h_A = enthalpy per pound of A stream
h_B = enthalpy per pound of B stream
h_L = enthalpy per pound of L stream
h_W = enthalpy per pound of W stream.
H_W = enthalpy per pound of water vapor
L_n = aqueous solution leaving stage n evaporator
L_n' = aqueous solution in the boiling mass of stage n evaporator
N = total number of stages
q_m = makeup heat
S_m = makeup steam
T_b = temperature of a boiling mass
T_c = temperature of a condensing mass
α = absorbent used to raise condensation temperature
β = boiling-point depressor

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Concentrated Polymer Solution: Part II.

Dependence of Viscosity and Relaxation Time on Concentration and Molecular Weight

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A previously presented molecular theory for non-Newtonian viscosity in moderately concentrated polymer solutions is extended here to a specific consideration of the influence of solute concentration c and molecular weight M on the limiting viscosity η_0 and the relaxation time λ. Estimates of the M,c dependence of several intermediate functions are necessary including that of Kirkwood's friction coefficient. The prediction $\eta_0 \sim (cM^{0.625})^2$ is in good agreement with the empirical observation that η_0 is a function of the parameter $cM^{0.68}$, but is inadequate for extremes of M and c. Plausibility arguments are advanced to suggest $\lambda \sim \eta_0 c^{-2}$ rather than $\lambda_{\text{dil.}} \sim M\eta_0 c^{-1}$ predicted by dilute solution theory and widely accepted. This would explain the utility of the factor c^2 used in recent rheological correlations, and would reconcile some conflicting reports of $\lambda(M)$ measurements.

A rather general formulation for the stress tensor in solutions of flexible polymers has been given by Fixman (*6*). This was discussed recently by Williams (*20*), who attempted to specialize it to the case of concentrated solutions by emphasizing intermolecular force effects. Williams introduced several mathematically tractable and physically plausible approximations for the intermediate functions needed to calculate the stress during shear flow.

One of these functions was $\nu(\mathbf{R})$, the spatial distribution of a polymer's segments with respect to its center ($\mathbf{R} = 0$). When a shear-dependent approximation to ν was inserted into the general intermolecular potential expression (*7*)

$$V(\mathbf{r}) = A \int \nu(\mathbf{R})\, \nu(\mathbf{r} + \mathbf{R})\, d\mathbf{R} \qquad (1)$$

where $\mathbf{r}$ is the vector between polymer molecular centers and A is a characteristic constant, there was obtained

$$V = \frac{A}{\sqrt{1 + \lambda^2\gamma^2}} \left(\frac{B}{2\pi}\right)^{3/2} \exp\left\{\frac{-B}{2(1 + \lambda^2\gamma^2)} \left[(x - \lambda\gamma z)^2 + (1 + \lambda^2\gamma^2)y^2 + (1 + 3\lambda^2\gamma^2)z^2\right]\right\} \qquad (2)$$

with $\gamma = dv_x/dx$ as the shear rate, λ an unspecified time constant, and B effectively a scale factor for a polymer molecule.

Since it was assumed (*6*) that potentials were pairwise additive, the stresses could be calculated by computing certain averages with respect to the pair correlation function $g(\mathbf{r})$. For a state of shear, $g(\mathbf{r})$ can be perturbed as (*15*)

$$g = g_o(r) \left[1 + \frac{\xi\gamma}{kT} \cdot Cf(r) \cdot h(\theta, \phi) + \ldots\right] \qquad (3)$$

where ξ is Kirkwood's friction coefficient (in polymer pair space) and C is a constant arising from the integration performed to determine $f(r)$. It was then necessary to choose a second function $g_o(r)$, the radial distribution function. Because polymer molecular domains overlap in concentrated solutions, the value $g_o \cong 1$ was used (*2, 8*); physically this means that the liquid contains a uniform density of polymer molecules. The form of $f(r)$ in Equation (3) was also determined through application of $g_o = 1$.

When these expressions for $V(r)$ and $g(r)$ were introduced into the integrals describing stress, the non-Newtonian viscosity η was evaluated directly in terms of well-known functions. Results were written as

$$\frac{\eta - \eta_s}{\eta_o - \eta_s} = S(\lambda\gamma) = 1 - \frac{9}{14}\lambda^2\gamma^2 \ldots \qquad (4)$$

$$\eta_o = \frac{n^2 AB^{3/2}\xi C}{15\sqrt{2\pi}\,kT} + \eta_s \tag{5}$$

where $n = cN/M$ is the number concentration of polymer molecules and η_s is solvent viscosity.

