Linear, Branched and Hyperbranched Macromolecules in Dilute Solution

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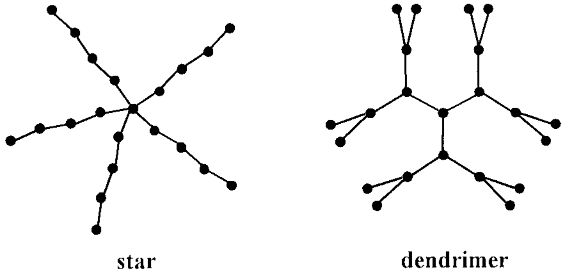
SUMMARY: We report some theoretical results obtained for star polymers and dendrimers under different solvent conditions using the Gaussian self-consistent approach. The focus is mainly on the model assumptions and approximations, and on the results. We discuss the Θ state in terms of both the Θ temperature and the molecular size, and then we consider the good-solvent conditions also through the intramolecular dynamics.

Introduction

In recent years branched and hyperbranched polymers such as stars and dendrimers (see Scheme 1) were synthesized with an essentially complete control over the molecular architecture, reviving the theoretical interest in such systems.[1-3] As a result of both theory and experiment, some simple models and general results had to be revised.



Scheme 1

We report here theoretical results obtained in our group for branched polymers using a coarse-grained model to study equilibrium and dynamics in a unified approach. A basic assumption is the Gaussian distribution of the distances among the beads. The molecular conformation is obtained from self-consistent free-energy minimization, which provides the name of Gaussian self-consistent (GSC) approach.[4] The method correctly accounts for the relevant degrees of freedom within the configurational entropy, and includes two- and three-body interactions. In dynamics, we adopt the Langevin equation taking into account the equilibrium results.

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Stars and dendrimers. Mathematical background

We consider regular stars formed by f equal arms, each one comprising N/f beads, while dendrimers are formed by f arms of order m (the dendrons) for a total of N bonds in both cases. The dendrimer topology can be described in terms of a sequence of concentric layers, the outmost one defining the generation g, numbered from 0 onward, with the number of bonds that increases exponentially with generation.

In linear and star polymers, the mean-square radius of gyration $\langle R_S^2 \rangle$ increases with N through a simple power law[5,6]

$$\langle R_S^2 \rangle \propto N^{2\nu} \tag{1}$$

where the Flory exponent ν is 0.5 for the random-walk (RW) model and in the Θ state, while in a good solvent $\nu \cong 0.6$ (with f-dependent prefactors). Therefore, we introduce the topological ratio[1] $g_S = \langle R_S^2 \rangle_{\text{star}} / \langle R_S^2 \rangle_{\text{lin}}$; for the RW model, $g_S^{\text{RW}} = (3f-2)/f^2$, showing the increasing compactness of the star compared to linear chains.

Cascade molecules[7] do follow Eq. (1) with a ν exponent that can be as low as 0.25, whereas dendrimers belong to a different universality class. In fact, in the RW model they follow a different behavior[8,9]

$$\langle R_S^2 \rangle \propto (g+1) \propto \ln N \tag{2}$$

Therefore, they form an extreme case of regularly branched molecules whose size increases logarithmically with molar mass, more slowly than the weakest power law.

Using Eq. (1), the average density within a molecule is $d \propto N / \langle R_S^2 \rangle^{3/2} \propto N^{1-3\nu}$. The exponent $\nu = 1/3$ corresponds to a constant density, while for $\nu > 1/3$ the average density goes to zero with increasing molar mass (as in linear and star polymers), and for $\nu < 1/3$ it diverges (as in cascade molecules and *a fortiori* in dendrimers). Because of the nonphysical nature of a diverging density, we conclude that the RW model can never apply to such molecules, and that a limiting generation must eventually be achieved.

