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In Figure 11, an increase in intensity appearing around the copolymer T_g may be due to C-PPO molecules passing through their glass transition. Residual strains may be released, causing the sample surface to become irregular, resulting in an increased scattering intensity. This effect can be reduced by annealing above the glass transition temperature of the film and slowly cooling to room temperature to relax any residual strain and stress.

Conclusions

Low carboxyl content ($\lesssim$ 10 mol %) copolymers (C^y-PPO) blended with PS of molar mass 115 000 exhibit a single phase. Phase diagrams for blends of $C^{8.0}$-PPO/PS_{115} and $C^{10.3}$-PPO/PS_{115} exhibit a single-phase region, a UCST, and an LCST. The gap between the UCST and LCST depends on the copolymer composition. For $C^{4.5}$-PPO/PS_{115} and $C^{6.7}$-PPO/PS_{115} blends, no phase separation was observed during thermal treatment because the single-phase region between the UCST and LCST extends beyond the experimental temperature range. The phase separation behavior observed by either DSC or light scattering is reversible.

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Osmotic Pressure of Star and Ring Polymers in Semidilute Solution

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ABSTRACT: The conformational space renormalization group method is used to calculate the osmotic pressure of semidilute solutions of star and ring polymers in marginal to good solvents to first order in ϵ, where $\epsilon = 4 - d$ and d is the spatial dimension. The results are expressed in terms of an experimentally measurable reduced concentration variable $c/c^* = c\langle A_2\rangle_w M_n$, with $\langle A_2\rangle_w$ the weight-averaged second virial coefficient and M_n a number-averaged molecular weight. The osmotic pressure is found to scale with the same power of the concentration for both stars and rings in the semidilute region, in agreement with scaling theory and asymptotic analyses, but there are fairly large differences in the values of the prefactor coefficients between different polymer types. This is in contrast to the predictions of scaling and of an approximate analytic evaluation of the osmotic pressure, which yields a single universal curve for these two architectural classes of polymer. Criteria are also provided for the onset of semidilute solution power law behavior as a function of the reduced concentration and solvent quality.

I. Introduction

Star and ring polymers constitute an important class of polymers whose study helps clarify the connection between polymer physical properties and molecular architecture. While there is a fairly extensive body of experimental and theoretical literature that explores this connection for the case of polymers at infinite dilution,[1-5] there have been fewer studies at concentrations where overlap between different chains becomes important.[6-9] However, these studies of semidilute solutions have focused only on linear polymers, and the question of whether topological differences significantly influence the large-scale properties of semidilute polymer solutions has so far only been addressed by scaling methods.[10-12] Scaling argues that polymer properties like the osmotic pressure must become independent of the molecular weight in semidilute solution, and, consequently, linear, star, and ring polymers scale in the same manner. Whether or not a full theory predicts differences and the extent to which such differences represent measurable effects is not yet known. Nor is it known whether the scaling functions for different polymer architectures in semidilute solution can be represented in terms of a single universal curve.

In this paper we examine the role of polymer architecture in influencing semidilute solution properties by calculating the osmotic pressure of dilute through semidilute solutions of star and ring polymers in marginal to good solvents to order ϵ, where $\epsilon = 4 - d$ and d is the spatial

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dimensionality. The calculations are performed by using the chain conformational space renormalization group method.[13-15] Ohta and Oono have introduced this method for semidilute good solvent solutions of linear polymers and have shown that the predictions are in reasonable agreement with experimental data on these systems.[16] Freed generalizes the method to treat the excluded volume crossover between the marginal and good solvent limits.[17] Here we extend these methods further and apply them with some modifications to semidilute solutions of stars and rings to determine the possible dependence of the osmotic pressure and the onset of power law behavior in the semidilute region on branching type.

Previous renormalization group treatments of polymer solutions have often used the equivalence between infinitely long polymers and magnetic systems at their critical points[18] to formulate the problem with field theoretic methods. These studies are frequently restricted to chains of infinite length or to solutions of broad polydispersity,[19-21] and the field theory approaches are not very accessible to polymer scientists. A direct renormalization approach to polymers, which avoids the polymer–magnet analogy, has been presented by des Cloizeaux,[22] but his treatment of the concentration-dependent screening of excluded volume interactions in semidilute solutions necessitates summing over certain infinite classes of polymer diagrams in analogy with field theoretic methods. The approach of Ohta and Oono[16] and Freed[17] formulates the problem directly with the two-parameter polymer model;[1] it permits both finite chain lengths and arbitrary chain length distributions to be considered at the same time, and it introduces screening in a natural way, without the use of infinite summations.

In applying the chain space approach to semidilute solutions of stars and rings, we provide a discussion of the particular polydispersity averages that enter into the theory and that are relevant to the analysis of experimental data. We modify the manner of regularizing the theoretical expression for the osmotic pressure so that the latter can be expressed solely in terms of experimental quantities.[10] The calculated natural scaling variable that emerges in this fashion is the reduced concentration c/c^*, first suggested implicitly by Stockmayer[23] as the appropriate variable to use for semidilute solutions away from the Θ point. The renormalization group theory yields $c/c^* = c\langle A_2\rangle_{\mathrm{w}} M_{\mathrm{n}}$ for marginal to good solutions, where $\langle A_2\rangle_{\mathrm{w}}$ and M_{n} are the weight-averaged osmotic second virial coefficient and the number-averaged molecular weight, respectively. Scaling theory has led to the use of the more common estimate of c^* in terms of the radius of gyration, R_{G}, viz., $c^*_{R_{\mathrm{G}}} = 3/4\pi R_{\mathrm{G}}^3$. These scaling estimates can differ greatly from the renormalization group value defined in terms of A_2. Moreover, the scaling concentration $c^*_{R_{\mathrm{G}}}$ is inappropriate in marginal solutions where A_2/R_{G}^3 becomes temperature and molecular weight dependent. Previous difficulties in predicting the onset concentration for semidilute power law behavior using the scaling estimate of c^* underscore the importance of calculating numerical coefficients in addition to scaling laws.

We provide a rigorous analysis of the behavior of the full $\mathcal{O}(\epsilon)$ perturbative expression for the osmotic pressure in the $c/c^* \gg 1$ limit and demonstrate that this produces the expected scaling form, thereby justifying the reexponentiation of logarithmic terms in the useful approximate analytic treatment of Ohta and Oono.[16]

Section IIA presents the functional integral representation of the partition function of stars and rings. The partition function of the ensemble of chains is rewritten in terms of a polydispersity-averaged single-chain partition function using the Edwards screening theory representation.[25] We relate the polydispersity averages obtained in this way to other experimentally relevant averages. Section IIB briefly describes the perturbative calculation of star and ring partition functions. The notion of a screened interaction is briefly described to motivate the resummation of terms in the perturbation expansion involving the concentration and excluded volume parameter that are not small in the semidilute region. In section IIC we outline the manner in which the initially divergent expression for the calculated osmotic pressure is regularized. (Details are provided in Appendix C.) The present regularization scheme[10] allows the osmotic pressure to be expressed solely in terms of measurable variables and in this regard differs slightly from the earlier scheme of Ohta and Oono.[16] Section III employs the approximation of Ohta and Oono to evaluate the osmotic pressure of solutions of rings and stars as a function of reduced concentration. This approximation results in a single universal function for all polymer architectures. The predicted power law behavior is compared with the expectations of scaling theory. Somewhat fortuitous agreement between their exponents occurs in three dimensions[16] if the exponent ν (defined by $R_{\mathrm{G}} \sim M^{\nu}$) is taken to have the Flory value.

