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Internal Chain Conformations of Star Polymers†

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ABSTRACT: The segmental density distribution around the center of an f-branched polymer chain is calculated with the aid of the previously obtained renormalized distribution functions for the intersegment distance vectors. The result confirms the authors' picture that branched chains are more expanded with increasing f due to the excluded volume in the inner region, rather than in the outer region. The mean inverse intersegment distances, which are central factors in describing hydrodynamic interactions among the segments, are also calculated. The results display the inner expansion from excluded volume in a more useful fashion than provided by the mean square intersegment distances alone, and they show that each branch end behaves almost like a linear chain end, in contrast to the strong dependence on f assumed by the Daoud–Cotton blob theory.

I. Introduction

In the previous article[1] we examined excluded volume effects in star polymers by calculating the distribution functions for intersegment distance vectors, the mean square intersegment distances, the mean square radius of gyration, the osmotic second virial coefficient, and the interpenetration function for f-branched star polymers using the chain conformation space renormalization group method.[2-4] This method has proven to be very powerful in obtaining not only information concerning the overall conformation but the detailed internal conformations of the polymer. The renormalization group results differ from the picture assumed in the Daoud–Cotton blob theory.[5] They introduce a model with a central close-packed core. They then invoke a surrounding inner region where the chains are unswollen because of screening of the excluded volume due to the higher segmental density. In the outer region the chains are assumed to be swollen because of the geometrical conditions on the blob size with an increase in the distance from the star center.

Our previous paper suggests that the use of semidilute screening concepts in blob models of star polymers may be inappropriate because the star branches are mutually attached and, therefore, strongly correlated, while the polymers in a semidilute solution are mobile and unattached. Hence, any screening is qualitatively different in these two situations. In addition, our renormalization group model, including only delta function type excluded volume interactions, becomes inapplicable in the limit of high f,[1] so it could not describe a central close-packed region for large f. Nevertheless, the rigorous calculations qualitatively depart from the assumed blob model in the inner and outer regions. Calculations provided here illuminate these differences and provide essential ingredients for studying excluded volume effects on frictional and viscoelastic properties of star polymers.

The previously calculated distribution functions for intersegment distance vectors are used in section II to generate the calculations in section III for the segmental density distribution around the star center and in section IV for the mean inverse intersegment distances. These calculations confirm the picture, given in our previous work, that chains are expanded with increasing f due to the excluded volume in the inner region, rather than in the outer region where each chain end behaves almost like a linear chain end. This is in contrast to the strong dependence on f predicted by the Daoud–Cotton theory.[5] The mean inverse intersegment distances are not only the central factors in describing hydrodynamic interactions among the segments, but they provide clearer indicators of excluded volume effects on internal chain conformations than the mean square intersegment distances. Finally, the Gaussian limit of our ϵ-expansion results in three-dimensional space is compared with the exact ones to ensure the validity of the ϵ-expansion technique used in the renormalization group method.[6,7] While the model employed is valid for comparison[1] with experimental data for f up to about 6 or 7, we present calculations for f both smaller and larger to exhibit the general trends more clearly.

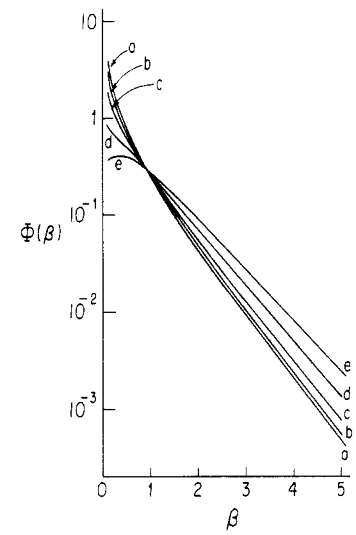

Figure 1. Self-avoiding polymer limit for segmental radial density about star center, $\Phi(\beta) = 2P(\beta)/(1 + 3\epsilon/4 - 3\gamma/2)$, plotted vs. the dimensionless distance squared $\beta = (\pi d/Ll)\mathbf{r}^2(2\pi N/L)^{-2\nu}$ for $\epsilon = 1$ and $\zeta = \infty$: (a) $f = 1$, (b) $f = 2$, (c) $f = 5$, (d) $f = 10$, and (e) $f = 15$.

II. Distribution Functions for Intersegment Distance Vectors

The renormalized distribution function for the intersegment distance vector

$$\mathbf{r} = (l/d)^{1/2}\mathbf{c} \tag{2.1}$$

in an f-branched polymer with branches having equal renormalized contour lengths N is calculated in our previous article.[1] The distribution function for two segments, located at the contour distances Nx and Ny, respectively ($1 \geq x \geq y \geq 0$), from the star center depends on the variable

$$\alpha = \mathbf{c}^2/[2N(x-y)(2\pi N/L)^{(\epsilon/8)[\zeta/(1+\zeta)]}] \tag{2.2}$$

† We dedicate this paper on star polymers to one of our personal "stars", Walter H. Stockmayer, on his 70th birthday.

