Huggins Coefficient for Polymer Solutions with Excluded Volume

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ABSTRACT: The Freed–Edwards theory of the concentration dependence of the hydrodynamics of polymer solutions is generalized to consider the Huggins coefficient for polymer viscosity with excluded volume. The increase in chain dimensions from intramolecular excluded volume interactions and their decrease from intermolecular ones are taken into account in the calculation. It is assumed that excluded volume effects serve only to alter the chain distributions in a concentration-dependent sense. Otherwise different chains are taken to be statistically uncorrelated at low concentrations and low frequencies. For fully developed excluded volume cases, as in good solvents, it is shown that $k_H \lesssim 0.4$, independent of polymer and solvent, and that the role of intermolecular excluded volume interactions in good solvents is rather minor. For very small excluded volume cases the theory justifies the use of different scaling factors for the inter- and intra-chain effects, yielding results in general agreement with experimental data.

(I) Introduction

At low, but finite, concentrations the polymer solution viscosity is observed to have the concentration dependence

$$\eta = \eta_0(1 + [\eta]c + k_H[\eta]^2c^2 + \dots) \qquad (1)$$

thereby defining the dimensionless Huggins coefficient k_H, where η is the polymer solution viscosity, η_0 is the pure solvent viscosity, $[\eta]$ is the polymer intrinsic viscosity, and c is the polymer mass concentration. The increase in solution viscosity with concentration has its origin in the disturbance of the hydrodynamic shear fields in the pure solvent by the presence of the large solute particles. At very low concentrations, the hydrodynamic shear fields are adequately approximated by considering one solute particle at a time and by ignoring the hydrodynamic interactions between solute particles. Einstein[1] solved this problem for hard spheres to obtain $\eta = \eta_0(1 + 2.5\phi)$, where ϕ is the volume fraction of hard spheres. Polymer molecules are more complicated because they are not "hard"; various models and treatments exist.

A random polymer chain possesses a long-ranged intramolecular excluded volume effect, due to the exclusion to multiple occupancy of space by two or more segments of the polymer, in addition to the short-ranged interactions between segments due to the connectivity of the chain. In polymer solutions at finite concentration, a concentration-dependent intermolecular excluded volume effect can also be present. The theoretical study of the Huggins coefficient for polymer solutions with excluded volume is the subject matter of the present paper.

For a given polymer solution, it is experimentally possible to realize a temperature, called theta temperature (Θ), at which the average excluded volume effect is zero due to the mutual cancellation between polymer–solvent and polymer–polymer interactions. The parameter $(1 - (\Theta/T))$, where T is absolute temperature, in part, provides a measure of the "goodness" of a solvent. The long-ranged excluded volume effect is generally written in terms of the short-ranged pair potential of mean force in a fashion very similar to that in simple solution theory. There are two regimes which are of particular interest in this problem. The first case involves large excluded volume effects (in good solvents) and presents mathematical difficulties similar in nature to those encountered in the theory of critical points in ordinary fluids, the exact solution having not been obtained yet. The second case considers small excluded volume effects (in poor solvents), and the mathematical treatment is similar in spirit to the theory of imperfect gases. In this approach, the excluded volume effect is expressed in terms of a parameter, z, which depends on $(1 - \Theta/T)M^{1/2}$, where M is the molecular weight of the polymer, and properties are determined in an asymptotic power series expansion in z.

Experiments[2,3] show that k_H lies around 0.7 at the theta temperature and decreases monotonically as the excluded volume parameter, z, is increased to reach a limiting value of about $k_H \sim 0.3$ in good solvents. The earlier efforts[4,5] to calculate k_H (including only the hydrodynamic pairwise interaction between solute particles) led to some improper integrals for k_H, which depend on the surface of the solution because the average stress tensor acting on a chain is proportional to r^{-3} due to the long-ranged nature of the hydrodynamic interaction.[2] Peterson and Fixman[6] have argued, on the other hand, that the situation is somewhat analogous to the theory of dielectrics. They have evaluated both the average stress and the average velocity gradient and have shown that k_H does not involve any improper integrals. Although their value of k_H is in agreement with that of experiments at the theta temperature, their calculations predict an increase in k_H with z, contrary to experiment on random coil molecules. It is to be noted that in the case of polymers, the effective size of the polymer molecules varies with concentration, owing to thermodynamic causes. Hence the effective volume fraction ϕ of polymer for hydrodynamic activity varies from a strict proportionality to polymer mass concentration. This dependence of molecular size on concentration has the effect of making an important possible contribution to the Huggins coefficient for polymers, which is not incorporated in the work of Peterson and Fixman.

Recently, a theory of k_H[7,10] has been obtained from the theory of polymer viscosity[8] in concentrated solutions,[9] which is free of improper integrals. When applied to the Gaussian random coil chain in theta solvents, the theory results in a value of 0.7574 for k_H in agreement with Brinkman's estimate[11] using a very simple dimensional method. Here we generalize this theory to random coil chains with excluded volume both in good and poor solvents, including the overall expansion of the chain due to the intramolecular excluded volume and the concentration-dependent intermolecular excluded volume effect which gives rise to a reduction of the overall chain dimension. The results are compared with experimental data.[12-15]

(II) Theory of the Huggins Coefficient

For a system of polymers in solution, the solvent is assumed to be incompressible and is described by a Navier–Stokes equation, while the polymer dynamics is governed by some chain model and the hydrodynamic interactions. The model considered here is that of a Gaussian chain backbone with excluded volume interactions between all pairs of segments (on all chains!). At infinite dilution the chains are sufficiently far from each other so intramolecular hydrodynamic interactions can be taken to propagate through the pure solvent. As the concentration is increased, however, the fluid element leaving, say, segment i on chain α may have its flow disturbed by (be scattered by) some segment on chain β before encountering another segment, say j, on chain α. This possibility and all higher order processes are represented in a multiple scattering formulation of the exact hydrodynamics for the polymer solution. This multiple scattering theory has been used to evaluate the Huggins coefficient under theta conditions, and it is generalized herein to include the excluded volume effects. Rather than pursuing the lengthy mathematical analysis of ref 7–10, we can derive the final equations by a simple physical argument.[16]

We are only interested in the average properties of the polymer solution where the average covers the distribution of all possible internal polymer configurations and spatial center of mass positions. The averaged solution is described hydrodynamically by a stress tensor involving that of the pure fluid plus an incremental contribution from the polymer. As only the divergence of the stress tensor occurs in the hydrodynamic equation, we need only focus on it. The divergence of the polymer contribution to the stress tensor is defined as $\int d\mathbf{r}' \int dt' \mathbf{\Sigma}(\mathbf{r}-\mathbf{r}'; t-t')\cdot\mathbf{u}(\mathbf{r}',t')$ where the tensor $\mathbf{\Sigma}$ is called the solution "self-energy", and $\mathbf{u}(\mathbf{r},t)$ is the velocity of the averaged solution at $\mathbf{r}$ and t. Hence, the quantity $\mathbf{\Sigma}$ is the object of investigation as we may directly obtain the viscosity from it. For this purpose it is convenient to introduce Fourier transforms in both space and time to yield $\mathbf{\Sigma}(\mathbf{k},\omega)$ from which the solution viscosity follows from

$$[\eta_{\text{soln}}(\omega) - \eta_0(\omega)]\mathbf{1} = -\lim_{k\to 0} \frac{1}{k^2}[\mathbf{\Sigma}(\mathbf{k},\omega) - \mathbf{\Sigma}(0,\omega)] \qquad (2)$$

as is evident from the relationship of $\mathbf{\Sigma}\cdot\mathbf{u}$ to the divergence of the polymer contribution to the stress tensor.

