Dimensions and Intrinsic Viscosities of Long Linear and Star Chains in Good- and Θ-Solvent Conditions

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ABSTRACT: Dimensions and intrinsic viscosities are calculated for different models of linear and star chains with a wide range of chain lengths. Viscosities are evaluated according to an efficient lower-bound method. The chain models mimic both the good-solvent and Θ-solvent conditions. These calculations permit refinement of previous estimations from results calculated with an upper-bound method for considerably shorter chains.

Introduction

The presence of fluctuating hydrodynamic interactions (FHI) between chain units constitutes a serious complication for the quantitative prediction of hydrodynamic properties of flexible chains in dilute solution. In recent years, important efforts in both theoretical and simulation work have been devoted to this problem. The only rigorous method so far available for obtaining correct numerical results for the hydrodynamic parameters of chain models consists in generating dynamical trajectories.[1] However, this method involves certain numerical difficulties that can only be overcome through the use of an unreasonable amount of computational time for chains with a relatively high number of units, N.

On the other hand, several types of equilibrium Monte Carlo calculations have been devised to obtain approximate values which, in fact, constitute lower or upper limits for the exact results. An upper-bound limit for determining friction and viscosity can be obtained by generating an equilibrium sample of instantaneously rigid conformations, for each of which the properties are calculated rigorously; the final results are then obtained as averages over these samples. This method was first proposed by Zimm[2] and has been extensively used in previous work involving the present authors[3-7] to study chains with intramolecular interactions which mimic different solvent conditions. Recently, we have also explored[8] a variational method, first proposed by Fixman,[9] that yields lower bounds, obtaining results for Gaussian chains of different architectures. The method is relatively simple in the case of viscosity and has the important advantage with respect to the upper-bound procedures that is does not requires the inversion of $3N \times 3N$ matrices in each simulation step. This allows us to increase the range of chain lengths that can be investigated. A detailed analysis of the performance of this method is given elsewhere.[8]

The influence of FHI on property values is better understood when the results obtained with the methods described above are compared with values calculated with preaveraged hydrodynamic interaction (PHI), an approximation contained in the standard theories.[10] Differences depend on the property considered and the compactness of the chain (which is directly related with its architecture and the solvent conditions). These differences are especially large (reaching more than 100%) for the viscosity of many-armed chains in Θ solvents, while the differences are less marked for simpler chains or better solvents. Consequently, the PHI calculations cannot properly reproduce the experimental values of the well-known Flory parameter $\Phi = [\eta]M/6^{3/2}\langle S^2\rangle^{3/2}$ (obtained from measurements of the intrinsic viscosity, $[\eta]$, the mean square radius of gyration, $\langle S^2\rangle$, and the chain molecular weight, M) or the ratio

$$g' = [\eta]_b/[\eta]_l \qquad (1)$$

where subscripts l and b refer to a linear and a branched (star) chain of the same N (or molecular weight).

Previous work with the upper-limit approach[3-7] has yielded extrapolated values of g' to high molecular weights for stars with different numbers of arms, and of Φ for stars, rings, and linear chains with intramolecular interactions that represent different types of solvent conditions. These extrapolations could only however be considered as tentative since the computational limitations of the method allowed us to perform simulations only for relatively short chains. Here we present calculations with the lower bound method which have been extended to stars and linear chains long enough to minimize most finite size effects. We also compare the lower- and upper-bound results for the properties of shorter chains of different types and solvent conditions in order to bracket more precisely the expected rigorous theoretical predictions in all these different cases.

Methods and Results

For the lower-bound calculations of $[\eta]$, we have made use of a general algorithm previously described.[8] This algorithm was devised to be applicable for different types of Monte Carlo sampling procedures, but has been previously employed only for unperturbed Gaussian chains. In the present work we have calculated properties for three different types of polymer models: (1) The unperturbed Gaussian chains in which neighboring beads are separated by distances which follow a Gaussian distribution characterized by a given statistical length b; no other types of interactions between beads are present. This model corresponds to a chain without long-range intramolecular potential. (2) Chains

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generated with a Gaussian distribution of distances between neighboring units, but with a hard-sphere potential between nonneighboring units so that conformations in which the distance between two of these units R_{ij} is smaller than a given value σ_{HS} are not allowed. This model is adequate to represent chains in the excluded volume or good solvent conditions. (3) A similar model in which the hard-sphere potential is replaced by a Lennard-Jones (LJ) intramolecular potential of the type

$$U(R_{ij}) = 4\epsilon[(\sigma_{LJ}/R_{ij})^6 - (\sigma_{LJ}/R_{ij})^{12}] \quad (2)$$

where σ_{LJ} and ϵ are the LJ parameters. This model can reproduce the properties of chains at different temperatures (or solvent conditions) by varying the energy well parameter ϵ/k_BT (k_B is the Boltzmann factor and T is the temperature). This variety of models permits a broad discussion of the validity of our numerical results as predictions of the behavior of chains in different conditions.