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and is given to first order in ϵ by

$$
\begin{aligned}
G(\alpha;x,y) = {} & \frac{1}{2}\left(1 + \frac{3\epsilon}{4} - \frac{\epsilon}{2}\gamma\right) \exp[-\alpha - \frac{\epsilon}{8}\frac{\zeta}{1+\zeta}\{2 - 3\gamma - \ln\{(1 - \\
& x)y\} + \frac{2}{\alpha} - 3\ln\left(\frac{\alpha}{x-y}\right) - \alpha\left\{1 - \gamma - \ln\left(\frac{\alpha}{x-y}\right)\right\} + \\
& \frac{1}{\alpha(x-y)}\left\{(1 - x + y)\exp\left(-\alpha\frac{x-y}{1-x+y}\right) - \right. \\
& \left. x\exp\left(-\alpha\frac{x-y}{y}\right) - (1-y)\exp\left(-\alpha\frac{x-y}{1-x}\right)\right\} + \\
& E_1\left(\alpha\frac{x-y}{y}\right) + E_1\left(\alpha\frac{x-y}{1-x}\right) - E_1\left(\alpha\frac{x-y}{1-x+y}\right) - \\
& F\left(\alpha;\frac{1-x}{x-y}\right) - F\left(\alpha;\frac{y}{x-y}\right) + (f-1)[\ln\left(\frac{2y}{1+y}\right) + \\
& \frac{1}{\alpha(x-y)}\left\{(2 - x + y)\exp\left(-\alpha\frac{x-y}{2-x+y}\right) - \right. \\
& (1 - x + y)\exp\left(-\alpha\frac{x-y}{1-x+y}\right) - \\
& \left. (1+x)\exp\left(-\alpha\frac{x-y}{1+y}\right) + x\exp\left(-\alpha\frac{x-y}{y}\right)\right\} + \\
& E_1\left(\alpha\frac{x-y}{1-x+y}\right) - E_1\left(\alpha\frac{x-y}{2-x+y}\right) - E_1\left(\alpha\frac{x-y}{y}\right) + \\
& E_1\left(\alpha\frac{x-y}{1+y}\right) + F\left(\alpha;\frac{y}{x-y}\right) - F\left(\alpha;\frac{1+y}{2-y}\right)]\}] \qquad (2.3)
\end{aligned}
$$

The normalization condition is

$$\int_0^\infty G(\alpha;x,y)\,\mathrm{d}(\alpha^{2-\epsilon/2}) = 1 \qquad (2.4)$$

l is Kuhn's statistical step length, $d = 4 - \epsilon$ is the dimensionality of space, $\gamma = 0.5772...$ is Euler's constant, L is a phenomenological length scale to be fixed by comparison with experiment,

$$E_1(x) = \int_x^\infty e^{-t}\,\mathrm{d}t/t \qquad (2.5)$$

is the exponential integral, and

$$F(\alpha;\gamma) = \int_0^1 \frac{t + 2\lambda}{(t - t^2 + \lambda)^2}\exp\left(-\frac{\alpha t^2}{t - t^2 + \lambda}\right)\mathrm{d}t \qquad (2.6)$$

Here, ζ is a scaling parameter defined by[4]

$$\zeta = (2\pi N/L)^{\epsilon/2}\bar{u}(1 - \bar{u})^{-1+\epsilon/8}, \qquad \bar{u} = u/u^* \qquad (2.7)$$

with u the renormalized dimensionless excluded volume representing the cooperative effects of the binary excluded volume interactions on the length L. The case of $\zeta \to 0$ implies the Gaussian chain limit, whereas $\zeta \to \infty$ gives the asymptotic limit of fully developed excluded volume with the interaction parameter

$$u^* = \frac{\epsilon}{2}\pi^2 + \mathcal{O}(\epsilon^2) \qquad (2.8)$$

A renormalized version of the two-parameter z variable is $(2\pi N/L)^{\epsilon/2}u$, which is closely related to ζ of (2.7).

Similarly, for two segments located at the contour distances Nx and Ny from the star center, along different branches, we have the variable

$$\alpha' = \mathbf{c}^2/[2N(x + y)(2\pi N/L)^{(\epsilon/8)[\zeta/(1+\zeta)]}] \qquad (2.2')$$

