# Extended Two-Parameter Theory for Flexible Polymer Chains

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ABSTRACT: The extended two-parameter theory of the statistical mean-square end-to-end separation and radius of gyration and the second virial coefficient, deduced from the recent renormalization group scaling theory [Chen, Z. Y.; Noolandi, J. *J. Chem. Phys.* **1992**, *96*, 1540], is discussed. We show that the extended two-parameter theory, which includes not only the two-parameter theory in the weak excluded-volume limit but also the effect of a *finite* excluded volume for which the two-parameter theory is no longer valid, is consistent with experimental light-scattering and osmotic-pressure data. A comparison with the results of self-avoiding walks is also included.

## 1. Introduction

The mean-square end-to-end separation $\bar{R}^2$ and radius of gyration $\bar{S}^2$ and the second virial coefficient $A_2$ are fundamental physical quantities used in characterizing a polymer chain in a good solvent.[1] A two-parameter theory for flexible polymer chains, which is valid for polymers with weak excluded-volume interactions (i.e., near the Θ temperature), displays a scaling form for these thermodynamic properties:[1,2]

$$\bar{R}^2 = bL\alpha_R{}^2(z) \tag{1.1}$$

$$\bar{S}^2 = {}^1/_6 bL\alpha_S{}^2(z) \tag{1.2}$$

$$A_2 = {}^1/_2 wL^2\mathcal{A}(z) \tag{1.3}$$

where $b$ is the effective Kuhn length, $L$ is the total contour length of the polymer chain, $wb^2$ is a measure of the strength of the excluded-volume interaction, and $z$ is a scaled excluded-volume parameter defined by[1,2]

$$z = (3/2\pi)^{3/2}(w/b)(L/b)^{1/2} \tag{1.4}$$

The functions $\alpha_R{}^2(z)$, $\alpha_S{}^2(z)$, and $\mathcal{A}(z)$ characterize the crossover for polymer chains in a Θ temperature solution[1-3] where the excluded-volume effect is zero ($z \to 0$) to a higher temperature, with a nonzero, but weak excluded-volume interaction at a very long contour length $L$ ($z \to \infty$). According to perturbation theories for small $z$[1]

$$\alpha_R{}^2(z) = 1 + \sum_{l=1} a_l{}^R z^l \tag{1.5}$$

$$\alpha_S{}^2(z) = 1 + \sum_{l=1} a_l{}^S z^l \tag{1.6}$$

$$\mathcal{A}(z) = 1 + \sum_{l=1} a_l{}^{\mathcal{A}} z^l \tag{1.7}$$

The linear-term coefficients $a_1{}^R = 4/3$, $a_1{}^S = 134/105$, and $a_1{}^{\mathcal{A}} = -32(7 - 4(2)^{1/2})/15$ based on a continuum-chain model are described in Yamakawa's book,[1] and the coefficients for higher-order terms are also available.[4] De Gennes has established the polymer-magnet analogy[3] which enables one to write the asymptotic behavior for large $z$:

$$\alpha_R{}^2(z) = A_R z^{2(2\nu-1)}(1 + b_R z^{-2\Delta} + ...) \tag{1.8}$$

$$\alpha_S{}^2(z) = A_S z^{2(2\nu-1)}(1 + b_S z^{-2\Delta} + ...) \tag{1.9}$$

$$\mathcal{A}(z) = A_{\mathcal{A}} z^{2(3\nu-2)}(1 + b_{\mathcal{A}} z^{-2\Delta} + ...) \tag{1.10}$$

where the "critical exponents" $\nu$ and $\Delta$ are theoretically well-determined universal constants.[5-8] The constants $A_R$, $A_S$, $A_{\mathcal{A}}$, $b_R$, $b_S$, and $b_{\mathcal{A}}$ are amplitudes of the leading power law and correction-to-scaling terms whose values will be discussed below.

One of the main concerns of previous studies[5-15] has been to extract the value of the critical exponent $\nu$. All recent results[5-8] agree that this universal exponent $\nu$ should have a value approximately equal to 0.5886. In addition, if we accept the universality hypothesis,[3,16] the correction-to-scaling exponent $\Delta$ should have the value $2\Delta = 0.93$ as predicted by Muthukumar and Nickel using a Borel summation technique,[11] which is consistent with the $\phi^4$-theory results for the ($d = 3$, $n = 0$) universality class by LeGuillou and Zinn-Justin.[5,6] We shall use these values of universal exponents through out this paper.

Many theoretical approaches have been advanced to derive the two-parameter theory. Earlier approaches[9,17,18] have oversimplified the asymptotic behavior (eqs 1.8–1.10), such as in the Flory model,[9] the modified Flory model,[17] etc. In more recent work, the asymptotic behavior (eqs 1.8–1.10) is studied in accordance with the predictions from the modern theory of critical phenomena.[16] One of the difficulties encountered in constructing a sensible model for these functions is the use of perturbation theories[8,11] leading to eqs 1.5–1.7, or the $\epsilon$ expansion[12,19] in the parameter $\epsilon = 4 - d$ where $d = 3$ is the dimension of space.[10] A perturbation theory needs to be resummed in order to obtain information in the large-$z$ limit, as has been shown by Muthukumar and Nickel[8] for $\alpha_R{}^2$ (on the basis of their earlier sixth-order perturbation calculation[11]). Empirical two-parameter theories have also been proposed according to the asymptotic behavior from the SAW (self-avoiding random walk) model.[13,14,20] It is generally assumed that the SAW model belongs to the same universality class as flexible polymer chains, which implies universal constants such as $\nu$ deduced from large $z$ should be universal. However, this does not state that the SAW corresponds to a two-parameter theory; therefore, care must be taken to interpret a SAW calculation.

Some fundamental problems still remain unsolved.

First, although the critical exponents $\nu$ and $\Delta$ are universal (system-independent) constants, confusion has arisen regarding the asymptotic amplitudes deduced from a SAW model[20] being different from that of a continuum model.[8] The questions are the following: (a) Is the two-

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parameter theory system-independent? (b) Is the difference in the amplitudes merely due to a definition of the $z$ variables? (c) What is the functional form of a two-parameter theory?

Second, there are also concerns about the applicability of a two-parameter theory. One of the problems is that the penetration function $\Psi = A_2/(4\pi^{3/2}S^3)$ deduced from the experimentally measured $A_2$ and $S$ for polymers at a temperature *far away* from the Θ point seems to have a different behavior than the one described by a two-parameter theory.[21] A related problem is that the results from the perturbation theories (e.g., from the Muthukumar–Nickel Borel summation study[8]) and from the self-avoiding random walk (SAW) model (e.g., from the recent Barrett et al. Monte Carlo calculations[21]) give correction-to-scaling amplitudes with *different* signs.[4] These physical systems deal with excluded volume of finite size (i.e., finite $w/b$) which *does not* have to obey the same physical properties of a small $w/b$ system for which the two-parameter theory is valid. Therefore, it is desirable to establish a model in which the characteristic features of the two-parameter theory are recovered for a small (infinitesimal) $w/b$, and yet contains the effect of a finite $w/b$ as an additional parameter. An attempt in terms of the direct renormalization technique to solve this problem has recently been put forward by Nickel.[4]

Most recently, we have presented a renormalization group (RG) scaling theory for the functions $\bar{R}^2$, $\bar{S}^2$, and $A_2$ *in closed form*.[22] It is not the purpose of the RG scaling theory to provide an estimate for the asymptotic amplitudes and the critical exponents for these functions. Our goal is more fundamental: We want to obtain a formalism in which the structure of these functions for a finite $w/b$ is properly treated and approximated, and to demonstrate that the inconsistencies mentioned above can be accounted for by using a finite $w/b$ formalism. Since the two-parameter-theory form is only one limit of the model ($w/b \ll 1$), we call our new model an extended two-parameter model. For the small $w/b$ limit, the extended two-parameter theory becomes a two-parameter theory. In this paper, we restrict ourselves to showing how the results of the extended two-parameter model based on the RG scaling theory can be compared with other formalisms and experiments; we refer interested readers elsewhere[22] for a complete and detailed treatment of the RG scaling theory leading to the equations used here.