The quantity $\mathbf{\Sigma}(\mathbf{k},\omega)$ is, therefore, the object of study to determine its concentration and excluded volume dependence. We limit the discussion to zero frequency and low concentrations in order to obtain k_{H} as a function of excluded volume. Since we perform an average over all chain configurations and positions, suppose this average were initially carried out over all chains but one particular chain α. If there were no statistical correlations between α and other chains, lasting for times on the order of or longer than ω^{-1}, we could view chain α as moving in the averaged polymer solution rather than in the pure fluid. Thus, intrachain hydrodynamic interactions within α are dictated by the averaged fluid with the divergence of the stress tensor equal to that of the pure solvent plus $\mathbf{\Sigma}\cdot\mathbf{u}$. Now the problem is analogous to that considered at infinite dilution, and we may determine the viscosity of the solution by multiplying the contribution from chain α by the number, N, of chains in solution. Equivalently, we use the approximation of N independent chains in the averaged fluid to determine $\mathbf{\Sigma}$ itself, thereby yielding the self-consistent, "mean-field" equations for $\mathbf{\Sigma}$ obtained by much more laborious methods in ref 7–10. (Corrections due to correlations between chains can be included in terms of a multiple scattering formulation with the averaged fluid as a reference rather than the pure solvent.) We assume that the dominant effect of the excluded volume interactions is to alter the spatial distributions of these independent chains in a concentration-dependent fashion as described below.

In order to express the equations for $\mathbf{\Sigma}$, it is convenient to introduce the spherically averaged, effective intramolecular, concentration dependent hydrodynamic interaction, $K(s-s',c)$, acting between segments at positions s and s' along a chain in the averaged solution. We denote the magnitude of the spherically averaged self-energy tensor as $\Sigma_0(k,c)$ at $\omega = 0$. The coupled integral equations for $\Sigma_0(k,c)$ and $K(s-s',c)$ are[17]

$$\Sigma_0(k,c) = -\frac{clN_{\text{A}}}{\pi M_{\text{A}}}\int_0^\infty dq\,\frac{\Gamma(k,q)}{K(q,c)} \qquad (3)$$

$$K(q,c) = \left(\frac{\zeta}{l}\right)^{-1} + \frac{1}{3\pi^2}\int_0^\infty dk'\,k'^2\,\frac{\Gamma(k',q)}{[\eta_0 k'^2 - \Sigma_0(k',c)]} \qquad (4)$$

where

$$K(q,c) = \int_{-\infty}^{\infty} d(s-s')\,\exp[iq(s-s')]K(s-s',c) \qquad (5)$$

$$\Gamma(k,q) = \int_{-\infty}^{\infty} d(s-s')\,\exp[iq(s-s')]S(s-s',k) \qquad (6)$$

$$S(s-s',k) = \langle \exp\{i\mathbf{k}\cdot[\mathbf{R}(s)-\mathbf{R}(s')]\}\rangle = \exp\left\{-\frac{k^2}{6}\langle[\mathbf{R}(s)-\mathbf{R}(s')]^2\rangle\right\} \qquad (7)$$

$K(q,c)$ is the Fourier transform of the static limit of the renormalized effective concentration-dependent hydrodynamic interaction tensor for the Rouse mode with wave vector $q = 2\pi p/nl$ (p, the Rouse mode index, is an integer). $S(s-s',k)$ is the static concentration-dependent segment pair correlation function. M_{A} is the "monomer" molecular weight, N_{A} is the Avogadro's number, l is the Kuhn effective step length, and n is the number of such effective links. ζ is the bead friction coefficient. Equation 7 represents an assumption concerning the distribution function for $\{\mathbf{R}(s)\}$ where higher cumulants are ignored. (They could be included but do not enter into (1) through order c^2.) Excluded volume effects are taken to enter only through the excluded volume dependence of $\langle[R(s)-R(s')]^2\rangle$ in (7).

The intramolecular excluded volume effect results in an expansion of the chain. The intermolecular excluded volume effect, on the other hand, results in a contraction of the chain which is concentration dependent. Taking both effects into account, the equilibrium mean-square end-to-end distance can be written to first order in c in the general form

$$\langle[\mathbf{R}(s)-\mathbf{R}(s')]^2\rangle = R^{2(0)}(s-s') - cR^{2(1)}(s-s') \qquad (8)$$

The functional behaviors of $R^{2(0)}(s-s')$ and $R^{2(1)}(s-s')$ are determined by the nature of the chain backbone model and by the extent of the excluded volume effect. Equation 8 is then substituted in (6) to obtain $\Gamma(k,q)$ as a series expansion in concentration,

$$\Gamma(k,q) = \Gamma^{(0)}(k,q) + c\Gamma^{(1)}(k,q) + 0(c^2) \qquad (9)$$

The explicit expressions for $\Gamma^{(0)}(k,q)$ and $\Gamma^{(1)}(k,q)$ are derived in Appendix A.

An iterative approach is employed to obtain $\Sigma_0(k,c)$ through c^2, and then the solution viscosity follows from use of (2). First, $K(q,0)$ is calculated using the zero concentration limit value of $K(s-s',c)$,

$$\lim_{c\to 0} K(s-s',c) = \frac{1}{6\pi\eta_0}\langle|\mathbf{R}(s)-\mathbf{R}(s')|_0^{-1}\rangle \qquad (10)$$

$$= \frac{1}{6\pi\eta_0}\left(\frac{6}{\pi}\right)^{1/2}\langle[\mathbf{R}(s)-\mathbf{R}(s')]_0^{\,2}\rangle^{-1/2}$$

$$= \frac{1}{6\pi\eta_0}\left(\frac{6}{\pi}\right)^{1/2}[R^{2(0)}(s-s')]^{-1/2}$$

$$\equiv K^{(0)}(s-s') \qquad (11)$$

in the nondraining limit of $\zeta^{-1} \to 0$, an approximate perturbed distribution (with excluded volume) being employed for the chain at $c = 0$. The subscript zero identifies the corresponding function at zero concentration limit. The zero concentration limit values of $K(s - s',c)$ and $\Gamma(k,q)$, from eq 10 and 11 and 9, respectively, are substituted in (3) to calculate the lowest order self-energy, which in turn is substituted in (4) to obtain $K(q,c)$ in a series expansion in concentration.

$$K(q,c) = K^{(0)}(q) + cK^{(1)}(q) + 0(c^2) \qquad (12)$$

The explicit expressions for $K^{(0)}(q)$ and $K^{(1)}(q)$ are derived in Appendix A.

Equation 12 is then substituted into (3) to determine the first-order self-energy, which in turn is substituted in (2). Setting $q = 2\pi p/L$ gives the specific viscosity per unit polymer concentration through the first order in concentration as

$$\begin{aligned}\frac{1}{c}\,\eta_{\mathrm{sp}}(c) \equiv \frac{\eta - \eta_0}{\eta_0 c} &= \frac{2lN_{\mathrm{A}}}{LM_{\mathrm{A}}\eta_0}\sum_{p=1}^{\infty}\frac{1}{K^{(0)}(p)}\lim_{k\to 0}\frac{\Gamma^{(0)}(k,p)}{k^2}\\ &+ c\,\frac{2lN_{\mathrm{A}}}{LM_{\mathrm{A}}\eta_0}\sum_{p=1}^{\infty}\left[\frac{1}{K^{(0)}(p)}\lim_{k\to 0}\frac{\Gamma^{(1)}(k,p)}{k^2}\right.\\ &\left. - \frac{K^{(1)}(p)}{[K^{(0)}(p)]^2}\lim_{k\to 0}\frac{\Gamma^{(0)}(k,p)}{k^2}\right] + 0(c^2) \qquad (13)\end{aligned}$$

where L is the total chain length. Using (1) and (13) enables the evaluation of the Huggins coefficient.

