A versatile 3D model of an end-tethered polymer chain under shear flow

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Abstract

A self-consistent field approach is used to model a single end-tethered polymer chain on a substrate subject to various forces in three dimensions. Starting from a continuous Gaussian chain model, the following perturbations are considered: (i) hydrodynamic interaction with an externally imposed shear flow for which a new theoretical framework is formulated; (ii) excluded volume effect in a good solvent, treated in a mean field approximation; (iii) monomer-substrate repulsion. The computed density profile is then explored as a function of these parameters for values that correspond to those accessible in realistic experiments.

Introduction

End-tethered macromolecules have attracted much interest during half a century now going from an evaluation of pure academic interest to applications in a wide field from biological applications to material science. The structure of a polymer brush in contact with a polymer melt, a solvent and polymer solutions has been quite well understood in theory, first using scaling arguments and later extended quantitatively by mean-field calculations.

1
which also confirmed the predicted scaling laws.\textsuperscript{[4]} Those theoretical results were confirmed by molecular dynamics simulations.\textsuperscript{[5,6]} Experiments suffered from the lack of accessibility of a broad range of grafting densities and chain lengths at the beginning but finally could corroborate the existing scaling laws.\textsuperscript{[7]} The monomer density of the brush was eventually revealed experimentally by SANS and NR.\textsuperscript{[8]}

Structural investigations of these brushes under shear load are not so common although the technical or biological implications of brushes mostly imply shear force. The largest body of work was done in theoretical studies based on the de Gennes model for weakly grafted films\textsuperscript{[8,9]} and for high grafting densities\textsuperscript{[10,11]} and using MD simulations on high density films.\textsuperscript{[5,13,14]} Experimental studies only exists for a series of NR measurements on stretched polymer brushes in solvents\textsuperscript{[15,17]} and in polymer melts.\textsuperscript{18} Especially low density brushes, or “mushrooms”, have, in our knowledge, evaded a quantitative description, yet.

Figure 1: A visual depiction of the complete algorithm used to describe a polymer chain in flow at a mean field level.

In this paper we propose a field-based mathematical model of an isolated polymer chain
end-tethered to a substrate and subject to shear flow, as well as excluded volume effect and a monomer-substrate repulsive force. All of these effects are accounted for simultaneously, and our simulation provides the polymer density distribution computed self-consistently with the distorted velocity field of the sheared liquid. The general framework is that of self consistent field theory\cite{19} with nontrivial modifications that are needed for a correct description of an external flow field.

The outline of the simulation algorithm detailed in the following sections is sketched in Fig. 1 along with a snapshot from the simulation.

**Theoretical framework**

To start off, we model our isolated polymer chain as a continuous Gaussian coil, meaning that the the s-th monomer is labeled by a continuous variable $s \in [0, 1]$. The partition function $q$ and $q^\dagger$ of such a chain in an external potential $w(r)$ obeys the modified diffusion equation (MDE)\cite{20, 21}:

$$\frac{\partial q}{\partial s} = R_g^2 \nabla^2 q - \frac{w(r)}{k_B T} q, \quad q(r, s = 0) = \delta(r),$$

$$\frac{\partial q^\dagger}{\partial s} = -\left( R_g^2 \nabla^2 q^\dagger - \frac{w(r)}{k_B T} q^\dagger \right), \quad q^\dagger(r, s = 1) = 1. \tag{2}$$

The solution $q(r, s)$ is the partition function for a polymer chain of length $s$ starting at $r_0 = 0$ (the tethering point) and ending at an arbitrary point $r$. Likewise, $q^\dagger(r, s)$ is the partition function for a polymer of length $(1 - s)$ having a uniform distribution at its $s = 1$ end, and terminating at $r$ as explained in more detail in Ref. \cite{22}. The total partition function is obtained by summing over all the intermediate positions $r$:

$$Q[w] = \int d\mathbf{r} q(r, s) q^\dagger(r, s). \tag{3}$$
One can check using integration by parts that $Q$ is independent of the monomer $s$ at which it is evaluated: $dQ/ds \equiv 0$. The practical result of the MDE is the polymer density, obtained by summing the contribution from each segment $s$ and normalizing by the $Q$:

$$
\rho(r) = \frac{1}{Q} \int_0^1 ds \, q(r, s) q^\dagger(r, s).
$$

(4)

It is straightforward to verify that this density is normalized: $\int d\mathbf{r} \, \rho(\mathbf{r}) \equiv 1$.