There are a number of other complications which are not considered in this paper. First, only two-body interactions are assumed here; for certain properties comparison with the Θ solution experiment may require the use of three-body interactions, which are absent from the current theory. Second, real systems are affected by polydispersity which is also completely ignored in our theory. Third, stiffness of the polymer chains may influence certain properties as well. Yamakawa[23] has recently discussed the properties of the helical wormlike chain, and he has concluded that the non-two-parameter behavior of a decrease in the penetration function with increasing molecular weight can be accounted for by considering the effects of chain stiffness. Further research work on the importance of the stiffness to a dilute polymer solution in the framework of the extended two-parameter theory needs to be studied more carefully.

## 2. Mean-Square End-to-End Separation

Elsewhere we have shown that the RG scaling theory[22] involves parameters $z$ and $\bar{u}$ for the mean-square end-to-end separation

$$\bar{R}^2 = bL\alpha_R^2(z,\bar{u}) \tag{2.1}$$

where $z$ is defined in eq 1.4. The constant $\bar{u}$ is a dimensionless excluded-volume parameter:[22b]

$$\bar{u} = (a/b)^{1/2}(w/b) \tag{2.2}$$

The cutoff constant $a$ is of the order of the shortest distance below which the polymer segments cannot interact with each other. The physical value of $a$ can be a few times the effective Kuhn length $b$.

From the RG scaling theory, the crossover function $\alpha_R^2(z,\bar{u})$ can be written in an extended two-parameter form which is expressed implicitly as a function of $z$ and $\bar{u}$:[22]

$$\alpha_R^{5.643} - (1-\bar{u})\alpha_R^{0.395} = C_R z \tag{2.3}$$

where the universal exponents $e_1 \equiv (1-2\Delta)/(2\nu-1) = 0.395$ and $e_2 = 1/(2\nu-1) = 5.643$ have been used. The constant $C_R = A_R^{1/2(2\nu-1)}$ is related to the asymptotic amplitude $A_R$. Equation 2.3 is a result of the RG scaling theory with closed-form approximations for the RG functions; it is valid for $0 \le \bar{u} \le 1$, and can possibly be extrapolated to the vicinity of 1 when $\bar{u} > 1$. We can now deduce the asymptotic behavior for large $z$:

$$\alpha_R^2(z,\bar{u}) = A_R z^{2(2\nu-1)}[1 + (1-\bar{u})b_R z^{-2\Delta} + ...] \tag{2.4}$$

with $b_R = 2(2\nu-1)/C_R^{2\Delta}$. The asymptotic behavior (eq 2.4) contains a leading correction-to-scaling term with a coefficient proportional to $1-\bar{u}$. For large excluded volume, $\bar{u} > 1$, this coefficient becomes negative (which qualitatively corresponds to the situation in the SAW models). For weak $\bar{u} \ll 1$, $\alpha_R^2(z,0)$ becomes a function of $z$ only, and a two-parameter theory is applicable. The representation 2.3 for the crossover function $\alpha_R^2(z,\bar{u})$ gives the functional form of an extended two-parameter theory that includes the effect of a finite $\bar{u}$.

**2.A. Two-Parameter Theory and Comparison with Continuum Theories.** The $\bar{u} \to 0$ limit of eq 2.3 has the form of a two-parameter theory, which still contains an unknown amplitude $C_R$. We shall compare our two-parameter theory (eq 2.5) with the literature to obtain a

$$\alpha_R^{5.643} - \alpha_R^{0.395} = C_R z \tag{2.5}$$

value for the constant $C_R$. The structure of eq 2.5 is similar to the original Flory two-parameter theory[9]

$$\alpha_R^5 - \alpha_R^3 = 2.60z \tag{2.6}$$

although there is no direct relationship between the RG scaling theory and the Flory theory.

The continuum description of the two-parameter theory with a probability distribution function written as a Wiener measure multiplied by a δ-function-type excluded-volume interaction has been extensively studied.[1,7,8,10-12,19] The value of the constant $A_R$ obtained by des Cloizeaux et al.[7] from an analysis of the perturbation theory of Muthukumar and Nickel[11] is $A_R = 1.5339$. In addition, des Cloizeaux et al. obtained critical exponents $2(2\nu-1) = 0.3538$ and $2\Delta = 0.9468$, which are in close agreement with the values $2(2\nu-1) = 0.3520$ and $2\Delta = 0.94$, and $2(2\nu-1) = 0.3540$ and $2\Delta = 0.96$ obtained by LeGuillou and Zinn-Justin.[5,6] The recent Borel summation of the same perturbation theory performed by Muthukumar and Nickel gives[8]

$$2(2\nu - 1) = 0.3544 \qquad 2\Delta = 0.930 \tag{2.7}$$

$$A_R = 1.5310$$

To compare with the continuum models, we adopt the value of $A_R$ given above, and the two-parameter theory (eq 2.5) then gives

$$\alpha_R^{5.643} - \alpha_R^{0.395} = 3.3261z \tag{2.8}$$

This simple equation reproduces eqs 1.5 and 1.8 with $\alpha_1^R = 1.27$ and $b_R = 0.116$, which are close to the predictions from the perturbation theory[1,8] $\alpha_1^R = 4/3$ and $b_R = 0.1204$. The function $\alpha_R^2$ versus $z$ is plotted in Figure 1a.

Muthukumar and Nickel's Borel summation is an accurate calculation for $\alpha_R^2$ within the two-parameter continuum model. The numerical results can be represented by their empirical expression[8]

$$\alpha_R^2 = (1 + 7.524z + 11.06z^2)^{0.1772} \tag{2.9}$$

for the whole $z$ range. Equation 2.9 was chosen to reproduce the known values of $2(2\nu - 1)$, $A_R$, and $\alpha_1^R$ at large- and small-$z$ limits, and reproduces the coefficient $b_R = 0.1205$ in agreement with $b_R = 0.1204$; however, the large-$z$ expansion of eq 2.9 yields a critical exponent $2\Delta = 1$, which is slightly large. The comparison between eqs 2.8 and 2.9 is shown in Figure 1b, where the relative error $\alpha_R^2$(eq 2.9)/$\alpha_R^2$(eq 2.8) − 1 is plotted as curve 1. We can see that the difference between eqs 2.8 and 2.9 is very small.

The des Cloizeaux–Conte–Jannink equation[7] for $\alpha_R^2$

$$\alpha_R^2 = \left(1 - \frac{g}{0.1769}\right)^{-0.3737}\left(1 + \frac{g}{0.2184}\right)^{-0.0115}\left(1 - \frac{0.215g - g^2}{0.3214}\right)^{0.1926} \exp\left[0.0399 \arctan\left(\frac{0.5567g}{0.3214 - 0.1075g}\right)\right]$$

$$z = \frac{3}{2}g\left(1 - \frac{g}{0.1769}\right)^{-1.0561}\left(1 + \frac{g}{0.2184}\right)^{0.0263}\left(1 - \frac{0.215g - g^2}{0.3214}\right)^{0.0149} \exp\left[0.3402 \arctan\left(\frac{0.5567g}{0.3214 - 0.1075g}\right)\right] \tag{2.10}$$

also agrees with eq 2.8 as shown in Figure 1b, curve 2, where the relative error $\alpha_R^2$(eq 2.10)/$\alpha_R^2$(eq 2.8) − 1 is plotted.

