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1997 J. Phys. A: Math. Gen. 30 2669

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Crossover from the dilute to the dense phase for self-repelling polymer chains: finite size effects and relation to zero-component Landau–Ginzburg–Wilson theory

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Received 28 November 1996

Abstract. Using a recently established perturbative approach we analyse a single polymer chain or a few chains floating in a good solvent contained in a finite box with periodic boundary conditions. We calculate to one-loop order the partition function and the equation of state relating segment concentration to segment chemical potential $\hat{\mu}_s$, and we discuss in detail the chain length distribution for a ‘field theoretic’ ensemble of chains characterized by fixed $\hat{\mu}_s$. Our results obey finite size scaling and cover the whole crossover from the dilute ($\hat{\mu}_s < \hat{\mu}_s^*$) to the dense ($\hat{\mu}_s > \hat{\mu}_s^*$) limit, where $\hat{\mu}_s^*$ is the critical chemical potential. The different limits evolve smoothly from one another. The theoretical results for the chain length distribution are compared with Monte Carlo simulations of self-avoiding walks on a cubic lattice. We find a good agreement between our results and the simulation data.

1. Introduction

We consider a polymer solution characterized by the number concentration of chains c_p and the average polymerization index (chain length) N . If we are in the excluded volume regime, where the individual monomers repel each other, the macromolecules in solution form random coils of average size $R = R(N, c_p)$. The radius increases with increasing N , and for an isolated coil ($c_p = 0$) we asymptotically find the power law

$$R(N, c_p) \sim N^\nu$$

where $\nu \approx 0.588$ in $d = 3$ dimensions. Indeed, in the limit of infinite chain length $N \rightarrow \infty$ and vanishing segment concentration $c = c_p N \rightarrow 0$ the system becomes ‘critical’. It shows power laws and scaling behaviour.

This critical behaviour can be analysed with the help of the renormalization group, as established in the standard-field theory of critical phenomena. As is well known, a special grand canonical ensemble of polymers in solution is closely related to the field theory [1–3]. This ensemble contains chains of all lengths n and is specified by the chemical potential

$$\hat{\mu}(n) = \mu_p + \hat{\mu}_s n. \quad (1)$$

(Here and in the following, carets are used to distinguish quantities referring to discrete chains from their counterparts for the continuum limit.) To all orders of the perturbation theory in the repulsive monomer interaction it is identical to a Landau–Ginzburg–Wilson (LGW) field theory in the formal limit of a zero-component vector field \mathcal{S} . Chain fugacity

e^{μ_p} or segment chemical potential $\hat{\mu}_s$ is related to the magnetic field \mathbf{h} or the bare mass m_0 of the LGW-model:

$$\begin{aligned} e^{\mu_p} &\sim \mathbf{h}^2 \\ \hat{\mu}_s &\sim -m_0^2. \end{aligned}$$

The polymer concentration is formally given as

$$c_p = \frac{1}{2} \mathbf{h} M \quad (2)$$

where M is the magnetization density, and the segment concentration is related to the energy density

$$c \sim \langle S^2 \rangle.$$

The average chain length follows from $N = \langle n \rangle = c/c_p$. The critical limit $N \rightarrow \infty$, $c \rightarrow 0$ is mapped onto the critical point $\mathbf{h} \rightarrow 0$, $m_0^2 = m_0^{*2}$. The ‘paramagnetic’ phase $\mathbf{h} \rightarrow 0$, $m_0^2 > m_0^{*2}$, i.e. $\mu_p \rightarrow -\infty$, $\hat{\mu}_s < \hat{\mu}_s^*$, corresponds to the dilute limit where a single finite macromolecule floats in the infinite volume. The ‘ferromagnetic’ phase $\mathbf{h} \rightarrow 0$, $m_0^2 < m_0^{*2}$, i.e. $\mu_p \rightarrow -\infty$, $\hat{\mu}_s > \hat{\mu}_s^*$, describes the semidilute limit, where an infinite number of infinitely long chains maintains a finite segment concentration c in the infinitely large container. For dimensions $d > 2$, which is the case exclusively considered in this paper, the polymer coils strongly overlap in the semidilute limit.

So far we have described standard results found in the normal thermodynamic limit: the linear size, L , of the container is taken to infinity first with c_p , N —or μ_p , $\hat{\mu}_s$, equivalently—kept fixed. However, we may take the limit $L \rightarrow \infty$ also in such a way that a finite number of chains (a single chain in the extreme case) maintains a finite segment concentration. This is the so-called dense limit. Since to leading order $c \sim M^2$, the limit $c = \text{constant}$, $c_p \sim L^{-d} \rightarrow 0$ via equation (2) implies that we couple \mathbf{h} to L such that $\mathbf{h} \sim L^{-d} \rightarrow 0$. Keeping $M^2 > 0$, we again approach the magnetization curve, working at $\hat{\mu}_s > \hat{\mu}_s^*$, i.e. $m_0^2 < m_0^{*2}$. It must be noted that for finite L the relation $\mathbf{h} \sim L^{-d}$ identifies the smallest value of \mathbf{h} of physical relevance: For $L < \infty$ and $\mathbf{h} \equiv 0$, there is no chain in the system. Thus, in some sense the dense limit is the best we can do to realize ‘spontaneous’ symmetry breaking in the ‘ferromagnetic’ phase. The contribution of the external field, \mathbf{h} , to the magnetic energy is of the order of

$$L^d \mathbf{h} M = O(1)$$

so that \mathbf{h} barely breaks the $O(m)$ symmetry of the LGW-model in m -component spin space. In the dense limit the average chain length is an extensive quantity: $N \sim L^d$. Since the radius of a chain in infinite volume obeys $R \sim N^\nu$, $\nu \geq \frac{1}{2}$, this implies $R \sim L^{\nu d} \gg L$ for $L \rightarrow \infty$, $d > 2$. Thus, the dense limit is closely related to finite size effects, which show up if the infinite volume correlation length in a finite system is not small compared with the size of the system. More precisely, it is related to finite size effects in the ferromagnetic phase of the LGW-model. While such effects in the paramagnetic phase are well understood [4–6], some progress on the treatment of the ferromagnetic phase has been made only recently [6, 7]. The problem is complicated by the fact that spontaneous symmetry breaking strictly arises only in the limit $L \rightarrow \infty$. Furthermore, for a LGW-model not of Ising-type additional complications arise due to the Goldstone modes of the broken $O(m)$ symmetry. In a previous publication [8] one of the present authors considered these problems in the polymer context. For $d > 2$ it was found that the dense limit can be handled within a perturbative approach, provided we do not work with the field theoretic ensemble (1) but with a canonical ensemble of sharp chain lengths $n \sim L^d$. (In the field-theoretic analogy this amounts to transforming

the canonical ensemble to a microcanonical ensemble of fixed energy density.) Assuming periodic boundary conditions, a reformulation of the (unrenormalized) perturbation theory was derived which eliminates dangerous zero modes and incorporates the screening of the Goldstone singularities. A simple treatment of finite size effects arises. The results can be transformed to the field theoretic ensemble at the end of the calculation. It was found that the dense limit for $d > 2$ does not yield a qualitatively new phase, but all density correlations and the free energy smoothly evolve from the normal semidilute limit. In terms of m -component field theory this implies that we can handle $O(m)$ -invariant quantities.

