Universal Ratios of Characteristic Lengths in Semidilute Polymer Solutions

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Abstract

We use experimental and simulation data from the literature to infer five characteristic lengths, denoted $\xi_s$, $\xi_f$, $\xi_\Pi$, $\xi_\phi$, and $\xi_D$ of a semidilute polymer solution. The first two of these are defined in terms of scattering from the solution, the third is defined in terms of osmotic pressure, the fourth by the spatial monomer concentration profile, and the last by co-operative diffusion. In a given solution the ratios of any of these five lengths are expected to be universal constants. Knowing these constants thus allows one to use one measured property of a solution as a means of inferring others. We calculate these ratios and estimate their uncertainties for solutions in theta as well as good-solvent conditions. The analysis is strengthened by use of scattering properties of isolated polymers inferred from computer simulations.

1 Introduction

In the 1970’s, it was recognized that polymer solutions are a form of critical phenomenon[1]. In the intervening years, a network of powerful consequences of this recognition have been verified. Many measured properties vary with concentration and with molecular weight according to power laws whose exponents are known only approximately, but which are shown to be universal—i.e. unchanged under continuous changes in the system properties. Moreover, the coefficients in these power laws are shown to be inter-related by universal ratios. Some of these ratios predict universal properties of dilute solutions. In 1987 Davidson et al expressed some of this universality in an elegant way by determining characteristic lengths[2]. Several experimental measurements were made on a number of solutions, and each was reduced to a length. Thus, eg. light scattering measurements were used to determine the radius of gyration. Several different lengths were inferred from different measurements on a given solution. When these lengths were compared, their ratios were found to be independent of the solution studied, thus confirming the anticipated universality. In the process the experiments obtained well-determined values for the universal ratios that remain as an important part of our knowledge of polymers.

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Our aim in this paper is to obtain analogous information for the semidilute regime. Semidilute solutions are commonly characterized by a length derived from small-angle scattering called the correlation length $\xi_s[3]$. Other common characteristics of these solutions can also be reduced to a length. For instance, the osmotic pressure $\Pi$ may be expressed in terms of a length $\xi_{\Pi}$ defined by $\Pi \equiv k_B T/\xi_{\Pi}^3$, where $k_B$ is Boltzmann’s constant and $T$ the absolute temperature. Likewise, the co-operative diffusion coefficient $D_c$ can be used to define a hydrodynamic length $\xi_D$ analogous to Stokes’ Law: $D_c \equiv k_B T/(6\pi \eta_s \xi_D)$, where $\eta_s$ is the solvent viscosity. Like Davidson’s dilute lengths[2], the ratios of these $\xi$’s are expected to be universal in the semidilute limit. The semidilute limit means the limit in which the volume fraction of polymer is at once much larger than the overlap volume fraction, and much smaller than unity. Naturally this limit requires polymers of sufficiently high molecular weight.

In this paper we determine these semidilute length ratios and several others using data from the experimental literature. We expect that knowledge of these ratios should be useful for those who study these solutions. Experimentally, one may use the ratios to predict one experimental quantity such as the co-operative diffusivity from another, such as the scattering correlation length. Conceptually, these ratios give one a clearer picture of the interior structure of the solution. We emphasize that these predictions are not scaling relations with undetermined numerical prefactors. They are quantitative predictions with stringent uncertainty limits.

The universal properties of semidilute solutions have been much explored and tested over the past two decades. The purpose of our work is not to extend the scope of these tests. Instead, we aim to distill known semidilute results into a form that is as useful and simple as possible for one studying a particular semidilute solution. Thus we define our lengths in a way that does not require a knowledge of the dilute properties of the polymer and solvent in question. Another virtue of our approach is accuracy. Most universal ratios for semidilute quantities reported in the literature require knowledge of dilute quantities with the same polymer and solvent, such as the radius of gyration. These dilute quantities are often sensitive to polydispersity, while the semidilute quantities of interest are not. Thus, recasting the universal information without reference to dilute quantities removes an important source of uncertainty.

Before proceeding, we define explicitly the lengths we will discuss. As noted above, the osmotic length $\xi_{\Pi}$ is related to the osmotic pressure $\Pi$ of the polymer solution by

$$\Pi = k_B T/\xi_{\Pi}^3,$$

where $k_B$ is the Boltzmann constant and $T$ the temperature. We also define a diffusive length $\xi_D$ from the co-operative diffusion coefficient $D_c$[3, 4]:

$$D_c \equiv k_B T/(6\pi \eta_s \xi_D),$$

where $\eta_s$ is the viscosity of the solvent. The scattering correlation length $\xi_s$ is inferred from the static structure factor $S(q)$ at wavevector $q$[4]:

$$S(q) = S_0(1 - \xi_s^2 q^2 + \mathcal{O}(q^4)),$$

where $S_0$ is the extrapolation of $S(q)$ at $q = 0$. We note that $\xi_s^2 = \frac{1}{3} R_G^2$ in the dilute limit, where $R_G$ is the radius of gyration of the polymer. A related length $\xi_f$ may be inferred
from the scattering in the so-called fractal wavevector regime where $1/q$ is much smaller than $\xi_s$ but much larger than a monomer. In this regime $S(q) \sim q^{-1/\nu}$, where the Flory swelling exponent $\nu \simeq 0.588$ for good-solvent cases. From this fractal law, we may define the length $\xi_f$ by

$$S(q) \rightarrow S_0(q\xi_f)^{-1/\nu}$$

where $q$ is in the fractal regime. Here $a \rightarrow b$ means that $a$ approaches $b$ in the asymptotic limit under discussion.