We have generated samples of linear chains and star chains with 12 arms. The description of properties for these many-armed star polymers presents serious difficulties for the theoretical point of view,[11] which adds special interest to the simulations.

As previously described,[12] the Gaussian stars are independently generated by joining vectors randomly chosen so that their coordinates follow Gaussian distributions whose quadratic deviations are given by $b^2/3$. Some numerical results with this simple model have been already reported for linear and star chains.[8] The intramolecular potentials have been introduced with the values $\sigma_{HS}/b = 0.55$ for model 2 and $\sigma_{LJ}/b = 0.8$ for model 3, which have been used in previous investigations.[3-7,13]

For the models 2 and 3 we have used several different Monte Carlo sampling techniques. For star chains we have preferently utilized a method (denoted method a in ref 3) in which we change the coordinates of a randomly selected bond vector. Then the rest of the arm to which this bond belongs is translated to the end of the new bond vector. For linear chains in the Θ state we also use this method (considering a linear chain with an odd number of units as a star with two arms). However, for linear chains in good solvent conditions we have found it useful to use a slighly different stochastic method; in this case we also change a bond vector, but now the rest of the arm is rotated according to three randomly selected Euler angles and then added to the new bond vector. This method combines the Gaussian distribution of neighboring units with the basic Pivot algorithm, which has been shown to be a very efficient way to sample long self-avoiding chains.[14]

The lower-bound calculations require a prior evaluation of different quadratic and reciprocal averages of internal distances $\langle R_{ij}^2 \rangle$ and $\langle R_{ij}^{-1} \rangle$. For the Gaussian model, these averages can be obtained from analytical expressions.[10] The models with intramolecular potentials, for which previous lower-bound calculations have not been attempted, require one to obtain these averages through a preliminary simulation. We have performed this simulation with the same samples that are later employed for the lower-bound calculations. (This initial simulation is also utilized to obtain simultaneously the radius of gyration of the chains, as it is directly dependent on the averages $\langle R_{ij}^2 \rangle$ as well as a preaveraged estimation of the viscosity.[10]) An efficient storage of the internal averages is desirable. For this purpose, it is useful to remember that the averages corresponding to different pairs of units separated from the center of the chain by the same number of bond vectors should be identical. (The same simplifications apply to a linear chain with an odd number of units considered as a star with two arms.) These symmetry considerations have allowed us to reduce the storage requirements considerably.

As we did in the upper-bound calculations,[4-5] we only use a small fraction of the total number of generated conformations ($^1/_{50}$ to $^1/_{400}$) to perform the hydrodynamic calculations, since these calculations require a large computational effort, considerably higher than that needed for the sampling process. Fortunately, following the trend of other hydrodynamic calculations,[4-7,12,15] the quantities related to the intrinsic viscosity lower-bound evaluation present a relatively narrower distribution than those corresponding to the averages of the internal distances or the radius of gyration. (These equilibrium properties are computed in each simulation step.) Usually, we employ a total number of steps ranging from 25 000 to 200 000. The structure of the lower-bound calculations is simple, involving only the evaluation of double sums extended over the different pairs of units.[8] This has allowed us to write a FORTRAN code which can be efficiently used on vector processors.

A hydrodynamic size for the beads must be introduced in the calculations in terms of the friction radius, σ. We have employed the hydrodynamic interaction parameter, h^*, defined as

$$h^* = (3/\pi)^{1/2}(\sigma/b) \quad (3)$$

We have set the value $h^* = 0.25$ for most of our calculations although some calculations have been also carried out with significantly smaller and higher values for this parameter ($h^* = 0.10$ and 0.40). The value $h^* = 0.25$ is very close to that expected for a Gaussian coil unit[2] and ensures the fastest approach to the high $h^*N^{1/2}$ asymptotic limit, while smaller values of h^* tend to reproduce the free-draining behavior for short chains. Most of our previous calculations[6,8,12,15] have been also performed with $h^* = 0.25$. However, the upper-bound results in ref 4 and 5, which are erroneously reported as corresponding to this value of h^*, were in fact calculated with $h^* = 0.20$. This difference, however, does not alter significantly the final values for the extrapolated parameters or ratios of properties found there. In fact, many of them are fairly consistent with the results of this work, as will be discussed in the next section. Furthermore, we have already reported in ref 7 some upper-bound results for $h^* = 0.25$ and the same models of linear chains, which lead to similar extrapolated parameters. In addition, we have evaluated in the present study some new upper-bound values with $h^* = 0.25$ for relatively short chains which are obtainable in a reasonable computational time. These values are included in Table I, together with results previously calculated the same way for unperturbed Gaussian chains.[12]

