Molecular Rheology of Polymer Solutions: Interpretation and Utility

Molecular theories of polymer rheology are reviewed with emphasis on predictions of the more familiar properties: non-Newtonian viscosity and normal stress in steady shear, complex viscosity in oscillatory shear, and elongational viscosity in extensional flow. Both dilute and concentrated solutions are discussed, with emphasis on the former. An important objective is clarification of polymer modeling strategies and how they are related to polymer structure. The intended readership consists of those engineers familiar in a general way with continuum polymer rheology, but with no special expertise in polymer physical or theoretical chemistry.

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SCOPE

Rheology, the study of material deformation and flow, can be defined more precisely as the establishment of relationships between stress $\boldsymbol{\sigma}$ and strain rate $\boldsymbol{\Delta}$ (including their respective histories in terms of integral or derivative functions). Among the theoretical tools for doing this are the continuum and the molecular/structural approaches. Continuum methods have been used to generate admissible frameworks for rheological models, but have a generality which permits ambiguity and cannot be used to evaluate model parameters. Thus the basic utility of molecular theory is its capability of yielding specific information on how rheological parameters vary with molecular variables under the control of chemists and chemical engineers.

Polymeric fluids—melts and solutions—possess the quality of viscoelasticity which has stimulated most of modern rheological research. This quality affects all properties of engineering interest, most prominently the non-Newtonian viscosity $\eta(\gamma) = \sigma_{21}/\gamma$ as a function of steady shear rate γ. More recently it became evident that processing anomalies such as die swell, melt fracture, and certain instabilities in flow as well as many final product anomalies also had their origin in viscoelasticity; many of these can be correlated in terms of the normal stress functions $N_1(\gamma) = \sigma_{11} - \sigma_{22} = \zeta\gamma^2$ and $N_2(\gamma) = \sigma_{22} - \sigma_{33} = \beta\gamma^2$ in steady shear. Fluid elasticity is essential to the synthetic fiber industry, and therefore the behavior of the elongational (tensile) viscosity $\bar{\eta}(\kappa)$ as a function of tensile strain rate κ is important to many engineers.

Other material properties can be defined for other types of flows, including the transient conditions of creep, relaxation, and start-up. Probably the most important of the time-dependent flows is sinusoidal oscillation of small amplitude, characterized by the complex viscosity $\eta^*(\omega)$ dependent only on the frequency ω. This property, widely used by chemists to evaluate viscoelasticity of polymers, is becoming increasingly relevant to engineering operations as well.

Defining "basic material properties" for all possible flow situations, and evaluating them separately, is an endless and unnecessary task. Instead, use of a rheological model will in principle permit predictions of $\boldsymbol{\sigma}$ for any kinematical case. However, because of widespread interest in η, N_1, N_2, $\bar{\eta}$, and $\eta^* \equiv \eta' - i\eta''$, we will focus on these in particular.

All these properties will depend on a multitude of molecular variables which can be independently obtained. Here we will consider basic molecular/structural shape W, molecular weight M, mass concentration c in solution, solvent influences which may be thermodynamic (S for solvent) or mechanical (through its viscosity η_s and hydrodynamic interaction HI), inherent springiness (spring coefficient K), and other structural features which may give rise to the internal viscosity (IV).

For the engineer trying to read the literature in molecular rheology of polymers, such a massive array of molecular and mythological variables is a formidable obstacle in number and in concept. To make this review tractable, then, some limitations on scope are necessary. We emphasize the realm of *dilute isothermal* solutions as the best platform for discussing the basic viscoelastic behavior of polymer molecules. A great variety of linear and nonlinear structural models W are considered and related to each other. More brief is the survey of concentrated systems, and no attention is given to free-volume interpretations which are useful near the bulk-polymer end of the concentration spectrum and also near glass transition temperatures. Finally, it is promised that no citations will be made of literature predating 1950; this material is available elsewhere.

Three primary objectives of this review can be identified:

1. To clarify the basic physics of polymer viscoelasticity,
2. To interpret the conventions, notation, and models of polymer molecular theory, thus assisting chemical engineers in appreciating the literature and extracting results,
3. To indicate how these results can be used in conjunction with engineering concepts and calculations.

In addition, remarks will be made on the directions of current research and some goals for future work.

CONCLUSIONS AND SIGNIFICANCE

The strategy of modeling dilute-solution rheology of linear polymers is reviewed in some depth, with primary attention focused on the Rouse Coil and its descendants which represent excursions into the variables of *HI*, *S*, *K*, and *IV*. Relationships are drawn to other linear models, including the Rigid Rod and intermediate forms of shape and stiffness. Nonlinear models—branched, ring, and ellipsoidal structures—are also discussed and distinctions from the linear case noted. Among concentrated systems, separate treatment is given to second-order phenomena (the Huggins constant) and to higher-order and possible entanglement effects.

In each case, an effort is made to interpret the basic physics of the model, to indicate which rheological properties have been predicted, and often to provide those results explicitly. Of primary availability are predictions of $\eta^\circ(\omega)$ and $\eta(\gamma)$, with less work having been done on $\zeta(\gamma)$, $\beta(\gamma)$, and $\bar{\eta}(\kappa)$. Special emphasis is placed on relaxation times τ_p because of the broad utility of such parameters. Finally, speculation is advanced that the next important advances will be with nonlinear models in dilute solution, and with better characterization of concentrated solution structure.

INTRODUCTION

The engineer involved in polymer processing operations, or in polymer research and development, is continually confronted by the peculiar flow properties of macromolecules. Whereas processing and design criteria may often succeed with entirely empirical tools, it is helpful to be conversant with rheological theories. Modeling of polymer rheology according to the continuum mechanics of viscoelasticity is increasingly common, but relatively few chemical engineers are familiar with the assistance afforded by molecular rheology. These theories are capable of assisting the engineer by:

1. Providing relationships between measured properties (for example, viscosity) and molecular variables. The latter, in turn, are often under the engineer's control and can be manipulated to secure desired properties.
2. Predicting the variation of these properties with kinematical conditions (for example, shear rate). Models which generate workable nonlinear predictions—often of greatest interest to engineers—are very few and invariably highly complex. However, prediction of linear properties are more successful and, as a pragmatic matter, can often be used to estimate nonlinear parameters.
3. Establishing some rapport with the unique physics of macromolecules. Rather elementary ideas lie at the heart of this, but are rarely assembled in a form accessible to most engineers. These ideas will be outlined here in the clearest possible framework, that of dilute solutions, with a number of greatly simplifying assumptions. These will subsequently be relaxed and many of the realistic complexities explored. Other reviews of dilute-solution polymer rheology which can be recommended are those of Cerf (1959), Peterlin (1968), Janeschitz-Kriegl (1969), Fixman and Stockmayer (1970), Yamakawa (1971), and Osaki (1973). Interestingly, development of the molecular theories has enhanced our understanding of continuum rheology, as will also be illustrated.

No experimental data are presented here, as the literature abounds in it. The figures are employed exclusively as guides to that literature and as conceptual aids since our emphasis is on understanding the strategies of theoretical modeling.

Concentration

Polymer solutions must be extremely dilute in order to achieve the limiting behavior of primary interest here, namely, the stress contribution of a single molecule unaffected by its neighbors. Because a flexible polymer is coiled into a loose three-dimensional ball, its sphere of influence (domain) may exceed its molar volume by hundreds of times. Interdomain contacts become insignificant and the dilute state achieved when, as a rough rule of thumb, the polymer volume fraction obeys $v_p < \frac{1}{10}(\tilde{V}_s/\tilde{V}_p)^{1/2}$. In principle, dilute solution theory can be compared accurately with data only in the limit $c \to 0$. For example, viscosity data in the dilute range behave as $\eta(c) = \eta_s + \eta_s c F(M, S, HI, \ldots.) + \mathcal{O}(c^2)$. They are then converted to the ratio $(\eta - \eta_s)/c\eta_s$ and extrapolated to $c = 0$ to yield the intrinsic viscosity $[\eta] = F$ which presumably contains basic molecular information.

The hierarchy of concentration dependence is outlined in Figure 1. Most of this review will pertain to $\mathcal{O}(c)$ since theory is well developed in this case and the major phenomena of polymer viscoelasticity are predictable from molecular parameters. The behavior of concentrated solutions and even melts is phenomenologically remarkably similar and in many instances may be estimated by suitable scale-up rules from the dilute solution predictions. Later, some remarks will be made about such concentrated media and references cited.

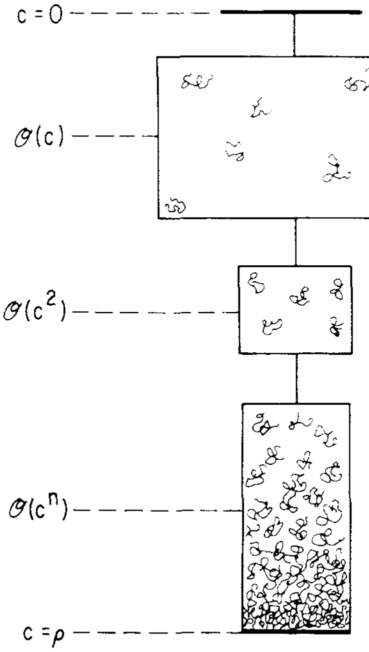

Fig. 1. Conceptual framework for concentration effects, $c = 0$ corresponding to pure solvent and $c = \rho$ being the melt. Relative sizes of boxes is roughly proportional to coverage in this review.

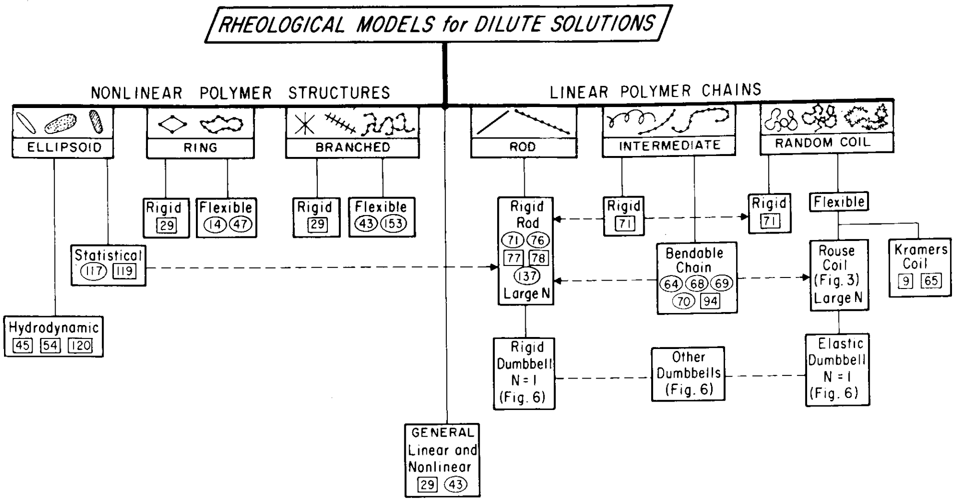

Fig. 2. Conceptual framework for modeling gross polymer structure W. For the most part, the variations shown here have been pursued in the context of dilute solution. Concentrated solutions have usually been modeled with the Rouse Coil (far right).

Structural Effects

Dynamical theories of dilute solutions had their origins in the 1940's with the work of Kuhn, Kramers, Hermans, Debye, and Kirkwood which established the peculiar blend of statistical mechanics and hydrodynamics which exists today. Indeed, the term *molecular theory* is something of a misnomer since the solvent is regarded as a continuous medium and the polymer fine structure can generally be ignored to an excellent approximation (for roughly similar chain shapes, anyway—for example, all random coils of linear chains behave dynamically much the same). These assumptions make it possible subsequently to obtain surprisingly accurate rheological results which in many ways are analogous to the mechanical response of assemblies of springs (elastic elements) and dashpots (viscous elements).

The 1950's saw the conversion of the basic concepts and formalism into realistic rheological results, primarily for the two basic linear structures of random coil and straight rod. These are among the many structures depicted in Figure 2, which is organized according to gross aspects of polymer shape modeling. The right-hand side, headed Linear Polymer Chains, represents by far the area of greatest theoretical effort. Most of this has been directed at the flexible Rouse Coil conformation since most synthetic polymers are of the coiling type. Even nonlinear polymers can often be treated by methods developed for the Rouse Coil since they may possess coil-type segments which evince similar dynamic behavior. Thus we are motivated to devote the major portion of the theoretical review to explaining the behavior of coiling linear polymers. The other structural extreme for linear molecules is the rigid rod, and a number of pertinent results will be cited for this case too. Then other microstructural models for polymers will be discussed.

FLEXIBLE COILING LINEAR POLYMERS

The pioneering work of Rouse (1953) demonstrated that a polymer modeled as N linearly-coupled springy units called submolecules could be solved exactly for $\eta^*(\omega)$. The major mathematical breakthrough here was introduction of the normal coordinate method for decoupling the N separate equations of motion. This contribution, developed for the simplest conceivable case ($HI = 0$; $S =$ theta solvent; $K = K_0$, linear springs; $IV = 0$) was the progenitor of all subsequent work, as is outlined in detail in Figure 3. Basic refinements were added by Zimm (1956) for $HI \neq 0$ and by Cerf (1957, 1958) for $IV \neq 0$. Following these, an explosion of effort occurred in the 1960's and may, in the mid-1970's, be tapering off in the fashion which characterizes a mature field (that is, semicontinuum modeling of linear coiling polymers).

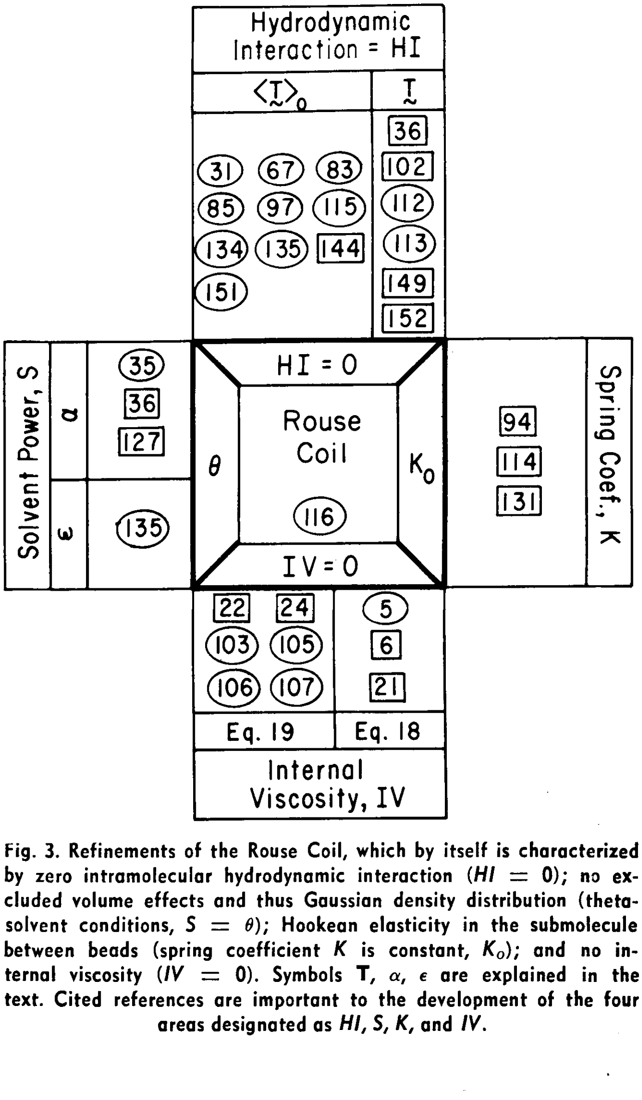

Fig. 3. Refinements of the Rouse Coil, which by itself is characterized by zero intramolecular hydrodynamic interaction ($HI = 0$); no excluded volume effects and thus Gaussian density distribution (theta-solvent conditions, $S = \theta$); Hookean elasticity in the submolecule between beads (spring coefficient K is constant, K_0); and no internal viscosity ($IV = 0$). Symbols $\mathbf{T}$, α, ϵ are explained in the text. Cited references are important to the development of the four areas designated as HI, S, K, and IV.

Figure 3 traces separately the developments along four different lines, all stemming from the Rouse Coil which will be discussed here in some detail. Only key contributions are designated, by (○) if the work predicts only linear properties and by (□) if it predicts nonlinear phenomena, for example, $\eta(\gamma)$ and $\zeta(\gamma)$.

The Submolecule

The most confusing concept in polymer modeling, yet one which has been universally employed and accepted almost without question, is that of the submolecule (or subchain, or segment); the reader is referred to Figure 4. The submolecule, like the unicorn, is a mythical beast. Developed by Kuhn, this concept is a convenient artifice which is defined as some fraction (say, $1/N$) of the total linear polymer, such that the entire molecule consists of N submolecules joined end-to-end. Thus molecular weights are related by $M = NM^{(s)}$, with N an integer between 1 and some reasonable upper bound of about $(M/M_0)/20$. Here, M_0 is the mass associated with a single backbone bond, so N may be around several hundred.

For realistic modeling of the large number of internal degrees of freedom in polymers, it is believed desirable for N to be as high as possible. This means $M^{(s)}$ must be chosen as small as possible, so long as the submolecule behavior remains independent of details of chemical structure. The latter condition is supposedly achieved if its end-to-end distance obeys Gaussian statistical probabilities; by definition, this means its average is given by $<r^2>^{(s)} = nl^2 \cdot f$ (bond angles) $\equiv b^2$, for n chain bonds of length l. Ordinarily this can be accomplished with $n \approx 20$, and since $M \equiv N(nM_0)$ we obtain the above-quoted result $N_{\max} \approx (M/M_0)/20$.

Rheological predictions are generally insensitive to the choice of N, as long as shearing is not severe (coil deformation not extreme) and N moderately large. Thus most of the literature has avoided coming to grips with the matter, but it should not be forgotten that N is a model parameter. Methods for obtaining N and b uniquely, from $[\eta]$ data, were proposed by Thurston and Schrag (1968). Wang and Zimm (1974a) have reviewed the problem recently, arguing that an optimum value of N must exist to model the modes of molecular motion properly. When $IV \neq 0$, all rheological predictions are strongly dependent on the choice of N.