Closely related to $\xi_f$ is a length characterizing the local monomer concentration profile. We define $C$ to be the monomer concentration and $\langle C(r)\rangle_0$ as the ensemble average of the local concentration at distance $r$ from an arbitrary monomer. If this $r$ is much larger than the monomer size $\{a\}$ and much smaller than $\xi_s$, then $\langle C(r)\rangle_0 \sim r^{1/\nu - 3}$. This behavior gives rise to the fractal scattering of Eqn 4, as discussed below. We define the concentration length $\xi_\phi$ by

$$\langle C(r)\rangle_0 \rightarrow C(r/\xi_\phi)^{1/\nu - 3}$$

where $r$ is in the fractal regime defined above. That is, $\xi_\phi$ is the distance at which the extrapolated fractal concentration profile meets the solution concentration $C$, as shown in Figure 1.

We note here that another dynamic length $\xi_p$ can be defined as the radius of a circular pipe with the same solvent permeability as the polymer solution of interest. The solvent permeability $P$ is usually measured with sedimentation experiments. The sedimentation coefficient, however, is rigorously related to the co-operative diffusion coefficient $D_c$ and the osmotic pressure $\Pi$. Hence, $\xi_p$ can be expressed in terms of $\xi_D$ and $\xi_\Pi$:

$$P \equiv \frac{\xi_p^2}{8} = \frac{3 - 1/\nu}{18\pi \xi_D^3} \xi_\Pi.$$

Figure 1: Schematic Diagram of $\langle C(r)\rangle_0$ (solid line) and $\{C_{max}A^{3-1/\nu}\}/r^{3-1/\nu}$ (dotted line).
This paper is organized as follows: In Section 2 we express the static lengths, $\xi_s$, $\xi_\Pi$, $\xi_f$ and $\xi_\phi$, in terms of the basic quantities $\beta_2$, $\beta_4$, $\{A\}$ and $P_\infty$. In Section 3 we describe the experiments and simulations on which our results are based. In Section 4 we report our values of the $\xi$ ratios for both good and theta solvents. In Section 5 we comment on the limitations and implications of these ratios. To improve the readability of the paper, we indicate quantities that depend only on polymer and solvent species but not on concentration or molecular weight by curly-bracketed symbols, such as $\{A\}$, and quantities that are universal by underlined symbols, such as $P_\infty$. We treat as universal any ratio of two quantities a) that individually diverge in the semidilute limit defined above, and b) that have the same predicted scaling dependence on a parameter such as concentration, so that their ratio is predicted to be independent of the parameter.

2 Relations to Structural Coefficients

In this section we define a set of structural coefficients that characterize the concentration profile in a semidilute solution. We found it convenient to relate the static lengths, $\xi_s$, $\xi_\phi$, $\xi_f$ and $\xi_\Pi$ to these coefficients.

2.1 Local Concentration

Above we defined the length $\xi_\phi$ from the local concentration $\langle C(r) \rangle_0$. We may express this $\langle C(r) \rangle_0$ in terms of the bulk concentration $\{C_{\text{max}}\}$ for the polymer in question. Here we exploit the fact that $\langle C(r) \rangle_0$ is unaffected by the surrounding solution when $r$ is small. Thus in the fractal $r$ regime, we may use Eqn 5 and define the fractal length $\{A\}$:

$$\frac{\langle C(r) \rangle_0}{\{C_{\text{max}}\}} \rightarrow \left(\frac{\{A\}}{r}\right)^{3-1/\nu}, \text{ for } \{a\} \ll r \ll \xi_\phi, \quad (7)$$

where $\{a\}$ is the monomer size. This $\{A\}$ is useful because it is independent of concentration. Evidently,

$$\xi_\phi = \left(\frac{\{C_{\text{max}}A^{3-1/\nu}\}}{C}\right)^{\nu/(3\nu-1)}. \quad (8)$$

The coefficient $\{C_{\text{max}}A^{3-1/\nu}\}$ depends only on the polymer and solvent species and is independent of concentration; The scattering structure function $S(q)$ in the fractal $q$ regime can also be expressed in terms of the fractal length $\{A\}$. Here we take the monomer as our elementary scatterer. For a scattering volume $V$, $S(q)$ may be written as

$$S(q) = \frac{1}{VC} \sum_{j,k=1}^{VC} \langle \exp [i\vec{q} \cdot (\vec{r}_j - \vec{r}_k)] \rangle$$

where $\vec{r}_j$ is the position vector of the $j$th monomer and $\vec{q}$ the wave vector transfer. In our notation, this reduces to

$$S(q) = \int_V d^3r \langle C(r) \rangle_0 \exp(i\vec{q} \cdot \vec{r}), \quad (9)$$
The fractal regime of \( \langle C(r) \rangle_0 \) gives rise to a complementary behavior in the fractal \( q \) regime:\[6\]: The power law regime of Eqn \[7\] produces the scattering at fractal wavevector mentioned in Eqn. \[4\]. By combining Eqn 7 and 9, one finds
\[
S(q) \rightarrow c_o \left\{ \frac{C_{\text{max}} A^{3-1/\nu}}{q^{1/\nu}} \right\} \quad \text{for } 1/\xi_\phi \ll q \ll 1/\{a\},
\]
where \( c_o = 4\pi \sin \left( \frac{\pi}{2} \left( \frac{1}{\nu} - 1 \right) \right) \Gamma (1/\nu - 1) \). We note that Eqn 10 still holds in the dilute limit, where \( \xi_s \simeq R_G \), so the fractal \( q \) regime means \( 1/R_G \ll q \ll 1/\{a\} \).

