Non-Gaussian Contribution to the Hydrodynamic Radius at the Θ Point†

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ABSTRACT: The Kirkwood approximation expresses the hydrodynamic radius for translational diffusion in terms of equilibrium averages of reciprocal intrachain distances. The suggestion has been made on the basis of lattice simulations that these averages do not scale properly in the long-chain limit at the Θ point because nonbonded interactions generate non-Gaussian statistics. An alternative interpretation of the earlier results is presented here on the basis of new simulations and perturbation theory. We conclude that Gaussian behavior at the Θ point is recovered in the long-chain limit. Slow convergence to the limit and dynamical corrections to the Kirkwood approximation are the more probable source of experimental deviations from the Kirkwood limiting values.

I. Introduction

The Kirkwood approximation[1] for the translational diffusion constant of polymer chains gives a value $R_G/R_H = 8/3\pi^{1/2} = 1.5045$ for the ratio between the radius of gyration R_G and the hydrodynamic radius R_H in the limit that the number of beads $N \to \infty$. The numerical value is based on the assumption that Gaussian statistics apply to sufficiently long real chains at the Θ point. However, a careful attempt[2] to extrapolate experimental values of the ratio at the Θ point gave a value some 15% smaller for polystyrene. Recently, it was suggested,[3] on the basis of lattice simulations of self-avoiding walks with nearest-neighbor attractive interactions incorporated, that the Gaussian approximation may not be valid for the calculation of R_H in Kirkwood's approximation, even in the limit $N \to \infty$. The nonbonded interactions at the Θ point, it was suggested,[3] keep R_H proportional to R_G in the long-chain limit, but the proportionality constant is not the Gaussian value. We have studied the same matter by means of simulations and perturbation theory and reached a contrary conclusion that we discuss here. Other related studies of dynamic corrections to the Kirkwood approximation[4-6] and work in preparation[7] indicate that the dynamic corrections provide a significant fraction of the observed discrepancy and that the remainder is reasonably ascribed to lack of convergence to asymptotic values at the largest chain lengths studied by either experiment or by simulation.

Guttman et al.[3] found an appparent limiting value $R_G/R_H = 1.40$ for their lattice chain simulations at the Θ point. It seemed possible to us that the apparent convergence to 1.40 might not be real and that the low values that were found for R_G/R_H might not be due primarily to nonbonded interactions.

Convergence was inferred by Guttman et al.[3] from a comparison of lattice simulations with analytical results for finite Gaussian chains and from a seemingly linear dependence of $N^{1/2}/R_H$ on $1/N^{1/2}$. In regard to the latter point, a perturbative discussion of nonbonded interactions in section IV indicates that $N^{1/2}/R_H$ should have a term linear in $\ln N/N^{1/2}$ for large N. Consequently, the curve of $N^{1/2}/R_H$ vs. $1/N^{1/2}$ should decrease from its limiting value at $1/N^{1/2} = 0$ with negative infinite slope. A linear extrapolation of $N^{1/2}/R_H$ vs. $1/N^{1/2}$ would undershoot the limit. In the comparison of Gaussian and lattice values of R_G/R_H, two changes are made in the model other than the incorporation of nonbonded interactions, which have the effect of reducing the lattice value of R_G/R_H below the Gaussian value for finite chains. First, for finite N the hydrodynamic radius is more sensitive than R_G to the stiffness of short stretches of chain. Second, the lattice calculations eliminate the singularity in the hydrodynamic interaction $1/R$, which increases R_H.

The last effect, elimination of the singularity in the hydrodynamic interaction (HI), seems at first sight to be due solely to nonbonded interactions, which prevent multiple occupation of a single lattice site. However, it is possible to devise sensible models that distinguish excluded volume effects from those due to HI at short distances. In the dynamical simulation of Gaussian and other models without excluded volume interactions,[4-7] it is necessary to modify the Oseen or $1/R$ HI in order to obtain positive definite diffusion matrices. For that purpose the Rotne–Prager[8] approximation works rather well[9] and is finite at $R = 0$. It gives a significant decrease in the Kirkwood value of R_G/R_H below what Oseen HI gives for finite Gaussian chains. Lattice values of R_G/R_H will be examined below; they are still smaller. Yet all these different calculations give the same Gaussian result in the limit of infinite N. It therefore seemed worthwhile to proceed to lengthier calculations with nonbonded interactions included, in order to gauge their isolated effect on the magnitude of R_G/R_H at the Θ point.