This present paper reports on a harder test of the theory. We concentrate on a quantity for which the semidilute limit or the dense limit necessarily yield very different results, discussing the chain length distribution in the field theoretic ensemble. In the dilute limit the probability of finding a chain of length n in the ensemble defined by the chemical potential (1) is known from the early days of the polymer–magnet analogy:

$$P(n) \sim n^{\gamma-1} e^{-\gamma n/N}. \quad (3)$$

Here $\gamma \approx 1.157$ ($d = 3$) is a standard critical exponent. In the normal semidilute limit $P(n)$ reduces to an exponential distribution

$$P(n) \sim e^{-n/N}. \quad (4)$$

In the dense limit for a single chain, however, $P(n)$ becomes sharp

$$P(n) \sim \delta\left(\frac{n}{L^d} - \bar{c}\right) \quad (5)$$

reflecting the fact that the segment density for given chemical potential $\hat{\mu}_s$ is a macroscopic thermodynamic observable. The crossover of expressions (3) and (4) was discussed in [9]. We here analyse the crossover towards expression (5), showing the perturbation theory of [8] in the renormalized form at work. We include finite size effects and establish finite size scaling. Extending the work of [10] we present new simulation results which quantitatively agree with our scaling functions which are calculated to one-loop order. Our results again illustrate that the dense limit is smoothly connected to the semidilute limit, even if we consider a quantity taking such different asymptotic forms as equations (4) or (5).

The dense limit is related to recent work on self-avoiding walks ‘transversing a hypercube’ [11–14]. That work considers an ensemble of single self-avoiding walks on a lattice, fixed with the ends to opposite corners of a hypercube of linear size L . The step number of the walks is governed by a chemical potential $\hat{\mu}_s$. In the thermodynamic limit a second-order phase transition is found, separating a dilute phase $N \sim L$, $c \sim L^{1-d} \rightarrow 0$ from a dense phase $N \sim L^d$, $c > 0$. This transition is driven by varying $\hat{\mu}_s$. For $d > 2$ clearly the dense phase found there is identical to the dense phase considered here, since for $R \sim n^\nu = (cL^d)^\nu \gg L$ the constraint fixing the chain ends should have no effect. Indeed, as was found in [8], the chain ends effectively unbind in the dense limit. This also implies that the critical values of $\hat{\mu}_s$ must be the same. The dilute phases, however, are different since here the constraint strongly stretches the chain: $R \sim L \sim N$, in contrast to $R \sim N^\nu$, $\nu < 1$ in the present problem.

The paper is organized as follows. In section 2 we define the model, and we derive the one-loop order result for the partition function in renormalized perturbation theory. In section 3 we exhibit the general scaling behaviour and discuss our results for the scaling functions for the partition function, the chain length distribution and the equation of state relating $\hat{\mu}_s$ to c . Section 4 compares our theoretical results with Monte Carlo simulations and in section 5 we summarize our findings.

2. Perturbation theory

2.1. The model

We consider a single polymer (random walk chain with effective segment repulsion) in a d -dimensional hypercube, Ω , of linear size L . The Hamiltonian is written as

$$\mathcal{H} = \frac{1}{4l^2} \sum_{\lambda=1}^n [\mathbf{r}(\lambda) - \mathbf{r}(\lambda-1)]^2 + \frac{\hat{u}_0}{2} \int_{\Omega} d^d r [\hat{\rho}(\mathbf{r})]^2 \quad (6)$$

where λ labels the n segments of average microscopic length l , \hat{u}_0 describes the bare (repulsive) segment interaction and

$$\hat{\rho}(\mathbf{r}) = \sum_{\lambda=1}^n \delta^d(\mathbf{r} - \mathbf{r}(\lambda)) \quad (7)$$

stands for the total segment density. The partition function is given by

$$\hat{\mathcal{Z}}(n) = \frac{(4\pi l^2)^{d/2}}{\Omega} \int_{\Omega} \prod_{\lambda=0}^n \frac{d^d r(\lambda)}{(4\pi l^2)^{d/2}} e^{-\mathcal{H}} \quad (8)$$

where the normalization guarantees that the partition function of a noninteracting chain reduces to $\hat{\mathcal{Z}}(n, \hat{u}_0 = 0) = 1$. For further calculations it is useful to take the continuous chain limit

$$l \rightarrow 0 \quad \left. \begin{array}{l} S = l^2 n \\ u_0 = \hat{u}_0 l^{-4} \end{array} \right\} \text{fixed.}$$

As a result summations over segment indices, λ , convert to integrals over $s = \lambda l^2$, and after a Gaussian transformation linearizing the interaction term the single chain partition function, $\hat{\mathcal{Z}}(n)$, is replaced by

$$\mathcal{Z}(S) = \frac{(4\pi l^2)^{d/2}}{\Omega} \int \mathcal{D}[\varphi] e^{-\frac{1}{2u_0} \int_{\Omega} d^d r \varphi^2(r)} \int_{\Omega} \frac{d^d r d^d r'}{(4\pi l^2)^{d/2}} G(\mathbf{r}, \mathbf{r}', S, \varphi). \quad (9)$$

The Green's function

$$G(\mathbf{r}, \mathbf{r}', S, \varphi) = \int_{\mathbf{r}(0)=\mathbf{r}'}^{\mathbf{r}(S)=\mathbf{r}} \mathcal{D}[\mathbf{r}(s)] e^{-\int_0^S ds [(\frac{d\mathbf{r}(s)}{ds})^2 + i\varphi(\mathbf{r}(s))]} \quad (10)$$

integrates over all paths connecting the endpoints of the chain. By imposing periodic boundary conditions on the container we expand the auxiliary field $\varphi(\mathbf{r})$ in normal modes $\psi_k(\mathbf{r})$

$$\varphi(\mathbf{r}) = \sqrt{u_0} \sum_k \tilde{\varphi}_k \psi_k(\mathbf{r}) \quad \psi_k(\mathbf{r}) = L^{-d/2} e^{i\mathbf{k}\mathbf{r}} \quad (11)$$

$$k_{\alpha} = \frac{2\pi}{L} \kappa_{\alpha} \quad \kappa_{\alpha} = 0, \pm 1, \pm 2, \dots \quad \alpha = 1, \dots, d.$$

With the notation

$$G_{kk'}(S, \varphi) = \langle \psi_k | G | \psi_{k'} \rangle \quad (12)$$

the partition function takes the form

$$\mathcal{Z}(S) = \frac{1}{\sqrt{2}} \int \prod_k \frac{d\tilde{\varphi}_k}{\sqrt{\pi}} e^{-\frac{1}{2} \sum_k \tilde{\varphi}_k \tilde{\varphi}_{-k}} G_{00}(S, \varphi). \quad (13)$$

The field theoretic ensemble for a single chain is defined by the Laplace transform

$$\mathcal{Z}_F(\mu_s) = \int_0^\infty dS e^{\mu_s S} \mathcal{Z}(S) \quad (14)$$

where μ_s is related to the chemical potential $\hat{\mu}_s$ in the discrete chain model via

$$\mu_s = \hat{\mu}_s l^{-2}. \quad (15)$$

In this ensemble the chain length is not fixed but characterized by the distribution

$$P(S, \mu_s) = e^{\mu_s S} \frac{\mathcal{Z}(S)}{\mathcal{Z}_F(\mu_s)}. \quad (16)$$

2.2. Unrenormalized perturbation theory

Standard finite size calculations in the paramagnetic phase of the LGW model proceed by perturbative elimination of the $\mathbf{k} \neq 0$ modes to find an effective potential for the zero mode [4, 5]. This mode is then treated on a nonperturbative level. In the ferromagnetic phase this approach runs into problems since the effective potential is highly singular, due to the Goldstone modes of the broken $O(m)$ symmetry. As has been shown in [8], for the polymer case ($m = 0$) these problems can be overcome by eliminating the zero mode first in a rigorous way, thus constructing an effective potential for the $\mathbf{k} \neq 0$ modes which can be dealt with perturbatively. We now apply this method to a calculation of the chain length distribution or related quantities.