(III) Huggins Coefficient in Good Solvents

When the excluded volume effect is large, as in the case of polymer solutions in good solvents, the mean-square segment-to-segment distance can in general be written as

$$\langle[\mathbf{R}(s) - \mathbf{R}(s')]^2\rangle = lA|s - s'|^{\nu}(1 - Bc|s - s'|^{\omega} + 0(c^2)) \qquad (14)$$

where the form of the concentration-dependent term arises from the result of lattice calculations.[18] The familiar first term in the right-hand side of (14) describes the fully developed intramolecular excluded volume effect, and the second term describes that due to the intermolecular excluded volume effect. The coefficients A and B have the dimensions of $(\text{length})^{1-\nu}$ and $(\text{length})^{-\omega}$/concentration, respectively, and are discussed below. The mean-square segment-to-segment distance at finite concentration cannot be determined from light-scattering measurements because these measurements are determined by a combination of intramolecular and intermolecular interference factors which cannot be separately estimated.[19] In the discussion below we show that the data on k_{H} can, in principle, be used to calculate the coefficient B, but it turns out that the mean-square segment-to-segment distance is not too sensitive to the value of B in the range of expected values as discussed below. The exponents ν and ω can be obtained from Monte-Carlo simulations,[20] exact enumerations on lattices,[18] and mean-field theories.[21] The ranges of possible values of ν and ω are analyzed below in the discussion of the comparison with experiment.

Comparing (14) with (8) gives

$$\begin{aligned}R^{2(0)}(s - s') &= lA|s - s'|^{\nu}\\ R^{2(1)}(s - s') &= lAB|s - s'|^{\nu+\omega} \qquad (15)\end{aligned}$$

Substituting these into (A.2) gives

$$\Gamma^{(0)}(k,q) = 2\int_0^{\infty}\mathrm{d}x\,\cos(qx)\exp\left[-\frac{k^2lAX^{\nu}}{6}\right] \qquad (16)$$

$$\Gamma^{(1)}(k,q) = 2\int_0^{\infty}\mathrm{d}x\,\frac{k^2lABX^{\nu+\omega}}{6}\cos(qx)\exp\left[-\frac{k^2lAX^{\nu}}{6}\right] \qquad (17)$$

Inserting (16) into (A.5) leads to (see Appendix B)

$$K^{(0)}(q) = \frac{1}{3\eta_0\pi^{3/2}}\left(\frac{6}{lA}\right)^{1/2}\frac{\Gamma(1 - (\nu/2))}{q^{(1-(\nu/2))}}\cos\left\{\left(1 - \frac{\nu}{2}\right)\frac{\pi}{2}\right\} \qquad (18)$$

where $\Gamma(\xi)$ is the gamma function

$$\Gamma(\xi) = \int_0^{\infty}\mathrm{d}t\,t^{\xi-1}\exp[-t]$$

Introducing (16), (17), and (18) into (A.7) gives the specific viscosity per unit concentration through first order in concentration as (Appendix B) in eq 19 where $\zeta(a)$ is the Riemann ζ function

$$\zeta(a) = \sum_{p=1}^{\infty} p^{-a}$$

Upon combining (1) and (19), the nonfree-draining intrinsic viscosity and the Huggins coefficient for fully developed excluded volume situations respectively become eq 20 and 21. It is to be noted that (20) is the same as that derived by Tschoegl[22] from the approximation $\langle[R(s) - R(s')]^2\rangle = lA|s$

$$\begin{aligned}\frac{1}{c}\,\eta_{\mathrm{sp}}(c) = &-\frac{(L/2)^{((3\nu/2)-1)}l^{5/2}A^{3/2}N_{\mathrm{A}}}{6^{1/2}\pi^{(3/2)(\nu-1)}M_{\mathrm{A}}}\,\frac{\Gamma(1+\nu)\cos[(1+\nu)\pi/2]\,\zeta(3\nu/2)}{\Gamma(1-(\nu/2))\cos[(1-(\nu/2))\pi/2]}\\ &+ c\left[\frac{2l^{5/2}(\pi A)^{3/2}BN_{\mathrm{A}}}{6^{1/2}LM_{\mathrm{A}}}\,\frac{\Gamma(\nu+\omega+1)\cos[(\nu+\omega+1)\pi/2]}{\Gamma(1-(\nu/2))\cos[(1-(\nu/2))\pi/2]}\left(\frac{L}{2\pi}\right)^{\omega+(3\nu/2)}\zeta\left(\omega+\frac{3\nu}{2}\right)\right.\\ &+ \frac{l^{5/2}(\pi A)^{3/2}BN_{\mathrm{A}}}{6^{1/2}LM_{\mathrm{A}}}\,\frac{\Gamma(\omega-(\nu/2)+1)\,\Gamma(1+\nu)\cos[(\omega-(\nu/2)+1)\pi/2]\cos[(1+\nu)\pi/2]}{\{\Gamma(1-(\nu/2))\cos[(1-(\nu/2))\pi/2]\}^2}\left(\frac{L}{2\pi}\right)^{\omega+(3\nu/2)}\zeta\left(\omega+\frac{3\nu}{2}\right)\\ &- \frac{l^5\pi^{3/2}A^3{N_{\mathrm{A}}}^2}{6\nu L{M_{\mathrm{A}}}^2}\,\frac{\Gamma(1+\nu)\Gamma(2-(\nu/2))\Gamma((\nu-2)/2\nu)\Gamma((1-\nu)/\nu)\Gamma(\nu)\cos[(1+\nu)\pi/2]\cos[(2-(\nu/2))\pi/2]\cos(\nu\pi/2)}{\{\Gamma(1-(\nu/2))\cos[(1-(\nu/2))\pi/2]\}^2}\\ &\left.\times(L/2\pi)^{3\nu-1}\,\zeta(3\nu-1)\right] + 0(c^2) \qquad (19)\end{aligned}$$

$$[\eta] = -\frac{(L/2)^{((3\nu/2)-1)}l^{5/2}A^{3/2}N_{\mathrm{A}}}{6^{1/2}\pi^{(3/2)(\nu-1)}M_{\mathrm{A}}}\,\frac{\Gamma(1+\nu)\cos\{(1+\nu)\pi/2\}\zeta(3\nu/2)}{\Gamma(1-\nu/2)\cos\{(1-(\nu/2))\pi/2\}} \qquad (20)$$

$$\begin{aligned}k_{\mathrm{H}} = &-\frac{2\Gamma(2-(\nu/2))\Gamma((\nu-2)/2\nu)\Gamma((1-\nu)/\nu)\,\Gamma(\nu)\cos[(2-(\nu/2))\pi/2]\cos(\nu\pi/2)}{\nu\pi^{1/2}\Gamma(1+\nu)\Gamma(1-(\nu/2))\cos[(1-(\nu/2))\pi/2]\cos[(1+\nu)\pi/2]}\,\frac{\zeta(3\nu-1)}{[\zeta(3\nu/2)]^2}\\ &-\frac{B}{[\eta]}\left(\frac{L}{2\pi}\right)^{\omega}\frac{\zeta((3\nu/2)+\omega)}{\zeta(3\nu/2)}\left\{\frac{\Gamma(\nu+\omega+1)\cos[(\nu+\omega+1)\pi/2]}{\Gamma(1+\nu)\cos[(1+\nu)\pi/2]} + \frac{\Gamma(\omega-(\nu/2)+1)\cos[(\omega-(\nu/2)+1)\pi/2]}{2\Gamma(1-(\nu/2))\cos[(1-(\nu/2))\pi/2]}\right\} \qquad (21)\end{aligned}$$

$- s'|^{\nu}$ by setting $c = 0$ in (14), while (21) depends on ω and B in addition to the quantities in (20).

