Self-repelling polymer chains in finite volume with Dirichlet boundary conditions: crossover from the dilute to the dense phase

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Abstract. Extending the results for periodic boundary conditions obtained in a previous paper we analyse a single polymer chain in a good solvent contained in a finite box with Dirichlet boundary conditions. We develop a consistent mean-field approximation, apply it to different geometries and discuss in detail the chain length distribution for the 'field theoretic ensemble' of chains characterized by a chemical segment potential $\hat{\mu}_s$. We show how the different regimes of the dilute ($\hat{\mu}_s^* < \hat{\mu}_s$) and dense ($\hat{\mu}_s^* > \hat{\mu}_s$) limits (where $\hat{\mu}_s^*$ stands for the critical chemical potential) smoothly evolve from one another.

1. Introduction

We consider a polymer solution described by random walks with effective segment repulsion. The system is characterized by the concentration of chains c_p and the average chain length (polymerization index) N. In the critical ('excluded volume') limit of vanishing segment concentration $c = Nc_p \to 0$ and $N \to \infty$ it shows the typical power law and scaling behaviour, which is well understood in terms of the renormalization group formalism. In this limit the average size R of an isolated polymer coil behaves as a function of the chain length as $R \sim N^\nu$, where the critical exponent ν in three dimensions is given by $\nu \approx 0.588$.

We now confine the polymer system to a container of typical linear dimension L. As long as the relation $N^\nu \ll L$ holds, finite-size effects will be neglegible. Clearly this is the case in the usual thermodynamic limit, where we take L to infinity at fixed c_p and c (or equivalently fixed c_p and N). However, other scenarios are possible. For instance we can take $L \to \infty$ and fix the segment concentration c and the number m of chains instead of the chain concentration. This is the so-called dense limit, where the average chain length scales like $N \sim L^d$ in d dimensions. With $R \sim N^\nu$ we see, that in this limit for $d > 2$ the ratio $R/L \sim N^{\nu d - 1}$ grows without bound and finite-size effects will play an essential role.

Our aim is to describe the crossover between the different limits. In a previous paper [1] we considered the case of a d-dimensional hypercube with periodic boundary conditions in all d directions. We considered the chain length distribution $P(n, \hat{\mu}_s)$ in the 'field theoretic' ensemble for a single chain, where the average chain length is controlled by a segment chemical potential $\hat{\mu}_s$. Then

$$P(n, \hat{\mu}_s) = \frac{e^{\hat{\mu}_s n} \hat{\mathcal{Z}}(n)}{\sum_n e^{\hat{\mu}_s n} \hat{\mathcal{Z}}(n)} \tag{1}$$

gives the probability to find a chain of length n in the ensemble. $\hat{\mathcal{Z}}(n)$ here stands for the partition function of a single polymer line of length n. Adopting the notation of [1] carets are used to distinguish quantities referring to the discrete chain model from their continuous chain limit counterparts.

For periodic boundary conditions we used a perturbation approach originally developed in [2]. The main feature of this approach consists in integrating out the zero mode completely before turning to a perturbation expansion for the higher modes. This way the usual finite-size difficulties arising in a perturbative treatment of the zero mode are avoided. The formalism covers the whole crossover from the dilute to the dense limit. We showed that the dilute limit is realized by $L \to \infty$ at fixed $\hat{\mu}_s < \hat{\mu}_s^*$ ($\hat{\mu}_s^*$ stands for the critical chemical potential) whereas $\hat{\mu}_s > \hat{\mu}_s^*$ describes the dense limit. In the different limits the chain length distribution yields very different results. While in the dilute limit the known result of the bulk theory

$$P(n, \hat{\mu}_s) \sim n^{\gamma-1} e^{-\gamma n/N} \qquad N = N(\hat{\mu}_s) \tag{2}$$

is recovered, in the dense limit for a single chain $P(n, \hat{\mu}_s)$ becomes sharp

$$P(n, \hat{\mu}_s) \sim \delta \left(\frac{n}{L^d} - \bar{c} \right) \qquad \bar{c} = \bar{c}(\hat{\mu}_s). \tag{3}$$

Finally, in the highly overlapping 'semidilute' limit of infinitely many chains (2) or (3) respectively reduce to the exponential distribution

$$P(n, \hat{\mu}_s) \sim e^{-n/N} \qquad N = N(\hat{\mu}_s). \tag{4}$$

The aim of this paper is to extend the discussion to the more realistic (physical) case of Dirichlet boundary conditions, demanding a vanishing segment density on the boundary of the container. These boundary conditions describe, for instance, the situation of polymers inside porous structures, a problem important for many practical questions. In this context an often considered and also measured [3–5] quantitiy is the so-called partition coefficient

$$K = \frac{c_I}{c_E}$$

giving the ratio of the segment concentration c_I inside a porous medium which is in contact with a polymer solution characterized by the segment concentration c_E. In thermodynamic equilibrium K would be given by

$$K = \frac{\mathcal{Z}_I(N)}{\mathcal{Z}_E(N)}$$

where $\mathcal{Z}_I$, $\mathcal{Z}_E$ are the respective partition functions in and outside the porous material. This way the problem reduces to the calculation of the partition function for polymers confined to small pores of a given geometry.

The situation of Dirichlet boundary conditions is more complicated than the periodic case since the zero mode (which means the mean-field solution of the problem) is no longer given by a constant: it becomes spatially dependent. This gives rise to many technical problems. Even the determination of the zero mode itself will be rather difficult. Such problems are known from the field theoretic finite-size methods for the φ^4-Landau–Ginzburg–Wilson model (LGW). There different zero modes have to be considered above and below the critical mass and a treatment of the higher modes is practically impossible. So one has to restrict oneself to the so-called renormalized lowest-mode approximation [6], integrating out only the amplitude of the mean-field ('zero' or 'lowest' mode) solution.

For the polymer problem, which is directly related to the LGW model in the limit of a zero-component vector field $\vec{\varphi}$ [7–9], a first attempt would be to directly use the results for the LGW model and translate them into the polymer context. However, to get the partition

functions in the canonical ensemble considered in [1] we would have to perform inverse Laplace transformations of the φ^4-results, which are at least below the critical temperature (which in the polymer language describes the dense limit) analytically not treatable. So it seems useful to develop a formalism for Dirichlet boundary conditions directly in the polymer formulation. Following the lines for periodic boundary conditions the first task would be to identify the zero (mean-field) mode and construct a consistent zero-loop (lowest-mode) approximation. We will see that for the most geometries this is rather complicated. So we will use the so-called 'ground state approximation' to get analytical results. Later we will show that by restricting to this ground state approximation all fluctuations around the mean-field solution can be integrated out. What can be done beyond this approximation strongly depends on the specific geometry considered.

To avoid misunderstanding we want to stress that whenever we speak of 'mean-field theory' we are dealing with zero-mode results for (swollen) chains with effective segment interaction. This way 'mean field' does not mean treating ideal (Gaussian) chains.

The organisation of this paper is as follows. In section 2 we develop the mean-field formalism for Dirichlet boundary conditions using the ground state approximation. In section 3 it is applied to a d-dimensional hypercube with Dirichlet boundary conditions in the z-direction and periodic boundary conditions in the remaining directions. The theory is renormalized following the lines of [1]. In section 4 we discuss what can be done beyond the mean-field approximation. Finally, we consider in section 5 a three-dimensional sphere as a geometry finite in all directions. There mean-field results can be obtained only by numerical methods.

2. Mean-field approximation

We start with the standard formulation [10, 11] for the partition function of a single polymer line of length S in the continous chain limit

$$\mathcal{Z}(S) = \frac{(4\pi l^2)^{d/2}}{\Omega} \int \mathcal{D}[\varphi] e^{-\frac{1}{2u_0} \int_\Omega d^d r \, \varphi^2(\vec{r})} \int_\Omega \frac{d^d r \, d^d r'}{(4\pi l^2)^{d/2}} G(\vec{r}, \vec{r}', S, \varphi) \tag{5}$$

with the Green function

$$G(r, r', S, [\varphi]) = \int_{r(0)=r}^{r(S)=r'} \mathcal{D}[r(s)] e^{-\int_0^S ds \, [(\frac{dr(s)}{2ds})^2 + i\varphi(r(s))]} \tag{6}$$

of the diffusion equation

$$\left[\frac{\partial}{\partial S} - \triangle_r + i\varphi(r) \right] G(r, r', S, [\varphi]) = 0 \tag{7}$$

$$G(r, r', 0, [\varphi]) = \delta^d(r - r').$$

Corresponding to the relation

$$\langle \rho(\vec{r}) \rangle = \frac{i}{u_0} \langle \varphi(\vec{r}) \rangle \tag{8}$$

which is obtained in the standard manner by introducing a source term $\int_\Omega d^d r \, \sigma(\vec{r}) \rho(\vec{r})$ into the partition function, we have to impose Dirichlet boundary conditions for the segment density

$$\rho(\vec{r}) = \int_0^S ds \, \delta^d(\vec{r} - \vec{r}(s))$$

directly to the the auxiliary field $\varphi(\vec{r})$.

To determine the mean-field solution $\varphi_{MF}(\vec{r})$ we now need the functional derivative $\delta G/\delta \varphi(\vec{r})$. We see that (7) has just the form of a Schrödinger equation

$$(i\partial_t - \mathcal{H})\psi = 0$$

with the imaginary time $t = -iS$ and the Hamiltonian

$$\mathcal{H} = -\triangle_{\vec{r}} + i\varphi(\vec{r}).$$

We will see later that the mean-field potential $i\varphi_{MF}(\vec{r})$ becomes a real function.