The simplest application of the theory stated so far is the ideal Gaussian chain which is purely governed by the maximization of entropy. In this case the potential energy $w(\mathbf{r}) = 0$, and the solution to Eqs. (1)-(2) is $q(r, s) = (4\pi R_g s)^{-3/2} e^{-r^2/(4sR_g^2)}$; $q^\dagger(r, s) = 1$. The total partition function $Q = 1$, while the density is

$$
\rho(r) = \int_0^1 ds \, \frac{1}{(4\pi R_g^2 s)^{3/2}} \exp \left( -\frac{r^2}{4R_g^2 s} \right).
$$

(5)

We will now proceed to compute how the polymer density distribution $\rho(\mathbf{r})$ changes under an external shear flow, as well as excluded volume and surface repulsion.

**Applied shear flow**

Consider that the chain is placed in an external solvent flow described by the velocity field $\mathbf{u}(\mathbf{r})$, which for the moment will be assumed to be fixed and insensitive to the chain conformation. A simple example is a linear shear flow $\mathbf{u}(\mathbf{r}) = \dot{\gamma} \mathbf{z} \hat{x}$. This will exert a Stokes force $\mathbf{F} = \zeta \mathbf{u}$ on the monomers, where $\zeta = 6\pi \eta a$ is the monomeric friction coefficient, with $a$ the monomer size and $\eta$ the solvent viscosity. Unfortunately, such a force cannot be derived from a scalar potential because its curl is non-zero: $\nabla \times \mathbf{F} \neq 0$, and hence the energy of the polymer chain is ill-defined, as it depends on the path taken by the chain (for a related discussion, see Supplementary information 2).

The approach that we have taken to handle this non-conservative aspect of the hydrodynamic forces is to first obtain the elementary propagator for a small chain segment, and
then use the Kolmogorov-Chapman equation to derive the full partition function. Within
the length scale of one bond length we can safely consider the speed $u$ to be uniform, in
which case the propagator for an elementary chain segment of length $\epsilon$ stretching between $r$
and $r + \Delta r$ remains Gaussian, with a bias due to the uniform velocity field:

$$
P(\Delta r, r, \epsilon) = \left( \frac{k}{2\pi k_B T} \right)^{3/2} \exp \left[ -\frac{k(\Delta r - u(r)\zeta/k)^2}{2k_B T} \right].
$$

(6)

where $k = k_B T/(2R_g^2\epsilon)$ is the stiffness of the segment. Inserting this into the Kolmogorov-
Chapman equation

$$
q(r, r_0, s + \epsilon) = \int d(\Delta r) q(r - \Delta r, r_0, s + \epsilon) P(\Delta r, r - \Delta r, \epsilon)
$$

(7)

we obtain a diffusion-advection kind of equation for the complete partition function:

$$
\frac{\partial q}{\partial s} = R_g^2 \nabla^2 q - 2 \left( \frac{\zeta R_g^2}{k_B T} \right) u \cdot \nabla q = R_g^2 \nabla^2 q - \tau_r u \cdot \nabla q,
$$

(8)

where $\tau_r = 2\zeta R_g^2/(k_B T)$ is the Rouse relaxation time of the polymer. A similar reasoning
for the complementary partition function yields

$$
\frac{\partial q^\dagger}{\partial s} = -R_g^2 \nabla^2 q^\dagger - \tau_r u \cdot \nabla q^\dagger.
$$

(9)

Once again one can easily verify that the total partition function $Q = \int d\mathbf{r} q q^\dagger$ is independent
of $s$. A simple analytical solution of Eqs. (8)-(9) can be found for the case of a uniform flow $u = \text{const.}$ We give the derivation in the supplementary material and plot the resulting one-
dimensional density profile in Fig. 2 alongside with a comparison of an undeformed chain
[Eq. (5)]. Note that one could also model this situation by the modified diffusion Eqs. (1)-(2), using a scalar potential field with a derivative equal to $\zeta u$. This alternative solution is
shown in Fig. 2 as well. Clearly, the diffusion-advection theory is different from the scalar
model, a scheme used in numerous non-equilibrium Monte-Carlo studies (see e.g. Ref. [24]).