Section IV presents the numerical evaluation of the osmotic pressure to $\mathcal{O}(\epsilon)$ for monodisperse stars and rings, without introducing the Ohta–Oono approximation. We find appreciable differences between the numerical and analytical approximation approaches for the numerical prefactors for polymers of different branching type. No differences arise for the exponents as dictated by our asymptotic analysis. Comparisons are provided between experimental data and our calculated osmotic pressure and osmotic compressibility curves for linear polymers. Criteria are also given for the onset of semidilute solution power law behavior as a function of the reduced concentration and solvent quality.

II. Theoretical Methods

A. Expressions for Star and Ring Partition Functions. Details of the conformational space renormalization group method for polymers at nonzero concentration are given in ref 17 and 10. Here we only mention those features of the method relevant to the study of stars and rings. We also discuss the slight modifications to the method that are needed to bring the theoretical parameters into correspondence with experimental measurables. The dimensionless configurational Hamiltonian for a polydisperse solution of n linear polymers in a volume Ω is given by

$$H = \frac{1}{2}\sum_{\alpha=1}^{S}\sum_{i=1}^{n_\alpha}\int_0^{N_{0,\alpha}}\mathrm{d}\tau_i \left|\frac{\mathrm{d}\mathbf{r}_i(\tau_i)}{\mathrm{d}\tau_i}\right|^2 + \frac{1}{2}v_0\sum_{\alpha,i}^{S,n_\alpha}\sum_{\beta,j}^{S,n_\beta}\int_0^{N_{0,\alpha}}\mathrm{d}\tau_i\int_0^{N_{0,\beta}}\mathrm{d}\tau_j\;\delta[\mathbf{r}_i(\tau_i) - \mathbf{r}_j(\tau_j)] \quad (1)$$

where S is the number of sets of polymers of a given chain length and n_α is the number of polymers of length $N_{0,\alpha}$ in the set α such that $\sum_{\alpha=1}^{S} n_\alpha = n$. The index i labels the ith chain of the αth set. Equation 1 describes the configuration of the ith chain in the ensemble in terms of a continuous curve in d dimensions whose position with respect to a chosen origin is specified by the vectors $\{\mathbf{r}_i(\tau_i)\}$ at the points $\{\tau_i\}$ along the chain. Here, for convenience, we employ a system of units in which the vectors $\{\mathbf{r}_i\}$ have the dimensions of $(\text{length})^{1/2}$ by defining

$$\mathbf{r}_i = (d/l)^{1/2}\mathbf{R}_i \quad (1a)$$

with $\mathbf{R}_i$ the usual d-dimensional vectorial distance and l

an effective segment length known as the Kuhn length.[24] The first term in (1) produces the Gaussian random walk chain backbone, while the second term models excluded volume effects between different chains and between different portions of the same chain through a repulsive δ-function pseudopotential with bare excluded volume v_0.[25] Such an approximation to the true intermolecular potential is adequate in describing the properties of polymers at length scales much larger than a typical bond distance[10,11,26] and polymer volume fractions much less than unity.

Equation 1 also describes the configurational Hamiltonian of a polydisperse solution of rings (under the assumption that the solution is free of nonequilibrium distributions of topological constraints such as those introduced by the presence of concatenations). The generalization for star polymers is[5]

$$H^{\mathrm{s}} = \frac{1}{2}\sum_{\alpha=1}^{S}\sum_{i=1}^{n_\alpha}\sum_{\beta=1}^{m_i}\sum_{j=1}^{h_\beta}\int_0^{N_{0,\beta}}\mathrm{d}\tau_j \left|\frac{\mathbf{r}_j(\tau_j)}{\mathrm{d}\tau_j}\right|^2 + \frac{1}{2}v_0 \sum_{\substack{\alpha,i,\beta,j\\ \mu,k,\nu,l}}\int_0^{N_{0,\beta}}\mathrm{d}\tau_j\int_0^{N_{0,\nu}}\mathrm{d}\tau_l\; \delta[\mathbf{r}_j(\tau_j) - \mathbf{r}_l(\tau_l)] \quad (2)$$

where, as before, the volume Ω contains a total of n stars; these are distributed among S sets of stars, each star of a given set having f_α branches, with α varying from 1 to S. There are n_α stars in each set, and i labels a given star in the set such that $\sum_{\alpha=1}^{S}\sum_{i=1}^{n_\alpha} = n$. The parameter m_i is the number of sets of branches of a given length in the ith star of the αth set, and there are h_β such branches, with β varying from i to m_i. A given branch in a star is labeled by the index j. In (2) as well as throughout the rest of the paper we use the superscripts s and r to distinguish between properties of stars and rings, respectively.

Given the Hamiltonians in eq 1 and 2, the bare partition function Q_{B} may be written as

$$Q_{\mathrm{B}}^{\mathrm{r}} = \left\{\prod_{\alpha=1}^{S}\prod_{i=1}^{n_\alpha}\int\mathcal{D}[\mathbf{r}_i(\tau_i)]\right\}\exp\{-H^{\mathrm{r}}[\mathbf{r}_i(\tau_i)]\} \quad (3)$$

for rings and

$$Q_{\mathrm{B}}^{\mathrm{s}} = \left\{\prod_{\alpha=1}^{S}\prod_{i=1}^{n_\alpha}\prod_{\beta=1}^{m_i}\prod_{j=1}^{h_\beta}\int\mathcal{D}[\mathbf{r}_j]\right\}\exp\{-H^{\mathrm{s}}[\mathbf{r}_j(\tau_j)]\} \quad (4)$$

for stars, where $\mathcal{D}[\mathbf{r}(\tau)]$ is the integration measure for continuous Gaussian chains. The integral in (3) for rings has the further constraint that $\mathbf{r}_j(0) = \mathbf{r}_j(N_{0,\alpha})$.

The osmotic pressure is readily derived from (3) and (4) using the standard thermodynamic relation[27]

$$\Pi_{\mathrm{B}} = -k_{\mathrm{B}}T(\partial \ln Q_{\mathrm{B}}/\partial\Omega)_{n,T} \quad (5)$$

The general approach[16] to the calculation of Q_{B} is discussed in detail in ref 10 and 17 where Edward's screening formulation[24,25] is introduced to factor the partition function into contributions from individual chains. Briefly, the method takes advantage of the equivalence between the description of a polymer, viewed as interacting with itself through some pairwise potential, and its description as a Gaussian chain interacting with a random fluctuating field $\phi(\mathbf{r})$. This equivalence is made explicit through the identity[25]

$$\exp\left\{-\frac{v_0}{2}\sum_{\substack{\alpha,i\\ \beta,j}}\int_0^{N_{0,\alpha}}\mathrm{d}\tau_i\int_0^{N_{0,\beta}}\mathrm{d}\tau_j\;\delta[\mathbf{r}_i(\tau_i) - \mathbf{r}_j(\tau_j)]\right\} \equiv \int\mathcal{D}[\phi]\exp\left\{\pm i\sum_{\alpha,i}\int_0^{N_{0,\alpha}}\mathrm{d}\tau_i\;\phi[\mathbf{r}_i(\tau_i)] - \frac{1}{2v_0}\int\mathrm{d}^d r\;\phi^2(\mathbf{r})\right\} \quad (6)$$

where the measure $\mathcal{D}[\phi]$ is defined by

$$\mathcal{D}[\phi] = \delta\phi\Big/\int\delta\phi\,\exp\left\{-\frac{1}{2v_0}\int\mathrm{d}^d r\;\phi^2(\mathbf{r})\right\} \quad (7)$$

and the volume element is

$$\delta\phi = \prod_{\mathbf{r}}\mathrm{d}\phi(\mathbf{r}) \quad (7a)$$

Using the random field representation (6), we write the partition functions for rings and stars in the form

