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Can the Twofold Structure of Renormalized Two Parameter Theory Explain Experiments in Good Solvents?

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ABSTRACT: Within the framework of renormalized two parameter theory we analyze data on dilute polymer solutions in good solvents. We find that the data support the structure of two universal branches, which recently has been exhibited theoretically and in Monte Carlo simulations. In particular, in contrast to the original interpretation of the data, we find no breakdown of two parameter theory due to stiffness corrections, which were claimed to vanish only slowly with increasing chain length. We also consider this claim from the theoretical point of view, explaining how renormalization takes care of these corrections.

1. Introduction

Properties of dilute polymer solutions are often analyzed within the framework of "two parameter" theories. In this approach the microstructure of the polymer chain is described by only two parameters, the elementary segment size l and a (repulsive) excluded volume coupling β_e. In macroscopic observables these microscopic parameters occur only in combination with the chain length N (polymerization index), the macroscopic parameters being the radius R_0 of a noninteracting Gaussian chain

$$R_0 = lN^{1/2}$$

and an interaction parameter

$$z \sim \beta_e N^{1/2}$$

Early theories, as reviewed in ref 1, are based on a straightforward cluster expansion in powers of z. In general only a few terms of this expansion are available, and the approach is restricted to values of $z \lesssim 1$. For long chains, $N \gg 1$, this confines these early approaches to a neighorhood of the Θ-temperature, where $T = \Theta$ is defined by the vanishing of β_e. In particular, the excluded volume limit $z \to \infty$ with its nontrivial power laws and scaling laws cannot be treated properly and is dealt with on a fairly heuristic level.

The application of the renormalization group allows these restrictions to be overcome, showing that the physics of not too concentrated polymer solutions is part of the realm of critical phenomena. Exploiting highly nontrivial transformation properties of the two parameter model under a change of the microscopic length scale l, this theory yields a "renormalized" cluster expansion which describes both the Θ-temperature and excluded volume limits, as well as the crossover between these limiting situations. The approach has met with considerable success in a quantitative explanation of experiments. (See, for instance, refs 2 and 3.) Thus, 5 years ago one might have considered the theory of equilibrium properties of dilute polymer solutions as basically a closed subject, with some annoying but minor defects, as will be pointed out below. This status of the problem is reviewed in refs 4 and 5.

However, some years ago Nickel[6] reminded us that our picture was not complete. Analyzing very precise Monte Carlo data, he recalled and stressed that the general renormalization group framework allows for two branches of physical behavior. Besides the weak coupling branch, which interpolates among Θ or excluded volume behavior, there is a strong coupling branch. The latter is not connected to a Θ-point region but connects the excluded volume limit to a region of very large coupling, eventually leaving the domain of perturbative renormalization group theory. With increasing chain length, physical systems described by the two different branches reach the asymptotically valid excluded volume power laws from opposite sides. Nickel found the strong coupling branch to be relevant for a description of self-avoiding lattice walks. His findings were confirmed by recent high-precision Monte Carlo work of Li et al.[7]

We have recently shown[8] how to describe the two branches within analytic renormalization group theory based on standard field theoretic methods. (For general critical phenomena related discussions may be found in ref 9.) In ref 10 the theory was compared to Monte Carlo data for the end-to-end distance of a polymer chain, with quantitative success. In full agreement with the work of refs 6 and 7 it was found that strictly self-avoiding walks on a lattice or the pearl-necklace model of hard beads in continuous space are described by the strong coupling branch. Adding a short-ranged attraction, we, however, may jump to the weak coupling branch, reaching a Θ-point as the attraction increases.

The work described above was essentially motivated by Monte Carlo data. With extremely small statistical error such data now are available for very long chains. $N = 80000$ has been reached in ref 7, and data for all chain lengths of $1 \leq N \leq 10^5$ have been determined by Grassberger.[11] Furthermore, being taken for strictly monodisperse samples, the data are not plagued by polydispersity effects. This is a great advantage as compared to physical experiments. Yet this line of development meets with recent research motivated by experiments in good solvent systems. Such systems typically are described as being in the excluded volume limit, obeying simple scaling and power laws. However, as has been remarked repeatedly over the years (see, for instance, ref 12), these systems have a tendency to show corrections to the asymptotic laws which cannot be interpreted in terms of the weak coupling branch of a two parameter theory. In particular, the interpenetration ratio ψ seems to reach its asymptotic limit from above, in agreement with Monte Carlo data for self-avoiding walks but in contradiction with two parameter theories based on the weak coupling branch. In a series of papers Yamakawa and his group reexamined this

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question both experimentally[13,14] and theoretically.[15] They concluded that the data for the radius of gyration R_g, the second virial coefficient A_2, the interpenetration ratio ψ, or the intrinsic viscosity in the dilute limit are well explained by the model of a helical wormlike chain. This model includes much more of the realistic microscopic features than are taken account of in two parameter theories. In particular in their interpretation of the data, stiffness plays an important role even for chain lengths of the order of $N \approx 10^4$. They suggest that two parameter theory becomes valid only for extremely long chains.

In the present paper we analyze good solvent data for R_g, A_2, and ψ with regard to the recent developments of renormalized two parameter theory. We find that within their nonnegligible scatter the data for $N \gtrsim 500$ can well be described by the two branches of our theory. For shorter chains ($500 \gtrsim N \gtrsim 100$) we expect to see systematic deviations due to $1/N$ effects of various origin (end effects, stiffness, three body forces, etc.), but the scatter of the data generally does not allow for firm conclusions.

A related route to extending the two parameter scheme was suggested in ref 16. This work is somewhat similar to those of refs 6, 8, and 10, but the structure of the two universal branches was missed. Furthermore, according to refs 13 and 14, it fails to account for the recent data, though it is consistent with Monte Carlo data and also roughly explains older experiments.

In the next section we present the relevant results of the renormalized two parameter theory in the form of simple expressions adequate for a comparison to present day experiments. The more accurate full results of our renormalization group calculation are given in the Appendix. Section 3 is devoted to the comparison with experiment. In the concluding section we discuss the relationship of our interpretation to that based on the helical wormlike chain model, pointing out some serious inconsistencies of that approach.