(IV) Huggins Coefficient with Small Excluded Volume

When the excluded volume effect is small, it is expressed in terms of a parameter, z, which is proportional to $(1 - (\Theta/T))M^{1/2}$. Including both the intra- and intermolecular excluded volume effects Yamakawa[23] has shown that the mean square intersegment distance is of the form

$$\langle[\mathbf{R}(s) - \mathbf{R}(s')]^2\rangle = l|s - s'|[1 + \beta f_1(s,s') - c\beta f_2(s,s') + \ldots] \quad (22)$$

where β is the binary cluster integral for a pair of segments and only terms through first order in β and in c are retained. f_1 and f_2 are rather involved functions which are not reproduced here. A full treatment would require the substitution of (22) in (13), but the complexity of f_1 and f_2 makes it convenient to introduce simple approximations. For the zero concentration limit Yamakawa and Tanaka[24] have utilized (22) with $c = 0$ to obtain the result

$$[\eta] = [\eta]_\Theta(1 + 1.06z + \ldots) \quad (23)$$

where

$$z = \left(\frac{3}{2\pi l^2}\right)^{3/2} \beta n^{1/2} \quad (24)$$

If, on the other hand, the enormous simplification of using the uniform scaling approximation,

$$\langle[\mathbf{R}(s) - \mathbf{R}(s')]^2\rangle \doteq l|s - s'|[1 + (4/3)z + \ldots] \quad (25)$$

were used instead, the coefficient of z in $[\eta]$ would incorrectly be obtained as 2. Thus, although (25) is correct for length expansions ($s = L$, $s' = 0$), the integrations in (13) mangle $f_1(s,s')$ sufficiently to produce a different coefficient. Similarly, f_1 appears differently in $[\eta]$ and k_H, so this scale factor must be different for these two cases. Likewise, the use of the correct length scaling factor instead of f_2 would also produce the wrong coefficient in the viscosity as it could not correctly reproduce the effects of the integrations in (13). Thus, we are led to the use of the nonuniform scaling procedure of introducing

$$\langle[\mathbf{R}(s) - \mathbf{R}(s')]^2\rangle \doteq l|s - s'|[1 + c_1 z - c_2 cz + \ldots] \quad (26)$$

into (13), recognizing that when c_1 occurs in the expression for $[\eta]$ it is to be replaced by the value of $(2/3)(1.06)$, but c_1 is left as a scaling factor in k_H (along with c_2). The full form of f_1 and f_2 thereby justifies the use of this nonuniform scaling approximation which was suggested to us by Yamakawa.

Using

$$R^{2(0)}(s - s') = l|s - s'|(1 + c_1 z)$$
$$R^{2(1)}(s - s') = zc_2 l|s - s'| \quad (27)$$

in (A.2) yields (Appendix C)

$$\Gamma^{(0)}(k,q) = \frac{(k^2 l/3)(1 + c_1 z)}{[q^2 + \{k^2 l(1 + c_1 z)/6\}^2]} \quad (28)$$

$$\Gamma^{(1)}(k,q) = \frac{k^2 l z c_2}{3} \int_0^\infty \mathrm{d}(s - s') \times \exp\left[-\frac{k^2 l}{6}(1 + c_1 z)(s - s')\right](s - s') \cos\{q(s - s')\} \quad (29)$$

Introducing (28) into (A.5) and using the change of variables $y^2 = k^2 l(1 + c_1 z)/6$ leads to the result

$$K^{(0)}(q) = \frac{2}{3\pi^2\eta_0}\left\{\frac{6}{l(1 + c_1 z)}\right\}^{1/2} \int_0^\infty \mathrm{d}y \frac{y^2}{q^2 + y^4} = \frac{1}{3^{1/2}\pi\eta_0}\{ql(1 + c_1 z)\}^{-1/2} \quad (30)$$

Equation 30 is the same as that obtained from eq 4, 10 and 11, and 27. Substituting eq 28–30 into (A.7) yields the specific viscosity through first order in concentration and z as

$$\frac{1}{c}\eta_{\mathrm{sp}}(c) = \frac{N_A L^{1/2} l^{5/2} \zeta(3/2)}{(6\pi)^{1/2} M_A}[1 + 2/3(1.06z)]^{3/2} + c\left[\left(\frac{N_A}{M_A}\right)^2 \frac{Ll^5}{6}\zeta(2)(1 + c_1 z)^3 - \frac{3}{2}\frac{N_A L^{1/2} l^{5/2}\zeta(3/2)}{(6\pi)^{1/2} M_A} c_2 z(1 + c_1 z)^{1/2}\right] + 0(c^2) \quad (31)$$

The first term in (31) yields the correct value of $[\eta]$ while k_H is given as

$$k_H = \frac{\pi\zeta(2)}{[\zeta(3/2)]^2}\frac{(1 + c_1 z)^3}{[1 + 2/3(1.06)z]^3} - \frac{3}{2}\frac{c_2 z(1 + c_1 z)^{1/2}}{[\eta](1 + 2/3(1.06)z]^{3/2}} + 0(z^2) = k_{H\Theta}[1 + (3c_1 - 2.12)z + \ldots] - \frac{3}{2}\frac{c_2 z}{[\eta]_\Theta} + 0(z^2) \quad (32)$$

where $k_{H\Theta}$ is the Huggins coefficient at the theta temperature.

Yamakawa has noted that, when use is made of scaling approximations as in (26) and (27), the full theory of (13) is unnecessary, and a much simpler approach is as follows: He shows that (17) of ref 7 may be rewritten as

$$\frac{1}{c}\eta_{\mathrm{sp}}(c) = \frac{N_A\zeta(3/2)\langle R^2\rangle^{3/2}}{(6\pi)^{1/2}M} + \frac{\pi^2}{36}\left(\frac{N_A}{M}\right)^2\langle R^2\rangle^3 c + \ldots \quad (33)$$

If the uniform scaling approximation is employed, corresponding to using (26) with c_1 as the fixed constant, $2/3(1.06)$, then (33) results in the *incorrect* result

$$k_H \dot{\sim} k_{H\Theta}[1 - 0.2276(12/\pi)\zeta(3/2)z^2 + 0(z^3)]$$

which does not contain the linear term required by the experimental data. (In obtaining (33a) the uniform scaling result $[\eta] = [\eta]_\Theta[1 + c_1 z - c_2 cz]^{3/2}$ has been utilized.) This improper uniform scaling approximation was utilized in ref 23a as well as by us in our original manuscript. Yamakawa then suggested the nonuniform scaling approximation such that

$$\langle R^2\rangle^{3/2} \text{ in 1st term of (33)} \rightarrow (Ll)^{3/2}\alpha_\eta^3(1 - Azc + \ldots) \quad (27a)$$

$$\langle R^2\rangle \text{ in 2nd term of (33)} \rightarrow Ll\alpha^2 \quad (27b)$$

where A is proportional to c_2 and α is some (unknown) expansion factor at $c = 0$. We then have

$$[\eta] = [\eta]_\Theta\alpha_\eta^3$$
$$k_H = k_{H\Theta}(\alpha/\alpha_\eta)^6 - Az/[\eta]_\Theta + \ldots \quad (34a)$$

Experiment suggests that

$$(\alpha/\alpha_\eta)^6 = 1 - (\text{constant})z + \ldots \quad (34b)$$

rather than the uniform scaling prediction of (33a) and ref 23a.