Because of the large number of approximations which led to Equations (4) and (5), it was suggested (*20*) that η be considered a function of two *empirical* parameters λ and η_o (or, rather than η_o, the group $AB^{3/2}\xi C$). However, an inquiry into the dependence of η on polymer concentration c and the molecular weight M requires closer examination of all parameters.

INTRAMOLECULAR SEGMENT DISTRIBUTION

In Equation (2), B is a measure of effective molecular size, and was originally introduced through $\nu(\mathbf{R})$. Here and elsewhere we employ the notion that polymer conformations and dimensions in concentrated solutions resemble closely the random walk picture. We are guided in this by the similarities between concentrated solutions and melts, and between molecular conformations in melts and θ solutions (*1, 9*, p. 426) for which random walk statistics are excellent approximations. Thus we shall estimate B in terms of the molecular end-to-end distance L

$$B = \frac{3}{2L^2} = \frac{3}{2Nb^2} \sim \frac{1}{M} \tag{6}$$

as found from a Gaussian segment distribution for a single molecule of N segments, each of length b (*9*).

STRENGTH OF INTERMOLECULAR FORCES

The key parameter here is A, which we presume is insensitive to shear. Fixman, in an equilibrium theory, finds (*7*)

$$A = V_p{}^2 \frac{d^2\epsilon}{dv_p{}^2} \tag{7}$$

where V_p is the partial molecular volume of a polymer molecule and $\epsilon(v_p)$ is the *Helmholtz* free energy density of mixing polymer segments with solvent to a bulk volume fraction v_p. To be consistent with many previous assumptions intended to confine this application to high concentrations (for example, $g_o \doteq 1$), we choose a Flory-Huggin form for ϵ (*7 to 9, 13*):

$$\epsilon = \frac{kT}{V_s}(1 - v_p)\,[\ln(1 - v_p) + \chi v_p] \tag{8}$$

$$\frac{d^2\epsilon}{dv_p{}^2} = \frac{kT}{V_s}F(v_p) \tag{9a}$$

$$F(v_p) \equiv \frac{1}{(1 - v_p)} - 2\chi + 2(1 - 2v_p)\chi' + v_p(1 - v_p)\chi'' \tag{9b}$$

Equation (8) was originally derived with the assumption that polymer concentration (v_p) was sufficiently high that the total segment density—to which *many* molecules may contribute in a given region—is nearly uniform throughout the solution (*9*). A more recent consideration of segment distributions in concentrated solutions has justified this assumption and has set limits for its application (*7, 8*). Flory estimates that this condition may be achieved at concentrations of a few percent when $M \gtrsim 10^5$, and Fixman's calculations for several polymers are in substantial agreement.

The magnitude of $F(v_p)$ in Equation (9*b*) is difficult to predict. The Flory constant χ, a measure of solute-solvent interactions, is not really constant, but is found experimentally to be a rather strong function of v_p for many polymer-solvent combinations (*9, 11, 13*); this explains the presence of its derivatives χ' and χ'' in Equation (9). It is only through χ (and V_s) that the character of the solvent enters significantly into the present work, so we cannot treat it lightly. Since we have ignored direct solvent-polymer interactions thus far, using a Gaussian function for $\nu(\mathbf{R})$, it would seem consistent to use $\chi = 1/2$ here (identically so under θ conditions). This appears a fair numerical approximation for modest concentrations even under non-θ conditions, providing dipole forces are unimportant (*9*). However, $\chi'(v_p)$ may easily be large and govern the magnitude of ϵ''. Several rough calculations by the author, based on published data (*9, 11*) show that $F(v_p) > 0$ for a variety of materials and concentrations of present interest.

Although the concentration dependence of ϵ'', and thus A, is difficult to estimate here, it is important to note that ϵ and χ are usually independent of M. Thus A depends on M only through V_p, which we take proportional to the contour length of the polymer molecule:

$$V_p \sim M \tag{10}$$

as one would do for a length of rubber hose. Finally, we have from Equation (7)

$$A(M, c) \sim M^2 \cdot F(c) \tag{11}$$

where c appears because $v_p \approx c/\rho$ with ρ being the total mass density of the solution.