2. Strong or Weak Coupling Branches of Renormalized Perturbation Theory

Renormalization maps the bare two parameter model, which is defined in terms of l and β_e, onto a renormalized model defined in terms of a new length scale l_R and a new coupling u (l_R). If we were able to calculate the physical quantities to all orders, the scale l_R could be chosen arbitrarily, without changing the macroscopic predictions of the theory. This expresses the scale invariance of the model. In evaluating low-order renormalized perturbation theory, we however use a special choice of l_R to enforce a good expansion scheme. For quantities involving only a few chains (dilute limit) l_R must be chosen to be of the order of the radius of gyration R_g, which is the relevant macroscopic length scale. For $N \to \infty$, i.e. $l_R \sim R_g \to \infty$, $u(l_R)$ tends to a fixed point value u^*, which governs the excluded volume limit. Depending on the starting value $u_0 = u(l_R = l)$, the function u (l_R) with increasing $l_R \sim R_g$ may approach u^* from below (weak coupling branch, $u_0 < u^*$) or from above (strong coupling branch, $u_0 > u^*$). Polymers in Θ-solvents are described by the weak coupling branch since u_0 is very small, vanishing at the Θ-temperature. This branch smoothly evolves from the bare two parameter theory, which is valid infinitesimally close to the Θ-temperature (provided we ignore effects of three body forces). It is the weak coupling situation that has been considered in most previous renormalization group studies. The strong coupling branch, $u > u^*$, has been ignored, for purely theoretical reasons discussed, for instance, in refs 8−10. However, considering the strong coupling branch seriously, we find that it describes for instance, purely self-avoiding walks on cubic lattices.[6,10]

Results of low-order renormalized perturbation theory for R_g^2 and A_2, valid for monodisperse systems for both the strong and the weak coupling branches, have been presented previously.[8] We there included corrections due to stiffness or to the finiteness of the number of discrete segments, and we compared two different renormalization schemes. Here we omit all corrections to the two parameter model, and we exploit the results of "field theoretic" renormalization, where the mapping from the bare to the renormalized model is known with high precision. The results, as presented in the Appendix, naturally take an implicit form, involving the auxiliary variable $f = u(l_R)/u^*$. This form is not practical for a comparisons with experiment. Numerically evaluating the results, we therefore eliminate f to find simple and sufficiently accurate analytical parametrizations in terms of variables which are easily accessible experimentally. We thus will present R_g^2, and A_2 as explicit functions of

$$\tilde{R}_0 = \tilde{l} N^{1/2}$$

$$\tilde{z} = \tilde{v} N^{1/2} \tag{1}$$

where $\tilde{l}$ and $\tilde{v}$ are nonuniversal fit parameters. We must, however, generalize our previous calculation to include arbitrary polydispersity, which is a straightforward task. As a result it is useful to replace $\tilde{R}_0$ and $\tilde{z}$ with two other parameters

$$\tilde{R}_{0,w} = \tilde{l} N_w^{1/2}$$

$$\tilde{z}_w = \tilde{v} N_w^{1/2} \tag{2}$$

where N_w is the weight average chain length. We also introduce the average radius of a fictitious noninteracting chain:

$$\tilde{R}_{0,z} = \tilde{l} N_z^{1/2} \tag{3}$$

where N_z is the well-known z-average chain length. Lacking information on the precise form of the chain length distribution, we will assume a Schultz distribution which is defined in terms of the single parameter

$$\tilde{p}'' = N_w/N \tag{4}$$

Then

$$\tilde{R}_{0,z}^{\;2} = \left(2 - \frac{1}{\tilde{p}''}\right)\tilde{l}^2 N_w \tag{5}$$

We now are prepared to write down our parametrization of the theoretical results. Introducing a theoretical swelling factor

$$\bar{\alpha}_g^{\;2} = R_g^{\;2}/\tilde{R}_{0,z}^{\;2} \tag{6}$$

we find for the strong coupling branch

$$\bar{\alpha}_g^{\;2} = (\bar{\alpha}_g^*)^2 \left[1 - 0.54\tilde{z}_w^{\;-0.941}\left(1 + \frac{0.44}{\tilde{z}_w}\right)\right], \qquad \text{strong coupling, } \tilde{z}_w \geq 3 \tag{7}$$

where

$$(\bar{\alpha}_g{}^*)^2 = (0.843 + 0.762c_g)\left(\frac{\tilde{z}_w}{(\tilde{p}'')^{1/2}}\right)^{0.352} \qquad (8)$$

represents the asymptotic power law and

$$c_g = 0.288(\tilde{p}'' - 1) - 0.70(\tilde{p}'' - 1)^2 \qquad (9)$$

parametrizes the polydispersity correction. The parametrization (7) reproduces the numerical results of our theory with deviations of less than 0.5% for monodisperse systems and within 3% for reasonably sharp chain length distributions ($1 \le \tilde{p}'' \lesssim 1.5$). The restriction $\tilde{z}_w \gtrsim 3$ reflects our estimate of the region of validity of our theory. (See the Appendix.) Recall that for the strong coupling branch the coupling constant u increases as we go away from the excluded volume limit $\tilde{z} = \infty$, presumably diverging for $\tilde{z} \to 0$. Thus, perturbation theory breaks down *below* some finite value of $\tilde{z}$.

For the weak coupling branch $\tilde{z}$ can cover the whole range $0 \le \tilde{z} \le \infty$, and a good parametrization of our result for the swelling factor in all that range takes the form

$$\bar{\alpha}_g{}^2 = [1 + (1.320 + 5.263c_g)\tilde{z} + 0.378\,(1 + 0.904c_g)^{1/0.176}\tilde{z}^2]^{0.176} \qquad (10)$$

The accuracy is better than 0.5% for all $\tilde{z}$ and polydispersities $1 \le \tilde{p}'' \le 2$. We should note that for a monodisperse ensemble Shanes and Nickel[17] have derived a parametrization based on a higher order calculation within the bare two parameter model, improved by a renormalization procedure. After an appropriate rescaling of $\tilde{z}$, eq 10 reproduces their result within deviations of 1%.

We now turn to the second virial coefficient A_2, which we define in terms of the forward scattering intensity $I_d(0)$.

$$I_d(0) = N_w c - A_2 c^2 + O(c^3) \qquad (11)$$

Here c is the segment concentration (number of monomers per volume). A_2 is related to the standard experimental definition $A_2{}^{\mathrm{exp}}$ by

$$A_2 = 3.320 M_w{}^2 A_w{}^{\mathrm{exp}}$$

where $A_2{}^{\mathrm{exp}}$ is measured in (cm^3 mol)/g^2, A_2 is measured in Å^3, and M_w is the weight average molecular weight in units of g/mol. The prefactor is $2 \times 10^{24}/N_A$, where N_A is Avogadro's number.