(V) Comparison with Experiments

(A) Good Solvents. According to (20), the intrinsic viscosity in a good solvent is proportional to $M^{((3\nu/2)-1)}$. The experimental value for this exponent ranges from 0.65 to 0.80, depending on the nature of the polymer, temperature, and goodness of the solvent. The viscosity exponents would correspond to 1.1 and 1.2, respectively, for the values of ν. As an example, we consider linear polyethylene (fraction IX of ref 13) in decalin at 135 °C for which the intrinsic viscosity is found to vary as $[\eta] \propto M^{0.7}$. Using (20) this would imply, therefore, that ν is 1.133 which lies between the value of 1.2 predicted by mean field theories[21] and the value of 1.1 given by Monte-Carlo calculations.[20,25] It is, in fact, very close to the value of 1.12 obtained by Mazur and McIntyre based on fits to light-scattering measurements[25] on polystyrene. Although any suitable empirical value can be assinged to ν and the equations derived above are still valid, the value of 1.133 is taken for ν for illustrative purposes in the explicit numerical calculations. The ν dependence of the results is discussed afterwards.

Substituting $\nu = 1.133$ in (20) we obtain

$$[\eta] = 0.2693 \frac{N_A}{M_A} l^{5/2} A^{3/2} L^{0.7} \tag{35}$$

For linear polyethylene[15] in the theta-solvent, diphenyl ether at 161.4 °C,

$$[\eta]_\Theta = KM^{1/2} = \Phi \left(\frac{\langle R^2 \rangle_0}{M}\right)^{3/2} M^{1/2} \tag{36}$$

$$K = 2.95 \times 10^{-1} \text{ (cgs units)} \tag{37}$$

Combining (36), (37), and the theoretical value[2] $\Phi = 2.87 \times 10^{23}$, the Kuhn statistical step length, l, and the end-to-end distance at full extension, L, for the linear polyethylene are calculated to be

$$l = 1.1250 \times 10^{-7} \text{ cm}$$

$$L = 9.0532 \times 10^{-10} M \text{ cm} \tag{38}$$

with M in grams. Substituting (38) into (34), the coefficient A can be calculated to be

$$A = 2.5913 \times 10^{-5M} \text{ cm}^{-0.133}$$

According to (21), k_H depends on the molecular weight of the polymer as $M^{(1+\omega-(3\nu/2))} = M^{\omega-0.7}$. As k_H has been experimentally found to be independent of the molecular weight of the polymer, ω should be anticipated to be near 0.7. This is very close to the "universal" value of 0.72 predicted by Bellemans et al.[18] based on lattice calculations. Even if ω were taken to be 0.72, k_H would have a rather weak molecular weight dependence of $M^{0.02}$ which would be unnoticeable within experimental error. However, just as experimental values of ν differ from the "universal" theoretical values, a similar departure is expected for ω. Consequently, we choose the convenient value $\omega = (3\nu/2) - 1$.

Substituting $\nu = 1.133$ and $\omega = 0.7$ into (21) and then combining with (38) and (34) leads to

$$k_H = 0.4005 - 4.0 \times 10^{-2} B' \tag{39}$$

where B' is related to B by

$$B = B'/d_2 l^\omega$$

and d_2 is the density of the polymer. A value of 0.043 is calculated for B' by Bellemans et al.[18] based on lattice calculations where monomer units occupy the same volume as the solvent molecules. For polyethylene in decalin the solvent size is ten times larger than that of the monomer units. Lattice calculations with differing segment and solvent unit volumes are significantly more difficult to perform. A qualitative estimate is obtained by multiplying the lattice value by the solvent to monomer volume ratio to yield a corrected estimate ~0.43. This value, when substituted into (39), yields $k_H = 0.3833$ in very good agreement with experimental results of Chaing[15] for this case.

The first term of (21) gives a value ranging within 2% of 0.4 for $1.05 \leqslant \nu \leqslant 1.2$. The second term of (21) is evaluated with the choice of $\omega = (3\nu/2) - 1$ to preserve the molecular weight independence of k_H and with the value of B' quoted above. We find that it gives a small contribution to k_H in the range of (−0.03, +0.01). This indicates, therefore, that the concentration-dependent decrease in coil size does not seem to be of major effect in good solvents and that the first hydrodynamic term is more important in good solvents, possibly explaining the constancy of k_H for different polymers in various good solvents.

(B) Poor Solvents. Using the value of c_2, as given by Yamakawa, with the required extra overall numerical constant c_3 (32) may be written as

$$k_H = k_{H\Theta}[1 + (3c_1 - 2.12)z + \ldots] - 2.43z^2 c_3 + 0(z^2) \tag{40}$$

where the second term in c_3 arises from intermolecular excluded volume effects and begins to contribute to order z^2. The leading term in (40) is linear in z, and this has been shown by Yamakawa to be in general accord with the experimental data of Kotera et al., Matsumoto et al., and Tsuji and Fujita with $c_1 - 1.06 < 0$. It would be of considerable interest to evaluate c_1 from a full theory including the complete expression for $f_1(s,s')$. However, (40) implies that in poor solvents the intramolecular excluded volume contribution dominates the intermolecular one in conformity with our results for good solutions.

(VI) Conclusion

We generalize the Freed–Edwards theory of the concentration dependence of the hydrodynamics of polymer solutions to consider the Huggins coefficient for polymer viscosity with excluded volume. The theory considers both the increase in chain dimensions, due to intramolecular excluded volume interactions, and their decrease from intermolecular excluded volume interactions. The theory assumes that statistical correlations between chains do not persist for an indefinite time (i.e., they are not entangled) so excluded volume effects are taken only to alter chain dimensions in a concentration-dependent fashion.

For good solvents, the theory shows that the intramolecular excluded volume effect plays the most important role, and this alone can give a value of 0.4 for k_H when $1.05 \leqslant \nu \leqslant 1.2$. A finer theoretical value of k_H can be obtained by incorporating the intermolecular excluded volume effect also which involves the poorly understood coefficient B. Approximating B from the results of lattice calculations yields $k_H = 0.3833$ for polyethylene in decalin at 135 °C in agreement with the values of k_H in good solvents reported in the literature.

In poor solvents a nonuniform scaling approximation, due to Yamakawa, leads to k_H being linear in z for small z in conformity with a number of experiments. Again the intermolecular excluded volume is less important than the intramolecular contributions with the former beginning at order z^2.

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Appendix A

Using (7), (6), and (5) we get

$$\begin{aligned}\Gamma(k,q) &= \int_{-\infty}^{\infty} \mathrm{d}(s-s') \\ &\quad\times \exp\left\{iq(s-s') - \frac{k^2}{6}[R^{2(0)}(s-s') - cR^{2(1)}(s-s')]\right\} \\ &= \int_{-\infty}^{\infty} \mathrm{d}(s-s') \exp\left[iq(s-s') - \frac{k^2}{6}R^{2(0)}(s-s')\right] \\ &\quad\times\left[1 + c\frac{k^2R^{2(1)}(s-s')}{6} + 0(c^2)\right] \qquad \text{(A.1)}\end{aligned}$$

Comparing (A.1) with (8) produces

$$\begin{aligned}\Gamma^{(0)}(k,q) &= \int_{-\infty}^{\infty} \mathrm{d}(s-s') \exp\left[iq(s-s') - \frac{k^2}{6}R^{2(0)}(s-s')\right] \\ \Gamma^{(1)}(k,q) &= \frac{k^2}{6}\int_{-\infty}^{\infty} \mathrm{d}(s-s')R^{2(1)}(s-s') \\ &\quad\times \exp\left[iq(s-s') - \frac{k^2}{6}R^{2(0)}(s-s')\right] \qquad \text{(A.2)}\end{aligned}$$