We obtain the molecular conformation by self-consistent free-energy minimization[4,9,10] under the assumption of a Gaussian distribution of the distances among the beads. With reference to the RW model, the free energy of the single molecule is written as $\mathcal{A} = \mathcal{A}_{\text{el}} + \mathcal{A}_{\text{intra}}$. $\mathcal{A}_{\text{el}}$ accounts for the configurational entropy, which determines the molecular elasticity (hence its name), while the intramolecular contribution includes the long-range two- and three-body interactions, $\mathcal{A}_{\text{intra}} = \mathcal{A}_2 + \mathcal{A}_3$. $\mathcal{A}_2$ and $\mathcal{A}_3$ are given by the probability densities of contact among all the beads pairs and triplets, the coefficients being the irreducible binary and ternary cluster integrals of the beads β_2 and β_3. The former parameter is temperature-dependent and vanishes at $T = \Theta_{\text{bead}}$. In a good solvent, $\beta_2 > 0$ and the two-body interactions are repulsive, whereas in a poor solvent they are attractive and $\beta_2 < 0$. The Θ state, corresponding to vanishing interactions *between two molecules*, is more complex[4,6,11] and does not simply reduce to $\beta_2 = 0$. As to β_3, it is always positive and temperature-independent: these interactions are repulsive, since they correct the extra contribution of simultaneous two-body interactions among three beads, and account for the lesser room available for the third bead when the other two are in contact.

The variational unknowns describing the molecular conformation can be the average scalar products among the bond vectors. Their number, however, is too large to study the asymptotic behavior, even exploiting the molecular symmetry. Therefore, in stars we optimize the eigenvalues of the matrix of the average scalar products, assuming the eigenvectors to be known by symmetry.[4,10,11] The bond vectors are thus transformed into the configurational normal modes, and the eigenvalues are their strain ratios with respect to the RW conformation. This procedure can be followed provided the molecule is conformationally homogeneous and there are no long-range correlations. These requirements[4] are not met: (i) with polymers in a good solvent and (ii) with copolymers, because of the unlike monomers. In the latter case we must adopt the full procedure, while in the former one, the normal modes can be used for linear and star polymers in the crossover regime, but not for dendrimers due to the large correlations imposed by steric constraints.[9,10]

The dynamics is studied following Zimm's approach with a bead-and-spring model, each bond being replaced with a harmonic spring, using the Langevin equation.[8,9,12] The equilibrium results previously obtained affect both the intramolecular elasticity and the hydrodynamic interaction, accounted for in the preaveraging approximation. The dynamic problem reduces to solving an eigenvalue equation, which yields a zero eigenvalue related to the overall diffusion and the relaxation times.

In the present paper, we only report the dynamic structure factor $S(q,t)$, measured in quasi-elastic scattering experiments. Here, q is the modulus of the scattering vector: $q = |\mathbf{q}| = 4\pi\sin(\vartheta/2)/\lambda$, ϑ being the scattering angle and λ the radiation wavelength. In the Gaussian approximation, $S(q,t)$ can be written as[4,12]

$$S(q,t) = \exp\left(-q^2Dt\right)\frac{1}{(N+1)^2}\sum_{i\neq j}\exp\left[-\frac{q^2}{6}\left\langle r_{ij}^2(t)\right\rangle\right] \tag{3}$$

Here we separate the motion of the whole molecule, with diffusion coefficient D, from the intramolecular dynamics, with the time-dependent mean-square distances $\left\langle r_{ij}^2(t)\right\rangle=$ $\left\langle\left[\mathbf{r}_j(t)-\mathbf{r}_i(0)\right]^2\right\rangle-6Dt$. For $t\rightarrow 0$, $S(q,t)$ reduces to the static structure factor, or form factor. The dynamic structure factor is characterized through its first cumulant $\Omega(q)$[12,13]

$$\Omega(q) = -\frac{\partial}{\partial t}\ln\left(\frac{S(q,t)}{S(q,0)}\right)\Bigg|_{t\rightarrow 0} \tag{4}$$

Since $\Omega(q)$ can also be calculated without preaveraging the hydrodynamic interaction,[13] this enables us to quantify the preaveraging error.

The unperturbed Θ state of stars and dendrimers

The unperturbed state is achieved when the second virial coefficient A_2 vanishes, and the solution shows a (pseudo)ideal behavior.[5] The temperature producing $A_2 = 0$ is the Θ temperature, generally taken as independent of molar mass, consistent with a vanishing β_2: attractive and repulsive interactions exactly cancel, the molecules do not interact and have a RW conformation, leading to the notion of universality of the Θ state. Recent experiments contradict these conclusions:[1,14] stars exhibit an f-dependent Θ depression compared with linear chains, although the same value is asymptotically reached. Also, in this limit, stars do show a larger size than expected from the RW model and, accordingly, display residual interactions, unlike linear chains.