and the distribution function

$$
\begin{aligned}
G'(\alpha';x,y) = {} & \frac{1}{2}\left(1 + \frac{3\epsilon}{4} - \frac{\epsilon}{2}\gamma\right)\exp[-\alpha' - \frac{\epsilon}{8}\frac{\zeta}{1+\zeta}\{2 - \\
& 3\gamma + \ln\left\{\frac{2}{(1-x)(1-y)}\right\} + \frac{2}{\alpha'} - 3\ln\left(\frac{\alpha'}{x+y}\right) - \\
& \alpha'\left\{1 - \gamma - \ln\left(\frac{\alpha'}{x+y}\right)\right\} + \\
& \frac{1}{\alpha'(x+y)}\left\{(2 - x - y)\exp\left(-\alpha'\frac{x+y}{2-x-y}\right) - \right. \\
& \left. (1+y)\exp\left(-\alpha'\frac{x+y}{1-x}\right) - (1+x)\exp\left(-\alpha'\frac{x+y}{1-y}\right)\right\} + \\
& E_1\left(\alpha'\frac{x+y}{1-x}\right) + E_1\left(\alpha'\frac{x+y}{1-y}\right) - E_1\left(\alpha'\frac{x+y}{2-x-y}\right) - \\
& F\left(\alpha';\frac{1-x}{x+y}\right) - F\left(\alpha';\frac{1-y}{x+y}\right) + (f-2)\times \\
& [2\left\{1 - \gamma + \frac{1}{\alpha'} - \ln\left(\frac{\alpha'}{2(x+y)}\right)\right\} + \frac{1}{\alpha' x^2}\left(\{2(x+y) - \right. \\
& x^2\}\exp\left\{-\frac{\alpha' x^2}{2(x+y) - x^2}\right\} - (x + y - x^2)\times \\
& \exp\left(-\frac{\alpha' x^2}{x + y - x^2}\right) - \\
& \left.\{(x+y)(1+x) + xy\}\exp\left(-\frac{\alpha' x^2}{x + y + xy}\right)\right) + \\
& \frac{2y}{\alpha' x}\exp\left(-\frac{\alpha' x}{y}\right) - E_1\left(\frac{\alpha' x^2}{2(x+y) - x^2}\right) + \\
& E_1\left(\frac{\alpha' x^2}{x + y - x^2}\right) + E_1\left(\frac{\alpha' x^2}{x + y + xy}\right) - \\
& 2E_1\left(\frac{\alpha' x}{y}\right) - F'(\alpha';x) + \\
& \frac{1}{\alpha' y^2}\left(\{2(x+y) - y^2\}\exp\left\{-\frac{\alpha' y^2}{2(x+y) - y^2}\right\} - \right. \\
& (x + y - y^2)\exp\left(-\frac{\alpha' y^2}{x + y - y^2}\right) - \\
& \left.\{(x+y)(1+y) + xy\}\exp\left(-\frac{\alpha' y^2}{x + y + xy}\right)\right) + \\
& \frac{2x}{\alpha' y}\exp\left(-\frac{\alpha' y}{x}\right) - E_1\left(\frac{\alpha' y^2}{2(x+y) - y^2}\right) + \\
& E_1\left(\frac{\alpha' y^2}{x + y - y^2}\right) + E_1\left(\frac{\alpha' y^2}{x + y + xy}\right) - \\
& 2E_1\left(\frac{\alpha' y}{x}\right) - F'(\alpha';y)]\}] \qquad (2.3')
\end{aligned}
$$

where the normalization is given by

$$\int_0^\infty G'(\alpha';x,y)\ \mathrm{d}(\alpha'^{\,2-\epsilon/2}) = 1 \qquad (2.4')$$

and F' is defined by

$$F'(\alpha';\lambda) = (x+y)^2 \int_0^\lambda \frac{t+2}{\{(x+y)(1+t)-t^2\}^2} \times \exp\left\{-\frac{\alpha' t^2}{(x+y)(1+t)-t^2}\right\} \mathrm{d}t \qquad (2.6')$$

III. Segmental Density Distribution Function

Consider a segment located at the contour distance Nx ($1 \geq x \geq 0$) along a branch from the star center, which is taken as the origin of coordinates. The spatial distribution function for this segment as a function of

$$\alpha = \left(\frac{d}{l}\mathbf{r}^2\right) \Big/ [2Nx(2\pi N/L)^{(\epsilon/8)[\zeta/(1+\zeta)]}] \qquad (3.1)$$

is provided from (2.3) or (2.3′) by putting $y \to 0$

$$G(\alpha;x,0) = \frac{1}{2}\left(1 + \frac{3\epsilon}{4} - \frac{\epsilon}{2}\gamma\right) \exp[-\alpha - \frac{\epsilon}{8}\frac{\zeta}{1+\zeta}\{1 + \frac{1}{\alpha} - \alpha - \ln(1-x) + (\alpha-2)\left(\gamma + \ln\frac{\alpha}{x}\right) - \frac{1}{\alpha}\exp\left(-\frac{\alpha x}{1-x}\right) - F\left(\alpha;\frac{1-x}{x}\right) + (f-1)\left[1 - \gamma + \frac{1}{\alpha} - \ln(\alpha/2x) - \frac{1}{\alpha x}\left\{(1+x)\exp(-\alpha x) + (1-x)\exp\left(-\frac{\alpha x}{1-x}\right) - (2-x)\exp\left(-\frac{\alpha x}{2-x}\right)\right\} - E_1\left(\frac{\alpha x}{2-x}\right) + E_1\left(\frac{\alpha x}{1-x}\right) + E_1(\alpha x) - F\left(\alpha;\frac{1}{x}\right)\right]\}] \qquad (3.2)$$

where the following limiting relations are used:

$$\lim_{\lambda\to 0} E_1(\lambda) \to -\ln\lambda - \gamma$$

$$\lim_{\lambda\to 0} F(\alpha,\lambda) \to \frac{1}{\alpha} - \ln\alpha - \ln\lambda - \gamma + 1 \qquad (3.3)$$

$$\lim_{y\to 0} F'(\alpha';x) = F\left(\alpha;\frac{1}{x}\right) \qquad (3.4)$$

Therefore, the segmental density function at the spatial distance

$$|\mathbf{r}| = \left(\frac{Ll}{\pi d}\beta\right)^{1/2} (2\pi N/L)^{\nu} \qquad (3.5)$$

from the star center is given by

$$NfP(\beta) = Nf\int_0^1 \frac{\mathrm{d}x}{x^{2-\epsilon/2}}\, G\left(\frac{\beta}{x};x,0\right) = \frac{Nf}{2}\left(1 + \frac{3\epsilon}{4} - \frac{\epsilon}{2}\gamma\right)\frac{1}{\beta}\exp[-\beta - \frac{\epsilon}{2}e^{\beta}E_1(\beta) - \frac{\epsilon}{8}\frac{\zeta}{1+\zeta}\{2 + \beta(\gamma - 1 + \ln\beta) - e^{\beta}E_1(\beta) + \Phi_1(\beta) + (f-1)[1 - \gamma - \ln(\beta/2) - 2e^{\beta}E_1(\beta) - 2e^{-\beta}\{K_1(2\beta) - K_0(2\beta)\} + \{K_1(\beta) - K_0(\beta)\} + \Phi_2(\beta)]\}] \qquad (3.6)$$