Starting from expression (13) for the partition function, we note that equation (10) is just the path integral representation for the Green's function of the diffusion equation

$$[\partial/\partial S - \Delta_r + i\varphi(\mathbf{r})]G(\mathbf{r}, \mathbf{r}', S, \varphi) = 0 \quad (17)$$

with the initial condition

$$G(\mathbf{r}, \mathbf{r}', S = 0, \varphi) = \delta^d(\mathbf{r} - \mathbf{r}'). \quad (18)$$

Since Δ_r acts only on the nonzero modes, we can split $\tilde{\varphi}_0$ off to find

$$G(\mathbf{r}, \mathbf{r}', S, \varphi) = e^{-i\sqrt{u_0/L^d}\tilde{\varphi}_0 S} G(\mathbf{r}, \mathbf{r}', S, \varphi') \quad (19)$$

where φ' contains only $\mathbf{k} \neq 0$ modes. Then the zero mode can be integrated out to yield

$$\mathcal{Z}(S) = e^{-\frac{u_0 S^2}{2L^d}} \int \prod_{\mathbf{k} \neq 0} \frac{d\tilde{\varphi}_{\mathbf{k}}}{\sqrt{\pi}} e^{-\frac{1}{2} \sum_{\mathbf{k} \neq 0} \tilde{\varphi}_{\mathbf{k}} \tilde{\varphi}_{-\mathbf{k}}} G_{00}(S, \varphi'). \quad (20)$$

G_{00} can be formally expanded as

$$G_{00}(S, \varphi') = 1 + \sum_{j=2}^{\infty} (-i)^j u_0^{j/2} L^{-jd/2} \sum_{\mathbf{k}_1, \dots, \mathbf{k}_{j-1}} A(1, j-1) J_j \quad (21)$$

where

$$A(1, j) = \tilde{\varphi}_{\mathbf{k}_1} \tilde{\varphi}_{\mathbf{k}_2 - \mathbf{k}_1} \dots \tilde{\varphi}_{\mathbf{k}_j - \mathbf{k}_{j-1}} \tilde{\varphi}_{-\mathbf{k}_j} \quad (22)$$

$$J_j = \int_{0 < s_1 < \dots < s_j < S} \exp\{-(s_j - s_{j-1})k_{j-1}^2 - \dots - (s_2 - s_1)k_1^2\} \quad (23)$$

and $\tilde{\varphi}_0 \equiv 0$. This constraint ensures that successive values $k_j = 0$ are separated by at least one value $k_j \neq 0$. Thus, the general form of a contribution to $G_{00}(S, \varphi')$ is a product of a number of 'irreducible' pieces, containing only $\mathbf{k} \neq 0$ propagators, connected by single

$k = 0$ propagators which cannot transport any correlation: the chain effectively decomposes into uncorrelated irreducible pieces.

As shown in [8] we may then resum the expansion to find an effective interaction for the $\tilde{\varphi}_k$, $k \neq 0$, consisting only of irreducible pieces:

$$\begin{aligned} \mathcal{Z}(S) &= e^{-\frac{u_0 S^2}{2L^d}} \int \prod_{k \neq 0} \frac{d\tilde{\varphi}_k}{\sqrt{\pi}} e^{-\mathcal{L}[\tilde{\varphi}]} \\ \mathcal{L}[\tilde{\varphi}] &= \frac{1}{2} \sum_{k \neq 0} \tilde{\varphi}_k \left(1 + 2u_0 L^{-d} \int_{0 < s_1 < s_2 < S} ds_1 ds_2 e^{-(s_1 - s_2)k^2} \right) \tilde{\varphi}_{-k} + iu_0^{3/2} L^{-3d/2} \\ &\quad \times \sum_{\substack{k_1, k_2 \neq 0 \\ k_2 - k_1 \neq 0}} \tilde{\varphi}_{k_1} \tilde{\varphi}_{k_2 - k_1} \tilde{\varphi}_{-k_2} \int_{0 < s_1 < s_2 < s_3 < S} ds_1 ds_2 ds_3 e^{-(s_3 - s_2)k_2^2 - (s_2 - s_1)k_1^2} + \dots \end{aligned} \quad (24)$$

To one-loop order we keep only the contribution to $\mathcal{L}[\tilde{\varphi}]$ quadratic in $\tilde{\varphi}$. The resulting Gaussian integral yields formally

$$\mathcal{Z}(S) = \exp \left(-\frac{u_0 S^2}{2L^d} - \frac{1}{2} \sum_{k \neq 0} \ln \left(1 + \frac{2u_0 S}{k^2 L^d} + 2u_0 \frac{e^{-k^2 S} - 1}{k^4 L^d} \right) \right). \quad (25)$$

For $d \geq 2$ the summation over large values of k yields a divergent contribution. This is a standard ultraviolet singularity which has to be eliminated by a mass subtraction. In the present problem it arises from taking the continuous chain limit. We thus extract from the summation a critical chemical potential

$$\mu_s^* = \frac{1}{2} \sum_{k \neq 0} \frac{2u_0 S}{k^2 L^d} \quad (26)$$

which is absorbed, when taking the Laplace transform, into a redefinition of μ_s :

$$\mu_s - \mu_s^* = -E_s. \quad (27)$$

This yields the generalized partition function

$$\begin{aligned} \mathcal{Z}_G(S, \mu_s) &\stackrel{\text{def}}{=} e^{\mu_s S} \mathcal{Z}(S) \\ &= \exp \left(-E_s S - \frac{u_0 S^2}{2L^d} - \frac{1}{2} \sum_{k \neq 0} \left[\ln \left(1 + \frac{2u_0 S}{k^2 L^d} + 2u_0 \frac{e^{-k^2 S} - 1}{k^4 L^d} \right) - \frac{2u_0 S}{k^2 L^d} \right] \right). \end{aligned} \quad (28)$$

In the following, \mathcal{Z}_F and P (see equations (14) and (16)) will be considered as functions of E_s instead of μ_s . Thus, $\mathcal{Z}_F(E_s)$ is found by integrating $\mathcal{Z}_G(S, E_s)$ over S

$$\mathcal{Z}_F(E_s) = \int_0^\infty dS \mathcal{Z}_G(S, E_s) \quad (29)$$

and $P(S, E_s)$ is given by the ratio $\mathcal{Z}_G(S, E_s)/\mathcal{Z}_F(E_s)$. The segment density is derived as

$$c(E_s) = \frac{1}{L^d} \langle S \rangle = -L^{-d} \frac{\partial}{\partial E_s} \ln \mathcal{Z}_F(E_s) \quad (30)$$

which yields the equation of state relating concentration and chemical potential.

It may be appropriate to mention the order of the terms kept in equation (28). The loop expansion proceeds in powers of u_0 , but taking $u_0 S/L^d$ of the order of 1 fixed. Thus the leading zero-loop term in fact is of the order of $L^d u_0^{-1}$:

$$\frac{u_0 S^2}{L^d} = \frac{L^d}{u_0} \left(\frac{u_0 S}{L^d} \right)^2.$$

The one-loop correction is of the order of $L^d (u_0)^0$, the factor L^d being contributed by the summation over k . The neglected two-loop term would be of the order of $u_0 L^d$.

2.3. Renormalization

When approaching $d = 4$ the theory shows ultraviolet singularities which have to be eliminated by (multiplicative) renormalization. These singularities are related to the short distance behaviour of the theory and are independent of constraining the system to finite volume [4]. We can therefore take over the standard infinite volume renormalization scheme [15].