Not only the fluid velocity \( \mathbf{u}(\mathbf{r}) \) exerts a force on the polymer, but also the presence of the polymer disturbs the flow. To take this effect into account, we assume that the polymer can be treated as a porous medium whose resistivity is proportional to the monomer density \( \rho(\mathbf{r}) \) (different dependencies could also be used but they typically bring only small modifications to the final result). Using the density obtained from Eqs. (8)-(9) we solve the flow profile governed by the stationary Stokes-Darcy law for incompressible flow:

\[
\nabla^2 \mathbf{u} - \frac{1}{\eta} \nabla \rho = \frac{\rho(\mathbf{r})}{\xi^2} \mathbf{u} \quad \text{and} \quad \nabla \cdot \mathbf{u} = 0,
\]

where \( \xi \) is a constant hydrodynamic screening length. We use a Dirichlet boundary condition with \( \mathbf{u} = \gamma z \hat{x} \) far away from the brush\(^1\). The solution \( \mathbf{u} \) is fed back to Eqs. (8)-(9) and the process is repeated until convergence is achieved (which usually happens within 4-7

\[^1\]This set of four coupled PDEs can be solved by adding a penalty term \( \lambda \rho \) to the divergence relationship, with \( \lambda \to 0 \). In numerical schemes beware that the pressure and the velocity fields must be defined on separate LBB-compatible finite element spaces.\(^2\)
Excluded volume effect

At the mean field level, the excluded volume effect is accounted for by introducing a repulsive self-consistent field \( w(r) = v N \rho(r) k_B T \) where \( v \) is the excluded volume per monomer and \( k_B T \) is the thermal energy. The description of a single chain in terms of such a self-consistent field description was pioneered by Edwards, who showed that the approach reproduces the Flory exponent \( \nu = 3/5 \), as expected from its mean field character. In the present study we need to take into account the excluded volume effect for chain configurations which are distorted from a spherical symmetry and hence a numerical approach is required to obtain the density profiles.

If we plug in the Flory potential \( v N \rho(r) \) into the MDE, the result is a set of two coupled partial non-linear integro-differential equations with both the non-linearity and the coupling on the integral term. For a very small \( v \) we can solve it by Picard iteration, but the experimentally relevant case of a big \( v \) does not converge, unfortunately.

We propose the following algorithm to achieve a rapid and stable convergence. First, we replace the partition functions by

\[
q(r,s) \to q_0(r,s) \exp(-svN\rho) \quad \text{and} \quad q^\dagger(r,s) \to q^\dagger_0(r,s) \exp[-(1-s)vN\rho].
\]

This eliminates the problematic Flory term, but generates unwanted derivatives of \( \rho \) and an explicit \( s \)-dependence. These extra terms can all be neglected if we make the following approximation. It is known that the chain size varies as \( L_F \propto N^{3/5} \) in a good solvent. Hence, the exact solution of the density will be some monotonically decaying function such as \( \rho \approx \exp(-z/L_F) \). In the MDE, its second derivative gives terms like \( R_2^2 \rho_{zz} \approx R_2^2 \exp(-z/L_F)/L_F \propto N^{-1/5} \). This has to be contrasted with the second derivative of \( q_0 \), which decays like \( R_2^2 q_0/R_2^2 \propto 1 \). Hence, for a very long chain, \( N \to \infty \), all the
Figure 3: Central cross-sections of the 3D polymer density profile. The silver circle is the radius of gyration in each case. The thick yellow curve is the integrated density along the $x$-axis: $\rho(x) = \int dz \, dy \, \rho(x, y, z)$. 