G may be written as

$$G(\vec{r}, \vec{r}', S, \varphi) = \sum_{\nu} \psi_{\nu}^*(\vec{r}') e^{-SE_{\nu}} \psi_{\nu}(\vec{r})$$

where the ψ_{ν} are the normalized solutions of the eigenvalue problem

$$\mathcal{H}\psi_{\nu}(\vec{r}) = E_{\nu}\psi_{\nu}(\vec{r})$$
$$\int d^d r \, \psi_{\nu}^*(\vec{r})\psi_{\nu}(\vec{r}) = 1. \tag{9}$$

The complete eigenvalue problem would be largely analytically unsolvable. But since the spectrum is discrete we can use the ground state approximation

$$G(\vec{r}, \vec{r}', S, \varphi) \cong \psi_0^*(\vec{r}') e^{-SE_0} \psi_0(\vec{r}) \tag{10}$$

which is clearly good for very long chains, i.e. for every finite L we can find chain lengths S large enough to ensure that the ground state approximation will produce reliable results. But the question is rather if this approximation is appropriate to describe the region of relevant chain lengths in the field theoretic ensemble. We will see later that in the geometries which we consider the energy gap $(E_1 - E_0)$ scales for large L like $(E_1 - E_0) \sim L^{-2}$. So the ground state approximation surely will be adequate in the dense limit, where $S(E_1 - E_0)$ for the relevant chain lengths $S \sim L^d$ in the ensemble for $L \to \infty$ and $d > 2$ tends to infinity. On the other hand, in the dilute limit, where we deal with a constant chain length independent of the system size, the ground state approximation breaks down with growing L. Depending on the chemical segment potential determining the relevant chain lengths in the ensemble we then would have to carefully examine if the approximation holds. However, we will see that the results obtained with (10) in the dilute limit smoothly join the expressions obtained in the lowest-mode approximation for the φ^4-LGW model mentioned in the introduction (cf [6, 12]). In this sense the ground state approximation may also be sensible in the dilute limit.

With (10) we obtain for the partition function

$$\mathcal{Z}(S) = \frac{1}{\Omega} \int \mathcal{D}[\varphi] e^{-\frac{1}{2u_0} \int_{\Omega} d^d r \, \varphi^2(\vec{r}) - SE_0[\varphi]} \int_{\Omega} d^d r \, d^d r' \psi_0^*(\vec{r}')\psi_0(\vec{r})$$

where the energy of the ground state E_0 is a functional of the auxiliary field φ.

The mean-field equation then reads

$$\frac{1}{u_0}\varphi_{MF}(\vec{r}) + S\frac{\delta E_0[\varphi]}{\delta\varphi(\vec{r})}\bigg|_{\varphi_{MF}} = 0.$$

Standard time independent perturbation theory for the Schrödinger equation yields

$$\frac{\delta E_0[\varphi]}{\delta\varphi(\vec{r})} = i|\psi_0(\vec{r})|^2$$

and we obtain

$$\varphi_{MF}(\vec{r}) = -iu_0 S|\psi_0^{MF}(\vec{r})|^2. \tag{11}$$

The superscript 'MF' resembles the fact that the ground state solution depends on the corresponding mean-field function φ_{MF}.

To be consistent we have to ensure ((9), (11))

$$[-\triangle_{\vec{r}} + u_0 S|\psi_0^{MF}(\vec{r})|^2]\psi_0^{MF}(\vec{r}) = E_0\psi_0^{MF}(\vec{r})$$
$$\int d^d r \, |\psi_0^{MF}(\vec{r})|^2 = 1. \tag{12}$$

With (11) the boundary conditions for φ_{MF} pass over to ψ_0^{MF}. Moreover we have to guarantee that, if we found a solution ψ_0^{MF} of (12) and this way determined φ_{MF} by (11), the originally chosen function ψ_0^{MF} is really the ground state solution of the problem

$$[-\triangle_{\vec{r}} + i\varphi_{MF}]\psi(\vec{r}) = E\psi(\vec{r}). \tag{13}$$

This can be ensured by searching for a ψ_0^{MF} without knots ($\psi_0^{MF} = 0$) inside the container [13, 14]. Together with the boundary conditions and (12) the functions ψ_0^{MF} and respectively $\varphi_{MF}(\vec{r})$ are then uniquely determined.

The mean-field partition function is finally given by

$$\mathcal{Z}_{MF}(S) = \frac{1}{\Omega} e^{-\frac{1}{2u_0}\int_\Omega d^d r\, \varphi_{MF}^2(\vec{r}) - SE_0[\varphi_{MF}]} \int_\Omega d^d r\, d^d r'\, \psi_0^{MF*}(\vec{r}')\psi_0^{MF}(\vec{r}). \tag{14}$$

Before really turning to Dirichlet boundary conditions we test our formalism on the geometry extensively studied in [1], i.e. a d-dimensional hypercube Ω with linear dimension L and periodic boundary conditions in all directions.

For the nodeless solution of the problem (12) we find

$$\psi_0^{MF}(\vec{r}) = \frac{1}{L^{d/2}} \qquad E_0 = \frac{u_0 S}{L^d}.$$

So we have a constant mean-field solution

$$\varphi_{MF}(\vec{r}) = -i\frac{u_0 S}{L^d}$$

and the mean-field partition function becomes

$$\mathcal{Z}_{MF}(S) = e^{-\frac{u_0 S^2}{2L^d}}.$$

This way in our mean-field approximation we recover the correct three level result for the partition function for periodic boundary conditions (cf [1]).

With the given constant φ_{MF} we are able to construct the higher energy solutions of the eigenvalue problem (13). The energies of these higher modes are given by

$$E_{\vec{k}} = k^2 + E_0 \qquad k_\alpha = \frac{2\pi}{L}\kappa_\alpha \qquad \kappa_\alpha = \pm 1, \pm 2, \ldots$$

and for the energy gap we get $(E_1 - E_0) = 4\pi^2/L^2$.

3. Dirichlet boundary conditions in one direction, periodic boundary conditions in $d-1$ dimensions

3.1. Unrenormalized mean-field approximation

We are now going to apply our formalism to a geometry with Dirichlet boundary conditions. We consider a d-dimensional hypercube of linear dimension L with Dirichlet boundary conditions in the z-direction and periodic ones in the remaining $d-1$ dimensions. This geometry (instead of Dirichlet boundary conditions in all d dimensions) has the advantage that the problem (12) effectively becomes one-dimensional:

$$\left[-\frac{d^2}{dz^2} + u_0 S|\psi_0^{MF}(z)|^2\right]\psi_0^{MF}(z) = E_0\psi_0^{MF}(z)$$

$$\int_0^L dz\, |\psi_0^{MF}(z)|^2 = L^{1-d}$$

and can be solved analytically [15]. The nodeless solution is given by

$$
z = \begin{cases} \dfrac{L}{2K(k)} F\left(k, \arcsin\left[\dfrac{\sqrt{u_0 S}L}{\sqrt{8}kK(k)}\psi_0^{MF}\right]\right) & 0 \leqslant z \leqslant L/2 \\[3mm] L - \dfrac{L}{2K(k)} F\left(k, \arcsin\left[\dfrac{\sqrt{u_0 S}L}{\sqrt{8}kK(k)}\psi_0^{MF}\right]\right) & L/2 \leqslant z \leqslant L \end{cases} \tag{15}
$$

$$
E_0 = \frac{4}{L^2}(k^2 + 1)K^2(k).
$$

The solutions for the two intervals $0 \leqslant z \leqslant L/2$ and $L/2 \leqslant z \leqslant L$ join smoothly. The parameter k is determined by the normalization condition

$$
\frac{8K(k)}{u_0 S} L^{d-2}(K(k) - E(k)) = 1. \tag{16}
$$

ψ_0^{MF} lies in the interval $[0, \frac{\sqrt{8}kK(k)}{\sqrt{u_0 S}L}]$ and K, E, F stand for the elliptic integrals

$$
E(k) = \int_0^{\pi/2} \sqrt{1 - k^2 \sin^2 \phi}\, \mathrm{d}\phi
$$

$$
K(k) = \int_0^{\pi/2} \frac{\mathrm{d}\phi}{\sqrt{1 - k^2 \sin^2 \phi}} \tag{17}
$$

$$
F(k, \theta) = \int_0^{\theta} \frac{\mathrm{d}\phi}{\sqrt{1 - k^2 \sin^2 \phi}}.
$$

The solution (15) exists for arbitrary S, u_0. For the ground state energy the relation $E_0 \geqslant \pi^2/L^2$ holds.

For the generalized partition function in the mean-field approximation (14) we get

$$
\mathcal{Z}_G^{(MF)}(S, \mu_s) = A\mathrm{e}^{(\mu_s - \mu_s^*)S + B} \tag{18}
$$

where

$$
A = \frac{8L^{4-d}k^2}{u_0 S}\left[\int_0^1 \frac{x\,\mathrm{d}x}{\sqrt{(1 - x^2)(1 - k^2 x^2)}}\right]^2
$$

$$
B = \frac{32k^4 K^3(k)}{u_0 L^{4-d}}\left(\frac{2(k^2 + 1)}{3k^4}(K(k) - E(k)) - \frac{K(k)}{3k^2}\right) - \frac{4S}{L^2}(k^2 + 1)K^2(k). \tag{19}
$$

In the mean-field approximation the critical chemical potential is given by $\mu_s^* = 0$.

We now discuss this result in the various limits studied in [1].