We define a renormalized length scale $l_R = \lambda l$ and replace S, E_s, u_0 by their renormalized counterparts n_R, E_R, u according to

$$\begin{aligned} S &= n_R l_R^2 Z_n \\ u_0 &= (4\pi)^{d/2} u l_R^{-\epsilon} Z_u \\ E_s &= E_R l_R^{-2} Z_n^{-1}. \end{aligned} \tag{31}$$

The renormalized form of the partition functions is then given by

$$\begin{aligned} \mathcal{Z}^{(R)}(n_R, u, l_R) &= \frac{Z_n}{Z} \mathcal{Z}(S, u_0, l) \\ \mathcal{Z}_G^{(R)}(n_R, E_R, u, l_R) &= \frac{Z_n}{Z} \mathcal{Z}_G(S, E_s, u_0, l). \end{aligned} \tag{32}$$

The renormalization constants Z, Z_n , and Z_u are determined as functions of u by requiring that $\mathcal{Z}_G^{(R)}$ is finite in four dimensions. Using minimal subtraction we find

$$\begin{aligned} Z_n &= 1 - \frac{1}{\epsilon} u + O(u^2) \\ Z_u &= \frac{1}{2} \left(1 + \frac{4}{\epsilon} u + O(u^2) \right) \\ Z &= 1 + O(u^2) \end{aligned} \tag{33}$$

where $\epsilon = 4 - d$. Substituting all these results into equation (28) for $\mathcal{Z}_G(S, E_s)$ and consistently expanding with respect to u we obtain

$$\begin{aligned} \mathcal{Z}_G^{(R)} = \exp \left\{ - E_R n_R - \frac{\tilde{u}}{2} \left(\frac{l_R}{L} \right)^d n_R^2 \left(1 + \frac{2}{\epsilon} u \right) - \frac{1}{\epsilon} u \right. \\ \left. - \frac{1}{2} \sum_{k \neq 0} \left[\ln \left(1 + \frac{2\tilde{u} l_R^{2-\epsilon} n_R}{k^2 L^d} + 2\tilde{u} \frac{e^{-k^2 n_R l_R^2} - 1}{l_R^\epsilon k^4 L^d} \right) - \frac{2\tilde{u} l_R^{2-\epsilon} n_R}{k^2 L^d} \right] \right\} \end{aligned} \tag{34}$$

with $\tilde{u} = (4\pi)^{d/2} u/2$. This is our basic perturbative result.

3. Scaling laws and results for the scaling functions

3.1. Scaling in the excluded volume limit

Physical observables are independent of the choice of the arbitrary renormalized length scale l_R . Any change of l_R must be compensated by a change of u, n_R, E_R . The flow equations governing the change of u, n_R, E_R with changing l_R are derived by taking the logarithmic derivative with respect to l_R of these quantities, keeping all unrenormalized quantities u_0, S, E_s fixed. For $l_R \rightarrow \infty$ this flow drives $u = u(l_R/l)$ to a fixed point value u^* that governs the behaviour of long self-repelling chains. In the sequel we will restrict ourselves to this ‘excluded volume limit’. Using the full renormalization group mapping, as given for instance in [15], it is also possible to evaluate the ‘corrections to scaling’ resulting from $u \neq u^*$ but $u \sim u^*$, or even the full crossover from noninteracting chains ($u = 0$) to excluded volume chains ($u = u^*$). With respect to the Monte Carlo data, presented in the next section, however, such corrections seem to be of no importance, and we therefore stay with the simple fixed point behaviour.

Evaluated at the fixed point $u = u^*$, the mapping from unrenormalized to renormalized variables reads

$$\begin{aligned} n_R &= \left(\frac{B}{l_R}\right)^{1/\nu} n \\ E_R &= (\hat{\mu}_s^* - \hat{\mu}_s) \left(\frac{l_R}{B}\right)^{1/\nu} \\ Z/Z_n &= \left(\frac{l_R}{B_1}\right)^{(\nu-1)/\nu} \end{aligned} \quad (35)$$

where we switched back to the notation holding for the discrete chain model. The parameters B, B_1 are independent of n or $\hat{\mu}_s$, but depend on the microstructure of the system.

We can now construct the scaling laws. Simple dimensional analysis yields

$$\hat{Z}_G(n, \hat{\mu}_s) = e^{(\hat{\mu}_s - \hat{\mu}_s^*)n} \frac{Z}{Z_n} \mathcal{Z}^{(R)} \left(n_R, \frac{l_R}{L} \right). \quad (36)$$

By inserting equation (35) and fixing l_R by the choice $n_R = 1$ for simplicity, we find the scaling law

$$\hat{Z}_G(n, \hat{\mu}_s) = n^{\nu-1} e^{(\hat{\mu}_s - \hat{\mu}_s^*)n} \mathcal{Z}^* \left(\frac{Bn^\nu}{L} \right). \quad (37)$$

In the same way we find for the chain length distribution P , the segment concentration c , or the chemical potential $\hat{\mu}_s$,

$$\begin{aligned} P(n, \hat{\mu}_s) &= (\hat{\mu}_s^* - \hat{\mu}_s)^\nu n^{\nu-1} P^* \left(\frac{n}{N}, \frac{BN^\nu}{L} \right) \\ c(\hat{\mu}_s) &= \frac{L^{-d}}{\hat{\mu}_s^* - \hat{\mu}_s} c^* \left((\hat{\mu}_s - \hat{\mu}_s^*) \left(\frac{L}{B}\right)^{1/\nu} \right) \\ \hat{\mu}_s - \hat{\mu}_s^* &= \frac{1}{N} E^* \left(\frac{N}{(L/B)^{1/\nu}} \right). \end{aligned} \quad (38)$$

Recall that for the single chain system considered N/L^d is just the average segment concentration c . The results show the typical features of finite size scaling [16]: a quantity $X(t)$ scaling in the infinite volume limit with the distance t to the critical point ($t = 0$) like

$$X_\infty(t) = t^{-\rho} X_\infty$$

should in the finite volume scale like

$$X_L(t) = t^{-\rho} X_L^* \left(\frac{t^{-\nu}}{L} \right).$$

In our polymer case t corresponds to an inverse chain length or $\hat{\mu}_s^* - \hat{\mu}_s$, respectively.

3.2. Qualitative form of the scaling function

The perturbation theory breaks the scaling invariance, and low-order approximations to scaling functions such as \mathcal{Z}^* , P^* , ... explicitly depend on our choice of l_R . In the spirit of Wilson's renormalization approach we should choose l_R as large as possible, but not larger than the smallest macroscopic length scale of interest. Otherwise we would absorb into the effective renormalized segment physical effects which should be explicitly kept in the theory. The present problem possesses two important length scales: the radius of gyration

$$R_g^2 \sim n_R l_R^2$$

gives the range of excluded volume correlations in the dilute limit. At finite concentration its role is taken over by the screening length

$$\xi_E^2 \sim \frac{l_R^2}{c_R}$$

where

$$c_R = \tilde{u}^* \frac{1}{L^d} n_R l_R^d \tag{39}$$

stands for the renormalized segment concentration. l_R should interpolate among these two scales, which suggests a choice

$$l_R^{-2} \sim \frac{1}{R_g^2} + \frac{1}{\xi_E^2}.$$

Multiplying by l_R^2 we find the precise form of our crossover relation

$$1 = \frac{n_0}{n_R} + \frac{c_R}{c_0}. \tag{40}$$

The parameters n_0, c_0 reflect the fact that our qualitative considerations fix l_R only up to numerical factors of the order of 1. Since the theory, if evaluated to all orders, is independent of l_R and thus of n_0 and c_0 , these parameters can be determined by requiring that universal ratios calculated to one-loop order become insensitive to their precise choice. Corresponding considerations [17] suggest the values

$$\begin{aligned} n_0 &= 0.53 \\ c_0 &= 1.2. \end{aligned} \tag{41}$$

For the derivation of the scaling laws (equations (36), (37)) the choice $n_R = 1$ and the crossover relation (40) are of course equivalent. For simplicity we first discuss in detail the chain length distribution to zero-loop order and we give the full one-loop order results afterwards. We thus consider the tree level result for the partition function (cf (34))

$$\begin{aligned} \hat{\mathcal{Z}}_G(n, \hat{\mu}_s) &= \frac{Z}{Z_n} \exp \left(-E_R n_R - \frac{\tilde{u}^*}{2} \left(\frac{l_R}{L} \right)^d n_R^2 \right) \\ &= \left(\frac{l_R}{B_1} \right)^{\frac{\gamma-1}{\nu}} \exp \left((\hat{\mu}_s - \hat{\mu}_s^*) n - \frac{\tilde{u}^*}{2L^d} l_R^{d-2/\nu} n^2 B^{2/\nu} \right). \end{aligned} \tag{42}$$