We shall not compare our results directly with the two-parameter model proposed by Douglas and Freed.[12,19] We note that the Douglas–Freed $\epsilon$-expansion calculation stems from the same continuum model. Therefore, the Freed–Douglas result should give the same value for the asymptotic amplitude; however, because of the poor convergence of the $\epsilon$ expansion, an intepretation of these results cannot be simply made. We refer to a recent paper by Freed and Douglas for a discussion of this point.[19]

**2.B. Extended Two-Parameter Theory and Comparison with SAW Models.** Having determined $C_R$ for the extended two-parameter equation (eq 2.3), we now turn to the interpretation of the SAW results. It is customary in the literature to compare the results of the SAW model with a two-parameter theory. However, it is not widely appreciated that a SAW model does not correspond to a two-parameter theory since it deals with a large excluded-volume parameter (in our terminology here, a finite $\bar{u}$). Here we demonstrate how the SAW data can be interpreted using the extended two-parameter theory (eq 2.3) which contains the effect of a finite $\bar{u}$.

First, we study the Monte Carlo (MC) simulation data of a SAW on a diamond lattice with an attractive potential

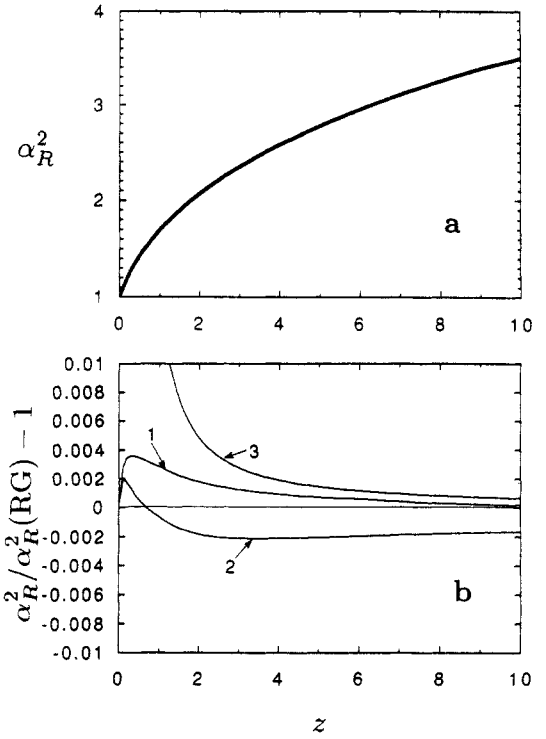


**Figure 1.** (a) Two-parameter theory $\alpha_R^2(z,0)$ deduced from the current work and (b) relative differences of $\alpha_R^2(z,0)$ between the RG scaling theory (eq 2.8) and the Muthukumar–Nickel equation (curve 1), between the RG scaling theory (eq 2.8) and the des Cloizeaux–Conte–Jannink equation (eq 2.10) (curve 2), and between the RG scaling equation (eq 2.8) and the asymptotic behavior (eq 1.8) truncated at the first correction-to-scaling term with constants $A_R = 1.531$ and $b_R = 0.1204$.

$\epsilon$ (not to be confused with the parameter $\epsilon$ in an $\epsilon$-expansion mentioned above).[24] We assume that the excluded-volume parameter $\bar{u}$ is proportional to the "reduced temperature", accurate to the linear order in a Taylor expansion of $\bar{u}(\tau)$:

$$\tau = |(\epsilon - \epsilon_\Theta)|/\epsilon_\Theta \qquad \bar{u} = C_u\tau \tag{2.11}$$

where $\epsilon_\Theta$ is the $\Theta$-point energy at which the excluded-volume interaction and the attraction cancels. Yuan et al. have reported $\epsilon_\Theta = -0.51$, but we found that $\epsilon_\Theta = -0.506$ is a better estimate from a fitting of the MC data to our model. The fitted constant $C_u$ has a value $C_u = 1.3363$. The effective excluded-volume $w/b$ in eq 1.4 is also fitted from the MC data. With the fitted $C_u$ and $w/b$, we found that the MC data of Yuan et al. can be represented by

$$\alpha_R^{5.643} - (1 - \bar{u})\alpha_R^{0.395} = 0.40813(n\tau)^{1/2} \tag{2.12}$$

*within the estimated errors* for their $\epsilon = 0.0$, −0.1, −0.2, −0.3, −0.4, and −0.5 data, where $n$ is the number of steps. Figure 2 shows excellent agreement between the MC data and our representation (eq 2.3) (solid curves), where $\bar{R}^2/b^2$ is plotted against a rescaled $z$ parameter:

$$\tilde{z}_R \equiv C_R z = 0.40813(n\tau)^{1/2} \tag{2.13}$$

The above-mentioned $\epsilon$ values correspond to $\bar{u} = 1.34$, 1.07, 0.808, 0.544, 0.280, and 0.016 in this figure.

Second, we attempt to compare the extended two-parameter model (eq 2.3) with the MC data summarized by Barrett et al.[20] of SAWs on simple cubic (SC), face-centered cubic (FCC), and body-centered cubic (BCC) lattices. The conventional identification for SAW is that $b$ corresponds to the lattice constant and $wb^2$ correponds to the volume of the unit cell of the lattice. With this identification, Barrett et al. have found asymptotic amplitudes different from that deduced from a continuum

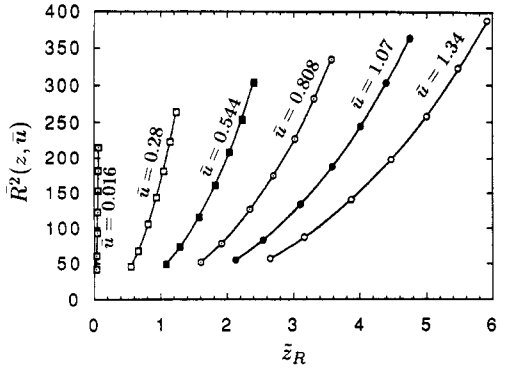


**Figure 2.** Comparison between the extended two-parameter theory (eq 2.3) (solid curves) and the MC data (symbols) of a SAW on a diamond lattice for $\bar{R}^2$. For the Θ point we have used $\bar{R}^2 = C_\infty nb^2$ where $C_\infty = 2$ for a diamond lattice as described by Yuan et al. (ref 24).

model.[20] The excluded-volume constant $w$ in eq 1.4 is defined through a continuum model; therefore, there is no a priori reason to equate $wb^2$ with the volume of the unit cell of a lattice. We assume that $w$ in our equations is an effective excluded-volume parameter and treat $w$ as an adjustable parameter to interpret the results of the SAW data.

A completely different view can be taken to interpret eq 2.3. Since the combination $\tilde{z}_R \equiv C_R z$ always appears together, one could argue that the inconsistency in large-$z$ asymptotic behavior arises from a *system-dependent* amplitude $C_R$, while $z$ for SAWs is defined in the conventional way. If we took this point of view, apart from the system dependence in $\bar{u}$, the function $\alpha_R$ would depend on at least another system-dependent constant, i.e., the asymptotic amplitude. We prefer to consider that $\alpha_R$ depends only on one system-dependent constant $\bar{u}$, and to consider an effective $w/b$ for the definition of $z$. For an extended two-parameter theory, a definition of the parameter $z$ is no longer necessary; it only serves as the two-parameter-theory variable for comparison with the weak $w/b$ limit.