For a given polymer and solvent, the coefficient \( \{C_{\text{max}} A^{3-1/\nu}\} \) can also be related to the dilute property of that polymer solution. The chainlength \( N \) of an isolated polymer is related to the radius of gyration \( R_G \) by
\[
N \rightarrow \left( \frac{R_G}{\{\Omega\}} \right)^{1/\nu}.
\]
We follow the work of Rawiso et al and define a universal constant \( P_\infty \) for a dilute polymer solution:\[12\]:
\[
P_\infty \rightarrow \frac{S(q)}{N \cdot (q R_G)^{1/\nu}} \quad \text{for } 1/R_G \ll q \ll 1/\{a\}.
\]
\( \{\Omega\} \) can then be written as
\[
\{\Omega\} = \left( \frac{P_\infty}{c_0} \right)^\nu \left( \frac{C_{\text{max}} A^{3-1/\nu}}{q^{1/\nu}} \right)^{-\nu}.
\]
We note that \( P_\infty \) is just \( \bar{P}_\infty \) defined in the paper of Rawiso et al\[12\]. Since \( \{\Omega\} \) and \( \{C_{\text{max}} A^{3-1/\nu}\} \) are both properties of a single chain, we can determine \( P_\infty \) using single-chain experiments or simulations.

### 2.2 Moments of Local Concentration

Beyond the fractal regime governed by the coefficient \( \{A\} \) discussed above, the local concentration \( \langle C(r) \rangle_0 \) departs from the power-law form and becomes constant(Figure 1). It is convenient to define the reduced moments \( \beta_n \) to characterize this part of the concentration profile:
\[
\beta_n \equiv \int_{C_A > C}^{\infty} dr r^n ((\langle C(r) \rangle_0 - C) - C_A(r) - C),
\]
where \( C_A(r) \equiv \{C_{\text{max}}\} \{A\} / r^{3-1/\nu} \), and we use the behavior in the fractal regime to normalize these moments. Several of the \( \xi \) ratios can be expressed completely in terms of these reduced moments. By Taylor-expanding Eqn 7 with respect to \( q \), we show in the appendix that for semidilute polymer solutions(Eqn 38),
\[
\frac{\xi_s}{\xi_\phi} \rightarrow \left[ \frac{\beta_4}{10(1 + 2\nu)\beta_2} \right]^{1/2}.
\]
The moment \( \beta_2 \) may be related to \( \xi_\Pi \) by using the compressibility sum rule:\[3\]:
\[
S_0 = k_B T \frac{\partial C}{\partial \Pi},
\]
where \( S_0 \) is defined in Eqn 3. This \( S_0 \) can then be expressed in terms of \( \beta_2 \), thus yielding a relation between \( \xi_\Pi/\xi_\phi \) and \( \beta_2 \)(Eqn 37):
\[
\frac{\xi_\Pi}{\xi_\phi} \rightarrow \left( 4\pi \nu \beta_2 \right)^{1/3}.
\]
Table 1: Sources of experimental and simulation data used in this work.

| Source | Probe** | $M_w \times 10^{-6}$ | $P_{\infty}$ | $\{\Omega\}$ | $\xi_\phi$ | $\xi_s$ | $\xi_\Pi$ | $\xi_D$ | $\xi_f$ |
|--------|---------|----------------------|-------------|---------------|------------|-------|-------|-------|-------|
| dm1[13] | MC      | $N \leq 4096$       | $\checkmark$ | $\checkmark$ | -          | -     | -     | -     | -     |
| dm2[17] | MC      | $N \leq 2048$       | $\checkmark$ | $\checkmark$ | -          | -     | -     | -     | -     |
| da[19]  | LS      | 8-60                | $\checkmark$ | $\checkmark$ | $\checkmark$ | -     | -     | -     | -     |
| sa[11, 20, 21] | LS    | 0.4-21              | $\checkmark$ | $\checkmark$ | -          | -     | -     | -     | -     |
| sa[20]  | LS      | 1-21                | $\checkmark$ | $\checkmark$ | -          | -     | -     | -     | -     |
| sa[11, 22] | DLS, CGD | 0.4-21            | $\checkmark$ | $\checkmark$ | $\checkmark$ | -     | -     | -     | -     |
| db[12]  | NS      | 0.05 – 1.3          | $\checkmark$ | $\checkmark$ | $\checkmark$ | -     | -     | -     | -     |
| sb[19, 23] | NS    | 0.5-1               | $\checkmark$ | $\checkmark$ | $\checkmark$ | -     | -     | -     | -     |
| dc[24]  | LS      | 0.2-2               | $\checkmark$ | $\checkmark$ | $\checkmark$ | -     | -     | -     | -     |
| sc[25]  | XS      | 0.1-2               | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ | -     | -     | -     |
| sc[27]  | CGD     | 0.2-3               | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ | $\checkmark$ | -     | -     |

*: “d” and “s” stand for “dilute” and “semidilute”, respectively. m1: a polyethylene chain model of $N$ C-C bonds. m2: the bond-fluctuation lattice model for a polymer of chainlength $N$. a: PS+Cyclohexane at 35°C. b: PS+CS$_2$ at 20°C. c: PS+Toluene at 25°C.

**: MC: Monte Carlo Simulation. LS: Light Scattering. NS: Neutron Scattering. XS: X-ray Scattering. DLS: Dynamic LS. CGD: Classical Gradient Diffusion.