For A_2 our parametrizations read

$$A_2 = (A_2^*)^2 \begin{cases} 1 + 0.528\tilde{z}_w{}^{-0.941}\left(1 + \dfrac{2.18}{\tilde{z}_w}\right), \\ \qquad \text{strong coupling, } \tilde{z}_w \ge 3 \\ \left(1 + \dfrac{2.622}{\tilde{z}_w} + \dfrac{1.219}{\tilde{z}_w{}^2}\right)^{-0.236}, \\ \qquad \text{weak coupling, } 0 \le \tilde{z}_w < \infty \end{cases} \qquad (12)$$

$$(4\pi)^{-3/2} A_2^* = 0.191\tilde{z}_w{}^{0.528}\tilde{R}_{0,w}{}^3 \qquad (13)$$

Irrespective of polydispersity these equations reproduce our full numerical results within deviations of less than 0.5%. Note that this implies that A_2 (for Schultz distributions) is insensitive to polydispersity, if expressed in terms of variables constructed from the weight average chain length.

Having at hand the expressions for A_2 and $R_g{}^2$, we easily can calculate the interpenetration ratio according to the definition

$$\psi = (4\pi)^{-3/2}\frac{A_2}{R_g{}^3} \qquad (14)$$

It is found to be extremely sensitive to polydispersity, dropping by more than 10% if $\tilde{p}''$ is increased from $\tilde{p}'' = 1$ to $\tilde{p}'' = 1.1$.

We here stress again that eqs 7, 10, and 12 are meant as simple and convenient representations of the analytical results, within the accuracy quoted above. They, however, do not incorporate all of the detailed structure predicted by the renormalization group. For instance, it is known that $\bar{\alpha}_g{}^2/(\bar{\alpha}_g{}^*)^2$ or $A_2/(A_2{}^*)^2$ for both branches can be expanded about $\tilde{z} = \infty$, the expansions proceeding in powers of $\tilde{z}^{-2\nu\omega} = \tilde{z}^{-0.941}$. The coefficients in these expansions are universal, except that we may change the definition of $\tilde{z}$ by an arbitrary factor. Also, microstructure terms not contained in the two parameter model introduce corrections, which depend on additional parameters. These "nonuniversal" corrections die out like $1/N^x$, where the exponent x is expected to be close to 1 but depends on the type of correction term. On the weak coupling branch these corrections can be suppressed in principle by increasing N and decreasing $T - \Theta$, keeping $\tilde{z}^{-2\nu\omega}$ fixed. On the strong coupling branch no such systematic tool is available, and it is an open question whether the RG two parameter type prediction is useful beyond the leading corrections of order $z^{-2\nu\omega}$. Only more precise and systematic experimental work can solve this question. We will find below that at present the experimental situation does not permit a check of these more detailed predictions and barely tests the two branched structure. A reader interested in seeing the full universal structure within the present approach is refered to the Appendix.

We want to close this section by recalling other well-known aspects of two parameter theories. As mentioned in the introduction, we take N to be the (number averaged) monomer number per chain. The microscopic parameters $\tilde{l}$ and $\tilde{v}$ are effective quantities which depend on polymer, solvent, and temperature. They collect the features of the microscopic structure relevant for the behavior of long chains but cannot simply and consistently be calculated from a microscopic model. The problem is that these parameters in principle are defined in the limit of an infinitely long chain. They, therefore, in particular cannot be determined in the oligomer region. Concerning the temperature dependence, only close to the Θ-temperature is the simple ansatz

$$\tilde{l}(T) = \tilde{l}(\Theta)$$
$$\tilde{v}(T) = v_1\frac{T - \Theta}{\Theta} \qquad (15)$$

justified. Further away from $T = \Theta$ we may need higher powers in $(T - \Theta)/\Theta$, even on the weak coupling branch. On the strong coupling branch, of course, any ansatz of the form (15) is meaningless, since no Θ-conditions can be identified. This, however, does not invalidate the role of $\tilde{l}$ and $\tilde{v}$ (or $\tilde{R}_0$ and $\tilde{z}$, equivalently) as effective parameters. Furthermore, these essentially theoretical considerations do not exclude the possibility of finding

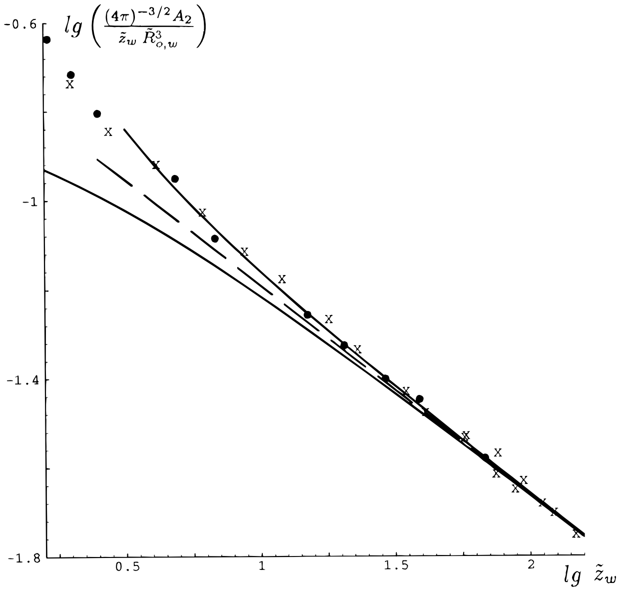

Figure 1. $\log((4\pi)^{-3/2}A_2/(\tilde{z}_w\tilde{R}_{0,w}{}^3))$ against $\log \tilde{z}_w$. The broken line represents the asymptotic power law. The weak couping branch lies below and the strong coupling branch lies above that line. Data: (•) polystyrene−toluene, T = 15 °C[13]; (×) polystyrene−benzene, T = 25 °C.[18,19]

useful empirical laws, which for a class of systems relate $\tilde{l}$ and $\tilde{\nu}$ to microscopic features of the polymer solution.