In all three cases (SC, FCC, BCC), a rescaled $z$ parameter

$$\tilde{z}_R \equiv C_R z \equiv \tilde{C}_R(n\bar{u})^{1/2} \tag{2.14}$$

is defined. We then obtain fitted coefficients $\tilde{C}_R$ with values

$$\tilde{C}_R(\mathrm{SC}) = 0.869\,73$$

$$\tilde{C}_R(\mathrm{FCC}) = 0.724\,96 \tag{2.15}$$

$$\tilde{C}_R(\mathrm{BCC}) = 0.792\,75$$

Without a better knowledge for the estimates of the cutoff parameter $a$ in eq 2.2, we also allow $\bar{u}$ to be a free parameter fitted from the MC data:

$$\bar{u}(\mathrm{SC}) = 1.9302$$

$$\bar{u}(\mathrm{FCC}) = 1.5154 \tag{2.16}$$

$$\bar{u}(\mathrm{BCC}) = 1.5388$$

Figure 3 shows $\alpha_R{}^2$ as a function of $\tilde{z}_R$ for these three cases. The open symbols represent the MC data used to obtain the fitted parameters $\tilde{C}_R$ and $\bar{u}$, and the filled symbols represent the enumeration data which are not used in the fitting. Figure 4 shows the relative error between our representation and the MC data.

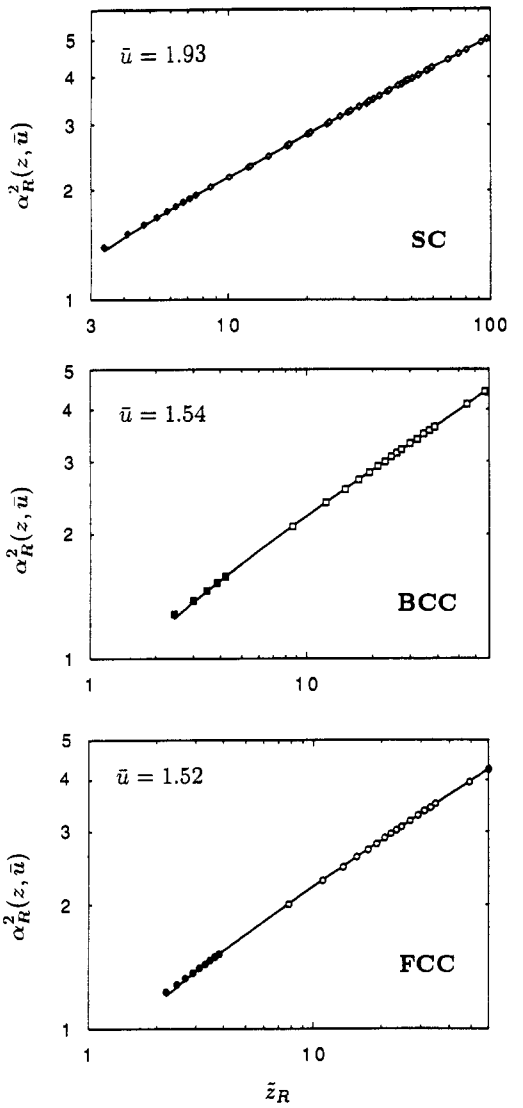


**Figure 3.** Comparison between the extended two-parameter theory (eq 2.3) (solid curves) and the results of SAWs on SC, BCC, and FCC lattices for $\alpha_R{}^2$. The open symbols are the MC data, and the filled symbols are the enumeration data, as summarized by Barrett et al. (ref 20).

Although we succeeded in bringing our representation (eq 2.3) and most of the MC data into accord except for a few $n < 8$ enumeration data points for which the correction due to rigidity perhaps becomes important,[22] no claim is made that representation 2.3 can be generalized to a $\bar{u}$ as large as $\bar{u}(\mathrm{SC}) = 1.93$. Since eq 2.3 is only valid for $\bar{u}$ between 0 and slightly above 1, the fitted $\bar{u}$ can only be viewed as an effective one. What is important here is the fact that the SAW shows a $\bar{u}$ that is greater than 1. As such, the correction-to-scaling amplitude in eq 2.4 becomes negative. Therefore, the effect of a finite $\bar{u}$ must be taken into account to interpret a SAW result; in other words, the SAW results correspond to an extended two-parameter theory.

## 3. Mean-Square Radius of Gyration

The extended two-parameter model based on the RG scaling theory predicts for the mean-square radius of gyration[22]

$$\bar{S}^2 = \frac{1}{6}bL\alpha_S{}^2(z,\bar{u}) \tag{3.1}$$

where $z$ is defined in eq 1.4 and $\bar{u}$ in eq 2.2. The function

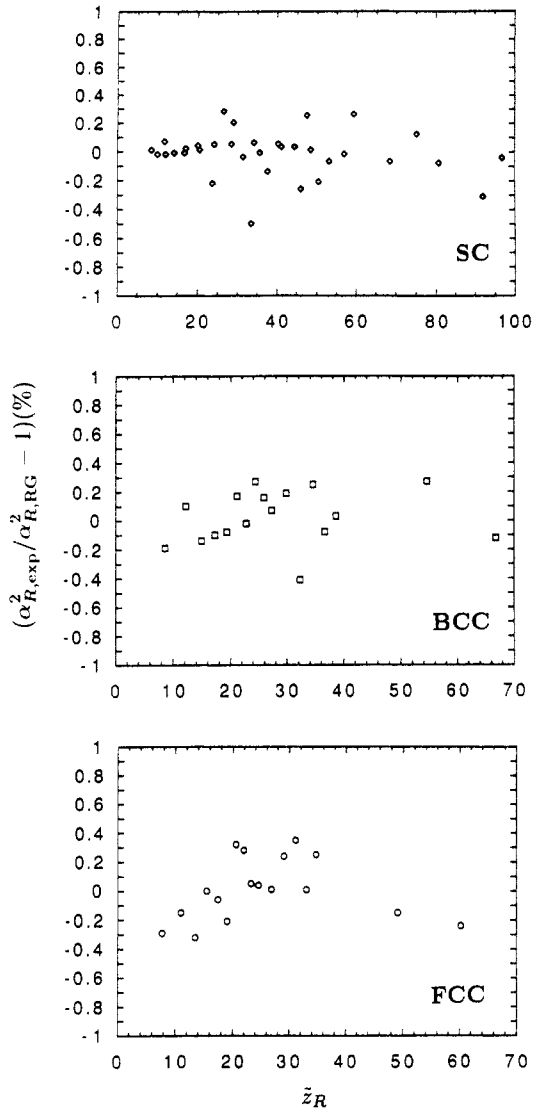


**Figure 4.** Relative deviations between the extended two-parameter theory (eq 2.3) and the results of SAWs on SC, BCC, and FCC lattices for $\alpha_R^2$. See also Figure 3.

$\alpha_S^2$ can be written in the form[22]

$$\alpha_S^{5.643} - (1 - \bar{u})\alpha_S^{0.395} = C_S z \tag{3.2}$$

in the entire $z$ range, which has the same structure as eq 2.3. Again, here $e_1 = (1 - 2\Delta)/(2\nu - 1) = 0.395$ and $e_2 = 1/(2\nu - 1) = 5.643$ are universal constants. $C_S = A_S^{1/2(2\nu-1)}$ is related to $A_S$, the amplitude of the asymptotic power law in eq 1.9. The ratio $A_R/A_S$ is expected to be universal. The $\alpha_S^2$ perturbation calculation to fourth order in $z$ gives[25] $A_S/A_R = 0.961 \pm 0.002$. The following analysis indicates that the SAW calculation[24] on diamond lattices gives $A_S/A_R = 0.954$, compared to the earlier SAW results[14] $A_S/A_R = 0.93 \pm 0.006$. Again, we can deduce the asymptotic behavior for large $z$:

$$\alpha_S^2(z,\bar{u}) = A_S z^{2(2\nu-1)}[1 + (1 - \bar{u})b_S z^{-2\Delta} + ...] \tag{3.3}$$

with $b_R = 2(2\nu - 1)/C_S^{2\Delta}$. Note the ratio $b_S/b_R = (C_R/C_S)^{2\Delta}$ is also universal in our model.