In Table I, we have also included the main results of the present study. Thus, we report our results for $\langle S^2 \rangle$, the lower-bound for the viscosity in reduced units, $[\eta]^* = [\eta]M/N_Ab^3$ (N_A is the Avogadro number), and Φ, calculated for chains of different types and sizes, with different values of h^*. The discrepancies of the lower-bound viscosity results with respect to the corresponding upper-bound value never exceed 10% for the range of chain length where both types of calculations have been feasible, but it is known[1] that these differences can increase with increasing chain length. Values of $\langle S^2 \rangle$ for unperturbed Gaussian chains, which can be easily evaluated from analytical formulas,[10,16] are also contained in Table I.

Discussion

In Table II, we show ratios of the results for $[\eta]$ obtained with the lower-bound method to those calculated according to the preaveraged treatment.[8,10] In most cases, we present values for the longest chains, since these ratios only depend weakly on N, although some long-chain extrapolations have been also performed through linear regression analysis vs $N^{-1/2}$ similar to those employed in previous work.[4,5,12] (We extrapolate using the variable $N^{-1/2}$ rather than N^{-1} since the nondraining hydrodynamic properties scale as $N^{1/2}$.) It can be observed that the ratios decrease with increasing friction radius, higher chain compactness, and poorer conditions, trends already discussed in previous work. We point out the high differences of the lower- (and upper-) bound results with respect to the PHI values found for star chains (higher than 100% in Θ conditions) and also the relatively small differences introduced by the PHI approximation in the case of linear chains with excluded volume (smaller than 10%).

The influence of chain length is considerably more complex depending also upon the other variables mentioned above. Thus, we include in Table III the exponents ν_S and ν_η obtained from log–log linear regression analysis

Table I
Results for Dimensions, Viscosity, and Parameter Φ, Obtained in This Work for Different Types of Chains, Models, and Hydrodynamic Treatments[a]