FRICTION COEFFICIENT

For ξ we should appeal to Kirkwood's original theory of the friction coefficient (*14*), which incorporates information about molecular interactions. However, an exact evaluation of ξ by this means would be extremely difficult and unnecessarily intricate for present purposes. Instead, we shall adopt the simpler estimate suggested by Kirkwood and co-workers (*15*):

$$\xi^2 = \frac{4\pi c}{3}\int_0^\infty g_o \frac{d}{dr}\left(r^2 \frac{dV}{dr}\right) dr \tag{12}$$

This formula, with its limitations, is discussed most thoroughly by Rice and Gray (*18*), and has been used with fair success in calculating the viscosity of simple liquids such as argon (*15*), for which V is spherically symmetric and independent of shear.* We shall employ Equation (12) by evaluating V at $\gamma = 0$ and thus avoid some of the defects of $V(\gamma)$ as given by Equation (2).

Immediately one inconsistency appears; if we proceed by using $g_o \doteq 1$ as previously assumed, a direct integration of Equation (12) gives $\xi^2 = 0$. This, of course, follows from $g_o \doteq$ constant and reflects no inadequacy of Equation (12). An integration by parts leads to

$$\xi^2 = -\frac{4\pi c}{3}\int_0^\infty r^2 \frac{dV_o}{dr}\cdot\frac{dg_o}{dr}\,dr \tag{13}$$

which forces us to recognize the need for a higher approximation to g_o, which is r dependent, at least for small r.

We shall introduce at this point the results of Fixman and Peterson (*8*). In the mathematical limit of $g_o(r) \cong 1$, they obtained an analytic solution of the linearized Born-

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* It is provocative to consider ξ being shear dependent, as is suggested by Equation (12) if $V = V(\gamma)$. Kirkwood discounted this for most liquid systems (*14*), but it seems a possibility for very soft and easily deformed molecules. If so, calculations of the shear dependency of stress would have to be reformulated entirely. Furthermore, ξ might assume tensor character, a concept not too unreasonable in view of the established anisotropy of stress in some flowing liquids.

Green-Kirkwood integro-differential equation for g_o:

$$g_o(r) = 1 - \frac{p^3}{2\pi^2 n} F(pr) \qquad (14a)$$

$$F(x) = \frac{\sin x - x \cos x}{x^3} \qquad (14b)$$

$$p^2 = 2B \ln (nA/kT) \qquad (14c)$$

This is expected to be adequate for polymer concentrations in excess of that needed to fill the liquid with polymer domains (*8*), and should therefore apply when polymers overlap at all (which occurs at rather modest concentrations). Thus, from Equation (13), we find

$$\xi^2 = \frac{4}{3}\left(\frac{M}{N}\right) A \left(\frac{B}{2\pi}\right)^{5/2} \cdot J \qquad (15)$$

where J is a pure number dependent only on ln (nA/kT), which is highly insensitive to M and c. From this we may infer

$$\xi \sim M^{1/4} \cdot F^{1/2}(c) \qquad (16)$$

INTEGRATION CONSTANT C

Dimensional considerations show that the units of C are (length)^5. This suggests strongly that

$$C \sim L^5 \sim M^{5/2} \qquad (17)$$

and this contention is justified in the Appendix by means of an application of $g_o(r)$ as given in Equations (14).

VISCOSITY

We are now in a position to evaluate the behavior of $\eta_o(M, c)$. From Equation (5), with $\eta_o >> \eta_s$

$$\eta_o \sim n^2 \cdot A \cdot B^{3/2} \cdot \xi \cdot C \qquad (18)$$

Substitution of Equations (6), (11), (16), and (17) shows

$$\eta_o(M, c) \sim M^{1.25} \quad c^2 F^{1.5}(c) \qquad (19)$$

TIME CONSTANT

A time constant λ was originally introduced in the segment distribution function $\nu(\mathbf{R})$, in order to characterize gross response of molecular conformation to shear forces. It subsequently appeared in the intermolecular potential $V(\mathbf{r})$ and ultimately in the non-Newtonian viscosity, Equation (4). The present model does not, unfortunately, include a derivation of $\nu(\mathbf{R})$ and thereby relate λ to other parameters and forces in the system. However, it would seem useful to attempt an estimate of λ, presuming that the model already possesses sufficient parameters to do this. Our intention is to proceed as is commonly done in dilute-solution theory (*4, 22*). There the time constant spectrum $\{\lambda_i\}$ is characterized by $\lambda_{\max}$ and a set of eigenvalues (in i). In principle, $\lambda_{\max}$ is given in terms of ξ_o (a segmental friction factor) and b (segment length), but in practice these latter parameters are never evaluated separately. Instead, they are lumped into η_o, and $\lambda_{\max}(\xi_o, b)$ is then more simply expressed as $\lambda_{\max}(\eta_o)$. We shall in the same spirit try to reduce $\lambda(\xi, C)$ to $\lambda(\eta_o)$.