**3.A. Two-Parameter Theory and Comparison with Continuum Theories.** We first compare eq 3.2 with a two-parameter continuum model. If we use the universal ratio $A_S/A_R = 0.961$ predicted by Shanes and Nickel,[25] we can deduce $C_S = 2.9713$. Then we have a two-parameter

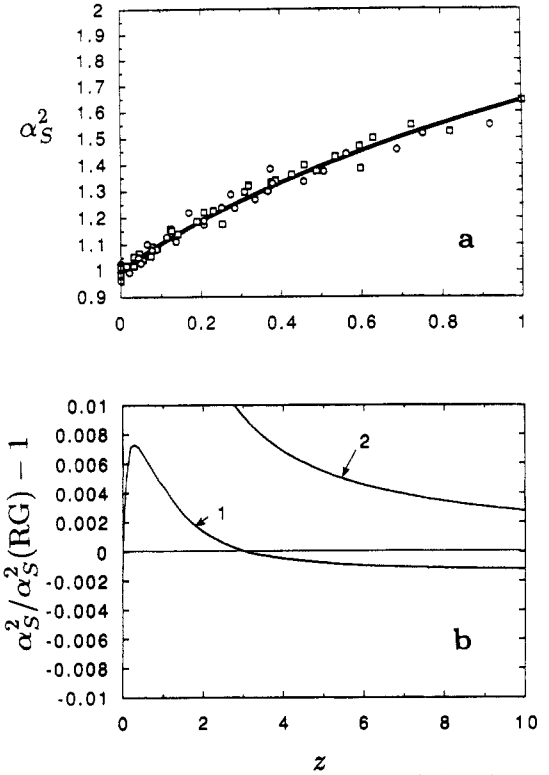


**Figure 5.** (a) Two-parameter theory $\alpha_S^2(z,0)$ deduced from the current work, and the experimental light-scattering data of Norisuye (ref 26, square symbols) and of Matsumoto (ref 27, circle symbols). (b) Relative differences of $\alpha_R^2(z)$ between the RG scaling equation (eq 2.8) and the empirical equation (eq 2.9) (curve 1).

theory by taking the $\bar{u} \to 0$ limit of eq 3.2:

$$\alpha_S^{5.643} - \alpha_S^{0.395} = 2.9713z \tag{3.4}$$

This simple equation reproduces eqs 1.6 and 1.9 with $\alpha_1^S = 1.13$ and $b_S = 0.13$. The value $\alpha_1^S = 1.13$ agrees reasonably well with the prediction from the perturbation theory[1] $\alpha_1^R = 134/105$. Also, the universal ratio of the amplitudes of the correction-to-scaling terms $b_S/b_R = 1.11$ is very close to the estimated[25] $b_S/b_R = 1.25 \pm 0.04$. The function $\alpha_S^2$ in eq 3.4 is plotted as a solid curve in Figure 5a.

An empirical expression

$$\alpha_S^2(S - N) = (1 + 7.1928z + 8.8287z^2)^{0.1772} \tag{3.5}$$

can be proposed to match the Shanes–Nickel values of $2(2\nu - 1)$, $A_S$, and $\alpha_1^S$ at the large- and small-$z$ limits, similar to the procedure used by Muthukumar and Nickel in deducing eq 2.9 for $\alpha_R^2$. This equation reproduces the coefficient $b_S = 0.144$ in agreement with the theoretically-predicted $b_S = 0.151$. The comparison between eqs 3.4 and 3.5 is shown in Figure 5b, where the relative error $\alpha_R^2$(eq 3.5)/$\alpha_R^2$(eq 3.4) − 1 is plotted as a solid curve. We see that the difference between eqs 3.4 and 3.5 is very small.

**3.B. Extended Two-Parameter Theory and Comparison with SAW Models.** The recent MC simulation data of a SAW on a diamond lattice with an attractive potential by Yuan et al.[24] also probe the mean-square radius of gyration. We assume that the excluded-volume parameter $\bar{u}$ can be obtained through the same expression (eq 2.11) for the mean-square end-to-end gyration $\bar{R}^2$, and that the value $C_u = 1.3363$ fitted to $\bar{R}^2$ can also be used here. To test if the ratio $A_S/A_R$ is universal, we use the extended two-parameter theory (eq 3.2) and obtain $C_S$ by

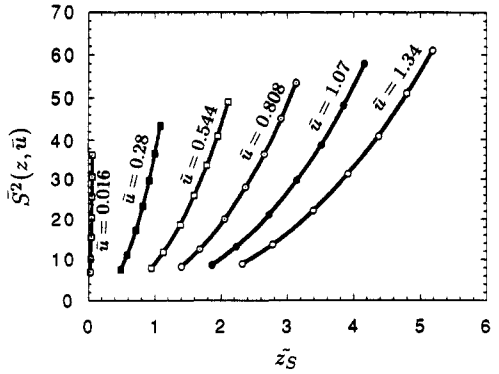


**Figure 6.** Comparison between the extended two-parameter theory (eq 3.2) (solid curves) and the MC data (symbols) of a SAW on a diamond lattice for $\bar{S}^2$ (ref 24).

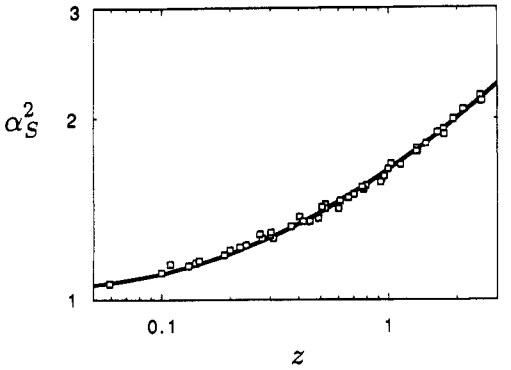


**Figure 7.** Comparison between the two-parameter theory (eq 3.7) (solid curve) and the experimental data of Miyaki et al. for PS cyclohexane (ref 27).

fitting to the MC data of Yuan et al. We found that the MC data can be represented *within the estimated errors* by

$$\alpha_S^{5.643} - (1-\tilde{u})\alpha_S^{0.395} = 0.35720(n\tau)^{1/2} \qquad (3.6)$$

This implies that a ratio of $A_S/A_R = 0.954$ can be estimated from Yuan et al.'s data, which is close to the ratio $A_S/A_R = 0.961$ predicted from the perturbation calculation for a continuum model by Shanes and Nickel.[25] Figure 6 shows excellent agreement between the MC data and representation 3.2 (solid curves), where $\bar{S}^2/b^2$ is plotted against a rescaled $\tilde{z}$ variable defined as

$$\tilde{z}_S = 0.3572(n\tau)^{1/2}$$

Using the values $A_S/A_R = 0.96$, $\tilde{C}_R(\mathrm{SC}) = 0.87$ in eq 2.15 and $\tilde{u}(\mathrm{SC}) = 1.93$ in eq 2.16, we have further deduced the value of $\alpha_S^2$ based on eq 3.2 for SC SAW, with the assumption that eq 3.2 can be extrapolated to $\tilde{u}(\mathrm{SC}) = 1.93$. We found that the predicted $\alpha_S^2$ is within 1% of Nickel's enumeration formula[4] for SC SAW with $n > 10$. The difference is probably due to the fact that eqs 2.3 and 3.2 should not be extrapolated too far from $\tilde{u} = 1$ for $\tilde{u} > 1$.

