

## Density functional theory for flexible and semiflexible polymers of infinite length

Clifford E. Woodward

University College, ADFA, Canberra, Australian Capital Territory 2600, Australia

Jan Forsman

Theoretical Chemistry, Chemical Centre, P. O. Box 124, S-221 00 Lund, Sweden

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We develop a density functional theory for infinitely long flexible and semiflexible polymers, as an appropriate simplification of the corresponding treatment of finite chains. We demonstrate that very long chains sometimes are required to reproduce even qualitatively correct limiting behaviors.

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Polymers are often used to mediate forces between surfaces and particles, both in nature and for technological applications. Interestingly, polymers can be used as either stabilizers or coagulants, depending upon the structure and chemistry of polymers and particles. The degree of polymerization is an important parameter in this respect. The Edwards–de Gennes (EdG) formulation [1–9] has provided a cornerstone theory for describing polymer behavior in the presence of particle surfaces. However, the theory is strictly valid only in the limit of infinitely long polymers, and for slow spatial variations of the monomer density. In practice, high-molecular-weight polymers find relatively few industrial applications, at least in colloid dispersions, due to viscosity problems and high cost. The degree of polymerization is then typically a few hundred monomers. Another limitation of the EdG theory is that interactions with surfaces are handled in an implicit manner, by imposing boundary conditions that have no direct correspondence in the Hamiltonian of the system. This is a consequence of the inability of the Edwards theory to resolve structural details [10,11].

The polymer density functional theory (DFT) has been developed as a high-resolution theory, capable of accurately predicting polymer fluid structure at surfaces [12,13]. Boundary conditions are completely determined by the model Hamiltonian, and the theory satisfies thermodynamic consistency relations, such as the contact theorem. In this work, we report an extension of the DFT to treat *infinitely* long polymers and thus establish the *exact* limit that is approached for finite chains. We will focus on the interactions between infinite parallel surfaces, assuming complete equilibrium with a bulk solution. This will be done for both flexible and semiflexible polymer models.

An important prediction of the EdG theory is that polymer-mediated equilibrium surface interactions are wholly attractive. This prediction has been questioned, for polymers of finite length. Perturbation approaches, as developed by Semenov *et al.* [8,9] and Blokhuis *et al.* [14], suggest the existence of free-energy barriers, in the presence of finite chains. As we shall see, DFT also predicts such barriers for finite chains. In some cases, particularly when the chains have some degree of intrinsic stiffness, these barriers can be thermally significant.

Our study is based on the polymer density functional theory introduced by Woodward [12], although we shall adopt the more refined versions for flexible [13] and semi-

flexible [15] chains, proposed in subsequent work. We start with a brief description of the theory for finite chains.