3.2.1. *Dilute limit.* For $\hat{\mu}_s < \hat{\mu}_s^*$ and large L the renormalized segment concentration c_R vanishes proportional to $(Bn^\nu/L)^d$ and equations (40) and (35) yield $n_R = n_0$, $l_R = Bn^\nu$. The partition function for $L \rightarrow \infty$ becomes

$$\hat{Z}_G(n, \hat{\mu}_s) = \text{constant} \cdot n^{(\gamma-1)} e^{(\hat{\mu}_s - \hat{\mu}_s^*)n} \quad (43)$$

which is the known result for the dilute limit. The scaling form (36) ensures that this result is correct to all orders of the perturbation theory.

For the average segment concentration and the chain length distribution we obtain respectively

$$\begin{aligned} c(\hat{\mu}_s) &= \frac{N}{L^d} = L^{-d} \frac{\gamma}{\hat{\mu}_s^* - \hat{\mu}_s} \rightarrow 0 \\ P(n, \hat{\mu}_s) &= \frac{(\hat{\mu}_s^* - \hat{\mu}_s)^\gamma}{\Gamma(\gamma)} n^{\gamma-1} e^{-n(\hat{\mu}_s^* - \hat{\mu}_s)} \\ &= \frac{\gamma^\gamma N^{-\gamma}}{\Gamma(\gamma)} n^{\gamma-1} e^{-\gamma \frac{n}{N}}. \end{aligned} \quad (44)$$

3.2.2. *Dense limit.* For $\hat{\mu}_s > \hat{\mu}_s^*$ in the limit of large L the first term on the right-hand side of the crossover relation (40)

$$1 = \frac{n_0}{B^{1/\nu} n l_R^{-1/\nu}} + \frac{\tilde{u}^* B^{1/\nu} n l_R^{d-1/\nu}}{c_0 L^d} \quad (45)$$

can be neglected to give

$$l_R(c) = \left(\frac{\tilde{u}^* B^{1/\nu} c}{c_0} \right)^{\nu/(1-\nu d)}. \quad (46)$$

The generalized partition function to zero-loop order becomes

$$\begin{aligned} \hat{Z}_G(n, \hat{\mu}_s) &= B_1^{\frac{1-\gamma}{\nu}} \left(\frac{\tilde{u}^* B^{1/\nu} n}{c_0 L^d} \right)^{\frac{\gamma-1}{1-\nu d}} \\ &\times \exp \left(-L^d \left[(\hat{\mu}_s^* - \hat{\mu}_s) \frac{n}{L^d} + \frac{\tilde{u}^*}{2} B^{2/\nu} \left(\frac{\tilde{u}^* B^{1/\nu}}{c_0} \right)^{\frac{\nu d-2}{1-\nu d}} \left(\frac{n}{L^d} \right)^{\frac{\nu d}{\nu d-1}} \right] \right). \end{aligned} \quad (47)$$

For large L the maximum of this distribution is at

$$\frac{\bar{n}}{L^d} = \bar{c}(\hat{\mu}_s) = \left[\frac{(\hat{\mu}_s - \hat{\mu}_s^*) \left(\frac{\nu d-1}{\nu d} \right)}{\frac{c_0}{2} \left(\frac{\tilde{u}^*}{c_0} \right)^{\frac{1}{\nu d-1}}} \right]^{\nu d-1} B^{-d}. \quad (48)$$

Using the method of steepest descent to evaluate the normalization Z_F (equation (29)) it is easily seen that due to (48) the chain length distribution for $L \rightarrow \infty$ tends to the δ -function

$$P(n, \hat{\mu}_s) \rightarrow \delta \left(\frac{n}{L^d} - \bar{c} \right). \quad (49)$$

Because of equation (48) this way of taking the dense limit is equivalent to $L \rightarrow \infty$ at a fixed chemical potential $\hat{\mu}_s > \hat{\mu}_s^*$ per segment.

The reduced width of the segment density distribution defined as $\sigma^2 = \frac{\langle n^2 \rangle - \langle n \rangle^2}{\bar{n}^2}$ scales like $\sigma \sim L^{-d/2}$. As expected, $c = n/L^d$ in the dense limit becomes a normal macroscopic variable.

3.3. One-loop order results

From the structure of the perturbative result (34) it is now clear that the one-loop order corrections only change the quantitative form of the scaling functions, but introduce no new qualitative features. We first consider the limit $L \rightarrow \infty$.

In the dense limit ($\hat{\mu}_s > \hat{\mu}_s^*$) the renormalized chain length, n_R , is proportional to $n \sim L^d$ and we can neglect the term proportional to k^{-4} in equation (34) which vanishes like L^{-d} . We replace in leading order of L^d the sum by the integral. The generalized partition function becomes

$$\hat{Z}_G(n, \hat{\mu}_s) = \left(\frac{l_R}{B_1}\right)^{\frac{\gamma-1}{\nu}} \exp\left(-L^d \left[(\hat{\mu}_s^* - \hat{\mu}_s) \frac{n}{L^d} + \frac{\tilde{u}^*}{2} \left(\frac{n}{L^d}\right)^2 B^{2/\nu} l_R^{d-2/\nu} \left(1 + \frac{2}{\epsilon} u^*\right) + \frac{\Gamma(1-d/2)}{(2\pi)^{\frac{d}{2}} d} \left(\frac{n}{L^d}\right)^{d/2} (\tilde{u}^* B^{1/\nu} l_R^{d-2-1/\nu})^{d/2} \right]\right). \tag{50}$$

By inserting again equation (46), we recover

$$P(n, \hat{\mu}_s) \rightarrow \delta\left(\frac{n}{L^d} - \bar{c}\right) \tag{51}$$

with the one-loop order equation of state

$$\bar{c} = \left[\frac{(\hat{\mu}_s - \hat{\mu}_s^*) \left(\frac{\nu d - 1}{\nu d}\right)}{\frac{c_0}{2} \left(1 + \frac{2}{\epsilon} u^*\right) \left(\frac{\tilde{u}^*}{c_0}\right)^{\frac{1}{\nu d - 1}} + \frac{\Gamma(1-d/2)}{(2\pi)^{\frac{d}{2}} d} c_0^{d/2} \left(\frac{\tilde{u}^*}{c_0}\right)^{\frac{\nu d}{\nu d - 1}}} \right]^{\nu d - 1} B^{-d}. \tag{52}$$

For finite values of L the sum in equation (34) cannot be replaced by an integral and must be treated numerically including the k^{-4} -term. This yields finite size corrections to results (43) and (51). The result is illustrated in figures 1 and 2. In figure 1 the segment density distribution $P(c, \hat{\mu}_s - \hat{\mu}_s^*)$ for a fixed chemical potential ($\hat{\mu}_s - \hat{\mu}_s^* = 0.01$) is plotted for $L = 64, 128, 256$ and 512 . It is clearly seen how the distribution tends to the δ -function. The theoretical value $\bar{c}(0.01) = 0.0498$ is marked by the vertical full line. Figure 2 shows the finite size corrections to the equation of state for $L = 64$ and $L = 128$. The bulk curve is marked by the full curve.