Finally, by virtue of Eqn 10 and 31, we obtain

$$\frac{\xi_f}{\xi_\phi} \rightarrow \left[ \frac{4\pi}{3c_0}(3\nu - 1)\beta_2 \right]^{\nu},$$

(17)

where the numerical coefficient $c_0$ is defined below Eqn 10. We hence conclude that $\xi_f$ gives no additional information if $\xi_\phi$ and $\xi_\Pi$ are known.

3 Sources of Data

Our results are based on the experimental data of solutions of polystyrene (PS) in the good solvents, toluene and carbon disulfide (CS$_2$), and the solvent cyclohexane at its theta temperature. For non-deuterated PS, the molecular weight $\{m_s\}$ of the monomer (CH$_2$CHC$_6$H$_5$) is 104 and the bulk density $\{\rho_{\text{max}}\}$ is 1.05g/cm$^3$[13], so that $\{C_{\text{max}}\} = 6.08 \times 10^{-3}$ Å$^{-3}$. In this paper, we assume the value of $\{C_{\text{max}}\}$ is invariant, regardless of whether the polymers are deuterated or not. Thus, we have ignored possible effects of tacticity of the molecules or of processing to obtain the neat (glassy) state of the polymer. Such effects introduce insignificant uncertainties compared to other uncertainties. Table 1 summarizes the sources of data and the quantities we derive from the associated sources.
3.1 The Values of $P_\infty$

The determination of $\xi_{\phi}$ requires the knowledge of $\{C_{\text{max}} A^{3-1/\nu}\}$, which can be obtained from the scattering data in the fractal $q$ regime (Eqn 10). However, data of this sort are rare. Measurements of $\{\Omega\}$ (Eqn 12) are much more accessible and provide the same information if the universal coefficient $P_\infty$ is known. We may determine $P_\infty$ using polymer simulations or theory. In theta conditions $P_\infty$ may be determined analytically by treating the polymers as ideal random walks [15]. It is straightforward to show that $P_\infty = 2$ for theta cases [12]. Destée et al obtained $S(q)$ for a single polyethylene in theta and good-solvent conditions using Monte Carlo techniques [16]. From their results, we determine $P_\infty = 2(\pm 4\%)$ for the theta cases where the number of C-C bonds $N \leq 4096$, and $P_\infty = 1.26(\pm 22\%)$ for the good-solvent cases where $N \leq 1024$. Müller et al reported $S(q)$ in their Monte Carlo simulation of a single chain [17], which yields $P_\infty = 1.20(\pm 14\%)$ was also obtained using the scattering data for dilute PS in the good solvent CS$_2$ [12]. These values are consistent with the renormalization group estimate of $P_\infty = 1.29$ to first order in $\epsilon \equiv (4$ minus the dimension of space) [3, 5, 18]. In the following sections, $P_\infty = 2$ and $1.23(\pm 4\%)$ are adopted to calculate $\xi_{\phi}$ for theta and good-solvent cases, respectively.

3.2 PS+Cyclohexane at 35°C

Although for many purposes, polymers in theta solvents may be considered as ideal random walks, theta polymers interact, and their semidilute solutions differ from a solution of noninteracting polymers. Thus not all of the universal ratios we seek for theta solutions can be found analytically. Here we make use of several studies of PS in cyclohexane at 34.5°C (or 35°C), a well-known theta solvent. Hayward and Graessley reported $R_G \rightarrow 0.28(\pm 4\%) \text{Å}$ [19], which implies

$$\{\Omega\} = 2.86(\pm 4\%) \ \text{Å}. \quad (18)$$

The behavior of $\xi_s$ is given in Adam and Delsanti’s paper [11], where they summarized the results of neutron and light scattering experiments [20, 21]:

$$\xi_s = \frac{5.5}{\rho} \ (\pm 5\%) \ \text{Å}, \quad (19)$$

where $\rho$ is measured in g/cm$^3$. They also reported

$$D_c = 1.25(\pm 8\%) \times 10^{-6} \ \text{ρ cm}^2/\text{s}, \text{ for } \rho \leq 0.08 \ \text{g/cm}^3. \quad (20)$$

We note that the viscosity $\eta_s$ of cyclohexane at 35°C is $0.762 \times 10^{-2}$ poise [27]. Their result is consistent with the classical gradient diffusion measurement done by Roots and Nyström [22]. Stepanek et al measured the osmotic compressibility using light scattering technique [20]. They obtained

$$\frac{1}{\rho} \frac{\partial \Pi}{\partial \rho} = 2.93 \times 10^7 \rho \ \text{for } 3 < \rho/\rho^* < 11, \quad (21)$$

where $\partial \Pi/\partial \rho$ is expressed in dyn-cm/g and $\rho$ is in g/cm$^3$.
3.3 Perdeuterated PS+CS$_2$ at 20$^\circ$C

CS$_2$ is known to be a good solvent for PS at 20$^\circ$C. Rawiso et al measured the radius for dilute perdeuterated PS in CS$_2$ and reported $R_G \to 0.133(\pm4\%) M_w^{0.588}$ (above Eqn (46) of [12]). Since the molecular weight $m_s$ of a perdeuterated monomer is 112, according to the definition of $\{\Omega\}$ above Eqn (1), we infer

$$\{\Omega\} = 2.13(\pm4\%) \ \text{Å}. \quad (22)$$

Here $M_w$ is identified with $M$ without further concern about the polydispersity, which is justified if the polydispersity is small. Rawiso et al also reported $S(q)$ in the fractal $q$ regime (above Eqn (46) of [12]):

$$S(q) \cdot q^{1/\nu} \to 0.330(\pm8\%) \ \text{Å}^{-1/\nu},$$

which in view of Eqn (10) gives

$$\{C_{\text{max}} \ A^{3-1/\nu}\} = 2.27(\pm8\%) \times 10^{-2} \ \text{Å}^{-1/\nu}. \quad (23)$$