where the normalization condition is

$$\int_0^\infty P(\beta)\ \mathrm{d}(\beta^{2-\epsilon/2}) = 1 \qquad (3.7)$$

and we define the functions

$$\Phi_1(\beta) = \int_0^1 \frac{\mathrm{d}s}{s}\exp\{-\beta[(1-s)/s]\}\int_0^1 \frac{\mathrm{d}t}{t^2} \times \left[\exp\left\{-\frac{\beta t^2}{1 - s(1-t+t^2)}\right\} - 1\right]$$

$$\Phi_2(\beta) = \int_0^1 \frac{\mathrm{d}s}{s}\exp\{-\beta[(1-s)/s]\}\int_0^1 \frac{\mathrm{d}t}{t^2} \times \left[\exp\left\{-\frac{\beta t^2}{1 + st(1-t)}\right\} - 1\right] \qquad (3.8)$$

$$K_0(\beta) = \int_0^1 \exp(-\beta/t)\,\frac{\mathrm{d}t}{t\sqrt{1-t^2}} \qquad (3.9)$$

is the modified Hankel function of order zero,[8]

$$K_1(\beta) = -\frac{\mathrm{d}}{\mathrm{d}\beta}K_0(b) = \int_0^1 \exp(-\beta/t)\,\frac{\mathrm{d}t}{t^2\sqrt{1-t^2}} \qquad (3.10)$$

the modified Hankel function of order 1, and

$$\nu = \frac{1}{2}\left\{1 + \frac{\epsilon}{8}\frac{\zeta}{1+\zeta} + \mathcal{O}(\epsilon^2)\right\} \qquad (3.11)$$

the ζ-dependent exponent.

In Figure 1 the scaled distribution

$$\Phi(\beta) = 2P(\beta)\Big/\left(1 + \frac{3\epsilon}{4} - \frac{\epsilon}{2}\gamma\right) \qquad (3.12)$$

is plotted against β in the three-dimensional space ($\epsilon = 1$) for $f = 1, 2, 5, 10$, and 15 in the self-avoiding limit $\zeta = \infty$. All the curves show that $P(\beta)$ is a very rapidly decreasing function of β. Figure 2 presents the quantity

$$\Pi(\beta) = [P(\beta)]_{\zeta=\infty}/[P(\beta)]_{\zeta=0} \qquad (3.13)$$

the ratio of $P(\beta)$ in the self-avoiding limit to that in the Gaussian limit, for $\epsilon = 1$ and the same f's. It should be noted that in both figures $f = 1$ is rather exceptional compared with others, since a star end is taken as the center for $f = 1$. All the curves in Figure 2 intersect for $\Pi(\beta) = 0.92469$ at $\beta = 0.9051$, independent of f as seen from (3.6). $\Pi(\beta)$ clearly indicates that the excluded volume effect tends to push out the segmental density toward the outer region with an increase in f.

IV. Mean Inverse Intersegment Distances

The calculation of the mean inverse intersegment distance

$$\langle|\mathbf{r}|^{-1}\rangle_{x,y} = \langle\alpha^{-1/2}\rangle_{x,y}\left(\frac{\pi d}{Ll}\right)^{1/2}(2\pi N/L)^{-\nu}(x-y)^{-1/2} \qquad (4.1)$$

for two segments located at the contour distances Nx and Ny along the same branch is straightforward. Using (2.3), we find after integration that

$$\langle\alpha^{-1/2}\rangle_{x,y} = \frac{\sqrt{\pi}}{2}\left\{1 - \frac{\epsilon}{2}(1 - 2\ln 2)\right\}(x-y)^{-(\epsilon/16)[\zeta/(1+\zeta)]} \times \exp[-\frac{\epsilon}{8}\frac{\zeta}{1+\zeta}\{\frac{5}{2} + \ln\left\{\frac{2}{(1-x)y}\right\} + \frac{2}{x-y}\left\{\sqrt{1-x+y} - (2x-y)\sqrt{\frac{y}{x}} - (1+x-2y)\sqrt{\frac{1-x}{1-y}}\right\} +$$

$$2\ln\left\{\frac{2(\sqrt{x}+\sqrt{y})(\sqrt{1-x}+\sqrt{1-y})}{1+\sqrt{1-x+y}}\right\} -$$

$$\frac{x-y}{1-x}\left\{\Psi\left(\sqrt{\frac{x-y}{4-3x-y}},\sqrt{\frac{x-y}{1-y}}\right)-1\right\} -$$

$$\frac{x-y}{\sqrt{(1-x)(1-y)}} -$$

$$\frac{x-y}{y}\left\{\Psi\left(\sqrt{\frac{x-y}{x+3y}},\sqrt{\frac{x-y}{x}}\right)-1\right\} - \frac{x-y}{\sqrt{xy}} +$$