3.4. Crossover from the dense to the semidilute limit

To see the crossover from the dense limit for a single chain to the normal semidilute limit we now consider an ensemble ($\hat{\mu}_s > \hat{\mu}_s^*$) of m chains with chain lengths $n_1 \dots n_m$ in the limit $L \rightarrow \infty, c_i = n_i L^d$ fixed. In this limit the generalized partition function $\hat{Z}_G^{(m)}(\{c_i\}, \hat{\mu}_s)$ is found to be independent of the number m of chains but involves only the total segment density $c = \sum c_i$ [8]:

$$\hat{Z}_G^{(m)}(c_1, \dots, c_m, \hat{\mu}_s) = \hat{Z}_G\left(\sum c_i, \hat{\mu}_s\right). \tag{53}$$

The probability of finding a chain of length $n = cL^d$ in the ensemble is given by ($m \geq 2$)

$$\begin{aligned} P(n = cL^d, \hat{\mu}_s) &= L^{-d} \langle \delta(c_1 - c) \rangle \\ &= L^{-d} \frac{\int dc_1 \dots dc_m \delta(c_1 - c) \hat{Z}_G(\sum c_i, \hat{\mu}_s)}{\int dc_1 \dots dc_m \hat{Z}_G(\sum c_i, \hat{\mu}_s)} \\ &= L^{-d} \frac{\int_c^\infty dc' \hat{Z}_G(c', \hat{\mu}_s) \frac{(c'-c)^{m-2}}{(m-2)!}}{\int_0^\infty dc' \hat{Z}_G(c', \hat{\mu}_s) \frac{c'^{m-1}}{(m-1)!}}. \end{aligned} \tag{54}$$

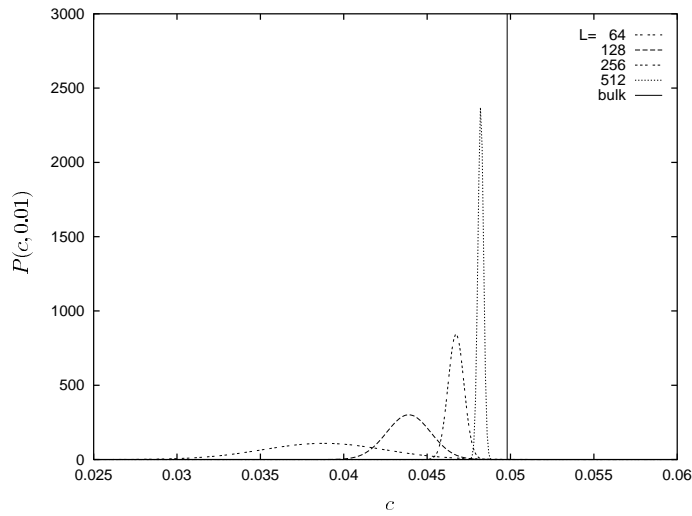


Figure 1. Segment density distribution at fixed chemical potential ($\hat{\mu}_s - \hat{\mu}_s^* = 0.01$) for various sizes of the container. The bulk value for the segment density $\bar{c}(0.01) = 0.0498$ is marked by the full vertical line.

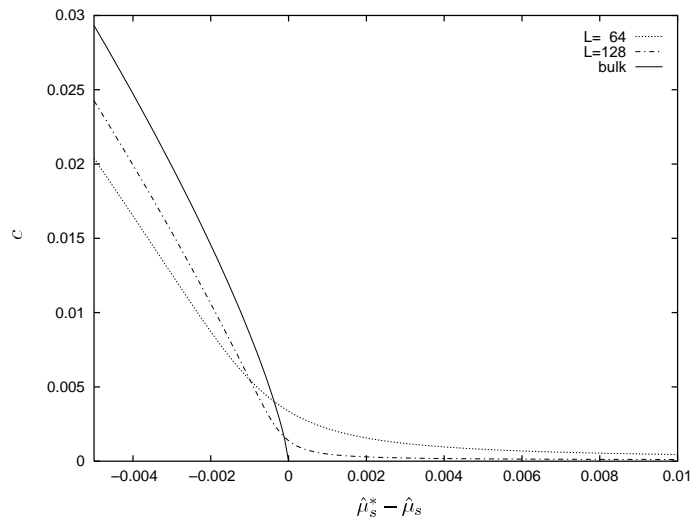


Figure 2. Segment density as a function of the chemical potential ($\hat{\mu}_s^* - \hat{\mu}_s$) for $L = 64$ and $L = 128$. The bulk curve is marked by the full curve.

In the limit $L \rightarrow \infty$ the total segment density distribution

$$\left\langle \delta \left(\sum c_i - c \right) \right\rangle \rightarrow \delta(c - \bar{c}(\hat{\mu}_s)) \tag{55}$$

becomes sharp with the equation of state (53) known from the dense limit. The chain length distribution takes the form

$$P(n, \hat{\mu}_s) = \frac{(m-1)L^{-d}}{\bar{c}(\hat{\mu}_s)} \left(1 - \frac{n/L^d}{\bar{c}(\hat{\mu}_s)} \right)^{m-2} \theta \left(\bar{c}(\hat{\mu}_s) - \frac{n}{L^d} \right). \tag{56}$$

In the limit of a large number of chains $m \rightarrow \infty$ we obtain

$$P(n, \hat{\mu}_s) \rightarrow \frac{1}{N} e^{-n/N} \quad N = \frac{\bar{c}L^d}{m} \quad (57)$$

which is the well known exponential distribution for the semidilute limit.

We conclude, not only the dilute and the dense but also the semidilute and the dense limit are connected smoothly. There is no sign of a ‘sharp’ transition.

4. Monte Carlo simulations

The theoretical results for the one-loop order partition function are compared with Monte Carlo simulations of self-avoiding random walks on finite (linear dimension $L = 8, 16, 32, 64, 128, 256$) three-dimensional cubic lattices with periodic boundary conditions.

These simulations were made with a growth algorithm similar to the one used in [10]. This is essentially a stochastic variant of the classic enrichment [18] algorithm, implemented recursively. Chains are constructed by adding monomers one by one. To prolongate a chain of length n , a random lattice direction is first chosen so that immediate U-turns are excluded. If this direction does not lead to a violation of the self-avoidance constraint, a monomer is added and the next prolongation step is attempted. Indeed, to implement the enrichment idea, a flag I_n is set with some probability p_n , which indicates that the same chain is also to be used in a second attempt. This is to overcome attrition. The latter happens since the chosen direction might lead to a self-crossing. In this case, it is checked whether the flag I_n is set. If it has been set, the second copy is started and the flag is cleared. If not, all monomers added after the last set flag (say $I_{n'}$) are deleted, and the second copy branching off at length n' is started.