(a) Theta solvent, free ends
(b) Theta solvent, end-tethered
(c) Good solvent, free ends
(d) Good solvent, end-tethered
derivatives of \( \rho \) vanish.

In the second step, we simply solve the MDE without the Flory term to obtain the partition functions \( q_{0}^\dagger(r, s) \) and \( q_{0}^\ddagger(r, s) \). The density is given by Eq. \([4]\) as usual:

\[
\rho = C \int_{0}^{1} ds \, q_{0}^\dagger = C \int_{0}^{1} ds \, q_{0}^\ddagger \exp(-vN\rho) = C \rho_{0} \exp(-vN\rho) .
\]  

(12)

In the third step, we iteratively solve Eq. \([12]\) to obtain the function \( \rho(r) \) and the constant \( C \) subject to normalization constraint \( \int dr \, \rho = 1 \). We have to take its logarithm in order to damp the errors at each iteration, as opposed to amplifying them with the exponent: \( vN\rho = \ln C + \ln(\rho_{0}/\rho) \). Let us assume that the first guess function is given by \( \rho = \rho_{1} \), where \( \rho_{1} \) is normalized. An improvement would be \( \rho_{2} = \rho_{1} + \Delta \rho_{1} \), where \( \Delta \rho_{1} \) is small. We now Taylor-expand our equation to obtain a correction

\[
\Delta \rho_{1} = \rho_{1} \left[ \frac{\ln C_{2} + \ln(\rho_{0}/\rho_{1}) - vN\rho_{1}}{1 + vN\rho_{1}} \right] .
\]  

(13)

The insofar unknown constant \( C_{2} \) is fixed by requiring \( \int dr \, \Delta \rho_{1} = 0 \). A good initial guess is simply \( \rho_{1} = \rho_{0} \), i.e. the density in theta solvent. A mere 5-6 iterations usually suffice to reach convergence of Eq. \([13]\). We observe a redistribution of polymer from the core to the periphery, thus leveling off the density as anticipated. A more uniform density is also what justifies the approximation we made by neglecting derivatives of \( \rho \) in the MDE.

We have applied this algorithm to estimate the density profile of a polystyrene chain in toluene (a good solvent) when the chain is end-tethered to a substrate. The results are shown in Fig. \([3]\) and the related discussion is in the Supplementary information 1.

**Monomer-substrate repulsion**

It is widely agreed upon that only non-adsorbing polymers can classify as a polymer brush. If there would ever be an attractive force between each monomer and the substrate, one would obtain a polymer coating instead. Hence, we only consider polymers which either have no
interaction with the substrate, or a small short-range repulsion. Such a repulsive force could arise due to Van der Waals interaction which we can model by a repulsive potential suggested by Hamaker (point-to-plane interaction): \( w(r) = H/z^3 \), where \( H \) is a material-dependent Hamaker constant. This potential is simply added to the diffusion-advection equation:

\[
\frac{\partial q}{\partial s} = R_g^2 \nabla^2 q - 2 \left( \frac{\zeta R_g^2}{k_B T} \right) \mathbf{u} \cdot \nabla q + (vN\rho)q + \frac{H}{z^3}q,
\]

and similarly for \( q^\dagger \). A polymer depletion layer shows up near the substrate as anticipated. Similar profiles can also be obtained by considering other fast-decaying potentials, such as an exponential \( w(z) = w_0 e^{-z/z_0} \).

The most convenient way to solve Eq. (14) is by the finite elements method (using software such as FreeFEM++\textsuperscript{26}), and employ a backwards-Euler marching scheme for the \( s \) integral. The main problem is defining numerically the initial Dirac delta condition \( q(r, s = 0) = \delta(r) \). Our approach has been to approximate it by a very narrow Gaussian, making sure that the final result does not depend on the choice of the initial Gaussian’s width.