chain	model	hydrodynamic treatment	N	$\langle S^2 \rangle$	$[\eta]^*$	Φ
$F = 2$	Gauss	lb ($h^* = 0.25$)	25	4.16[b]	44.0 ± 0.2	2.13 ± 0.01
			49	8.16[b]	122 ± 1	2.14 ± 0.02
			109	18.16[b]	412 ± 2	2.18 ± 0.01
			145	24.16[b]	626 ± 4	2.16 ± 0.02
			325	54.17[b]	2088 ± 10	2.15 ± 0.01
$F = 2$	Gauss	ub ($h^* = 0.25$)	25		50 ± 2[c]	2.56 ± 0.10
			49		143 ± 12[c]	2.59 ± 0.22
$F = 2$	Gauss	lb ($h^* = 0.1$)	25		23.8 ± 0.1	1.15 ± 0.01
			49		74.9 ± 0.3	1.32 ± 0.01
			109		286 ± 1	1.51 ± 0.01
			145		451 ± 4	1.56 ± 0.01
			325		1652 ± 9	1.70 ± 0.01
$F = 2$	Gauss	lb ($h^* = 0.4$)	25		59.6 ± 0.2	2.88 ± 0.01
			49		154 ± 1	2.71 ± 0.01
			109		483 ± 2	2.56 ± 0.01
			145		720 ± 2	2.49 ± 0.02
			325		2293 ± 10	2.36 ± 0.01
$F = 2$	HS	lb ($h^* = 0.25$)	25	6.18 ± 0.03	69 ± 1	1.83 ± 0.04
			49	13.8 ± 0.4	225 ± 2	1.78 ± 0.02
			109	35.9 ± 0.2	912 ± 16	1.75 ± 0.04
			145	50.4 ± 0.2	1547 ± 18	1.77 ± 0.03
			325	130 ± 1	6500 ± 70	1.80 ± 0.02
$F = 2$	HS	ub ($h^* = 0.25$)	25		72.1 ± 0.6	1.91 ± 0.03
			49		246 ± 2	1.87 ± 0.05
$F = 2$	HS	lb ($h^* = 0.1$)	25		36.8 ± 0.6	0.99 ± 0.02
			49		135 ± 3	1.06 ± 0.03
			109		620 ± 10	1.18 ± 0.03
			145		1060 ± 1	1.21 ± 0.02
$F = 2$	LJ(EV)	lb ($h^* = 0.25$)	25	6.88 ± 0.01	77 ± 1	1.76 ± 0.02
			49	15.3 ± 0.2	257 ± 3	1.75 ± 0.05
			109	39.3 ± 0.1	1080 ± 20	1.79 ± 0.04
			145	55.2 ± 0.2	1717 ± 10	1.72 ± 0.02
			325	144 ± 1	7500 ± 100	1.78 ± 0.04
$F = 2$	LJ(EV)	ub ($h^* = 0.25$)	25		81.0 ± 0.05	1.84 ± 0.04
			49		273 ± 3	1.87 ± 0.06
$F = 2$	LJ(θ_1)	lb ($h^* = 0.25$)	25	5.6 ± 0.1	63 ± 1	1.96 ± 0.05
			49	10.9 ± 0.2	185 ± 8	2.09 ± 0.14
			109	22.0 ± 0.2	587 ± 7	2.32 ± 0.06
			145	27.7 ± 0.3	840 ± 15	2.37 ± 0.07
$F = 2$	LJ(θ_1)	ub ($h^* = 0.25$)	25		67.6 ± 0.7	2.07 ± 0.05
			49		188 ± 3	2.17 ± 0.08
$F = 2$	LJ(θ_2)	lb ($h^* = 0.25$)	25	5.78 ± 0.02	65 ± 1	1.92 ± 0.04
			49	11.8 ± 0.1	199 ± 3	2.01 ± 0.05
			109	25.7 ± 0.1	687 ± 8	2.16 ± 0.03
			145	33.4 ± 0.2	1052 ± 15	2.23 ± 0.04
$F = 12$	Gauss	lb ($h^* = 0.25$)	25	1.34[b]	18.5 ± 0.1	4.79 ± 0.02
			49	2.30[b]	46.2 ± 0.2	5.43 ± 0.01
			109	4.67[b]	143 ± 1	5.80 ± 0.02
			145	6.08[b]	215 ± 1	5.88 ± 0.02
			325	13.17[b]	697 ± 2	6.24 ± 0.02
$F = 12$	Gauss	ub ($h^* = 0.25$)	25		19.8 ± 0.1[c]	8.84 ± 0.04
			49		54 ± 2[c]	8.5 ± 0.3
$F = 12$	HS	lb ($h^* = 0.25$)	25	1.96 ± 0.01	28.1 ± 0.5	4.19 ± 0.10
			49	3.84 ± 0.02	88 ± 2	4.76 ± 0.12
			109	8.04 ± 0.01	271 ± 5	4.88 ± 0.10
			145	12.4 ± 0.1	520 ± 8	4.86 ± 0.10
			325	31.4 ± 0.1	2168 ± 38	5.04 ± 0.11
$F = 12$	HS	ub ($h^* = 0.25$)	25		30.3 ± 0.1	4.51 ± 0.03
			49		90.6 ± 0.5	4.95 ± 0.07
$F = 12$	LJ(EV)	lb ($h^* = 0.25$)	25	2.26 ± 0.01	34.3 ± 0.5	4.15 ± 0.07
			49	4.39 ± 0.02	102 ± 1	4.54 ± 0.08
			109	10.3 ± 0.1	379 ± 6	4.72 ± 0.10
			145	13.8 ± 0.1	600 ± 10	4.81 ± 0.10
			325	33.5 ± 0.2	2410 ± 50	5.12 ± 0.15
$F = 12$	LJ(EV)	ub ($h^* = 0.25$)	25		35.0 ± 0.2	4.22 ± 0.05
			49		105 ± 1	4.68 ± 0.06
$F = 12$	LJ(θ_1)	lb ($h^* = 0.25$)	25	2.09 ± 0.01	31.7 ± 0.8	4.31 ± 0.14
			49	3.77 ± 0.02	84 ± 2	4.69 ± 0.14
			109	7.86 ± 0.04	278 ± 8	5.16 ± 0.19
			145	10.2 ± 0.1	416 ± 4	5.26 ± 0.06
$F = 12$	LJ(θ_1)	ub ($h^* = 0.25$)	25		32.1 ± 0.1	4.35 ± 0.06
			49		89.4 ± 0.9	4.94 ± 0.13
$F = 12$	LJ(θ_2)	lb ($h^* = 0.25$)	25	2.10 ± 0.01	31.7 ± 0.7	4.26 ± 0.11
			49	3.88 ± 0.02	89 ± 2	4.78 ± 0.14
			109	8.18 ± 0.03	282 ± 5	4.93 ± 0.13
			145	10.7 ± 0.1	429 ± 19	5.05 ± 0.28