For several theoretical reasons, the nonbonded interactions were restricted to finite values, and very simple algorithms were used. First, the central limit theroem guarantees that interactions between beads close together along the backbone cannot give non-Gaussian statistics in the long-chain limit, regardless of their strength. Any prospect for non-Gaussian limits at the Θ point would have to derive from the cumulative effect of interactions between all beads i and j such that $|j - i|$ is large. And it seems impossible to find, in either intuition or theory, any reason to believe that the effects of such interactions should depend on their detailed form. However, the main motivation for using finite energies is that a quantitative interpretation of the effects is much easier if based on weak interactions or the use of pseudopotentials than if based on strong interactions which have large effects on the local conformational statistics.

In section II we review the methods used to generate and analyze ensembles of single chains and pairs of chains. Interactions between two chains are analyzed in order to determine the relative balance of attractive and repulsive energies at the Θ point. Use of a single-chain criterion for the Θ point such as constancy of R_G^2/N over what is bound to be a finite molecular weight range is dangerous. In the usual situation where the shortest range interactions are

† This work is dedicated to Walter Hugo Stockmayer, our teacher and companion during many an adventure in the hills and in science.

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repulsive and the longest range interactions are attractive, the latter have greater relative importance for short chains than for long ones because of the difficulty a short chain has in bending back. At the Θ point R_G^2/N for finite chains may be significantly less than its asymptotic value, the discrepancy decreasing as $1/N^{1/2}$. See section IV and also Allegra[10] and Martin.[11] An attempt to keep R_G^2/N constant for a finite molecular weight range is prone to exaggerate the estimated strength of attractive interactions at the Θ point.

In section III the simulation results are discussed, and in section IV they are compared with perturbation theory. Only a rather summary sketch of perturbation theory is presented. A more extensive analysis has recently been performed by Martin.[11] The perturbation theory summarized here concerns Gaussian chains with pseudopotential interactions. Plausible modifications are made to permit an approximate application to lattice chains. An exact development for lattice chains cannot make use of the independent distribution of certain chain vectors that facilitates calculations with the Gaussian model. So we have been content with an approximate conversion from the Gaussian to the lattice model.

The simulation results indicate that the effect of nonbonded interactions on R_G/R_H is quite small, not more than 1 or 2% in our calculations. These results and others on various moments of the end-to-end distance and comparison with perturbation theory indicate that all physically relevant moments scale at the Θ point as they would for Gaussian chains in the limit $N \to \infty$.

We cannot completely exclude the possibility that strong Θ point interactions will lead to significantly greater decreases in R_G/R_H than have been found here. That seems unlikely, however, because we find values of R_G/R_H for systems with weak or vanishing nonbonded interactions that are similar to those found by Guttman et al.[3] for self-avoiding walks.

II. Simulation Methods

A. Chain Generation and Weighting. Polymer chains with N beads and unit bond length were generated on a simple cubic lattice. The angle between adjacent bonds was required to be 90°; therefore each bond added after the first could be placed with equal probability along any of four equivalent lattice vectors. All the chains so generated, typically 4×10^4 for each N, have the same weight in the basic, random ensemble. The configurational properties that are required to introduce energetic interaction between beads were gathered at the time of chain generation, along with other properties such as the end-to-end distance, the radius of gyration, and certain sums of reciprocal distances required to compute the hydrodynamic radius.

It was assumed that energetic interactions would be allowed between beads i and j ($i, j = 1, ..., N$) only if the magnitude of the vector $\mathbf{R}_{ij}$ connecting them was 0 or 1. To provide some flexibility in the choice of interactions, we tabulated for each chain the number $N_0(k)$ or i,j pairs such that $|j - i| = k$ and $R_{ij} = 0$ and the number of pairs $N_1(k)$ such that $R_{ij} = 1$. All pairs for which $k > K$ were counted in with $N_0(K)$ or $N_1(K)$, and K was usually chosen to be 21. The "excluded volume" energy E used to bias the random ensemble has the form

$$E = E_0N_0 + E_1N_1 \tag{2.1}$$

where E_0 is the energy assigned to any pair of beads occupying the same site and E_1 is the energy assigned to any pair of beads occupying nearest-neighbor lattice sites. N_0 and N_1 were calculated from

$$N_0 = \sum_k N_0(k); \qquad N_1 = \sum_k N_1(k) \tag{2.2}$$

Restriction of the allowed k's in these sums permits the effects of various interactions to be isolated. Elimination of small k's from the sums permits the use of somewhat stronger interaction energies before the statistical precision becomes excessively reduced as a result of biasing the initially random ensemble. Averages of any function of configuration, say Q, were of course calculated from

$$\langle Q \rangle = \sum Qe^{-E}/\sum e^{-E} \tag{2.3}$$

where the sums run over all members of the random ensemble. Here and in the following the unit of energy is equal to k_BT.