Farnoux et al measured $\xi_s$ for semidilute perdeuterated PS in CS$_2$ also using neutron scattering [23]:

$$\xi_s = 44\text{Å} (\rho = 0.025 \ \text{g/cm}^3, M_w = 1.1 \times 10^6), \ 29.8\text{Å} (\rho = 0.04, M_w = 5 \times 10^5),$$

$$18.3\text{Å} (\rho = 0.075, M_w = 5 \times 10^5) \ \text{and} \ 10.5\text{Å} (\rho = 0.15, M_w = 5 \times 10^5).$$

We note that since they used perdeuterated PS, the monomer concentration $C$ and the chainlength $N$ are related to $\rho$ and $M$ by $C = N_a \rho / 112$ and $N = M / 112$, respectively, where $N_a$ is Avogadro’s constant. des Cloizeaux and Jannink reported in their book (below Eqn (15.4.37) of [6]) that

$$S_0 / S(q) \cdot (q\xi_s)^{-1/\nu} = 1.51(\pm1\%) \ \text{for} \ q\xi_s \geq 2.6,$$

from which we can calculate $\xi_f$.

3.4 PS+Toluene at 25$^\circ$C

Higo et al summarized the results of several light scattering experiments and reported $R_G^2 = 1.38 \times 10^{-2} M^{1.19} \text{Å}^2$ [24]. This implies

$$\{\Omega\} = 1.95(\pm5\%) \ \text{Å} \quad (25)$$

The small-angle X-ray scattering experiment done by Hamada et al gives $\xi_s$ and $S_0$ [25]:

$$\xi_s = 2.67\rho^{-0.77} (\pm5\%) \ \text{Å}, \quad (26)$$

and

$$S_0 = 2.65\rho^{-1.30} (\pm10\%), \quad (27)$$

where $\rho$ is in g/cm$^3$. The co-operative diffusion constant is given in Schaefer and Han’s review article [27]:

$$D_c = 93.0 \cdot \left(\frac{C}{\{C_{\text{max}}\}}\right)^{0.75} (\pm5\%) \cdot 10^{-7} \text{cm}^2/\text{s}, \ \text{for} \ 0.02 \leq C/\{C_{\text{max}}\} \leq 0.08. \quad (28)$$

We note that the viscosity $\eta_s$ of toluene at 25$^\circ$C is $0.552 \times 10^{-2}$ poise [27].
Table 2: Universal Ratios of the Characteristic Lengths in Semidilute Polymer Solutions.

| System* | \{A\}(Å) | \(\xi_\phi/\xi_s\) | \(\xi_\Pi/\xi_s\) | \(\xi_f/\xi_s\) | \(\xi_D/\xi_s\) | \(\beta_2\) | \(\beta_4\) |
|---------|----------|-----------------|-----------------|-----------------|-----------------|--------|--------|
| a       | 3.21(±7%) | 0.61(±9%)       | 2.97(±5%)       | -               | 4.29(±10%)      | 18(±22%)| 968(±28%) |
| b       | 2.79(±7%) | 1.23(±8%)       | -               | 1.27(±1%)       | -               | 4.8(±14%)| 64(±21%) |
| c       | 3.16(±7%) | 1.23(±9%)       | 3.81(±6%)       | -               | 1.65(±7%)       | 4.3(±23%)| 61(±29%) |

*: a: PS+Cyclohexane at 35°C. b: PS+CS\(_2\) at 20°C. c: PS+Toluene at 25°C.

4 Results

We report in this section the ratios of \(\xi_s\), \(\xi_\phi\), \(\xi_\Pi\), \(\xi_f\), and \(\xi_D\), as well as the reduced moments \(\beta_2\) and \(\beta_4\) for polymer solutions under theta and good-solvent conditions. \(\xi_f\) is rigorously related to a combination of \(\xi_\phi\) and \(\xi_\Pi\) (Eqn 17), and \(\xi_\Pi\) can be determined using Eqn 6. For PS+Cyclohexane and PS+Toluene solutions, we are able to determine all \(\xi\)'s except \(\xi_f\). But for PS+CS\(_2\) solution, we obtain \(\xi_\phi\), \(\xi_s\) and \(\xi_f\), but find no data in the literature helpful in determining \(\xi_\Pi\) and \(\xi_D\). The results are also summarized in Table 2 for clarity’s sake. The quoted uncertainties are those claimed in the original references. When our quantity involves more than one number from these references, we have propagated the quoted uncertainties presuming that these are independent.