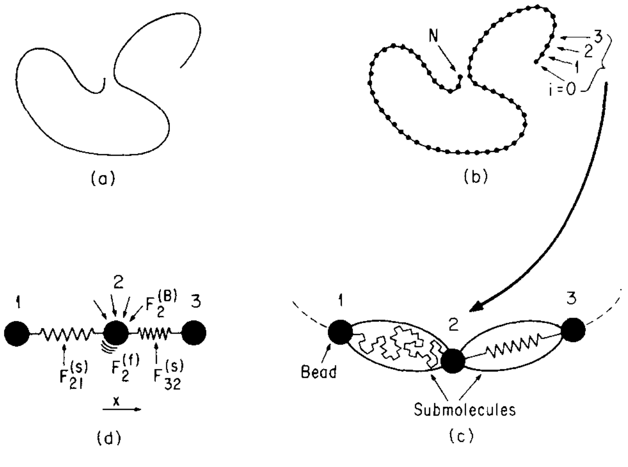

Fig. 4. Justification and evolution of the submolecule concept and its customary interpretation as a springlike element. (a) Flexible linear coil, with rheological properties insensitive to details of molecular structure. (b) Replacement of continuous solvent friction by $N + 1$ discrete frictional elements, beads, presumed not to misrepresent overall chain dynamics if N is large. (c) Chain element called a *submolecule* between beads 2 and 3 has many degrees of freedom, and thermal motions cause its ends to feel an entropic tensile force. Thus $F_{32}^{(s)}$ behaves as a spring, as shown explicitly for the adjoining submolecule. Chemical structure is still unimportant although it may influence the submolecule length and hence the number of submolecules N. (d) Linear representation of all forces on bead 2, corresponding to Equation (1a).

Application of the submolecule artifice leads to immense simplifications, converting the dynamical problem from a molecular one to a particulate one with far fewer degrees of freedom. The polymer chain now consists of N submolecules (springy particles) joined at $N - 1$ junctions. These junctions—plus the two free ends—constitute the $N + 1$ centers of frictional resistance through which the assembly is assumed to interact with the solvent. (Since the submolecule is at least 20 times more massive than a bond element, and occupies a swollen domain larger by perhaps $n^{3/2} \approx 90$, the solvent molecules are sufficiently smaller to be regarded as a viscous continuum by comparison.) Substituting this discrete frictional interaction for what is actually a continuous one converts the problem entirely to one of discrete-system mathematics.

This conceptual metamorphosis is illustrated in Figure 4 by the transition from 4a through 4b to 4c, wherein three submolecules are shown near a chain end. The last sketch emphasizes how coiling-chain properties within a submolecule lead to springiness in the assembly. It is not surprising that such a sequence of alternating springs and frictional centers (beads in a necklace model) will generate viscoelasticity of the sort associated with the classical Maxwell model of a spring and dashpot in series (Ferry, 1970).

The Rouse Coil

Here the basic conservation equations for an assembly of beads, joined by submolecules, will be presented with reference to the one-dimensional system of Figure 4d. The beads are numbered* $i = 0, 1, 2, \ldots, N$ and each has an equation of motion (conservation of linear momentum) written as $\sum_k F_i^{(k)} = ma_i \approx 0$; with negligible acceleration at molecular levels (Fixman, 1965), the various forces are in balance. These forces are interpreted as follows:

$F^{(f)}$ = frictional drag with solvent, of a Stokes Law type. This is the external force, transmitted through the solvent, which perturbs the bead from its equilibrium position.

$F^{(B)}$ = Brownian force, a randomizing influence similar to that causing Brownian motion of unconnected particles. This is always included in force balances despite the fact that it has no influence on rheological properties, contributing ultimately to $\boldsymbol{\sigma}$ only an isotropic pressure-like term.

$F^{(s)}$ = submolecule force of possibly several kinds, which tug at the bead from both sides. In the Rouse Coil and many others, these forces are often termed the *spring force*. In opposing the applied disturbance force, this represents an entropy-driven attempt at restoration of equilibrium bead arrangement. This term is the basic source of model elasticity, while $F^{(f)}$ is the source of model viscosity.

To illustrate the force balance, we consider bead 2 in Figure 4d.

$$0 = F_2^{(f)} + F_2^{(B)} + F_2^{(s)} = F_2^{(f)} + F_2^{(B)} + [F_{32}^{(s)} - F_{21}^{(s)}] \quad (1a)$$

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* The reader is cautioned that many results in the literature use $i = 1$ for the first bead and thus minor translations are sometimes required.

$$= -f(\dot{x}_2 - \dot{x}_{2s}) - kT\frac{\partial \ln\psi}{\partial x_2} + [K(x_3 - x_2) - K(x_2 - x_1)] \quad (1b)[*]$$

Here, $F_2^{(B)}$ is in the familiar form of the gradient of a potential since the (free energy) potential is $-kT\ln\psi$, where ψ is the distribution function describing all bead positions. This thermodynamic formalism can be invoked to interpret $F_2^{(s)}$ as well, by considering a consequence of Gaussian equilibrium:

$$\psi_0 = \text{constant} \times \exp\left[-\frac{3}{2b^2}\sum_{i=0}^{N}(x_{i+1} - x_i)^2 + (y_{i+1} - y_i)^2 + (z_{i+1} - z_i)^2\right] \quad (2)$$

Computation of $-kT\partial\ln\psi_0/\partial x_2$ leads precisely to the form given in Equation (1b), $F_2^{(s)} = K(x_3 - 2x_2 + x_1)$ where $K = 3kT/b^2$.

Thus $F_2^{(s)}$ emerges as an entropy spring force (since ψ_0 here is entirely configurational); it resists deformation arising from both $F_2^{(f)}$ and the diffusive force $F_2^{(B)}$. An alternate thermodynamic viewpoint suggests that Equation (1) be expressed as

$$0 = F_2^{(f)} + F_2^{(Th)} \quad (3a)$$

where the net thermodynamic force $F^{(Th)}$ is derived from the net potential,

$$F_2^{(Th)} = -kT\frac{\partial\ln(\psi/\psi_0)}{\partial x_2} \quad (3b)$$

Polymer dynamics has been developed primarily as a statistical mechanics of configuration space (x, y, z) rather than a complete phase space which would include bead momenta as well, and be charcterized by a partition function in terms of x, $\dot{x}$, y, $\dot{y}$, z, $\dot{z}$. A complete phase space was considered originally by Kramers, but this approach was buried until very recently (Bird, Johnson, and Curtiss, 1969; Curtiss, Bird, and Hassager, 1974). Complications have also been discussed by Fixman (1974).

Characteristics of the Rouse Coil are shared by most of the models of coiling polymers studied since 1953. By definition, however, the Rouse Coil is unique in evaluating the local solvent velocity $\dot{\mathbf{x}}_s$ in $\mathbf{F}^{(f)}$. This is done in the simplest possible way, by assuming that the beads have absolutely no perturbing effect on $\dot{\mathbf{x}}_s$. Hence, in simple shear flow, Equation (1b) employs $\dot{x}_{2s} = \dot{x}_{2s}^0 = y_2\gamma$, with $\dot{y}_{2s} = 0 = \dot{z}_{2s}$, and γ is the macroscopically imposed velocity gradient.

In addition to an equation of motion [Equations (1a), (1b), and (1c)], an equation of continuity is also required for all models. This is analogous to the continuum equation of conservation of mass density ρ and is derived in the same way—with ψ replacing ρ—to give

$$\frac{\partial\psi}{\partial t} = -\nabla\cdot(\psi\mathbf{v}) = -\left(\frac{\partial}{\partial\mathbf{x}}\;\frac{\partial}{\partial\mathbf{y}}\;\frac{\partial}{\partial\mathbf{z}}\right)\cdot\begin{bmatrix}\psi\dot{\mathbf{x}}\\ \psi\dot{\mathbf{y}}\\ \psi\dot{\mathbf{z}}\end{bmatrix} = -\sum_{i=0}^{N}\left[\frac{\partial}{\partial x_i}(\psi\dot{x}_i) + \frac{\partial}{\partial y_i}(\psi\dot{y}_i) + \frac{\partial}{\partial z_i}(\psi\dot{z}_i)\right] \quad (4)$$

This states simply that beads are conserved in number although they may accumulate locally in response to a dynamical process.

Equations (4) and (1) are coupled by virtue of velocities such as $\dot{\mathbf{x}}$ appearing in both. Fortunately, Equation (1c) can be rearranged to give $\dot{\mathbf{x}}$ explicitly, which is then substituted directly into Equation (4). This combined relationship is the *diffusion equation* describing ψ, analogous to the form of the continuum conservation equation for binary mixtures obeying Fick's Law, $\partial\rho_1/\partial t = \mathcal{D}_{12}\partial^2\rho_1/\partial x^2$. For the bead model, the Brownian diffusion coefficient emerges as $D = kT/f$.

In principle, the solution of the diffusion equation for $\psi(x, y, z, t)$ would permit any macroscopic quantity to be computed by the usual statistical averaging process,

$$<Q> = \int Q\psi\,dx\,dy\,dz \quad (5)$$

but in practice it isn't necessary to know ψ exactly. It is sufficient merely to calculate the value of certain integrals (moments) of ψ, and this can be done simply by multiplying the whole diffusion equation by Q [see Equation (5)] and then integrating by parts (Zimm, 1956; Williams, 1965).

It remains to convert this modeling into rheological properties such as viscosity. This is done by computing the stress tensor according to Equation (5). For dilute solutions, only the first term in polymer concentration is required: $\boldsymbol{\sigma} = \boldsymbol{\sigma}_s + \boldsymbol{\sigma}_p(c)$. It has been almost universal practice to employ the form derived by Kramers for potential flows, which for shear stress becomes

$$\sigma_{yx} = \eta_s\gamma + \nu<\mathbf{y}^T\cdot(-\mathbf{F}_x^{(f)})> = \eta_s\gamma - \nu\sum_i <y_iF_{xi}^{(f)}> \quad (6a)$$

where $\nu = N_Ac/M$. This can be generalized (Kotaka, 1959; Williams, 1965) to

$$\boldsymbol{\sigma} = \sigma_s\boldsymbol{\Delta} - \nu<\mathbf{r}^T\,\mathbf{F}^{(f)}> \quad (6b)$$

as was derived independently by Fixman (1965). [See Equation (29) et seq.] Similar expressions for dumbbell molecules (see below) have been advanced by Giesekus (1956), Prager (1957), and Bird, Warner, and Evans (1971). An analogous form arose from the thermodynamic analysis of Sarti and Marrucci (1973). The use of Equation (6) has recently been criticized and more general expressions proposed (Curtiss, Bird, and Hassager, 1974). Still, most of the polymer literature employs Equation (6) and no rheologically important errors are yet known to arise from its use.

When $F^{(f)}$ from Equation (1b) is substituted into Equations (6a) or (6b), the stress is expressed in terms of averages such as $<y_i\,x_{i+1}>$, $<x_i^2>$, etc. which are obtainable directly as moments of the diffusion equation. Thus the problem is solved, in principle, but one detail impedes the procedure—the fact that coordinates of adjacent beads are coupled together [for example, x_1, x_2, x_3 in Equation (1b)]. This difficulty is circumvented by a change of co-

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[*] The entire set of $N + 1$ such equations is usually written in multidimensional vectors such that $\mathbf{x}^T = (x_0, x_1, x_2, \ldots\ldots, x_N)$ and Equation (1b) becomes

$$0 = -f(\dot{\mathbf{x}} - \dot{\mathbf{x}}_s) - kT\frac{\partial\ln\psi}{\partial\mathbf{x}} - K\,\mathbf{A}\cdot\mathbf{x} \quad (1c)$$

$$\text{with } \mathbf{A} \equiv \begin{pmatrix} 1 & -1 & 0 & 0 & \cdots & 0 & 0 & 0\\ -1 & 2 & -1 & 0 & \cdots & 0 & 0 & 0\\ 0 & -1 & 2 & -1 & \cdots & 0 & 0 & 0\\ 0 & 0 & -1 & 2 & \cdots & 0 & 0 & 0\\ \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots & \vdots\\ 0 & 0 & 0 & 0 & \cdots & -1 & 2 & -1\\ 0 & 0 & 0 & 0 & \cdots & 0 & -1 & 1 \end{pmatrix}$$

At equilibrium, with $\dot{\mathbf{x}} = \dot{\mathbf{x}}_s = 0$, Equation (1c) is satisfied by $\psi = \psi_0$ from Equation (2).

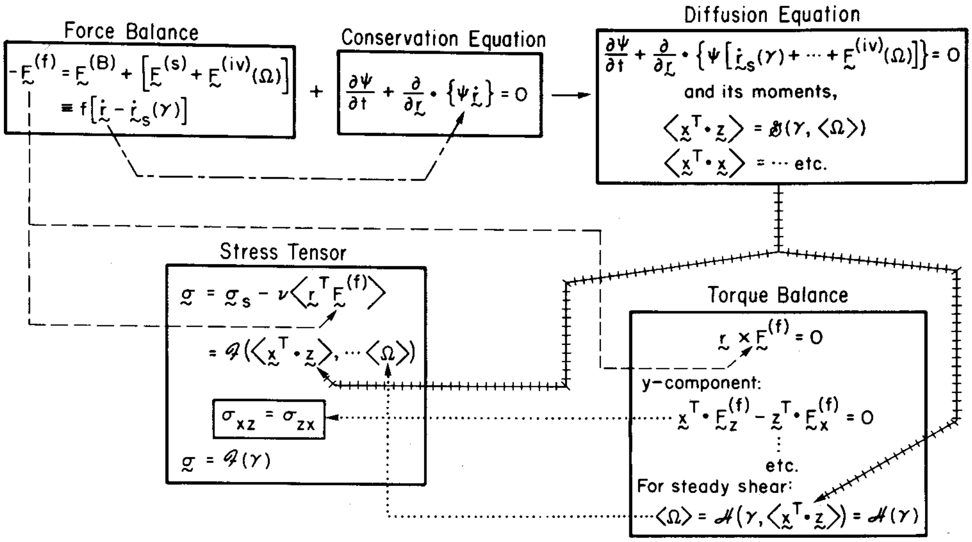

Fig. 5. Schematic outline of how stress components are calculated in molecular rheology. As in continuum mechanics, the necessary ingredients are the Force Balance (conservation of linear momentum), Continuity Equation, and the Torque Balance (conservation of angular momentum). The latter, which assures symmetry of $\boldsymbol{\sigma}$, is trivially satisfied by many models and is thus usually unmentioned; it becomes important at high shear rates and for IV models.

ordinates which effects a decoupling, to the so-called "normal" coordinates.

Finding these coordinates is an eigenvalue problem, easily solved *only* for the Rouse Coil. It reduces to finding coordinates $\{\mathbf{u}, \mathbf{v}, \mathbf{w}\}$ related to $\{\mathbf{x}, \mathbf{y}, \mathbf{z}\}$ by a linear transformation $\mathbf{x} = \mathbf{Q} \cdot \mathbf{u}$, etc. such that diagonalization of the matrices in the stress and diffusion equation occurs. For the Rouse Coil, this means simply $\mathbf{Q}^T \cdot \mathbf{A} \cdot \mathbf{Q} = \boldsymbol{\Lambda}^0$ with $\boldsymbol{\Lambda}^0$ being diagonal with elements* (Rouse, 1953)

$$\mu_p{}^0 = \lambda_p{}^0 = 4 \sin^2 \left[\frac{p\pi}{2(N+1)} \right] \tag{7a}$$

Thus, the $N + 1$ coupled differential equations are separated into N independent equations (plus a rheologically irrelevant center-of-resistance equation). The conversion to normal coordinates and substitution of $\lambda_p{}^0$ values permits a closed-form representation of the stresses. To maximize the physical significance of λ_p in such expressions, it is useful to define the relaxation times

$$\tau_p = \left(\frac{fb^2}{6kT} \right) \frac{1}{\lambda_p} \tag{7b}$$

This completes, in principle, the analysis for any kind of flow. The conceptual framework is represented schematically in Figure 5. For different flows, the equations are distinguished only by the characteristic form of the solvent velocity field. For steady simple shear, $\dot{x}_{2s}{}^0 = \gamma y_2$ with γ constant; for oscillatory shear, $\dot{x}_{2s}{}^0 = \gamma(t) y_2 = [\gamma_m \cos \omega t] y_2$; and for steady extension, $\dot{x}_{2s}{}^0 = 2\kappa x_2$ with $\dot{y}_{2s}{}^0 = -\kappa y_2$ and $\dot{z}_{2s}{}^0 = -\kappa z_2$ where the tensile strain rate κ is constant (Bird, Johnson, and Stevenson, 1970).

Rheological results for all these flows are presented in Table 1. The expression for η_0 in terms of the τ_p can be used to eliminate the product fb^2 in Equation (7b), giving the very useful general result

$$\tau_p = \left[\frac{(\eta_0 - \eta_s)\, M}{c\, RT \left(\sum_k \lambda_k{}^{-1} \right)} \right] \frac{1}{\lambda_p} \tag{7c}$$

This can be evaluated for Rouse Coil eigenvalues in Equation (7a); employing the approximation $\sin^2\theta \cong \theta^2$ yields the widely quoted form

$$\tau_p{}^0 \cong \left[\frac{6(\eta_0 - \eta_s)\, M}{\pi^2 cRT} \right] \frac{1}{p^2} \equiv \frac{\tau_1{}^R}{p^2} \tag{7d}$$

which defines the maximum Rouse relaxation time $\tau_1{}^R$.

Predictions made in Table 1 have the following qualitative features:

1. $\eta'(\omega)$ begins at η_0, shows a decrease near $\omega\tau_1 = 1$, and thereafter drops off in power-law fashion ($d \log \eta' / d \log \omega = \text{const.} = P$) so that $\eta'_\infty \to \eta_s$ at high ω. Whereas P can be influenced by modifications of the τ_p — spectrum (to be discussed) to fit experimental data rather well, the result $\eta'_\infty \to \eta_s$ is unavoidable and represents a basic failure of the model.
2. $\eta''(\omega)$ begins at zero, increases linearly with ω until near $\omega\tau_1 = 1$ where a maximum occurs, then decreases toward zero with $d \log \eta''/d \log \omega = P$. For all τ_p-spectra, $\eta'' \leqq (\eta' - \eta_s)$ although Equation (7d) leads to convergence at high ω. The result $\eta''_\infty \to 0$ is realistic.
3. $\eta(\gamma) = \eta_0$, a constant. That only Newtonian viscosity can be predicted is an important weakness of the model.†
4. $\zeta(\gamma) = \zeta_0$. Data show that ζ depends strongly on γ.
5. $\beta = 0$. Since most data show β to be small, this is a rather minor shortcoming. Experimental evidence in truly dilute solutions is rare, but Denn and Roisman (1969) obtain $0 < |\beta_0/\zeta_0| < 0.05$ by indirect methods.
6. $\bar{\eta}(\kappa)$ begins at $3\eta_0$ as required of all fluids, then increases with κ—perhaps realistically for small κ—but suffers catastrophe ($\bar{\eta} \to \infty$) when $\kappa\tau_1 \to 1/2$. Although the latter has not been disproved by definitive data on dilute solutions, its coincidence with (7) below indicates it to be a failure.
7. $<r^2>^{1/2}$ increases monotonically with γ (or with κ), going to unreasonable magnitudes at large γ (and to infinity as $\kappa\tau_1 \to 1/2$).