Denoting the coordinate of the  $i$ th monomer by  $\mathbf{r}_i$ , we can write the full configuration of an  $r$ -mer as  $\mathbf{R}=(\mathbf{r}_1, \dots, \mathbf{r}_r)$ . The hard-sphere monomers are connected by bonds of a fixed length  $\sigma$ , which is also their diameter. Hence,  $e^{-\beta V_B(\mathbf{R})} \propto \prod_{i=1}^{r-1} \delta(|\mathbf{r}_{i+1} - \mathbf{r}_i| - \sigma)$ , where  $\beta$  is the inverse thermal energy and  $V_B(\mathbf{R})$  is the bond potential connecting monomers. We then define an  $r$ -point density distribution  $N(\mathbf{R})$ , such that  $N(\mathbf{R})d\mathbf{R}$  is the number of polymer molecules having configurations between  $\mathbf{R}$  and  $\mathbf{R}+d\mathbf{R}$ . The monomer density  $n(\mathbf{r})$  is obtained from  $n(\mathbf{r}) = \int \sum_{i=1}^r \delta(\mathbf{r} - \mathbf{r}_i) N(\mathbf{R}) d\mathbf{R}$ . The free-energy functional  $\mathcal{F}[N(\mathbf{R})]$ , is generally written as the sum of an ideal ( $\mathcal{F}^{id}[N(\mathbf{R})]$ ) and an excess ( $\mathcal{F}^{ex}[N(\mathbf{R})]$ ) contribution:  $\mathcal{F}[N(\mathbf{R})] = \mathcal{F}^{id}[N(\mathbf{R})] + \mathcal{F}^{ex}[N(\mathbf{R})]$ . The ideal part is exactly given by  $\beta \mathcal{F}^{id}[N(\mathbf{R})] = \int N(\mathbf{R}) \cdot \{\ln[N(\mathbf{R})] - 1\} \cdot d\mathbf{R} + \beta \int N(\mathbf{R}) [V_B(\mathbf{R}) + V_{ex}(\mathbf{R})] d\mathbf{R}$ , where  $V_{ex}(\mathbf{R})$  is an external potential, in our case emanating from the surfaces. We have approximated  $\mathcal{F}^{ex}$  by integrating the generalized Flory dimer equation of state [16]. Explicit expressions are provided in Ref. [13]. The grand potential  $\Omega$  is obtained from  $\Omega[N(\mathbf{R})] = \mathcal{F}^{id}[N(\mathbf{R})] + \mathcal{F}^{ex}[N(\mathbf{R})] - \mu_p \int N(\mathbf{R}) d\mathbf{R}$ , where  $\mu_p$  is the bulk polymer chemical potential. The confining surfaces, located at  $z=0$  and  $h$ , are infinitely large, flat, and perpendicular to the  $z$  direction. The net free energy per unit area,  $g_s(h)$ , is given by  $g_s(h) = \Omega_{eq}/S + P_b h$  where  $\Omega_{eq}$  is the equilibrium grand potential and  $P_b$  is the osmotic pressure in the bulk. The functional is simplified by integration over the  $(x, y)$  plane parallel to the surfaces. This means that we neglect lateral heterogeneities [17]. At large surface separations,  $g_s$  approaches twice the tension at a single surface,  $\gamma_s$ . The net surface interaction per unit area is conveniently expressed in terms of  $\Delta g_s(h) \equiv g_s(h) - 2\gamma_s$ .

Semiflexible chains are modeled via a stiffness potential  $E_B$ , introducing repulsions between next-nearest neighbors in a chain. Specifically, if  $s_i$  denotes the bond vector between monomers  $i$  and  $i+1$ ,  $E_B$  is given by  $\beta E_B = \epsilon \left(1 - \frac{s_i \cdot s_{i+1}}{\sigma^2}\right)$ , where  $\epsilon$  determines the degree of stiffness. Isolated chain properties are easily evaluated. Neglecting hard-core effects, the polymer persistence length  $\lambda_p = \langle \mathbf{R}_e \cdot \mathbf{s}_1 / \sigma \rangle$  is given by  $\lambda_p / \sigma = \frac{\epsilon(1 - e^{-2\epsilon})}{1 - e^{-2\epsilon(1+2\epsilon)}}$ . Thus, even for moderate values of  $\epsilon$ ,  $\lambda_p / \sigma \approx \epsilon$ . Integrating the Boltzmann factor  $\exp(-\beta E_B)$  over the  $(x, y)$  plane gives the following weight function:

$$\Psi(\Delta z_i, \Delta z_{i+1}) = e^{\epsilon(1 - \Delta z_i \Delta z_{i+1} / \sigma^2)} \times I_0 \left( \epsilon \left[ 1 - \left( \frac{\Delta z_i}{\sigma} \right)^2 \right]^{1/2} \left[ 1 - \left( \frac{\Delta z_{i+1}}{\sigma} \right)^2 \right]^{1/2} \right) \quad (1)$$

where  $I_0(x) = \frac{1}{2\pi} \int_0^{2\pi} \exp(-x \cos \Phi) d\Phi$  is a modified Bessel function and  $\Delta z_i \equiv z_{i+1} - z_i$ . Minimizing the free-energy functional for semiflexible chains of hard-sphere monomers confined by surfaces gives the following expression for the equilibrium monomer density profile,  $n(z)$ :

$$n(z) = e^{\beta \mu_p} \sum_{i=1}^r \int_0^h \delta(z - z_i) \prod_{j=1}^r e^{-\lambda(z_j)} \prod_{k=1}^{r-1} \times \Theta(|\Delta z_k| - \sigma) \prod_{l=1}^{r-2} \Psi(\Delta z_l, \Delta z_{l+1}) dz_1 \cdots dz_r \quad (2)$$