$$Q_{\mathrm{B}}^{\mathrm{r}} = \int\mathcal{D}[\phi]\exp\left\{-\frac{1}{2v_0}\int\mathrm{d}^d r\;\phi^2(\mathbf{r})\right\}\prod_{\beta}[G^{\mathrm{r}}(N_{0,\beta},\phi)]^{n_\beta} \quad (8)$$

$$Q_{\mathrm{B}}^{\mathrm{s}} = \int\mathcal{D}[\phi]\exp\left\{-\frac{1}{2v_0}\int\mathrm{d}^d r\;\phi^2(\mathbf{r})\right\}\prod_{\alpha,i,\beta}[G^{\mathrm{s}}(N_{0,\beta},f_\alpha,\phi)]^{h_\beta} \quad (9)$$

where the quantities G^{r} and G^{s} are, respectively, the partition functions of single ring and star polymers in the random field $\phi(\mathbf{r})$. Path integral representations of G^{r} and G^{s} are

$$G^{\mathrm{r}}(N_{0,\beta},\phi) = \int\mathcal{D}[\mathbf{r}]\exp\left\{-\frac{1}{2}\int_0^{N_{0,\beta}}\mathrm{d}\tau\left|\frac{\mathrm{d}\mathbf{r}(\tau)}{\mathrm{d}\tau}\right|^2 \pm i\int_0^{N_{0,\beta}}\mathrm{d}\tau\;\phi[\mathbf{r}(\tau)]\right\} \quad (10)$$

$$G^{\mathrm{s}}(N_{0,\beta},f_\alpha,\phi) = \int\mathcal{D}[\mathbf{r}_i]\exp\left\{-\frac{1}{2}\sum_{\beta}\sum_{j}\left(\int_0^{N_{0,\beta}}\mathrm{d}\tau_j\left|\frac{\mathrm{d}\mathbf{r}_j(\tau_j)}{\mathrm{d}\tau_j}\right|^2 \pm i\int_0^{N_{0,\beta}}\mathrm{d}\tau_j\;\phi[\mathbf{r}_j(\tau_j)]\right)\right\} \quad (11)$$

The products over the individual G's in (8) and (9) may be expressed in terms of an average over some chosen length distribution. Using the case of stars as an illustration, we write this as[10,16,17]

$$\prod_{\alpha,i,\beta}[G^{\mathrm{s}}(N_{0,\beta},f_\alpha,\phi)]^{h_\beta} \equiv \exp\Big[n\sum_{\alpha}\sum_{i}\sum_{\beta}(n_\beta/n)\ln G^{\mathrm{s}}(N_{0,\beta},f_\alpha,\phi)\Big] \equiv \exp[n\langle\ln G^{\mathrm{s}}(\{N_{0,f}\},f,\phi)\rangle_{\mathrm{n}}] \quad (12)$$

where the average $\langle\ldots\rangle_{\mathrm{n}}$ denotes a number average.

Several different polydispersity averages are used in evaluating polymer properties in addition to the number average of (12). In particular, weight or weight fraction averages are commonly employed in experimental work, and are defined by

$$\langle P(N_0)\rangle_{\mathrm{w}} = \sum_{\alpha}P(N_{0,\alpha})M_\alpha n_\alpha\Big/\sum_{\alpha}M_\alpha n_\alpha \quad (13)$$

with M_α the molecular weight of the chain of length $N_{0,\alpha}$ and P some polymer property. With the number-averaged molecular weight M_{n} defined through

$$M_{\mathrm{n}} \equiv \sum_{\alpha}M_\alpha n_\alpha/n \quad (14)$$

$\langle P(N_0)\rangle_{\mathrm{n}}$ and $\langle P(N_0)\rangle_{\mathrm{w}}$ are related as

$$\langle P(N_0)\rangle_{\mathrm{n}} = \langle P(N_0)/M\rangle_{\mathrm{w}}M_{\mathrm{n}} \quad (15)$$

Similarly, the polymer chain density c_{p} is related to the standard mass concentration c through

$$c_{\mathrm{p}} = N_{\mathrm{A}}c/M_{\mathrm{n}} \quad (16)$$

where N_A is Avogadro's number.

B. Perturbative Calculation of G^r and G^s: Effect of Screening. The field ϕ is formally of order $v_0^{1/2}$ as may be seen from the measure containing $v_0^{-1}\phi^2$ in eq 8 and 9. It is, therefore, possible to evaluate G^r and G^s to first order in v_0 by perturbatively expanding to second order in ϕ in the exponent of (12) and by subsequently integrating over all ϕ. Simple dimensional analysis implies that terms in the expansion that describe intramolecular excluded volume are of the form $v_0N_0^{\epsilon/2}$, with $\epsilon \equiv 4 - d$. For large chains this expansion parameter is not small in the dimension of interest, viz., $d = 3$, and a further expansion around $d = 4$ (i.e., around $\epsilon = 0$) is necessary to render the perturbative approach controllable. Results for $d = 3$ are recovered by the application of renormalization group methods.[10,14]

Interchain excluded volume contributions, on the other hand, yield expansions in the dimensionless quantity $c_pv_0N_0^2$, with $c_pv_0N_0^2$ proportional to the unperturbed reduced concentration c/c_0^*. Since the semidilute region corresponds to concentrations for which $c/c^* \geq 1$, it is clear that an expansion in this parameter is not useful. We, therefore, employ Edwards' screening approach to retain c_pv_0 and, hence, c/c^* both formally of order ϵ^0.

The Edwards screening theory[10,17,25] has polymer segments interacting through the screened excluded volume potential $v_{\text{eff}}(\mathbf{q})$, which on all length scales becomes

$$v_{\text{eff}}^{-1}(\mathbf{q}) = \tfrac{1}{2}v_0 + cS(\mathbf{q},N_0) \tag{17}$$

where $S(\mathbf{q},N_0)$ is the Debye scattering function of a single Gaussian chain and $\mathbf{q}$ is a momentum variable conjugate to $\mathbf{r}$.

C. Regularization of the Osmotic Pressure. As explained in ref 10 and 17 the calculation of (10) and (11) and subsequently (8) and (9) is conveniently carried out by first expressing the field ϕ as a sum over its Fourier components $\phi_{\mathbf{q}}$. When the average over the ϕ fields is then taken, the bare osmotic pressure is found to involve an integral over all $\mathbf{q}$ in the continuum limit. This integral diverges at a dimensionality of four as $q \to \infty$. A renormalization of the osmotic pressure is required to obtain finite, physically meaningful results.

References 10, 16, and 17 perform the renormalization by isolating the singular portion of the $\mathbf{q}$ integral as a pole in ϵ and absorbing it into a redefinition of the bare v_0 and N_0 as the corresponding renormalized v and N. In the present calculation, as discussed in Appendix C, renormalization proceeds by extracting the singularity in $\mathbf{q}$ along with a nonsingular contribution into the definition of the osmotic second virial coefficient and by renormalizing this measurable quantity as in infinite dilution theories. This approach makes it possible to express the osmotic pressure in terms of the measurable reduced concentration $\bar{c} \equiv c/c^* = c\langle A_2\rangle_w M_n$, while at the same time eliminating all poles in $1/\epsilon$.