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* When $HI \neq 0$, the Rouse equalities $\mathbf{Q}^T = \mathbf{Q}^{-1}$ and $\mathbf{M} = \boldsymbol{\Lambda}$ are not valid (Zimm, 1956).

† Bueche (1954a,b), also credited with developing the normal coordinate analysis, obtained slightly different $\eta^*(\omega)$ and also a non-Newtonian viscosity. Instead of a stress representation like Equation (6), he invoked energy-dissipation arguments to calculate viscosity. Apparently errors were made [DeWames et al. (1967) have discussed this point], and the predictions of η^* and $\eta(\gamma)$ are not in particularly good agreement with experiment.

TABLE 1. PREDICTIONS OF ROUSE-ZIMM MODELS
(Isotropic HI, $S = \theta$, $K = K_0$)

Mode	Property
Small-amplitude oscillation	$\eta^*(\omega) = \begin{cases} \eta'(\omega) \\ -i\eta''(\omega) \end{cases} = \begin{cases} \left[\eta_s + \nu kT \sum_{p=1}^{N} \frac{\tau_p}{1+\omega^2\tau_p{}^2} \right] \\ -i\left[\nu kT \sum_{p=1}^{N} \frac{\omega\tau_p{}^2}{1+\omega^2\tau_p{}^2} \right] \end{cases}$
Steady shear	$\eta(\gamma) = \eta_0 = \eta_s + \nu kT \sum_{p=1}^{N} \tau_p$
	$\zeta(\gamma) = \zeta_0 = 2\nu kT \sum_{p=1}^{N} \tau_p{}^2$
	$\beta(\gamma) = 0$
	$<r^2(\gamma)> = <r^2>_0 + \frac{2b^2\gamma^2}{3} \sum_{p=1}^{N} \tau_p{}^2$
	$[\eta_0] \cong \begin{cases} \frac{N_A}{36}\left(\frac{b}{M^{(s)}}\right)^2 \left(\frac{f}{\eta_s}\right) M \ldots\ldots \text{Rouse, } h = 0 \\ 2.84 \times 10^{23} \left(\frac{b}{\sqrt{M^{(s)}}}\right)^3 M^{1/2} \ldots\ldots \text{Zimm, } h \to \infty \end{cases}$
Steady elongation	$\bar{\eta}(\kappa) = 3\eta_s + 3\nu kT \sum_{p=1}^{N} \frac{\tau_p}{(1-2\kappa\tau_p)(1+\kappa\tau_p)}$
	$<r^2(\kappa)> = <r^2>_0 + 2b^2\kappa^2 \sum_{p=1}^{N} \frac{\tau_p{}^2}{(1-2\kappa\tau_p)(1+\kappa\tau_p)}$

8. $[\eta_0]$ is proportional to M^1, whereas most data show proportionality with M^a where $0.5 \leqq a \leqq 0.8$. This was severely disturbing to physical chemists.

These results can be deemed generally successful for the ω-dependence of η' and η'' (Ferry, 1970) and the corresponding oscillating normal stress properties (Williams, 1965; Akers and Williams, 1969). The high-ω failure $\eta_\infty' \to \eta_s$ is a consequence of simply pushing the N-unit model too far. Once ω is sufficiently high to excite the Nth normal mode, the model is saturated and thereafter inappropriate for use.[*] Performance at higher ω could be predicted by choosing a larger N (that is, using a smaller submolecule) or by going inside the submolecule itself until, ultimately, individual chemical bond rotations would become saturated too.

From the engineering viewpoint, failures (3) and (6) are far more serious. Although the coil is predicted to deform and become oriented in shear flow, compensating factors cause viscosity to remain constant (Subirana, 1964). The prediction $\bar{\eta} \to \infty$ has been cited as corresponding to observed fiber instabilities and fractures, but instead it reflects imperfection of the Hookean extensional law in $F^{(s)}$. The latter permits, mathematically, an infinite extendability in any kind of deformation field, as cited in (7) above (Bird, Johnson, and Stevenson, 1970).

Even the lesser (?) failing of predicting $\beta = 0$ becomes significant when looking for subtle molecular influences. Prediction of a realistic β has been used as a discriminator between continuum rheological models for many years (Oldroyd, 1950). Now it is known that many flow instabilities and secondary flows are traceable to β (for example, Denn and Roisman, 1969), which is of definite engineering importance.

Continued molecular model-building beyond the Rouse Coil was expected to remedy this catalogue of defects.

Variations on the Rouse Theme

The vast preponderance of effort with dilute solution theory in the past 20 years can be regarded as deriving from the Rouse Coil, with large N, as indicated in Figure 3. This approach represents the mainstream, with the full coil formulation becoming more detailed in terms of either polymer structure (K and IV), solvent dynamics (better description of $\dot{x}_s$, through HI), or thermodynamic solvent power (S). An alternate representation of chain dynamics, the time-correlation method, has been recently employed by Bixon (1973) and Zwanzig (1974) in seeking further to interpret and extend the more mechanistic Rouse formulation.

The only variation which tends to simplify rather than complicate is the special case $N = 1$, named the *Dumbbell* because it possesses only two beads joined by one submolecule. This models the entire polymer as one huge submolecule (n large) or, alternatively, can be regarded as appropriate for short hydrocarbon chains ($n \approx 20$). Motivating this is the hope of escaping the smog of many-body mathematics while preserving and examining the essential physics. Rheological predictions for $N = 1$ are qualitatively the same as for large N, but the normal coordinate transformation is trivial. As often as possible, Dumbbell results will be cited to illustrate the role of parameters such as HI and K (see Figure 6).

The fact that a Dumbbell has only one eigenvalue and one relaxation time, for example,

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[*] This fact is often masked by allowing $N \to \infty$ when the sums in Table 1 are being evaluated. Negligible error is incurred for considerable ranges of $\omega\tau_1$ as long as N is indeed large, but obviously this scheme collapses as $\omega\tau_N \to 1$ and $p \to N$.

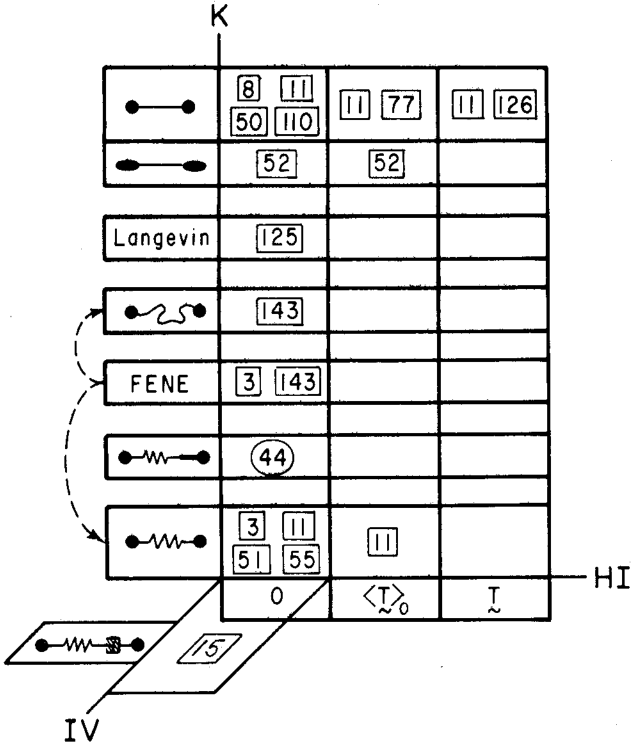

Fig. 6. Dumbbells of many kinds, with differing types of submolecule forces $F^{(s)}$. As a rule, only *K* and *HI* have been explored as dumbbell variables; one *IV* study has been reported. More linear Elastic Dumbbell results are obtainable from the Rouse Coil literature by taking the $N = 1$ case.

Rouse Dumbbell: $\lambda_1^0 = 2$ (8a)

$$\tau_1^0 = (\eta_0 - \eta_s)M/cRT \tag{8b}$$

is a severe limitation on its ability to fit data on large coiling molecules. Still, certain general statements about Dumbbell rheology are enlightening. Giesekus (1966) has shown that the equivalent of Equation (6b) can be written as

$$\boldsymbol{\sigma} = \sigma_s \boldsymbol{\Delta} + \frac{\nu f}{4J}\frac{\mathfrak{d}}{\mathfrak{d}t}\langle\mathbf{RR}\rangle \tag*{(9a)*}$$

where **R** is the bead separation vector and

$$\frac{\mathfrak{d}\langle\mathbf{RR}\rangle}{\mathfrak{d}t} \equiv \frac{\partial\langle\mathbf{RR}\rangle}{\partial t} + \mathbf{v}\cdot\nabla\langle\mathbf{RR}\rangle - \langle\mathbf{RR}\rangle\cdot\nabla\mathbf{v} - (\nabla\mathbf{v})^T\cdot\langle\mathbf{RR}\rangle \tag{9b}$$

with $\mathfrak{d}/\mathfrak{d}t$ the convected derivative applied to a contravariant tensor. The need for the $\mathfrak{d}/\mathfrak{d}t$ operator in differential viscoelastic models of continuum rheology was demonstrated by Oldroyd (1950) through purely mathematical arguments which were incapable of indicating whether contravariant or covariant forms (giving different physical predictions) should be used. Equation (9a) suggests that the molecular rheology of Dumbbells favors the former.

The Rouse Dumbbell in particular can be linked with a classical continuum model first proposed by Oldroyd (1950) as a first-order extension of linear rheology. As shown by Giesekus (1958) and presented by Bird, Warner, and Evans (1971), Equation (9a) can be rewritten for Dumbbells with linear elastic springs

$$\left(1 + \tau_1^0 \frac{\mathfrak{d}}{\mathfrak{d}t}\right)\boldsymbol{\sigma} = \eta_0\left(1 + \tau_2^0 \frac{\mathfrak{d}}{\mathfrak{d}t}\right)\boldsymbol{\Delta} \tag{9c}$$

where τ_1^0 is given by Equation (8b) and

$$\eta_0 = \eta_s + \nu kT\tau_1^0 \tag{9d}$$

$$\tau_2^0 = \tau_1^0 (\eta_s/\eta_0) \tag{9e}$$

Equation (9c) is identical to Oldroyd's contravariant model and yields the predictions $\eta = \eta_0$, $\zeta = \zeta_0 = 2\eta_0(\tau_1^0 - \tau_2^0)$, and $\beta = 0$, which might be considered useful approximations to low-shear behavior. These results are in complete agreement with Table 1 for $N = 1$, and are obtained with far less effort than needed in the molecular approach. When the covariant tensor analogue of Equation (9c) is employed, normal stress predictions are totally wrong (Oldroyd, 1950). This mathematically-permitted alternative could have been discarded, even without appeal to experiment, if molecular insight had been applied.

It should be added, however, that other (non-Rouse) Dumbbell models cannot be forced into the framework of Equation (9c) or other continuum models which might support the correctness or utility of preferring contravariant or covariant versions of the $\mathfrak{d}/\mathfrak{d}t$ operator.

MODIFICATIONS OF THE ROUSE COIL

Hydrodynamic Interaction (HI)

This oft-misunderstood phrase refers to an *intra*-polymer phenomenon, originating from the perturbation of solvent hydrodynamics within the coil caused by drag from a given bead. This modification of $\dot{\mathbf{x}}_s$ influences the drag on all other beads as well, and this complex interaction creates in effect the hydrodynamic interbead forces which are absent in the Rouse Coil. Thus the Rouse Coil is termed the *free draining* case, since its nonperturbed approximation $\dot{x}_s \approx \dot{x}_s^0$ could exist only if solvent were able to flow (drain) through the coil without being disturbed at all by the drag.

The other extreme, the *nondraining* case, represents dominant *HI* to the extent that solvent within the coil is essentially trapped and must follow the coil deformation and rotation. This also means that external solvent is severely disturbed and must flow around the coil. Detailed results for this case were presented first by Zimm (1956), who also established a general *HI* framework which is widely used today. The major result of his approach is modification of the eigenvalues λ_p^0 in Equation (7a).

This is accomplished with considerable difficulty, however. Following Kirkwood, Zimm approximated the actual solvent velocity by

$$\dot{x}_{is} = \dot{x}_{is}^0 + \underbrace{\sum_k T_{ik}^{(x)} F_{xk}^{(f)}}_{\substack{HI\text{ perturbation}\\ \text{between beads}}} \;\ldots\; k \neq i \tag{10}$$

where the Oseen interaction tensor **T** between points i and k

$$\mathbf{T}_{ik} \equiv \frac{1}{8\pi\eta_s|\mathbf{r}_i - \mathbf{r}_k|}\left[\boldsymbol{\delta} + \frac{(\mathbf{r}_i - \mathbf{r}_k)(\mathbf{r}_i - \mathbf{r}_k)}{|\mathbf{r}_i - \mathbf{r}_k|^2}\right] \ldots i \neq k \tag{10a}$$

was subsequently represented by its equilibrium (no-shear) averaged form,

$$\langle\mathbf{T}_{ik}\rangle_0 \equiv \int \mathbf{T}_{ik}\,\psi_0\,dx\,dy\,dz = \frac{1}{6\pi\eta_s\langle|\mathbf{r}_i - \mathbf{r}_k|\rangle}\boldsymbol{\delta} \tag{10b}$$

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[*] Hassager and Bird (1972) have generalized this for large *N*, also including *HI*.

$$<T_{ik}^{(x)}>_0 = <T_{ik}^{(y)}>_0 = <T_{ik}^{(z)}>_0 = 1/\eta_s b(6\pi^3 |i-k|)^{1/2} \quad (10c)$$

This latter formula, used in Equation (10), preserves the linear nature of the problem since $<T_{ik}^{(x)}>_0$ has no dependence on coordinates x_i, but has two weaknesses. First, the pre-averaging in Equation (10b) cannot properly represent conditions of shearing; the resultant isotropic tensor $<\mathbf{T}>_0 \sim \boldsymbol{\delta}$ restricts the model's capability of dealing with all phenomena arising from shear-induced anisotropy, such as non-Newtonian viscosity. Second, Equation (10a) was originally derived for long-range perturbation conditions which are violated when it is applied to beads which are close together. Rotne and Prager (1969) and Yamakawa (1970) have discussed problems with, and corrections to, Equation (10a) for the finite size of the bead.

Nonetheless, the introduction of *HI* was a major advance. Eigenvalues[*] became functions of a new parameter, defined by Zimm as

$$h = \left(\frac{N}{12\pi^3}\right)^{1/2} \frac{f}{b\eta_s} \quad (11a)$$

or, as suggested later by Thurston and Morrison (1969),

$$h^* = h/N^{1/2} \quad (12b)$$

which is more convenient because explicit molecular weight dependence is avoided. The qualitative effect of *HI* can be seen by examining low-*N* cases (Lodge and Wu, 1972),

$$N = 1 \text{ (Dumbbell): } \lambda_1 = 2(1 - 2^{1/2} h^*) \quad (12c)$$
$$h = h^*$$

$$N = 2 \; (h = 2^{1/2} h^*): \; \lambda_1 = 1 - h^* \quad (12d)$$

$$\lambda_2 = 3 - (2^{1/2} 4 - 1)h^* \quad (12e)$$

Thus *HI* is seen to decrease λ_p, hence to increase τ_p from the free-draining case. Also, the influence is different for each *p*, which means that the λ_p-spectrum is changed too.

No such closed-form solutions are possible for larger *N*. Since the basic mathematical step in obtaining the $\lambda_p(h)$ is inversion of an $N \times N$ matrix and *N* is large, various numerical methods have been employed. Zimm, Roe, and Epstein (1956) produced $\lambda_p(\infty)$, and Tschoegl (1963) used basically the same method to obtain $\lambda_p(h)$ for all cases $0 \leq h \leq \infty$. Hearst (1962) devised a simpler means for computing $\lambda_p(h)$ by noting that the freedraining eigenfunctions (column vectors composing $\mathbf{Q}^0$) are excellent approximations to the nondraining eigenfunctions, despite substantial differences in the corresponding eigenvalues. This permitted a successful first-order perturbation calculation with results nearly identical to those of Tschoegl. The nonaveraged Equation (10a) was used by Pyun and Fixman (1965, 1966) to obtain more accurate approximations to $\lambda_p(h)$, showing with great effort that the λ_p were increased only a few percent by this more sophisticated treatment.

As a consequence of *HI*, objection (8) to the Rouse Coil was overcome and now $[\eta_0] \sim M^{1/2}$ for the same case of Gaussian statistics. This is conveniently expressed in the form

$$[\eta_0] = \Phi <r^2>^{3/2}/M \quad (13)$$

since $<r^2> \sim M$. Equation (13), introduced years earlier on the basis of totally different intuitive arguments (Flory, 1953), defines the Flory-Fox parameter Φ which is nearly a universal constant for all linear coiling polymers. Now $\Phi = \Phi(h)$, and $\Phi_\infty \equiv \Phi(\infty)$ corresponds to the nondraining case which is supposedly achieved when the Gaussian chain is sufficiently long. Zimm (1956) obtained $\Phi_\infty = 2.84 \times 10^{23}$, Hearst 2.82×10^{23} (1962), Pyun and Fixman 2.68×10^{23} in their first perturbation (1965) and 2.66 through the third perturbation (1966). Data for nonelectrolyte polymers in θ solvents agree very well, being within 5% of $\Phi_\infty = 2.7 \times 10^{23}$ (Kurata and Stockmayer, 1963; Yamakawa, 1971).

Many of these efforts utilized approximations valid only for large *N;* in certain ways, limits for $N \to \infty$ were being taken. Besides the mathematical convenience, additional justification for this was the fact that rheological predictions seemed insensitive to the choice of *N*. Actually, this was only true for moderate ranges of ω or γ or κ, where the higher response modes of the model were still unexcited. The need for more exact eigenvalues for nonvanishing γ, ω was recognized by Thurston and Morrison (1969) who performed exact calculations of $\lambda_p(h^*, N)$ with Equation (10c) through $N = 15$. More recently Lodge (1972) and Lodge and Wu (1972) produced exact results through $N = 300$.

An interesting discovery by Thurston and Morrison was that mathematical solutions in terms of positive eigenvalues were possible only for $h^* < 0.471$ (at least, for $N \leq 15$). Similar restrictions were noted by DeWames et al. (1967). In retrospect, we can see from Equations (12c) to (12e) that such a limitation could be expected. The physical reasons for this are obscure, although for the limiting case of Dumbbells some explanation can be extracted,[†] and DeWames et al. argue more generally that this corresponds to a plausible physical restriction on how much faster a bead can move by virtue of *HI* perturbations. In any event, high values of h^* have been shown to lead to physically inadmissible situations (for example, infinities) when Equation (10c) is used (Zwanzig et al., 1968; DeWames et al., 1967). Another consideration, discussed by Osaki (1972), appears to restrict h^* still further. The intended case of dominant *HI* actually corresponds to $h^* = 1/4$ even in Zimm's framework, and higher values would seem to have uncertain physical significance. Lodge and Wu show with exact calculations that $h^* = 0.26$ yields the same zero-shear limit $\Phi_\infty \cong 2.84 \times 10^{23}$ obtained by Zimm, without sensitivity to the choice of *N*. Because of this and the fact that data can be fit with the range $0 \leq h^* \leq 0.26$, Lodge and Wu present results only through $h^* = 0.3$.