$$(f-1)[\ln\left(\frac{2y}{1+y}\right) + \frac{2}{x-y}\{\sqrt{2(2-x+y)} -$$

$$\sqrt{1-x+y} - (1+2x-y)\sqrt{\frac{1+y}{1+x}} +$$

$$(2x-y)\sqrt{\frac{y}{x}}\} +$$

$$2\ln\left\{\frac{(1+\sqrt{1-x+y})(\sqrt{1+x}+\sqrt{1+y})}{(\sqrt{2}+\sqrt{2-x+y})(\sqrt{x}+\sqrt{y})}\right\} +$$

$$\frac{x-y}{y}\left\{\Psi\left(\sqrt{\frac{x-y}{x+3y}},\sqrt{\frac{x-y}{x}}\right)-1\right\} + \frac{x-y}{\sqrt{xy}} -$$

$$\frac{x-y}{1+y}\left\{\Psi\left(\sqrt{\frac{x-y}{4+x+3y}},\sqrt{\frac{x-y}{1+x}}\right)-1\right\} -$$

$$\frac{x-y}{\sqrt{(1-x)(1+y)}}]\}] \quad (4.2)$$

where Ψ is defined by

$$\Psi(k, \cos\varphi) = \frac{1}{k}\{E(k,\pi/2) - E(k,\varphi)\} \quad (4.3)$$

and

$$E(k,\varphi) = \int_0^{\varphi}\sqrt{1-k^2\sin^2\theta}\,\mathrm{d}\theta \quad (4.4)$$

is the elliptic integral of the second kind.[8]

Similarly, using (2.3′) we obtain

$$\langle|\mathbf{r}|^{-1}\rangle_{x,y} = \langle\alpha'^{-1/2}\rangle_{x,y}(\pi d/Ll)^{1/2}(2\pi N/L)^{-\nu}(x+y)^{-1/2} \quad (4.1')$$

for two segments at the contour distances Nx and Ny along the different branches, where

$$\langle\alpha'^{-1/2}\rangle_{x,y} = \frac{\sqrt{\pi}}{2}\left\{1-\frac{\epsilon}{2}(1-2\ln 2)\right\}\times$$

$$(x-y)^{-(\epsilon/16)[\zeta/(1+\zeta)]}\exp[-\frac{\epsilon}{8}\frac{\zeta}{1+\zeta}\{\frac{5}{2} +$$

$$\ln\left\{\frac{4}{(1-x)(1-y)}\right\} + \frac{2}{x+y}\{\sqrt{2(2-x-y)} -$$

$$(1+x+2y)\sqrt{\frac{1-x}{1+y}} - (1+2x+y)\sqrt{\frac{1-y}{1+x}}\} +$$

$$2\ln\left\{\frac{2(\sqrt{1-x}+\sqrt{1+y})(\sqrt{1+x}+\sqrt{1-y})}{\sqrt{2}+\sqrt{2-x-y}}\right\} -$$

$$\frac{x+y}{1-x}\left\{\Psi\left(\sqrt{\frac{x+y}{4-3x+y}},\sqrt{\frac{x+y}{1+y}}\right)-1\right\} -$$

$$\frac{x+y}{\sqrt{(1-x)(1+y)}} -$$

$$\frac{x+y}{1-y}\left\{\Psi\left(\sqrt{\frac{x+y}{4+x-3y}},\sqrt{\frac{x+y}{1+x}}\right)-1\right\} -$$

$$\frac{x+y}{\sqrt{(1+x)(1-y)}} + (f-2)[2 + 2\ln\{2(x+y)\} +$$

$$\frac{2}{x^2}\left(\sqrt{2(x+y)\{2(x+y)-x^2\}} - \sqrt{(x+y)(x+y-x^2)} -\right.$$

$$\left.(1+2x)\sqrt{\frac{(x+y)(x+y+xy)}{1+x}}\right) + \frac{4}{x}\sqrt{(x+y)y} +$$

$$2\ln\{[2(\sqrt{x+y}+\sqrt{x+y-x^2})\times$$

$$(\sqrt{(x+y)(1+x)}+\sqrt{x+y+xy})]/[(\sqrt{2(x+y)} +$$

$$\sqrt{2(x+y)-x^2})(\sqrt{x+y}+\sqrt{y})^2]\} +$$

$$\frac{2}{y^2}\left(\sqrt{2(x+y)\{2(x+y)-y^2\}} - \sqrt{(x+y)(x+y-y^2)} -\right.$$

$$\left.(1+2y)\sqrt{\frac{(x+y)(x+y+xy)}{1+y}}\right) + \frac{4}{y}\sqrt{x(x+y)} +$$

$$2\ln\{[2(\sqrt{x+y}+\sqrt{x+y-y^2})\times$$

$$(\sqrt{(x+y)(1+y)}+\sqrt{x+y+xy})]/[(\sqrt{2(x+y)} +$$

$$\sqrt{2(x+y)-y^2})(\sqrt{x+y}+\sqrt{x})^2]\} -$$

$$(x+y)\left\{\Psi\left(\sqrt{\frac{x+y}{4+x+y}},\frac{x}{\sqrt{(x+y)(1+x)}}\right) +\right.$$

$$\left.\Psi\left(\sqrt{\frac{x+y}{4+x+y}},\frac{y}{\sqrt{(x+y)(1+y)}}\right) - 2\right\} -$$

$$\sqrt{\frac{(x+y)(x+y+xy)}{1+x}} -$$

$$\sqrt{\frac{(x+y)(x+y+xy)}{1+y}}]\}] \quad (4.2')$$

Figure 3 presents the mean inverse distance of a segment, located at the contour distance Nx along a branch from the star center ($y = 0$) in the self-avoiding limit $\zeta = \infty$, relative to its Gaussian $\zeta = 0$ limit value

$$\langle R^{-1}\rangle_{x,0} = \{[\langle|\mathbf{r}|^{-1}\rangle_{x,0}]_{\zeta=\infty}/[\langle|\mathbf{r}|^{-1}\rangle_{x,0}]_{\zeta=0}\}(2\pi N/L)^{\epsilon/16} \quad (4.5)$$

as a function of x for $\epsilon = 1$ and $f = 1, 5, 10$, and 15 in the full curves. For comparison, the corresponding relative value of the inverse root mean square of the distance from