3.1.1. Dilute limit. In the dilute limit $(\mu_s < 0, L \to \infty)$ or $(S \to \text{const.}, L \to \infty)$ we get with (16)

$$
k \sim \sqrt{\frac{u_0 S}{\pi^2 L}} \to 0 \qquad E(k),\ K(k) \to \frac{\pi}{2}.
$$

Defining

$$
\hat{z} = z/L
$$

$$
\hat{\psi}_0^{MF} = \frac{\sqrt{u_0 S}L}{\sqrt{8}kK(k)}\psi_0^{MF} \tag{20}
$$

and taking into account (15) we can write

$$
E_0 \to \frac{\pi^2}{L^2}
$$

$$
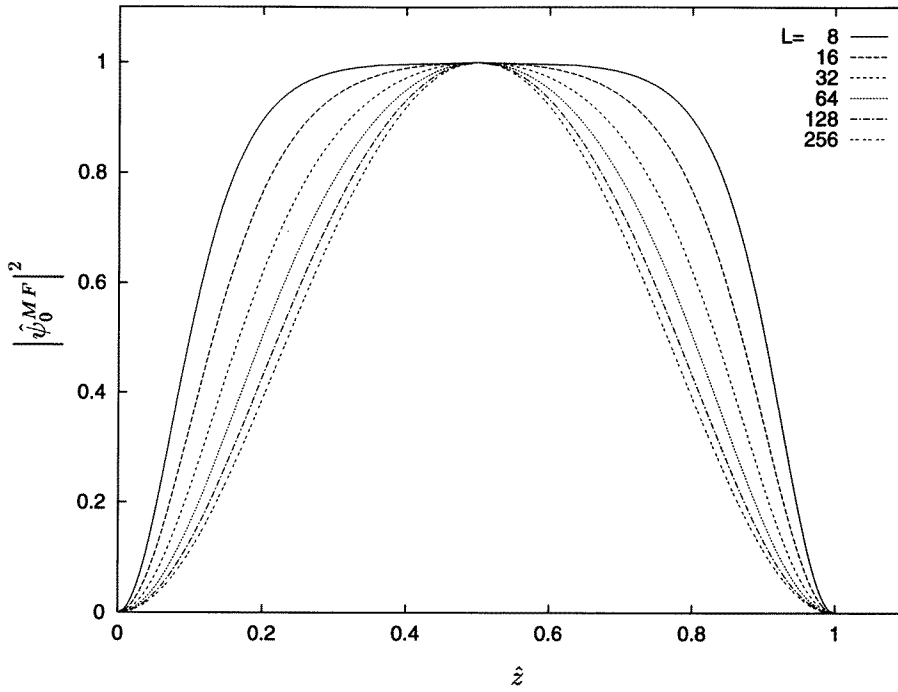\hat{\psi}_0^{MF} \to \sin(\pi\hat{z}). \tag{21}
$$

Figure 1. Local segment density for fixed $u_0 S = 1000$ and various system sizes L.

A more interesting quantity is the local segment density (cf (8), (11))

$$\langle \rho(\vec{r}) \rangle = \frac{i}{u_0} \varphi_{MF}(\vec{r}) = S |\psi_0^{MF}(\vec{r})|^2. \tag{22}$$

Figure 1 shows the normalized quantity $|\hat{\psi}_0^{MF}|^2 = \frac{u_0 L^2}{8 k^2 K^2(k)} \langle \rho(\vec{r}) \rangle$ proportional to it for a fixed chain length $u_0 S = 1000$ and various system sizes L. (In all results we set $d = 3$.)

In the limit $L \to \infty$ we get

$$\langle \rho(\vec{r}) \rangle \longrightarrow 2c \sin^2 \left(\frac{\pi z}{L} \right)$$

where c stands for the total segment density $c = S/L^d = \int \mathrm{d}^d r \, \langle \rho(\vec{r}) \rangle$. The local segment density grows quadratically for small values of z near the boundary of the system, a result found also in [16]. For the mean-field partition function in the dilute limit we find

$$\mathcal{Z}_G^{(MF)}(S, \mu_s) = \frac{8}{\pi^2} \exp \left[(\mu_s - \mu_s^*)S - \frac{\pi^2}{L^2} S - \frac{3}{4} \frac{u_0 S}{L^d} \right]. \tag{23}$$

The leading finite-size corrections are given by the $(\pi^2/L^2)S$-term in the exponent. So one could argue that due to the finiteness of the system the chemical segment potential gets shifted by (π^2/L^2). However, this interpretation does not hold in the renormalized theory discussed later. There the chemical potential is renormalized, but not the system size, and $(\pi^2/L^2)S$ gets a function of the finite-size scaling variable (n^ν/L) not proportional to n.

3.1.2. Dense limit. In the dense limit ($\mu_s > 0$, $L \to \infty$) or ($c = S/L^d \to$ const., $L \to \infty$) respectively we find with the notation $\hat{c} = u_0 S/L^d$

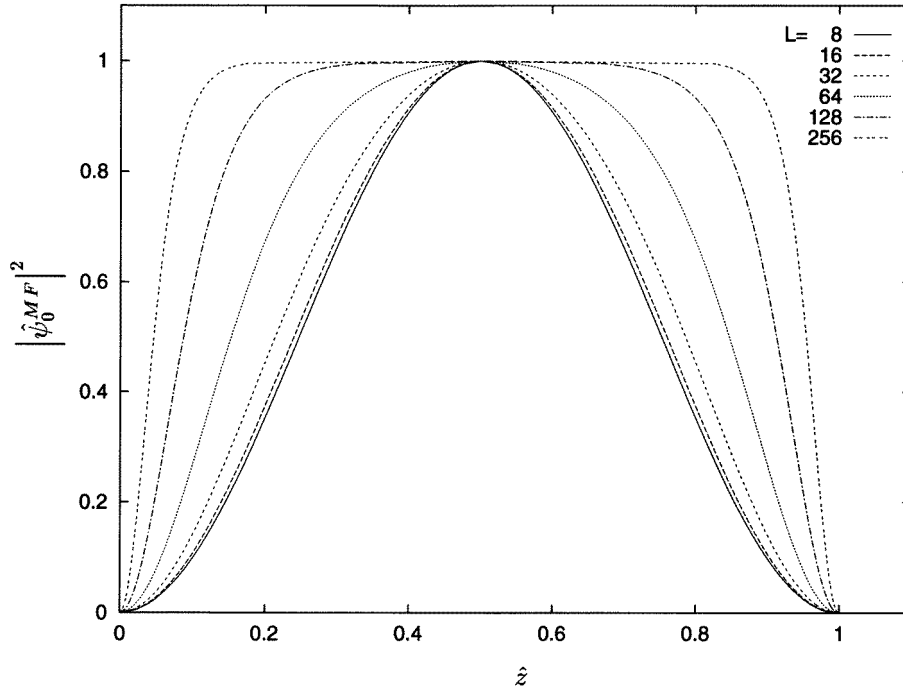$$k \to 1 \qquad E(k) \to 1 \qquad K(k) \to \sqrt{\frac{\hat{c} L^2}{8}}.$$

Figure 2. Local segment density for fixed $\hat{c} = 0.01$ and various system sizes L.

The ground state energy tends to a finite limit

$$E_0 \to \hat{c}$$

and for the local segment density we get the behaviour shown in figure 2. With growing system size L the local segment density reaches a constant (namely the total segment density c) almost in the whole volume with steep descents at the boundaries of the system. We can define the thickness the of the boundary layer as the value of z, where the local segment density reaches the half of its maximum

$$d_c \stackrel{\text{def}}{=} z(|\hat{\psi}_0^{MF}|^2 = \tfrac{1}{2}).$$

Then we get using (15)

$$d_c = \frac{L}{2K(k)} F(k, \arcsin(1/\sqrt{2})) \to \sqrt{\frac{2}{\hat{c}}} F(1, \pi/4).$$

The thickness of the boundary layer for $L \to \infty$ tends to a constant proportional to the screening length $\xi_E \sim \hat{c}^{-1}$ (cf [1]) independent of the system size. Such a behaviour could also be expected by simple scaling arguments (cf [17, 18]).

The mean-field partition function in the dense limit can be written as

$$\mathcal{Z}_G^{(MF)}(\hat{c}, \mu_s) = \exp\left[-\frac{L^d}{u_0} \left((\mu_s^* - \mu_s)\hat{c} + \frac{\hat{c}^2}{2} - \frac{2\sqrt{8}}{3L}\hat{c}^{3/2} + O(L^{-2}) \right) \right]. \tag{24}$$

We find the same leading term $-\frac{L^d \hat{c}^2}{2u_0}$ as for periodic boundary conditions in [1]. The Dirichlet boundary conditions manifest themselves as corrections $\sim 1/L$ to this leading behaviour.