The biggest difficulty is finding a direct relationship between an *intra*molecular parameter (λ) and the *inter*molecular parameters (C, ξ). We shall proceed by observing that the influence of shear is accommodated by the group $\lambda\gamma$ in ν and V, and the group $C\xi\gamma$ in g. Thus we assert that $\lambda \sim C\xi$ and cast about for a reasonable proportionality factor. This step requires selection of a factor with dimensions of sec.^{2}/(g.)(cm.^{5}) with which to multiply $C\xi$ to yield a parameter with units of sec. Many choices are possible, but the simplest and most natural seems dictated by the combination of parameters in η_o, Equation (5). Hence we choose

$$\lambda = \delta C \xi \left(\frac{B^{3/2}}{kT}\right) \qquad (20)$$

to within an uncertain numerical factor δ, and therefore write

$$\eta_o = \left(\frac{n^2 A}{15\sqrt{2\pi}}\right) \frac{\lambda}{\delta} + \eta_s \qquad (21)$$

This can be rearranged to give

$$\lambda = 15\sqrt{2\pi}\,\delta \frac{(\eta_o - \eta_s)}{n^2 A} \qquad (22a)$$

$$= \left(\frac{15\sqrt{2\pi}\,\delta M^2 V_s}{k N^2 V_p{}^2}\right) \cdot \frac{(\eta_o - \eta_s)}{c^2 T F(c)} \qquad (22b)$$

where we have taken A from Equations (7) and (9). Equation (22*b*) might be compared with typical dilute-solution theory, such as the Rouse free-draining result (*4*):

$$\lambda_{\max} = \left(\frac{6M}{\pi^2 k N}\right) \cdot \frac{(\eta_o - \eta_s)}{cT} \qquad (23)$$

The differences between Equations (22*b*) and (23) are independent of our choice of $\xi(M, c)$ or the finer details of $g_o(M, c)$, beyond $g_o \doteq 1$.

DISCUSSION

The principal results are the identification of λ in Equation (22*b*), and the dependence of η_o on concentration and molecular weight in Equation (19). These will be discussed separately.

Viscosity

It is generally felt that at low M, a relationship such as $\eta_o(M) \sim M$ should prevail (*4, 17*). Other theories have suggested $\eta_o \sim M^{1.33}$ for somewhat different systems at low M. These, like ours, do not consider the effect of M on free volume (*17*), and such modification must be ad hoc. Our prediction, $\eta_o \sim M^{1.25}$, appears to differ from $\eta_o \sim M$ because ξ was here found to be weakly M dependent. The latter may be an artifact of the many approximations introduced, yet will be retained in the absence of theoretical justification for using $\xi \sim M^0$. It is felt that arguments pertaining to a segmental ξ_o, between segment and solvent, do not apply in polymer pair space. This philosophy will be essential when describing the observed M dependence of ξ at higher molecular weights. Indeed, it may be possible to extend the present theory to the region of $\eta_o \sim M^{3.4}$ by means of a straightforward calculation of $\xi(M)$, even without introducing the rubber-like entanglement concept which is often invoked to explain such behavior (*3, 4, 10*).* Hence Equation (19) might be considered a transitional step, showing the possibility of $\eta_o(M)$ progressing from $\sim M^1$ to $M^{1.25}$ and ultimately to $M^{3.4}$. However, results given here should definitely be considered to apply only in the absence of significant entanglement forces.

A rather curious empirical correlation has been observed for the viscosity of concentrated solutions of many polymers (*4*, p. 378). For a given solvent-solute combination, a plot of η_o vs. the combined parameter $cM^{0.68}$ appears to unify data obtained over wide ranges of c and M. For the first time a partial explanation of this can be given.

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* Chikahisa has already made an attempt in this direction (*17*). His result for high M is $\eta_o \sim M^3$, derived for bulk polymers.

Equation (19) may be rewritten

$$\eta_o \sim (cM^{0.625})^2 \cdot F^{1.5}(c) \tag{24}$$

If the concentration dependence of $F(c)$ is weak, the present model is seen to *predict* the utility of the empirical parameter $cM^{0.68}$. Arguing a posteriori, we might take the empirical results as evidence that $F(c)$ is indeed insensitive to c; examination of Equation (9) shows this is entirely possible, even if χ is strongly c dependent.

Time Constant

If we use $V_p \sim M$ and ignore a possible weak c dependence of $F(c)$ as suggested by the discussion above, Equation (22) assumes the form

$$\lambda \sim \frac{(\eta_o - \eta_s)_{\text{conc.}}}{c^2 T} \tag{25}$$

as compared with the free-draining dilute-solution prediction taken from Equation (23):

$$\lambda_{\max} = \frac{M(\eta_o - \eta_s)_{\text{dil.}}}{cT} \tag{26}$$

Two distinctions between Equations (25) and (26) are important, their c dependence and their M dependence.