where  $\lambda(z) = \beta[\delta \mathcal{F}_{ex} / \delta n(z) + V_{ex}(z)]$  and  $\Theta(x)$  is the Heaviside step function

$$\Theta(x) = \begin{cases} 1, & x \leq 0, \\ 0, & x > 0. \end{cases}$$

Equation (2) is easily solved by iteration. In the case of flexible polymers, it is useful to introduce an auxiliary field  $c(i, z)$ , which satisfies the following recursion formula:

$$c(i, z) = e^{\lambda_b} \int c(i-1, z') T_f(z', z) dz'. \quad (3)$$

The quantity  $\lambda_b$  denotes the value of  $\lambda(z)$  in the bulk, i.e., it is the *excess* monomer chemical potential. The connectivity matrix  $T_f(z, z')$  is given by

$$T_f(z', z) = \frac{e^{-\lambda(z')/2} \Theta(|z - z'| - \sigma) e^{-\lambda(z)/2}}{2\sigma}. \quad (4)$$

The quantity  $c(i, z) \exp[-\lambda(z)/2]$  is proportional to the density of end monomers in a chain of  $i$  monomers. The total monomer density for a chain of length  $r$  is given by the sum of the individual monomer contributions, i.e.,

$$n(z) = \rho_p^b \sum_{i=1}^r c(i, z) c(r-i, z). \quad (5)$$

Here  $\rho_p^b$  is the bulk polymer density. As the degree of polymerization approaches infinity,  $c(i, z)$  uniformly approaches a limiting function  $c_f(z)$  and Eq. (5) simplifies to

$$n(z) = n_b c_f^2(z), \quad (6)$$

where  $n_b$  is the bulk monomer density and  $c_f(z)$  is the infinite-chain limit of  $c(i, z)$ . Furthermore, Eq. (3) completes the self-consistency relations for  $c_f(z)$ ,

$$c_f(z) = e^{\lambda_b} \int c_f(z') T_f(z', z) dz'. \quad (7)$$

Equations (6) and (7) are rapidly solved by iteration.

In the case of infinite, semiflexible chains, the corresponding solution requires a two-dimensional matrix  $c_s(z, z')$

rather than a simple vector, but the relations are almost as simple. If we define a connectivity matrix  $T_s(z, z')$ ,

$$T_s(z', z) = \frac{e^{-\lambda(z')/3} \Theta(|z - z'| - \sigma) e^{-\lambda(z)/3}}{2\sigma}, \quad (8)$$

we can write

$$n(z) = n_b \int c_s(z, z' - z) c_s(z', z - z') T_s(z, z') dz' \quad (9)$$

with the following closure:

$$c_s(z, z' - z) = \int c_s(z'', z - z'') \Psi(z - z'', z' - z) T_s(z, z'') dz''. \quad (10)$$

Note that the formalism is general in the sense that one is free to choose and improve the approximate functional  $\mathcal{F}_{ex}$ . An interesting option is to use an excess functional that constrains the total volume fraction of monomers and (implicit) solvent particles to be constant, in which case we obtain a continuum analogue of the Scheutjens-Fleer theory [18], as described in Ref. [19].

We considered both hard repulsive and adsorbing surfaces. In the latter case, we used a relatively smoothly varying  $\beta V_{ex}^{ref}(z) = A_w ([1 - e^{-2(z-z_m)}] - 1)$ , with a potential strength  $A_w = 2.5$ . We have also truncated and shifted this potential, i.e.,  $V_{ex}(z) = V_{ex}^{ref}(z) - V_{ex}^{ref}(z_c)$ , ensuring a short-ranged attraction. The distance  $z_m$  is chosen such that  $V_{ex}(z=0) = 0$ . By setting  $z_c - z_m = 2.9$ , we obtain  $z_m \approx 0.346$ . Hard walls are retained at  $z=0$  and  $z=h$ . Overlap between the attractive regions of the opposing surfaces occurs below  $h \approx 6.5$ .

We first consider the interaction between inert hard surfaces in the presence of fully flexible chains. Results at relatively low bulk monomer concentrations are given in Fig. 1.