3.2. Renormalization

For the renormalization of the theory we note that renormalizability is a statement about the short-distance behaviour, independent of whether the system is finite or not [19]. We thus can take over the standard bulk renormalization scheme (cf [1]). We define a renormalized length scale l_R and replace the bare quantities by their renormalized counterparts

$$
\begin{aligned}
S &= n_R l_R^2 Z_n(u) \\
u_0 &= (4\pi)^{d/2} u l_R^{-\epsilon} Z_u(u) \\
\mu_s^* - \mu_s &= E_R l_R^{-2} Z_n^{-1}(u).
\end{aligned}
\tag{25}
$$

The renormalized form of the generalized partition function is given by

$$
\mathcal{Z}_G^{(R)}(n_R, E_R, u) = \frac{Z_n}{Z} \mathcal{Z}_G(S, \mu_s^* - \mu_s, u_0).
\tag{26}
$$

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. For our zero-loop approximation they can be replaced simply by constants. With (25) and the notion $\tilde{u} = (4\pi)^{d/2} u/2$ we get for the renormalized partition function

$$
\begin{aligned}
\mathcal{Z}_{MF}^{(R)} &= A\exp(B) \\
A &= \left(\frac{L}{l_R}\right) \frac{8k^2}{\tilde{u} n_R} \left[\int_0^1 \frac{x\,dx}{\sqrt{(1-x^2)(1-k^2 x^2)}}\right]^2 \\
B &= \tilde{u} n_R^2 \left(\frac{l_R}{L}\right)^d \left(-\frac{k^2}{3} - \frac{1}{6}\right) + n_R \left(\frac{l_R}{L}\right)^2 K(k) E(k) \left(\frac{8}{3} - 4(k^2 + 1)\right) \\
&\quad - \frac{32}{3} k^2 \frac{K^2(k) E^2(k)}{\tilde{u}} \left(\frac{l_R}{L}\right) - E_R n_R.
\end{aligned}
\tag{27}
$$

The normalization condition determining the parameter k is modified into

$$
\frac{8K(k)}{\tilde{u} n_R} \left(\frac{L}{l_R}\right)^{d-2} (K(k) - E(k)) = 1.
\tag{28}
$$

As for periodic boundary conditions we restrict ourselves to the excluded volume fixed point $u = u^*$. There the mapping from renormalized quantities back to the physical ones in the discrete chain model is given by

$$
\begin{aligned}
n_R &= \left(\frac{B}{l_R}\right)^{1/\nu} n \\
E_R &= (\hat{\mu}_s^* - \hat{\mu}_s) \left(\frac{l_R}{B}\right)^{1/\nu} \\
Z/Z_n &= \left(\frac{l_R}{B_1}\right)^{(\gamma-1)/\nu}
\end{aligned}
\tag{29}
$$

with the critical exponents $\nu \approx 0.588$ and $\gamma \approx 1.157$ in $d = 3$ dimensions. The parameters B, B_1 depend on the microstructure of the system. Throughout this paper we will use the value $B = 0.4631$ found in [1] for periodic boundary conditions by comparing the theoretical results to Monte Carlo data. Since we will normalize all partition functions to $\mathcal{Z}(n = 1) = 1$ the value of B_1 is of no importance for our purposes. The renormalized length scale l_R will be fixed by the crossover relation

$$
1 = \frac{n_0}{n_R} + \frac{c_R}{c_0} \qquad c_R = \tilde{u}^* \frac{1}{L^d} n_R l_R^d \qquad c_0 = 1.2 \qquad n_0 = 0.53
\tag{30}
$$
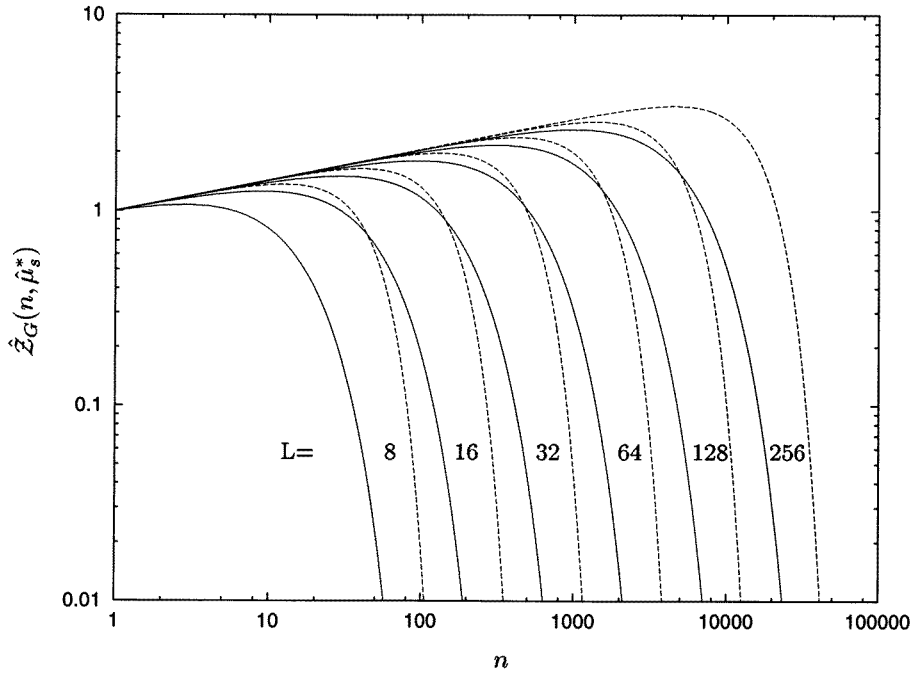
Figure 3. Partition function at the critical chemical segment potential $\hat{\mu}_s = 0$ for periodic and Dirichlet boundary conditions and various system sizes $L = 8, 16, 32, 64, 128, 256$. Dirichlet boundary conditions are represented by the full curves, periodic boundary conditions by the broken curves. The respective curves left and right of the system size numbers belong together.

smoothly interpolating between the dilute limit and the case of finite concentration (see [1]).

Figure 3 shows the results for the partition function

$$\hat{\mathcal{Z}}_G^{(MF)}(n, \hat{\mu}_s^*) = \frac{Z}{Z_n} \mathcal{Z}_{MF}^{(R)}(E_R, n_R, l_R/L) = \left(\frac{l_R}{B_1}\right)^{(\gamma-1)/\nu} A \exp(B)$$

at the critical chemical segment potential $\hat{\mu}_s = 0$ compared with the zero-loop results [1] for a system with periodic boundary conditions in all d directions. It is clearly seen that the maximum of the partition function for Dirichlet boundary conditions is shifted to smaller chain lengths.

Finally we consider the chain length distribution in the dilute and dense limits.

3.2.1. Dilute limit.

For $\hat{\mu}_s < 0$, $L \to \infty$ we get with the crossover relation (30)

$$n_R \to n_0 \qquad l_R \to B\left(\frac{n}{n_0}\right)^\nu$$

and using (28) we recover $k \to 0$ as in the unrenormalized case. Respectively (27) yields

$$\hat{\mathcal{Z}}_G^{(MF)}(n, \hat{\mu}_s) = \text{const.} \cdot n^{(\gamma-1)} e^{(\hat{\mu}_s - \hat{\mu}_s^*)n}$$

the well known result for the bulk partition function. The scaling form of the partition function

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

ensures that this result is exact to all orders perturbation theory. Hence the chain length distribution (1) is given by (2).

3.2.2. Dense limit. In the dense limit $\hat{\mu}_s > 0$, $L \to \infty$, l_R gets a function of the segment density

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

and the generalized partition function as a function of c can be written as

$$\hat{\mathcal{Z}}_G^{(MF)}(c) = \text{const.} \cdot c^{\frac{\gamma-1}{1-\nu d}} \exp\left[-L^d \left(C_1 c^{\frac{\nu d}{\nu d-1}} + \frac{1}{L} C_2 c^{\frac{3\nu d-5\nu}{2(\nu d-1)}} - (\hat{\mu}_s - \hat{\mu}_s^*)c \right) \right] \tag{31}$$

where

$$C_1 = \frac{1}{2\tilde{u}^*} (\tilde{u}^* B^{1/\nu})^{\frac{\nu d}{\nu d-1}} c_0^{\frac{\nu d-2}{\nu d-1}}$$

$$C_2 = \frac{2\sqrt{8}}{3\tilde{u}^*} (\tilde{u}^* B^{1/\nu})^{\frac{3\nu d-5\nu}{2(\nu d-1)}} c_0^{\frac{5\nu-3}{2(\nu d-1)}}.$$

The leading term $\sim C_1$ is identical to the zero-loop result for periodic boundary conditions, whereas the term proportional to C_2 describes the corrections due to the Dirichlet conditions. To get the chain length distribution (1), the field theoretic partition function $\mathcal{Z}_F = \int dc\, \mathcal{Z}_G(c)$ must be evaluated by the method of steepest descent. Then for $L \to \infty$ we recover the result

$$P(c, \hat{\mu}_s) \to \delta(c - \bar{c}) \tag{32}$$

known from periodic boundary conditions, but with a slightly modified value for the mean segment density $\bar{c}$ given now by the equation

$$\frac{\nu d}{\nu d-1} C_1 \bar{c}^{\frac{1}{\nu d-1}} + \frac{1}{L} \frac{3\nu d-5\nu}{2(\nu d-1)} C_2 \bar{c}^{\frac{\nu d-5\nu+2}{2(\nu d-1)}} - (\hat{\mu}_s - \hat{\mu}_s^*) = 0 \tag{33}$$

instead of

$$\frac{\nu d}{\nu d-1} C_1 \bar{c}^{\frac{1}{\nu d-1}} - (\hat{\mu}_s - \hat{\mu}_s^*) = 0$$

as in the periodic case. To leading order (33) yields

$$\bar{c} = \bar{c}_{PBC} - \frac{1}{L} \frac{(3\nu d - 5\nu)C_2}{2(\hat{\mu}_s - \hat{\mu}_s^*)} (\bar{c}_{PRB})^{\frac{3\nu d-5\nu}{2(\nu d-1)}} + \mathrm{O}(L^{-2})$$

with the zero-loop saddle point $\bar{c}_{PBC}$ for periodic boundary conditions

$$\bar{c}_{PBC} = \left[\frac{(\nu d - 1)(\hat{\mu}_s - \hat{\mu}_s^*)}{\nu d C_1} \right]^{\nu d-1}.$$

Compared with the periodic case the mean segment density in the dense limit for Dirichlet boundary conditions gets shifted by a correction $\sim 1/L$ to lower values.

With (32) the complete discussion for the crossover from the dense to the semidilute limit in [1] can be repeated also in the case of Dirichlet boundary conditions.

Figure 4 shows how the segment density distribution with growing system size L in the dense limit tends to the delta-function. For comparision we added the zero-loop results for peridic boundary conditions in all directions. The chemical segment potential is fixed to $\hat{\mu}_s = 0.1$. The bulk ($L \to \infty$) value for the segment density is given by $c_{bulk} = 0.2001$ and (within the accuracy of the plot) identical to the maximum of the $L = 512$ peak for periodic boundary conditions.