[a-c] Results calculated from exact analytical formulas[10,16] are denoted by superscript *b*. Upper bound results for unperturbed chains, previously reported,[12] are denoted by superscript *c*. Dimensions are only reported once for the same chain and model, treated with different hydrodynamic methods. Definitions are as follows: Gauss, unperturbed Gaussian chain; HS, chain with a hard-sphere potential; LJ(EV), chain with a LJ potential, $\epsilon/k_BT = 0.1$; LJ(θ_1), chain with a LJ potential, $\epsilon/k_BT = 0.3$; LJ(θ_2), chain with a LJ potential, $\epsilon/k_BT = 0.275$; lb, lower-bound method; ub, upper-bound method; F, the number of arms of a star chain ($F = 2$, linear chain).

Table II
Long-Chain Values for Parameter Φ and $[\eta]/[\eta]_{preav}$ for Different Types of Chains According to the Results Obtained in This Work (Lower Bound Hydrodynamic Treatment)[a]

chain	model	h^*	$\Phi \times 10^{-23}$	$[\eta]/[\eta]_{preav}$
$F = 2$	Gauss	0.25	2.15 ± 0.00	0.75
$F = 2$	Gauss	0.10	1.87 ± 0.01*	0.83
$F = 2$	Gauss	0.40	2.20 ± 0.01*	0.69
$F = 2$	HS	0.25	1.80 ± 0.02	0.89
$F = 2$	HS	0.10	1.36 ± 0.03*	0.92
$F = 2$	LJ(EV)	0.25	1.78 ± 0.04	0.91
$F = 2$	LJ(θ_1)	0.25	2.65 ± 0.10*	0.70*
$F = 2$	LJ(θ_2)	0.25	2.54 ± 0.07*	0.80*
$F = 12$	Gauss	0.25	6.72 ± 0.02*	0.48
$F = 12$	HS	0.25	5.18 ± 0.09*	0.68
$F = 12$	LJ(EV)	0.25	5.26 ± 0.18*	0.68
$F = 12$	LJ(θ_1)	0.25	5.92 ± 0.27*	0.52*
$F = 12$	LJ(θ_2)	0.25	5.61 ± 0.23*	0.53*

[a] Extrapolated results are marked by asterisks. Notation for chains and models as in Table I.

for $\langle S^2 \rangle$ and $[\eta]$ vs N, according to the relationships

$$\langle S^2 \rangle \approx N^{\nu_S} \tag{4}$$

and

$$[\eta]^* \approx N^{\nu_\eta} \tag{5}$$

It can be observed that the exponents obtained for linear chains in good solvents are both in very good agreement with the theoretical predictions, $\nu_S = 2\nu$ and $\nu_\eta = 3\nu$, where ν is the critical exponent defined in the renormalization group theory,[17] whose value is $\nu = 0.588$. This agreement is found when the excluded volume is described by means of the rigid-sphere potential as well as through the LJ potential with the energy parameter value previously chosen for these conditions,[3] $\epsilon/K_BT = 0.1$. Therefore both models can be equivalently used as representations of chains with excluded volume.

The exponent ν_S for Gaussian linear chains is very close to 1, as it can be expected from the simple analytical expression $\langle S^2 \rangle = (N-1)b^2[1 + 1/N]$, while ν_η is also in good agreement with the expected value $\nu_\eta = {}^3/_2$. In previous calculations for shorter chains,[3,4,6] $\nu_S = 1$ and $\nu_\eta = {}^3/_2$ were also reproduced with the LJ potential and $\epsilon/k_BT = 0.3$. However, we have verified now that the representations of $\langle S^2 \rangle$ against N exhibit a clear curvature downward for $N > 100$. Similar curvatures for long chains have been also observed[18] in simple cubic lattice simulations with attractive potentials set to reproduce the Θ behavior of dimensions for small values of N. Consequently, we have also investigated the alternative lower value $\epsilon/k_BT = 0.275$. (In this case, we have made an additional run for $N = 145$ over 2 400 000 steps, with a previous equilibration of 800 000 steps.) This value reproduces more satisfactorily the Θ predictions for ν_S (as it can be verified in Table III) but the exponent $\nu_\eta \simeq {}^3/_2$ is more adequately described with $\epsilon/k_BT = 0.3$, even for the longest chains. Thus, different properties seem to reproduce the Θ behavior at slightly different values of the attractive energy well LJ parameter. However, these discrepancies can be model dependent (for instance, they can vary for other choices of the LJ steric parameter, σ_{LJ}) and, consequently, it is not clear whether they should be reflected in experimental data. The Θ temperature, defined as the temperature at which the solution behaves pseudoideally and obeys the van't Hoff law, depends on the number of bonds for a given model, when the chains are not very long. This can also explain the curvatures and the slight discrepancies found by the different properties.