To explain this behavior, we calculate the Θ temperature that makes $A_2 = 0$ through a vanishing interaction free energy between two molecules.[4,5] We find that Θ is lower than Θ_{bead}, because temperature-dependent two-body attractions must balance the three-body repulsions between two molecules. In branched molecules, the larger multiplicity of interactions between two molecules compared with linear chains brings about larger three-body repulsions (an effect of molecular connectivity), and the two-body attractions must correspondingly be larger, with a lower Θ. Numerical calculation of Θ is coupled with the issue of the molecular conformation, since it requires the knowledge of the intramolecular probability density of contact. In turn, this is obtained by minimization of the intramolecular free energy at the true Θ temperature.[11]

We find a striking difference between stars and dendrimers. In stars, Θ changes with the arm length N/f according to a square-root law,

$$\Theta = \Theta_{\infty} - \varphi \, \chi_f (N/f)^{-1/2} \qquad (5)$$

where χ_f depends only on the arm number, and φ is a parameter characteristic of the monomer/solvent pair. For $f > 4$, Θ increases with molar mass to the same Θ_{∞} as in linear chains, because the star topology becomes irrelevant for very long arms. Moreover, at a fixed arm length, the Θ depression increases with the arm number as an effect of the larger multiplicity of intermolecular interactions.

On the other hand, Θ in dendrimers decreases without limit with increasing generation g. (Actually, only finite g values can be realized because of the increasingly larger crowding of the monomers.) The reason for this different behavior is apparent: increasing g means also increasing the interaction multiplicity, so that dendrimers can be compared with stars with an increasingly large number of arms.[11] This opposite behavior of the Θ temperature is also expected from the RW model if we assume the probability density of contact between two beads being simply proportional to V^{-1} (V is the molecular volume). We get $\Theta = \Theta_{\text{bead}} / [1 + C \cdot d]$, C being a constant. Thus, in linear and star polymers, Θ should tend to the limit $\Theta_{\infty} \equiv \Theta_{\text{bead}}$ from below with increasing molar mass since the average density scales as $d \propto N^{-1/2}$. Conversely, in cascade polymers, where $d \propto N^{1/4}$, and in dendrimers, where d diverges, Θ decreases without limit.

As for the molecular dimensions at $T = \Theta$, the compensation between two-body attractions and three-body repulsions in linear chains yields a RW conformation. On the other hand, residual three-body repulsions among three beads on three different arms are non-compensated in stars and dendrimers, lacking any *inter*molecular counterpart. This produces a finite star swelling[1,11] with expansion factor $\alpha_S^2 = \langle R_s^2 \rangle / \langle R_s^2 \rangle^{\text{RW}}$ and in stars a topological ratio $g_S = g_s^{\text{RW}} \cdot \alpha_{S,\text{star}}^2 / \alpha_{S,\text{lin}}^2$. Thus, we get $g_S^{\Theta} > g_s^{\text{RW}}$, since $\alpha_{S,\text{lin}} = 1$ to a very good approximation. The calculated g_S^{Θ} agrees well with experimental results, which show the non-universality of the Θ state. Indeed, we argue that in general the RW size is only achieved in a melt because of an essentially complete screening of all interactions, unlike what happens in the Θ state. In dendrimers, the larger multiplicity of three-body interactions leads to a sharp increase in molecular size over the RW value, although eventually a maximum size is reached, dictated by molecular connectivity.[11]

A potential problem in the study of the Θ state, in particular for computer simulations, is the determination of Θ, often established in single molecules through the relationship $\langle R_S^2 \rangle \propto N$, whereas its thermodynamic definition requires considering a two-chain system, which is more difficult to simulate. Also, the nonuniversality of the Θ state is related with the three-body interaction parameter, which strongly depends on the ratio between local thickness to "bond" length. Therefore, slight differences among different monomers may significantly affect the Θ behavior.