Figure 5 shows the finite-size results for the equation of state relating the chemical potential to the mean segment density.
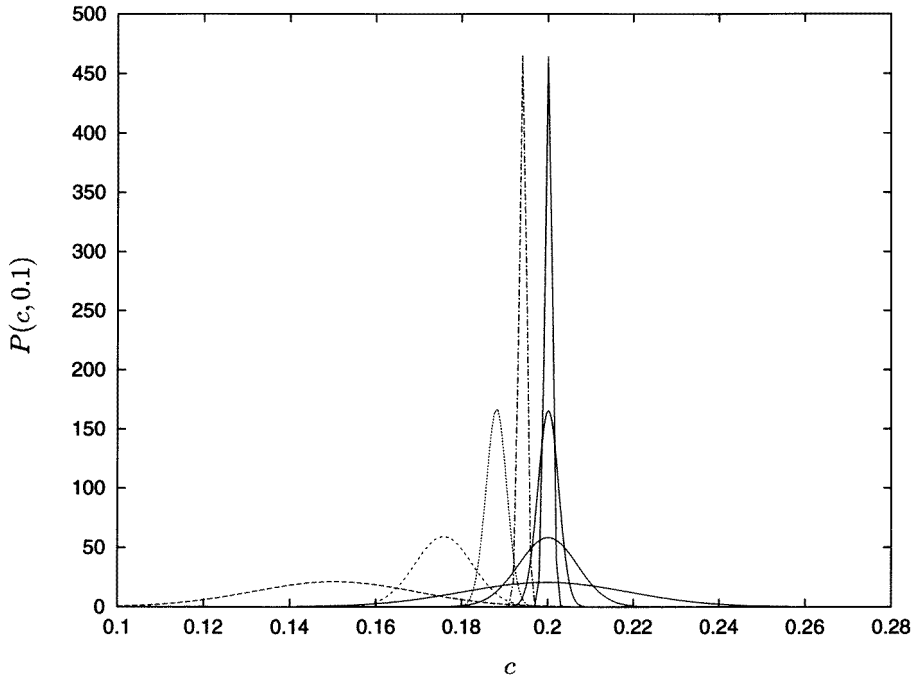
Figure 4. Segment density distribution for periodic and Dirichlet boundary conditions and various system sizes $L = 64, 128, 256, 512$. Periodic boundary conditions are represented by the full curves, periodic boundary conditions by the dashed or broken curves.

4. Beyond the mean-field approximation

In the mean-field formalism constructed in the last sections we made two essential simplifications: (i) we neglected all fluctuations around the mean-field solution by setting $\varphi(\vec{r}) \equiv \varphi_{MF}(\vec{r})$ and (ii) used the ground state approximation for the mean-field Green function $G(\vec{r}, \vec{r}', S, \varphi_{MF})$. We will now show that the ground state approximation plays the fundamental role in our mean-field formalism in the sense that within this approximation all fluctuations around $\varphi(\vec{r})_{MF}$ can be integrated out without changing the result.

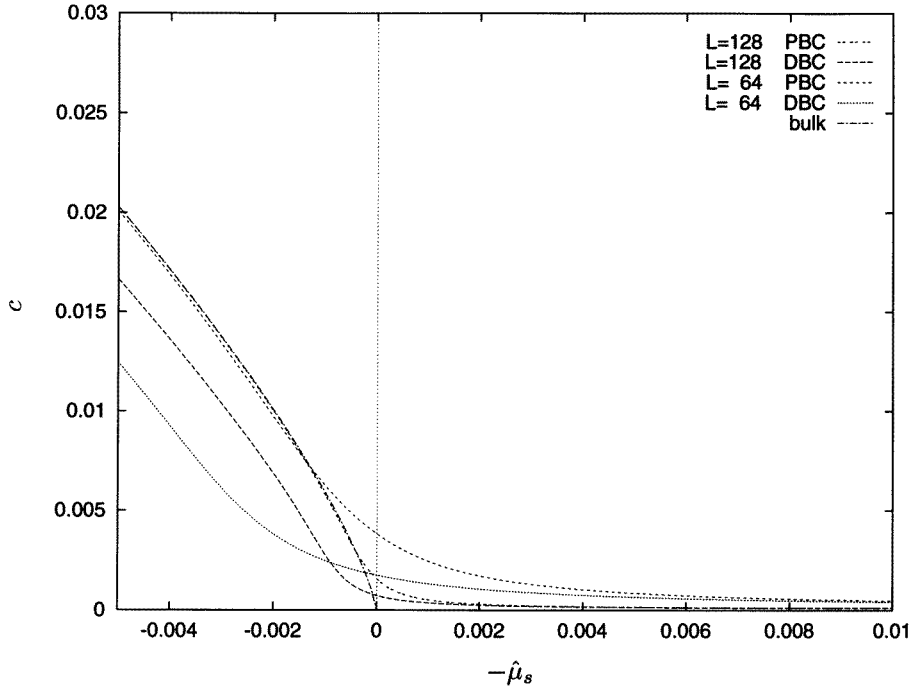To this purpose we expand the auxiliary field $\varphi(\vec{r})$

$$\varphi(\vec{r}) = \varphi_{MF}(\vec{r}) + \delta\varphi(\vec{r}) \qquad \delta\varphi(\vec{r}) = \varphi_0 \varphi_{MF}(\vec{r}) + \sigma(\vec{r}) \qquad \sigma \perp \varphi_{MF}.$$

For the Green function (6) we can write

$$G(\vec{r}, \vec{r}', S, \varphi) = \int_{\vec{r}(0)=\vec{r}}^{\vec{r}(S)=\vec{r}'} \mathcal{D}[r(s)] e^{-\int_0^S ds[(\frac{d\vec{r}(s)}{2ds})^2 + i\varphi_{MF}(\vec{r}(s))] - i\int_0^S ds\, \delta\varphi(\vec{r}(s))}.$$

Expanding the exponent in $\delta\varphi$ we get

$$G(\vec{r}, \vec{r}', S, \varphi) = G(\vec{r}, \vec{r}', S, \varphi_{MF})$$
$$+ (-i) \int_{0 \leqslant s \leqslant S} ds \int d^d r_1 G(\vec{r}, \vec{r}_1, S-s, \varphi_{MF}) \delta\varphi(\vec{r}_1) G(\vec{r}_1, \vec{r}', s, \varphi_{MF})$$
$$+ (-i)^2 \int_{0 \leqslant s_1 \leqslant s_2 \leqslant S} ds_1\, ds_2 \int d^d r_1\, d^d r_2\, G\delta\varphi G\delta\varphi G + \cdots. \tag{34}$$

Figure 5. Equation of state for periodic (PBC) and Dirichlet (DBC) boundary conditions and system sizes $L = 64, 128$. For comparision the bulk curve is also shown.

Now using the ground state approximation (10) for $G(\vec{r}, \vec{r}', S, \varphi_{MF})$, the expansion can be resummed to yield

$$
\begin{aligned}
G(\vec{r}, \vec{r}', S, \varphi) &= G(\vec{r}, \vec{r}', S, \varphi_{MF})\bigg(1 + (-\mathrm{i})S \int \mathrm{d}^d r_1 \, \delta\varphi(\vec{r}_1)|\psi_0^{MF}(\vec{r}_1)|^2 \\
&\quad + (-\mathrm{i})^2 \frac{S^2}{2}\left[\int \mathrm{d}^d r_1 \delta\varphi(\vec{r}_1)|\psi_0^{MF}(\vec{r}_1)|^2\right]^2 + \cdots\bigg) \\
&= G(\vec{r}, \vec{r}', S, \varphi_{MF})\mathrm{e}^{-\mathrm{i}S \int \mathrm{d}^d r_1 \, \delta\varphi(\vec{r}_1)|\psi_0^{MF}(\vec{r}_1)|^2} \\
&= G(\vec{r}, \vec{r}', S, \varphi_{MF})\mathrm{e}^{\frac{1}{u_0} \int \mathrm{d}^d r_1 \, \delta\varphi(\vec{r}_1)\varphi_{MF}(\vec{r}_1)}.
\end{aligned}
\tag{35}
$$

Inserting this result into (5) we can integrate out $\delta\varphi$ completely

$$
\mathcal{Z}(S) = \int \mathcal{D}[\delta\varphi]\mathrm{e}^{-\frac{1}{2u_0}\int_\Omega \mathrm{d}^d r \, (\delta\varphi(\vec{r}))^2}\mathcal{Z}_{MF}(S) = \mathcal{Z}_{MF}(S)
$$

and recover the mean-field result for the partition function. The fluctuations do not yield any corrections. In this sense within the ground state approximation the mean-field result for the partition function is exact. The ground state approximation neglects all spatial correlations of the auxiliary field $\varphi(\vec{r})$ beyond the mean-field contribution $\langle\varphi(\vec{r})\rangle\langle\varphi(\vec{r}')\rangle$. This is the main feature of our mean-field formalism.

Respectively, the range of validity of our mean-field approximation is determined by the breakdown of the ground state approximation for the Green function (see the discussion following equation (10) in section 2).