The exponents for stars shown in Table III differ significantly from those calculated with linear chains, because of the influence of the star core which produces more severe finite size effects. These effects can even be noticed for Gaussian chains. Thus, performing log–log linear regression analysis for the results obtained with analytical expressions for Gaussian stars with 12 arms[16] and the same values of N that are included in our numerical simulations we get $\nu_S \simeq 0.90$. Therefore, it seems more useful to study the exponents for the corresponding chain expansion coefficients, defined as

$$\alpha_S{}^2 = \langle S^2 \rangle / \langle S^2 \rangle_{Gauss} \approx N^{\nu_{\alpha(S)}} \tag{6}$$

and

$$\alpha_\eta{}^3 = [\eta]/[\eta]_{Gauss} \approx N^{\nu_{\alpha(\eta)}} \tag{7}$$

so that these coefficients correspond to ratios of the excluded volume chains to the values obtained with Gaussian chains of the same architecture and length. Our fitted values for these exponents, both with the hard-sphere and the good-solvent set of LJ potentials are remarkably close to the theoretically predicted values $\nu_{\alpha(S)} = 2\nu - 1 \simeq 0.18$ and $\nu_{\alpha(\eta)} = 3\nu - {}^3/_2 \simeq 0.26$, both for linear and star chains. Then, our excluded volume models are shown to reflect the universal scaling laws for the expansion coefficients of long flexible linear and star-like polymers.

Similar fits have been also performed for the chains with LJ potentials which try to mimic Θ conditions. In this case we expect results close to 0. We can observe in Table III that $\epsilon/k_BT = 0.275$ yields a practically null value for $\nu_{\alpha(S)}$ in linear chains, although the value of $\nu_{\alpha(\eta)}$ is more satisfactory when $\epsilon/k_BT = 0.3$, in accordance with the conclusions obtained with ν_S and ν_η. Differences are smaller for stars, where the exponents ν_S and ν_η are considerably smaller than 1, doubtlessly due to core effects, while $\nu_{\alpha(S)}$ and $\nu_{\alpha(\eta)}$ are slightly higher than 1, even with $\epsilon/k_BT = 0.3$. It should be considered that, according to experimental work, Θ conditions are met at smaller temperatures for finite stars than for equivalent linear chains, although they are coincident in the long chain limit.[19]

The values of parameter ϕ contained in Table I seem to approach an asymptotic limit as N increases. However, the variation of ϕ with varying N exhibits maxima or minima in the case of linear chains calculated with $h^* = 0.25$. Although this variation is more pronounced for stars or for considerably lower or higher values of h^*, it is better described as a monotonous function in these cases so that extrapolations can be employed to obtain the long chain limits. A summary of the estimated or extrapolated long chain values for different types of chains is included also in Table II. The values of Φ obtained for long Gaussian linear chains and $h^* = 0.25$ are significantly smaller than the result $\Phi \simeq 2.5 \times 10^{23}$ predicted through tentative extrapolations of upper-bound values of shorter chains[2,4] which, however, seems to be closer to the most accurate experimental data of long nondraining linear polymers in Θ solvents.[20] The presence of ternary interactions included in the models with LJ parameters for Θ conditions seems to increase satisfactorily the long chain values of Φ in the desired direction. However, the higher statistical uncertainties associated with these chains make it difficult to obtain a very precise extrapolated value.

The ratio of Φ for a given model to the value obtained with the same chain and the unperturbed Gaussian model, Φ/Φ_{Gauss}, can be easily obtained from the data for Φ contained in Table I. Ratios corresponding to the two