**Results and discussion**

The complete self-consistent solution with hydrodynamics, surface repulsion and excluded volume taken into account is visualized in the Supplementary Video. As far as shear is concerned, the main conclusion is that the “mushroom” is mostly stretched along the direction of the flow (the effect is most pronounced for high shear rate \( \dot{\gamma} \), long chain \( R_g \), and low screening length \( \xi \)). We could identify only one mechanism by which the flow in the \( x \) direction could possibly cause any change in the \( z \) density profile. When the hydrodynamic screening length \( \xi \) is reduced [cf. Eq. (10)] the fluid streamlines deviate around the chain and gain a positive \( z \) velocity component which on the incoming side stretches the polymer. On the opposing side there is a negative \( z \) velocity component which compresses the polymer, resulting in an overall irregular shape.
Figure 4: The polymer density profile along $z$- and $x$-axes. We compare a free-draining polymer (liquid penetration length $\xi \to \infty$) against one which strongly screens the flow ($\xi \to 0$), under the same applied shear rate.

For easier comparison of different simulation parameters one may integrate the 3D density profile over a plane to obtain the density along one axis only, for example the $z$-axis: $\phi(z) = \int \int dx \, dy \, \phi(x, y, z)$. We have done so in Fig. 4 to elucidate the change in polymer shape as a function of the screening length. The minuscule change of the $z$-profile (cf. blue and red curves) is about as large as it gets for any simulation parameters, which compares to the general result of experimental results on brushes in pure solvent. On the other hand, the change in the $x$-direction is paramount (see Fig. 5) and should be detectable by grazing incidence small angle neutron scattering (GISANS) or atomic force microscopy (AFM) measurements.

Recent advances in experimental techniques allow for a direct in situ observation of soft matter by small angle neutron scattering or neutron reflectometry while subject to an external shear flow in conjunction with rheology. We therefore look forward to generalize our model to end-tethered mushrooms in contact with semi-dilute polymer solutions under shear including entanglements. This will give us the possibility to make a direct comparison with
Figure 5: The lateral shift of the chain center of mass \( \langle x \rangle = \int x \rho \, dr \), as a function of the applied shear rate normalized to the Rouse relaxation time \( \dot{\gamma} \tau_r \). The shift is maximum for a free draining chain and decreases with decreasing liquid screening length \( \xi \).

experimentally determined monomer density profiles and, moreover, to predict the linked changes of the solid/liquid boundary condition of the flow profile which are also accessible by experiment \textit{in situ}.

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Supporting Information Available

The following files are available free of charge.
End-tethered vs. free chain in a good solvent

Numerous measurements of polystyrene radius of gyration in various solvents have been carried out over the years. Using the data from Fetters et al.\textsuperscript{29} we can interpolate that a model chain of $M_w = 6.0 \times 10^6 \text{ g mol}^{-1}$ molecular mass should have the radius of gyration in a theta solvent (cyclohexane) of $R_g^\Theta = 22 \text{ nm}$, while in a good solvent (toluene) it becomes $R_g^{\text{TOL}} = 33 \text{ nm}$. This information will serve us to determine the excluded value parameter of our 3D model. Note that these data have been measured for free chains in dilute solutions, while we are primarily interested in end-tethered chains. If the $s = 0$ end of an ideal Gaussian chain is constrained to the origin, the random walk statistics predict that the probability density of the $s$-th segment is a Gaussian:

$$
\rho_{\text{tethered}}(r, s) = \frac{1}{(4\pi R_g^2 s)^{3/2}} \exp \left( -\frac{r^2}{4R_g^2 s} \right). 
\tag{15}
$$

The density of the entire chain is the sum of its individual segment densities, normalized to the total number of segments $N = M_w/M_1 = 5761$, where $M = 104.15 \text{ g mol}^{-1}$ is the molecular mass of one styrene monomer.

$$
\rho_{\text{tethered}}(r) = N \int_0^1 ds \rho_{\text{tethered}}(r, s). 
\tag{16}
$$

One may check that the radius of gyration of an end-tethered chain is $\sqrt{\langle r^2 \rangle} = \sqrt{3} R_g$, higher than it would be if the chain was not tethered.