III. Results

The renormalized osmotic pressure of stars and rings is found in this manner to be given by

$$\frac{\Pi M_n}{RTc} = 1 + \bar{c} - \frac{\epsilon}{16\bar{c}}\left(\frac{32\bar{z}/3}{1 + 32\bar{z}/3}\right)\int_0^\infty \mathrm{d}y\, y^3\left\{\ln\,[1 + 4\bar{c}g(y^2)] - \frac{4\bar{c}g(y^2)}{1 + 4\bar{c}g(y^2)} - \frac{1}{2}[4\bar{c}g(y^2)]^2\right\} + \mathcal{O}(\epsilon^2) \tag{18}$$

where the difference between the two classes of polymer enters through the function $g(y^2)$, which is defined for stars by

$$\begin{aligned} g^s(y^2) = {}& y^{-2} + y^{-4}\{\langle\sum_\alpha^f[\exp(-y^2N_\alpha/\langle\sum_\alpha^f N_\alpha\rangle_n) - 1]\rangle_n - \\ & \tfrac{1}{2}\langle\sum_\alpha^f[\exp(-y^2N_\alpha/\langle\sum_\alpha^f N_\alpha\rangle_n) - 1]^2\rangle_n + \\ & \tfrac{1}{2}\langle\{\sum_\alpha^f[\exp(-y^2N_\alpha/\langle\sum_\alpha^f N_\alpha\rangle_n) - 1]\}^2\rangle_n\} \end{aligned} \tag{19}$$

In monodisperse solutions (19) becomes

$$g^s(y^2) = y^{-2} + y^{-4}f[\exp(-y^2/f) - 1]\{1 + \tfrac{1}{2}(f - 1)[\exp(-y^2/f) - 1]\} \tag{19a}$$

while for ring polymers we have

$$g^r(y^2) = \frac{1}{2\langle N\rangle_n^{\,2}}\left\langle N^2[y(N/4\langle N\rangle_n)^{1/2}]^{-1} \times \exp(-y^2N/4\langle N\rangle_n)\int_0^{y(N/4\langle N\rangle_n)^{1/2}}\mathrm{d}t\; e^{t^2}\right\rangle_n \tag{20}$$

which for monodisperse solutions becomes

$$g^r(y^2) = y^{-1}\exp(-y^2/4)\int_0^{y/2}\mathrm{d}t\,\exp(t^2) \tag{20a}$$

The average $\langle...\rangle_n$ in (19) denotes a number average over chain lengths as well as an average over the distribution of the number of arms in the star. RT is the thermal energy, and $\bar{z}$ is a phenomenological interaction variable that is to be treated as the usual z parameter of the two-parameter model.[1] ($\bar{z}$ is related to the crossover variable ζ of ref 10 and 17 through $\zeta = (32\bar{z}/3)$ and obeys the relation $\bar{z} \propto M^{1/2}[1 - (\Theta/T)]$, with Θ the theta temperature.)

Equation 18 may be compared with the corresponding expression, obtained from a scaling analysis alone, which in the limit $c \gg c^*$ and $\bar{z} \gg 1$ is

$$\frac{\Pi}{ck_BT} \propto \left(\frac{N_A}{M}\right)^{1+(d\nu-1)^{-1}} l^{d(d\nu-1)^{-1}}c^{(d\nu-1)^{-1}}(\beta_0l^{-d})^{d(2\nu-1)/(4-d)(d\nu-1)} \tag{21}$$

where β_0 is a binary cluster integral[1] and ν describes chain expansion in good solvents through the power law

$$R_G \sim M^\nu \tag{21a}$$

With the Flory value[1] of $^3/_5$ for ν in three dimensions (a more accurate theoretical estimate[28] is $\nu = 0.588$), eq 21 reduces to

$$\frac{\Pi}{k_BT} \propto \frac{N_A}{M^{9/4}}c^{9/4}\beta_0^{\,3/4}l^{3/2} \tag{22}$$

The scaling structure of (18) can be determined by approximations to g^r and g^s that enable the analytic evaluation of the integral in (18).

Ohta and Oono[16] approximate $g(y^2)$ for linear polymers by a function whose limiting forms for $y \to 0$ and $y \to \infty$ are the same as those of the original function. With this approximation $g^s(y^2)$ and $g^r(y^2)$ become

$$g^s(y^2) \approx (y^2 + 2\sigma)^{-1}, \qquad \sigma = \langle\sum_\alpha^f N_\alpha\rangle_n^{\,2}/\langle(\sum_\alpha^f N_\alpha)^2\rangle_n \tag{23}$$

$$g^r(y^2) \approx (y^2 + 2\lambda)^{-1}, \qquad \lambda = \langle N\rangle_n^{\,2}/\langle N^2\rangle_n \tag{24}$$

and the integral in (18) can now be evaluated analytically.[16] The calculation is found to yield a number of logarithmic terms in c/c^*. If the final expression for the osmotic pressure is required to have a power law form in the reduced concentration $\bar{c}$ as predicted in (21) by scaling theory, such logarithmic terms must be reexponentiated. For instance, we write

$$\bar{c}^{\epsilon b} = 1 + \epsilon b \ln \bar{c} + \mathcal{O}(\epsilon^2) \qquad (25)$$

where ϵ is as usual $4 - d$. In this way the approximations (23) and (24) lead to

$$\frac{\Pi M_\mathrm{n}}{cRT} \equiv \hat{\Pi} = 1 + \bar{c}\left(\frac{\theta + 2\bar{c}}{\theta}\right)^{(\epsilon/4)(32\bar{z}/3)(1+32\bar{z}/3)^{-1}[1-(\theta/2\bar{c})^2]}\left[1 - \frac{\epsilon}{8}\,\frac{32\bar{z}/3}{1 + 32\bar{z}/3}\left(1 - \frac{\theta}{\bar{c}}\right)\right] + \mathcal{O}(\epsilon^2) \qquad (26)$$

where θ equals σ (λ) for stars (rings). Equation 26 is an approximate *single* universal scaling form of the osmotic pressure of linear, star, and ring polymers in semidilute solutions of general solvent quality (away from the θ point). The expression (26) differs slightly from that given by Ohta and Oono[16] because of our method of regularization,[10] which makes $\bar{c}$ have an explicit measurable interpretation.

Two limits are of interest in eq 26. As $\bar{c} \to 0$, eq 26 becomes

$$\Pi M_\mathrm{n}/cRT \to 1 + c\langle A_2\rangle_\mathrm{w} M_\mathrm{n} + \ldots \qquad (27)$$

which is the usual dilute limit virial expansion of the osmotic pressure.[1] In the limit of large concentration $\bar{c} \gg 1$ and under good solvent conditions $\bar{z} \gg 1$ eq 26 reduces to

$$\Pi M_\mathrm{n}/cRT = \bar{c}(2\bar{c})^{\epsilon/4}(1 - \epsilon/8) \qquad (28)$$

which exhibits the general scaling structure

$$\Pi/c \propto \bar{c}^{\mu}, \qquad \bar{c} \gg 1 \qquad (28a)$$

where μ is a pure number. The exponent $\epsilon/4$ in eq 28 coincides to $\mathcal{O}(\epsilon)$ with the scaling exponent $(d\nu - 1)^{-1} - 1$ of eq 22 when ν is taken to be the Flory value $^3/_5$ in three dimensions. The agreement is somewhat fortuitous as $\mathcal{O}(\epsilon^2)$ calculations are generally required to obtain good exponents for polymer properties. However, this identification enables us to replace the exponent $\epsilon/4$ in (26) and (28) by $(2 - d\nu)/(d\nu - 1)$. This, in turn, allows us to use more accurate estimates of ν to obtain an improved exponent μ without having to calculate it to higher order in ϵ.