As an immediate consequence of this discussion finally we note that the swelling factor $\alpha_g{}^{\text{exp}}$, relating $R_g(T)$ to $R_g(T{=}\Theta)$ in a Θ-solvent, is not universal but differs from the universal two parameter result (weak coupling) by a factor of $\tilde{l}(T)/\tilde{l}(\Theta)$:

$$\alpha_g^{\text{exp}} = \frac{\tilde{l}(T)}{\tilde{l}(\Theta)}\bar{\alpha}_g \tag{16}$$

Thus, the standard plot of ψ against $\alpha_g{}^{\text{exp}}$ a priori is not universal, a well-known feature that has been often mentioned before.

3. Comparison with Experiment

Being insensitive to polydispersity, the second virial coefficient is the most attractive quantity to be considered. Figure 1 shows our results. We choose to plot $\log((4\pi)^{-3/2}A_2/(\tilde{z}_w\tilde{R}_{0,w}{}^3))$ as function of $\log \tilde{z}_w$, since in this way we construct a scaling plot corresponding to the plot of $\log A_2{}^{\text{exp}}$ against $\log M_w$ typically found in experimental work. The two branched structure of our result clearly is seen, the two branches merging into the asymptotic power law for $\tilde{z}_w \gtrsim 50$. The strong coupling branch lies above the asymptote and has been cut off at $\tilde{z}_w = 3$. We include data on polystyrene (PS) in the good solvents toluene or benzene. These data clearly follow the strong coupling branch. The parameter values are collected in Table 1. We note that the asymptotic behavior (13) quite precisely fixes the combination $\tilde{l}\tilde{\nu}^{2\nu-1} = \tilde{l}\tilde{\nu}^{0.176}$ of the parameters, as given in the last column of Table 1. The uncertainty of this combination is of the order of 1%. In contrast, $\tilde{\nu}$ and thus the absolute values of $\tilde{z}_w$ here are determined only within an uncertainty of about a factor of 1.5. We further note that for the PS−toluene system the three points of smallest $\tilde{z}_w$ are taken for chain lengths of 20 $\lesssim N_w < 100$, where our theory should not apply. In fact we in principle expect to see nonuniversal $O(1/N)$ corrections for $N_w \lesssim 500$, corresponding to $\tilde{z}_w \lesssim 8$ and $\log \tilde{z}_w \lesssim 0.9$ for PS−toluene or $\tilde{z}_w \lesssim 4.5$ and $\log \tilde{z}_w \lesssim 0.65$ for PS−benzene. (This estimate is based on previous experience[3] with fitting to the renormalized two parameter theory as well as a consideration of results at the Θ-point.)

Table 1. Values of the Nonuniversal Parameters System

system	$\tilde{l}$ (Å)	$\tilde{\nu}$	$\tilde{l}\ \tilde{\nu}^{0.176}$
polystyrene−toluene	2.63	0.35	2.19
polystyrene−benzene	2.92	0.2	2.20
PMMA−chloroform[b]	3.23	0.14	2.28
PMMA−nitroethane	2.51	0.23	1.94
PMMA−acetone			1.66
polystyrene−cyclohexane	3.00	0.35t	
polystyrene−transdecaline	2.80	0.4t	
polyisobutylene−isoamyl valerate	2.30	0.13t	

[a] First four systems: strong coupling; last three systems: weak coupling. Here, $t = (T - \Theta)/\Theta$; all temperatures measured on the absolute scale. [b] PMMA = poly(methyl methacrylate).

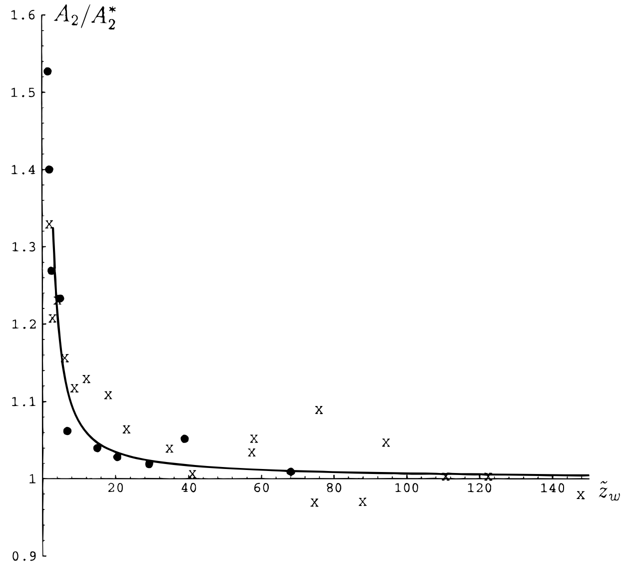

Figure 2. A_2/A_2^* as function of $\tilde{z}_w$. The curve represents the strong coupling branch, approaching the asymptotic limit A_2/A_2^* for $\tilde{z}_w \to \infty$. Data are the same as in Figure 1.

Previously[8] we have considered two sources of $1/N$ corrections: the finiteness of N in our discrete Gaussian chain model and local stiffness. This introduces two additional microscopic parameters into the model, and varying these parameters can modify the theoretical results considerably in the region of small N. To search for indications of such corrections, in Figure 2 we have plotted A_2/A_2^* where A_2^* for the data has been calculated from eq 13 with the given values of $\tilde{l}$ and $\tilde{\nu}$ and the experimental N_w. Clearly the data scatter too much to identify any significant systematic deviation from the two parameter curve.

Turning now to the radius of gyration, we are confronted with the problem of polydispersity. Furthermore, the square root plot, which frequently is used in the determination of $R_g{}^2$, has a tendency to underestimate the values, the effect systematically increasing with chain length and polydispersity. Thus, the number of good solvent data, which allow for a study of systematic deviations from the asymptotic power law, is quite restricted. In Figure 3 is data of ref 13 for the polystyrene−toluene system, divided by the asymptotic power law $(R_g^*)^2 = \tilde{R}_{0,z}{}^2(\bar{\alpha}_g^*)^2$ (cf. eq 8). This plot emphasizes the deviations from the asymptotics. In Figure 3 we distinguish between light scattering data

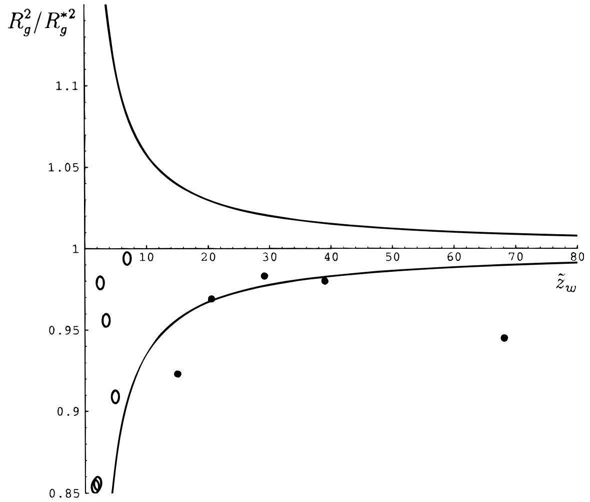

Figure 3. $R_g^2/(R_g^*)^2$ as function of $\tilde{z}_w$: (upper curve) weak coupling; (lower curve) strong coupling. Data: PS−toluene, $T = 15$ °C[13]; ●, light scattering; ○, X-ray scattering.