The Θ point was established from a study of the interactions of two chains, each generated in the random or unbiased ensemble. The centers of mass of the two chains were placed at specified relative distances R_{12} or as close to these specified distances as a lattice translation would allow.[12] In addition to the information required for intramolecular interactions, the numbers of intermolecular bead overlaps and nearest-neighbor pairs, $N_0^{(2)}$ and $N_1^{(2)}$, respectively, were recorded. The intermolecular interaction $E^{(2)}$ could then be calculated in a subsequent study of the pair ensemble from

$$E^{(2)} = E_0N_0^{(2)} + E_1N_1^{(2)} \tag{2.4}$$

In principle, it would be possible to make the second virial coefficient vanish for any finite N through a proper combination of E_0 and E_1 and thereby establish an N-dependent Θ point. This Θ point would be defined by the requirement that the sum over all relative vector distances of $F(\mathbf{R}_{12})$ vanishes, where

$$F(\mathbf{R}_{12}) \equiv \langle 1 - \exp(-E^{(2)}) \rangle \tag{2.5}$$

and the average in eq 2.5 is over the internal conformation of each chain, weighted according to eq 2.3. However, we wished to use only a fixed Θ point characterizing the limit of infinite N. In that limit we expect not only that the sum of F will vanish for proper combinations of E_0 and E_1 but that these combinations will also make $F(\mathbf{R}_{12})$ vanish for all $\mathbf{R}_{12}$.[12] As nearly as could be determined from the study of F at three values of R_{12}, namely, 0, $R_{G,0}/2$, and $R_{G,0}$, where $R_{G,0}$ is the unbiased radius of gyration, this independence was reached fairly rapidly with increasing N. The value of E_1 required to make $F(\mathbf{R}_{12})$ vanish for a specified E_0 had a contribution decaying as $1/N$. Extrapolation of E_1 from its value for the largest two-chain system studied, $N = 321$, to infinite chain length left an apparent uncertainty in the asymptotic E_1 in the vicinity of 1% for the smaller E_0's and perhaps 2% for the larger E_0's.

For the larger E_0's, systematic errors in E_1 of another 1 or 2% cannot be entirely excluded because the two-chain interactions with large E_0 were studied with suppression of smaller k's in the sums (2.2) in order to improve statistical precision. This suppression did not change the estimate of E_1 by more than the statistical uncertainty for those values of E_0 such that both methods were applicable, namely, $E_0 \leq 0.4$.

It will be seen below that errors in the Θ point of the indicated magnitude have a small effect on the radius of gyration and hydrodynamic radius and a quite negligible effect on their ratio.

B. Hydrodynamic Radius. The hydrodynamic radius of the chain, R_H, is a Stokes law radius defined in terms of the diffusion constant D

$$6\pi\eta_0R_H = D^{-1} \tag{2.6}$$

Table I
Simulation Results vs. Chain Length: Weak Interactions[a]

	$E_0 = 0.0, E_1 = 0.0$				$E_0 = 0.1, E_1 = -0.0163$				$E_0 = 0.1, E_1 = -0.0161$				$E_0 = 0.1, E_1 = -0.0159$			
N	α_0^2	sd	ρ_0	sd	α_G^2	sd	α_{GH}	sd	α_G^2	sd	α_{GH}	sd	α_G^2	sd	α_{GH}	sd
11	1.001	3	1.060	1	1.008	<1	1.000	<1	1.008	<1	1.000	<1	1.008	<1	1.000	<1
21	0.998	3	1.152	1	1.017	<1	1.000	<1	1.017	<1	1.000	<1	1.018	<1	1.000	<1
41	0.997	2	1.233	1	1.026	<1	0.999	<1	1.027	<1	0.999	<1	1.028	<1	0.999	<1
81	0.999	2	1.301	<1	1.033	1	0.998	<1	1.035	1	0.999	<1	1.037	1	0.999	<1
161	0.998	1	1.354	<1	1.039	1	0.997	<1	1.042	1	0.997	<1	1.046	1	0.997	<1
321	0.997	2	1.395	1	1.043	2	0.997	<1	1.049	2	0.997	<1	1.054	2	0.998	<1
641	1.000	1	1.426	1	1.046	2	0.998	1	1.056	2	0.998	1	1.064	2	0.999	1
1281	1.001	2	1.449	1	1.034	4	0.995	1	1.047	4	0.995	1	1.060	4	0.996	1

[a] α_0^2 is the ratio $R_{G,0}^2/R_{G,anal}^2$; where $R_{G,0}^2$ is the simulation result for the mean square radius of gyration in the absence of excluded volume interactions, i.e., for $E_0 = E_1 = 0$, and $R_{G,anal}^2$ is the corresponding analytical result. ρ is the ratio of simulation radius of gyration to hydrodynamic radius, R_G/R_H; a subscript 0 indicates $E_0 = E_1 = 0$. α_G^2 is the ratio $R_G^2/R_{G,0}^2$, and α_{GH} is the ratio ρ/ρ_0. The Θ point for $E_0 = 0.1$ is estimated to occur at $E_1 = -0.0161$. Standard deviations, under the heading sd, are given in units of the last significant digit shown in the quantity to the left.