The theoretical density distribution of a chain whose both ends are free is less well known, so we report it here. A specific chain conformation can in principle be described by a certain parametric function $r(s)$. One can write a Fourier transform of this curve to obtain the so-called Rouse decomposition:

$$
r(s) = a_0 + 2 \sum_{p=1}^{\infty} a_p \cos(p\pi s). 
\tag{17}
$$
It satisfies the physical requirement that \( (dr/ds)|_{s=0,s=1} \equiv 0 \), that is, there can be no tension at either chain end, meaning that both ends are free to move. The vector \( \mathbf{a}_0 \) denotes the center of mass of the chain, while the other vectors \( \mathbf{a}_p \) are all independent Gaussian random variables with the mean equal to zero and the variance equal to 

\[
\langle a_p^2 \rangle = \frac{R_g^2}{\pi^2 p^2}
\]  

(18)

(see related discussion in Doi and Edwards\textsuperscript{23}). According to Eq. (17), \( r(s) \) is a sum of Gaussian random variables, hence it itself is also a Gaussian random variable with the mean equal to \( \langle r(s) \rangle = a_0 \) (position of the center of mass) and the variance equal to 

\[
\langle (r(s) - a_0)^2 \rangle = \sum_{p,q} \langle \mathbf{a}_p \cdot \mathbf{a}_q \rangle \cos(p\pi s) \cos(q\pi s) = \frac{R_g^2}{\pi^2} \sum_{p=1}^{\infty} \frac{\cos^2(p\pi s)}{p^2} = 6R_g^2 \left( s^2 - s + \frac{1}{3} \right).
\]  

(19)

Clearly, the end monomers \( s = 0 \) and \( s = 1 \) have a wider distribution \( (\sigma_r = \sqrt{2}R_g) \) with respect to the middle ones \( (s = \frac{1}{2}) \) which are more concentrated in the center \( (\sigma_r = R_g/\sqrt{2}) \). The full distribution function is hence given by 

\[
\rho_{\text{free}}(r,s) = \left[ \frac{1}{4\pi R_g^2(s^2 - s + 1/3)} \right]^{-3/2} \exp \left( -\frac{r^2}{4R_g^2(s^2 - s + 1/3)} \right).
\]  

(20)

To obtain the distribution of the whole chain, simply integrate over \( ds \), just like in Eq. (16):

\[
\rho_{\text{free}}(r) = N \int_0^1 ds \rho_{\text{free}}(r,s).
\]  

(21)

One may check that the radius of gyration of this distribution is \( \sqrt{\langle r^2 \rangle} \equiv R_g \), as expected for a free chain.

We now apply the excluded volume algorithm to the density given in Eq. (21), as described in the main text. The excluded volume parameter is progressively increased until the radius of gyration becomes equal to the experimental value \( R_g^{\text{TOL}} = 33 \) nm (the excluded volume
turns out to be \( v = 0.016 \text{nm}^3 \) per monomer). We can now use this value and apply the excluded volume algorithm to the end-tethered chain [Eq. (16)] which then swells up to a radius of gyration of 49 nm. The density plots of all the polymers are shown in Fig. 3.

**A Gaussian chain under a uniform flow: analytical solution**

One way to illustrate the theory of polymer chains under liquid flow is to find an analytical solution for the simplest non-trivial case. Consider an ideal Gaussian chain in one dimension, whose one end is tethered at \( x = 0 \) and the other end is free to be anywhere on the \( x \)-axis. A uniform flow of magnitude \( u \) is applied in the \( x \) direction. According to Eqs. (8)-(9), the partition function of such a chain satisfies the diffusion-advection (D-A) equation:

\[
\frac{\partial q}{\partial s} = \frac{\partial^2 q}{\partial x^2} - u \frac{\partial q}{\partial x}, \quad q(x, s = 0) = \delta(x), \quad \frac{\partial q^\dagger}{\partial s} = -\frac{\partial^2 q^\dagger}{\partial x^2} - u \frac{\partial q^\dagger}{\partial x}, \quad q^\dagger(x, s = 1) = 1,
\]

written in dimensionless units for simplicity. Both of these equations have simple analytical solutions:

\[
q(x, s) = \frac{1}{\sqrt{4\pi s}} \exp \left( \frac{-(x-us)^2}{4s} \right),
\]

\[
q^\dagger(x, s) = 1.
\]