$\Gamma^{(0)}(k,q)$ and $K^{(0)}(s-s')$ are now used to calculate the lowest order approximation to the self-energy as

$$\overset{(0)}{\underset{0}{\Sigma}}(k,c) = -\frac{clN_{\mathrm{A}}}{\pi M_{\mathrm{A}}}\int_0^{\infty} \mathrm{d}q' \frac{\Gamma^{(0)}(k,q')}{K^{(0)}(q')} \qquad \text{(A.3)}$$

This is then substituted in (3) to get $K(q,c)$

$$\begin{aligned}K(q,c) &= \frac{1}{3\pi^2}\int_0^{\infty} \mathrm{d}k'\, k'^2 \\ &\quad\times \frac{[\Gamma^{(0)}(k',q) + c\Gamma^{(1)}(k',q) + 0(c^2)]}{\left[\eta_0 k'^2 + \frac{clN_{\mathrm{A}}}{\pi M_{\mathrm{A}}}\int_0^{\infty} \mathrm{d}q' \frac{\Gamma^{(0)}(k',q')}{K^{(0)}(q')}\right]} \\ &= \frac{1}{3\pi^2\eta_0}\int_0^{\infty} \mathrm{d}k'\, \Gamma^{(0)}(k',q) + \frac{c}{3\pi^2\eta_0} \\ &\quad\times\left[\int_0^{\infty} \mathrm{d}k'\, \Gamma^{(1)}(k',q) - \frac{lN_{\mathrm{A}}}{\pi M_{\mathrm{A}}\eta_0}\int_0^{\infty} \frac{\mathrm{d}k'}{k'^2}\Gamma^{(0)}(k,q)\right. \\ &\quad\left.\times\int_0^{\infty} \mathrm{d}q' \frac{\Gamma^{(0)}(k',q')}{K^{(0)}(q')}\right] \qquad \text{(A.4)}\end{aligned}$$

Comparing (A.4) and (12) gives

$$\begin{aligned}K^{(0)}(q) &= \frac{1}{3\pi^2\eta_0}\int_0^{\infty} \mathrm{d}k'\, \Gamma^{(0)}(k',q) \\ K^{(1)}(q) &= \frac{1}{3\pi^2\eta_0}\left[\int_0^{\infty} \mathrm{d}k'\, \Gamma^{(1)}(k',q) - \frac{lN_{\mathrm{A}}}{\pi M_{\mathrm{A}}\eta_0}\int_0^{\infty} \frac{\mathrm{d}k'}{k'^2}\right. \\ &\quad\left.\times\Gamma^{(0)}(k',q)\int_0^{\infty} \mathrm{d}q' \frac{\Gamma^{(0)}(k',q')}{K^{(0)}(q')}\right] \qquad \text{(A.5)}\end{aligned}$$

It can be shown that the expression in (A.5) for $K^{(0)}(q)$ is identical to that of eq 10 and 11.

Substituting (12) into (2), the self-energy through first order in concentration becomes

$$\begin{aligned}\overset{(1)}{\underset{0}{\Sigma}}(k,c) &= -\frac{clN_{\mathrm{A}}}{\pi M_{\mathrm{A}}}\int_0^{\infty} \mathrm{d}q\, [\Gamma^{(0)}(k,q) + c\Gamma^{(1)}(k,q)] \\ &\quad\times[K^{(0)}(q)]^{-1}\left[1 - c\frac{K^{(1)}(q)}{K^{(0)}(q)} + \ldots\right] \qquad \text{(A.6)}\end{aligned}$$

Using (A.6) in (2) and setting $q = 2\pi p/L$ yields the specific viscosity through first order in concentration as given by (13). Inserting (A.5) into (13) produces the results

$$\begin{aligned}\frac{1}{c}\eta_{\mathrm{sp}}(c) &= \frac{2lN_{\mathrm{A}}}{LM_{\mathrm{A}}\eta_0}\sum_{p=1}^{\infty}\frac{1}{K^{(0)}(p)}\lim_{k\to 0}\frac{1}{k^2}\Gamma^{(0)}(k,p) \\ &\quad + c\frac{2lN_{\mathrm{A}}}{LM_{\mathrm{A}}\eta_0}\sum_{p=1}^{\infty}\left[\frac{1}{K^{(0)}(p)}\lim_{k\to 0}\frac{1}{k^2}\Gamma^{(1)}(k,p)\right. \\ &\quad - \frac{1}{3\pi^2\eta_0}\frac{1}{[K^{(0)}(p)]^2}\lim_{k\to 0}\frac{\Gamma^{(0)}(k,p)}{k^2}\left\{\int_0^{\infty}\mathrm{d}k'\,\Gamma^{(1)}(k',p)\right. \\ &\quad\left.\left. - \frac{lN_{\mathrm{A}}}{\pi M_{\mathrm{A}}\eta_0}\int_0^{\infty}\frac{\mathrm{d}k'}{k'^2}\Gamma^{(0)}(k',p)\int_0^{\infty}\mathrm{d}q'\frac{\Gamma^{(0)}(k',q')}{K^{(0)}(q')}\right\}\right] \\ &\quad + 0(c^2) \qquad \text{(A.7)}\end{aligned}$$

Appendix B

From (16) we obtain[26]

$$\begin{aligned}\lim_{k\to 0}\frac{\Gamma^{(0)}(k,q)}{k^2} &= 2\lim_{k\to 0}\int_0^{\infty}\mathrm{d}x\cos(qx)k^{-2} \\ &\quad\times\exp\left[-\frac{k^2lAx^{\nu}}{6}\right] = -\frac{2lA}{6}\lim_{\epsilon\to 0}\int_0^{\infty}\mathrm{d}x\cos(qx)x^{\nu} \\ &\quad\times\exp(-\epsilon x) = -\frac{lA}{3}\frac{\Gamma(1+\nu)}{q^{(1+\nu)}}\cos\left[(1+\nu)\frac{\pi}{2}\right] \qquad \text{(B.1)}\end{aligned}$$

From (17) it is found that

$$\begin{aligned}\lim_{k\to 0}\frac{\Gamma^{(1)}(k,q)}{k^2} &= \frac{lAB}{3}\lim_{k\to 0}\int_0^{\infty}\mathrm{d}x \\ &\quad\times\cos(qx)(x)^{\nu+\omega}\exp\left[-\frac{k^2lAx^{\nu}}{6}\right] \\ &= \frac{lAB}{3}\frac{\Gamma(\nu+\omega+1)}{q^{(\nu+\omega+1)}}\cos\left[(\nu+\omega+1)\frac{\pi}{2}\right] \qquad \text{(B.2)}\end{aligned}$$

and[26]

$$\begin{aligned}\int_0^{\infty}\mathrm{d}k\,\Gamma^{(1)}(k,q) &= \frac{lAB}{3}\int_0^{\infty}\mathrm{d}x \\ &\quad\times\cos(qx)x^{\nu+\omega}\int_0^{\infty}\mathrm{d}k\,\mathrm{k}^2\exp\left[-\frac{k^2lAx^{\nu}}{6}\right] \\ &= \frac{\pi^{1/2}}{2}B\left(\frac{6}{lA}\right)^{1/2}\lim_{\epsilon\to 0}\int_0^{\infty}\mathrm{d}x\cos(qx)x^{(\omega-(\nu/2))}\exp(-\epsilon x) \\ &= \frac{\pi^{1/2}}{2}B\left(\frac{6}{lA}\right)^{1/2}\frac{\Gamma(\omega-(\nu/2)+1)}{q^{(\omega-(\nu/2)+1)}}\cos\left[\left(\omega-\frac{\nu}{2}+1\right)\frac{\pi}{2}\right] \\ &\qquad \text{(B.3)}\end{aligned}$$