Table II
Simulation Results vs. Chain Length: Stronger Interactions at the Θ Point[a]

	$E_0 = 0.2, E_1 = -0.0315$				$E_0 = 0.3, E_1 = -0.0455$				$E_0 = 0.4, E_1 = -0.060$				$E_0 = 0.6, E_1 = -0.083$			
N	α_G^2	sd	α_{GH}	sd	α_G^2	sd	α_{GH}	sd	α_G^2	sd	α_{GH}	sd	α_G^2	sd	α_{GH}	sd
11	1.015	<1	1.000	<1	1.023	<1	1.000	<1	1.029	<1	1.000	<1	1.043	<1	1.000	<1
21	1.033	<1	1.000	<1	1.049	<1	1.000	<1	1.061	1	1.000	<1	1.092	1	1.001	<1
41	1.050	1	0.999	<1	1.074	1	0.999	<1	1.092	1	0.998	<1	1.138	2	0.999	1
81	1.065	1	0.998	<1	1.097	2	0.997	1	1.117	2	0.996	1	1.179	3	0.997	1
161	1.077	3	0.995	1	1.118	6	0.995	1	1.140	9	0.993	1	1.22	2	0.994	2
321	1.088	4	0.996	1	1.15	1	0.996	2	1.19	3	0.998	5	1.44	15	1.02	3
641	1.097	7	0.998	2	1.17	2	0.999	4	1.21	6	1.00	1				
1281	1.05	4	0.98	1	1.05	19	0.97	4								

[a] The notation is defined under Table I.

since $k_BT = 1$ in the current units. η_0 is the solvent viscosity. In the Kirkwood approximation[1] the diffusion constant is given by

$$D^K = N^{-2}\sum\sum\langle H_{ij}\rangle \tag{2.7}$$

where H_{ij} is the element of the diffusion matrix connecting beads i and j.

$$H_{ij} = \beta^{-1}\delta_{ij} + T_{ij} \tag{2.8}$$

$T_{ij} = 0$ if $i = j$; otherwise T_{ij} is $^1/_3$ the trace of the hydrodynamic interaction tensor connecting beads i and j. β is a bead friction constant, which will be written in the form

$$\beta = 3\pi\eta_0 d$$

where d is the Stokes diameter of the bead. T_{ij} is often evaluated in the approximation $\beta T_{ij} = d/(2R_{ij})$, usually referred to as the Oseen interaction, but this diverges at $R_{ij} = 0$ and cannot be used in a lattice calculation that allows bead overlaps. The Rotne–Prager approximation[8] yields finite and even moderately sensible values[9] for T_{ij} for all R_{ij}, and we have used it here. For $R_{ij} \geq d$, the Oseen and Rotne–Prager expressions agree. However, for $R_{ij} = 0$, the Rotne–Prager interaction gives $\beta T_{ij} = 1$. Subject to the assumption that the Stokes diameter of a bead does not exceed the lattice spacing, namely, unity, the Kirkwood–Rotne–Prager expression for R_H is

$$R_H^{-1} = (2/dN^2)\{N + 2[\langle N_0\rangle + (d/2)\sum_{i<j}\langle(1 - \delta(R_{ij}))/R_{ij}\rangle]\} \tag{2.9}$$

where

$$\delta(R_{ij}) = 1 \quad \text{if } R_{ij} = 0$$
$$= 0 \quad \text{if } R_{ij} \neq 0$$

We have used $d = 1$ for the calculations reported below. d does not have to be specified during the slow process of gathering chain properties, so it is easy to recalculate averages for other values. However, nothing interesting resulted from such a study. We note that $d = 1$ corresponds to a value in the range 0.4–0.5 for the conventional parameter h^* used by Guttman et al.[3]

$$h^* = \beta/[(12\pi^3)^{1/2}\eta_0 b']$$

where b' is a statistical segment length that is here unity in the random ensemble and is no more than 20% larger in our biased ensembles at the Θ point. Guttman et al.[3] used h^*'s of 0.3 and 0.4 in their study.

C. Verification of Methods. As the methods used to generate and sample the chains were fairly simple, there seemed to be few opportunities to go astray. However, we did compare simulation averages of various moments of the end-to-end distance with the averages computed from exact enumeration of the configurations of short chains, with excellent agreement.