Rather than use the Ohta–Oono approximation for g^r and g^s to evaluate the integrals in (18), it is now computed numerically. Appendices A and B show that the integral in (18) for stars and rings behaves as

$$\lim_{\bar{c}\to\infty} (\Pi/c) \propto \bar{c} + \bar{c} \ln \bar{c} \qquad (29)$$

in the asymptotic limit of high concentration. Since it is not possible to separate the logarithmic portion from the remainder of the integral, the required power law can only be obtained by exponentiating the entire $\mathcal{O}(\epsilon)$ expression. That is, eq 18 is rewritten to $\mathcal{O}(\epsilon)$ as

$$\hat{\Pi} \equiv \frac{\Pi M_\mathrm{n}}{cRT} = 1 + \bar{c}\exp\left\{-\frac{\epsilon}{16\bar{c}^2}\int_0^\infty \mathrm{d}y\, y^3\left(\ln\,[1 + 4\bar{c}g(y^2)] - \frac{4\bar{c}g(y^2)}{1 + 4\bar{c}g(y^2)} - \frac{1}{2}[4\bar{c}g(y^2)]^2\right)\right\} + \mathcal{O}(\epsilon^2) \qquad (30)$$

where both (26) and the numerical calculations are presented in the limit $\bar{z} \gg 1$. Depending on the kind of polymer being considered, $g(y^2)$ refers now to the exact expressions of eq 23 and 24. For simplicity, the solutions are also taken to be monodisperse in (30).

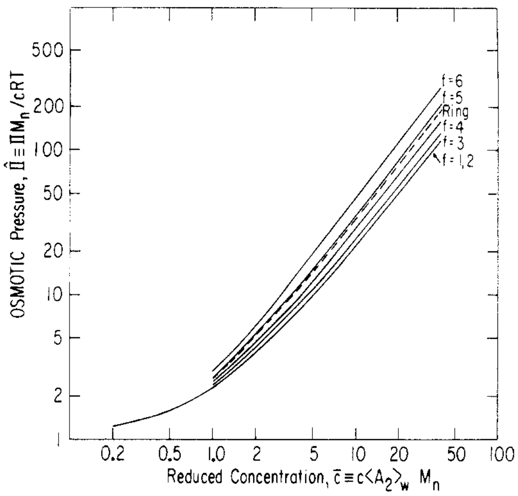

Figure 1. log–log plots of $\Pi M_\mathrm{n}/cRT = \hat{\Pi}$ vs. $\bar{c}$ using eq 30 evaluated numerically. Full lines present the calculations for stars, the lowest curve corresponding to $f = 1$ and the highest to $f = 6$. The dashed line is for rings.

Improved estimates of the exponent are obtained from (30) by the substitution of a factor of $\epsilon/4$ in front of the integral by $(d\nu - 1)^{-1} - 1$, while the solvent quality dependence is reintroduced by taking $\epsilon \to \epsilon(32\bar{z}/3)(1 + 32\bar{z}/3)^{-1}$ in the exponent of (30) with A_2 solvent quality dependent.

IV. Numerical Results and Comparison with Experiment

The approximations of eq 23 and 24 for the functions g^s and g^r lead to identical expressions for the concentration and solvent quality dependence of the osmotic pressure as a function of $\bar{c}$ for these apparently different architectural classes of polymer throughout the dilute and semidilute regions. To our knowledge, there is presently no experimental evidence that demonstrates that such a single universal curve can, in fact, describe these systems. On the contrary, the data from a preliminary investigation of semidilute solutions of stars by Burchard,[36] which he brought to our attention after submission of our manuscript, suggest that while the osmotic pressures of different stars scale in essentially the same way for $c > c^*$, their amplitudes differ markedly. A second counterexample to the possible existence of a universal description of topologically different systems arises in connection with the more complicated two-dimensional case, where experimental data for the surface pressure above the overlap concentration c^* do not lead to a single universal curve for linear polymers and rings.[29]

We have tested this universality of the approximate analytical theory further through explicit numerical evaluation of the integrals in eq 30 using Simpson's formula. The calculated curves for $\hat{\Pi}$ as a function of $\bar{c}$ are depicted in Figure 1 and are found to differ not only between rings and stars but also between stars of varying number of branches. In fact, the calculated numerical difference between the prefactor of linear polymer solutions and the prefactors of rings or stars of five or six branches is approximately 2. This should be measurable experimentally and would provide a useful test of the theory. It would also furnish a means of checking the purity of solutions of rings or stars, provided polydispersity corrections are made.[30] The data of Burchard are in semiquantitative agreement with our calculations and suggest a slightly larger prefactor.

While it may be possible to collapse the separate curves of the various star polymers onto a single curve by scaling

Table I
Comparison of Experimental and Predicted Values of Exponents and Prefactors for Semidilute Solutions of Linear, Star, and Ring Polymers

system	exponent	prefactor
linear[a]	1.25	$2^{1/4}(1 - {}^1/_8) = 1.041$
linear[b]	1.32	1.02
ring[a]	1.25	1.041
star[a]	1.25	1.041
star,[c] $f = 1, 2$	1.23	1.26
star,[c] $f = 3$	1.24	1.32
star,[c] $f = 4$	1.24	1.63
star,[c] $f = 5$	1.25	2.00
star,[c] $f = 6$	1.26	2.58
ring[c]	1.25	1.86

[a] Using eq 26 with $\bar{c} \gg 1$ and $\bar{z} \to \infty$. [b] From the data of Noda et al.[8] [c] Evaluated numerically.

g^s by some function of f, we have not found such a transformation.

The similarity of the osmotic pressure curves in Figure 1 for rings and five-armed stars is interesting in view of the fact that the properties other than the osmotic pressure also exhibit this correspondence. One such property is the good solvent penetration function Ψ, defined by

$$\Psi = \frac{M^2}{4\pi^{3/2}N_A} \frac{A_2}{(R_G{}^2)^{3/2}} \tag{31}$$

in $d = 3$. Five-armed stars have a good solvent limit $\Psi^* = 0.68$ as calculated[31] by renormalization group methods, while the calculated value for rings is 0.69.[31] Roovers and Toporowski[32] measure $\Psi^*(\text{ring}) = 0.63$. (For comparison we also quote other experimental[2] and theoretical[31] estimates: Ψ^*_{exptl} (star, $f = 4$) = 0.53, Ψ^*_{theor} (star, $f = 4$) = 0.5297, Ψ^*_{exptl} (star, $f = 6$) = 0.75, and Ψ^*_{theor} (star, $f = 6$) = 0.8523.) Another property exhibiting this correspondence is associated with the radius of gyration, which for linear and star polymers is related in ideal solution as[1]

$$g^\circ \equiv \langle R_G{}^2\rangle_f / \langle R_G{}^2\rangle_{f=1} = (3f - 2)/f^2 \tag{32}$$

The special case of $f = 5$ yields $g^\circ = {}^{13}/_{25} \approx 0.5$, while for rings g° is exactly 0.5.[1] Since the g° factors enter into the description of several properties of branched and ring polymers and since theoretical calculations[31] show g° to have a very weak dependence on solvent quality, similarities between equilibrium properties of five-armed stars and rings may be anticipated from the closeness of their respective g°'s.

As discussed throughout this paper, scaling arguments dictate the power law exponent μ of eq 28a in the semidilute region, but the prefactors may differ. This issue is investigated further by calculating μ and the prefactor by a least-squares determination of the slope and intercept of $\ln \bar{c}$ vs. $\ln \hat{\Pi}$ curves for $\bar{c} \geq 10$ using values obtained from the numerical integration of eq 30. The results are presented in Table I, together with the corresponding values calculated with eq 26.

