Finite-N effects for ideal polymer chains near a flat impenetrable wall

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Abstract. This paper addresses the statistical mechanics of ideal polymer chains next to a hard wall. The principal quantity of interest, from which all monomer densities can be calculated, is the partition function, \( G_N(z) \), for a chain of \( N \) discrete monomers with one end fixed a distance \( z \) from the wall. It is well accepted that in the limit of infinite \( N \), \( G_N(z) \) satisfies the diffusion equation with the Dirichlet boundary condition, \( G_N(0) = 0 \), unless the wall possesses a sufficient attraction, in which case the Robin boundary condition, \( G_N(0) = -\xi G_N'(0) \), applies with a positive coefficient, \( \xi \). Here we investigate the leading \( N^{-1/2} \) correction, \( \Delta G_N(z) \). Prior to the adsorption threshold, \( \Delta G_N(z) \) is found to involve two distinct parts: a Gaussian correction (for \( z \lesssim aN^{1/2} \)) with a model-dependent amplitude, \( A \), and a proximal-layer correction (for \( z \gtrsim a \)) described by a model-dependent function, \( B(z) \).

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1 Introduction

It is well known that polymer chains have an entropic tendency to avoid hard walls, which generally results in a depletion layer of width \( aN^{1/2} \), where \( N \) is the degree of polymerization and \( a \) is the statistical segment length. The reason is rather simple; surfaces restrict the allowed configurations of a polymer molecule, and thus polymers lose configurational entropy as they approach a wall. An important consequence is the depletion-induced attraction that occurs between colloidal particles, when a small amount of polymer is added [1]. The thin depletion layer surrounding each particle reduces the effective volume accessible to the polymers, but some of the volume is freed up when the depletion layers overlap. The resulting gain in translational entropy of the polymers, in turn, causes the effective attraction between the particles.

In the ideal case of a theta solvent, the polymers can be treated as non-interacting and the solvent can be ignored [2], which allows the statistical mechanics to be performed exactly. This is done by calculating the partition function, \( G_N(r) \), for a single chain of \( N \) monomers, with one end fixed at position \( r \). As such, \( G_N(r) \) is proportional to the end-monomer distribution of the chain. In the limit of large \( N \), it can be obtained by solving the modified diffusion equation,

\[
\frac{\partial}{\partial N} G_N(r) = \left[ \frac{a^2}{6} \nabla^2 - \frac{w(r)}{k_BT} \right] G_N(r),
\]

subject to the initial condition, \( G_N(0) = 1 \) [3]. For completeness, we have included a field, \( w(r) \), acting on the monomers. Once \( G_N(r) \) is known, the average monomer concentration for \( n \) polymers of polymerization \( N \) is given by

\[
\rho(r) = \frac{n}{Z} \int_0^N G_s(s) G_{N-s}(r) ds,
\]

where \( Z \equiv \int G_N(r) dr \). When there is a flat impenetrable wall at \( z = 0 \), the diffusion equation is solved with the Dirichlet boundary condition,

\[
G_N(0) = 0,
\]

and zero field, which leads to the solution [4]

\[
G_N(z) = \text{Erf} \left( \sqrt{\frac{3}{2N} \frac{z}{a}} \right).
\]

The monomer density, \( \rho(z) \), can also be expressed analytically in terms of the error function, but the expression is much messier [4,5]. The main result is that both \( G_N(z) \) and \( \rho(z) \) exhibit a depletion zone of characteristic width, \( aN^{1/2} \), over which they both decay to zero as the wall is approached.
This cannot be completely correct, because if $\rho(z)$ drops to zero then the polymers will not exert any pressure on the wall. This latter fact follows from the wall (or contact) theorem, which states that the pressure is given by $P = k_B T \rho(0)$ [6]. However, we know that non-interacting molecules obey the ideal-gas law, and thus they must create a positive pressure of $P = n k_B T / V$. The failure of the theory to capture this is linked with the Dirichlet boundary condition. Motivated by this inconsistency, Erukhimovich et al. [4] recently examined the statistical mechanics for finite $N$, where it is unnecessary to specify a boundary condition. By calculating the finite-$N$ corrections to the partition function, $\Delta G_N(z)$, they were able to satisfy the wall theorem and recover the Dirichlet boundary condition in the limit of $N \to \infty$.

Although Erukhimovich et al. modified the Dirichlet solution, equation (4), to provide a pressure consistent with the wall theorem, the details of their solution disagree with some recent simulations of ours as shown in Figure 1 and described in the caption. The simulations were performed by generating many ($e.g.$, $\sim 10^8$) polymer configurations, each constructed from a sequence of $N - 1$ bond vectors randomly chosen from a Gaussian distribution (see the inset of Fig. 1), and spatially averaging them over the center-of-mass coordinate. The procedure is so straightforward and the statistical noise is so small (less than 1 part in $10^4$) that the disagreement must almost certainly originate with the analytical calculation [4].

The calculation by Erukhimovich et al. was also limited to neutral walls, whereas we know that the results will be affected by any interaction the polymers have with the wall. For instance, de Gennes [7] has argued that if the impenetrable wall possesses a sufficiently strong short-range attraction, then the Dirichlet boundary condition switches to the Robin boundary condition:

$$G_N(0) = -\xi G^0_N(0),$$

with some positive coefficient, $\xi$. This leads to the solution [7]

$$G_N(z) \propto \exp(a^2 N / 6 \xi^2 - z / \xi),$$

for which the monomer concentration decays as

$$\rho(z) \propto \exp(-2z / \xi).$$

Hence the depletion layer gives way to adsorption at the wall [5,8]. Naturally, it would be interesting to also understand what happens to $\Delta G_N(z)$ as this absorption threshold is approached.

Here we re-examine the statistical mechanics of ideal polymers ($i.e.$, the theta solvent condition), but this time numerically so to avoid the need for any approximations. Of course our calculations will be affected by the limited machine precision of the computer, but for these simple computations the relative inaccuracies are $\lesssim 10^{-10}$ and therefore are of no practical significance whatsoever. Furthermore, the versatility of the numerical approach will allow us to include a short-range attraction with the wall, and thus investigate the transition from the Dirichlet to the Robin boundary condition.

2 Partition function for discrete chains

For a discrete chain of $N$ monomers, the partition function, $G_N(r)$, is obtained by applying the recursive equation

$$G_{N+1}(r) = h(r) \int g(R) G_N(r - R) dR,$$

starting from $G_1(r) = h(r)$. The function, $h(r) \equiv \exp(-w(r) / k_B T)$, will account for the interaction, $w(r)$, of monomers with the wall, and the function, $g(R) \propto \exp(-b(R) / k_B T)$, is the Boltzmann factor for the bond potential, $b(R)$, normalized so that

$$\int g(R) dR = 1.$$

In order to demonstrate the degree of universality, we will perform calculations for two different polymer models: one with a Hookian-spring potential

$$g(R) = \left( \frac{3}{2 \pi a^2} \right)^{3/2} \exp \left( - \frac{3 \ell^2}{2a^2} \right),$$

and another with a fixed bond length

$$g(R) = \frac{1}{4\pi a^2} \delta(R - a).$$

Once $G_N(r)$ has been evaluated, the monomer concentration is given by

$$\rho(r) = \frac{n}{2h(r)} \sum_{i=1}^{N} G_i(r) G_{N+1-i}(r).$$

In this paper, we limit our attention to systems with a flat wall at $z = 0$, which implies that quantities such as