To obtain the density of the entire chain, we simply integrate over each monomer:

\[
\rho_{\text{D-A}}(x) = \int_0^1 ds \, q^\dagger = \int_0^1 \frac{ds}{\sqrt{4\pi s}} \exp \left( \frac{-(x-us)^2}{4s} \right).
\]

On the other hand, for the simple case of a 1-D uniform flow, one might be tempted to use the modified diffusion equation [Eqs. (1)-(2)] with a scalar potential: \( w(x) = -gx \), where the parameter \( g \) denotes a constant force. This approach would be correct if the force was
conservative (i.e. gravity, Coulomb force), but it is invalid for a dissipative force such as the Stokes which we are dealing with in this study. Nevertheless, it is interesting to compare the MDE prediction with that of D-A. Consider now the partition function of a Gaussian chain in a uniform scalar potential:

\[
\frac{\partial q}{\partial s} = \frac{\partial^2 q}{\partial x^2} - gxq, \quad q(x, s = 0) = \delta(x), \quad (27)
\]

\[
\frac{\partial q^\dagger}{\partial s} = -\frac{\partial^2 q^\dagger}{\partial x^2} + gxq, \quad q^\dagger(x, s = 1) = 1. \quad (28)
\]

These equations might remind some readers of the Schrödinger equation in a uniform field. Luckily, they both have analytical solutions:

\[
q(x, s) = \frac{1}{\sqrt{4\pi s}} \exp \left( -\frac{x^2}{4s} + \frac{gx^3}{2} + \frac{g^2 s^3}{12} \right), \quad (29)
\]

\[
q^\dagger(x, s) = \exp \left( gx(1 - s) + \frac{g^2}{3}(1 - s)^3 \right). \quad (30)
\]

Integration over \( x \) yields the total partition function (which is, as required, independent of \( s \)):

\[
Q = \int_{-\infty}^{\infty} dx \, q q^\dagger = \exp \left( \frac{g^2}{3} \right). \quad (31)
\]

The density is given by the integral over all monomers, normalized to the total partition function:

\[
\rho_{\text{MDE}}(x) = \frac{1}{Q} \int_0^1 ds \, q q^\dagger = \int_0^1 ds \, \frac{1}{\sqrt{4\pi s}} \exp \left( -\frac{(x - gs(2 - s))^2}{4s} \right). \quad (32)
\]

This equation is surprisingly similar in form to the D-A density, Eq. \( \Box \). To compare them, let us find the mean position of each density distribution:

\[
\langle x \rangle = \int_{-\infty}^{\infty} x \rho(x) \, dx \quad \Rightarrow \quad \langle x \rangle_{\text{D-A}} = \frac{1}{2} u, \quad \langle x \rangle_{\text{MDE}} = \frac{2}{3} g. \quad (33)
\]

We have chosen \( u = 3 \) and \( g = 9/4 \) which give the same mean \( \langle x \rangle = 3/2 \) for both distributions and plotted them in Figure \( \Box \). Quite remarkably, completely different physics
modeled by different approaches provide very similar density profiles.

Finally, we give the expression for an unperturbed end-tethered Gaussian chain density (where both models agree if we set $g = u = 0$):

$$\rho_0(x) = \int_0^1 ds \frac{1}{\sqrt{4\pi s}} \exp\left(\frac{-x^2}{4s}\right) = \sqrt{\frac{x^2}{4}} \left[ \text{erf}\left(\sqrt{\frac{x^2}{4}} - 1\right) + \frac{1}{\sqrt{\pi}} \exp\left(-\frac{x^2}{4}\right) \right].$$  \hspace{1cm} (34)

This function is shown as a dashed line in Figure 2.

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