To get corrections to the mean-field results we thus have to improve the approximation
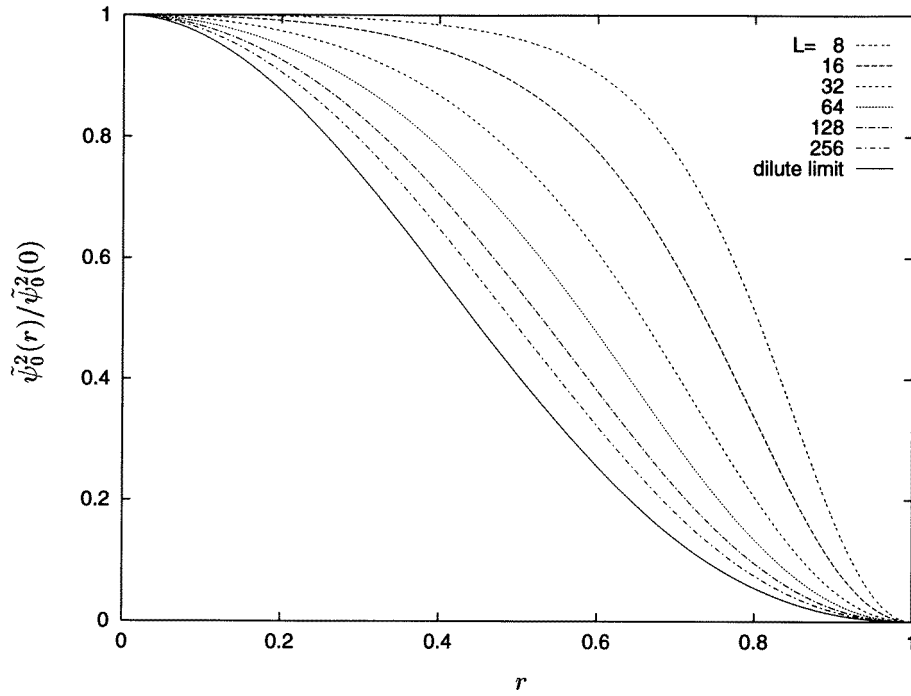
Figure 6. Local segment density for a sphere with Dirichlet boundary conditions at fixed $u_0 S = 1000$ for various system sizes L. The full curve represents the limiting function $\sin^2(\pi r)/\pi^2 r^2$ in the dilute limit $L \to \infty$.

for the Green function

$$G(\vec{r}, \vec{r}', S, \varphi_{MF}) = \sum_\nu \psi_\nu^*(\vec{r}')e^{-E_\nu S}\psi_\nu(\vec{r}).$$

What can be done analytically strongly depends on the geometry considered. If we return to the d-dimensional hypercube with Dirichlet boundary conditions in the z-direction and periodic ones in the remaining $d - 1$ dimensions, the solutions of the Schrödinger equation

$$[-\triangle_{\vec{r}} + u_0 S|\psi_0^{MF}(\vec{r})|^2]\psi_\nu(\vec{r}) = E_\nu\psi_\nu(\vec{r})$$

can be written as

$$\psi_\nu(\vec{r}) = \psi_{n,\vec{q}}(\vec{r}) = e^{i(q_1 x_1 + \ldots q_{d-1} x_{d-1})}\psi_n(z)$$
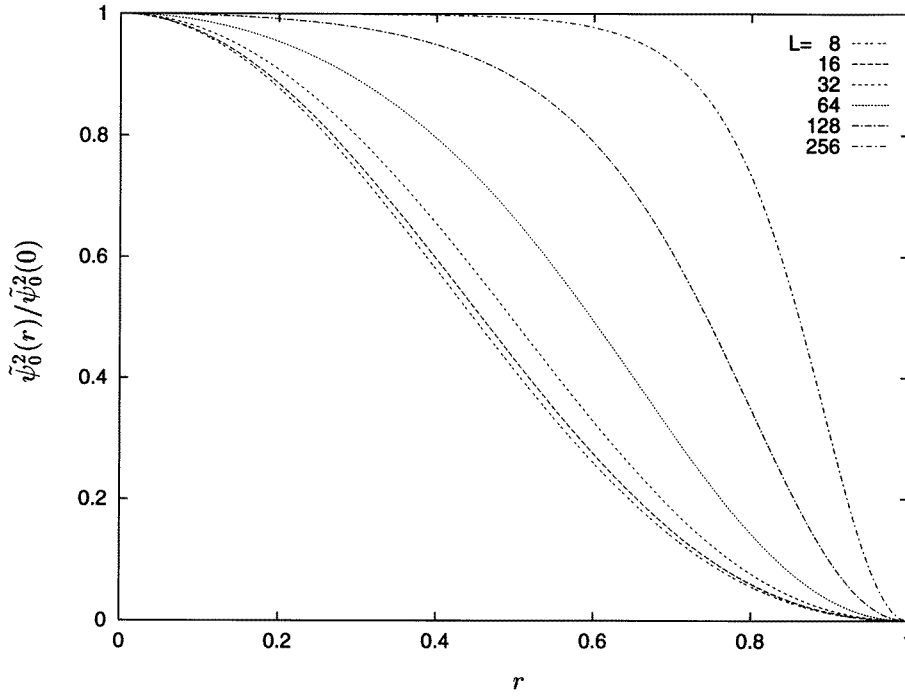$$E_{n,q} = E_n + q^2$$

where

$$q_i = \frac{2\pi}{L}\kappa_i \qquad \kappa_i = 0, \pm 1, \pm 2, \ldots.$$

The $\psi_n, E_n, n = 0, 1, 2, \ldots$ are the solutions of the one-dimensional eigenvalue problem

$$\left[-\frac{d^2}{dz^2} + u_0 S|\psi_0^{MF}(z)|^2\right]\psi_n(z) = E_n\psi_n(z)$$
$$\int_0^L dz\,|\psi_n(z)|^2 = L^{1-d}.$$

ψ_n, E_n cannot be evaluated analytically.

However, we can avoid this problem by considering a geometry with different length scales

Figure 7. Local segment density for a sphere with Dirichlet boundary conditions at fixed $\hat{c} = 0.001$ for various system sizes L.

in the Dirichlet and periodic directions. Let L_D be the linear dimension of the finite box in the z-direction with Dirichlet boundary conditions and L_P the respective scale for the $d - 1$ directions with periodic boundary conditions. If we require $L_P \gg L_D$, which means choosing a plate geometry, the energy gap $E_1 - E_0$ will be much larger then the q^2-fluctuations around the ground state energy E_0 caused by the periodic modes. So it will be reasonable to improve the ground state approximation by including periodic fluctuations into the approximation for the Green function and neglect only the higher energy solutions of the Dirichlet problem in the z-direction.

This way we have

$$G(\vec{r}, \vec{r}', S, \varphi_{MF}) = \sum_{\vec{q}} \psi^*_{0,\vec{q}}(\vec{r}')e^{-(E_0+q^2)S}\psi_{0,\vec{q}}(\vec{r})$$

$$\psi_{0,\vec{q}}(\vec{r}) = e^{i\vec{q}\vec{r}_\perp}\psi_0^{MF}(z) \qquad \vec{r}_\perp = \{x_1, \ldots, x_{d-1}\}$$

(36)

where $\psi_0^{MF}(z)$ is given by (15) with the slightly modified normalization condition (16)

$$\frac{8K(k)}{u_0 S}\frac{L_P^{d-1}}{L_D}(K(k) - E(k)) = 1$$

due to the two length scales. Inserting (36) into the expansion (34) we get

$$G(\vec{r}, \vec{r}', S, \varphi) = G(\vec{r}, \vec{r}', S, \varphi_{MF})$$

$$+(-i)\int_0^S ds \int d^d r_1 \sum_{\vec{q}_1, \vec{q}_2} \psi_{0,\vec{q}_1}(\vec{r})\psi^*_{0,\vec{q}_1}(\vec{r}_1)e^{-E_0 S - q_1^2(S-s)}$$

$$\times \delta\varphi(\vec{r}_1)\psi_{0,\vec{q}_2}(\vec{r}_1)\psi^*_{0,\vec{q}_2}(\vec{r}')e^{-q_2^2 s} + \cdots .$$

So we have to consider integrals of the form

$$\int d^d r \, \delta\varphi(\vec{r}) e^{i(\vec{q}_1 - \vec{q}_2)r_\perp} |\psi_0^{MF}(z)|^2. \tag{37}$$

If we restrict ourselves to the lowest-mode approximation [6], integrating out only the amplitude of the mean-field solution, i.e. if we set

$$\delta\varphi(\vec{r}) = \tilde{\varphi}_0 \varphi_{MF}(\vec{r})$$

$\delta\varphi$ depends only on the z-coordinate and the integrals (37) reduce to

$$L_P^{d-1} \delta_{\vec{q}_1, \vec{q}_2} \int_0^{L_D} dz \, \delta\varphi(\vec{z}) |\psi_0^{MF}(z)|^2.$$

Then in complete analogy to (35) we recover in the approximation (36) the result

$$\mathcal{Z}(S) = \frac{1}{\Omega} e^{-\frac{1}{2u_0} \int_\Omega d^d r \, \varphi_{MF}^2(\vec{r})} \int_\Omega d^d r \, d^d r' \sum_{\vec{q}} e^{i\vec{q}(\vec{r}_\perp - \vec{r}'_\perp)} \psi_0^{MF*}(z') e^{-(E_0 + q^2)S} \psi_0^{MF}(z)$$

$$= \mathcal{Z}_{MF}(S)$$

for the partition function, which differs from (14) only by the modified normalization condition for the parameter k and again indicates the high structural stability of our mean-field formalism.