One of the two basic flaws in using Equation (10b), the preaveraged *HI* tensor, was that it remains unrealistically isotropic under all conditions of shear. Williams (1965) suggested that this characteristic was in part responsible for predictions of $\beta = 0$ as well as Newtonian viscosity from coil models. Rectifying this for the full flexible coil is tremendously complex, but ultimately the full form of **T** from Equation (10a) must be taken into account. Zimm (1961) suggested two approaches to introducing the anisotropy that develops in *HI* with shear. Earlier, Peterlin (1960) pursued one of these and obtained an approximation to $\eta(\gamma)$ by using $<T(\gamma)>$ in the diffusion equation, calculating $<T>_\gamma$ by averaging with $\psi(\gamma)$ obtained from solving the equation with isotropic *HI*. Incorporation of exact *HI* from Equation (10a) into the full shear-dependent problem was subsequently performed by Fixman (1966ab), who presented $\eta(\gamma)$ but without

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[*] When $\dot{\mathbf{x}}_s \neq \dot{\mathbf{x}}_s^0$, then $\mathbf{Q}^T \neq \mathbf{Q}^{-1}$ and also the eigenvalues μ_p and λ_p from **M** and $\boldsymbol{\Lambda}$ are unequal. The relevant set for most stress calculations remains λ_p.

[†] For $N = 1$, Equations (11a) and (11b) become $h^* = (1/12\pi^3)^{1/2} f/b\,\eta_s$. If the bead is modeled as a Stokes sphere of radius *a* then $h^* = (3/\pi)^{1/2}\, a/b$ and its range depends on *a*. Beads behaving as point junctions between submolecules give $h^* = 0$, and beads large enough to contact adjacent beads ($a = b/2$) give $h_{\max}^* = 0.49$. Naive though this argument is, it suggests physical reasons why h^* should be bounded. Note, also, that $h^* \sim a/b$ indicates h^* can be interpreted as a submolecule thickness ratio.

accompanying normal stress results.

Yamakawa's correction (1970) to **T** for finite bead size of radius a was used to compute only η_0. The method was otherwise identical to the Pyun-Fixman approximation for $\lambda_p(h)$ and led to the same result for a chain thickness $a/b = 0$, $\Phi(h)$ increasing with h to attain Φ_∞ when $h > 10^2$. This prediction, typical of all earlier *HI* work, does not conform with experiment; even rather short chains (with h small because $h \sim N^{1/2}$) are known to achieve Φ_∞. These data can be explained by the Yamakawa analysis with $\Phi(h, a/b)$ since Φ_∞ is attained for nearly *all* h (that is, all N) if $a/b \approx 0.21$.

For spherical beads, this also corresponds to $h/N^{1/2} = h^* \cong 0.21$, and thus a remarkable parallel exists with the Lodge and Wu result (1972) in which $\Phi(h^*, N)$ equals Φ_∞ for all N if $h^* = 0.26$. Clearly the translation of variables is $\{h^*, N\}_{LW} \leftrightarrows \{a/b, h(N)\}_Y$, but the similarity of results is surprising in view of conceptual differences in the two works:

$$\left\{\begin{array}{l}\text{Isotropic } HI.\\ \text{Exact } \lambda_p.\\ \mathbf{T} \text{ uncorrected for}\\ \qquad \text{bead size.}\end{array}\right\}_{LW} \neq \left\{\begin{array}{l}\text{Exact } HI.\\ \text{Approximate } \lambda_p.\\ \mathbf{T} \text{ corrected for}\\ \qquad \text{bead size.}\end{array}\right\}_{Y}$$

From this we conclude that errors introduced by pre-averaging **T** and ignoring finite bead size are negligible in the low-shear limit. The former conclusion is reinforced by the smallness of the Pyun-Fixman correction to $\lambda_p(h)$ for exact **T** with the coil (1965, 1966) and Ullman's analogous results for the rod (1964). However, since pre-averaging **T** is known to cause errors (Fixman, 1966b) in computing $\eta(\gamma)$, one must suspect also that ignoring chain thickness can lead to errors at high shear.

Further comments on *HI* appear in connection with rigid linear molecules.

Solvent Effects (S)

A good solvent expands the coil domain for thermodynamic reasons (in dilute solution), relative to a theta solution ($S = \theta$). The latter is a poor solvent which shrinks the coil sufficiently to overcome excluded volume effects and preserve the Gaussian relation $\langle r_\theta^2\rangle \sim M$. It is common (Flory, 1953) to measure solvent power in terms of a zero-shear coil expansion parameter,

$$\alpha_0^2 \equiv \langle r^2\rangle_0/\langle r_\theta^2\rangle_0 \tag{14a}$$

whence

$$[\eta_0]/[\eta_0]_\theta = \alpha_0^3 \tag{14b}$$

If all bead positions scale linearly with α_0 in various solvents, then the dynamical problem is basically unchanged as long as shear-induced deformations are small.

However, large shear rates tend to enlarge and deform the coil domain, so $\langle r^2\rangle$ increases for all solvents with increasing shear. This expanded coil has less sensitivity to excluded volume effects and thus tends to behave more like a θ-system ($\alpha \rightarrow 1$). Subirana (1964) employed $\psi(\gamma)$ from the steady shear diffusion equation to compute the shape and size of the ellipsoidally deformed coil. His results for $[\eta(\gamma)]/[\eta_0]$ are qualitatively in accord with data on solvent effects, with non-Newtonian phenomena increasingly pronounced as solvent improves. Simply expressed, $[\eta]/[\eta_0] = \alpha^3(\gamma)/\alpha_0^3$, and moreover a high-shear limit is obtained as $[\eta_\infty]/[\eta_0] = 1/\alpha_0^3$. But for θ solvents, the (erroneous) Zimm result of Newtonian viscosity was still obtained by a fortuitous cancellation of various deformational effects, presumably because of inadequacies in the *HI* treatment.

The highly sophisticated approach of Fixman (1965, 1966a, b) is a comprehensive accommodation of both *HI* and S for steady shear flow. Results, for $\eta(\gamma)$ alone, are presented graphically in reduced variables which involve $\alpha_0(S)$; the parameter h does not appear explicitly. The correct shear-thinning behavior is predicted, even for θ solutions, and it is likely that η_∞ also emerges. The greater degree of non-Newtonianism with better solvents (in dilute solution) is found to arise from two factors: (a) the initially expanded coil in a good solvent offers less resistance to deformation because its far-separated segments sense little *HI;* (b) there is greater thermodynamic incentive to further expansion (in shear) and thereby to increase contacts with solvent molecules. In turn, this enhanced expansion permits partial draining to occur more readily and viscosity is reduced in ever greater proportion. Apparently Fixman's method has not been extended to compute other rheological properties so the question of β is still unresolved.

An alternate, and more directly interpretable, method was introduced by Tschoegl (1964). This is based on the fact that Gaussian statistics are actually violated in non-θ systems, such that

$$\langle r^2\rangle_0 = N^{1+\epsilon}\, b^2 \ \ldots . \ \epsilon_\theta = 0 \tag{15}$$

where the excluded-volume parameter $\epsilon = \epsilon(S)$ is usually in the range $0 \leqq \epsilon \leqq 1/3$. [Note that if $\epsilon = 1$, the result $|\mathbf{r}| = Nb$ would correspond to a rodlike, or straight-line, polymer.] Tschoegl calculated $\lambda_p(h, \epsilon)$ with h now emerging more generally as

$$h^2(\epsilon) = (2/N)^\epsilon \cdot h^2(0) \tag{16}$$

The predicted $\eta^*(h, \epsilon)$ has been quite successful in describing both *HI* and S effects, but no non-Newtonian results were possible. Furthermore, Osaki's correction (1972) to the Zimm eigenvalue equation shows that the Tschoegl predictions are also somewhat in error.

The non-Gaussian nature of $\langle r^2\rangle$ and resultant relaxation phenomena for an isolated polymer molecule with excluded-volume effects ($\epsilon \neq 0$) was demonstrated with a Monte Carlo stepping technique by Verdier and Stockmayer (1962). An interesting consequence was that $\tau_1^{\text{effec.}}$ could be predicted remarkably well by Zimm's nondraining result ($h \rightarrow \infty$, $\epsilon = 0$), leading us to speculate essentially that the regions of excluded volume might be dynamically equivalent to sites *of HI*. This raises disturbing questions about the meaning and uniqueness of h and ϵ in fitting rheological data. Furthermore, the defining relation for ϵ [Equation (15)] does not seem consistent with chain density distributions ψ_0 calculated by Verdier and Stockmayer.

Recently, Osaki, Schrag, and Ferry (1972) pointed out that *HI* and S were not really independent of each other when obtained from curve-fits of $\eta^*(\omega)$ data. By compiling rheologically obtained sets of $\{h^*, \alpha_0\}$, they showed that $\alpha_0 h^* =$ constant. This implies further that rheological *HI* and S parameters can be estimated from equilibrium properties of the solution. Earlier we discussed how chain thickness effects, too, could be absorbed in h^*. This suggests that future curve-fitting of linear data, for example, $\eta^*(\omega)$, will be done with only two parameters, h^* and N or α_0 and N, rather than three or four (h, ϵ or α, a/b, N).

Both ϵ and α_0 for large numbers of polymer-solvent combinations are in the polymer literature, most compactly in the *Polymer Handbook* (Brandrup and Immergut, 1966).

Nonlinear Springs (K)

The submolecule contributes a spring-like restoring force $F^{(s)}$ in Equation (1b) when the coil is deformed. If deformation is small, K is usually taken as a constant $K_0 = 3kT/b^2$ and this maintains the linear nature of the mathematics. Disregarding for the moment possible *HI* influences, this linear spring is a major explanation for Rouse Coil predictions of strain-rate-independent rheological properties. The existence of nonconstant $K(x_i)$ leads to a nonlinear diffusion equation which is not amenable to the eigenvalue solutions discussed earlier.

Several sources of nonlinearities in K are possible, and all of them lead to predictions of $\eta(\gamma)$ and $\zeta(\gamma)$ and sometimes to $\beta(\gamma) \neq 0$ and $\eta_\infty > \eta_s$. All have their origin in the appearance of non-Gaussian bead distributions, but our discussion will treat separately those arising from equilibrium and from nonequilibrium causes.

Equilibrium thermodynamics. This is basically the same cause as discussed under $\epsilon(S)$ above. Non-Gaussian coils, which exist under non-θ conditions, must have intrinsically nonlinear springs because bead positions cannot be scaled as α-multiples of hypothetical Gaussian positions. That is, $kT\partial \ln \psi_0/\partial x_2 \neq K'_0(x_1 - 2x_2 + x_3)$ unless $\psi_0 \sim \exp(-\alpha^2 x_\theta^2)$ is valid This problem was not really confronted by Subirana (1964), even though he obtained non-Newtonian viscosity by dealing with $S(\alpha)$, nor by Tschoegl (1964) who invoked $S(\epsilon)$ but dealt only with Zimm's linear framework and thus did not fully exploit the non-Gaussian physics. Apparently little work has been done expressly on this phenomenon although Fixman's formalism (1966a, b) could presumably deal with it. This postulates an excluded-volume potential by which solvent effects of all kinds can be introduced.

Unrelated to solvent per se is another configurational thermodynamic source of nonlinear springs. This is somewhat related to the concept of entanglements which is often applied to concentrated media where many polymer molecules may overlap. In dilute solutions, intramolecular segmental motions also lead to intramolecular loops. This may not influence equilibrium-averaged bead positions (ψ_0) appreciably, but the entropy of coil deformation at even low shear now involves disentanglement as well. This can generate spring nonlinearity with even modest displacements, as Prager and Frisch (1967) have shown by computing disentanglement forces from entropy alone. However, this concept has apparently never been injected quantitatively into the full molecular dynamics problem.

Large coil deformation. Even under θ conditions, the Gaussian ψ_0 in Equation (2) is only a good but not exact solution to idealized random chain distributions. More correctly[*], the form $\psi_0 \sim \exp\left[\frac{-3r^2}{2Nb^2}\right]$ should be replaced by $\psi_0 \sim \exp\left[-\int_0^r \mathcal{L}^{-1}\left(\frac{r}{Nb}\right) dr/b\right]$, where $\mathcal{L}\left(\frac{r}{Nb}\right)$ is the Langevin function $\mathcal{L} = \coth\left(\frac{r}{Nb}\right) - Nb/r$; ψ can be expanded (Flory, 1953) to give

$$\psi_0 \sim \exp\left\{-\frac{3r^2}{2Nb^2}\left[1 + \frac{3}{10}\left(\frac{r}{Nb}\right)^2 + \ldots\right]\right\}$$

This becomes important when coil deformation is large, as pointed out by Reinhold and Peterlin (1966). The resulting $F_{xi}{}^{(s)}$ is still obtained from $kT\ \partial \ln \psi_0/x_i$, but now $K = K(x_k)$ is no longer a constant.

Ultimately, of course, the coil domain is limited by the finite molecular length. Then rheological predictions become sensitive to N, unlike most low-deformation results. Reinhold and Peterlin predicted non-Newtonian viscosity of correct general character (shear-thinning, with $\eta \rightarrow \eta_\infty$ at high shear) by using Langevin springs, with a key parametric dependence on N. Tanner and Stehrenberger (1971) approximated the Langevin spring with the linear-locked spring characterized by K_0 until the ultimate extension $L = Nb$ was achieved, after which further extension was impossible. Their calculations[†] for $N = 10$ showed, among other things, that objection (6) to the Rouse Coil —concerning $\bar{\eta}(\kappa) \rightarrow \infty$—was overcome by this treatment and $\bar{\eta}(\kappa)$ increased only to a limit $\bar{\eta}_\infty$. Realistic $\eta(\gamma)$ was obtained in the Rouse model by Noda and Hearst (1971), who constrained the contour length $L = Nb = [N \sum_i (\mathbf{r}_{i+1} - \mathbf{r}_i)^2]^{1/2}$ to be constant which in turn forced K to be nonlinear. All these approaches counter objection (7) to the Rouse Coil, that $<r^2> \rightarrow \infty$ at high rates.

When coil deformation becomes severe, entropic forces which act toward restoring random coil distribution become tremendously large and are grossly underestimated by all linear-spring models. This defect is remedied in empirical fashion by injecting nonlinear connectors to replace the linear springs between beads, as was the spirit of the linear-locked spring of Tanner and Stehrenberger. Some other possibilities are the rigid rod (see Other Linear Structures) which cannot either extend or contract and the finitely extendible nonlinear elastic (FENE) spring (Warner, 1972) which is another approximation to the Langevin spring and can represent cases intermediate between the linear-spring and finite-string connectors.[††]

The Dumbbell has been very popular for examining the influence of nonlinear springs. Stevenson and Bird (1971) showed that Langevin Dumbbells in elongational flow have properly limited magnitudes of $\bar{\eta}(\kappa) \rightarrow \bar{\eta}_\infty$ and $<r^2>$. FENE Dumbbells (Warner) in shear flow exhibit $\eta'(\omega)$ with a limit $\eta_\infty' > \eta_s$, $\eta(\gamma)$, and $\zeta(\gamma)$. For Dumbbells of arbitrary springs in homogeneous flows, Armstrong (1974) developed ψ as a power series through second order in $\nabla\mathbf{v}$; $\boldsymbol{\sigma}$ was displayed to the same approximation, using Equation (9a). He evaluated this formalism explicitly for Rouse and FENE Dumbbells, with $\boldsymbol{\sigma}$ to order $(\nabla\mathbf{v})^3$. All Nonlinear Dumbbell predictions are qualitative improvements on the linear springs used in the Rouse Coil, but are limited in fitting data because $N = 1$ is too restrictive.

Incorporation of nonlinear springs into coiling-polymer models has not been common because of obvious mathematical difficulties. However, the original Kramers formulation employed rigid-rod connectors, and recently this model has been revived and extended. Connections between the Kramers Coil and Rouse Coil predictions were established for η_0 and $\bar{\eta}_0$ by Bird, Johnson, and Curtiss (1969). Hassager (1974) examined slow steady flows with $HI = 0$ and determined η_0 and ζ_0 for $N = 2$ exactly and large N approximately; in the latter case $[\eta_0] \sim M$ for large enough N, as for the Rouse Coil. Particularly helpful was Hassager's treatment of $\bar{\eta}(\kappa)$ for large N, demonstrating that $\bar{\eta}_\infty$ has finite magnitude larger than $\bar{\eta}_0$. The limit $\bar{\eta}_\infty$ was the same for both the rigid rod and the flexible Kramers Coil with identical numbers of beads since the molecule is stretched out and aligned with the flow for both cases. The major differences between these two models was in $\bar{\eta}_0$, with $\bar{\eta}_0$ (Kramers) $\sim (\bar{\eta}_\infty/N)$ and $\bar{\eta}_0$ (rod) $= \bar{\eta}_\infty/2$. Thus the presence of rigidity in the connectors of a flexible coil assures $\bar{\eta}_\infty \neq \infty$ and removes objection (6) to the Rouse Coil, but the prediction that $\bar{\eta}_\infty >> \bar{\eta}_0$ for all flexible coils remains.

The ultimate case of using rigid-rod connectors would be a detailed model of chemical bonds themselves, which avoids the submolecule and nonlinear spring concepts en-

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[*] But still not exactly (Yamakawa, 1970; Chap. 2).

[†] Errors in this work are cited by Armstrong (1974) although final results are apparently not seriously affected.

[††] Nonlinear spring laws used by Fraenkel (1952) and Giesekus (1958) have a nonzero rest length, unlike $F^{(s)}$ in Equation (1b) and the FENE spring. This is not a factor at high deformation and these laws are thus inadequate in the same sense as linear springs. However, Giesekus found a nonvanishing $\beta_0/\zeta_0 < 0$, which is of considerable interest.

tirely. Any approach of this kind is bound to predict high-γ and high-ω limiting rheological properties. This basic idea is used, in part, to justify the IV models (see next section). A far more comprehensive treatment of bond-level dynamics has recently been given by Fixman and Kovac (1974a, b), following development of a key theorem on statistical mechanics of constraints by Fixman (1974). For the limiting case of freely-jointed chains (bond lengths constant, no bond angle constraints), their results for $\eta''(\omega)$ were nearly identical to those of Rouse and Zimm. However, they now were able to obtain $\eta'(\omega) \rightarrow \eta_\infty' > \eta_s$ which remedied a serious defect in earlier models. It was shown, in particular, that a sort of decoupling of bond interaction occurs; thus η_∞' is essentially a sum of effects attained within each bond. This leads to $[\eta_\infty']$ becoming independent of N at even moderate values of N.