Rough verification of some aspects of the work, such as the determination of the Θ point, may be found in the agreement with perturbation theory for small E_0. The application of perturbation theory is discussed in section IV.

III. Simulation Results

The simulation results to be discussed are shown in Tables I–III. Table III also contains perturbation theoretical results, which will be considered in section IV.

We begin with the unbiased ensemble, $E_0 = E_1 = 0$. The quantity of α_0^2 is the ratio

$$\alpha_0^2 \equiv R_{G,0}^2/R_{G,anal.}^2 \tag{3.1}$$

of the mean square radius of gyration computed by simulation, $R_{G,0}^2$, to the known analytical value. For the unbiased lattice ensemble, all second moments of bead–bead distances R_{ij} agree with their Gaussian values. Agreement

Table III
Simulation and Modified Perturbation Results vs. Chain Length

	simulation $E_0 = 0.1, E_1 = -0.0161$				perturbation $E_0 = 0.1, E_1 = -0.0157$		
N	α_2^2	sd	x_4	x_{-1}	α_2^2	x_4	x_{-1}
11	1.011	<1	0.996	0.998	0.979	0.978	1.057
21	1.021	1	0.995	1.005	1.005	0.984	1.041
41	1.030	1	0.995	1.010	1.024	0.989	1.029
81	1.038	1	0.996	1.010	1.038	0.992	1.021
161	1.045	1	0.996	1.011	1.048	0.994	1.015
321	1.051	2	0.997	1.006	1.056	0.996	1.010
641	1.064	5	1.001	1.005	1.061	0.997	1.007
1281	1.053	7	0.997	1.002	1.064	0.998	1.005
	simulation $E_0 = 0.2, E_1 = -0.0315$				perturbation $E_0 = 0.2, E_1 = -0.0298$		
N	α_2^2	sd	x_4	x_{-1}	α_2^2	x_4	x_{-1}
11	1.022	<1	0.992	0.997	0.958	0.958	1.109
21	1.040	1	0.991	1.010	1.008	0.970	1.079
41	1.056	1	0.991	1.017	1.045	0.978	1.056
81	1.071	2	0.993	1.017	1.072	0.985	1.040
161	1.082	3	0.994	1.018	1.092	0.989	1.028
321	1.090	6	0.996	1.010	1.106	0.992	1.020
641	1.10	1	1.005	1.019	1.115	0.995	1.014
1281	1.05	5	0.998	1.006	1.122	0.996	1.010

[a] α_2^2 is the expansion factor $\langle R^2\rangle/\langle R^2\rangle_0$, where R is the end-to-end distance. x_n is the ratio of the squared expansion factor for the nth moment to α_2^2.

of analytical and simulation results is shown in Table I to within a few tenths of a percent. The ratio $\rho \equiv R_G/R_H$, designated ρ_0 in the unbiased ensemble, increases quite slowly with increasing chain length and is still significantly below the Gaussian limit of 1.5045 for a chain of 1281 beads. The lattice averages of reciprocal distances are larger than the Gaussian averages because the reciprocal distances are more sensitive to small R_{ij} and are therefore more sensitive to the constraints of fixed bond lengths and angles than the second moments. The actual magnitude of ρ_0 of course depends on the Stokes diameter d, which is here unity. With Rotne–Prager HI, the limiting value of ρ_0 is approached from below for lattice chains with $d \gtrsim 0.4$ (or $d \gtrsim 0.5$ for Gaussian chains.) Small d's reduce hydrodynamic interaction and decrease R_H; see eq 2.9. Larger d's increase R_H and exaggerate the effect shown in Table I.

Results for chains with interactions are generally shown as ratios to results without interaction. Thus

$$\alpha_G^2 \equiv R_G^2/R_{G,0}^2 \tag{3.2}$$

and

$$\alpha_{GH} \equiv \rho/\rho_0 \tag{3.3}$$

Table I shows values of α_G^2 and α_{GH} for $E_0 = 0.1$ and a small range of E_1 values about the estimated Θ point $E_1 = -0.0161$. Small but quite noticeable changes in dimensions result from small changes in the nearest-neighbor interaction E_1. However, the effect on the ratio of R_G to R_H is seen to be extremely slight. It therefore seems quite unlikely that errors in the estimates of Θ points will have any significant effect on the results for α_{GH}.

Table II shows results for α_G^2 and and α_{GH} at larger values of E_0 for a value of E_1 estimated to be the Θ point. Statistical uncertainties in α_G^2 are quite large for large N and E_0, but uncertainties in the ratio of dimensions α_{GH} are typically much smaller, by factors of 2–10. α_{GH} decreases slightly below unity as N increases from the minimum value, $N = 11$. α_{GH} varies little with E_0. It is not clear from the data whether this small decrease below unity will disappear as N becomes large. We believe it disappears in view of the studies of end-to-end moments to be discussed next and considering the perturbation theory in section IV.