First, the presence of c^2 in Equation (25) explains the success of certain non-Newtonian viscosity correlations for concentrated solutions (*3, 16, 21*), at least for modest shear rates. It has been found empirically that data for a given polymer solute can often be superimposed on a master curve when plotted as reduced viscosity η_r vs. reduced shear rate γ_r:

$$\eta_{\mathrm{r}} \equiv \eta/\eta_o \approx (\eta - \eta_s)/(\eta_o - \eta_s) \tag{27}$$

$$\gamma_r \equiv \left[\frac{(\eta_o - \eta_s)}{(\eta_o - \eta_s)_r} \cdot \frac{T_r}{T} \cdot \frac{c_r^2}{c^2}\right]\gamma \tag{28}$$

The r subscripts on the right side denote constant and arbitrary reference quantities. Examination of Equations (25) and (28) reveals that

$$\gamma_r = (\text{constant}) \cdot (\lambda\gamma) \tag{29}$$

and hence that experimental plots of η_r vs. γ_r differ from *our present prediction* of $\eta_r = S(\lambda\gamma)$ [see Equation (4)] only by an arbitrary shift of the master curve along the γ_r or $\lambda\gamma$ axis. This could not be predicted by dilute solution theory, in which $\lambda_{\max}$ varies as c^{-1}.

With regard to the influence of molecular weight, it is widely accepted (*4*) that time constants should *always* vary with molecular weight as $\lambda_i \sim M \cdot \eta_o(M)$. This belief is based partly on the heralded success of dilute solution theories themselves [see Equation (*26*)] and partly on experimental data which show that the *spectrum* of time constants shifts to higher values with an M dependence stronger than $\eta_o(M)$. The latter data, however, may not necessarily reflect the behavior of λ in concentrated solutions, but simply that of the longer λ_i which apply to intramolecular rearrangements; these λ_i may well obey Equation (26). We suggest that if the true λ could be accurately measured, it might vary as $\lambda(M) \sim \eta_o(M)$ as predicted by the present model in Equation (25).[*]

This contention is supported by some measurements on polymer melts, for which λ would seem experimentally more accessible. Tobolsky and co-workers (*19*) have shown for polyisobutylene and for polystyrene that the M dependences of λ and η_o are the same. The analogy between polymer behavior in the bulk and in concentrated solutions provides hope that the same results will be found true for solutions. The best experimental technique may require a comparison of shear stress and normal stress data at very low steady shear rates.

CONCLUSION

The previously developed model for the viscosity of concentrated polymer solutions can be used to explain several experimental observations:

1. Utility of the parameter $cM^{0.68}$ in correlating $\eta_o(M, c)$ data.
2. Need for a reduction factor of c^2 for correlating non-Newtonian viscosity data, rather than the factor of c^1 predicted by dilute solution theory.
3. Similar dependence of η_o and λ on molecular weight, reported for some bulk polymers (but apparently not for solutions as yet).[*]

Rather surprisingly it is shown to be possible to explain points 1, 2, and 3 on the basis of traditional manybody theory, without resorting to ad hoc concepts such as gel formation and entanglements which are frequently introduced (*3, 4*). An important corollary of 1 and 2 is the insensitivity of $F(c) \sim \epsilon''(c)$ to concentration. This would seem to have far-reaching implications about the thermodynamics of concentrated polymer solutions.

It should be pointed out, however, that results presented here for η_o and ξ are not adequate descriptions of the extreme phenomena (for example $\eta_o \sim c^5M^{3.4}$) observed beyond the onset of entanglement mechanisms. If the latter can be characterized in terms of a potential which is pairwise additive, some success with the present formalism seems likely.