**3.C. Comparison with Experiments.** We now turn our attention to the light-scattering measurements. First we shall consider those near Θ conditions so that a two-parameter theory

$$\alpha_S^{5.643} - \alpha_S^{0.395} = 2.9713z \qquad (3.7)$$

can be tested. The two-parameter theory employed here depends on the smallness of $\tilde{u}$ near the Θ condition. A rough estimate below leads us to expect $\tilde{u} < 0.1$ for our first example below. One difficulty is to extract information about the relationship between the $z$ variable and the excluded-volume interaction. In principle, this relationship can be determined from the penetration function $\Psi$ data for small $z$, since *near the* Θ *point*, $\Psi = z + \mathcal{O}(z^2)$. However, the $\Psi(z)$ data for the experiments discussed here do not have the quality for such a study; therefore, we chose a different approach. We first determine the relationship between $z$ and the excluded-volume interaction through a fit to eq 3.7, and then *compare*, without any free parameter, to the $\Psi$ data. Our key assumption is that if the $z$ parameter determined this way and eq 3.7 are correct, the deduced $\Psi$ function from our theory should represent the experimental $\Psi$ data. We therefore write

$$z = c(1 - T\Theta/T)\bar{M}_w^{1/2} \qquad (3.8)$$

where $c$ is fitted from the data near the Θ temperature.

As the first example, the light-scattering data for polychloroprene (PCP) in *trans*-decalin solution,[26] represented by squares, are plotted in Figure 5a. We use the expression for a Θ solution

$$\bar{S}^2_\Theta = \frac{1}{6}bL = c_b\bar{M}_w \qquad (3.9)$$

where $c_b = 0.0888$ Å$^2$ is adopted from Norisuye et al.'s value for the Θ-temperature data, and $\bar{M}_w$ is the weight-averaged molecular weight.[26] The values

$$c = 5.355 \times 10^{-3} \quad T_\Theta = 275.05\ \mathrm{K} \qquad (3.10)$$

are used to convert the original data in temperature and molecular weight $\bar{M}_w$ to the excluded volume variable $z$. The value of $c$ is determined from a best fit of the experimental data to the RG scaling theory. This choice of $c$ is slightly larger than the estimate $c = 5 \times 10^{-3}$ from an original fit of the $\bar{S}^2$ data but is smaller than $c = 5.7 \times 10^{-3}$ from a fit of the initial slope of the $A_2$ data, both reported by Norisuye et al.[26]

As a second example we consider the light-scattering data for polyisobutylene (PIB) in isoamyl isovalerate (IAIV) solution,[27] represented by circles in Figure 5a. For $\bar{S}^2$ at the Θ condition, we use eq 3.9 with $c_b = 0.0952$ Å$^2$ reported by Matsumoto et al.[27] We also use eq 3.8 with

$$c = 3.776 \times 10^{-3} \quad T_\Theta = 295.25\ \mathrm{K} \qquad (3.11)$$

to convert the original data to the excluded-volume variable $z$. This value of $c$ is obtained from a fit of the experimental data to eq 3.7 which is slightly larger than the estimate $c = 3.06 \times 10^{-3}$ suggested by Matsumoto et al.[27]

As a third example we consider polystyrene (PS) in cyclohexane solution (Figure 7). The excluded-volume parameter $z$ is converted from eq 3.8 with

$$c = 7.23 \times 10^{-3} \quad T_\Theta = 307.7\ \mathrm{K} \qquad (3.12)$$

where $c$ is fitted to data reported by Miyaki et al.[27] at different temperatures and molecular weights. The experimental data points represented by the squares in Figure 7 are in excellent agreement with the RG scaling theory (solid curve in Figure 7).

We have used the Shanes–Nickel and Muthukumar–Nickel value for the asymptotic amplitude $C_S$ in eq 3.7. From eq 3.7 one can see that it is $\tilde{z} = C_S z$ that plays the role of the variable for $\alpha_S^2$. Since $c$ is fitted from experiments, it does not matter what value of $C_S$ is used. The light-scattering data alone cannot determine the correctness of the chosen value for $C_S$. For the value of $c$ quoted above, a few percent change will result in a much poorer comparison.

It would be interesting to further test the two-parameter theory (eq 3.7) for large $C_S z$ by increasing the molecular weight $M_w$ *near the* Θ *point so that the effect of finite* $\tilde{u}$ *can still be ignored.* Such a study can provide experi-

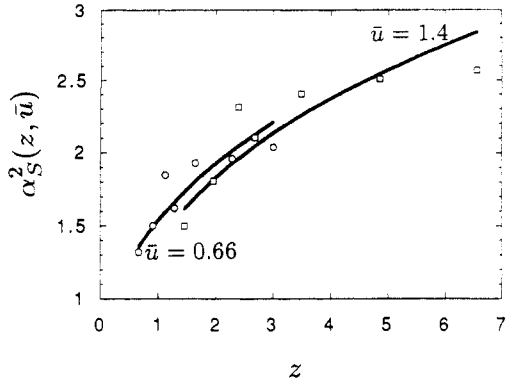


**Figure 8.** Comparison between the extended two-parameter theory (eq 3.2) (solid curve) and the experimental data of Norisuye et al. (ref 26). The square symbols represent PCP in *n*-butyl acetate, and the circle symbols represent PCP in carbon tetrachloride.

mental information about the critical exponents $\nu$ and $\Delta$. However, the fact that most experiments performed for large $z$ are realized at a temperature far away from the $\Theta$ condition (with a large $\bar{u}$) makes a test for the large-$z$ behavior of a two-parameter theory (e.g., eq 3.7) impossible; instead, one needs to use an extended two-parameter theory such as eq 3.2 to study these data. However, the restriction on the validity of eq 3.2 (that eq 3.2 cannot be extrapolated to a very large $\bar{u}$) has limited our ability to study experimental data at very large $\bar{u}$. Here we present only a comparison of eq 3.2 to the experiments that give a moderate fitted value of $\bar{u}$.

The light-scattering data for PCP in *n*-butyl acetate[26] are plotted in Figure 8. In converting the original data to the $\tilde{z}$ variable, we have written

$$z = c'\bar{M}_w^{1/2} \tag{3.13}$$

with fitted

$$c' = 3.679 \times 10^{-3} \qquad \bar{u} = 1.411 \tag{3.14}$$

in eq 3.2. We assume that a flexible chain in different solutions corresponds to different values of the excluded volume $w$ but the same Kuhn length $b$. The ratio $\bar{u}/c' = 3.833 \times 10^2$ deduced here should be approximately a constant for PCP in all other solutions. We can then estimate $\bar{u}$ for the near $\Theta$ condition data of (PCP) in *trans*-decalin solution presented above. The largest $\bar{u}$ is less than 0.1 which justifies the use of a two-parameter theory for a study of these data. We have also compared eq 3.2 with PCP in carbon tetrachloride,[26] with a fixed ratio $\bar{u}/c' = 3.833 \times 10^2$ and adjustable $c'$. We found

$$c' = 1.730 \times 10^{-3} \tag{3.15}$$

from a fit of eq 3.2 to experimental data, which implies $\bar{u} = 0.6637$. Figure 8 shows the result of this comparison.