The EdG theory [5] predicts that under full equilibrium conditions, the surface interaction free energy will be purely attractive. This result follows from the form of the free-energy functional, which is local in the monomer density and its spatial gradient. On the other hand, our DFT for infinitely long chains is nonlocal, and a similar proof cannot be applied in our case. Note that de Gennes's study was applied to a *flexible* chain model. Nevertheless, for hard inert surfaces, the DFT does predict an attraction between surfaces immersed in solutions of infinite flexible and semiflexible chains at low and moderate concentration. At very high concentrations, we observe packing-driven surface force oscillations at short range—see Fig. 2(a) (inset). Further analysis of our results reveals that the attraction is due to polymer depletion. Depletion is driven by the reduction in configurational entropy of a chain close to a surface, giving rise to an effective soft repulsion from the wall, with a range of the order of the polymer radius of gyration,  $R_g$ . However, when hard-core interactions are present, there is a tendency for the solution to “fill in” regions depleted of polymer, due to the excess chemical potential being lower there. This occurs at a length scale equal to the bulk correlation length  $\xi$ . In our theory  $\xi$  is proportional to  $\sigma / \sqrt{n_b d \lambda_b / dn_b}$ ; hence it becomes shorter the higher is the monomer concentration [5]. The final size of the

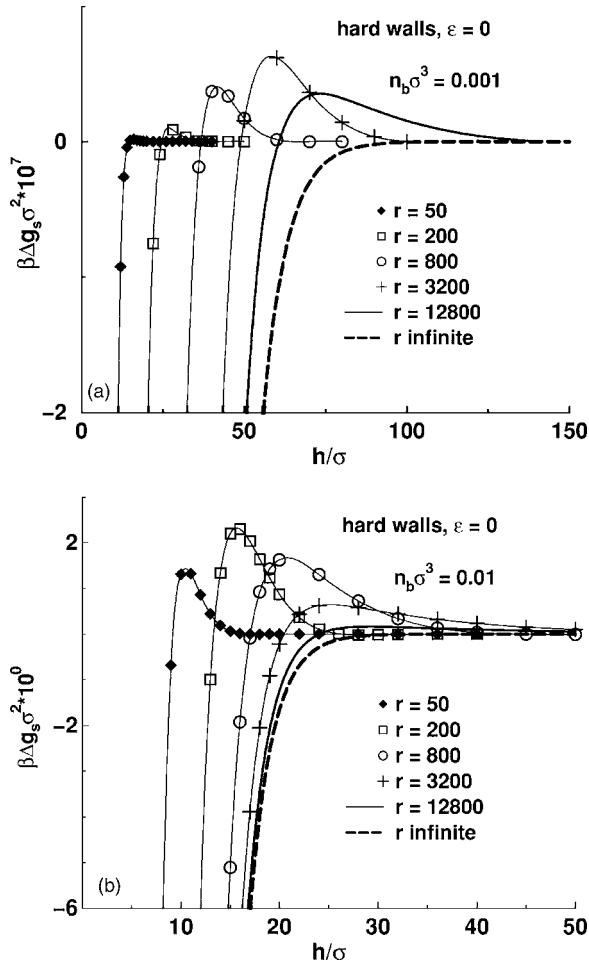


FIG. 1. Interactions between hard surfaces in a solution containing flexible polymers, at two different bulk monomer concentrations.  $n_b\sigma^3 =$  (a) 0.001 and (b) 0.01.

depletion hole is determined by these two competing effects. If  $R_g$  is much larger than  $\xi$ , the range of the depletion hole is determined by the latter. This is obviously the case for infinitely long polymers and the attraction becomes short ranged at high concentrations.