Internal Viscosity (IV)

The Rouse Coil and all modifications cited so far contain the implicit assumption that submolecule response giving $F^{(s)}$ is instantaneous, not limited by sluggishness of structural rearrangements within the submolecule. However, even if submolecules contain only 20 to 30 chain bonds, some finite response time for their cooperative motions can be expected. Furthermore, the presence of solvent within the submolecule provides viscous drag which slows their response further. Such lines of thought (Cerf, 1957, 1958) gave birth to the internal viscosity concept, wherein a rate-dependent force within the submolecule appears as part of $F^{(s)}$. Hence Equation (1b) is modified to contain another contribution:

$$F_2{}^{(s)} = [K_0(x_3 - 2x_2 + x_1) + F_2{}^{(iv)}] \qquad (17)$$

so $F^{(s)}$ loses its completely entropic significance. Note that linear springs are still used, yet the presence of $F^{(iv)}$ assures the prediction of nonlinear rheology (for any *HI*).

At least two formulations of $F^{(iv)}$ have been proposed, as surveyed recently by Bazua and Williams (1974):

$$\text{I.}\begin{cases} \qquad F_{x2}{}^{(iv)} = \varphi(\dot{x}_1{}^d - 2\dot{x}_2{}^d + \dot{x}_3{}^d) & (18a) \\ \text{or,}\quad \mathbf{F}_x{}^{(iv)} = \varphi\mathbf{A} \cdot \dot{\mathbf{x}}^d & (18b) \end{cases}$$

and

$$\text{II.}\begin{cases} \qquad \mathbf{F}_x{}^{(iv)} = [\mathbf{Q}^{-1T} \cdot \boldsymbol{\Phi} \cdot \mathbf{Q}^T] \cdot \dot{\mathbf{x}}^d & (19a) \\ \text{with}\quad \Phi_{pk} = \varphi(p/N)\,\delta_{pk} & (19b) \end{cases}$$

Here, $\dot{x}_i{}^d$ is deformational (elongational) velocity defined as

$$\dot{x}_i{}^d = \dot{x}_i - \dot{x}_i{}^{\text{rot}} = \dot{x}_i - (\boldsymbol{\Omega} \times \mathbf{r}_i)_x \qquad (20)$$

Evaluation of the angular rotational rate Ω_y in shear flow is also controversial. It was almost universally taken as $\gamma/2$ (Cerf, 1957, 1958; Peterlin, 1967) until recently when Cerf (1969) and Bazua and Williams (1973, 1974) showed $\Omega_y(\gamma)$ to be a decreasing function of γ. Figure 5 outlines how the molecular dynamics equations are solved, with Ω_y determined by a torque balance which is satisfied trivially in non-IV models.

Among the two $F^{(iv)}$ expressions, Equations (19a) and (19b) have been favored for fifteen years but have awkwardness in that $[\mathbf{Q}^{-1T} \cdot \boldsymbol{\Phi} \cdot \mathbf{Q}^T]$ has no simple interpretation in laboratory coordinates, and also Equation (19b) seems arbitrary in its p dependence. These disadvantages are surmounted by Equations (18a) and (18b), which were proposed originally by Cerf (1957) and later derived from submolecule dynamics by Bazua and Williams (1973). In both $F^{(iv)}$ expressions, φ is the scalar internal viscosity but it need not have the same significance in both. Molecular interpretations of φ have recently been given (Peterlin, 1972, 1973; Bazua and Williams, 1973), but as yet φ has not been evaluated from atomic data and subsequently used to predict rheological results.

All internal viscosity models have qualitatively similar advantages over other coiling-polymer models (with isotropic *HI* and linear springs). This is evident from the predictions and subsequent comparison given in Table 2. Extremely good agreement with $\eta^*(\omega)$ data is possible with either Equation (18) or (19) (Massa, Schrag, and Ferry 1971; Osaki and Schrag 1971); in this limit of linear phenomena, the nature of Ω_y is not in doubt (Bazua and Williams, 1974). The combined roles of *IV*, *S*, and isotropic *HI* have been displayed for $\eta^*(\omega)$ by Peterlin and Reinhold (1967). Previous efforts to fit nonlinear measurements with parameters obtained from η^* did not meet with the same quantitative success (Zimmerman and Williams, 1972). As yet, it is uncertain whether these deficiencies can be rectified by the newly proposed form of $\Omega_y(\gamma)$.

To summarize, the *IV* advantages lie in (1) its inherent ability to predict nonlinear phenomena from a quasi-linear model while utilizing the same $\lambda_p(h, \epsilon)$ as other models, and (2) predictions of qualitatively correct γ-dependence and ω-dependence in σ_{21} and N_1, including viscometric limits η_∞ and η_∞'. Partially offsetting are the disadvantages that (1′) predictions are now sensitive to the choice of N, (2′) still another parameter is added, φ, and (3′) uncertainties exist about the true nature of φ and the handling of various approximations needed to obtain Ω. A number of basic objections have been raised by Booij and van Wiechen (1970) in the context of the Dumbbell, $N = 1$, for which it is easier to demonstrate that $\Omega \neq \gamma/2$ as well as other fallibilities of the model.

OTHER LINEAR STRUCTURES

The rest of the right-hand branch of Figure 2 identifies other linear geometries which have been used to model polymer shape, besides the random coil. The rigid rod-like extreme has sometimes been studied because it permits simplification of mathematical problems arising with coils. Most of these models, however, have been introduced because many macromolecules exhibit shapes and properties significantly different from coils.

The general trend of Figure 2, reading from the extreme right toward the center, is increasing the stiffness of the polymer. This endows the molecule with a larger domain in space, restricts its ability to respond to rapid mechanical perturbations, and thus leads to predictions of larger viscosity and longer relaxation times. In many ways, the result of incorporating chain rigidity is phenomenologically similar to introducing *IV* into the perfectly flexible Rouse Coil. Detailed references are charted in Figure 2.

Rigid Linear Polymers (Rods)

A number of complex biopolymers are sufficiently extended to resemble rods more closely than coils (Tanford, 1961), and many recently synthesized high-performance plastics consist of consecutive rigid planar rings which endow them also with rodlike character. In recent years, however, the rheological motivation for studying the Rigid Rod has been to clarify basic questions about macromolecular modeling while avoiding purely mathematical difficulties which confuse results with the Rouse-Zimm Coil. A major physical advantage is that the ultimate nonlinear spring is employed, and no spurious dimensional infinities can be predicted.

The Rigid Rod, like the Rouse Coil, can be conceived as a chain of N links and $N + 1$ frictional centers, but now

TABLE 2. PREDICTIONS OF INTERNAL VISCOSITY MODELS
(Isotropic *HI*, $S = \theta, K = K_0$)
$\tau_p' = \tau_p\,(1 + \phi_p\nu_p/f)^*$

Mode	Property
Small-amplitude oscillation	$\eta^*(\omega) = \begin{cases}\eta'(\omega) \\ -i(''(\omega)\end{cases} = \begin{cases}\left[\eta_s + \nu kT \sum_{p=1}^{N} \dfrac{\tau_p\,[1 + \omega^2\tau_p'\,(\tau_p' - \tau_p)]}{1 + (\omega\tau_p')^2}\right] \\ -i\left[\nu kT \sum_{p=1}^{N} \dfrac{\omega\tau_p^2}{1 + (\omega\tau_p')^2}\right]\end{cases}$
Steady shear	$\Omega = \frac{1}{2}\gamma$: Nonsymmetric stress tensor, use $\eta \equiv \sigma_{21}/\gamma$. $\eta(\gamma) = \eta_s + \nu kT \sum_{p=1}^{N} \tau_p \left[\dfrac{1 + \gamma^2\,(\tau_p' - \tau_p)^2}{1 + \gamma^2\,(\tau_p' - \tau_p)\,(\tau_p' + \tau_p)}\right]$ $\zeta(\gamma) = 2\nu kT \sum_{p=1}^{N} \left[\dfrac{\tau_p^2}{1 + \gamma^2\,(\tau_p' - \tau_p)\,(\tau_p' + \tau_p)}\right]$. $\beta(\gamma) = 0$
	$\Omega(\gamma)$ from torque balance: Symmetric stress tensor. $\eta(\gamma) = \eta_s + \nu kT \sum_{p=1}^{N} \tau_p \left[1 - \left(1 - \dfrac{2\Omega}{\gamma}\right)\dfrac{(\tau_p' - \tau_p)}{\tau_p'}\right]$ $\zeta(\gamma) = 2\nu kT \sum_{p=1}^{N} \left[\dfrac{\tau_p^2}{1 + 4\Omega\,(\tau_p' - \tau_p)\,[\Omega(\tau_p' - \tau_p) + \gamma\tau_p]}\right]$ $\beta(\gamma) = 0$
Steady elongation	$\bar{\eta}(\kappa) = 3\eta_s + 3\nu kT \sum_{p=1}^{N} \dfrac{\tau_p}{(1 - 2\kappa\tau_p)\,(1 + \kappa\tau_p)}$

Summary

	Rouse-Zimm	IV
γ-dependent η?	No	Yes, with $\eta_\infty > \eta_s$
γ-dependent ζ?	No	Yes, perhaps with ζ_∞
High-frequency $\eta'(\omega)$ limit with $\eta_\infty' > \eta_s$?	No	Yes

* Using Equations (18ab), $\phi_p = \phi\mu_p$ so that $\tau_p' = \tau_p\,(1 + \phi\lambda_p/f)$.
Using Equations (19ab), $\phi_p = \phi(p/N)$ and thus $\tau_p' = \tau_p\,(1 + p\phi\nu_p/Nf)$.

TABLE 3. EFFECT OF EXACT OSEEN *HI* FOR THE RIGID DUMBBELL

Viscosity*	$\dfrac{\eta_0\,(h_d) - \eta_s}{\eta_0\,(0) - \eta_s} = \dfrac{1 - \frac{8}{5}h_d}{(1 - h_d)\,(1 - 2h_d)}$
N_1	$\dfrac{\zeta_0\,(h_d)}{\zeta_0\,(0)} = \dfrac{1}{(1 - h_d)^2}$
N_2	$\dfrac{\beta\,(h_d)}{\zeta_0\,(0)} = \dfrac{\frac{2}{7}h_d}{(1 - h_d)^2\,(1 - 2h_d)}$
Relaxation time	$\dfrac{\tau\,(h_d)}{\tau\,(0)} = \dfrac{1}{1 - h_d}$

* $h_d = h_d^* = f/8\pi\eta_s l$.

the links are taken to be unjointed and without any springiness. Because the array is one-dimensional there are considerable simplifications of a purely geometrical nature, and the absence of springiness means that bead positions are assumed fixed a distance l apart* so $|\mathbf{r}| = L = Nl$ is also a fixed and not a statistically average quantity like the Rouse Coil equivalents $<r^2>^{1/2}$ and $b = <l_i>$.

Among the earliest molecular rheology results showing dispersive effects (ω- or γ-dependent properties) were those with the Rigid Rod. Kirkwood and Auer (1951) predicted $\eta^*(\omega)$, and Kirkwood and Plock (1956) obtained low-order $\eta(\gamma)$, while employing exact *HI* through $\mathbf{T}_{ik}$ of Equation (10a). Only one relaxation time arises even for a rod of N segments connecting $N + 1$ beads:

$$\tau_{\text{rod}} = \frac{fl^2}{72\,(1 + \Gamma_N)\,kT} \cdot N\,(N + 1)(N + 2) \quad (21a)$$

where Γ_N is a *HI* factor analogous to h which does not scale simply with N. In the limit of large N, Equation (21a) becomes approximately

$$\tau_{\text{rod}} = \frac{\pi\eta_s L^3}{18\,kT \ln N} \quad (21b)$$

Only quadratic γ-effects in $\eta(\gamma)$ were computed and normal stresses were not calculated by Kirkwood et al.

Kotaka (1959) also used the full form of *HI*, but displayed low-order steady shear effects for both shear and normal stresses. The presence of *HI* was revealed by a comparison of the stresses with and without it, and for the first time $N_2(\gamma) \sim \beta(\gamma)$ was predicted to be nonzero. Its sign was opposite that of $N_1 \sim \zeta$, with $|\beta_0/\zeta_0| = 1/7$. These predictions are in excellent agreement with many recent measurements on nondilute solutions of supposedly flexible-coil polymers (Miller and Christiansen, 1972; Olabisi and Williams, 1972; Tanner, 1973). Even today, no

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* Estimating l for the rod or b for the coil is, like choosing N, somewhat arbitrary. Ullman (1969) showed that rod theory can be formulated to contain the chain diameter and not l.

comparable normal stress results have emerged from theories of coiling linear polymers although possibly the approach of Fixman (1966a, b) would suffice because of its rigorous treatment of *HI*.

A number of studies of the Rigid Dumbbell ($N = 1$)[*] have appeared since the initial one by Kirkwood and Plock (1956) which predicted non-Newtonian viscosity. Prager (1957) developed independently an expression for $\boldsymbol{\sigma}_p$ and was able to show $\beta = 0$ in shear flow with $HI = 0$. Similar results emerged from Giesekus' more general study (1962) when the beads were spherical; interestingly, the use of rigid ellipsoidal beads gave $\beta_0 \neq 0$ and $\beta_0/\zeta_0 \leqq 0$, with magnitude of β_0 determined by ellipsoid geometry. An extremely complete discussion of dumbbell rheology, with strong emphasis on the Rigid Dumbbell, is the treatise of Bird, Warner, and Evans (1971). They review the diffusion equation, derive a new expression for $\boldsymbol{\sigma}_p$, and predict rheological behavior for steady and oscillatory shear and for elongational flow, including start-up and relaxation phenomena. The reader is referred to this work for other references, including a number by Bird's group, but it suits our discussion here to review their results concerning the effect of exact (nonisotropic) *HI* which emerges with relative ease for Rigid Dumbbells.

The polymer-induced stress tensor is

$$\boldsymbol{\sigma}_p = \frac{\nu f}{4J(1-2h_d)} \frac{\mathfrak{d}}{\mathfrak{d}t} <\mathbf{RR}> + \frac{h_d}{1-2h_d} \left\{ \frac{3\nu kT}{Jl^2} <\mathbf{RR}> - \nu kT \boldsymbol{\delta} \right\} \tag{22}$$

where $h_d = f/8\pi\eta_s l$ for the dumbbell differs from h of the coil but appears clearly in Equation (10a). This compact result shows the role of *HI* explicitly, as well as the fact that $h_d < 1/2$ no matter what estimate for f is taken. Perturbation expressions for $\eta(\gamma)$, $\zeta(\gamma)$, and $\beta(\gamma)$, equivalent to those obtained earlier by Giesekus (1962), were presented along with the corresponding complete curves obtained numerically by Stewart and Sorensen (1971). Some of these revealing results are given in Table 3, showing that η_0 and ζ_0 are increased by *HI* and that $\beta_0 \neq 0$ arises directly from *HI*, with limits defined by $0 \leqq \beta_0/\zeta_0 \leqq 0.43$. Moreover, as the complete curves show, *HI* enhances shear sensitivity and causes dispersion effects to become prominent at lower γ and ω; this is basically a consequence of the increased $\tau_{\text{rod}}(h_d)$ shown in Table 3.

Bird, Warner, and Evans list several ways in which the Rigid Dumbbell property predictions are superior to those of the Elastic Dumbbell. A source of concern, however, is that the Rigid Dumbbell differs from Kotoka's Rigid Rod with respect to the sign of β/ζ; this ratio is positive for Dumbbells and negative for Rods, when both incorporate the exact *HI* of Equation (10a). No normal stress data exist for dilute solutions of rodlike polymers, so the correctness of these two predictions cannot be verified. However, the source of the difference may lie with the choice of N itself. The generalized *HI* factor Γ_N [see Equation (21a)] changes sign as N increases, and since Dumbbells predict $\beta \sim h_d \sim \Gamma_1$, it appears that the sign of β is linked to the sign of Γ_N. This implies a warning about generalizing on the basis of Dumbbells, but equally important to note is the fact that Equation (10a) is itself defective when applied to points close together as when N is large.

Intermediate Linear Forms

Somewhere between the perfectly rigid rod and the perfectly flexible random coil lies the truth about real linear polymers of all kinds (see Figure 2). Of course, modeling of such reality becomes increasingly complex and returns may not seem to engineers to be proportionate to effort in these directions. Nevertheless, a number of novel concepts of polymer modeling have been introduced and are worth discussing qualitatively; many of the rheological predictions are due to Hearst and coworkers.

For *rigid* forms (or, those unperturbed by γ) of *any* segment distribution for linear chains with cylindrical symmetry, Hearst (1964) developed a formalism of great generality. It is capable of handling *HI* exactly and characterizes the geometry in terms of a persistence length (PL)[†] and the diameter a of the bead. From this model, Hearst extracted η_0 for the worm-like coil (spherically symmetric but structurally expanded because of PL) and also $\eta^*(\omega)$ for the weakly bending (that is, curved) rod. The worm-like coil reduced, as the limiting case for no stiffness, to the random coil in the nondraining limit. In the opposite direction, the weakly bending rod could easily be taken to the limit of the absolutely straight Rigid Rod. Subsequently, low-order $\eta(\gamma)$ was also obtained for the Rigid Rod and random coil limits by Hearst and Tagami (1965).

A totally new approach to polymer modeling was developed by Harris and Hearst (1966). They proposed that the molecule be conceived as a bendable elastic rod with a bending force constant α so polymer flexibility or stiffness could be characterized by both transverse and longitudinal elasticity. A variational procedure invoked the mathematical constraint of holding the average contour length $<L>$ constant, thereby introducing a Lagrange multiplier β which was shown to be dynamically equivalent to K of earlier models. Because β was a function of PL, which in turn was related to α, both the worm-like coil and rigid rod shapes were attainable as limits.

Predictions of $\eta^*(\omega)$ were carried out by Hearst, Harris, and Beals (1966) for conditions of $HI = 0$ and $\epsilon = 0$, so these results could be compared directly with the Rouse Coil in the limit of zero stiffness. Differences appeared, in that $\eta'(\omega)$ was crossed by $\eta''(\omega)$ in all cases (never predicted by flexible-coil models) and high-ω dependence was also dissimilar (although no $[\eta_\infty]$ appeared). Predictions for the Rigid Rod limit showed peculiar inflections, which might be traceable to artifacts of the variational procedure which permitted L to sustain fluctuations δL which turned out not to be small in the rigid limit.