There are other experiments that determine the $\tilde{S}^2$ data at temperatures far away from the $\Theta$ condition,[29-32] corresponding to large excluded volumes. The comparison is not presented here since the fitted $\bar{u}$ values are too high, and we expect that eq 3.2 is no longer valid at such high values of $\bar{u}$. It is evident, however, that an extended two-parameter model is preferred because of the high $\bar{u}$ seen in such a study. A simple extended two-parameter theory for large $\bar{u}$ will require more theoretical investigation.[4]

## 4. Second Viral Coefficient and the Penetration Function

The extended two-parameter model based on the RG scaling theory predicts for the second virial coefficient[22]

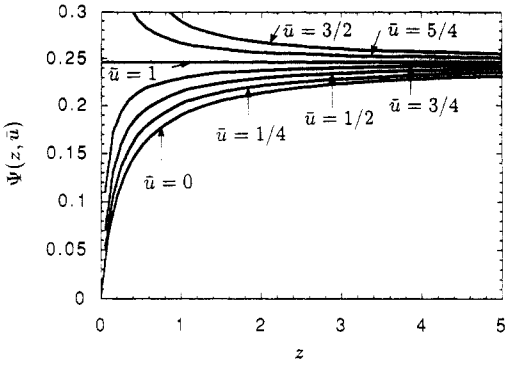


**Figure 9.** Extended two-parameter theory for the $\Psi(z,\bar{u})$ function (eq 4.3). The $\bar{u} = 0$ curve corresponds to a two-parameter model.

$$A_2 = {}^1/_2 wL^2 \mathcal{A}(z,\bar{u}) \tag{4.1}$$

where the crossover function $\mathcal{A}$ can be written in terms of $\alpha_S$ and $z$:

$$\mathcal{A}^{-2.513} - (1-\bar{u})\mathcal{A}^{-0.528} = C_A z \alpha_S \tag{4.2}$$

Here $e_3 = (\nu - \Delta)/(2-3\nu) = 0.528$ and $e_4 = \nu/(2-3\nu) = 2.513$ are universal constants, and the function $\alpha_S$ is derived from eq 3.2.

Investigation of the dimensionless penetration function[1]

$$\Psi(z,\bar{u}) = \frac{A_2}{4\pi^{3/2}S^3} = \frac{z\mathcal{A}(z,\bar{u})}{\alpha_S{}^3(z,\bar{u})} \tag{4.3}$$

is a powerful probe that clearly illustrates different physical behaviors between two families $\bar{u} < 1$ and $\bar{u} > 1$ as shown in Figure 9 (see below for the choice of the constant $C_A$). The function $\Psi$ has the following asymptotic behavior:

$$\Psi(z) = z(1 + \alpha_1{}^{\Psi} z + \ldots) \qquad z \ll 1 \qquad \bar{u} \ll 1 \tag{4.4}$$

and

$$\Psi(z,\bar{u}) = \Psi^*[1 + (1-\bar{u})b_\Psi z^{-2\Delta} + \ldots] \qquad z \gg 1 \tag{4.5}$$

where $\Psi^*$ is a universal constant and $b_\Psi$ is negative. When $\bar{u}$ is small, the correction-to-scaling term has a negative coefficient; the $\Psi$ function crosses over from $\Psi^*$ at a large $z$ to $\Psi = 0$ at $z = 0$, which is the behavior given by a two-parameter theory (curve labeled $\bar{u} = 0$ in Figure 9). As evident in eq 4.5, when $\bar{u}$ is greater than 1, $\Psi$ increases when $z$ decreases, exhibiting a SAW-like behavior[4] (curves having $\bar{u} > 1$ in Figure 9). This feature qualitatively describes the non-two-parameter $\Psi$ behavior suggested by Fujita and Norisuye.[21]

One interesting feature in eqs 4.1 and 4.2 is that it contains a coefficient $C_A$, hence $\Psi^*$, as a parameter. If accurate experimental data for $\Psi$ are available, the value of $C_A$ in principle can be obtained from experiments.

**4.A. Two-Parameter Theory and Comparison with Direct Renormalization Result.** In order to completely specify eq 4.2, we need to obtain the value of $C_A$. The estimate based on $\epsilon$ expansions for $\Psi$ is approximately[12,33,34]

$$\Psi^*_\epsilon = 0.27 \tag{4.6}$$

The numerical quadrature analysis of Barrett predicts[35]

$$\Psi^*_{\text{Barrett}} = 0.24 \tag{4.7}$$

The recent SAW model calculation on SC lattice gives[4]

$$\Psi^*_{\text{SC}} = 0.2465 \tag{4.8}$$

There are inconsistencies in the literature regarding the value of $\Psi^*$ to be used. Experimentally, two different behaviors of $\Psi$ have been observed corresponding to the

$\bar{u} < 1$ and $\bar{u} > 1$ cases (Figure 9). For experiments exhibiting $\bar{u} < 1$ behavior, the value $\Psi^*$ is an upper bound for the penetration function. It would be ideal to measure the $\Psi$ function near a $\Theta$ point ($\bar{u} < 1$) for a very-high-molecular-weight polymer which would asymptotically approach $\Psi^*$. For those experiments exhibiting $\bar{u} > 1$ behavior, however, $\Psi^*$ is a lower bound but *not* an upper bound for $\Psi$. As a consequence, for experiments that exhibit this behavior, the high values of $\Psi$ at small $z$ *do not* indicate a high $\Psi^*$. One example is the experimental data of polybutadiene in cyclohexane at 25 °C as tabulated in Table XI of ref 37. The *function* $\Psi$ (not the *value* $\Psi^*$ as denoted in ref 37) decreases when the molecular weight increases. The asymptotic behavior at large molecular weight approaches approximately 0.25 or even lower, which sets the upper limit for the value of $\Psi^*$. That the $\Psi$ function follows a $\bar{u} > 1$ behavior in this experiment is further supported by the fact that the effective exponent measured for the radius of gyration is 1.183, higher than the expected $2\nu = 1.176$; this higher effective exponent is caused by the negative correction-to-scaling amplitude (large $\bar{u}$). In another example, the $\Psi$ functions measured by Fukuda et al.[31] and Miyaki et al.[32] approach an average value $\Psi = 0.22$ for large molecular weight. Considering the large fluctuations in the $\Psi$ measurements, we conclude that this does not necessarily indicate a lower value for $\Psi^*$. The most recent experimental results reported by Fetters et al.[38] gives a smooth $\Psi$ curve that approaches $\Psi^* \approx 0.24$–$0.25$.

As an application of our theory, we use the most recent SAW $\Psi^*$ value (eq 4.8). The choice is not limiting, and any other choice for $\Psi^*$ could also be used in the model. The two-parameter limit of eq 4.2 becomes

$$\mathcal{A}^{-2.513} - \mathcal{A}^{-0.528} = C_A z \alpha_S \tag{4.9}$$

By taking the large-$z$ limit of eq 4.9, we found

$$C_A = 6.498 \tag{4.10}$$

Expanding eqs 4.9 and 4.2 at the large- and small-$z$ limits and comparing with eqs 4.4 and 4.5 yields $\alpha_1^{\Psi} = -4.968$ and $b_{\Psi} = -0.297$, which can be compared with $\alpha_1^{\Psi} = -4.78$ deduced from a perturbation theory. Using eq 4.9, we calculate the two-parameter theory $\Psi(z,0)$ as shown by the solid curve in Figure 10a.

Nickel has used a direct-renormalization technique to obtain the two-parameter penetration function in the form[4]

$$\left(\frac{z}{\Psi}\right)^{0.93} = \frac{\exp\{0.1457 \arctan [2.3677\Psi/(1 - 0.40\Psi)]\}}{(1 - \Psi/0.2465)(1 - 0.80\Psi + 5.76\Psi^2)^{0.0544}} \tag{4.11}$$

This expression gives $b_{\Psi} = -0.293$ which can be compared with our estimate $b_{\Psi} = -0.297$. A comparison of eqs 4.9 and 4.11 shows good agreement (see Figure 10b).