For chains of finite length, there will be a crossover in the dominance of  $R_g$  and  $\xi$ . In a dilute melt,  $R_g$  is small relative to  $\xi$ , there is little overlap of chains, and the depletion region is determined mainly by  $R_g$ . Hard-core interactions have little influence on the size of the depletion hole. The system behaves as if it was a collection of ideal polymers and the surface interaction is attractive as the surfaces approach (Fig. 1,  $r=50$ ) due to the expulsion of polymer molecules from the interstitial region. However, when  $R_g$  approaches  $\xi$ , we see the onset of a free-energy barrier. In this regime, there is a “flattening” of polymer molecules against the surfaces, due to hard-core correlations. As the surfaces approach to a distance of the order of  $R_g$ , polymers will be first *compressed* slightly, before they are eventually expelled at shorter separations. This leads to a repulsive barrier at a separation that will scale roughly as  $R_g$ , before depletion attraction dominates at shorter separation. Looking at Figs. 1 and 2, we see that, as  $R_g$  increases, this barrier grows in height, reaches a

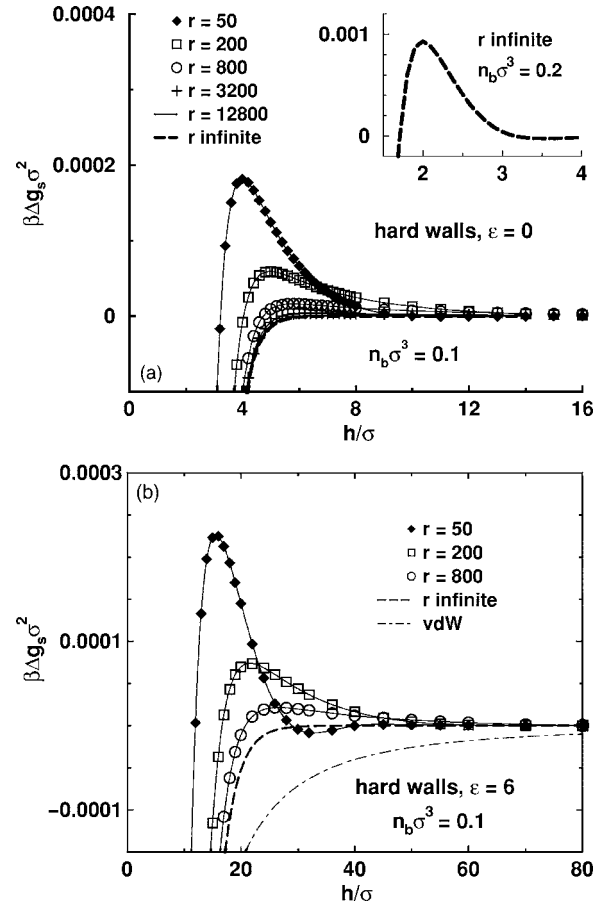


FIG. 2. Interactions between hard surfaces, at a high monomer concentration  $n_b\sigma^3=0.1$ . (a) Fully flexible polymers,  $\epsilon=0$ . The inset shows the case of  $n_b\sigma^3=0.2$ , with infinite chains. (b) Semiflexible polymers,  $\epsilon=6$ . The latter graph includes a nonretarded van der Waals (vdW) attraction, assuming a typical Hamaker constant of  $1 \times 10^{-20}$  J.

maximum, and then decreases again as the infinite-length limit is approached. For very long chains, this barrier moves to larger separation and is reduced in magnitude. The latter occurs as the average intramolecular correlation in the chain becomes weaker. For infinite chains, the barrier has disappeared and the interaction is always attractive. At very high densities, packing of monomers results in oscillatory surface interactions, even for infinite chains (Fig. 2).

Free-energy barriers have also been predicted from finite-chain perturbation theories by Semenov *et al.* [9] and Blokhuis *et al.* [14]. However, the nonmonotonic dependence of the barrier height on chain length, at low and moderate concentrations, cannot be captured by first-order perturbation theories, based on expansions in  $1/r$ .

The free energy barriers we observe in Fig. 1 are thermodynamically inconsequential. They do become significant at high volume fractions, at least when the polymers have some intrinsic stiffness. This is illustrated in Fig. 2 where, in the case of semiflexible chains, we find barriers that are comparable with a typical van der Waals (vdW) attraction. As with fully flexible chains, the barrier is also absent in the infinite length limit. Although the barriers for flexible and semiflexible polymers have comparable heights, they are located at