In comparison to [10] the present algorithm involves two main improvements. First, as described above the recursion is implemented ‘by hand’, not by means of a recursive function call. This is slightly faster and (this was more important) it uses much less memory. In this way we could easily build chains with $n > 2 \times 10^5$. Secondly, we chose p_n such that the final samples had roughly the same size for all n up to some maximal n_{\max} . In this way, we could base our statistics only on complete ‘tours’ in the terminology of [10], avoiding thereby the potentially dangerous problems discussed in that paper. Thus, our algorithm should give an unbiased sample corresponding to an n -dependent fugacity depending on p_n . From this it is straightforward to estimate the distribution $P(n)$ for a fixed chemical potential $\hat{\mu}_s$ [10]. For each lattice size, our samples consisted of $(3-10) \times 10^6$ ‘tours’. This is also the number of independent *short* chains, while the number of independent long chains was much smaller of course. Thus, the relative error bars on $P(n)$ increase from $< 10^{-3}$ for small n to $O(1)$ for $n = n_{\max}$. In all graphs they are comparable with the line width or smaller.

The bulk critical potential for the sc lattice is $\hat{\mu}_s^* = -1.544\,161 \pm 0.000\,001$ [10, 19].

We now first analyse the scaling properties of the data. Dividing the partition function $\hat{\mathcal{Z}}_G(n, \hat{\mu}_s^*)$ by a factor of constant $\cdot n^{\nu-1}$ (cf (37)) in figure 3 we show $\ln \mathcal{Z}^*$ as a function of the scaling variable $n/L^{1/\nu}$ for all system sizes simulated. Clearly scaling is well obeyed for small values of $n/L^{1/\nu}$, but deviations occur for larger values. With increasing L , however, the results for all $n/L^{1/\nu}$ seem to approach a universal master curve. The scale of $\ln \mathcal{Z}^*$ should be noted: for $L \gtrsim 64$ deviations from universality occur for values $\mathcal{Z}^* \lesssim e^{-100}$. In terms of the chain length distribution this implies that we are deep in the tail, where $P(n, \hat{\mu}_s^*)$ is essentially zero.

A more detailed analysis indicates that for all L deviations from scaling become visible

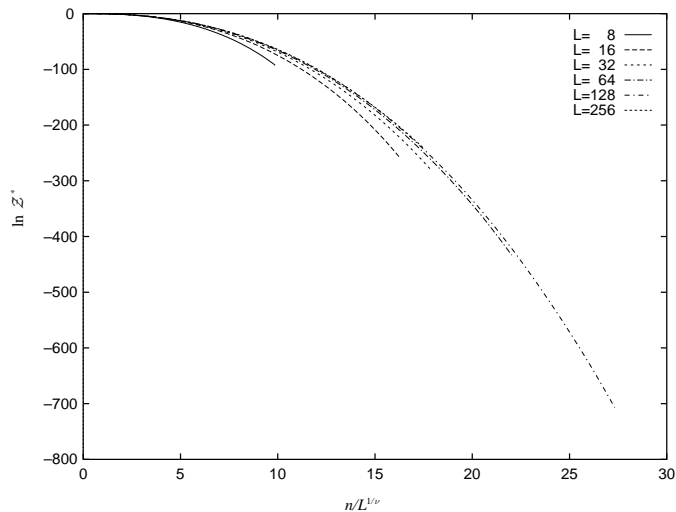


Figure 3. Monte Carlo data of the scaling function for various sizes of the container.

roughly for $n/L^d = c \gtrsim 0.05$. They could be due to effective three-body forces which under renormalization are generated automatically by products of two-body interactions within short parts of the chain. Such forces are known to lead to violations of scaling with increasing concentration and have been ignored within our theoretical model. For the present problem three-body forces even for small concentrations $c \approx 0.01$ could have a large effect since they correct the leading term $\sim u_0 S^2/L^d = u_0 L^d c^2$ in the exponential of equation (28). This term becomes large in the dense limit, so that even small corrections of the relative order of c could be visible in $\hat{Z}_G(n, \hat{\mu}_s)$.

In the further analysis we restrict ourselves to the scaling range, where the dominant variation of the chain length distribution takes place. In our theoretical model the bulk critical chemical potential corresponds to $\hat{\mu}_s - \hat{\mu}_s^* = 0$. For an optimal fit of the data we introduce a L -dependent shift of the critical chemical potential (or in the magnetic language the critical temperature), i.e. the critical chemical potential $\hat{\mu}_s^*(L)$ now depends on the finite size of the container. Then the difference $\hat{\mu}_L = \hat{\mu}_s^*(L) - \hat{\mu}_s^*$ is expected to scale like $\text{constant} \cdot L^{-1/\nu}$ [16, 20]. The second fit parameter is the microstructure dependent constant B . It must be the same for all values of L . Figures 4 and 5 show fits of the simulation data with this ansatz for the smallest ($L = 8$) and the largest ($L = 256$) system. In figure 4 we also included the zero-loop order result for the partition function to show the one-loop improvement of the theoretical curves. All theoretical curves use the same nonuniversal constant $B = 0.4631$. The values for the other fit parameter, $\hat{\mu}_L$, are listed in table 1.

Figure 6 shows the experimental data and the theoretical curves for all considered linear dimensions of the lattice in one doubly logarithmic plot. The theoretical results are in very

Table 1. Shift of the critical chemical potential.

L	8	16	32	64	128	256
$\hat{\mu}_L$	-0.022	-0.00718	-0.00228	-0.00071	-0.00022	-0.000069

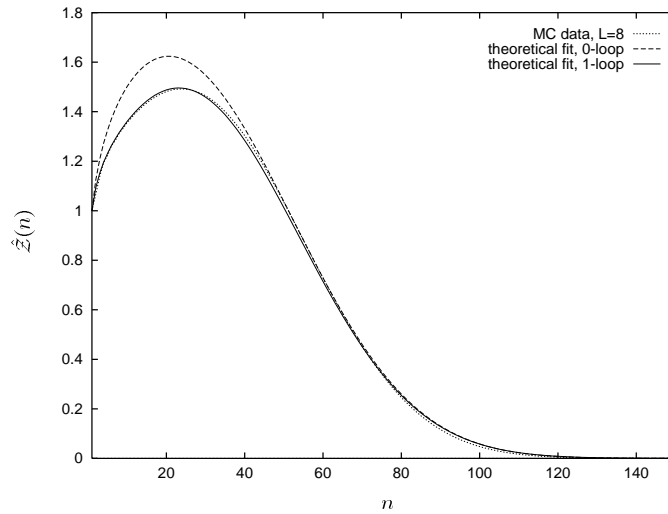


Figure 4. Partition function at the critical chemical potential ($\hat{\mu}_s = \hat{\mu}_s^*$) for $L = 8$.

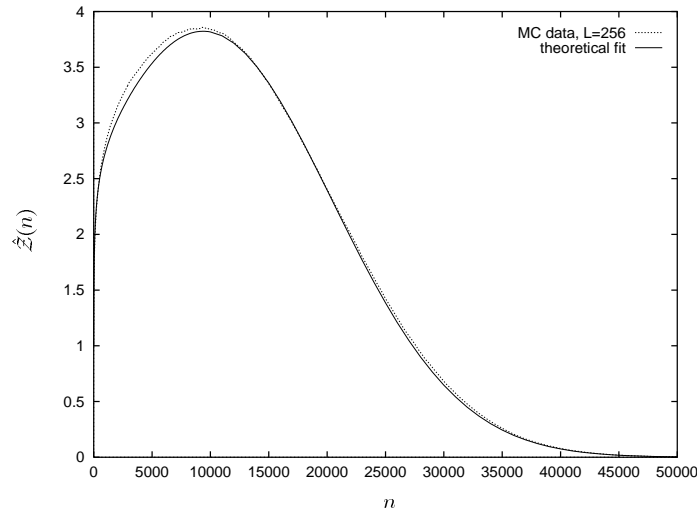


Figure 5. Partition function at the critical chemical potential ($\hat{\mu}_s = \hat{\mu}_s^*$) for $L = 256$.

good agreement with the simulation data. The slight overestimation for small chain lengths is consistent with the fact that self-avoiding walks on the cubic lattice approach the fixed point from the strong coupling side [21].