Table III
Exponents Defined in Text for Different Types of Chains[a]

chain	model	ν_S	$\nu_{\alpha(S)}$	ν_η	$\nu_{\alpha(\eta)}$
$F = 2$	Gauss	1.00		1.505 ± 0.002	
$F = 2$	HS	1.191 ± 0.003	0.185 ± 0.004	1.772 ± 0.006	0.27 ± 0.01
$F = 2$	LJ(EV)	1.175 ± 0.10	0.18 ± 0.02	1.770 ± 0.007	0.26 ± 0.01
$F = 2$	LJ(θ_1)	0.908 ± 0.004	−0.09 ± 0.02	1.49 ± 0.02	−0.04 ± 0.04
$F = 2$	LJ(θ_2)	1.00 ± 0.01	−0.04 ± 0.02	1.57 ± 0.01	0.07 ± 0.02
$F = 12$	Gauss	0.89 ± 0.02		1.433 ± 0.003	
$F = 12$	HS	1.06 ± 0.01	0.18 ± 0.03	1.68 ± 0.01	0.26 ± 0.05
$F = 12$	LJ(EV)	1.05 ± 0.01	0.16 ± 0.01	1.65 ± 0.01	0.23 ± 0.01
$F = 12$	LJ(θ_1)	0.90 ± 0.01	0.04 ± 0.01	1.47 ± 0.02	0.06 ± 0.03
$F = 12$	LJ(θ_2)	0.92 ± 0.02	0.06 ± 0.01	1.48 ± 0.02	0.08 ± 0.02

[a] Hydrodynamic results from lower-bound hydrodynamic treatment with $h^* = 0.25$. Notation for chains and models as in Table I.

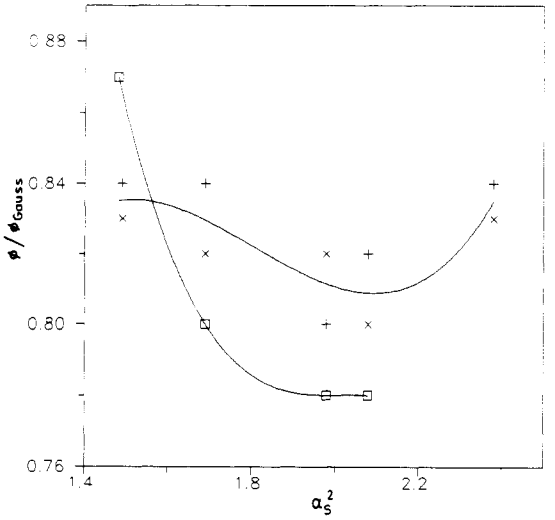

Figure 1. Φ/Φ_{Gauss} for linear chains with hard-sphere (+) and with LJ potentials, $\epsilon/k_BT = 0.1$ (×) (both calculated with $h^* = 0.25$), and with hard-sphere potential and $h^* = 0.10$ (□), vs the expansion coefficients α_S^2 (all of them obtained with the hard-sphere model). The solid line is the illustration of the best fit to a third order polynomial.

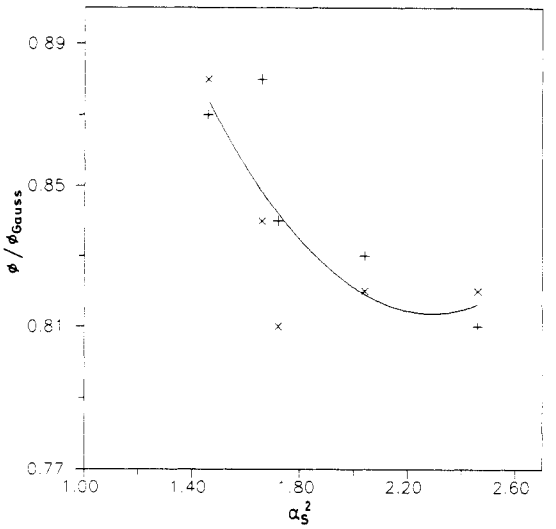

Figure 2. ϕ/ϕ_{Gauss} for star chains ($F = 12$) with hard-sphere and LJ potentials. Same notation and parameter values as in Figure 1.

different models of linear chains in good solvents calculated with the lower-bound method are plotted in Figure 1 against the expansion coefficients α_S^2 obtained with the hard-sphere model. Again, we do not observe significant discrepancies due to model effects. However, the differences due to the hydrodynamic treatment are revealed for the shorter chains where the upper-bound calculations are feasible. The results obtained with these alternative calculations (not included in the figure, but easily available from the results in Table I) are about 10% smaller. Unfortunately, it is not clear whether these differences will remain in the long chain limit. The lower bound results, which extend to the region of fairly long chains, yield values in the range $\Phi/\Phi_{Gauss} \simeq 0.80$–$0.84$, with a minimum at about $\alpha_S^2 \simeq 2$. Calculations performed by Douglas et al.[21] with the renormalization group theory and preaveraged or other approximate hydrodynamic treatments lead to the slightly higher long chain limit result of $\Phi/\Phi_{Gauss} = 0.88$.