Substituting (16) into (A.5) leads to

$$\begin{aligned}K^{(0)}(q) &= \frac{2}{3\pi^2\eta_0}\int_0^{\infty}\mathrm{d}x\cos(qx)\int_0^{\infty}\mathrm{d}k\exp\left(-\frac{k^2lAx^{\nu}}{6}\right) \\ &= \frac{1}{3\eta_0\pi^{3/2}}\left(\frac{6}{lA}\right)^{1/2}\int_0^{\infty}\mathrm{d}x\cos(qx)(x)^{-\nu/2} \\ &= \frac{1}{3\eta_0\pi^{3/2}}\left(\frac{6}{lA}\right)^{1/2}\frac{\Gamma(1-(\nu/2))}{q(1-(\nu/2))}\cos\left[\left(1-\frac{\nu}{2}\right)\frac{\pi}{2}\right] \qquad \text{(18)}\end{aligned}$$

Using (16) and (18), we calculate[26] eq B.4. From (16) and (B.4), eq B.5 is found.[26] Substituting (18), (B.1), (B.2), (B.3), and (B.5) into (A.7), eq 21 can be obtained.

$$\begin{aligned}\int_0^{\infty}\mathrm{d}q\frac{\Gamma^{(0)}(k,q)}{K^{(0)}(q)} &= \frac{6\eta_0\pi^{3/2}(lA/6)^{1/2}}{\Gamma(1-(\nu/2))\cos[(1-(\nu/2))\pi/2]}\int_0^{\infty}\mathrm{d}x\exp\left[-\frac{k^2lAx^{\nu}}{6}\right]\lim_{\epsilon\to 0}\int_0^{\infty}\mathrm{d}q\cos(qx)q^{(1-(\nu/2))}\exp(-\epsilon q) \\ &= \frac{6\eta_0\pi^{3/2}(lA/6)^{1/2}\,\Gamma(2-(\nu/2))\cos[(2-(\nu/2))\pi/2]}{\Gamma(1-(\nu/2))\cos[(1-\nu/2)\pi/2]}\int_0^{\infty}\mathrm{d}x\,(x)^{-(2-(\nu/2))}\exp\left(-\frac{k^2lAx^{\nu}}{6}\right) \\ &= \frac{6\eta_0\pi^{3/2}(lA/6)^{1/2}\,\Gamma(2-(\nu/2))\cos[(2-(\nu/2))\pi/2]}{\Gamma(1-(\nu/2))\cos[(1-(\nu/2))\pi/2]}\left|\frac{2}{\nu-4}\right|\int_0^{\infty}\mathrm{d}y\,y^{2/(\nu-4)}\exp\left[-\frac{k^2lA}{6}(y)^{(2\nu/(\nu-4))}\right] \\ &= \frac{6\eta_0\pi^{3/2}(lA/6)^{(1/2)(1+[(2-\nu)/\nu])}\Gamma(2-(\nu/2))\Gamma((\nu-2)/2\nu)\cos[(2-(\nu/2))\pi/2](k)^{(2-\nu)/\nu}}{\nu\Gamma(1-(\nu/2))\cos[(1-(\nu/2))\pi/2]} \equiv Xk^{((2-\nu)/\nu)} \qquad \text{(B.4)}\end{aligned}$$

$$\begin{aligned}\int_0^\infty \frac{\mathrm{d}k}{k^2}\,\Gamma^{(0)}(k,q)\int_0^\infty \mathrm{d}q'\,\frac{\Gamma^{(0)}(k,q')}{K^{(0)}(q')} &= 2X\int_0^\infty \mathrm{d}x\,\cos(qx)\int_0^\infty \mathrm{d}k\,k^{(2-3\nu)/\nu}\exp\left[-\frac{k^2lAx^\nu}{6}\right]\\ &= 2X\left|\frac{\nu}{2-3\nu}\right|\int_0^\infty \mathrm{d}x\,\cos(qx)\int_0^\infty \mathrm{d}y\,y^{\nu/(2-3\nu)}\exp\left[-\frac{lAx^\nu}{6}(y)^{(2\nu/(2-3\nu))}\right]\\ &= X\left(\frac{lA}{6}\right)^{(\nu-1)/\nu}\Gamma\left(\frac{1-\nu}{\nu}\right)\lim_{\epsilon\to 0}\int_0^\infty \mathrm{d}x\,\cos(qx)x^{\nu-1}\exp(-\epsilon x) = \frac{\eta_0\pi^{3/2}lA}{\nu}\\ &\quad\times\frac{\Gamma(2-(\nu/2))\Gamma((\nu-2)/2\nu)\Gamma((1-\nu)/\nu)\Gamma(\nu)\cos[(2-(\nu/2))\pi/2]\cos(\nu\pi/2)}{\Gamma(1-(\nu/2))\cos[(1-(\nu/2))\pi/2]}q^{-\nu} \qquad \text{(B.5)}\end{aligned}$$

Appendix C

Substituting (27) in (A.2) gives

$$\begin{aligned}\Gamma^{(0)}(k,q) &= \int_{-\infty}^\infty \mathrm{d}(s-s')\\ &\quad\times\exp\left[iq(s-s')-\frac{k^2l}{6}(1+c_1z)|s-s'|\right]\\ &= 2\int_0^\infty \mathrm{d}(s-s')\cos\{q(s-s')\}\\ &\qquad\times\exp\left[-\frac{k^2l}{6}(1+c_1z)(s-s')\right] \qquad \text{(C.1)}\\ &= \frac{(k^2l/3)(1+c_1z)}{\{q^2+[k^2l(1+c_1z)/6]^2\}} \qquad (17)\end{aligned}$$

$$\begin{aligned}\Gamma^{(1)}(k,q) &= \frac{k^2lzc_2}{6}\int_{-\infty}^\infty \mathrm{d}(s-s')\\ &\quad\times\exp\left[iq(s-s')-\frac{k^2l}{6}(1+c_1z)|s-s'|\right]|s-s'| \qquad \text{(C.2)}\\ &= \frac{k^2lzc_2}{3}\int_0^\infty \mathrm{d}(s-s')(s-s')\\ &\quad\times\cos[q(s-s')]\exp\left[-\frac{k^2l}{6}(1+c_1z)(s-s')\right] \qquad (18)\end{aligned}$$