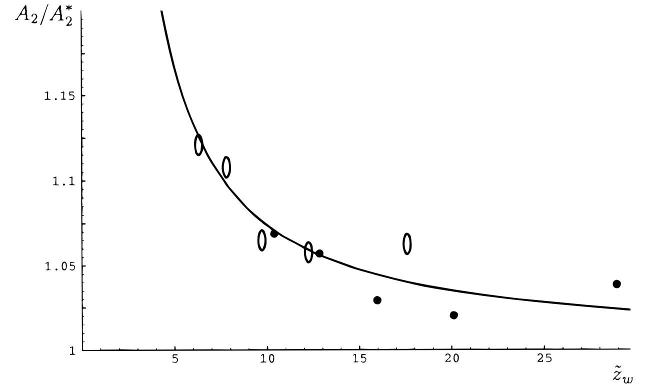

Figure 4. A_2/A_2^* as function of $\tilde{z}_w$. The curve represents the strong coupling branch. Data:[14] (○) PMMA−chloroform; (●) PMMA−nitroethane.

(points) and X-ray data (ellipsoids). One gets the feeling that there is a break between these two sets of data, a feature which we cannot comment upon. Furthermore, it should be noted that the point at highest $\tilde{z}_w$ may be somewhat low, due to problems of the square root plot. With all of these uncertainties we may say that the data scatter about the lower (strong coupling) branch of the theory. They clearly are inconsistent with the upper (weak coupling) branch.

Analyzing other systems in very good solvents, we often find that even for A_2 the data in a plot like Figure 2 scatter strongly, and we can say little more than that the data indicate deviations from the asymptotic law tending toward the strong coupling side. The data for $R_g^2/(R_g^*)^2$ typically scatter about 1 quite erratically. For systems where the data show a clear trend, often only a few samples have been measured. Still we include two such experiments[14] for long chains ($2000 \lesssim N_w \lesssim 16000$) in very good solvents: poly(methyl methacrylate) in chloroform or nitroethane. Figure 4 (A_2/A_2^*) or Figure 5 ($R_g^2/(R_g^*)^2$) show the data fitted to the strong coupling branch. Despite sizable scatter the data show clear strong coupling behavior.

We finally discuss an extensive set of data[14] for the system poly(methyl methacrylate)−acetone. Figures 6 or 7 show the results for $R_g^2/(R_g^*)^2$ and A_2/A_2^*, respectively, where we tentatively assigned a value of $\tilde{v} = 0.2$. (The combination $\tilde{l}\tilde{v}^{2\nu-1}$, as given in Table 1, again is fixed precisely.) Strong or weak coupling branches are

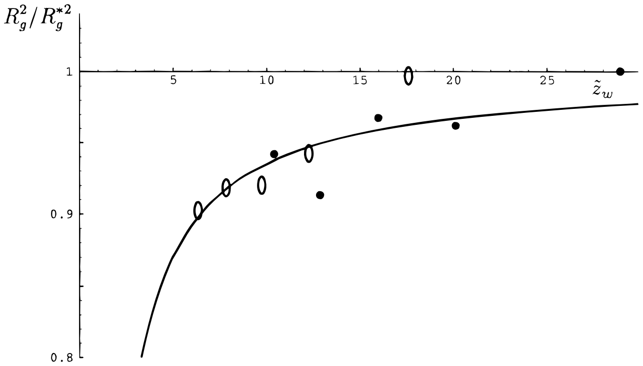

Figure 5. Same as Figure 4, for $R_g^2/(R_g^*)^2$.

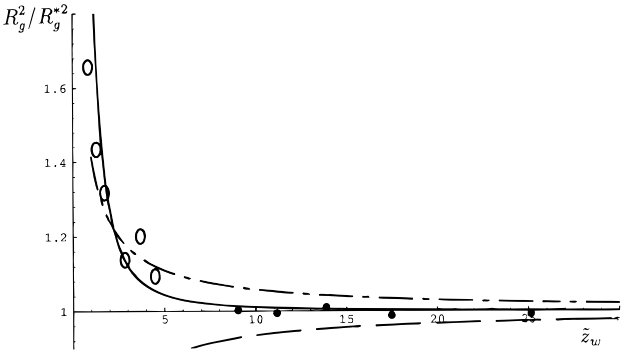

Figure 6. $R_g^2/(R_g^*)^2$ as function of $\tilde{z}_w$: (dotted−dashed curve) (weak coupling branch strong coupling branch. See the text for the full curve. Data for PMMA−acetone[14]: (●) $N_w \gtrsim 1180$; (○) $18 \lesssim N_w \lesssim 504$.