Returning to limiting properties, Hearst, Beals, and Harris (1968) computed $[\eta_0]$ for cases of varying *HI* (through the isotropic *HI* approximation) and ϵ for molecular stiffness ranging from the Rigid Rod to the flexible coil. Thus $[\eta_0]$ was found to be a remarkably more complicated function of M than previously believed, highly nonlinear, especially for shorter chains. Hearst et al. used these results to point out hazards in the traditional fashion of identifying a θ solvent by the condition $[\eta_0] \sim M^{1/2}$ for

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[*] When *HI* is neglected, there is little point to executing rheological calculations for rigid rods with N large since all results can be predictably scaled up from the dumbbell case. For example, note that Equation (21a) can then be written

$$\tau_{\text{rod}} = \frac{f_{\text{rod}} L^2}{72kT} \left(\frac{N+2}{N} \right) \cdots\cdots\cdots\; \Gamma_N = 0 \tag{21c}$$

using $L = Nl$ and $f_{\text{rod}} = f.\,(N+1)$ because the total viscous drag on the rigid rod is proportional to the number of beads. Thus values of τ_{rod} ($\Gamma = 0$) are nearly independent of the choice of N and scale easily from the dumbbell case $N = 1$. Note that Equation (21c) is much different from the result of correct *HI* calculation, Equation (21b). When $\Gamma_N \neq 0$, there are no simple scale-up relationships, for τ_{rod} or other properties, from the $N = 1$ case.

[†] The PL concept, widely used in the physics of stiff chains (Yamakawa, 1971) is employed to describe the tendency of chain backbone units to persist in a direction given them by preceding units. Clearly the PL is directly applicable even at the atomic level, and its introduction replaces the submolecule which is conceived as having infinite directional flexibility.

a modest range of M.

Finally, nonlinear steady shear effects were obtained by Noda and Hearst (1971) for both the bending-rod model and the bead-spring model after they resolved the earlier problem of δL fluctuations. They imposed the condition of absolutely constant contour length L, which could be achieved only by allowing the spring coefficients to become nonlinear. Simple implicit equations for $K/K_0 \equiv X$ and $(\beta/\alpha)/(\beta_0/\alpha_0)$—designated Y for the coil and Z for the rod forms—were obtained for θ solvents, in a fashion insensitive to the draining condition. Conveniently enough, $[\eta(\gamma)]/[\eta_0]$ was given by $1/X(\gamma)$, $1/Y(\gamma)$, and $1/Z(\gamma)$ for these three cases, and computations were presented for intermediate cases of molecule stiffness. The effect of increasing stiffness was very similar to that of increasing φ in the IV coil models and also to reducing chain length in the finite-length coil models, with non-Newtonian relative viscosity becoming apparent at lower γ and descending more rapidly. Comparisons with data were successful for moderately stiff polymers, but failed to be quantitative for highly flexible molecules, presumably because of the inexact HI treatment.

Normal stress was also computed by Noda and Hearst. As usual, their result $\beta = 0$ was attributed to using $<T>_0$, but they found $\zeta(\gamma) \leqq \zeta_0$ of a realistic sort. The ratio $(\sigma_{21}{}^2/N_1)_p$—sometimes identified as a modulus G for liquids, or the inverse of a compliance—was nearly insensitive to γ, in agreement with considerable data on dilute and concentrated solutions (Williams, 1968). It was γ-independent in the rod limit and also in the coil limit (about five times larger), and increased weakly with γ in s-shaped manner within this range for cases of intermediate stiffness; this, too, has been noted experimentally (Williams, 1968).

NONLINEAR STRUCTURES

The left branch of Figure 2 represents molecular or microstructural polymer models different in various topological ways from linear models. Whereas the latter all have finite cylindrical symmetry,* the nonlinear models may have no ends (rings) or multiple ends (branches) or globular superstructures which are perhaps better approximated as ellipsoids than by the details of long, convoluted, and possibly internally bonded cylinders.

Ellipsoids

These models, which resemble the gross shape of globular proteins and the envelope of shear-distorted flexible polymers, have been examined from both the hydrodynamic and statistical points of view. The former is basically nonmolecular, invoking the laws of two-phase continuum mechanics to determine the stresses in Phase 1 caused by a suspended particulate Phase 2. The physics of such systems has been elaborated by Happel and Brenner (1965), with references to most of the earlier classical works. The latter were devoted primarily to rigid bodies, and much recent effort has been directed at studying shear-deformable particles (which may in some cases be more realistic approximations to polymer domains). Among contributions of particular note are those of Goddard and Miller (1967) for suspensions of elastic solids, and Schowalter, Chaffey, and Brenner (1968) and Frankel and Acrivos (1970) for emulsions. All three derive the complete stress tensor, and normal stresses can be shown to arise from the particle deformation from spheres to shear-induced ellipsoids. Results are cast in the form of 2nd-order continuum models, similar to those generated by Oldroyd (1950), and can easily be evaluated for any rheological property.

There is, of course, no molecular information whatever in these results, but quite apart from their utility in describing two-phase continua they suggest how rheological measurements might be used to infer the gross shape, size, and ease of deformability of macromolecules. It is quite common to espouse such techniques when studying biopolymers which often have ellipsoidal structure (Tanford, 1961).

Still another point to note is that these microstructural continuum models, with particles deformed and oriented by shear, can be regarded as intermediate steps between molecular theories and recent continuum theories which imply structure through an orientation vector (director) obeying certain constitutive laws. Along this line, Allen, Kline, and Ling (1971) developed a model of noninteracting (dilute) substructures with linear director equations by which $\eta(\gamma)$, $\zeta(\gamma)$, and $\beta = -\frac{1}{2}\zeta$ are predicted. Finally, by an ad hoc process of linking Elastic Dumbbell theory with the director concept, Gordon and Schowalter (1972) obtained qualitatively realistic behavior for $\eta(\gamma)$, $\zeta(\gamma)$, and $-1 < \beta/\zeta < 0$.

The statistical (molecular) treatment of dilute ellipsoids is exemplified by the results of Scheraga (1955), who used the appropriate diffusion equation (Saito, 1951) for rigid ellipsoids of axial ratio $p = L/a$ to calculate $\eta(\gamma)$. The non-Newtonian viscosity was sensitive to p and approached a limit $[\eta_\infty]$ at high shear which also depended on p; the latter is somewhat surprising since rigid rods do not exhibit $[\eta_\infty]$. In the limit of large p, however, the elongated rigid ellipsoid makes many predictions similar to the rod, including $\eta^*(\omega)$ of similar form (Ferry, 1970) with

$$\tau_{\text{ell}} = \frac{\pi^2 \eta_s L^3}{18kT \ln p} \tag{23}$$

which is very close to Equation (21b). No normal force or other rheological predictions seem to be available for the molecular-level treatment of ellipsoids.

Chain Polymers

Molecular approaches to the general rheology of nonlinear polymer structures have been scarce, and only now is a generalized breakthrough on the horizon (Curtiss, Bird, and Hassager, 1974).

For branched polymers, the initial challenge was to predict how $[\eta_0]_b$ was reduced below the corresponding linear value $[\eta_0]_l$. Clearly, this occurs because the branched molecule has a domain size smaller than that of its linear brethren; in terms of their radius of gyration R_G (since end-to-end distance no longer has meaning), $<R_G{}^2>/<R_G{}^2>_l \equiv g < 1$. As reviewed by Yamakawa (1971), early calculations showed how g depended on the number and type of branch points; but relating η_0 to g has been much more difficult. At present, the favored theory is that $q \equiv [\eta_0]_b/[\eta_0]_l \cong g^{1/2}$ (Zimm and Kilb, 1959) for all branched molecules although this can only be defended rigorously for one branching geometry.

Actually, the dependence $\eta_0(g)$ will vary somewhat with details of branching topology. Calculations have been made for the star (✱), comb or normal (+++), and intermediate random types, with g's designated $g^{(s)}$, $g^{(n)}$, and $g^{(r)}$, respectively. For each of these it is possible to compute viscosity where the branches and segments have uniform length $(g_u{}^{(i)})$ or random length distribution $(g_r{}^{(i)})$. It is of some comfort that numerical results do not vary greatly between different topologies, within reasonable ranges of the geometrical parameters involved (Yamakawa, 1971).

As an example, consider the simplest possible case, the uniform star conformation,

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* Two ends, and a uniform average chain diameter.

$$g_u^{(s)} = (3f - 2)/f^2 \ldots\ldots f \geqq 2 \qquad (24)$$

where f = number of branches, or functionality. Solving a chain dynamics eigenvalue problem analogous to that for the linear Rouse Coil ($f = 2$) gives, for any topology,

$$[\eta_0] = \frac{N_A f b^2}{6M\eta_s} \sum_p \frac{d_p(f)}{\lambda_p(f)} \qquad (25)$$

where d_p is the degeneracy of the pth normal mode. For this particular case, $d_p = f - 1$ for odd p and $d_p = 1$ for even p. Eigenvalues are similar to those for linear polymers and scale as $\lambda_p^0 \sim (f/2)^2$ in the free-draining limit and roughly as $\lambda_p^\infty \sim (f/2)^{3/2}$ in the nondraining case. For the latter in a θ solution ($\epsilon = 0$) we get (Yamakawa)

$$q_u^{(s)}(h, \epsilon) = q_u^{(s)}(\infty, 0) = 1.88\ (f - 0.498)/f^{3/2} \qquad (26)$$

Clearly, for large f, we have $q_u^{(s)} \sim 1/f^{1/2} \sim (g_u^{(s)})^{1/2}$, which supports the earlier contention that $q = g^{1/2}$ although $q_u^{(s)}$ and $(g_u^{(s)})^{1/2}$ differ by about 10% in this case.

A novel and unifying approach to the rheology of branched polymer solutions has been proposed by Forsman (1974). Using the formalism of graph theory, he was able to show with great generality how the chain dynamics and chain distribution (that is, branching character) were related. The connection is provided through an $N \times (N + 1)$ matrix $\mathbf{G}$ whose numerical elements are simply determined by chain topology; in the linear-chain limit $\mathbf{G} \cdot \mathbf{G}^T = \mathbf{A}$. Forsman shows, for the general case, that all dynamic and distribution properties of the polymer are determined by the eigenvalues of $\mathbf{G} \cdot \mathbf{G}^T$.

Ring polymers are definitely less important as a practical matter than branched ones. Equation (25) can be applied with $d_p = 2$ for all p; λ_p are proportional to λ_p^0 for the Rouse Coil in the free-draining case but more complex for $\lambda_p(\infty)$. Bloomfield and Zimm (1966) and Fukatsu and Kurata (1968) agreed that $q_r(h, 0) = 0.65$ but disagreed with each other when $\epsilon \neq 0$. Yamakawa (1971) examines this carefully, ultimately pointing out that q_r is very insensitive to ϵ, being reduced only to 0.63 even when $\epsilon = 1/2$.

A useful aggregation of all these η_0 results—for linear, branched, and ring coiling polymers—has been proposed by Bloomfield and Sharp (1968). They pointed out that separation of HI, S, and topological factors could be approximately achieved and $[\eta_0]$ calculated from a single generalized function of h, ϵ, and $q(\infty, 0)$ [which equals 1, 0.65, and $g^{1/2}$ for the linear, ring, and branched topologies]. Their success at reproducing exact results in this way was within 5%, for $h \gtrsim 3$.

The ω-dependence of η^* for flexible branched and ring polymers is given by Table 1 predictions, with suitable attention to mode degeneracy as indicated in Equation (25). This has rarely been tested, but was recently verified for a four-branch star polymer by Osaki, Mitsuda et al. (1972). Other properties have not been explicitly presented elsewhere, but ζ_0 and $\bar{\eta}(\kappa)$ are also given by Table 1. There should be considerable interest in this, in view of the commercial importance of branched polymers and the recognized sensitivity of fluid elasticity and spinnability to chain branching.

A major advance in the general theory of polymer rheology was presented by Curtiss, Bird, and Hassager (1974) as this review was being constructed. Cast in generalized coordinates for all system particles (polymer beads and solvent molecules), this theory is based in the classical concepts of complete phase space. It can accommodate in principle all topologies, all types of submolecule forces $F^{(s)}$, and all orders of concentration effects. Thus far, it has been evaluated only for dilute solutions and for polymer models containing rather few beads with $HI = 0$. Still, a number of these results for steady shear flow are worthwhile reporting since they reveal potentially powerful generalizations about polymer structural influences.

1. *For any topology or $F^{(s)}$*. Very general but quite simple formuli are presented for η_0 and ζ_0, with proof that $\zeta_0 \geqq 0$ and also that $\beta_0 = 0$. The latter is consistent with all previous dilute-solution predictions with spherical beads for $HI = 0$ and means that $N_2 \sim \gamma^4$ in the lowest approximation for such systems.

2. *For Linear Topology.* (a) Two-bead chain ($N = 1$): The effect on $\boldsymbol{\sigma}_p$ of submolecule extensional stiffness is demonstrated by comparing predicted properties for the string ($K_0 = 0$), linear spring ($K_0 \neq 0$), and rigid rod ($K_0 = \infty$). For viscosity, the comparison is $\eta_0^{(0)} : \eta_0^{(K_0)} : \eta_0^{(\infty)} = 1 : 0.42 : 0.14$ and for normal stress $\zeta_0^{(0)} : \zeta_0^{(K_0)} : \zeta_0^{(\infty)} = 1 : 0.24 : 0.015$, all for equivalent values of length parameters $l_{\max}$, $<l^2>^{1/2} = b$, and l. Thus spring softness at low shear enhances stresses, in a fashion unrelated to the ultimate extension of the spring.

(b) Three-bead chain ($N = 2$): An opposite conclusion seems to hold for bending springs. Permitting the rigid rod to bend slightly is shown to reduce η_0 and ζ_0. Introducing lateral flexibility by allowing free rotation at the beads where rigid rods are connected also reduces these properties. From these two results, we conclude that $\boldsymbol{\sigma}_p$ is reduced as internal degrees of freedom are increased or domain size $<r^2>^{1/2}$ is decreased.

Both (a) and (b) deal with the quality of chain flexibility, with apparently differing results with respect to phenomenologically defined chain elasticity parameters. The resolution of this may require a more detailed molecular theory, as opposed to this microstructural one.

3. *For Nonlinear Topology.* (a) Planar ring with four beads: Three different conformations—one with rigid rods and angles, one with rigid rods freely jointed, and one like the last but with a spring between opposing beads—were found to have the same η_0. This shows η_0 to be insensitive to internal geometry (for rings).* However, ζ_0 is sensitive to these variations, being in the ratio 1 : 0.5 : 0.25+. Thus ζ_0 is reduced by increasing degrees of freedom, as was also concluded for linear topology.

(b) Branching, with orthogonal rigid rods (as crossed xyz axes, so $f = 6$) of varying symmetry: Viscosity was markedly lower than for a linear assembly of the same number of beads, corresponding to the smaller R_G. With the six branches of equal length, $\zeta_0 = 0$ as is apparently true for all molecules with undeformable spherical symmetry. When branching uniformity was destroyed by sliding the origin along one axis, a nonzero ζ_0 appeared. As this continued, making the molecule more lopsided and nonuniform (that is, broadening the distribution of branch length), η_0 and especially ζ_0 increased considerably.

In general, it was found for all topologies that ζ_0 is a much more sensitive indicator of polymer structure (for molecules of equal M) than is η_0.

CONCENTRATED SOLUTIONS AND MELTS

As earlier stated, the scope of this review does not permit detailed discussion of higher-order concentration effects. We shall linger only to outline some of the key concepts of modeling, pointing out how concentrated polymer systems differ qualitatively from dilute solutions (as

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* This seems analogous to the flexible-ring results cited earlier, wherein $q_r(h, \epsilon) \cong 0.64$ over all ranges of h and ϵ.

they do in regard to $M, c, W, HI, S \ldots$) although some surprising connections exist between the dilute and concentrated cases. More information is available in the reviews of Graessley (1974), Berry and Fox (1968), and Porter and Johnson (1966), and extensive coverage is provided by Ferry (1970).

Second-Order Effects

A framework for describing the lowest-order concentration complications, $\mathcal{O}(c^2)$, is well established and, as suggested by Figure 1, is rather separate from treating still higher-order effects. It is customary to represent η_0 as

$$(\eta_0 - \eta_s)/\eta_s = A_1 c + A_2 c^2 + \ldots$$
$$= [\eta_0]c + k_H[\eta_0]^2 c^2 + \ldots \qquad (27)$$

hoping that most of the dependence of A_2 on M, HI, S, etc. is accounted for within $[\eta_0]^2$. Indeed, the Huggins constant k_H is relatively insensitive to these parameters. Experimental data indicate that k_H is about 0.3 for flexible coils in good solvents and increases as $S \rightarrow \theta$; values near 1.0 have been reported for some polar systems (Gandhi and Williams, 1971; Imai, 1969; Tanford, 1961).

Frisch and Simha (1956) summarize considerable theoretical work, showing a k_H range from 2.0 (spheres) to 0.73 (rods) for rigid particles, and 0.60 for a Rouse Coil ($HI = 0, \alpha = 1$). Peterson and Fixman (1963) generated a soft-sphere model from a strictly hydrodynamic analysis, obtaining $k_H = 0.69 + h(z)$ where z is an excluded-volume parameter related to $\alpha(S)$. This gives a rigid-sphere limit of 0.69, $k_H(\theta) = 0.90$, and higher for other $k_H(S)$. All their predictions are too high in general and fail to reflect the S-dependence cited above.

An elaborate coil analysis with intermolecular HI approximations was presented by Imai (1969), using a pair correlation function $g(\mathbf{R})$ to average the interactions between approaching molecules. His result was $k_H = k_H(\theta)/\alpha^4 + zC_0/\alpha^5$, both $k_H(\theta)$ and C_0 being computable functions not yet reported. Interestingly, $k_H(\theta)$ was predicted to be independent of M, T, and S, but data show that S affects $k_H(\theta)$ when polar interactions are involved (Gandhi and Williams).

Non-Newtonian viscosity and normal stresses have simply not been considered by analogous theoretical means although both the Imai and the Peterson-Fixman formulations could be so extended. It is obvious that nonlinear phenomena will be enhanced by interpolymer contacts since these provide additional mechanisms for coil deformation. The ω-dependence of $\eta^*(\omega, c)$ predicted by Wang and Zimm (1974a, b) was realistic for a range of $c[\eta_0]$ including $\mathcal{O}(c^2)$, but $\eta_0(c)$ could not be found; this model is discussed below. Other than the aforementioned treatment of rigid bodies, no consideration has been made of molecular structure variations or chain stiffness (although the latter can be thought to increase when $\alpha > 1$).