It is possible to go a step further beyond the lowest-mode approximation by also including periodic fluctuations for $\delta\varphi$ around the mean-field solution

$$\delta\varphi(\vec{r}) = \sqrt{u_0} \sum_{\vec{q}} \tilde{\varphi}_{\vec{q}} \psi_{\vec{q}}(\vec{r}) \qquad \psi_{\vec{q}}(\vec{r}) = \frac{1}{\mathcal{N}} e^{i\vec{q}\vec{r}_\perp} |\psi_0^{MF}(z)|^2$$

$$\mathcal{N} = \left(L_P^{d-1} \int_0^{L_D} dz \, |\psi_0^{MF}(z)|^4 \right)^{1/2}.$$

Using this approach together with the approximation (36) for the mean-field Green function we get with (34)

$$\int d^d r \, d^d r' \, G(\vec{r}, \vec{r}', S, \varphi) = e^{-E_0 S} L_P^4 \int_0^{L_D} dz \, \psi_0^{MF}(z) \int_0^{L_D} dz' \, \psi_0^{MF*}(z') \bar{G}_{00}(S, \varphi)$$

$$\bar{G}_{00}(S, \varphi) = 1 + \sum_{j=2}^{\infty} (-i)^j u_0^{j/2} \mathcal{N}^j \sum_{\vec{k}_1, \dots, \vec{k}_{j-1}} A(1, j-1) J_j \tag{38}$$

where we adopted the notation

$$A(1, j) = \tilde{\varphi}_{\vec{q}_1} \tilde{\varphi}_{\vec{q}_2 - \vec{q}_1} \dots \tilde{\varphi}_{\vec{q}_j - \vec{q}_{j-1}} \tilde{\varphi}_{-\vec{q}_j} \tag{39}$$

$$J_j = \int_{0 < s_1 < \dots < s_j < S} \exp\{-(s_j - s_{j-1})q_{j-1}^2 - \dots - (s_2 - s_1)q_1^2\} \tag{40}$$

of [1]. We are now able to integrate out the zero-mode amplitude $\tilde{\varphi}_0$ completely by reordering the expansion

$$G_{00}(S, \varphi) = \left(1 + \sum_{j=1}^{\infty} (-i)^j \frac{(S)^j}{j!} u_0^{j/2} \mathcal{N}^j \tilde{\varphi}_0^j \right)$$

$$\times \left(1 + \sum_{j=2}^{\infty} (-i)^j u_0^{j/2} \mathcal{N}^j \sum_{\vec{k}_1, \dots, \vec{k}_{j-1}} A(1, j-1) J_j \bigg|_{\tilde{\varphi}_0 = 0} \right)$$

$$= e^{-iS\tilde{\varphi}_0 u_0^{1/2} \mathcal{N}} \bar{G}_{00}(S, \varphi')$$

where φ' like for periodic boundary conditions contains only $\vec{q} \neq 0$ modes. For the partition function we thus get

$$\hat{\mathcal{Z}}(S) = \frac{1}{\Omega} e^{-E_0 S} L_P^4 \int_0^{L_D} dz \, \psi_0^{MF}(z) \int_0^{L_D} dz' \, \psi_0^{MF*}(z') \int \prod_{q \neq 0} \frac{d\tilde{\varphi}_{\vec{q}}}{\sqrt{\pi}} e^{-\frac{1}{2} \sum_{q \neq 0} \tilde{\varphi}_{\vec{q}} \tilde{\varphi}_{-\vec{q}}} \bar{G}_{00}(S, \varphi')$$

$$= \mathcal{Z}_{MF}(S) \int \prod_{q \neq 0} \frac{d\tilde{\varphi}_{\vec{q}}}{\sqrt{\pi}} e^{-\frac{1}{2} \sum_{q \neq 0} \tilde{\varphi}_{\vec{q}} \tilde{\varphi}_{-\vec{q}}} \bar{G}_{00}(S, \varphi') \tag{41}$$

with $\mathcal{Z}_{MF}$ from (14). As could be expected we reproduce the result (20) of [1] with the only modifications that the mean-field partition function $\exp(-u_0 S^2/2L^d)$ for periodic boundary conditions has to be replaced by the respective Dirichlet expression $\mathcal{Z}_{MF}$ and in $\bar{G}_{00}$ we sum only over the $d-1$ periodic directions.

Restricting in $\bar{G}_{00}$ to the contributions quadratic in $\tilde{\varphi}_{\vec{q}}$ we get (cf (25) in [1])

$$\mathcal{Z}(S) = \mathcal{Z}_{MF}(S) \exp\left(-\frac{1}{2} \sum_{\vec{q} \neq 0} \ln\left(1 + \frac{2u_0 S}{q^2 L^d} + 2u_0 \frac{e^{-q^2 S} - 1}{q^4 L^d} \right) \right). \tag{42}$$

The critical chemical segment potential in this approximation is given by

$$\hat{\mu}_s^* = \frac{1}{2} \sum_{\vec{q} \neq 0} \frac{2u_0}{q^2 L^d}.$$

Because $\vec{q}$ again is only $(d-1)$-dimensional, the sum in (42) is finite in four dimensions and by renormalizing the theory we have to use the zero-loop expressions for the Z-factors.

5. Dirichlet boundary conditions for a sphere

In this section we finally consider a geometry finite in all directions, namely a three-dimensional sphere with radius L and Dirichlet boundary conditions on the surface. We choose a sphere because for this geometry the mean-field problem (12) is again one-dimensional. However, it cannot be solved analytically and we have to refer to numeric methods. Therefore, we cannot go beyond mean-field approximation. Nevertheless, in the dense and dilute limits some analytical results can be derived.

For the d-dimensional sphere the ground state solution $\psi_0^{MF}(\vec{r})$ of the mean-field equation will be given by a real symmetric function depending only on r. So (12) reduces to

$$-\frac{d^2}{dr^2} \psi_0^{MF}(r) - \frac{2}{r} \frac{d}{dr} \psi_0^{MF}(r) + u_0 S(\psi_0^{MF}(r))^3 = E_0 \psi_0^{MF}(r)$$

$$\int_\Omega d^3 r \, |\psi_0^{MF}(r)|^2 = \int_0^L dr \, 4\pi r^2 |\psi_0^{MF}(r)|^2 = 1 \tag{43}$$

$$\psi_0^{MF}(L) = 0 \qquad \psi_0^{MF}(r < L) \neq 0.$$

We rescale the problem

$$\tilde{\psi}_0(r/L) \stackrel{\text{def}}{=} L^{3/2} \psi_0^{MF}(r) \tag{44}$$

to get for the new function $\tilde{\psi}_0(r)$

$$-\frac{d^2}{dr^2} \tilde{\psi}_0(r) - \frac{2}{r} \frac{d}{dr} \tilde{\psi}_0(r) + \frac{u_0 S}{L} \tilde{\psi}_0^3(r) = E_0' \tilde{\psi}_0(r)$$

$$E_0' = E_0 L^2$$

$$\int_0^1 dr \, 4\pi r^2 |\tilde{\psi}_0(r)|^2 = 1 \tag{45}$$

$$\tilde{\psi}_0(1) = 0 \qquad \tilde{\psi}_0(r < 1) \neq 0.$$

The mean-field partition function (14) is given by

$$\mathcal{Z}_{MF}(S) = 12\pi^2 \left(\int_0^1 dr\, r^2 \tilde{\psi}_0(r) \right)^2 e^{\frac{2\pi u_0 S^2}{L^3} \int_0^1 dr\, r^2 \tilde{\psi}_0^4(r) - SE_0' L^{-2}}. \tag{46}$$

Dilute limit. For $L \to \infty$ at fixed chain length S we can neglect the term $\frac{u_0 S}{L} \tilde{\psi}_0^3$ in (45). Then the problem can be analytically solved to yield

$$\tilde{\psi}_0(r) = \frac{1}{\sqrt{2\pi}} \frac{\sin(\pi r)}{r} \qquad E_0' = \pi^2. \tag{47}$$

For the mean-field solution we have

$$\varphi_{MF}(r) = -i \frac{u_0 S}{2\pi L^3} \frac{\sin^2(\pi r/L)}{(r/L)^2}$$

and the local segment density (22) can be written as

$$\langle \rho(r) \rangle = \frac{2c}{3} \frac{\sin^2(\pi r/L)}{(r/L)^2}.$$

The generalized partition function tends to

$$\mathcal{Z}_G^{(MF)}(S, \mu_s) = \frac{6}{\pi^2} \exp\left[(\mu_s - \mu_s^*)S - \frac{\pi^2}{L^2}S + \text{const.} \cdot \frac{S}{L^3} \right] \tag{48}$$

where $\mu_s^* = 0$ has to be set. We get the same leading corrections $-(\pi^2/L^2)S$ as for the cubic geometry with Dirichlet boundary conditions in one direction.

Dense limit. Fixing the segment density $c = S/\Omega = S/(4\pi L^3/3)$ in the limit $L \to \infty$, the $\tilde{\psi}_0^3$-term in (45) dominates and the ground state solution almost in the whole volume tends to a constant with a steep descent at the surface of the sphere at $r = 1$. In the bulk we then have

$$\begin{aligned} \tilde{\psi}_0 &\to \sqrt{\frac{3}{4\pi}} \qquad E_0' \to u_0 c L^2 \\ \varphi_{MF} &\to -i u_0 c \qquad \langle \rho(r) \rangle \to c. \end{aligned} \tag{49}$$

The partition function is given by

$$\mathcal{Z}_G^{(MF)}(\hat{c}, \mu_s) = \pi \exp\left[-\frac{\Omega}{u_0} \left((\mu_s^* - \mu_s)\hat{c} + \frac{\hat{c}^2}{2} \right) \right] \tag{50}$$

with the usual abbreviation $\hat{c} = u_0 c$. Again, we recover the leading contribution $\hat{c}^2\Omega/2u_0$ in the exponent.

For finite values of the system size L we have to solve the problem (45) numerically. Figures 6 and 7 show the results for the normalized quantity

$$\tilde{\psi}_0^2(r)/\tilde{\psi}_0^2(0)$$

proportional to the segment density in the dilute ($u_0 S$ *fixed*) and dense ($\hat{c}$ *fixed*) limits.