A value of the hydrodynamic interaction parameter, $h^* = 0.1$, considerably smaller than that used in the other calculations, lead to a sharper and more monotone decrease of Φ/Φ_{Gauss} with increasing chain length so that the minimum is observed in the the upper range of chain lengths considered here (see Figure 1). This is in good agreement with the partial draining effects which can be qualitatively explained with the renormalization group theory and is also consistent with the variations observed for experimental data of linear chains[17,21] in good and Θ-solvent conditions.

Table IV
Long-Chain Values of Ratios g and g' for the Different Models or Solvent Conditions ($F = 12$)[a]

model	g	g'
Gauss	0.24[b]	0.33 ± 0.01
HS	0.22 ± 0.01	0.34 ± 0.01
LJ(EV)	0.24 ± 0.01	0.33 ± 0.01
RN(EV)	0.25	
Exp(GS)	0.24	0.32 - 0.35
LJ(θ_1)	0.36 ± 0.02	0.50 ± 0.03
LJ(θ_2)	0.32 ± 0.02	0.41 ± 0.03
Exp(θ)	0.28 - 0.41	0.41 - 0.42

[a] Notation for chains and models as in Table I. Exp: experimental data in good (GS) or theta (θ) solvents. The renormalization group (RN) result[11] for g is also included. [b] Reference 10.

The results for Φ corresponding to the long star chains (Table I) are in remarkable agreement with previous estimations from upper-bound results, performed with much shorter chains, for the Gaussian and the LJ chains representing Θ and good-solvent conditions.[4,5] Furthermore, the ratios Φ/Φ_{Gauss} are shown to be close to those obtained for linear chains, although slightly higher and with less pronounced mimima (Figure 2). Consistently as was the case of linear chains, they can be about a 10% higher that those obtained with the upper-bound method for the smallest values of N (This can be verified from inspection of the results contained in Table I).

Finally, we discuss the long chain values for the ratios g and g' which we include in Table IV. We should remark that the results obtained with the unperturbed Gaussian model cannot reproduce the experimental data for star chains in the Θ state, due to the great influence of the

central core on the global chain properties. The results obtained with the LJ model and $\epsilon/k_BT = 0.3$ deviate from the experimental data for long chains in Θ solvents as N increases, due to the remarkable deviation from the Θ behavior of the long linear chains generated with these particular choices of the LJ energy parameter, discussed in previous paragraphs. However, the ratios obtained with $\epsilon/k_BT = 0.275$ and the whole range of chain lengths are in close agreement with the experimental data, showing a weak variation with N and a long chain limit in fair agreement to that previously reported[3] for $\epsilon/k_BT = 0.3$ through extrapolations with shorter chains and the upper-bound method. Bruns and Carl have recently studied equilibrium properties for self-avoiding star chains with up to six arms generated in lattices with an attractive potential.[22] This study points out a slight dependence of the Θ temperature on the chain architecture. Moreover, it is shown that the central core effects are eliminated for sufficiently long chains, so that the unperturbed value[10] of g is reproduced in the Θ state. However, as previously discussed, most experimental data seem to be in the range where core effects are still important and agree more closely with our values.

A similar agreement of the present results with our previously reported calculations[3-5] is also found for the unperturbed chains and the LJ chains with $\epsilon/k_BT = 0.1$. Therefore, one can expect that the previous calculations[3-5] for stars with different numbers of arms can be equally valid as first estimations in both Θ- and good-solvent conditions.

The ratios g and g' obtained with two different excluded volume models do not show significant differences between them and, furthermore, they exhibit a remarkable coincidence with those calculated for the unperturbed Gaussian chains. This coincidence has also been noticed in previous calculations by different authors.[5,23] The result for g also agree with a theoretical prediction from the renormalization group theory.[11] All these EV results are in good agreement with the experimental data. The reproduction of experimental data is even better than that found with our previous extrapolations[5] from upper-bound values.[11]

Summary of Conclusions

The lower-bound method has allowed us to extend previous calculations of intrinsic viscosity to a range of considerably higher chain lengths. Mean dimensions of these chains have been also computed. The results broadly confirm the expected scaling laws for chains with LJ intramolecular interactions in good- and Θ-solvent conditions, although a slight modification in the LJ attractive energy parameter was necessary in order to reproduce the adequate behavior of dimensions of linear chains in Θ conditions. This parameter value is now in good agreement with precise results obtained recently in simple cubic lattices.[24] Also, the calculations yield long chain limit results in fair agreement with previous estimations, which are now refined. (These earlier estimations were obtained from shorter chains through tentative extrapolations using calculations for much shorter chains with the more computer-intensive upper-bound method.) The precise assymptotic limit value of Φ for linear chains in different solvent conditions still however requires further study.

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