Higher Effects

Equation (27) shows that higher concentration effects become important when $c[\eta_0] > 1$, but power-series expansions then become useless. Exponential forms such as the empirical Martin equation

$$\frac{\eta_0 - \eta_s}{c\eta_s} = [\eta_0] \exp\left(k_M [\eta_0]\, c\right) \qquad (28)$$ [*]

are more nearly correct, but are also known to fail in various ways (Gandhi and Williams). Far more useful are the reduced-variable correlations developed by Simha and coworkers (1967; 1971) which are guided by theoretical concepts. In this concentration regime, very little is gained by using models of dense suspensions—that is, taking the polymer to be dynamically equivalent to a solid sphere or ellipsoid—because such modeling fails to account for important intramolecular draining effects and for overlap and possible entanglement of the coils.

In Figure 1, the continuum between $\mathcal{O}(c^2)$ and the melt ($c = \rho$) indicates that similar theoretical treatments apply throughout this range. An important change from the semi-dilute regime is the possibility of intermolecular entanglements E. Although their fundamental nature has been the subject of fervid debate, there is no alternative way of explaining all the rheological changes which occur when the molecules are close enough (high c) and long enough (high M) to be geometrically capable of entwining with each other in a loose network-like sense throughout the system.

The onset of E-behavior is relatively gradual in the c variable but very abrupt with M. Both empirical and theoretical rules suggest that a critical condition of coil overlap will occur when products such as cM (Berry and Fox, 1968) or $cM^{1/2}$ (Cornet, 1965) reach a certain magnitude, say $(cM)_E = \rho M_c$ where M_c identifies the critical weight for polymer melts. When this happens, the rheology enters another regime wherein relaxation spectra clearly have two sets of characteristic times (Ferry); stresses are tremendously enhanced and highly sensitive to c and M.

Once established, entanglements and other forms of association serve to retard large-scale motions of neighboring molecules. The time required to disentangle, to permit flow, must greatly exceed $\tau_1{}^0$ of the isolated single molecule itself, and thus the spectrum of relaxation times τ_p is broadened at the long-time end.[†] Hence rheological phenomena sensitive to the slower relaxations—for example, $\eta(\gamma)$ and $\eta^*(\omega)$ at low γ and ω—are much affected by such associations. This explains the sudden transition from $\eta_0 \sim M$ to $\eta_0 \sim M^{3.4}$ when $(cM)_E$ is exceeded, although high-γ and high-ω properties are less affected. As something of an oversimplification, one can view entangled systems as consisting of two response regimes, (1) response of the entanglements in the network, important at low γ, ω and long times [that is, sensitivity to the enhanced $\tau_p(E)$], and (2) response of the network chains between entanglements, important at high γ, ω and short times (that is, sensitivity to normal chain dynamics in the absence of excluded volume effects and governed by $\tau_p{}^0$).

The rheological role of solvent in concentrated solutions is still not completely elucidated. Certainly solvent acts as a lubricant to polymer-polymer friction and $\eta(c)$ is proportional to η_s to a first approximation, but this does not tell the whole story. Solvent thermodynamics S is also important, as emphasized by Gandhi and Williams (1971). Poor solvents can enhance $\eta_0(c)$ considerably, such that $\eta_0(\theta) > \eta_0(S)$ by more than an order of magnitude for many systems (at least, for $c < 0.5$ g/ml). This is accompanied by rapid increase of $\eta_0(c)$ at anomalously low values of cM, well below ρM_c, so that the usual E-onset predictions would be seriously in error (Gandhi and Williams, 1972).

All of this can be explained by postulating increased polymer-polymer friction as solvent molecules are excluded locally by unfavorable thermodynamics. Thus the apparent E-onset arises at low c because interpolymer associations (actually, non-E) can exist, and true entanglements resist

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[*] Through c^2-effects, the identification $k_M = k_H$ can be made, but higher-order effects are better described when k_M is a free parameter.

[†] The spectrum, plotted as the number of τ_p's between τ and $\tau + d\tau$ versus τ, varies as $\tau^{-1/2}$ for the Rouse Coil [from Equation (7d)] until $\tau_1{}^0$ is reached. When entanglements occur, this spectrum develops a broad shoulder extending to much higher τ, its width proportional roughly to $M^{2.4}$ (Ferry, 1970).

separation for similar thermodynamic reasons. Note that S acts here in a direction opposite to the dilute solution case, for which $\eta_0(S) \gtreqqless \eta_0(\theta)$ because of increased domain size with increasing α or ϵ.

Actually, α and ϵ are not directly useful parameters at very high concentrations; it is found that $\epsilon \rightarrow 0$ and $\alpha \rightarrow 1$ (Fixman and Peterson, 1964) as c increases in any solvent. Polymer coils suffer excluded volume effects equally from their neighbors and themselves, thus nullifying solvent-induced expansion and permitting them to interpenetrate each other with Gaussian spatial distributions at equilibrium (Flory, 1953, pp. 426, 602). Despite this, characteristic solvent/polymer parameters are useful for correlating data for a considerable concentration range, perhaps over 50%. For a given solvent/polymer pair, a master curve may be constructed in the form $(\eta_0 - \eta_s)/\eta_s$ or $(\eta_0 - \eta_s)/\eta_s\, c\, [\eta_0]$ versus cM^b, where b will vary with the polymer-solvent combination but is always close to the Mark-Houwink exponent a in $[\eta_0] = KM^a$ (Simha et al., 1967, 1971; Gandhi and Williams, 1971).* What is still unpredictable a priori is the shape of either of these master curves.

Stress Predictions

Representation of the stress tensor for these complex systems can be given in principle, but evaluation of it tends to rely heavily on physical intuition and ad hoc assumptions. One example is the elegant work of Curtiss, Bird, and Hassager (1974), who develop a very general but unwieldy form for $\boldsymbol{\sigma}$ which can only be made tractable (even for dilute solutions) with a multitude of approximations. In what was apparently the first general derivation, Fixman (1965) summed the separate momentum-conservation equations of solvent and all polymer segments, to obtain

$$\boldsymbol{\sigma}_p = \nu \sum_{i=0}^{N} \left\langle \mathbf{r}_i \frac{\partial U}{\partial \mathbf{r}_i} \right\rangle + \frac{1}{2}\nu^2 \left\langle \mathbf{R} \frac{\partial V}{\partial \mathbf{R}} \right\rangle \qquad (29)$$

where $U(\nu)$ and $V(\nu)$ are intersegmental and intermolecular potentials, $\mathbf{r}_i$ defines a segment position relative to the center of mass of its own molecule, and $\mathbf{R}$ is the vector between centers of polymer pairs. This is exact for all $c = \nu N_A$, not just through ν^2, with the $< >$-averages performed with $\psi(\mathbf{r}_i, \nu)$ and $g(\mathbf{R}, \nu)$.

The actual use of Equation (29) requires that U, V, ψ, and g be known, and therein lies the difficulty. For dilute solutions, it reduces to the linear term in ν and $U^{(1)}$ can be identified as the net thermodynamic potential $kT \ln (\psi^{(1)}/\psi_0^{(1)})$. Thus, through Equation (3), the dilute-solution $\boldsymbol{\sigma}_p^{(1)}$ of Equation (7) is recovered. However, for higher ν, the single-molecule functions ψ and U are more complex and, in addition, the molecular-pair functions $g(\mathbf{R})$ and V are also needed.

Nonentanglement Models

For high c, Williams (1966, 1967a, b) neglected the first term in Equation (29) and proposed a non-E model for the second term which employed a limiting form for g. This in turn led to evaluation of V and subsequent predictions for $\eta(\gamma)$, $\zeta(\gamma)$, and $\beta(\gamma)$ which had some sensitivity to S and predicted correctly several realistic features of concentrated solutions, for example, $\eta_0(c, M)$ being a function of $cM^{5/8}$ and $\tau_1(c, M) \sim \eta_0/c^2$ rather than the dilute-solution $\tau_1^0(c, M) \sim (\eta_0 - \eta_s)M/c$. However, it failed to model the intermolecular friction coefficient adequately [even for the range $cM < (cM)_E$ for which it was intended] and was found not to be quantitatively useful in that form† (Gandhi and Williams, 1971).

Very similar concepts were being explored independently by Imai (1966) and Chikahisa (1964). Different approximations were taken in evaluating the friction coefficient and $g(\mathbf{R})$, with the results

$$\eta_0 = [C_1M + C_2M^{3/2}] \exp (C_3M^{1/2}) \ldots . \text{Imai} \qquad (30)$$

$$\eta_0 = [C_1'M + C_2'M^3] \ldots . \text{Chikahisa} \qquad (31)$$

both of which are quite realistic in their M-dependence. It is notable that all three workers avoided explicit recognition of entanglements, yet obtained plausible results for η_0. The latter two papers ignored normal stresses and shear dependence, however.

The new Wang and Zimm (1974a) model represents a refined evaluation of the intramolecular term alone. *HI* within the coil is shown to be modified by the presence of beads from penetrating coils. The ν^2-term in Equation (29) and the possibility of entanglements are ignored, which limits the range of application, and explicit $\boldsymbol{\sigma}(c)$ predictions cannot be made. However, very useful results appear for dispersion phenomena (see section on Relaxation Times).

Entanglement Models

Detailed E-modeling has had considerable success in approximating the $\eta_0 \sim M^{3.4}$ behavior often reported for linear chains. Eyring, Ree, and Harai (1958) used a statistical treatment of a slalom disentanglement motion around fixed points, to obtain $\eta_0 \sim M^{10/3}$ when $M > M_c$ and $\eta_0 \sim M^{4/3}$ when $M < M_c$.

Graessley (1965, 1967) examined the dynamics of pulling one string through a loop of another, arriving at $\eta_0 \sim (cM)^{7/2}$ for $cM > (cM)_E$ and $\eta_0 \sim cM$ for lesser cM. A key link with single-molecule properties was recognition that the time needed to establish an entanglement is of the order of $\tau_1^0(c)$ in the given viscous environment. This led to a very realistic $\eta(\gamma)$ prediction although no η_∞ was evident.

By identifying normal stresses as mechanisms of energy storage, Graessley justified an analogy to solid state elasticity and was thereby able to obtain N_1 without using a tensor model at all. This yielded $\zeta \sim \eta^2/M^2$, hence $\zeta_0 \sim M^5$†† and γ-dependence as $\zeta \sim \eta^2(\gamma)$.‡ The energy analogy imposed $\beta = 0$, but ζ_0 was shown to be predictable to the proper order of magnitude from knowing only c, M, M_E, and η_0.

Another model based on the local kinetics of entanglement was proposed by Meister (1971), who discussed the capture of a passing polymer molecule by an unexplicit process of the proper rate [characterized, again, by $\tau_1(c)$].

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* To an approximation, the three solvent parameters cited here are related by: $a = 1/2 + (3/2)\,\epsilon$ and $\alpha = M^{\epsilon/2}$.

† An algebraic error is propagated through two papers from an early point. The function V in Equation (21) of Williams (1966) and Equation (9) of Williams (1967b) should have a net coefficient of z^2 which reads $(1 + m^2)$ rather than $(1 + 4m^2)$. This should affect $\eta(\gamma)$ very little, but will probably alter the prediction that $\zeta_0 \sim \gamma^4$ and perhaps also that $\beta(\gamma)$ changes sign.

†† Normal stresses are much more sensitive to molecular weight and weight distribution than are shear stresses (see comments on Curtiss et al. above). For dilute solutions $\zeta_0 \sim \nu\, \tau_1^2 \sim \dfrac{c}{M} \left[\dfrac{(\eta_0 - \eta_s)M}{cRT} \right]^2$ which becomes in the limit $\zeta_0 \sim cM[\eta_0]^2$; since $[\eta_0] \sim M^a$ with $0.5 \leqq a < 0.8$, the dilute prediction is $\zeta_0^{\mathrm{dil}} \sim M^{1+2a}$ and at most $\zeta_0^{\mathrm{dil}} \sim M^{2.6}$. For concentrated solutions, use of the same formulation with $(\eta_0 - \eta_s) \approx \eta_0 \sim M^{3.5}$ gives $\zeta_0 \sim M^8$, but this seems too strong a dependence. Using the high-concentration behavior $\tau_1 \sim \eta_0/c^2$ gives $\zeta_0 \sim M^6$, which is to be compared with the Graessley prediction $\zeta_0 \sim M^5$.

‡ This result says that the liquid steady shear modulus $G \equiv \sigma_{12}^2/N_1$ should be independent of γ, very similar to dilute-solution predictions for flexible coils made by Williams (1965) for the constant-η_0, ζ_0 bead models and by Noda and Hearst (1970) for the variable-η, ζ bending rod model. That this is very nearly so has been amply verified by experiment.

This analysis, which had excellent success in predicting many steady and transient stress properties, was cast in the context of an integral expression for $\boldsymbol{\sigma}$ such as is popular in continuum mechanics formulations. His model and dozens of others stem from the pioneering work of Lodge (1956), who proposed that a molecular theory for entangled polymer liquids could be developed from integral models formerly used to express stresses in (crosslinked) rubber elasticity. The general strategy for doing this is reviewed by Lodge (1964).

Such integral models are in a form which makes a direct connection with the phenomenological theory of linear viscoelasticity (Ferry, 1970), but have often suffered from gaps in their connection with molecular characteristics. The Meister model is an improvement in this regard, and so is the highly detailed transient-network theory of Chompff and Druiser (1966) which converts the network dynamics into that of an equivalent set of Rouse Coils. The reader is referred to the current review by Graessley (1974) for more discussion of entanglement network theories.

Relaxation Times

Before concluding the survey of concentrated solution concepts, it is desirable to elaborate on the nature of τ_p. For some engineering applications, this in itself is the desired quantity rather than properties such as ζ characteristic of a constrained flow pattern.

As the volume fraction of polymer domains[*] increases, the domains eventually contact each other and begin to overlap. Even at rather low $c[\eta_0]$, rheological properties deviate from dilute-solution Zimm conditions—represented by $\tau_p(h \to \infty)$—and approach Rouse-like predictions, $\tau_p(h = 0)$. This conversion can be accomplished at relatively low concentrations, say $c[\eta_0] \geqq 3$, and thereafter a surprisingly good approximation is

$$\tau_p(c, M) \cong \tau_1{}^R(c, M)/p^2 = \left[\frac{6}{\pi^2}\,\frac{(\eta_0 - \eta_s)M}{cRT}\right]\frac{1}{p^2} \tag{32}$$

where the measured $\eta_0(c, M)$ is employed. This experimental result can be rationalized by two arguments. First, the real $(\eta_0 - \eta_s)$ rather than $[\eta]c\eta_s$ should be used to eliminate f from dilute-solution theory because it represents the concentrated-solution environment more realistically. Second, the Rouse spectrum arises because the free-draining case is now reasonable; solvent should flow through the polymer because it finds no advantage in flowing around the domain of one coil when it would be equally impeded by a universe of many coils.

This behavior is quantitatively described by the recent model of Wang and Zimm (1974a) for nondilute solutions. An approximate treatment of HI within a coil penetrated by beads from neighboring molecules led to a modified interaction tensor. That is, Equation (10b) was replaced by

$$<\mathbf{T}_{ik}>_0 = \frac{1}{6\pi\eta_s}\left\langle\frac{e^{-|\mathbf{r}_i - \mathbf{r}_k|/L_s}}{|\mathbf{r}_i - \mathbf{r}_k|}\right\rangle \boldsymbol{\delta} \tag{33}$$

where the shielding length L_s—defined in terms of c, f, and η_s—measures the accumulated effect of the foreign beads. Although L_s was shown to depend on $c[\eta_0]$, ignorance of the exact $L_s(c)$ behavior prevented prediction of $\eta_0(c)$. However, the $\tau_p(h, c)$ spectrum was found to change from Zimm-like $\tau_p(\infty, c)$ to Rouse-like $\tau_p(0, c)$ as given by Equation (32). Wang and Zimm (1974b) also presented new data on $\eta^*(\omega, c)/\eta_0(c)$ which, together with their model, indicated that this Zimm-Rouse transition is not due to true free-draining behavior but rather to the intramolecular HI range being limited by the screening effect of other chains.

However, Graessley, Hazelton, and Lindeman (1967) and later Graessley and Segal (1969) analyzed systematic experimental differences from Equation (32) for large c and M and empirically identified a relation for the longest relaxation time

$$\tau_1(c, M) = \tau_1{}^R(c, M)/(1 + m_1E) = \tau_0/m_0 \tag{34a}$$[†]

for linear polymers, where now the entanglement concept is made quantitative by defining

$$E \equiv cM/(cM)_E \tag{34b}$$

At high E, Equation (34a) predicts $\tau_1 \sim \eta_0/c^2$ as Williams (1967a) obtained from a picture without entanglements at all. Another complication in the useful but simplistic Equation (32), recently pointed out by Osaki, Mitsuda, et al., (1972), is that the c-dependence of $\tau_1{}^R$ is not reflected in the higher $\tau_p(c)$ which remain much less affected by c.

Molecular Structure

Nearly all the theories of polymer rheology in concentrated systems are confined in their details to coiling, flexible, linear molecules. Almost the only exception is Bueche's prediction (1964) for branched polymers that $\eta_{0b}/\eta_{0l} = g^{7/2}$, a much stronger dependence of η_0 on g than exhibited by dilute solutions. Experimental data have been slow in testing this, with many contradictory reports (Berry and Fox, 1968) even about the relative magnitudes of η_{0b} and η_{0l} for the same M. The principal complication seems to be whether the branches themselves are long enough and close enough to participate in intermolecular entanglements. If they are not, then the Bueche model applies; if they are, then even $\eta_{0b} > \eta_{0l}$ is a possibility.

For example, Graessley and Prentice (1968) tested solutions up to $c = 0.22$ g/ml and found $\eta_{0b}/\eta_{0l} \sim g^{7/2}$ with a proportionality factor approaching 1.0 in the most viscous media. However, a study carried to $c = 0.35$ g/ml (Graessley and Shinbach, 1974) showed strong enhancement of η_{0b}/η_{0l}, the interpretation being that molecules were now close enough so branches of weight M_b could entangle. This tendency is predictable from the correlation of Berry and Fox (1968),

$$\ln\left(\frac{\eta_{0b}}{g^{7/2}\,\eta_{0l}}\right) = (1 - g)(2.16 + 0.85w)\left(\frac{cM_b}{\rho M_c} - 1\right) \tag{35}$$

for $cM_b/\rho M_c > 1$; w is the weight fraction of the molecule in the backbone, with value 0 for stars, $0 < w < 1$ for combs, and 1.0 for linear polymers.

In a very careful experimental study on melts, Mendelson, Bowles, and Finger (1970) determined that $\eta^*(M)$ and $\eta_0(M)$ data on branched polyethylene could be correlated with the parameter $g\bar{M}_W$, with $\eta_{0b} \sim (g\bar{M}_W)^{6.6}$. Because the familiar $\eta_{0l} \sim \bar{M}_W{}^{3.5}$ was obtained for linear polymers, it became clear that the two topological types could not be treated similarly in entangled systems.[††] This

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[*] Proportional to $c[\eta_0]$.

[†] τ_0 is a characteristic time in the Graessley model (1965), and the parameters for these systems obeyed $m_0 \geqq 1 > m_1 > 0.1$.