Scaling argues that when c becomes much greater than c^*, two interacting polymer segments cannot "tell" if they belong to different polymers or to distant portions along a single chain. Such scaling arguments suggest that the prefactor in (28a) should perhaps be independent of polymer architecture when a suitable definition of c^* is introduced. It is clear from Table I that the naturally occurring definition $(c^*)^{-1} = \langle A_2\rangle_w M_n$ does not yield this universality. The scaling choice of $c^*_{R_G} = 3/4\pi R_{G,f}{}^3$ converts (28a) into

$$\Pi/cRT = K_f \Psi_f{}^\mu (c/c^*_{R_{G,f}})^\mu \tag{33}$$

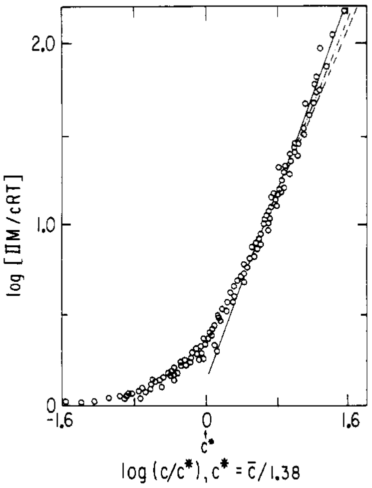

Figure 2. Comparison of the data of Noda et al.[8] with eq 26 (---) and with eq 30 (-·-). The variable c/c^* used by Noda et al. is related to $\bar{c}$ of this work by $c/c^* = \bar{c}/1.38$, corresponding to a value of 0.26 for the good solvent limit penetration function. The full line is the experimental fit to the data, and it essentially coincides with eq 30 corrected for the exponent μ.

where K_f is the numerical prefactor in Table I and the subscript f labels the number of arms (zero for a ring). However, both K_f in Table I and Ψ_f values[31] are increasing functions of f, so (33) does not produce the desired universality. An alternative involves using the same scaling concentration for all architectures. Defining the ratio

$$g_{A_{2,f}} = \langle A_{2,f}\rangle_w / \langle A_{2,f=1}\rangle_w \tag{34a}$$

with both chains having the same molecular weight, eq 33 is rewritten as

$$\Pi/cRT = K_f (g_{A_{2,f}})^\mu (c\langle A_{2,f=1}\rangle_w M_n)^\mu \tag{34b}$$

Now $(g_{A_{2,f}})^\mu$ is decreasing as f increases, but the product $K_f(g_{A_{2,f}})^\mu$ still increases with f. Our calculations for $(K_f/K_1)(g_{A_{2,f}})^\mu$ for f from 3 to 6 yield, respectively, 1.01, 1.16, 1.32, and 1.55. It is possible that our calculations overestimate K_f, but Burchard's data for $f = 6$ suggests an underestimate. Thus, scaling suggestions of a universal form, independent of architecture, are not quite supported by our calculations. This appears to imply that in the semidilute region there are sufficiently large regions within a correlation length where the polymer "feels" its architecture. The higher density in the interior of star molecules is in accord with this observation.

Table I also includes estimates of μ and the prefactor from the data of Noda et al.[8] for various good solvent solutions of linear polymers. Their data are compared with the predicted curves of eq 26 and 30 for $f = 1$ in Figure 2 where the full line represents the experimental fit to the data and the dashed and dot–dashed lines represent, respectively, eq 26 and 30. The latter are not significantly different from one another and both are seen to be in very good agreement with the experimental data. The Ohta–Oono approximation for the function $g(y^2)$ for the linear polymer is clearly a very useful one for a wide range of experimentally accessible concentrations.

Since Noda et al.[8] use the reduced concentration $c/c^* = 4c\pi R_G{}^3/3$ in plotting their data, comparisons with data based on $\bar{c} = c\langle A_2\rangle_w M_n$ require introducing the penetration function Ψ to convert between the two scaling variables. Figure 2 presents this comparison for the value $\Psi = 0.26$. Estimates[31] of Ψ range from 0.22 to 0.30. However, $\Psi = 0.25$–0.26 seems a widely accepted figure. The use of Ψ to determine A_2 may lead to a different averaged A_2 than

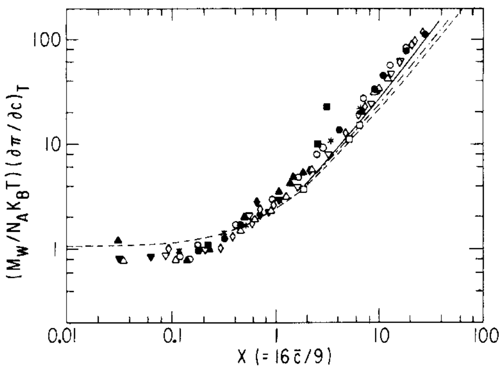

Figure 3. Comparison of the data of Wiltzius et al.[7] for the osmotic compressibility of linear polymers in semidilute marginal to good solvent solutions with the osmotic compressibility curve constructed from eq 30 using both corrected (—) and uncorrected (-·-) exponents μ. The dashed line represents the curve derived from the work of Ohta and Oono.[16]

the polydispersity-averaged $\langle A_2\rangle_w$ of this work and thereby introduce errors into the comparisons. In particular, the prefactor calculated from the experimental data varies over the range 1.30–1.02 as Ψ is taken to range from 0.21 to 0.26. This emphasizes the importance of choosing the appropriate reduced concentration variable with which to plot data. The quantity c/c^*, expressed in terms of a suitably averaged second virial coefficient, is the most natural choice for comparison with theory, a feature that is not brought out by scaling analyses.

From the arguments presented in section III the exponent $\mu = 1 + \epsilon/4$ may be replaced by $1 + (2 - d\nu)/(d\nu - 1)$. With ν given by 0.588 in three dimensions this yields the improved estimate $\mu = 1.31$. When eq 30 is replotted with this value of μ, the experimental and calculated fits to the data of Figure 2 become essentially coincident.

Figure 3 compares the data of Wiltzius et al.[7] for the osmotic compressibility of semidilute solutions of various linear polymers in marginal to good solvents with the predictions evaluated numerically from eq 30 for linear chains (dot–dashed line) and with the original predictions of Ohta and Oono[16] (dashed line). We use the correspondence $\bar{c} = 9X/16$ between the reduced concentration of the present calculation and the variable X of Ohta and Oono, which is used by Wiltzius et al. Figure 3 also shows eq 30 replotted according to the scaling argument in (21) using $\nu = 0.588$ (full line). The fit to the experimental data with $\mu = 1.31$ is seen to be improved.

The recent data of Hager et al.[9] (not reproduced here) on the osmotic compressibility of semidilute good solvent solutions of various linear polymers, when compared with the predictions of eq 30 with and without the higher order corrections, show qualitatively the same features as the comparison with the data of Wiltzius et al.[7]

The numerically calculated $\mathcal{O}(\epsilon)$ value of 1.25 for the exponent μ for rings and stars of up to six branches agrees with other theoretical predictions[10–12] and also with what is predicted from an asymptotic analysis of eq 18 and 30 in the limit $\bar{c} \gg 1$ (as shown in Appendices A and B).

Of some interest is the question of when the power law behavior of the osmotic pressure sets in for solutions of poorer quality. We have addressed this question by constructing osmotic pressure curves for various values of $\bar{z}$ using eq 30 with the factor $\epsilon/16\bar{c}^2$ replaced by $(\epsilon/16\bar{c}^2)\cdot(32\bar{z}/3)(1 + 32\bar{z}/3)^{-1}$. The concentrations at which there occurs a transition to semidilute scaling behavior characterized by an $\mathcal{O}(\epsilon)$ exponent $\mu = 1.25$ for $\bar{z}$ in the range 0.01–5.0 are shown in Figure 4 for the linear polymer. As is evident, the poorer the quality of the solvent, the higher must be the concentration to reach the scaling regime. At the same time even moderately good solvents ($\bar{z} \sim 2$) show scaling behavior at relatively low concentrations ($\bar{c} \sim 10$). From the difficulty of ascertaining the exact concentration at which scaling behavior begins, it must be noted that the concentrations indicated in Figure 4 are probably smaller than is actually the case, especially at the lower values $\bar{z}$. For solutions of stars and rings, the solvent dependence of the osmotic pressure is qualitatively the same, with the difference that the greater the degree of branching, the sooner the onset of scaling behavior, although again the precise values of these differences are difficult to estimate.