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NOTATION

A = $V_p^2\,\epsilon''$, thermodynamic constant which determines the magnitude of intermolecular potential energy between polymers; (g.) (cm.^{5})/sec.^{2}
B = scale factor of size of a polymer molecule, as given by a Gaussian model, cm.$^{-2}$
c = polymer mass concentration, g./cc.
C = integration constant in the perturbation expression for $g(r)$, cm.^{5}
f = radial dependence of the perturbation function in $g(\mathbf{r})$, cm.$^{-3}$
F = $V_s\epsilon''/kT$, dimensionless
$\mathcal{F}$ = function defined in Equation (14*b*), dimensionless
g = pair correlation function, dimensionless
k = Boltzmann constant, (g.) (sq.cm.)/(sec.^{2}) (deg.)
L = average separation of the ends of a linear polymer molecule, cm.
M = polymer molecular weight, g./mole
n = number density of polymer molecules, cm.$^{-3}$
N = Avogardro's number, molecules mole^{-1}
p = parameter as defined in Equation (14*c*), cm.$^{-1}$
$\mathbf{r}$ = vector separation of the centers of two polymer molecules, $r = |\mathbf{r}|$, cm.
$\mathbf{R}$ = vector position, referred to the center of a polymer molecule; $R = |\mathbf{R}|$, cm.
S = function of a dimensionless shear rate $\lambda\gamma$ which governs non-Newtonian viscosity, dimensionless
T = absolute temperature, deg.

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[*] Note added in proof: These predictions were confirmed by the data of Graessly, Hazelton, and Lindeman, presented at the Society of Rheology meeting, February, 1967, at Santa Barbara. Similar results were given by O'Reilly and Prest (for melts).

[*] See previous footnote on this page.

v = volume fraction
V_i = partial molecular volume of species i; cc.
V = intermolecular potential energy between polymer molecules; (g.) (sq.cm.)/sec.^{2}
x = pr, dimensionless
z = $r\sqrt{B/2}$, dimensionless

Greek Letters

γ = dv_z/dx, shear rate in simple shear flow, sec.$^{-1}$
δ = numerical constant, unspecified, dimensionless
ϵ = Helmholtz free energy density for mixing polymer segments with solvent, g./(cm.) (sec.^{2})
ζ defined in Equation (6A), cm.$^{-2}$
η = non-Newtonian viscosity, g./(cm.) (sec.)
θ = solution in which solvent-segment interactions are *minimal* and the second virial coefficient vanishes
λ, $\lambda_{\max}$ = time constant for gross response of a polymer chain to shear perturbation and the dilute solution prediction, sec.
ν = probability density for distribution of polymer segments about their own molecule, cm.$^{-3}$
ρ = mass density of solution, g./cc.
ξ = friction coefficient between polymer molecules, g./sec.
χ = Flory's thermodynamic interaction parameter for solvent-polymer forces, dimensionless
ψ = r-dependent factor in shear perturbation of g_o, determined by Equation (2A)
ω defined in Equation (6A), dimensionless

Subscripts

i = one of many, for example, one time constant in the spectrum
o = low shear limit
p = polymer
s = solvent

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APPENDIX

Equation (3) contains the function

$$\psi_\infty = Cf(r) \tag{1A}$$

whose constant C may depend on solute concentration and molecular weight. We shall here discuss the significance of C in more detail and attempt to estimate the order of error in η_o due to the use of ψ_∞ where a more complicated function would be correct.

Actually, $\psi_\infty(r)$ is itself one limiting form of $\psi(r)$ which is determined by the differential equation (*15*):

$$\frac{d}{dr}\left(r^2 g_o \frac{d\psi}{dr}\right) - 6g_o\,\psi = r^3\frac{dg_o}{dr} \tag{2A}$$

and two boundary conditions

$$\lim_{r\to\infty} \psi = 0 \tag{3A}$$

$$\lim_{r\to 0} r^2 g_o \frac{d\psi}{dr} = 0 \tag{4A}$$

As r becomes large, the previous approximation $g_o \cong 1$ becomes exact and the solution to Equation (2A), subject to Equation (3A), is

$$\psi_\infty = \frac{C}{r^3} \tag{5A}$$

For small r, a different approximation to g_o is needed. An expansion of $g_o(r)$ from Equation (14) gives

$$\begin{aligned} g_o &= \left(1 - \frac{p^3}{6\pi^2 n}\right) + \left(\frac{p^3}{60\pi^2 n}\right) x^2 - \ldots. \\ &= \omega + \zeta r^2 \end{aligned} \tag{6A}$$

Substitution of this g_o into Equation (2A) and application of Equation (4A) admit a complete solution of the form

$$\psi_o = \frac{1}{2} r^2 + \sum_{j=2} A_j\, r^j \tag{7A}$$

if the A_j (j; ζ/ω) are properly chosen. However, it is meaningless to retain terms of order r^4 and above, in view of the prior truncation of g_o above r^2. If all these spurious terms are discarded, Equation (7A) satisfies the differential equation only if $A_2 = 0 = A_3$. Thus our low r solution is simply

$$\psi_o = \frac{1}{2} r^2 \tag{8A}$$

For an intermediate range of the variable $x \equiv pr$, $\psi(r)$ will behave differently from either ψ_o or ψ_∞. We shall not attempt to describe this behavior exactly, but will take ψ to be adequately approximated by the superposition of ψ_o and ψ_∞ as shown in Figure 1. The position at which they meet r_o determines the magnitude of C.