Equilibrium and dynamics of stars and dendrimers in a good solvent

In a good solvent, the two-body repulsions swell the molecules, the expansion being qualitatively different from that in the Θ state. Within the GSC approach, the molecular conformation is obtained neglecting the three-body repulsions absorbed in the renormalized two-body interactions. The result is a non-affine expansion concentrated at the molecular center where the bead density is the largest.[4] Thus, the arms are stretched outward in stars with little correlation among their initial directions, as nicely confirmed by computer simulations, so that both intra- and interarm repulsions are minimized.[10] In dendrimers, the repulsive interactions among the dendrons, the subdendrons, etc., strongly stretch them outward with an incipient dendron segregation, again in agreement with computer simulations. The large density of beads in branched polymers gives rise to a peak in the Kratky plot of the static structure factor, reported in Fig. 1. A larger peak sharpness for branched molecules indicates a larger bead density; therefore, the peak broadens in a good solvent because the molecular expansion relieves the steric congestion near the core.

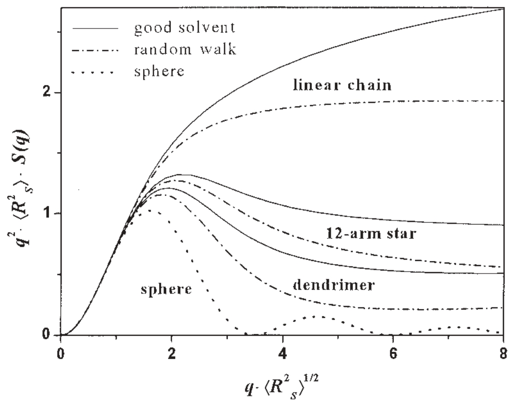

Fig. 1: Kratky plot of the static structure factor $S(q)$ for linear chains, a twelve-arm star, a sixth-generation dendrimer and a compact sphere for comparison.

In spite of the non-affine expansion, linear and star polymers in a good solvent show a universal behavior if the expansion factor α_S^2 is reported as a function of the reduced variable $z \propto \beta_2\sqrt{N}$. The asymptotic dependence is simply $\alpha_S \propto z^{2\nu-1}$, yielding Eq. (1). Our results in the crossover region show that α_S has roughly the same z dependence for linear chains and stars due to the compensating effect of arm expansion and loss of correlation across the branch point; accordingly, the topological ratio $g_S^{GS} = g_S^{RW} \times \alpha_{S,\mathrm{star}}^2/\alpha_{S,\mathrm{lin}}^2$ is close to the RW value, in keeping with previous theoretical results.[1]

Dendrimers do follow a universal behavior, too[9], but the appropriate reduced variable is β_2N^{φ}, with an empirical exponent $\varphi = 0.923$. This value is much larger than $\varphi = 0.5$, but close to $\varphi = 1$ for polymers in two dimensions,[6] consistent with the fact that a large fraction of the beads lies near the outer surface. Moreover, the dendrimer expansion reaches an asymptotic maximum value, in contrast to stars, where the arm length can increase without limit. This finite swelling is consistent with the finite extension of the real dendrons, whose local stereochemistry is not affected by the solvent quality.

Turning now to the dynamics, a characteristic feature of branched polymers consists in the degeneracy of their relaxation times, strictly related with molecular symmetry. In stars, there are non-degenerate modes related to the concerted motion of the arms, and $(f-1)$-degenerate modes describing the independent motion of the arms, while the complex structure of dendrimers produces a whole hierarchy of relaxation times.[9]

The relaxation times become larger with molecular expansion, at least for collective modes, due to both the change in intramolecular elasticity, and the decrease in hydrodynamic interaction. Therefore, in a good solvent, the intramolecular dynamics approaches in part the free-draining regime. Incidentally in our procedure, the main error due to preaveraging[9] is largest in dendrimers in view of their large bead density, although being less dramatic under good-solvent expansion.