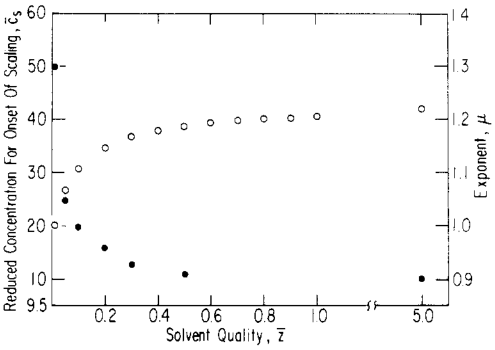

Figure 4. Plot of the reduced concentration for onset of scaling $\bar{c}_s$ as a function of solvent quality $\bar{z}$ (●) and plot of the exponent μ as a function $\bar{z}$ (○). Both curves are for the linear polymers and are constructed from eq 30 with $\epsilon/16\bar{c}^2$ replaced by $(\epsilon/16\bar{c}^2)(32\bar{z}/3(1 + 32\bar{z}/3)$.

Figure 4 also shows the variation of the exponent μ with $\bar{z}$ for the linear polymer. The asymptotic limit $\mu \rightarrow 1.25$ is reached at relatively low $\bar{z}$. Much the same behavior is observed for the variation of the prefactor with $\bar{z}$, and this is true of the exponents and prefactors of the other geometries as well.

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Appendix A. Behavior of $\hat{\Pi}$ in the Asymptotic Limit of $\bar{c} \rightarrow \infty$ for Stars

Before considering the general structure of the integral in (18) as $\bar{c} \rightarrow \infty$, we first introduce the change of variables $y^2 = z$ to rewrite the equation in the slightly simpler form

$$\hat{\Pi} = 1 + \bar{c}\left[1 - \frac{\epsilon}{32\bar{c}^2}I\right] + \mathcal{O}(\epsilon^2) \qquad \text{(A.1)}$$

with I given by

$$I = \int_0^\infty \mathrm{d}z\, z\left\{\ln\,[1 + 4\bar{c}g^s(z)] - \frac{4\bar{c}g^s(z)}{1 + 4\bar{c}g^s(z)} - 8\bar{c}^2[g^s(z)]^2\right\} \qquad \text{(A.2)}$$

The behavior of I in the asymptotic limit is more conveniently pursued by taking the derivative of (A.2) with respect to $\bar{c}$ to produce

$$\frac{\mathrm{d}I}{\mathrm{d}\bar{c}} = \int_0^\infty \mathrm{d}z\, z\left\{\frac{16\bar{c}[g^s(z)]^2}{[1 + 4\bar{c}g^s(z)]^2} - 16\bar{c}[g^s(z)]^2\right\} \qquad \text{(A.3)}$$

The quantity $g^s(z)$ is a monotonic decreasing function of

z, as may be readily verified, and it is bounded above and below as

$$0 < g^{s}(z) \le 0.5, \qquad \forall z > 0 \tag{A.4}$$

It therefore follows that there exists an $\alpha = \alpha(\bar{c})$ such that for $z < \alpha$, $4\bar{c}g^{s}(z) > 1$, while for $z > \alpha$, $4\bar{c}g^{s}(z) < 1$. Equation A.3 may consequently be rewritten as

$$\frac{\mathrm{d}I}{\mathrm{d}\bar{c}} = \int_0^{\alpha(\bar{c})} \mathrm{d}z\ z\left\{\frac{1}{\bar{c}}\left[1 - \frac{1}{2\bar{c}g^{s}(z)} + \frac{3}{16\bar{c}^2[g^{s}(z)]^2} + \mathcal{O}\left(\frac{1}{\bar{c}g^{s}(z)}\right)^3\right] - 16\bar{c}[g^{s}(z)]^2\right\} + \int_{\alpha(\bar{c})}^{\infty} \mathrm{d}z\ z\{16\bar{c}[g^{s}(z)]^2[1 - 8\bar{c}g^{s}(z)] + 48\bar{c}^2[g^{s}(z)]^2 + \mathcal{O}[(\bar{c}g^{s}(z))^3] - 16\bar{c}[g^{s}(z)]^2\} \tag{A.5}$$

The condition that there exists the desired α is expressed as

$$4\bar{c}g^{s}(\alpha) = 1 \tag{A.6}$$

which, using the expression for g^{s} given in (19), becomes

$$4\bar{c}\left[\frac{1}{\alpha} + \frac{1}{\alpha^2}f[\exp(-\alpha/f) - 1]\{1 - \tfrac{1}{2}(1 - f) \times [\exp(-\alpha/f) - 1]\}\right] = 1 \tag{A.7}$$

As $\bar{c} \to \infty$, eq A.7 is satisfied by $\alpha = 4\bar{c}$. Applying this limit to (A.5), we obtain

$$\frac{\mathrm{d}I}{\mathrm{d}\bar{c}} = \int^{4\bar{c}} \mathrm{d}z\ z\{-16\bar{c}[g^{s}(z)]^2\}[1 + \mathcal{O}(\bar{c}^{-1})] \tag{A.8}$$

where we have omitted the lower limit on the z integral since the integrand is known to be finite there as $\bar{c} \to \infty$. The correction terms in (A.8) are found to be asymptotically small. Substituting the expression for $g^{s}(z)$ into (A.8), we obtain

$$\frac{\mathrm{d}I}{\mathrm{d}\bar{c}} = -16\bar{c}\int^{4\bar{c}} \mathrm{d}z\ z\left[\frac{1}{z^2} + \mathcal{O}\left(\frac{1}{z^3}\right)\right] \tag{A.9}$$

$$= -16\bar{c}\left[\ln(4\bar{c}) + \mathcal{O}\left(\frac{1}{\bar{c}}\right)\right] \tag{A.10}$$

I may now be evaluated as

$$I = -8\bar{c}^2 \ln \bar{c} + \mathcal{O}(\bar{c}^2, \bar{c}, \bar{c}^0) \tag{A.11}$$

and (A.1) becomes

$$\hat{\Pi}(\bar{c}\to\infty) = 1 + \bar{c}\left\{1 - \frac{\epsilon}{32\bar{c}^2}[-8\bar{c}^2 \ln \bar{c} + \mathcal{O}(\bar{c}^2, \bar{c}, \bar{c}^0)]\right\} \tag{A.12}$$

which after reexponentiation yields

$$\hat{\Pi}(\bar{c}\to\infty) \propto \bar{c}^{1+\epsilon/4} \tag{A.13}$$

Appendix B. Rings

The asymptotic behavior of rings can be developed in the same way beginning with a preliminary simplification of the expression for the osmotic pressure through the change of variables $y = z^2$ and following steps (A.2) through (A.5) to obtain the analogue of (A.5) for rings, with g^{s} now replaced by g^{r}. To proceed further, we recognize that[33]

$$\int_0^x \mathrm{d}t\ \exp(t^2) \equiv \frac{1}{2x}\left\{\exp(x^2) - M\left(-\frac{1}{2},\frac{1}{2},x^2\right)\right\} \tag{B.1}$$

with M a confluent hypergeometric function. For positive values of its third argument, M can, in general, be written as[34]

$$M(a,b,\xi) = \frac{\Gamma(b)}{\Gamma(a)}e^{\xi}\,\xi^{a-b}[1 + \mathcal{O}(|\xi|^{-1})], \qquad \mathrm{Re}\ \xi > 0 \tag{B.2}$$

where Γ is the gamma function. Equations B.1 and B.2 can be used to approximate g^{r} as

$$g^{r}(y) = \frac{1}{y}\left[1 + \frac{2}{y} + \mathcal{O}\left(\frac{1}{y^2}\right)\right] \tag{B.3}$$

The condition that there exist an $\alpha(\bar{c})$ around which expansions in large and small values of $4\bar{c}g^{r}(y)$ are possible is again satisfied by $\alpha = 4\bar{c}$ in the limit of $\bar{c} \to \infty$. Equation A.13 then follows also for rings. The asymptotic behavior of the osmotic compressibility can be analyzed similarly.