The assignment of r_o (or x_o) can be made only by examining how well $g_o(x)$ or $F(x)$ can be fit with two approximate functions:

$x < x_o$, approximate: $$F_o(x) = \frac{1}{3} - \frac{1}{30}x^2 \tag{9A}$$

$x > x_o$, approximate: $$F_\infty(x) = 0 \tag{10A}$$

all x, true: $$F(x) = \frac{\sin x - x\cos x}{x^3} \tag{11A}$$

Figure 2 shows $F(x)$ with a dashed line; it is seen to damp out rapidly and agree with $F_\infty = 0$ at high x. A dotted line shows F_o, which intersects F_∞ at $x = \sqrt{10} = 3.16$. This might be taken as x_o, but we have some freedom here to select a different value if the curve-fit can be improved in the x_o region. If we take $\overline{F}_o = \frac{1}{3} - \frac{2}{75}x^2$, we obtain the solid line displayed in Figure 2. It improves the fit, gives $x_o = 5/\sqrt{2}$

$= 3.53$, and moreover was chosen so that

$$\int_{x_o}^{\infty} F_\infty\, dx + \int_0^{x_o} \overline{F}_o(x)\, dx = \int_0^{\infty} F(x)\, dx \qquad (12A)$$

which appears a rational criterion. We note that ψ_o is not affected by this change.

Now, C can be evaluated from $\psi_o(r_o) = \psi_\infty(r_o)$ where $r_o = x_o/p$. The result is

$$C = \frac{1}{2}\left(\frac{3.53}{p}\right)^5 \qquad (13A)$$

and its M,c dependence is thus

$$C \sim \frac{1}{p^5} \sim \frac{1}{B^{5/2}\left(\ln \dfrac{nA}{kT}\right)^{5/2}} \overset{.}{\sim} \frac{1}{B^{5/2}} \sim M^{5/2} \qquad (14A)$$

since the logarithmic term varies only slightly as $n(M,c)$ and $A(M,c)$ change. This verifies our previous contention that $C \sim M^{5/2}$.

With improved approximations to g_o and ψ now available, it is possible to inquire as to possible errors which arose earlier (*20*) from computing η_o with $g_o = 1$ and $\psi = \psi_\infty$ throughout. The pertinent integral I involved in this calculation (*20*) may be defined by

$$AB\left(\frac{B}{2\pi}\right)^{3/2} \cdot I \equiv \int_0^{\infty} g_o \psi \cdot \left(r \frac{dV_o}{dr}\right) r^2\, dr \qquad (15A)$$

We may now approximate I by I_a, using Equations (5A), (6A), and (8A):

$$I_a = \int_0^{r_o} (\omega + \zeta r^2)\left(\frac{1}{2} r^2\right)(r^2 e^{-Br^2/2}) r^2\, dr + \int_{r_o}^{\infty} (1)\left(\frac{C}{r^3}\right)(r^2 e^{-Br^2/2}) r^2\, dr \qquad (16A)$$

Using $z \equiv r\sqrt{B/2}$, and the knowledge that $\zeta r_o^2 < \omega$, and $C = (x_o/p)^5/2$ from Equation (13A), we arrive at

$$I_a = \frac{2^{5/2}\omega}{B^{7/2}} \int_0^{z_o} z^6 e^{-z^2}\, dz + \frac{1}{2B}\left(\frac{x_o}{p}\right)^5 e^{-z_o^2} \qquad (17A)$$

The earlier results (*20*), displayed also in Equation (5), approximated I by I_∞:

$$I_\infty \equiv \int_0^{\infty} (1)\left(\frac{C}{r^3}\right)(r^2 e^{-Br^2/2}) r^2 dr = \frac{1}{2B}\left(\frac{x_o}{p}\right)^5 \qquad (18A)$$

Hence the new (and better) approximation differs from the earlier one by the fraction

$$\frac{I_\infty - I_a}{I_\infty} = 1 - e^{-z_o^2} - \frac{64\,\omega}{x_o^5}\left(\ln \frac{nA}{kT}\right)^{5/2} \int_0^{z_o} z^6 e^{-z^2}\, dz \qquad (19A)$$