In the doubly logarithmic plot of $\hat{\mu}_L$ (figure 7) it is seen that $\hat{\mu}_L \sim \text{constant} \cdot L^{-1/\nu}$, a least squares fit gives $\nu = 0.599$, which, taking into account the limited accuracy of our determination of $\hat{\mu}_L$, is in good agreement with the known value 0.588.

So far we have compared theory and numerical data at the critical chemical potential $\hat{\mu}_s^*$. As shown in figures 4–6 we find excellent agreement in all the data range where $\hat{Z}(n) \gtrsim 0.01$. We find, however, sizeable deviations in the extreme tail of the chain length distribution, where $\hat{Z}(n, \hat{\mu}_s^*) \lesssim 10^{-100}$. Clearly this region is irrelevant for $\hat{\mu}_s \approx \hat{\mu}_s^*$, but

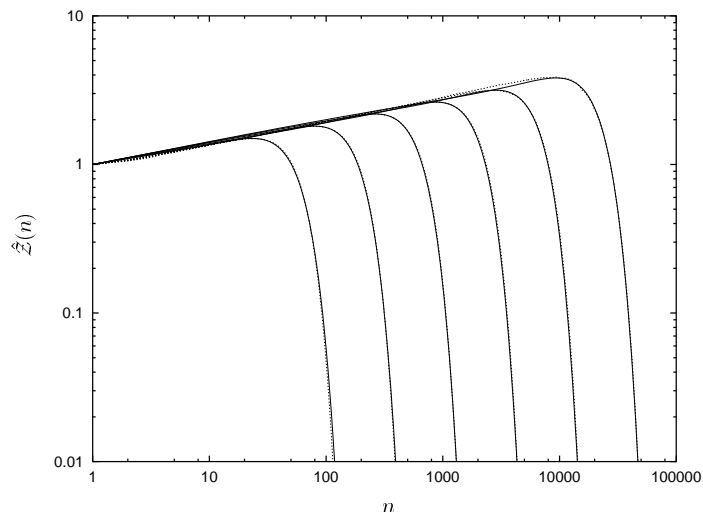


Figure 6. Partition functions at the critical chemical potential ($\hat{\mu}_s = \hat{\mu}_s^*$) for $L = 8, 16, 32, 64, 128, 256$. The Monte Carlo data are represented by the dotted curves, the theoretical curves are marked by the full curves.

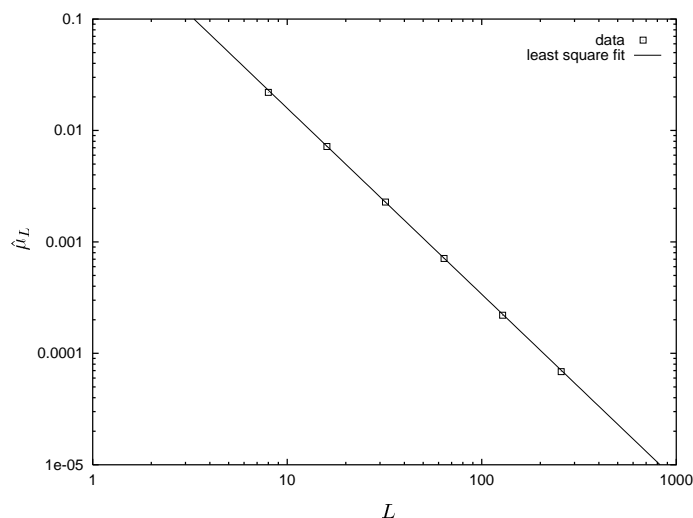


Figure 7. Shift of the critical chemical potential $\hat{\mu}_L = \hat{\mu}_s^*(L) - \hat{\mu}_s^*$. The full line is a least squares fit giving $\nu = 0.599$.

increasing $\hat{\mu}_s$, i.e. going to more dense systems, we shift the maximum of $P(n, \hat{\mu}_s)$ into the region of larger n , where the deviations are observed. Related to that feature is the fact that the equation of state $c = c(\hat{\mu}_s, L)$ as determined from the computer experiment (figure 8) does not quite fit with the theoretical result. As shown in figure 8 in the computer experiment $c(\hat{\mu}_s, L)$ reaches its asymptotic value $c(\hat{\mu}_s, \infty)$ from above monotonically. In contrast, the theoretical curves for different L cross each other (see figure 2), an effect reduced, but not suppressed completely by taking into account the L -dependent shift of $\hat{\mu}_s^*(L)$. This deviation among theory and data might indicate the importance of higher loop

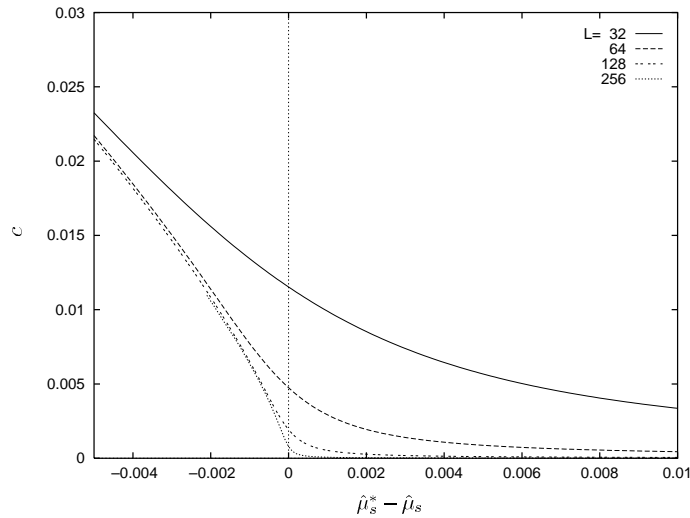


Figure 8. Segment density as a function of the chemical potential ($\hat{\mu}_s^* - \hat{\mu}_s$) for various sizes of the container, determined from the Monte Carlo data.

corrections in the theory, but part of it also might be due to a violation of the strict scaling limit due to three-body forces in the simulation.

5. Summary

We have calculated the partition function for a single polymer in a finite box with periodic boundary conditions to one-loop order. The obtained expression has a finite size scaling form and covers the whole crossover from the dilute to the highly overlapping limit. Depending on the chemical potential per segment $\hat{\mu}_s$ of an ensemble of chains the chain length distribution yields very different results. While for $\hat{\mu}_s < \hat{\mu}_s^*$ the known results of the dilute limit are recovered, a chemical potential $\hat{\mu}_s > \hat{\mu}_s^*$ describes the dense limit, where the chain length distribution for a single chain becomes sharp. For a canonical ensemble of a large number m of chains however this sharp distribution crosses over to the exponential behaviour of the normal semidilute limit. By varying $\hat{\mu}_s$, the different limits evolve smoothly from one to another. This illustrates the absence of any peculiar effects in the dense limit even for such a sensitive quantity as the chain length distribution. Furthermore, our calculation demonstrates that the renormalized form of the perturbation theory of [8] also adequately handles finite size effects in the ‘ordered’ phase of the zero-component field theory.

The theoretical results were compared with Monte Carlo simulations of self-avoiding walks on a cubic lattice. Close to the critical chemical potential the data are very well fitted with a shifted critical chemical potential depending on the finite size of the container. The difference to the bulk critical potential scales like $\text{constant} \cdot L^{-1/\nu}$.

Acknowledgment

This work has been supported by the Sonderforschungsbereich 237 ‘Unordnung und grosse Fluktuationen’ of the German Science Foundation DFG.

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