Equations 28 and 29 can be combined to yield

$$\lim_{k\to 0}\frac{\Gamma^{(0)}(k,q)}{k^2} = \frac{l}{3}(1+c_1z)q^{-2} \qquad \text{(C.3)}$$

$$\begin{aligned}\lim_{k\to 0}\frac{\Gamma^{(1)}(k,q)}{k^2} &= \frac{lzc_2}{3}\lim_{k\to 0}\int_0^\infty \mathrm{d}(s-s')(s-s')\\ &\quad\times\cos[q(s-s')]\exp\left[-\frac{k^2l}{6}(1+c_1z)(s-s')\right]\\ &= -\frac{lzc_2}{3}q^{-2} \qquad \text{(C.4)}\end{aligned}$$

$$\begin{aligned}\int_0^\infty \mathrm{d}k\,\Gamma^{(1)}(k,q) &= \frac{lzc_2}{3}\int_0^\infty \mathrm{d}k\,k^2\int_0^\infty \mathrm{d}(s-s')(s-s')\\ &\quad\times\cos[q(s-s')]\exp\left[-\frac{k^2l}{6}(1+c_1z)(s-s')\right]\\ &= \frac{lzc_2}{3}\int_0^\infty \mathrm{d}(s-s')(s-s')\cos[q(s-s')]\int_0^\infty \mathrm{d}k\,k^2\\ &\quad\times\exp\left[-\frac{k^2l}{6}(1+c_1z)(s-s')\right]\\ &= \frac{(6\pi)^{1/2}}{2}\frac{zc_2}{(1+c_1z)^{3/2}}(lq)^{-1/2}\int_0^\infty \mathrm{d}x\,\frac{\cos x}{x^{1/2}}\\ &= \frac{3^{1/2}\pi}{2}\frac{zc_2}{(1+c_1z)^{3/2}}(lq)^{-1/2} \qquad \text{(C.5)}\end{aligned}$$

$$\int_0^\infty \mathrm{d}k\,\Gamma^{(1)}(k,p) = \frac{(3\pi)^{1/2}}{2}\frac{zc_2}{(1+c_1z)^{3/2}}\left(\frac{L}{2pl}\right)^{1/2} \qquad \text{(C.6)}$$

Using (30) and (28) we obtain

$$\begin{aligned}\int_0^\infty \mathrm{d}q\,\frac{\Gamma^{(0)}(k,q)}{K^{(0)}(q)} &= 3^{1/2}\pi\eta_0[l(1+c_1z)]^{1/2}\\ &\quad\times\frac{k^2l}{3}(1+c_1z)\int_0^\infty \mathrm{d}q\,\frac{q^{1/2}}{\left\{q^2+\left[\frac{k^2l(1+c_1z)}{6}\right]^2\right\}}\\ &= \pi^2\eta_0l(1+c_1z)k \qquad \text{(C.7)}\end{aligned}$$

Using (C.7) we calculate

$$\begin{aligned}\int_0^\infty \frac{\mathrm{d}k}{k^2}\,\Gamma^{(0)}(k,q)\int_0^\infty \mathrm{d}q'\,\frac{\Gamma^{(0)}(k,q')}{K^{(0)}(q')} &= 12\pi^2\eta_0\int_0^\infty \mathrm{d}k\,\frac{k^2}{\{k^4+[6q/l(1+c_1z)]^2\}}\\ &= \frac{\pi^3\eta_0}{2q}l(1+c_1z) \qquad \text{(C.8)}\end{aligned}$$

Substituting (30), (C.3), (C.4), (C.6), and (C.8) into (A.7), eq 31 can be obtained after some algebra.

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A Study of Equilibrium Melting of Polyethylene

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ABSTRACT: The equilibrium melting of polyethylene is discussed based on new and literature data. Melting temperatures, superheating effects, and heats of fusion are determined on well-crystallized chain folded and extended chain crystals as well as fully extended chain crystals produced by etching. Extrapolation procedures of melting temperatures are critically evaluated. The superheating is shown to be mainly due to effects of the amorphous areas on the crystals, but some superheating remains for sufficiently large crystals after removal of the amorphous material. The heat of fusion is shown to have a surprising temperature dependence which gives a reason for errors in melting temperature extrapolations. The experimental data on volume change on fusion are summarized. The entropy of fusion is discussed in terms of the conformational change which, however, is not approximated by the constant volume entropy of fusion. The following best values have been derived: melting temperature 414.6 ± 0.5 K, crystal volume 1.0338 m^3/Mg, amorphous volume 1.2765 m^3/Mg, heat of fusion 4.1 ± 0.2 kJ/mol of CH_2, and conformational melt entropy 7.8 ± 1.0 J/K/mol of CH_2.

The equilibrium properties of crystals of flexible, linear macromolecules are difficult to obtain experimentally. On crystallization from the melt or from solution, already polymerized molecules go first to a chain-folded macroconformation.[1] This leads, at least initially, to grossly metastable crystals. For many years no conditions were known to produce anything but these metastable chain folded crystals. Their analysis furthered the belief that: "Crystallizing high polymers have no sharp melting point".[2] A major effort was, for this reason, undertaken to develop extrapolation procedures to guess at the equilibrium properties. In the meantime, annealing of metastable crystals, as well as crystallization during polymerization, have led to a number of crystals of linear macromolecules which closely approximate equilibrium crystals.[1] In practice this means that crystals of high perfection of sizes above 1 μm in all crystallographic directions have been grown. It is thus possible to have an experimental check on the quality of these extrapolations.

In this paper we are concerned with polyethylene. Experimental data on crystals close to equilibrium became available with the first crystallization from the melt under hydrostatic pressures above 300 MN/m^2.[3] In the present research new data on heats of fusion, melting temperatures, and superheating behavior of a series of more or less extended chain crystals have been derived. They will be combined with older data from our laboratory and with literature data to enable a critical comparison with extrapolated equilibrium properties. Of main interest are data on the equilibrium melting temperature, the heat of fusion, the volume change on fusion, and the entropy of fusion. It will be shown that presently extrapolations and experiments agree within the error limits of the methods.

The first step in the analysis is the proof that the above statement about the diffuse melting of macromolecules is true only for metastable crystals. Equilibrium crystals of flexible linear macromolecules melt as sharply as small molecules. Figure 1 illustrates such proof for the melting of high molecular weight polyethylene crystallized under elevated pressure (sample PM, below). About 80% of the whole sample can be seen to melt within 1.6 K, and the highest melting crystals are largest in number and give a sharp melting temperature of 414.6 K.[4] Since the largest crystals in this sample were 10 μm or more in all dimensions, had a density which agreed with the x-ray density, and contained no fractions below 10^5 molecular weight, they must melt with a typical experimental error of ±0.5 K at the equilibrium melting temperature.[54] This conclusion, which was reached almost 15 years ago and was frequently criticized,[5] will be shown to be supported by the new experiments and also by properly adjusted extrapolations.

A major problem in experimentation with extended chain crystals is their tendency to superheat before melting. Superheating of the extended chain crystals will be shown to result from two sources: inherently slow melting of large macromolecular crystals and restriction of melting by remaining loops and tie molecules.

Experimental Section

Materials. Linear polyethylene of number average molecular weight 8530 and weight average 153 000 was used. A molecular weight distribution curve of this polymer has been shown in ref 6. A high molecular weight sample, referred to as polymethylene, was made from diazomethane with an estimated molecular weight of 1.4×10^7. The lowest fraction in this polymer, detectable by gel permeation, was above 10^5 in molecular weight.

The crystallization conditions were guided by prior experience. The polymethylene was crystallized at 500 K and 482 MN/m^2 pressure for 20 h and then slowly cooled at a rate of 1.6 K/h to room temperature for pressure release. This sample is called PM. Its 296 K density is 0.997 Mg/m^3, and its dilatometric melting point on slow heating was determined earlier as 414.6 K (see Figure 1; sample 31 in ref 4). Crystallizing this polymer without the aid of elevated pressure from the melt by quick quenching led to a crystallinity of only 0.37 and a DTA melting peak temperature of 404.9 K.

The polyethylene was crystallized both under elevated pressure and by long-term crystallization at atmospheric pressure. The pressure crystallization was carried out at 509 K and 507 MN/m^2 for 24 h and was followed by fast cooling to room temperature. The 296 K density of this sample was 0.982 Mg/m^3, considerably less than the best samples crystallized from the same polymer at elevated pressure. This sample will be called P509. The atmospheric pressure sample was crystallized isothermally for 21 days at 402.2 K before quick cooling to keep the segregated, low molecular weight polymer poorly crystallized. This sample will be called P402. Its 296 K density is 0.977

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