The intrinsic viscosity is obtained from the sum of the relaxation times. We define its expansion factor with respect to the RW value as $\alpha_\eta^3 = [\eta]/[\eta]^{RW}$, which is a universal function of z. Asymptotically, we have Zimm's result[4,12] $[\eta] \propto N^{0.8}$. As to the topological ratio $g_\eta = [\eta]_{\mathrm{star}}/[\eta]_{\mathrm{lin}}$, we find that at first g_η^{GS} increases with z, in keeping with the perturbative analysis, but eventually it decreases to a constant value,[10] consistent with experimental results.[1]

In dendrimers, α_η increases to an asymptotic maximum value with increasing molecular expansion, just as α_S. A universal curve is obtained using the universal variable $\beta_2 N^\xi$, with $\xi = 0.735$. This exponent is lower than the φ exponent required for α_S because of the small length of the dendrons *and* of the complex hydrodynamic behavior of these crowded molecules. As for the dendron length, we get an apparent exponent ν_{app} of the radius of gyration, which decreases from 0.43 for $g = 1$ to 0.23 for $g = 6$ at intermediate solvent quality,[9] in agreement with simulations. If we used the scaling expression $[\eta] \propto R^3/N$ in terms of some radius R proportional to the radius of gyration, we would get $[\eta] \propto N^{3\nu_{\text{app}}-1}$. Thus, $[\eta]$ should increase as $N^{0.29}$ at low g, but decrease as $N^{-0.31}$ at large g, passing through a maximum, as observed in some cases.[2] Though affected by the preaveraging approximation, our calculations disagree with this result, predicting that $[\eta]$ should monotonically increase with g, showing that at small dendron length the scaling relationships are not valid.

Finally, we discuss the first cumulant $\Omega(q)$ for dendrimers (reported in Fig. 2) to estimate also the preaveraging error. Both at very small and at very large q, we have $\Omega(q) \propto q^2$ because of the diffusion of the whole molecule (low q) or of the single beads (high q) before they experience any connectivity constraint.[12] In the intermediate q range, the dependence switches to $\Omega(q) \propto q^3$ for linear chains.

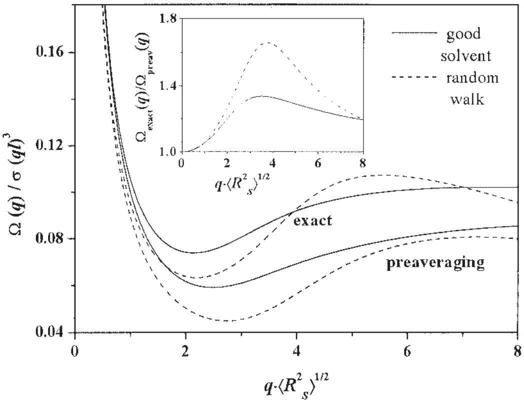

Fig. 2: The first cumulant of the dynamic structure factor for the sixth-generation dendrimer. The exact (in the GSC approach) and the preaveraged results are shown, together with the preaveraging error in the inset. Here, σ^{-1} is the time unit.

The characteristic feature of branched polymers consists in a shallow minimum in the plot of $\Omega(q)/q^3$ at $q \cdot \left\langle R_S^2 \right\rangle^{1/2} \cong 2 \div 3$, probing distances of the order of the radius of gyration, as predicted and observed in stars.[7,15] Such minimum, which matches the position of the peak in the Kratky plot of Fig. 1, deepens with an increasing bead density, hence with dendrimer generation, and becomes shallower with good-solvent expansion. The region of this minimum is also roughly the q range where the preaveraging error is largest, as shown in the inset; however, as anticipated, the error becomes significantly smaller in a good solvent.

Concluding remarks

The main weakness of the GSC approach consists in using the Gaussian approximation and, additionally, in dynamics on preaveraging the hydrodynamic interaction. On the other hand, the method allows to investigate both equilibrium and dynamics within a unified scheme. The main advantages showing the rich potentialities of the method are: it accounts for all the configurational degrees of freedom and for molecular connectivity, it permits to study molecules of any topology with an arbitrary sequence of unlike beads, and it is consistent with the linear Langevin equation in dynamics. Improvements beyond the Gaussian approximation are not trivial, since it is unclear whether the correct distribution function of linear chains applies also to branched molecules. Also, it does not yield a linear elastic force in the Langevin equation, making the consistent study of equilibrium and dynamics a difficult task. On the other hand, computer simulations do not suffer from this limitation, but the ergodicity problem becomes relevant for branched molecules, while simulating the dynamics is by no means trivial. On the experimental side, we note that the unperturbed state of dendrimers was hardly investigated, while such data can provide an even more stringent test of theoretical predictions.

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