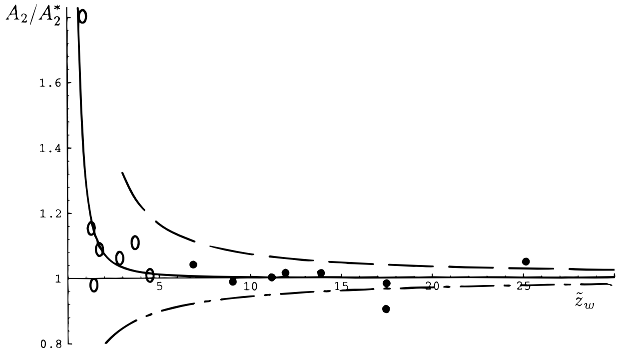

Figure 7. Same as Figure 6, for A_2/A_2^*.

represented by the dashed or dotted−dashed curves, respectively. Inspecting Figure 6, we might be inclined to describe the system by the weak coupling branch, but the data for A_2/A_2^*, with all their scatter, are not in favor of such an interpretation. Closer inspection shows that the data for $N_w \gtrsim 1000$ (points in Figures 6 and 7) are well-described by the excluded volume laws, with no indication of systematic two parameter type corrections. Deviations are found for $N_w \lesssim 1000$ only (ellipsoids) and, thus, could be described as nonuniversal corrections. As mentioned above, there are several sources of such corrections, some of which were not included in our previous theory,[8] and the data clearly scatter too much for a detailed analysis. In Figures 6 and 7 we therefore only include curves calculated according to the law $y/y^* = 1 + a/\tilde{z}_w^2$ (full lines; $a = 1.1$, $y = R_g$; $a = 0.3$, $y = A_2$). This simple ansatz should be viewed as roughly collecting all terms of order $1/N^x$, $x \approx 1$. As is obvious from Figures 6 and 7, the interpretation of the data as excluded volume behavior supplemented by $O(1/N)$ corrections, is not implausible.

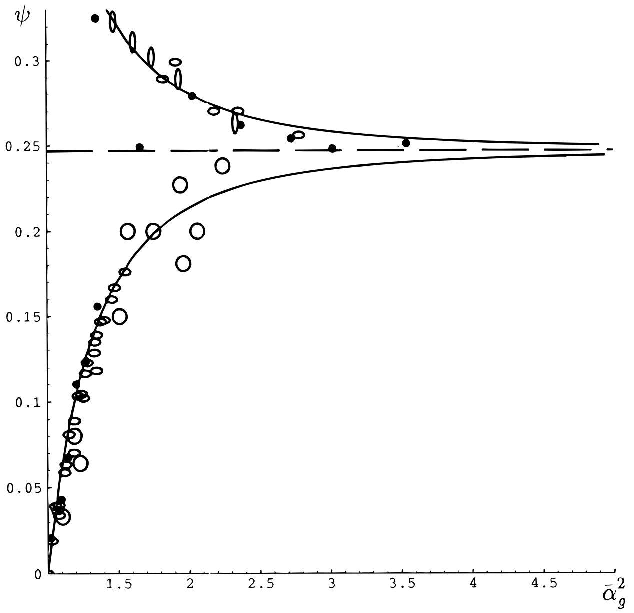

Figure 8. ψ as function of $\bar{\alpha}_g^2$: (upper curve) strong coupling branch; (lower curve) weak coupling branch; (broken line) excluded volume limit. Data, strong coupling: (●) PS−toluene;[13] PMMA−nitroethane;[14] PMMA−chloroform.[14] Data, weak coupling: (●) PS−cyclohexane;[20] poly(isobutylene)−isoamyl valerate;[21] PS−transdecaline.[22]

For completeness we now consider the interpenetration ratio ψ (eq 14), which of course does not contain new information, once we analyzed A_2 and R_g separately. Figure 8 shows ψ as function of $\bar{\alpha}_g^2$, where we also include data for Θ-solvent systems to decorate the weak coupling branch. (In view of the scatter of the data we did not apply polydispersity corrections for the fairly sharp fractions used.) This figure clearly illustrates that the two branched structure predicted by renormalized two parameter theory is supported by experiment.

To summarize, we find that systems which in previous renormalization group work have been interpreted as showing pure excluded volume power laws, upon closer inspection indicate strong coupling behavior. However, the statistical scatter is too large to test the precise shape of the theoretical curves or to exhibit the role of correction terms not included in the two parameter model. Thus, present experiments do not permit a check on the details of the renormalization group predictions or, on the quantitative level, allow us to discriminate among different implementations of the theory which yield slightly different results.

4. Relation to the Theory of Helical Wormlike Chains

Over the years Yamakawa and co-workers have developed a theory[15] of excluded volume effects in helical wormlike chains, i.e. in chains possessing some degree of stiffness and having a tendency to form a helix on microscopic scales. Clearly this is a much more realistic model of the microstructure than the Gaussian chain or Edward's continuous chain which underlies the two parameter theory. The Yamakawa−Shimada (YS) theory proceeds by two steps. First the quantity of interest is calculated to lowest nontrivial order in the cluster expansion, using the full microscopic model. (In our language this is just a one-loop approximation, also underlying, for the Gaussian chain model, the results of section 2.) This result is used to extract a correction factor $K(N)$, which renormalizes the z-parameter of the bare two parameter theory as

$$z \rightarrow \hat{z} = K(N)z \tag{17}$$

$K(N)$ depends on the physical quantity considered but has the general structure

$$K(N) = 1 + \frac{a}{N^{1/2}} + \frac{b}{N} + ... \tag{18}$$

Of course the unperturbed radius is calculated using the full model: $R_0 \rightarrow \hat{R}_0$.

The second step of YS theory then relies on parametrizations of the excluded volume effects for larger z as derived in two parameter theory. In these expressions z just is replaced by $\hat{z}$. Thus, YS theory smoothly interpolates among the behavior for $z << 1$ as given by the helical wormlike chain model and the asymptotic excluded volume behavior ($z \rightarrow \infty$, i.e. $N \rightarrow \infty$, $\hat{z} \rightarrow \infty$. Furthermore for A_2 also $1/N$ effects due to the interaction of the polymer end groups explicitly are taken into account. For the two parameter input the authors use results of Domb and Barrett,[23] which have been constructed by matching low-order results of the bare cluster expansion valid for $z \ll 1$ to results of Monte Carlo simulations found for $z \gg 1$.

The YS theory has met with truly remarkable success, as is illustrated in refs 13 and 14. It consistently fits data for R_g, A_2, ψ, and the intrinsic viscosity from the oligomer region $N \gtrsim 5$ to the largest chain lengths. As expected, large deviations from the two parameter model are seen for R_g and $N \lesssim 100$, even in a Θ-solvent at the Θ-temperature, and also end effects for A_2 become very important for such small N. What is less expected is the observation that in good solvents the "renormalization" (17) and (18) of z is found to be important even for long chains, $N \lesssim 10^4$, whereas the same chains show asymptotic Gaussian behavior at $T = \Theta$ in a Θ-solvent for $N \gtrsim 500$. This can be traced back to the slowly vanishing correction $\sim a/N^{1/2}$ in eq 18, which in YS theory is due to stiffness. Thus, it is concluded and stressed that stiffness in good solvents is important even for long chains, the asymptotic two parameter limit being attained only for extreme chain lengths. This finding, if true, would invalidate much of the renormalization group work.