One of the reasons for ambiguity in the N dependence is that the radius of gyration and the hydrodynamic radius involve averages over all possible pairs of beads. This helps to reduce statistical uncertainty but also tends to obscure the N dependence. We therefore examined several moments of the end-to-end distance R. The results are expressed in terms of the quantities

$$(\alpha_n)^n \equiv \langle R^n\rangle/\langle R^n\rangle_0 \tag{3.4}$$

and

$$x_n \equiv \alpha_n^2/\alpha_2^2 \tag{3.5}$$

For $n = -1$, the function $1/R$ is replaced by $(1 - \delta(R))/R$, where $\delta(R)$ vanishes for $R = 0$ and is 1 otherwise. Simulation results are shown for α_2^2, x_4, and x_{-1} at the Θ point in Table III. The expansion of the chain due to Θ point interactions is somewhat greater when inferred from $1/R$ averages in comparison to R^2 averages and is very slightly less when inferred from R^4 averages. There is a noticeable trend, not apparent in α_{GH}, for the discrepancies between different measures of expansion x_n to increase with E_0 and a trend, somewhat murky for $E_0 = 0.2$, to decrease at the larger values of N. A tolerably satisfactory quantitative explanation of these trends is given in the next section on the basis of a modified Gaussian perturbation theory. Qualitative rationalizations were presented in the Introduction.

IV. Perturbation Theory

The purpose of this section it to show that the simulation results are reasonably consistent with perturbation theory. Quantitative agreement cannot be expected because the available perturbation theory,[1,11,13] summarized in the Appendix, was carried through only for Gaussian chains. Although modifications in the theory make it approximately valid for long chains on a lattice, the statistical accuracy of the simulations decreases with increasing chain. Accordingly, we seek only a rough verification of consistency.

A. Gaussian Perturbation Theory. The perturbation theory of Gaussian chains was based on a generalization of the familiar[1] pseudopotential form for the cluster function $f(r)$

$$f(r) \equiv 1 - \exp(-E(r)) \tag{4.1}$$

where $E(r)$ is the interaction energy between a pair of beads. The generalization consists of the approximation

$$f(r) = \epsilon\delta(\mathbf{r}) + \gamma\nabla^2\delta(\mathbf{r}) \tag{4.2}$$

Integration of eq 4.2, first as it stands and then after multiplication by r^2, gives

$$\epsilon = \int f(r)\, d\mathbf{r} \tag{4.3}$$

and

$$6\gamma = \int r^2 f(r)\, d\mathbf{r} \tag{4.4}$$

In the conversion to a lattice model in which the primitive cell is a cube of unit dimensions, the integrals are replaced by sums. We take $\epsilon = 0$; this defines the Θ point in the pseudopotential approximation.

A first-order Ursell–Mayer expansion of the average of R^ν, where R is the distance between beads i and j and $|i - j| = M$, involves the Gaussian average of the product of R^ν and $f(r_{kl})$, which must be summed over k and l. It turns

out that only those interaction diagrams for which k and l lie in the interval between i and j count in the limit that M and the chain length become large. In other words, the asymptotic effect on dimensions can be computed as if i and j were end beads and $M = N - 1$. We will also be interested in corrections to that limit, but the displayed correction is valid only when R is the end-to-end distance. A more general choice of i and j gives results for the corrections which have seemed too messy to explore. With ν any power of R for which the necessary integrals exist

$$\langle R^\nu \rangle = \langle R^\nu \rangle_0 (\alpha_\nu)^\nu \tag{4.5}$$

where α_ν is an expansion factor that, a priori, may depend on ν. It has the form

$$\alpha_\nu^2 = 1 - (2\gamma/\nu)(3/2\pi)^{3/2} \sum_{x=1}^{N-1} U_\nu(x) \tag{4.6}$$

where

$$U_\nu(x) \equiv 9N(1-y)[1-(1-y)^{\nu/2}]x^{-5/2} + 3\nu(1-y)^{\nu/2}x^{-3/2} \tag{4.7}$$

$$y \equiv x/N$$

For large N, evaluation of the sum in eq 4.6 gives

$$\alpha_\nu^2 = 1 + p + \delta_\nu/N^{1/2} \tag{4.8}$$

where

$$p = -15\gamma P(0) \tag{4.9}$$

and

$$P(0) = (3/2\pi)^{3/2} \sum_{1}^{\infty} x^{-3/2} \tag{4.10}$$

p is an asymptotic expansion factor that is independent of ν. The correction term is given by

$$\delta_\nu = -2\gamma(3/2\pi)^{3/2}(C_\nu - 15) \tag{4.11}$$

where C_ν is an integral recorded in the Appendix that has integer values for those ν of special interest here: $C_{-1} = 3$, $C_2 = -15$, and $C_4 = -22$.