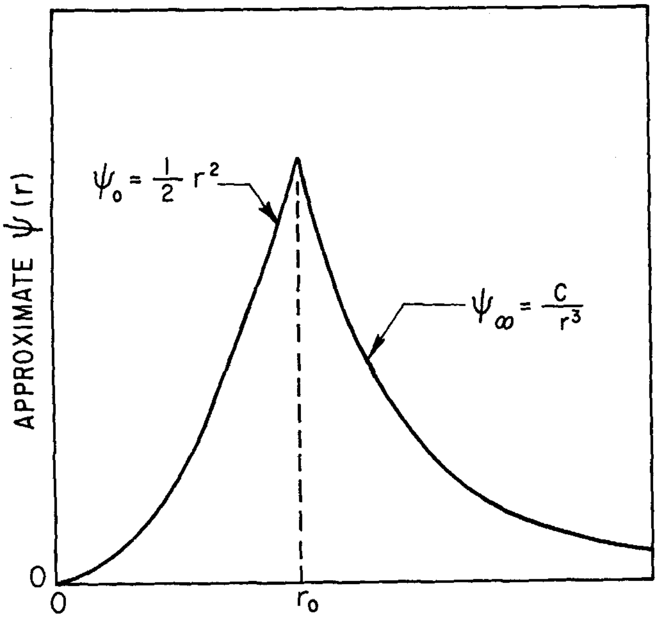

Fig. 1. Superposition of ψ_o and ψ_∞ to approximate $\psi(r)$. Magnitude of C is related to r_o, the point of intersection.

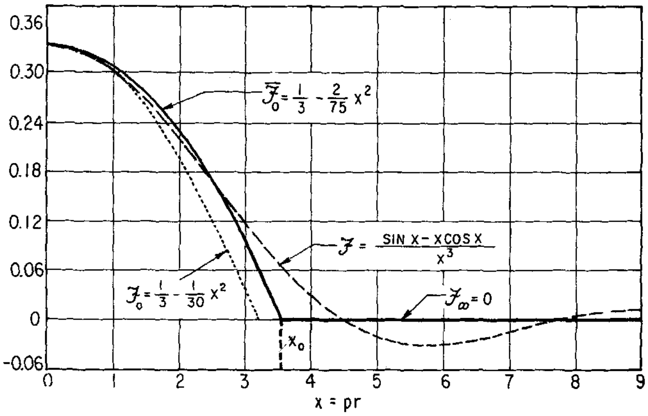

Fig. 2. Approximations to radial distribution function, $g_0 = 1 - (p^3/2\pi^2 n)\, F\,(x)$. Fixman-Peterson theory (*8*) gives F (— — — —); quadratic expansion of this gives F_0 (. . . . .); adjusted quadratic for better fit at low x gives $\overline{F}_0$ (————), which is joined at x_0 with the high x approximation F_∞.

Further progress requires numbers. We shall consider a 10% solution ($c = 0.1$ g./cc.) of a linear carbon polymer with $M = 10^6$. Typical dimensions would be $L = 1{,}000$ Å. $= 10^{-5}$ cm., $V_p = 10^{-17}$ cc., $V_s = 10^{-23}$ cc. We shall also take $F(c) = 1$, although it may range fairly widely (for example, 0.1 to 10) for different polymer-solvent systems. From these we calculate

$$\begin{aligned} n &= 6 \times 10^{16}\ \text{cm.}^{-3} \\ \left(\frac{A}{kT}\right) &= 10^{-11}\ \text{cc.} \\ \ln\left(\frac{nA}{kT}\right) &= 14.3 \\ p &= 6.55 \times 10^5\ \text{cm.}^{-1} \\ z_o &= 0.468\ (\text{with } x_o = 3.53) \\ r_o &= 540\ \text{Å.} = 5.4 \times 10^{-6}\ \text{cm.} \\ \omega &= 0.92 \\ \epsilon &= 3.4 \times 10^9\ \text{cm.}^{-2} \end{aligned} \qquad (20A)$$

These figures verify that $\omega > \zeta r_o^2$ and moreover obey the two criteria cited for validity of the $g_o(r)$ theory in concentrated solutions (*8*):

$$\ln\left(\frac{nA}{kT}\right) > 5 \qquad n\left(\frac{4L^2}{3}\right)^{3/2} > 2 \qquad (21A)$$

When they are used in Equation (19A), we find

$$\frac{I_\infty - I_a}{I_\infty} \cong 0.15 \qquad (22A)$$

and we conclude that the previous use of $g_o = 1$ and $\psi = \psi_\infty$ resulted in little error ($\sim 15\%$) in η_o. Other reasonable choices of the parameters c, M, V_p, V_s and $F(c)$ show this conclusion to be insensitive to these choices as long as c is in the concentrated range.

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