However, we do not believe this conclusion is true. On the empirical level we have demonstrated above that renormalized two parameter theory adequately deals with the data at least in the range $N \gtrsim 500$, where Θ-point chains behave Gaussian. But we also must examine more closely YS theory itself.

First we note that the Domb−Barrett equations, used as a two parameter input, in light of our recent understanding must be abandoned. Since the Monte Carlo data are taken for systems lying on the strong coupling branch, these equations by construction interpolate between the weak and strong coupling branches.[10] This clearly is incorrect, despite its fair success. We lose the basic two branched structure. But this only is a side issue. The heart of the problem lies in the treatment of $K(N)$, eq 18. It is true that $K(N) \neq 1$ does not occur in a two parameter calculation starting from the *continuous chain model* with its unrestricted flexibility on arbitrarily small scales. Such terms, however, show up in a *discrete Gaussian chain model*, as is illustrated for instance by eqs 3.10−3.12 ($\beta_2 = 0$) of ref 8. Indeed, terms of type $za/N^{1/2} \sim a\beta_e$ are technically known as the leading cutoff corrections in a $d = 3$-dimensional theory, the role of the cutoff here being played by the finite segment size. Now renormalization basically consists of redefining the parameters of the theory so as to absorb these leading cut off corrections. We illustrate this with a somewhat oversimplified calculation. With some slight change of notation eqs 33, 34, 50, and 51 of the work of Shimada and Yamakawa[15] yield for the end-to-end distance R_e

$$R_e^{\,2} = R_{e,0}^{\,2}(1 + cK(N)z + O(\beta_e^{\,2}))$$

where c denotes some constant. To leading order in N, the relation $R_{e,0}^{\,2} = \hat{l}^2N(\ 1 + O(1/N))$ holds, and $K(N)$ has the form $K(N) = 1 + a/N^{1/2} + O(1/N)$. Thus,

$$R_e^{\,2} = \hat{l}N(1 + O(1/N))\ [1 + cz(1 + O(1/N)) + ca\beta_e + O(\beta_e^{\,2})]$$

$$= \hat{l}(1 + ca\beta_e)N(1 + O(1/N))[1 + cz(1 + O(1/N)) + O(\beta_e^{\,2})]$$

Clearly the factor $(1 + ca\beta_e)$ can be absorbed into a redefinition of $\hat{l}$, i.e. a renormalization. Now this by no means is the whole content of the renormalization group. A more careful discussion can, for instance, be found in section 4 of ref 8. This calculation, however, illustrates one of the important aspects of renormalization, viz., the way it eliminates the leading microstructure dependence. This well-known fact sometimes is obscured by first taking the continuous chain limit, thus simplifying the calculation on the technical level.

These considerations have important consequences: In so far as the effective two parameter results used in YS theory are meant to reproduce scaling functions of a renormalized two parameter theory, it is clearly inconsistent to introduce terms $\sim a/N^{1/2}$ once more in a further redefinition of z. They already have been absorbed into $\tilde{l}$ or $\tilde{v}$, which are to be treated as adjustable parameters. Furthermore, the renormalization of $\tilde{l}$ and thus of $\tilde{R}_0$ by interaction effects also shows that there is no justification to assume that $\tilde{R}_0$ for a long chain in a good solvent coincides with R_g of the same chain under Θ-conditions, even if this identification empirically is found to be valid in the oligomer region. Indeed, $\tilde{l}$ and $\tilde{v}$ by definition refer to long chains, where all $1/N$ corrections are negligible. These parameters can not be determined in the oligomer region.

To summarize the main points, we find that in a consistently renormalized two parameter scheme stiffness corrections in good solvents die out at the same rate as in Θ-solvents. Thus, the theory is likely to be valid as soon as the Θ-chains can be considered as Gaussian coils. We have analyzed data which have been claimed to support the opposite view, but we find that they are in accord with our theory. However, we have to be aware of the two branches predicted by the renormalization group. Only the weak coupling branch for $\tilde{z} \to 0$ ends at a Θ-point. Since the infinitely flexible continuous chain model becomes valid under Θ-conditions, it may be attractive to speculate that the strong coupling branch for $\tilde{z} \to 0$ tends toward a stiff rod. In this way the physical basis of our interpretation of the good solvent data might be related to that of YS or of Huber and Stockmayer.[24] Unfortunately perturbative renormalization group theory does not permit us to answer that interesting question.

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Appendix A: Results of First Order Renormalized Perturbation Theory

We use the standard methods of dimensional regularization and minimal subtraction in the form quoted in ref 8, section 4.2. For general dimension $d = 4 - \epsilon$, $\epsilon \geq 0$, our results read

$$R_g^{\,2} = -\frac{d}{3}\frac{\tilde{p}'''}{\tilde{p}''}l_R^2N_R\left[1 - \frac{u}{\epsilon} - \frac{u}{2}N_R^{\epsilon/2}\left(\frac{2}{\epsilon} - \frac{2}{2+\epsilon} - \frac{1}{4+\epsilon} + \frac{1}{6+\epsilon}\right)\int_0^\infty dy\ y^{3+\epsilon/2}\frac{p(y)}{\tilde{p}'''}\right] \quad \text{(A1)}$$

$$(4\pi)^{-d/2}A_2 = \frac{u}{2}l_R^{\,d}N_R^{\,2}\left\{\left(1 + \frac{2}{\epsilon}u\right)(\tilde{p}'')^2 - \frac{2}{\epsilon}u\frac{N_R^{\epsilon/2}}{(1 - \epsilon^2/4)(2 + \epsilon/2)}\left[\int_0^\infty dy\ p(y)y^{2+\epsilon/2}((4 + \epsilon)\tilde{p}'' + 2y) - \int_0^\infty dy_1\ dy_2\ p(y_1)\ p(y_2)y_1y_2(y_1 + y_2)^{2+\epsilon/2}\right]\right\} \quad \text{(A2)}$$