4.1 PS+Cyclohexane at 35°C

Eqn 12 and 18, together with the assumption that \(P_\infty = 2\) yield

\[
\{C_{\text{max}} A^{3-1/\nu}\} = 1.95 \times 10^{-2}(\pm 7\%) \text{ Å}^{-2},
\]

where \(\nu = 0.5\). Hence \(\{A\} = 3.21(\pm 7%)\) Å. According to Eqn 8,

\[
\xi_\phi = \{A\} \cdot \frac{\{C_{\text{max}}\}}{C} = 3.21 \cdot \frac{\{C_{\text{max}}\}}{C}(\pm 7%) \text{ Å}.
\]

Eqn 9 can be rewritten as

\[
\xi_s = 5.24 \cdot \frac{\{C_{\text{max}}\}}{C}(\pm 5%) \text{ Å}.
\]

Eqn 20 gives rise to

\[
\xi_D = 22.5 \cdot \frac{\{C_{\text{max}}\}}{C}(\pm 8%) \text{ Å}, \text{ for } C < 4.6 \times 10^{-4}\text{Å}^{-3}.
\]

Eqn 21 leads to

\[
\xi_\Pi = 15.54 \cdot \frac{\{C_{\text{max}}\}}{C} \text{ Å},
\]

It is now straightforward to calculate the \(\xi\) ratios: We find \(\xi_\phi/\xi_s = 0.61(\pm 9%), \xi_D/\xi_s = 4.29(\pm 10%), \) and \(\xi_\Pi/\xi_s = 2.97(\pm 5%). \) To calculate \(\beta_2\) and \(\beta_4\), we combine Eqn 15, 21.
29 and 32, which yields $\beta_2 = 18(\pm 22\%)$. Hence $\xi_\Pi/\xi_\phi = 4.84(\pm 8\%)$ in view of Eqn 16. Furthermore, from Eqn 14 we obtain $\beta_1 = 968(\pm 28\%)$. Eqn 39 then gives

$$r_2 \equiv \int_0^\infty dx x^n ((C(x\xi_\phi))/_0/C - 1) \to 3(\pm 22\%) \text{ and } 48(\pm 28\%)$$

for $n=2$ and 4, respectively.

### 4.2 Perdeuterated PS+C\textsubscript{S\small{2}} at 20°C

Eqn 12 and 22 with $P_\infty = 1.23(\pm 4\%)$ give rise to $\{C_{max}A^{3-1/\nu}\} = 2.34(\pm 8\%) \times 10^{-2} \text{Å}^{-1/\nu}$ and hence $\{A\} = 2.82(\pm 6%) \text{Å}$, whereas Eqn 23 yields $\{A\} = 2.75(\pm 6%) \text{Å}$. The average of these two $\{A\}$'s leads to

$$\xi_\phi = \{A\} \cdot \left(\frac{\{C_{max}\}}{C}\right)^{\frac{1}{3-1/\nu}} = 2.785 \cdot \left(\frac{\{C_{max}\}}{C}\right)^{\frac{1}{3-1/\nu}} (\pm 7\%) \text{Å},$$

where $\nu = 0.588$. We also obtain $P_\infty = 1.20(\pm 11\%)$ using the same set of data (Eqn 22 and 23), which agrees with the simulation results (Section 5.4). Several $\xi_\phi$'s for different concentrations are given in Section 3.3. From these data, we obtain $\xi_\phi/\xi_\phi = 1.23(\pm 8\%)$. In addition, by virtue of Eqn 24, we determine $\xi_f/\xi_\phi = 1.27(\pm 1\%)$, which implies $\xi_f/\xi_\phi = 1.03(\pm 8\%)$. Eqn 14 and 17 then determine the reduced moments $\beta_2 = 4.8(\pm 14\%)$ and $\beta_4 = 64(\pm 21\%)$. Alternatively, they determine the $r_2$ moments defined in Eqn 39. $r_2$ = 1.2(14%) and $r_4$ = 4.5(21%).

### 4.3 PS+Toluene at 25°C

Eqn 12 and 25 give $\{C_{max}A^{3-1/\nu}\} = 0.0273(\pm 9\%) \text{Å}^{-1/\nu}$, where we set $\nu = 0.59$ and $P_\infty = 1.23(\pm 4\%)$. This in turn yields $\{A\} = 3.16(\pm 7\%) \text{Å}$ and

$$\xi_\phi = \{A\} \cdot \left(\frac{\{C_{max}\}}{C}\right)^{\frac{1}{3-1/\nu}} = 3.16 \cdot \left(\frac{\{C_{max}\}}{C}\right)^{\frac{1}{3-1/\nu}} (\pm 7\%) \text{Å}.$$

Eqn 26 can be written as

$$\xi_s = 2.57 \cdot \left(\frac{\{C_{max}\}}{C}\right)^{\frac{1}{2}} (\pm 5\%) \text{Å}.$$

Eqn 27 gives

$$\xi_\Pi = 9.80 \cdot \left(\frac{\{C_{max}\}}{C}\right)^{\frac{1}{2}} (\pm 3\%) \text{Å}.$$

$\xi_D$ is determined from Eqn 28:

$$\xi_D = 4.25 \cdot \left(\frac{\{C_{max}\}}{C}\right)^{\frac{1}{2}} (\pm 5\%) \text{Å}, \text{ for } 0.02 \leq C/\{C_{max}\} \leq 0.08.$$

The above results give $\xi_\phi/\xi_s = 1.23(\pm 9\%)$, $\xi_D/\xi_s = 1.65(\pm 7\%)$, and $\xi_\Pi/\xi_s = 3.81(\pm 6\%)$. By identifying Eqn 27 with Eqn 22, we obtain $\beta_2 = 4.3(\pm 23\%)$, which yields $\xi_\Pi/\xi_\phi = 3.16(\pm 8\%)$ (Eqn 16). Eqn 14 then gives $\beta_4 = 61(\pm 29\%)$. These results are consistent with those of PS+C\textsubscript{S\small{2}} presented in the previous section. Furthermore, Eqn 39 gives rise to $r_2 = 1.1(\pm 23\%)$ and $r_4 = 4.3(\pm 29\%)$. 