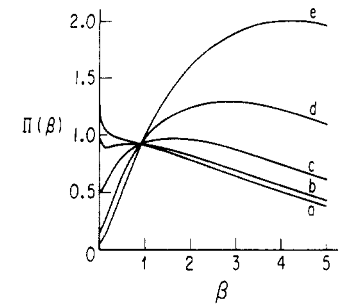

Figure 2. Ratio of good solvent $\zeta = \infty$ to Gaussian $\zeta = 0$ chain segmental radial densities $\Pi(\beta) = [P(\beta)]_{\zeta=\infty}/[P(\beta)]_{\zeta=0}$ about the star center as a function of $\beta = (\pi d/Ll)\mathbf{r}^2(2\pi N/L)^{-2\nu}$ for $\epsilon = 1$: (a) $f = 1$, (b) $f = 2$, (c) $f = 5$, (d) $f = 10$, and (e) $f = 15$. Note that this definition of β implies it corresponds to different distances from the star center in good ($\zeta = \infty$) and poor ($\zeta = 0$) solvents.

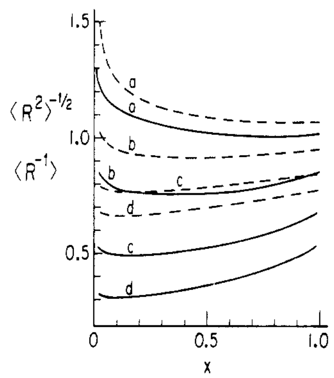

Figure 3. Full curves give ratio of good solvent $\zeta = \infty$ to Gaussian chain $\zeta = 0$ intersegment average hydrodynamic interaction $\langle R^{-1}\rangle_{x,0} = \{[\langle|\mathbf{r}|^{-1}\rangle_{x,0}]_{\zeta=\infty}/[\langle|\mathbf{r}|^{-1}\rangle_{x,0}]_{\zeta=0}\}(2\pi N/L)^{\epsilon/16}$ for $\epsilon = 1$ where one segment is at the star center and the other lies at a Nx along a branch. Dashed curves give $\langle R^2\rangle_{x,0}^{-1/2} = \{[\langle|\mathbf{r}|^2\rangle_{x,0}^{-1/2}]_{\zeta=\infty}/[\langle|\mathbf{r}|^2\rangle_{x,0}^{-1/2}]_{\zeta=0}\}(2\pi N/L)^{\epsilon/16}$ vs. x for $\epsilon = 1$ as a comparison. (a) $f = 1$, (b) $f = 5$, (c) $f = 10$, and (d) $f = 15$.

the star center

$$\langle R^2\rangle_{x,0}^{-1/2} = \{[\langle \mathbf{r}^2\rangle_{x,0}^{-1/2}]_{\zeta=\infty}/[\langle \mathbf{r}^2\rangle_{x,0}^{-1/2}]_{\zeta=0}\}(2\pi N/L)^{\epsilon/16} \tag{4.6}$$

is also plotted against x in the dashed curves, where

$$\langle \mathbf{r}^2\rangle_{x,y} = \frac{Ll}{2\pi}(2\pi N/L)^{2\nu}(x-y)^{2\nu}\left[1 - \frac{\epsilon}{8}\,\frac{\zeta}{1+\zeta}\left\{\frac{3}{2} - \frac{x-y}{2} - \frac{y}{x-y}\ln\left(\frac{x}{y}\right) + \frac{1-x}{x-y}\ln\left(\frac{1-x}{1-y}\right) + (f-1)\left[\frac{x-y}{4} + \frac{y}{x-y}\ln\left(\frac{x}{y}\right) - \frac{1+y}{x-y}\ln\left(\frac{1+x}{1+y}\right)\right]\right\}\right] \tag{4.7}$$

The ratio $2\pi N/L$ in the good solvent limit can be shown[11] to be identical with n/n_τ of the blob model, with the good solvent limit beginning for $n/n_\tau > 40$. Hence, the factor of $(2\pi N/L)^{\epsilon/16}$ for $\epsilon = 1$ in (4.5), (4.6), and Figures 3 and 4 is greater than $^5/_4$. (If the better second-order exponent[12] is used, this factor is greater than 1.4. The prefactors are not expected to change much in second order.)

Likewise, Figure 4 gives the relative values $\langle R^{-1}\rangle_{x,-1}$ and $\langle R^2\rangle_{x,-1}^{-1/2}$ vs. x in full and dashed curves, respectively, where $-1 \le x \le 0$ implies the segment at the contour distance Nx is on the same branch as that containing the specified end ($y = -1$), whereas $0 \le x \le 1$ means it is on another branch not including the specified end.