Appendix C. Regularization of the Osmotic Pressure

This appendix introduces a slightly modified regularization in order to make all parameters appearing in the computed osmotic pressure correspond to direct measurables. As discussed in ref 10, 16, and 17, the bare osmotic pressure can be shown to be given by

$$\frac{\Pi_{\mathrm{B}}}{c_{\mathrm{p}}k_{\mathrm{B}}T} = 1 + \frac{1}{2}c_{\mathrm{p}}v_0\langle N_0\rangle_{\mathrm{n}}^2 - (2c_{\mathrm{p}})^{-1}\int \frac{\mathrm{d}^d q}{(2\pi)^d}\{\ln[1 + 2c_{\mathrm{p}}v_0\langle S(\mathbf{q},N_0)\rangle_{\mathrm{n}}] - 2c_{\mathrm{p}}v_0\langle S(\mathbf{q},N_0)\rangle_{\mathrm{n}}[1 + 2c_{\mathrm{p}}v_0\langle S(\mathbf{q},N_0)\rangle]^{-1} + \mathcal{O}(v_0^2)\} \tag{C.1}$$

where c_{p} is the number density and $S(\mathbf{q},N_0)$ the Debye scattering function

$$S(\mathbf{q},N_0) = 2N_0q^{-2} + 4q^{-4}[\exp(-q^2N_0/2) - 1] \tag{C.2}$$

In the limit $q \to \infty$ the integrand in (C.1) behaves as

$$q^{d-1}(\tfrac{1}{2}[2v_0c_{\mathrm{p}}\langle S(\mathbf{q},N_0)\rangle_{\mathrm{n}}]^2) + \mathcal{O}(\langle S\rangle_{\mathrm{n}}^3) \tag{C.3}$$

that is, as

$$q^{d-1}[8(c_{\mathrm{p}}v_0)^2\langle N_0\rangle^2q^{-4}] \tag{C.4}$$

which provides a regular integral only for $d < 4$.

The regularization of (C.1) follows the method of Gel'fand and Shilov[35] and proceeds by adding and subtracting the first term in (C.3) from the integrand of (C.1).[10] This produces a contribution to the osmotic pressure that converges in $d = 4$

$$I(4) = \int_0^{\infty} \mathrm{d}q\ q^3\{\ln[1 + 2c_{\mathrm{p}}v_0\langle S(\mathbf{q},N)\rangle_{\mathrm{n}}] - 2c_{\mathrm{p}}v_0\langle S(\mathbf{q},N_0)\rangle_{\mathrm{n}}[1 + 2c_{\mathrm{p}}v_0\langle S(\mathbf{q},N_0)\rangle_{\mathrm{n}}]^{-1} - \tfrac{1}{2}[2v_0c_{\mathrm{p}}\langle S(\mathbf{q},N_0)\rangle_{\mathrm{n}}]^2\} \tag{C.5}$$

together with the contribution

$$\delta I(d) = 2v_0^2c_{\mathrm{p}}^2\int_0^{\infty} \mathrm{d}q\ q^{d-1}\ \langle S(\mathbf{q},N_0)\rangle_{\mathrm{n}}^2 \tag{C.6}$$

that leads to logarithmic divergences at this dimension. Equation C.6 is readily shown[10] to be proportional to c_{p}^2 times the bare second virial coefficient by using the definition

$$S(\mathbf{r}-\mathbf{r}',N_0) = \int_0^{N_0}\mathrm{d}\tau\int_0^{\tau}\mathrm{d}\tau'\ G_0(\mathbf{r}-\mathbf{r}',\tau-\tau') \tag{C.7}$$

in (C.6) and inverse Fourier transforming to $\mathbf{r}$ space. The quantity G_0 in (C.7) is the Gaussian propagator between the points $(\mathbf{r},\tau)$ and $(\mathbf{r}',\tau')$ and is given by

$$G_0(\mathbf{r}-\mathbf{r}',\tau-\tau') = [2\pi(\tau-\tau')]^{-d/2} \exp[-(\mathbf{r}-\mathbf{r}')^2/2(\tau-\tau')] \tag{C.8}$$

Hence, (C.6) then becomes

$$\delta I(d) = 2v_0^2 c_p^2 \int \mathrm{d}^d r \int \mathrm{d}^d r' \, \langle S(\mathbf{r}-\mathbf{r}',N_0)\rangle_n^2 \tag{C.9}$$

which is the second-order contribution to the bare second virial coefficient A_{2B}. Thus, the contribution (C.9) may be combined with the term $^1/_2 c_p v_0 \langle N_0\rangle_n^2$ in (C.1), which is just $^1/_2 c_p$ times the first-order contribution to A_{2B}. Equation C.9 is then written in terms of the second-order second virial coefficient as

$$\delta I = c_p^2 \left\langle \frac{M_N M_{N'}}{N_A} A_{2B}(N_0,N_0') \right\rangle_n - c_p^2 v_0 \langle N_0\rangle_n^2 \tag{C.10}$$

Equivalently the definitions (13)–(16) enable (C.10) to be expressed as

$$\delta I = N_A c^2 \langle A_{2B}^{(2)}(N_0,N_0')\rangle_w \tag{C.11}$$

where the superscript denotes the second order in ϵ contributions.

Polydispersity averaging implies that the measured virial coefficient A_2 is given by

$$A_2 = {}^1\!/_2 \langle A_2(N,N')\rangle_w \tag{C.12}$$

By introducing the change of variables $y^2 = q^2\langle N_0\rangle/2$ in (C.1), defining the dimensionless function $g(y^2) = y^{-2} + y^{-4}\langle \exp[-y^2 N/\langle N_0\rangle_n] - 1\rangle_n$, and expressing the renormalized counterpart of the quantity $c_p v_0 \langle S(\mathbf{q},N_0)\rangle_n$ to lowest order in ϵ as $4cM_nA_2 g(y^2) + \mathcal{O}(\epsilon^2)$, eq C.1 finally becomes

$$\frac{\Pi M_n}{cRT} = 1 + cA_2M_n - \frac{u}{cA_2M_n} \int \frac{\mathrm{d}^4 y}{(2\pi)^2} \left\{ \ln[1 + 4cA_2M_n g(y^2)] - \frac{4cA_2M_n g(y^2)}{1 + 4cA_2M_n g(y^2)} - 8c^2A_2^2M_n^2[g(y^2)]^2 \right\} \tag{C.13}$$

with u the dimensionless excluded volume parameter ($u \rightarrow u^* = \epsilon/8 + \mathcal{O}(\epsilon^2)$ in the scaling limit of fully developed excluded volume).

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