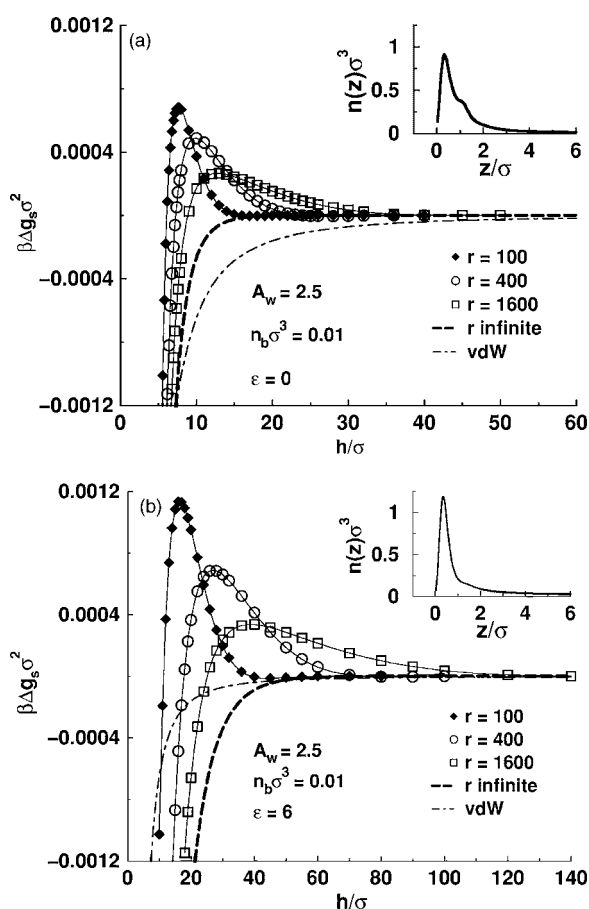


FIG. 3. Interactions between adsorbing surfaces, at a bulk monomer concentration of  $n_b \sigma^3 = 0.01$ . (a) Fully flexible polymers,  $\epsilon = 0$ . (b) Semi-flexible polymers,  $\epsilon = 6$ . Again, the results are compared with a typical vdW attraction (dot-dashed), with a Hamaker constant of  $1 \times 10^{-20}$  J. The insets display monomer density profiles for infinite chains.

shorter separations in the flexible case. Hence, the vdW interaction will typically have grown very strong at the position of the barrier, making the barrier less likely to be high enough to stabilize a corresponding colloid dispersion. In the

presence of adsorbing surfaces, a sizable barrier develops at rather low concentrations (Fig. 3). This is in agreement with experimental observations by Bechinger *et al.* [20]. In our case, the adsorption is strong, but not strong enough to saturate the surfaces. Even fully flexible chains provide a barrier, with a strength comparable to the expected vdW attraction. While the barrier height decreases with polymer length, its position is shifted further out. Thus, its strength in relation to the vdW interaction is approximately constant. In the infinite-length limit the barrier vanishes. When the polymers have an intrinsic rigidity, the scenario is quite different. Now the barriers completely dominate the vdW interaction, as they occur at a large separation. This is true even with chains containing thousands of monomers, and the barrier height can be orders of magnitude stronger than the vdW attraction.

It is useful to analyze the interaction in terms of pressure contributions across the midplane of the slit. The repulsive barriers we observe with attractive surfaces can be attributed to an overlap between adsorbed layers on opposing walls, whereby the midplane monomer density increases. At shorter separations bridging interactions dominate. These interactions are “displaced” to larger separations when the chains are stiffer, as these molecules are effectively larger. The increased barrier height observed for stiffer polymers can be attributed to a reduced tendency for bridging chains to “coil back.” This leads to weak bridges and a higher barrier [21].

In summary, we have formulated a versatile density functional theory for infinite flexible and semiflexible chains. The theory is consistent with that for finite chains, and is fully able to resolve structural details. Hence, we can now make consistent comparisons between properties of finite and infinitely long polymers. For solutions that are not too concentrated, we find that surface interactions in the presence of infinitely long polymers are attractive, in accordance with the theorem by de Gennes [5]. When the chains have finite length, there is in general a free-energy barrier, the height and range of which depend on conditions such as chain length, intrinsic stiffness, polymer concentration, and surface properties. Infinite-chain behavior is in some cases reproduced by relatively short chains. Under other conditions, notably when the polymers have an intrinsic rigidity, there are substantial deviations, even for long polymers.

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