10
5 Discussion

5.1 Solvent Quality

In good-solvent cases such as PS+CS$_2$ at 20°C, the relations between $\xi_s$, $\xi_\phi$, $\xi_f$, and $\xi_\Pi$(Eqn 14, 16 and 17) become strictly correct only for a sufficiently good solvents. Whether the solvent is good enough may be expressed using the notion of the thermal blob[26]. The size of the thermal blob $\{\xi_T\}$ marks the crossover between ideal chain and self-avoiding behavior. For chain sections of size much smaller than $\{\xi_T\}$ the polymer behaves as an ideal chain; for sections much larger than $\{\xi_T\}$, it exhibits excluded-volume expansion. In such solvents, the good-solvent scaling properties disappear for high concentrations such that $\xi_\phi \leq \{\xi_T\}$. However, the good-solvent behavior appears for lower concentrations such that $R_G \gg \xi_\phi \gg \{\xi_T\}$. Accordingly, the universal ratios reported in rows b and c of Table 2 should hold only in this same regime. To be more specific, when $R_G \gg \xi_\phi \gg \{\xi_T\}$, the first-order correction to those $\xi$ ratios goes as some positive power of $\{\xi_T\}/\xi_\phi$. If $\xi_\phi$ (or $R_G$) is of the order of $\{\xi_T\}$, i.e., the system is in the marginal-solvent condition, special care must be taken to interpret experimental data[27].

5.2 Consistency with Previously Reported Universal Ratios

In this work, we demonstrate the universal properties of semidilute polymer solutions by showing the constancy of those $\xi$ ratios without referring to the dilute properties such as $R_G$. However, there exists an equivalent alternative, which relies on the scaling relations between dilute and semidilute properties.

In the appendix, we obtain a scaling formula for osmotic pressure $\Pi$(Eqn 33) and define a universal constant $k_\Pi$, which is related to the reduced moment $\beta_2$(Eqn 34). Since $P_\infty$ and $c_0$ are known, and the reduced moment $\beta_2$ is given in Table 2, we determine $k_\Pi = 2.2(\pm 22\%)$ and $9.4(\pm 24\%)$ for theta and good solvents, respectively. For good-solvent cases where $\nu = 0.588$, des Cloizeaux and Noda obtained $k_\Pi \approx 9.85$ using the renormalization group theory(to first order in $\epsilon$)[28]. Noda et al reported $k_\Pi = 10.0$ and $\nu = 0.585$ for poly($\alpha$-methylstyrene) in toluene[29]. Adam et al determined $k_\Pi = 9.7$ and $\nu = 0.586 \pm 0.006$ for semidilute polyisoprene in cyclohexane[30]. Their results together with ours confirm the universality of $k_\Pi$, and hence that of the ratio $\xi_\Pi/\xi_\phi$ for good-solvent cases(Eqn 37).

Des Cloizeaux and Jannik defined the Kuhnian overlap length $\xi_k$ as

$$\xi_k = X(CX^3/N)^{\nu/(1-3\nu)},$$

where $X^2 = R_e^2/3 = 2R_G^2/\bar{\Lambda}$ in the dilute limit. $R_e$ is the end-to-end distance of a dilute polymer. The numerical constant $\bar{\Lambda} \equiv 6R_G^2/R_e^2 \simeq 0.952$ for an isolated polymer in a good solvent[1]. $\xi_k$ can be rewritten in a form similar to Eqn 33:

$$\frac{\xi_k}{R_G} = (\bar{\Lambda}/2)^{1/(3\nu-1)} \left( \frac{C^*}{C} \right)^{\frac{\nu}{2(3\nu-1)}},$$

where $C^* \equiv N/R_G^3$ is the overlap concentration. Dividing Eqn 33 by the above formula gives rise to

$$\xi_\phi/\xi_k = (P_\infty/c_0)^{\nu/(2\nu-1)} \left( \bar{\Lambda}/2 \right)^{\frac{1}{2(3\nu-1)}}.$$
This implies \( \xi_\phi/\xi_k = 0.318 \) and 0.243 for theta and good solvents respectively. In addition, by use of \( \xi_\phi/\xi_s \) given in Table 2, we determine \( \xi_s/\xi_k = 0.522(\pm9\%) \) for theta cases, and 0.198(\pm9\%) for good-solvent cases. The latter value agrees with that(0.18) reported in their book(Chapter 15 of [3]).

5.3 Dynamic Length \( \xi_D \)

While the universality of the static ratios \( \xi_\phi/\xi_s \) and \( \xi_\Pi/\xi_s \) are robust, that of the dynamic ratio \( \xi_D/\xi_s \) is not. For semidilute polymer solutions, \( \xi_D \) goes as \( C^{-\alpha} \), where the theoretical value of \( \alpha = 0.77 \) for good-solvent conditions. Experiments, however, often report \( \alpha = 0.5 - 0.75 \) [22, 31, 32]. The deviation of the exponent from the scaling theory prediction suggests the underlying dynamics of the co-operative diffusion of semidilute polymers might be more complex than the scaling theory can explain. Several attempts have been made to resolve this discrepancy by attributing it to the cross-over behavior of the system under investigation [27, 32, 33]. Despite of these controversies, we expect the scaling theory prediction should still hold in the semidilute limit, where \( C^* \ll C \ll \{C_{\text{max}}\} \) and \( N \to \infty \), and this is confirmed by the experimental data collected in Schaefer and Han’s review paper [27]. In this paper, we use their data to calculate \( \xi_D/\xi_s \) for PS+Toluene(Eqn 28).