For the lattice average of the reciprocal end-to-end distance, $\nu = -1$, configurations for which $R = 0$ have to be excluded. The lattice average is taken of the function $(1 - \delta(R))/R$. In the continuum model, exclusion of a small sphere around the point $R = 0$ adds only a $1/N$ correction to eq 4.8. The $1/N$ term has been neglected in comparison to the $1/N^{1/2}$ correction.

A second point to be made in connection with averages of $1/R$ is that the $1/N^{1/2}$ form of the correction is a characteristic only of the average for a single pair of beads. The sum over pairs required to calculate the hydrodynamic radius leads to a correction proportional to $\ln N/N^{1/2}$. Such a slowly decaying function might give trouble in the extrapolation of experimental or simulation results for R_H.

B. Lattice Perturbation Theory. For chains with 90° bond angles on the simple cubic lattice, eq 4.3 and 4.4 are replaced by

$$\epsilon^{sc} = \sum f(r) = 1 - e^{-E_0} + 6(1 - e^{-E_1}) \tag{4.12}$$

and

$$\gamma^{sc} = 6^{-1} \sum r^2 f(r) = 1 - e^{-E_1} \tag{4.13}$$

The quantity $P(0)$, which occurs in the calculation of p in eq 4.8, has been defined in such a way that its physical meaning is clear. It is the probability that any bead makes a contact within unit volume of any bead further along in an infinite chain. We assume that the corresponding value of p for lattice chains is obtained by replacing $P(0)$ by $P^{sc}(0)$ in eq 4.9, where $P^{sc}(0)$ is the probability that any bead occupies the same site as any bead further along the chain. Extrapolation of our simulation results for $P^{sc}(0)$ at $N = 641$ and $N = 1281$ to infinite chains, assuming a $1/N$ dependence on chain length, gave a 4% change in $P^{sc}(0)$ beyond its value for $N = 1281$ and the result

$$P^{sc}(0)/P(0) \cong 0.356 \tag{4.14}$$

It was assumed that δ_ν, because its value is determined from interactions between beads widely separated along the backbone, is approximately the same for lattice and Gaussian chains.

Various quantities derived from the modified perturbation theory are shown in comparison with simulation results in Table III. Perturbation values of E_1 are derived from eq 4.12 with $\epsilon^{sc} = 0$. The quantities x_n are given by

$$x_n \equiv (\alpha_n/\alpha_2)^2 = 1 - 2\gamma^{sc}(3/2\pi)^{3/2}(C_n - C_2)/N^{1/2} \tag{4.15}$$

The agreement between found and predicted values of α_2^2, the expansion factor for the mean square end-to-end distance, is reasonably good, except for small chain lengths. The more sensitive tests for x_4 and x_{-1} are only qualitatively successful, but the precision of the x_n is not very high for large N, where the perturbation theory is expected to work. Standard deviations are not shown for the x_n but are in the vicinity of one-fourth the standard deviations of the corresponding α_2^2. At least the signs, trends with increasing N, and rough values for large N are all correctly predicted.

We conclude that our chains are indeed asymptotically Gaussian at the Θ point.

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Appendix

The Ursell–Mayer expansion of $Q(R) \equiv R^\nu$, $\mathbf{R} \equiv \mathbf{R}_{ij}$, is given by[1]

$$\langle Q(R) \rangle = \langle Q(R) \rangle_0 + \sum_{k<l} [\langle Q(R) \rangle_0 \langle f(r) \rangle_0 - \langle Q(R) f(r) \rangle_0] + \ldots \tag{A1}$$

where $\mathbf{r} \equiv \mathbf{R}_{kl}$. The cluster function $f(r)$ is defined in eq 4.1 and will be approximated by the pseudopotential (4.2) with $\epsilon = 0$. The averages $\langle\ \rangle_0$ are taken over Gaussian distributions.

If $\nu = -1$, a problem arises for the special term in eq A1 such that $\mathbf{R}$ and $\mathbf{r}$ are identical. This situation arises for Oseen hydrodynamic interaction (HI) between beads i and j, coupled to energetic interaction between the same two beads. Quantities like $\langle Q(R) \nabla^2 \delta\ (\mathbf{r}) \rangle_0$ do not exist in that special case. Of the various ways to deal with this problem i.e., substitution of nonsingular HI, such as the Rotne–Prager interaction, introduction of a more realistic potential, or omission of the troublesome terms, we adopt the simplest, i.e., the last, because the results differ only by $\mathcal{O}(1/N)$ fractional contributions to $\langle Q(R) \rangle$.