These figures clearly indicate that with increased f the expansion of intersegment distances due to excluded volume effects is magnified in $\langle R^{-1}\rangle$ much more than in $\langle R^2\rangle^{-1/2}$ and that intersegment distances near the branch ends are almost independent of f. This result contrasts with the strong dependence of f predicted by the Daoud–Cotton theory.[5]

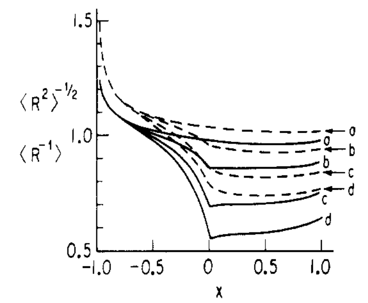

Figure 4. Same as Figure 3, but now one segment is at a branch end. Full curves present $\langle R^{-1}\rangle_{x,-1} = \{[\langle|\mathbf{r}|^{-1}\rangle_{x,-1}]_{\zeta=\infty}/[\langle|\mathbf{r}|^{-1}\rangle_{x,-1}]_{\zeta=0}\}(2\pi N/L)^{\epsilon/16}$ vs. x while dashed ones show $\langle R^2\rangle_{x,-1}^{-1/2} = \{[\langle\mathbf{r}^2\rangle_{x,-1}^{-1/2}]_{\zeta=\infty}/[\langle\mathbf{r}^2\rangle_{x,-1}^{-1/2}]_{\zeta=0}\}(2\pi N/L)^{\epsilon/16}$ vs. x for $\epsilon = 1$. (a) $f = 2$, (b) $f = 5$, (c) $f = 10$, and (d) $f = 15$. Note that negative values of x imply both points on the same branch, while for positive values they are on different ones.

Though (4.2) and (4.2′) contain individual terms which are ill-defined when $y \to 0$, their combination is well defined in this limit. The final result is found to be

$$\lim_{y\to 0}\langle\alpha^{-1/2}\rangle_{x,y} = \lim_{y\to 0}\langle\alpha'^{-1/2}\rangle_{x,y} = \frac{\sqrt{\pi}}{2}\left\{1 - \frac{\epsilon}{2}(1 - 2\ln 2)\right\}x^{-(\epsilon/16)[\zeta/(1+\zeta)]}\exp[-\frac{\epsilon}{8}\,\frac{\zeta}{1+\zeta}\{\frac{3}{2} + \ln\left(\frac{2}{1-x}\right) - 2\sqrt{1-x} - \frac{x}{\sqrt{1-x}} - \frac{x}{1-x}\left\{\Psi\left(\sqrt{\frac{x}{4-3x}},\sqrt{x}\right) - 1\right\} + (f-1)\left[1 + 3\ln 2 + \frac{2}{x}\left\{\sqrt{2(2-x)} - \sqrt{1-x} - \frac{1+2x}{\sqrt{1+x}}\right\} + 2\ln\left\{\frac{(1+\sqrt{1-x})(1+\sqrt{1+x})}{\sqrt{2}+\sqrt{2-x}}\right\} - \frac{x}{\sqrt{1+x}} - x\left\{\Psi\left(\sqrt{\frac{x}{4+x}},\sqrt{\frac{x}{1+x}}\right) - 1\right\}\right]\}]$$

This limiting form has been used to generate Figure 3 and is obtained with the aid of the expansion

$$\Psi(1-\lambda, 1-\mu) = \frac{1}{1-\lambda}[E(1-\lambda,\pi/2) - E(1-\lambda, \cos^{-1}(1-\mu))] = 1 + \tfrac{1}{2}\lambda(3\ln 2 + 1 - \ln\lambda) - \sqrt{2\mu} + \ldots$$

for elliptic integrals of the second kind when $0 < \lambda, \mu \ll 1$.

V. Discussion

It is noteworthy that in the case of $d = 3$ ($\epsilon = 1$), instead of (3.2) the exact result in the Gaussian limit $\zeta = 0$ is

$$G^0(\alpha;x,0) = \frac{4}{3\sqrt{\pi}}e^{-\alpha} \tag{5.1}$$

where the normalization is

$$\int_0^\infty G^0(\alpha;x,0)\,\mathrm{d}(\alpha^{3/2}) = 1 \tag{5.2}$$

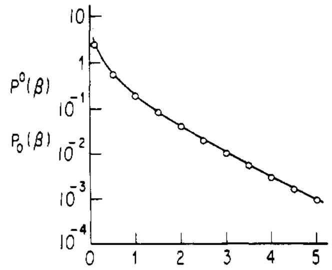

Figure 5. Exact Gaussian chain segmental distribution function $P^0(\beta)$ vs. β in full curve and $P_0(\beta)$ vs. β as circles for $\epsilon = 1$ and $\zeta = 0$.

Therefore, in this case the segmental density distribution function for the spatial distance

$$|\mathbf{r}| = \left(\frac{Ll}{\pi d}\beta\right)^{1/2}\left(\frac{2\pi N}{L}\right)^{1/2} \tag{5.3}$$

from the star center is exactly given as

$$NfP^0(\beta) = Nf\int_0^1 \frac{\mathrm{d}x}{x^{3/2}}G^0\left(\frac{\beta}{x};x,0\right) = Nf\frac{8}{3\sqrt{\pi\beta}}\ \mathrm{erfc}\ (\sqrt{\beta}) \tag{5.4}$$

where the error function is defined as

$$\mathrm{erfc}\ (x) = \int_x^\infty e^{-t^2}\ \mathrm{d}t = \frac{\sqrt{\pi}}{2}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}\ \mathrm{d}t\right) \tag{5.5}$$

Setting $\epsilon = 1$ and $\zeta = 0$ in the ϵ-expansion form (3.6) gives the *approximation*

$$NfP_0(\beta) = \frac{Nf}{2}\left(1 + \frac{3}{4} - \frac{\gamma}{2}\right)\frac{1}{\beta}\ \exp\left\{-\beta - \frac{1}{2}e^{\beta}E_1(\beta)\right\} \tag{5.6}$$

which should be compared with (5.4).