6 Conclusions

Table 2 summarizes the ratios of those \( \xi \)'s for semidilute polymers under theta and good-solvent conditions. These ratios are expected to be universal in the semidilute regime where \( C^* \ll C \ll \{C_{\text{max}}\} \) and the chainlength \( N \to \infty \). The static lengths \( \xi_s, \xi_\phi, \xi_f \) and \( \xi_\Pi \) are related to each other through the reduced moments \( \beta_2 \) and \( \beta_4 \) of the local concentration \( \langle C(r) \rangle_0 \) (Section 2.2). The universality of these length ratios is just the manifestation of the scaling property of \( \langle C(r) \rangle_0 \). The data in Table 2 provide a satisfying confirmation of this universality. Each of the reported ratios (except those involving \( \xi_D \)) was obtained from data over a substantial range of concentration—approaching an order of magnitude. The ratios were independent of concentration to a degree given by the quoted uncertainty. Further, the reduced moments \( \beta_2 \) and \( \beta_4 \) were independently obtained for two solvents, CS2 and toluene. The values obtained are very similar for the two solvents, further supporting the claim of universality. As mentioned in Section 1, these ratios are valuable since they allow us to infer one quantity such as \( A \) or \( \xi_\phi \) from another, such as the osmotic pressure \( \Pi \). Moreover, \( \beta_2 \) and \( \beta_4 \) provide the information about the cross-over behavior of \( \langle C(r) \rangle_0 \). It might be a challenge for polymer theorists who are interested in \( \langle C(r) \rangle_0 \) to work out \( \beta_n \) (or \( r_n \)) and determine these ratios.

As noted in Section 5.3, the concentration dependence of \( \xi_D \) may deviate from the scaling theory prediction. It seems to us that, so far there is no satisfactory explanation for this discrepancy. Thus, further theoretical and experimental investigations are needed.
Appendix

Eqn 9 can be rewritten as

\[ S(q) = \int_V d^3r (\langle C(r) \rangle_0 - C) \exp(i\vec{q} \cdot \vec{r}) \]

since the Fourier transform of any constant is zero as long as \( q \neq 0 \). \( S(q) \) can then be Taylor-expanded with respect to \( q \) (cf. Eqn 3):

\[ S(q) = S_0 \left( 1 - \frac{1}{2} \int d^3r (\langle C(r) \rangle_0 - C) \vec{q} \cdot \vec{r} \right) \cdots \]

where \( S_0 = \int d^3r ((\langle C(r) \rangle_0 - C) \). A straightforward calculation leads to

\[ \xi_s^2 = \frac{1}{6} \int_0^\infty dr \, r^4 (\langle C(r) \rangle_0 - C) \]

By introducing \( \beta_n \) (Eqn 13) and using Eqn 8, \( S_0 \rightarrow 4\pi \beta_n \int_{C_A > C} dr \, r^2 (C_A - C) \)

\[ = \frac{4\pi}{3} (3\nu - 1) \beta_n \{ C_{\max} A^{3-1/\nu} \}^{1/\nu} \]

\[ = \frac{4\pi}{3} (3\nu - 1) \beta_n \{ C_{\max} A^{3-1/\nu} \}^{\frac{3\nu}{3\nu-1}} C^{\frac{1}{3\nu-1}} \]

Incorporating Eqn 10, 11 and the overlap concentration \( C^* \equiv N/R_G^3 \) into Eqn 32 leads to

\[ S_0 \rightarrow \frac{4\pi}{3} (3\nu - 1) \left( P_\infty / c_0 \right)^{\frac{3\nu}{3\nu-1}} \beta_n \{ C/C^* \}^{\frac{1}{3\nu-1}} N, \]

where \( c_0 \) is defined below Eqn 11. Using this \( S_0 \) and Eqn 13, we obtain

\[ \frac{N}{k_B T \Pi C} \rightarrow k_{\Pi} \left( \frac{C}{C^*} \right)^{\frac{1}{3\nu-1}}, \]

where

\[ k_{\Pi} = (4\pi \nu \beta_n)^{-1} \left( P_\infty / c_0 \right)^{\frac{3\nu}{3\nu-1}}. \]

Furthermore, Eqn 33 gives

\[ \frac{\xi_{\Pi}}{R_G} \rightarrow k_{\Pi}^{-1/3} \left( \frac{C^*}{C} \right)^{\frac{\nu}{3\nu-1}} \]

Similarly, Eqn 8 can be expressed as

\[ \frac{\xi_{\phi}}{R_G} \rightarrow (P_\infty / c_0)^{\frac{\nu}{3\nu-1}} \left( \frac{C^*}{C} \right)^{\frac{\nu}{3\nu-1}} \]

Combining Eqn 35 with 36 yields

\[ \frac{\xi_{\Pi}/\xi_{\phi} \rightarrow k_{\Pi}^{-1/3} \left( P_\infty / c_0 \right)^{\frac{\nu}{1-3\nu}} = (4\pi \nu \beta_n)^{1/3}. \]
By the same token, Eqn 30 is reduced to

\[ \xi_s^2 \to \xi_\phi^2 \left[ \frac{1}{6} \left( \frac{\nu}{1+2\nu} - \frac{1}{3} \right) \frac{\beta_4}{\beta_2} \right] . \]  

(38)

We may define another kind of dimensionless moment \( r_n \) for \( \langle C(r) \rangle_0 \), which carries the same information as does \( \beta_n \):

\[ r_n \equiv \int_0^\infty dx \, x^n \left( \frac{\langle C(x\xi_\phi) \rangle_0}{C} - 1 \right) \to \frac{(3-1/\nu)\beta_n}{(n+1)(n-2+1/\nu)} , \]  

(39)

where \( x = r/\xi_\phi \).

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