( (\overline{n}_w/\overline{n}_n = 2.0) \), while the limiting distribution for \( Z = \infty \) corresponds to a monodisperse system. The integrations required to calculate \( \eta \) vs \( \eta_0 \) were performed numerically for several values of \( Z \). The results are given in Table I, and are plotted in Fig. 4.

As might be expected, increasing the distribution breadth causes changes to occur in the viscosity at successively lower values of shear rate. It also broadens the transition between Newtonian behavior and approximate power-law behavior, such that at high shear rates samples with different distributions but similar values of \( \overline{M}_w \) again have similar viscosities. Computations with other model distributions indicate that the location and nature of the curve in the region where the viscosity first begins to decrease is very sensitive to higher moments of the distribution such as appear in the definitions of \( \overline{M}_g \) and \( \overline{M}_{g+1} \). Thus, systems with similar \( \overline{M}_w/\overline{M}_n \) but different \( \overline{M}_g/\overline{M}_n \) tend to show substantially different behavior at intermediate shear rates.

A comparison between the curve predicted to samples with most-probable distribution \( (Z = 0) \) and the Bueche-Harding (BH) master curve is shown in Fig. 5. The latter represents a composite of experimental viscosity data from a variety of polydisperse polymer systems. The BH curve was shifted horizontally to achieve the best possible fit with the theoretical curve. It is apparent that viscosity decreases more slowly with shear rate in the BH curve than in the theoretical result. On the other hand, the two curves can be placed in almost perfect register if a slight vertical shift is allowed, that is, if a different extrapolated value of \( \eta_0 \) is taken for the BH curve.

Another comparison of the theory with experiments on polydisperse systems is shown in Fig. 6. The polymer is polystyrene, prepared at low conversion \( (\sim 15\%) \) by thermal polymerization at 60°C. The weight-average molecular weight is \( \overline{M}_w = 1.90 \times 10^6 \) by light scatter-
ing. The number-average molecular weight is too large to be measured accurately, but measurements on thermal polystyrenes prepared at other temperatures suggests \( \bar{M}_n/\bar{M}_a = 1.60-1.80 \) for this sample, and therefore a \( Z \) value between 0.0 and 1.0. The data shown were obtained for solutions of 0.255 g/cc and 0.35 g/cc polymer in \( n \)-butyl benzene.\(^{40}\) Viscosity measurements were made at 50°C using a commercial plate-cone instrument.\(^{11}\) The theoretical curves for \( Z = 0 \) and \( Z = 1 \) were shifted horizontally and vertically to achieve the best fit at each concentration. The data lie within the envelope between \( Z = 0 \) and \( Z = 1 \) over most of the range, although the viscosity appears to decrease more rapidly with shear rate than either curve at the highest shear rates.

In general the theoretical curves seem to correspond reasonably well with these experiments. However, a more severe test of the theory is how well viscosity vs shear rate is predicted for much broader distributions, such as those encountered in commercial linear poly-


ethylene and polypropylene. In principle the viscosity-shear-rate curve should be directly calculable from fractionation or gel-permeation chromatography information.

If treating the segmental friction coefficient as a communal property is seriously in error, this error should become increasingly evident as the distribution broadens. Moreover, even if the shapes of the viscosity curves are predicted accurately the value of \( \eta_0 \) determined from the data should correlate with the corresponding Rouse parameters in a manner which is independent of molecular weight distribution.

ACKNOWLEDGMENTS

This study was carried on with the aid of a grant from the Petroleum Research Fund of the American Chemical Society and with the support of Materials Research Center. The experimental work was supported by the University Research Committee and the National Science Foundation. Computations were made using the facilities of the Vogelback Computer Center of Northwestern University.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 47, NUMBER 6 15 SEPTEMBER 1967

Geometry of Ozone and Azide Ion in Ground and Certain Excited States

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(Received 26 May 1966)

A series of \textit{ab initio} SCF MO calculations for ground and various closed-shell excited states of \( \text{O}_3 \) and \( \text{N}_3^- \) have been carried out with a view toward investigating relationships between the geometries of these states. The calculations give quantitative verification to many of the assumptions made in previous empirical theories dealing with this subject and enlarge the scope of former quantitative schemes to include more quantitative predictions relative to steepness of potential surfaces of molecular states. Thus it is shown that the calculated SCF total energy surfaces of both \( \text{O}_3 \) and \( \text{N}_3^- \) can be compared quite concisely in terms of a small number of differentiating orbital-energy curves.

I. INTRODUCTION

The equilibrium geometry of ozone has long been of considerable interest to both the experimentalist and the theoretician. The experimental determination of its equilibrium angle has been a particularly challenging problem, with proposed values ranging from 37 to 160 deg\(^{4}\); precise microwave measurements have yielded the presently accepted value of 116°45'.\(^{4} \) The opportunity for a theoretical study of the ozone geometry is now afforded by recent advances in \textit{ab initio} calculations for polyatomic molecules; comparison of ozone with the related system, the azide ion \( \text{N}_3^- \), is also of interest in this connection and the results of a series of such calculations form the subject matter of this paper.

Both these molecules fall into the general category of \( \text{AB}_3 \) systems, whose geometry has been discussed by means of the empirical MO scheme of Mulliken\(^{3} \) and Walsh,\(^{4} \) according to which changes in total energy are

\(^{2} \) R. S. Mulliken, Rev. Mod. Phys. 14, 204 (1942).
\(^{3} \) W. Shand, Jr., and R. A. Sparr, J. Am. Chem. Soc. 65, 149 (1943).