Several additional assumptions have been used to simplify the evaluation of eq A1. It is assumed that $N \to \infty$ and that the ratio $|i - j|/N$ remains constant, although the ratio may be small. The main purpose of these assumptions is to permit the elimination of two out of the three kinds of cluster diagrams[1]. Only the simplest, for which $i < k < l < j$, are retained. In these diagrams the contacts occur between beads located along the chain connecting i to j. The more complicated diagrams may be shown to make a fractional contribution to $\langle Q(R) \rangle$ that vanishes as $1/N^{1/2}$ for large N. We suppress the complicated diagrams, with the consequence that the limiting value of $\langle Q(R) \rangle /$

$\langle Q(R)\rangle_0$ is correctly calculated for arbitrary i and j; however, the deviation from that limit, which vanishes as $1/N^{1/2}$, is correctly calculated only if i and j are the end beads.

A possible problem occurs in the mechanics of the calculation for $\nu = -1$, depending on the procedures used. The prospective pitfalls can be avoided by taking the limit $\nu \to -1$, from above.

The simplest diagrams lead rather quickly to eq 4.7, and that in turn to eq 4.8. There remains only to record that the integral in eq 4.11 is given by

$$C_\nu = \nu^{-1}\int_0^1 [-9\nu/(2y^{1/2}) + 9(1-y)f_2(y)y^{-5/2} + 3\nu f_1(y)y^{-3/2}]\,dy \quad \text{(A2)}$$

where

$$f_1(y) \equiv (1-y)^{\nu/2} - 1$$

and

$$f_2(y) \equiv -f_1(y) - \nu y/2$$

References and Notes

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Light Scattering Study on Polystyrene in Cyclohexane below the Θ Point†

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ABSTRACT: Light scattering measurement was performed on three monodisperse polystyrene samples ($M = 10 \times 10^3$, 43.6×10^3, and 180×10^3) in cyclohexane in the temperature range from the theta point Θ to 1 °C above the cloud point. From the data obtained the Flory–Huggins interaction parameter χ was expressed as a function of temperature T, polymer volume fraction ϕ, and molecular weight M. This expression for χ was extended to T below the cloud point to calculate critical points, cloud point curves, and spinodals for a series of M values. Good agreement, certainly better than obtained by previous formulations, was found between the calculated results and some typical experimental data. The success is due primarily to the formulation of the experimental finding that χ at high concentration depends significantly on M, in contrast to the usual concept on thermodynamic behavior of concentrated polymer solutions.

This paper is concerned with a very basic but still less satisfactorily solved problem in polymer solution thermodynamics. It is to establish the Flory–Huggins interaction parameter χ that allows quantitative and consistent prediction of phase relationships in strictly binary solutions consisting of a monodisperse polymer and a pure solvent—the simplest of polymer solutions. Much has been worked out over the past 3 decades to find such an expression. Yet, the results obtained do not seem fully satisfactory.[1] This may be understood from the following brief, but somewhat biased, survey of previous studies which we believe have made substantial contributions to the problem concerned.

In 1970, Koningsveld et al.[2] derived from critical point data for polystyrene in cyclohexane an empirical expression

$$\chi = 0.2035 + 90.65T^{-1} + 0.3092\phi + 0.1554\phi^2 \quad (1)$$

for χ at T below the theta point Θ. Here, T is the absolute temperature and ϕ the volume fraction of the polymer in the solution. It should be noted that eq 1 does not contain the molecular weight M of the polymer as the variable. In 1971, Scholte[3] published an important experimental study in which he determined χ for the polystyrene + cyclohexane system above and below Θ by light scattering and could represent the results in terms of an expression similar to eq 1 but different in that the coefficient of T^{-1} depends on M. Either eq 1 or Scholte's expression was less satisfactory, yielding spinodals significantly narrower than the observed ones.

In a paper also of 1971, Koningsveld and Kleintjens[4] reanalyzed the above-mentioned critical point data, assuming for χ a closed expression as

$$\chi = \alpha + (\beta_{00} + \beta_{01}T^{-1})(1-\gamma)/(1-\gamma\phi)^2 \quad (2)$$

where α, β_{00}, β_{01}, and γ are constants. This approach, however, failed to achieve consistent agreement with observed spinodals for different molecular weight samples.

It became evident from these studies that χ depends on M as well as on T and ϕ and that an M dependence must be taken into χ for an accurate prediction of binodals and spinodals of polymer solutions. An interesting theory in this line of thought was presented by Koningsveld et al.[5] in 1974. Considering the well-known fact that the spatial

† It is our great pleasure to dedicate this paper to Professor W. H. Stockmayer on occasion of his 70th birthday.

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