In Figure 5, $P^0(\beta)$ is plotted as a full curve, while $P_0(\beta)$ is shown as circles. The coincidence is satisfactory enough to assure us of the quantitative validity of the ϵ-expansion technique used in the renormalization group method.[6,7]

Using (3.6) and (3.7), we obtain the mean value

$$\langle\beta\rangle = \int_0^\infty \beta P(\beta)\ \mathrm{d}(\beta^{2-\epsilon/2}) = 1 - \frac{\epsilon}{4} - \frac{\epsilon}{8}\frac{\zeta}{1+\zeta}\left\{\frac{7}{6} + (f-1)\left(\frac{13}{6} - 4\ln 2\right)\right\} \tag{5.7}$$

Therefore, we have the mean square dimension about the star center with the aid of (4.7) and (5.7) as

$$\langle\mathbf{R}^2\rangle = \frac{Ll}{2\pi}\left(\frac{2\pi N}{L}\right)^{2\nu}\langle\beta\rangle = \int_0^1 \mathrm{d}x\ \langle\mathbf{r}^2\rangle_{x,0} = \frac{Ll}{2\pi}\left(\frac{2\pi N}{L}\right)^{2\nu}\left[\frac{1}{2} - \frac{\epsilon}{8}\frac{\zeta}{1+\zeta}\left\{\frac{7}{12} + (f-1)\left(\frac{13}{12} - 2\ln 2\right)\right\}\right] \tag{5.8}$$

Since the mean square radius of gyration is given in our previous work[1] by

$$\langle\mathbf{S}^2\rangle = \frac{Ll}{2\pi}\left(\frac{2\pi N}{L}\right)^{2\nu}\left[\frac{3f-2}{6f} - \frac{\epsilon}{8}\frac{\zeta}{1+\zeta}\left\{\frac{13}{72} + \frac{(f-1)(3f-5)}{3f}\left(\frac{13}{12} - 2\ln 2\right)\right\}\right] \tag{5.9}$$

we obtain the mean square distance of the center of mass from the star center as

$$\langle\mathbf{R}_G{}^2\rangle = \langle\mathbf{R}^2\rangle - \langle\mathbf{S}^2\rangle = \frac{Ll}{2\pi}\left(\frac{2\pi N}{L}\right)^{2\nu}\left[\frac{1}{3f} - \frac{\epsilon}{8}\frac{\zeta}{1+\zeta}\left\{\frac{29}{72} + \frac{5(f-1)}{3f}\left(\frac{13}{12} - 2\ln 2\right)\right\}\right] \tag{5.10}$$

The mean inverse intersegment distances $\langle|\mathbf{r}|^{-1}\rangle_{x,y}$ can again be obtained exactly for $\epsilon = 1$ and $\zeta = 0$ for two segments at contour distances Nx and Ny on the same branch as

$$\langle|\mathbf{r}|^{-1}\rangle_{x,y} = (6/\pi)^{1/2}\{Nl(x-y)\}^{-1/2} = 1.38198\{Nl(x-y)\}^{-1/2} \tag{5.11}$$

where the ϵ-expansion form (4.1) and (4.2) yields

$$\langle|\mathbf{r}|^{-1}\rangle_{x,y} = \left(\frac{3\pi}{2}\right)^{1/2}\frac{1 + 2\ln 2}{4}\{Nl(x-y)\}^{-1/2} = 1.29505\{Nl(x-y)\}^{-1/2} \tag{5.12}$$

The difference in numerical factors between (5.11) and 5.12) is only about 7%.[13]

Since $\langle|\mathbf{r}|^{-1}\rangle$ is a predominant factor in describing hydrodynamic interactions among the segments, the very nature of the excluded volume effect on $\langle|\mathbf{r}|^{-1}\rangle$ is crucial to understanding dynamic properties of star polymers,[9,10] e.g., the diffusion constant, the intrinsic viscosity, and so forth. Further elaborate calculations of these dynamical properties in the preaveraging approximation are left for a future paper.

Added Note. After this paper was submitted for publication, we received a preprint from Mattice,[14] who considers excluded volume in star polymers by Monte Carlo calculations for a hard-sphere rotational isomeric model. He finds enhanced expansion near the star center and none near the chain ends, in agreement with our renormalization group calculations.

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(13) This difference can be completely eliminated by noting (Douglas, J., private communication) that the coefficient $(6/\pi)^{1/2}$ in (5.11) is just the $d = 3$ value of $(d/2)^{1/2}\Gamma((d-1)/2)/\Gamma(d/2)$, with Γ the Gamma function, whereas the coefficient $(3\pi/2)^{1/2}(1 + 2\ln 2)/4$ is just obtained by ϵ-expanding the Γ functions and setting $\epsilon = 1$ because $\Gamma((d-1)/2)/\Gamma(d/2) = \pi^{1/2}(1 + \epsilon\ln 2 - \epsilon/2)/2$.
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