Here l_R, N_R, and $u = u(l_R)$ denote the renormalized length scale, the renormalized chain length, and the renormalized coupling, respectively. Polydispersity is taken care of by the reduced chain length distribution

$$p(n/N) = NP(n) \quad \text{(A3)}$$

where $P(n)$ is the probability of finding a chain of length n in the ensemble. $p(y)$ has the moments

$$1 = \int_0^\infty dy\ p(y) = \int_0^\infty dy\ yp(y);\quad \tilde{p}'' = \int_0^\infty dy\ y^2p(y);\quad -\tilde{p}''' = \int_0^\infty dy\ y^3p(y)$$

It must be noted that eqs A1 and A2 do not use the ϵ-expansion but are results of first order perturbation theory in u. We further note that the results to the order considered yield an internally consistent treatment of polydispersity but only approximately reproduce exact results known in special limits. We, for instance, easily may calculate the exact polydispersity dependence of R_g^2 in the excluded volume limit:

$$R_g^{\,2} \sim \frac{1}{\tilde{p}''}\int_0^\infty dy\ y^{2+2\nu}p(y)N^{2\nu}$$

Equation A1 underestimates the ratio $R_g^2[p(y)]/R_g^2$ [monodisperse] by about 5% for extremely broad polydispersity ($\tilde{p}'' = 2$). Also, eq A2 does not incorporate the behavior expected for a bimodal distribution of two very different chain lengths. The results are adequate for smooth and not too broad distributions, which is the typical case realized in experiments.

We now specialize to $d = 3$, writing $u = u^*f$, where $u^* = 0.364$ is the fixed point coupling derived from a higher order calculation[25] (cf. ref 8, section 4.3). We furthermore fix N_R as $N_R = N_o = 0.53$ (see below). As a result eqs A1, A2 reduce to

$$R_g^{\,2} = 0.53\left(\frac{-\tilde{p}'''}{\tilde{p}''}\right)l_R^{\,2}[1 - f(0.195 - 0.728c_g)] \quad \text{(A4)}$$

$$c_{\mathrm{g}} = -0.232\left(1 + \int_0^\infty \mathrm{d}y\, y^{7/2}\frac{p(y)}{\tilde{p}'''}\right) \tag{A5}$$

$$(4\pi)^{-3/2}A_2 = 0.0511(\tilde{p}'')^2 f l_{\mathrm{R}}{}^d[1 + f(0.348 + 0.728c_{\mathrm{A}})] \tag{A6}$$

$$c_{\mathrm{A}} = -0.388\left(\int_0^\infty \mathrm{d}y\, \frac{p(y)}{\tilde{p}''}y^{5/2}\left(5 + 2\frac{y}{\tilde{p}''}\right) - \int_0^\infty \mathrm{d}y_1\, dy_2\, \frac{p(y_1)\, p(y_2)}{(\tilde{p}'')^2}y_1 y_2\,(y_1 + y_2)^{5/2} + 4\sqrt{2} - 7\right) \tag{A7}$$

The polydispersity corrections c_{g} and c_{A} vanish for a monodisperse system.

Concerning the choice of N_{o}, we should recall that universal scaling functions evaluated in strict ϵ-expansion (which implies expanding out all nontrivial powers into logarithms) are strictly independent of such conventions. However, any scheme that aims at a useful expression for scaling functions in $d = 3$ must keep the nontrivial powers intact and weakly depends on N_{o}. We here have adjusted N_{o} to reproduce the excluded volume limit of the interpenetration ratio, which according to the most recent Monte Carlo simulations[7] takes a value ψ^* (monodisperse) 0.247. (We should note that in refs 8 and 10 we did choose $N_{\mathrm{o}} = 1$, but kept a parameter b_{u} in the definition of the renormalized coupling constant, adjusting this parameter to reproduce ψ^*. In the relevant expressions the parameters b_{u} and N_{o} occur only in the combination $b_{\mathrm{u}}N_{\mathrm{o}}{}^{\epsilon/2}$, so that we equivalently can choose $b_{\mathrm{u}} = 1$ and $N_{\mathrm{o}} \neq 1$ as used here.)

We finally have to consider the RG flow, relating l_{R} and f to physical variables $\tilde{z}$ and $\tilde{R}_0$. Appropriate expressions based on the higher order work of ref 25 are given in ref 8, eqs 4.26 and 4.27, which would be perfectly acceptable for the present purpose. In view of the recent high-precision Monte Carlo results[7,11] we however on the basis of the work of ref 25 reevaluated the RG mapping, employing the most precise RG-value $\nu = 0.588$ in place of $\nu = 0.59$ and keeping some very small terms which we dropped previously. The revised form of the mapping reads ($d = 3$)

$$\tilde{z} = f|1 - f|^{-1/2\nu\omega}(1 + 0.824f)^{0.25}H^{-1/2}(f)N_{\mathrm{R}}{}^{1/2}$$

$$\tilde{R}_0{}^2 = f|1 - f|^{(1/\omega)(2-(1/\nu))}H^{-1}(f)N_{\mathrm{r}}l_{\mathrm{R}}{}^2 \tag{A8}$$

where

$$H(f) = 1 - 0.005f - 0.028f^2 + 0.022f^3 \tag{A9}$$

$\nu = 0.588$, and $\omega = 0.80$. It must be stressed that for all practical purposes the form A8 and the simpler expressions given previously are equivalent, as long as we do not consider the recent Monte Carlo work. It is most remarkable that these recent data clearly resolve the difference among $\nu = 0.59$ or $\nu = 0.588$.

Putting $N_{\mathrm{R}} = N_{\mathrm{o}}$ we now numerically can evaluate eqs A4–A9 to arrive at the parametrizations given in the main text. For the strong coupling branch $f > 1$ the results start to run away for $f \gtrsim 1.5$, corresponding to $\tilde{z} \lesssim 3$, where we stopped the evaluation. Our parametrizations are constructed to be fairly simple but not to respect the full analytic structure of the RG results. The full results, for instance, can be expanded about the excluded volume limit $f = 1$, yielding the expansion in powers of $\tilde{z}^{-2\nu\omega}$ mentioned in section 2.

Our calculation of the scaling functions (A1) and (A2) uses a form of renormalized perturbation theory that consistently can be combined with the higher order renormalization group of ref 25. Other approaches can be found in the literature, all methods being equivalent in the sense of the ϵ-expansion. Evaluated in $d = 3$ the results differ somewhat on the quantitative level, the difference however typically is small compared to the statistical scatter of the data.

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