Douglas and Freed have also proposed an expression for $\Psi$ in a two-parameter theory:

$$\Psi = 0.207\lambda(z) + 0.062\lambda^2(z) \qquad \lambda(z) = \frac{4.831z}{1 + 4.831z} \tag{4.12}$$

This expression gives $\Psi^* = 0.269$ which is perhaps too large as explained above. Here we have rescaled the $z$ variable in the original Douglas–Freed expression in order to make $\Psi \to z + \ldots$ at the small-$z$ limit. The dashed curve in Figure 10a shows this equation.

There are also two-parameter theories proposed by Yamakawa, Kurata, and co-workers,[18,39,40] Flory and co-workers,[41] Fixman and co-workers,[43,44] and Albrecht.[44] These theories yield incorrect large-$z$ behavior and thus cannot be used in describing experimental data in the entire $z$ range.

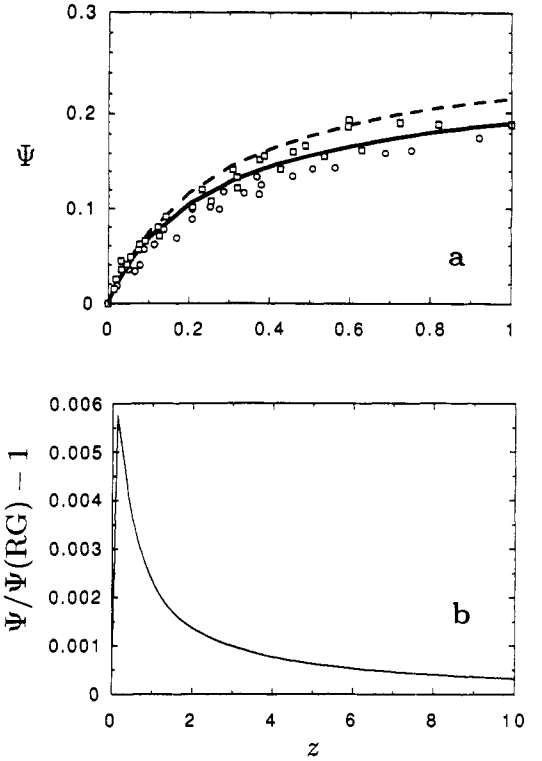


**Figure 10.** (a) Two-parameter model $\Psi(z,0)$ (solid curve) and experimental data of Norisuye (ref 26, square symbols) and of Matsumoto (ref 27, circle symbols). The Douglas–Freed equation (eq 4.12) is plotted as a dashed curve. (b) Relative differences between the RG scaling equation and the Nickel equation (eq 4.11).

**4.B. Extended Two-Parameter Theory and Comparison with SAW Result.** In the previous sections, we have assumed that our extended two-parameter models (eqs 3.2 and 2.3) can be extrapolated to large $\bar{u}$ and compared with the SAW results. Using the $\bar{u}$(SC) value obtained in eq 2.16, and eqs 3.2 and 4.2, we have plotted the $\Psi(z,\bar{u})$ function (solid curve) deduced from our model in Figure 11a. The curve deviates from the enumeration SAW results by Prooyen and Nickel[36] (dashed curve) at small $z$. However, the qualitative behavior is correct. The deviations at small $z$ are possibly due to the incorrectness of extrapolating eqs 3.2 and 4.2 to a $\bar{u}$ as high as 1.9; it could also be due to the effect of rigidity for short chains.

**4.C. Comparison with Experiments.** As pointed out earlier, the ideal procedure of comparing a theory with experimental results would be to obtain the relationship between the $z$ parameter and the temperature from the $\Psi$ data near the $\Theta$ point. The experimental data we studied, however, lack the good quality for which this analysis can be conducted. Therefore, we fitted the proportionality constant $c$ in eq 3.8 in order to determine the $z$ parameter. Then, a good test of the theory will be to see if the determined $\Psi(z,\bar{u})$ function (eq 4.3) can be used to describe the $\Psi$ data.

Figure 10a shows the penetration-function data extracted from the experimental light-scattering and osmotic-pressure measurements by Norisuye et al.[26] (square symbols) and by Matsumoto et al.[27] (circle symbols) for the polymers in solutions mentioned in section 3.C. These data are obtained near the $\Theta$ point, so that a two-parameter theory is assumed to be valid. We have used the same $z$ variable as described above with no adjustable parameters. It is seen that eqs 4.9 and 3.7 can be satisfactorily used to represent the experimental data.

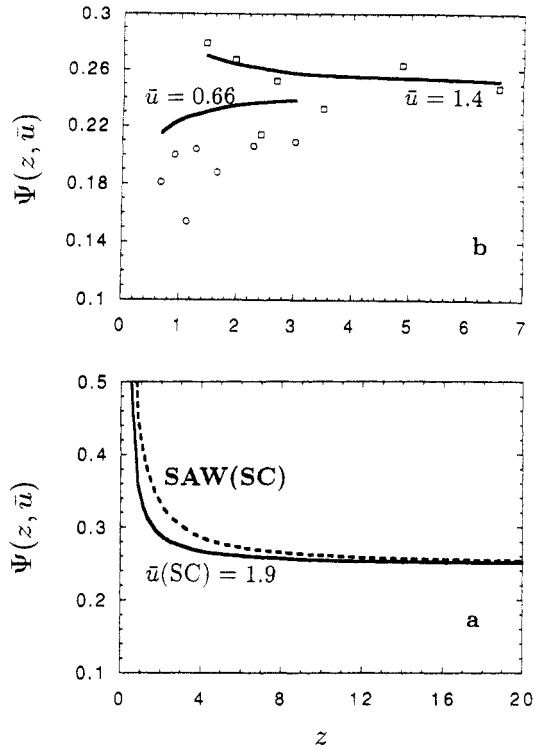


**Figure 11.** Extended two-parameter model (eq 4.2) (solid curve) and comparison with (a) the SAW model (dashed curve) (ref 4) and (b) the experimental data of Norisuye et al. (ref 26; see also Figure 8).

Figure 11b shows a comparison of the extended two-parameter theory (eqs 4.2 and 3.2) with the experimental data of Norisuye et al.[26] for nonzero $\bar{u}$. The same value of the parameter $\bar{u}$ is used as for the $\bar{S}^2$ case in section 3.C so that no adjustable parameter is used. It is interesting to see that the $\bar{u} = 1.3$ curve indeed describes the extended two-parameter behavior of PCP in *n*-butyl acetate.

## 5. Summary

It has been more than 40 years since Flory[9] first addressed the problem of flexible polymer chains in solution. Since then, many two-parameter models have been proposed for the mean-square end-to-end separation and radius of gyration and second virial coefficient. The basic assumption in a two-parameter theory is the smallness of the excluded-volume interaction $w$ in comparison with, e.g., the Kuhn length. This assumption leads to universal functions for flexible polymer chains as a result of the excluded-volume effect. Some experiments and the SAW models deal with strong excluded-volume interactions, making it necessary to study an extended two-parameter model which contains the effect of a finite excluded volume. This paper analyzes the extended two-parameter model based on our recent RG scaling theory which goes beyond the standard two-parameter model.[22]

We have not mentioned up to this point the effect of rigidity for short chains. For a wormlike chain, one expects that more system-dependent features come into the theory. It is also important to incorporate the excluded-volume effect into a wormlike chain description. This problem is discussed elsewhere.[22]

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