Renormalization. We renormalize the theory following the lines of section 3.2 to get for the renormalized partition function

$$\begin{aligned} \mathcal{Z}_{MF}^{(R)}\left(n_R, \frac{l_R}{L} \right) = 12\pi^2 &\left(\int_0^1 dr\, r^2 \tilde{\psi}_0(r) \right)^2 \exp\left[2\pi \tilde{u} n_R^2 \left(\frac{l_R}{L} \right)^3 \int_0^1 dr\, r^2 \tilde{\psi}_0^4(r) \right. \\ &\left. - E_0' n_R \left(\frac{l_R}{L} \right)^2 \right]. \end{aligned}$$
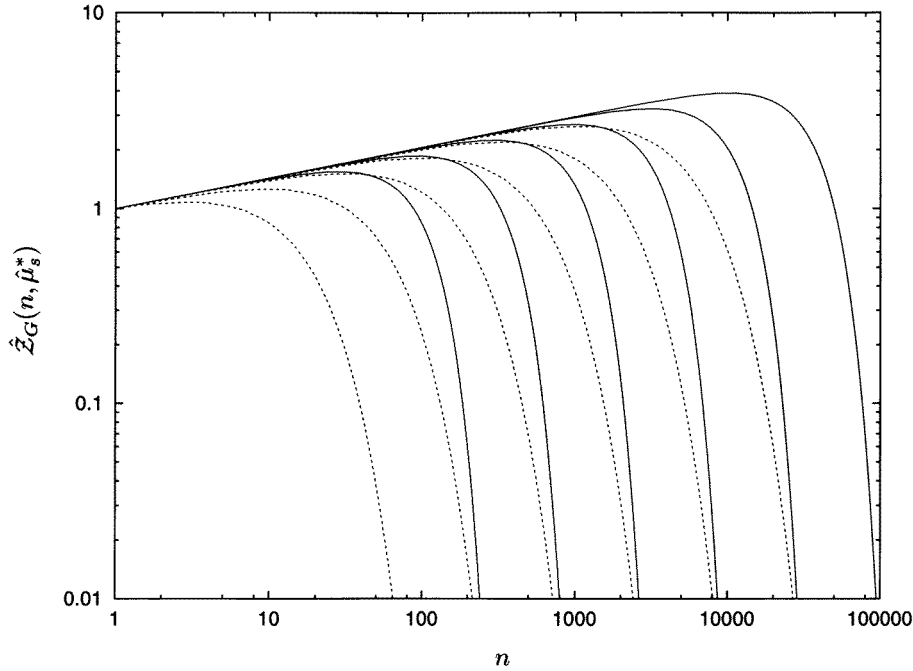
Figure 8. Mean-field partition function for a sphere with Dirichlet boundary conditions at the critical chemical segment potential $\hat{\mu}_s = 0$ for various system sizes. The full curves are the respective results for a cube with periodic boundary conditions.

As before we restrict to the excluded volume fixed point and use the relations (29) for the mapping from renormalized back to the physical quantities. In the crossover relation (30) we have to take care that the confining volume for the sphere in three dimensions is modified by a factor $4\pi/3$. The renormalized segment concentration is then given by

$$c_R = \tilde{u}^* \frac{n_R}{\Omega} l_R^d = \tilde{u}^* \frac{n_R}{4\pi/3} \left(\frac{l_R}{L} \right)^3 .$$

In figure 8 we plotted the finite-size results for the partition function at the critical chemical potential $\hat{\mu}_s = 0$ for various diameters of the sphere. For comparision we show also the zero-loop results for a cube with periodic boundary conditions in all directions at system sizes L' belonging to the same values of the volume

$$(L')^3 = \frac{4\pi}{3} L^3 .$$

Figures 9 and 10 show the segment density distribution at a fixed chemical segment potential in the dense limit and the finite-size corrections to the equation of state. Figure 10 has to be compared with figure 5. It is clearly seen that the finite-size corrections to the equation of state for the sphere geometry are larger than for the cubic geometry with Dirichlet boundary conditions in only one direction.

6. Summary

We developed a renormalized mean-field formalism for the calculation of the partition function of a single polymer in finite volume with Dirichlet boundary conditions. We showed that within
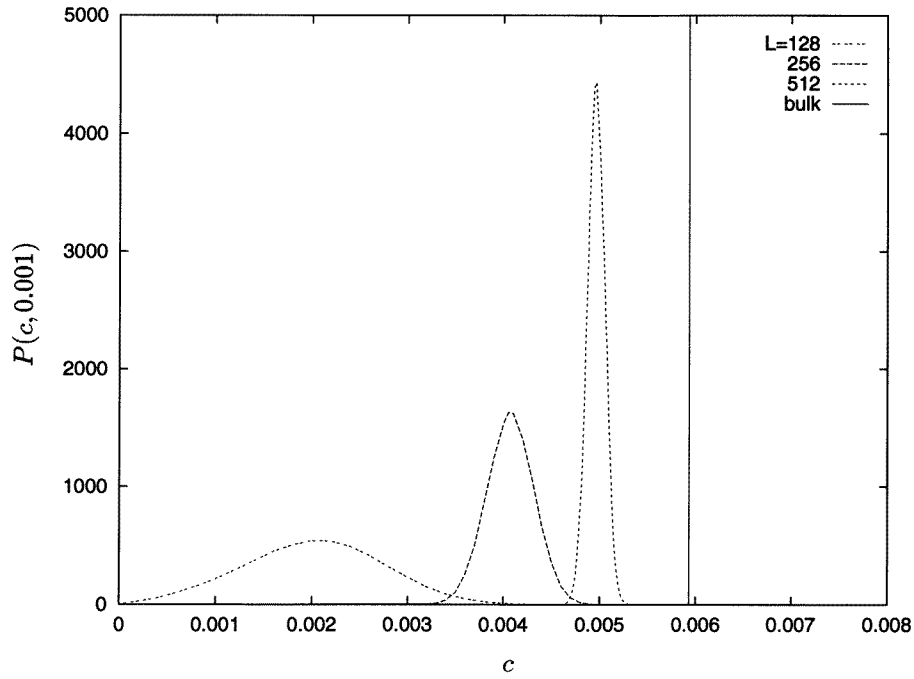
Figure 9. Segment density distribution at fixed chemical segment potential $\hat{\mu}_s = 0.001$ for a sphere with Dirichlet boundary conditions for various system sizes. The bulk value $\bar{c}_{bulk} = 0.0059$ is marked by the vertical line.
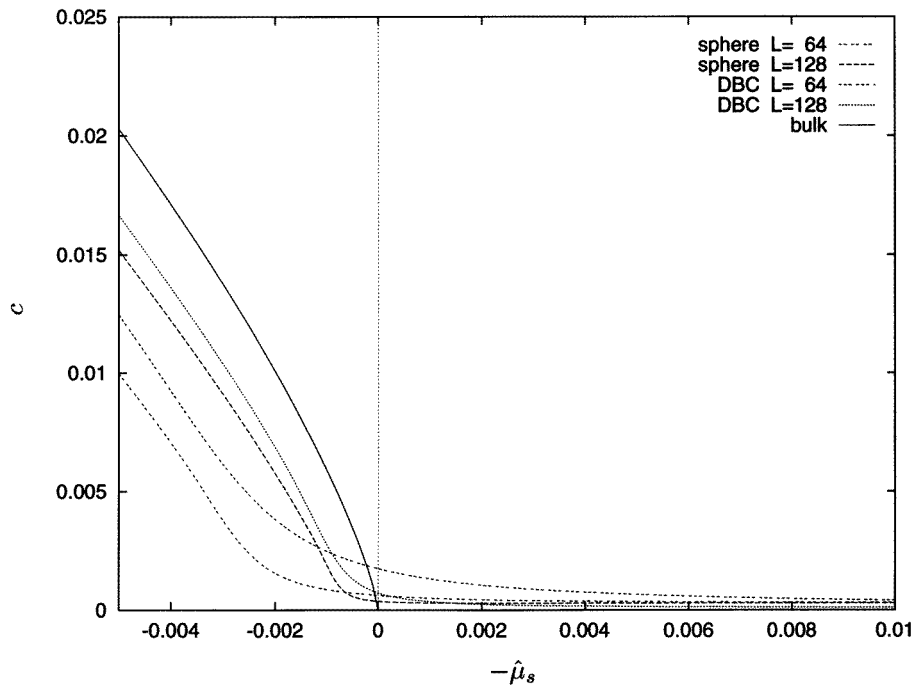
Figure 10. Equation of state for the sphere geometry with Dirichlet boundary conditions. The full curve represents the bulk curve of the dense limit. For comparision we also show the results for a cube with Dirichlet boundary conditions in one and periodic boundary conditions in the remaining directions (DBC).

the so-called ground state approximation for the mean-field Green function all fluctuations around the mean-field solution can be integrated out and do not yield any corrections to the mean-field result. To go beyond that result, the approximation for the mean-field Green function has to be improved. However, what can actually be done analytically strongly depends on the geometry considered.

The formalism was applied to two different geometries, a cube with Dirichlet boundary conditions in only one direction and a three-dimensional sphere with Dirichlet boundary condition on the surface. Whereas for the cubic geometry analytical results beyond the mean-field approximation can be obtained at least in plate geometry, for the sphere the mean-field solution can only be found by numerical methods.

By discussing the chain length distribution we showed for both geometries that as for periodic boundary conditions the dense and dilute limits are described by $L \rightarrow \infty$ at fixed chemical segment potential $\hat{\mu}_s^* > \hat{\mu}_s$ and $\hat{\mu}_s^* < \hat{\mu}_s$, respectively. The different regimes smoothly evolve from one another. In comparision to the periodic case the maximum of the chain length distribution for Dirichlet boundary conditions gets shifted by $1/L$-corrections to lower values.

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