[††] This generalization is supported also by the finding that $\tau_1(c, M)$ in solutions of branched polymers does not behave in accord with Equation (34a); it seems to be less sensitive to E (Graessley and Prentice, 1968; Graessley and Shinbach, 1974). In view of successes of the unifying topological treatments of branched and linear polymers in dilute solution, this is something of a surprise.

also explained earlier ambiguities of relative magnitude since clearly the two curves (η_0 vs. $g\overline{M}_W$ for branched and linear polymers) can cross. However, the fact that the temperature-dependence of η_{0b} and η_{0l} differ for polyethylene (Graessley and Shinbach, 1974) means that η_{0b}/η_{0l} depends on T in this case.

APPLICATIONS

It is hoped that the engineer reading this survey now possesses sufficient familiarity with basic modeling concepts and the sometimes obscure terminology to feel comfortable in reading further about the molecular rheology of polymers. In addition to this facility, a number of more direct results should arise.

1. Connections between molecular and continuum modeling should be apparent. There is a clear molecular role for the time derivative $\mathfrak{d}/\mathfrak{d}t$, first proposed for continuum mechanics, in the dilute-solution Dumbbell theory. In certain cases, there are direct term-by-term equivalences between molecular and continuum models (Bird, Warner, and Evans, 1971; Lodge and Wu, 1971; Bird, 1972; Armstrong, 1974). The kernel functions of continuum time-integral models can often be explained in terms of concentrated-solution theory for transient molecular networks (Lodge, 1964, 1970; Graessley, 1974).

2. More directly utilitarian is the selection of realistic relaxation times, in particular the longest one $\tau_1(c, M)$ which dominates material response. From τ_1, one can often evaluate the importance of fluid elasticity in engineering flows. The rule of thumb is that elasticity effects may give rise to anomalous behavior when the Deborah number becomes significant: $N_D \equiv \tau_1/\tau_{\mathrm{loc}} \rightarrow 1$, where τ_{loc} is a time characteristic of local deformations imposed on the fluid by the process.

One rather successful application of this has been predicting the onset of drag reduction in the turbulent flow of very dilute polymer solutions (Hershey and Zakin, 1967), by identifying $\tau_{\mathrm{loc}}^{-1} \sim \gamma_w$. The general N_D criterion also leads qualitatively to expressions very similar to others proposed for predicting onset of various laminar-flow processing instabilities.[*] For example, a recent survey (Boyer, 1970) has presented an empirical correlation characterizing melt fracture for capillary extrusion of polystyrene: $\sigma_{21,w}\overline{M}_W = \text{const.} = (\eta \overline{M}_W)\gamma_w$. Clearly, this is equivalent to setting $\tau_1^R/\tau_{\mathrm{loc}} = \text{const.}$ if again $\tau_{\mathrm{loc}}^{-1} \sim \gamma_w$ through local geometrical relationships. Bagley (1961) suggested that fracture would occur at a certain value of recoverable shear strain s_R stored in a flowing elastic fluid. (This concept was reviewed by Tanner (1969) and incorporated into his integral model.) Since $s_R = \sigma_{21}/G$ and $G = \sigma^2{}_{21}/N_1$, this critical value s_{Rc} corresponds to

$$s_{Rc} = \left(\frac{N_1}{\sigma_{21}}\right)_{\mathrm{loc}} \cong \left.\frac{(\nu\, kT \sum_p \tau_p{}^2)\ \gamma^2}{(\nu\, kT \sum_p \tau_p)\ \gamma}\right|_{\mathrm{loc}} \cong \tau_1\, \gamma_{\mathrm{loc}} \tag{34}$$

and the utility of knowing τ_1 and N_D is borne out again.

In a more general sense, Metzner and co-workers have shown the importance of N_D in anticipating anomalies in numerous engineering processes. Using various continuum models, they have discussed the role of N_D in flows into converging channels, through packed beds, and around submerged objects (Metzner and White, 1965; Metzner, White, and Denn, 1966a; Metzner and Asterita, 1967) as well as scale-up problems in general (Metzner, White, and Denn, 1966a, b). Problems inevitably arise in the sense of the fluid becoming solid-like when N_D becomes large.

In estimating τ_1, however, it is good to remember that the effects of c, M, and especially S vary considerably as concentration increases.

3. In addition to needs for τ_1 alone, it is clear that the entire spectrum τ_p serves even more purposes. If this can be estimated from the λ_p spectrum and guesses for b and f, an independent assessment of η_0, ζ_0, and other properties can be made (see Table 1). More frequently, this sequence is inverted and the magnitude of τ_p's is estimated from η_0 and the λ_p's. This is the objective of continuum mechanicians whose models may contain τ_p, to which numerical values can be assigned by this procedure. This permits a realistic continuum description of dispersion effects. For example, Spriggs (1965) and Spriggs and Bird (1965) obtained $\eta(\gamma)$, $\zeta(\gamma)$, and $\eta^*(\omega)$ from embedding the spectra of Rouse ($\tau_p{}^0 \cong \tau_1{}^R/p^2$), Zimm ($\tau_p{}^z \simeq \tau_1{}^R/p^{3/2}$) and empirical modifications ($\tau_p = \tau_1{}^R/p^n$) within their generalized Maxwell models. This approach has been used also by Meister and many others, with considerable success.

Points 1, 2, and 3 make connections between molecular and continuum rheology, bolstering the latter on two fronts—giving an alternate physical interpretation of established mathematical orchestrations, and providing methods for estimating τ-spectra which appear in continuum models. This is important because engineering flow problems can be solved much more conveniently with continuum mechanics than by molecular-level mechanics.

4. It is sometimes possible to call on explicit molecular predictions of important physical properties. This is particularly true for dispersion phenomena such as $\eta(\gamma)/\eta_0$ and $\eta^*(\omega)/\eta_0$, less so for $\zeta(\gamma)/\zeta_0$ and $\overline{\eta}(\kappa)/\eta_0$ which are not as extensively investigated. For some molecular models η^*/η_0 is available but η/η_0 is not, in which case it is usually legitimate to use the approximation $\eta \approx |\eta^*|$ at equal values of γ and ω. This has been established experimentally for many polymer systems (for example, Cox and Merz, 1958) and has been justified also with Rigid Dumbbell theory in the free-draining limit by Stewart and Sorensen (1972). The analogy ultimately breaks down, of course, because $\eta_\infty > \eta_\infty'$.

Prediction of the reference parameters (η_0, ζ_0) is achieved rather successfully for dilute solutions, but far less so in more concentrated systems. Methods for doing this are reviewed elsewhere (Kurata and Stockmayer, 1963; Ferry, 1970; Graessley, 1974). Parameters W, HI, and S are "real," whereas K and IV are more nebulous concepts and probably related to details of W and S. It appears that S is a more important variable in connection with γ-dependent properties than originally surmised, since —for example—dilute-solution departures from θ conditions have much more influence (in the presence of HI) than even the most accurately assessed role of HI alone in a solvent (Fixman, 1966b).

5. Very high-γ behavior, such as leads to the limit $\eta_\infty > \eta_s$, cannot yet be predicted with confidence but success may be on the horizon. Several mechanisms can be invoked to show $\eta \rightarrow \eta_\infty$—nonlinear springs arising from limited chain length, IV representing dissipative mechanisms within the submolecule, a limiting alignment of extended molecules in the shear direction, etc.—but quantitatively correct predictions have still to be made for coiling polymers. The simplest available model is clearly the IV one, which converts the lumped molecular parameter φ to the phenomenological η_∞; a priori prediction of φ and matters

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[*] Alternate methods of predicting drag reduction are those based on a length-scale ratio (Virk et al., 1967) involving $<r^2>^{1/2}$, and on energy-absorbing capability (Walsh, 1967) involving normal stresses. Evaluation of all these requires the molecular theory of dilute polymer solutions.

of internal consistency are still being explored. However, Fixman's (1974) method of treating bond constraints may hold more promise for the future.

Finally, what are the frontiers of molecular polymer rheology? In the author's opinion, the next decade should be characterized by advances along the variables *W* and *c*. For *W*, this means exploring both the gross molecular superstructure (branches, rings, etc.) as is being done now by Curtiss, Bird, and Hassager and by Forsman (1974), and also the details of localized (bond level) chain structure as begun recently by Bazua and Williams (1973), Peterlin (1973)—both in the *IV* context—and by Fixman (1974) and by Fixman and Kovac (1974a, b) in a more general way. The ultimate result of these investigations would be elimination of dependency on the submolecule concept altogether, with rheological properties calculable from truly molecular parameters. This would also introduce the essentials of nonlinear springs *K* in a completely natural way and lead to prediction of chain responses at high shear which produce η_∞.

For the *c* variable, there is the need to model intermolecular *HI* [along lines explored by Imai (1961) and by Wang and Zimm (1974a, b)] and *S*-affected entanglement phenomena more accurately. Some of the newer topological machinery brought to bear on *W*-effects could conceivably find use also in modeling *E* dynamics. In general, methods for making a priori predictions of properties at high concentration must be improved considerably, even in the absence of *S* and *W* complications, since this is the regime of greatest relevance to industrial practice.

NOTATION

a = bead radius, cm
$\mathbf{A}$, A = matrix in Equation (1c); coefficients in Equation (27)
b = average submolecule length, cm
c = concentration of polymer, g/cm^3
d = degeneracy (repeatedness); Equation (25)
D = diffusion coefficient of bead (kT/f), cm^2/s
E = entanglement density; also concept
f = friction coefficient of bead
f = functionality (number of ends) of branched polymer
F, $F_2^{(X)}$, $\mathbf{F}_y$ = force; of type X exerted on bead 2; supervector composed of y-components of forces on all $N + 1$ beads
g = $<R_G^2>/<R_G^2>_l$, used with nonlinear polymers
$g(\mathbf{R})$ = pair correlation function for molecules
G = elastic shear modulus for liquids (σ_{21}^2/N_1), dynes/cm^2
$\mathbf{G}$ = matrix in Forsman's graph-theory explanation
h = hydrodynamic interaction coefficient used by Zimm and by Tschoegl; see Equation (11a)
h^* = $h/N^{1/2}$
h = function in Peterson-Fixman model for $<r^2>$
HI = hydrodynamic interaction concept
IV = internal viscosity concept
J = Jacobian of coordinate transformation
k = Boltzmann's constant
k_X = Huggins $(X = H)$ or Martin $(X = M)$ coefficient
K, K_0 = submolecule spring coefficient and its low-deformation limit, dynes/cm
l = interbead spacing for rigid rod, cm
L = contour length of linear chain, cm
L_s = shielding length in Wang-Zimm model, cm
m = $\tau\gamma$ in Williams (1966, 1967) model
m_1, m_2 = coefficients in Graessley model, Equation (33a)
M, $\overline{M}_W$, M_0 = molecular weight; weight-average M; weight associated with one backbone atom in linear chain
$\mathbf{M}$ = $\boldsymbol{\Lambda}^0 = (\mathbf{Q}^T \cdot \mathbf{A} \cdot \mathbf{Q})$, diagonal matrix
n = number of backbone bonds per submolecule
N = number of submolecules in polymer molecule
$\mathbf{N}$ = $(\mathbf{Q}^{-1} \cdot (\boldsymbol{\delta} + \mathbf{T}) \cdot \mathbf{Q}^{-1T})$, diagonal matrix
N_A = Avogadro's number
N_D = Deborah number $(\tau_1/\tau_{\text{loc}})$
N_1 = first normal stress function, $(\sigma_{11} - \sigma_{22})$, dynes/cm^2
N_2 = second normal stress function, $(\sigma_{22} - \sigma_{33})$, dynes/cm^2
P = powerlaw slope of $\log \eta$ vs. $\log \gamma$
p = axial ratio of ellipsoid
q = $[\eta_0]/[\eta_0]_l$, used with nonlinear polymers
$\mathbf{Q}$ = coordinate transformation matrix
$\mathbf{r}$, $<r^2>^{1/2}$ = end-to-end vector of linear polymer and its average magnitude, cm
$\mathbf{R}$ = interbead vector for dumbbell model; also interpolymer vector in concentrated solutions, cm
R_G = radius of gyration, cm
s_R = recoverable shear strain in liquids
S = solvent thermodynamic variable; also concept
t = time, s
T = temperature, deg
$\mathbf{T}_{ik}$ = Oseen interaction tensor, Equations (10+), cm/dyne s
u = normal coordinate from x, cm
U = interbead potential, erg/cm^3
v = normal coordinate from y, cm; also, volume fraction
V = interpolymer potential, erg/cm^3
$\tilde{V}$ = molar volume, cm^3/mol
w = normal coordinate from z, cm
W = structure variable (concept)
x = coordinate of flow direction, cm
X = $K(\gamma)/K_0$
y = coordinate normal to streamlines, cm
Y = $(\beta/\alpha)/(\beta/\alpha)_0$ for random coil, Noda-Hearst
z = neutral coordinate, cm; also, an excluded volume parameter
Z = $(\beta/\alpha)/(\beta/\alpha)_0$ for rigid rod, Noda-Hearst

Greek Letters

α = coil expansion factor due to solvent effects, Equation (14a); also, transverse elastic coefficient of chain in Harris-Hearst model, dynes/cm
β = second normal stress coefficient (N_2/γ^2), dynes s^2/cm^2; also, longitudinal elastic coefficient of chain in Harris-Hearst model, dynes/cm
γ = velocity gradient in shear flow, s^{-1}
Γ_N = hydrodynamic interaction factor in rod model, for N segments $(N + 1$ beads$)$
$\boldsymbol{\delta}$ = unit tensor
$\boldsymbol{\Delta}$ = strain rate tensor, $(\nabla \mathbf{v}) + (\nabla \mathbf{v})^T$, s^{-1}
ϵ = an excluded volume parameter, Equation (15)
ζ = first normal stress coefficient (N_1/γ^2) dynes s^2/cm^2
η = viscosity, g/cm s
θ = theta conditions of solvent and temperature
κ = tensile strain rate, s^{-1}
λ = eigenvalue of $\boldsymbol{\Lambda}$
$\boldsymbol{\Lambda}$ = diagonal matrix $(\mathbf{Q}^{-1} \cdot (\boldsymbol{\delta} + \mathbf{T}) \cdot \mathbf{A} \cdot \mathbf{Q})$
μ = eigenvalue of $\mathbf{M}$
ν = eigenvalue of $\mathbf{N}$; also, density of polymer molecules, cm^{-3}
ρ = density of bulk polymer, g/cm^3
$\boldsymbol{\sigma}$, σ_{ij} = stress tensor and its ij-component, dynes/cm^2
τ = relaxation time, s

ϕ = internal viscosity coefficient, cm/dyne s
$\boldsymbol{\Phi}$ = internal viscosity matrix, Equation (19), cm/dyne s
Φ = Flory-Fox coefficient [Equation (13)], g-mole
ψ = distribution function for beads, cm^{-3}
ω = angular frequency of oscillating shear, s^{-1}
Ω = angular velocity of coil rotation, s^{-1}

Subscripts

b = branched chain
c = critical value, at which rheological properties change abruptly
d = dumbbell
H = Huggins
ij = tensor component
i, j, k = bead index
l = linear chain
M = Martin
p = index of normal mode and its eigenvalue; also, designates polymer contribution
s = solvent
w = wall conditions
W = weight-averaged
∞ = limit for high strain rates
0 = limit for low strain rates

Superscripts

B = Brownian
iv = internal viscosity
0 = case of $h = 0$ (free-draining)
∞ = case of $h \to \infty$ (non-draining)
R = Rouse
s = submolecule
$*$ = complex number
$'$, $''$ = real and imaginary parts of $(\ )^*$

Other Symbols

$< >$ = ensemble average, Equation (5)
$[\ ]$ = intrinsic property, $\lim\limits_{c \to 0} \left(\dfrac{\mathcal{P} - \mathcal{P}_s}{c\mathcal{P}_s} \right)$ cm^3/g where $\mathcal{P}$ is any property
$(\bar{\ })$ = tensile-strain parameter
$\mathfrak{D}/\mathfrak{D}t$ = convected derivative, Equation (9b), s^{-1}

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THE AUTHOR

Mike Williams, born and bred in Wisconsin, took the convenient but fortunate educational route through Madison. The B.S. led to a summer job at Los Alamos which stimulated his interest in rheology, and he returned to Madison to study continuum modeling with Bob Bird. After getting his Ph.D. in 1964, Mike spent a year at the University of Oregon with Marshall Fixman and focused on molecular rheology. Since arriving at Berkeley, he has tried to synthesize these two research interests and has also dabbled in drag reduction, block copolymer thermodynamics, and flow-induced blood damage.

His extracurricular activities include a ridiculous degree of participation in baseball and tennis and a fannish interest in all sports, but most of his outside time is engaged in career guidance work with high school students.

JOURNAL REVIEW

Porous-Electrode Theory with Battery Applications

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Developments in the theory of flooded porous electrodes are reviewed with regard to simulation of primary and secondary batteries, adsorption of ions and double-layer charging, and flow-through electrochemical reactors.

Porous electrodes have numerous industrial applications primarily because they promote intimate contact of the electrode material with the solution and possibly a gaseous phase. Specific factors are as follows:

1. The intrinsic rate of the heterogeneous electrochemical reaction may be slow. A porous electrode can compensate for this by providing a large interfacial area per unit volume (for example, 10^4 cm^{-1}).
2. Double-layer adsorption constitutes the basis for novel separation processes involving cycling of the electrode potential. Just as in conventional fluid-solid adsorption, a high specific interfacial area is desirable.
3. Important reactants may be stored in the solution in close proximity to the electrode surface by means of porous electrodes. This permits sustained high-rate discharge of the lead-acid cell.
4. A dilute contaminant can be removed effectively with a flow-through porous electrode. The proximity of the flowing stream to the electrode surface is again important.
5. Similar arguments apply to nonconducting reactants of low solubility. Then another solid phase (as in batteries) or a gas phase (as in fuel cells) may be incorporated into the system, or the reactants may be dissolved and forced through a porous electrode.
6. The compactness of porous electrodes can reduce the ohmic potential drop by reducing the distance through which current must flow. This has obvious advantages in reducing the losses in batteries and fuel cells. It may also permit operation without side reactions by providing potential control for the desired process.

If porous electrodes were trivially different from plane electrodes, there would be no motivation for their separate study. But here inherent complications arise because of the intimate contact of electrode and solution—the ohmic potential drop and the mass transfer occur both in series and in parallel with the electrode processes, with no way to separate them. One needs to develop an intuitive feeling for how and why the electrode processes occur nonuniformly through the depth of the electrode. Finally, we seek methods for designing a porous electrode for a particular application in such a way as to maximize the efficiency.

Electrodes with two fluid phases are excluded from consideration here. Gas electrodes for fuel cells are reviewed