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Scattering function of semiflexible polymer chains under good solvent conditions

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Using the pruned-enriched Rosenbluth Monte Carlo algorithm, the scattering functions of semiflexible macromolecules in dilute solution under good solvent conditions are estimated both in d= 2 and d = 3 dimensions, considering also the effect of stretching forces. Using self-avoiding walks of up to $N = 25\,600$ steps on the square and simple cubic lattices, variable chain stiffness is modeled by introducing an energy penalty ϵ_b for chain bending; varying $q_b = \exp(-\epsilon_b/k_B T)$ from $q_b = 1$ (completely flexible chains) to $q_b = 0.005$, the persistence length can be varied over two orders of magnitude. For unstretched semiflexible chains, we test the applicability of the Kratky-Porod worm-like chain model to describe the scattering function and discuss methods for extracting persistence length estimates from scattering. While in d = 2 the direct crossover from rod-like chains to self-avoiding walks invalidates the Kratky-Porod description, it holds in d = 3 for stiff chains if the number of Kuhn segments n_K does not exceed a limiting value n_K^* (which depends on the persistence length). For stretched chains, the Pincus blob size enters as a further characteristic length scale. The anisotropy of the scattering is well described by the modified Debye function, if the actual observed chain extension $\langle X \rangle$ (end-to-end distance in the direction of the force) as well as the corresponding longitudinal and transverse linear dimensions $\langle X^2 \rangle - \langle X \rangle^2$, $\langle R_{e,\perp}^2 \rangle$ are used. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4764300]

I. INTRODUCTION

Small angle (neutron) scattering from polymers in dilute solution is the method of choice to obtain a complete picture of the conformations of long flexible or semiflexible macromolecules, from the length scale of the monomeric units to the gyration radius of the chain molecules.^{1–4} Classical experiments have shown that the gyration radius R_{g} of long flexible chains in dense melts (and also in dilute solution under Theta conditions) scales with chain length N according to the classical random walk picture, ${}^{5-7}R_g \propto N^{1/2}$, while in dilute solution under good solvent conditions flexible polymers form swollen coils,^{1-4,8} $R_g \propto N^{\nu}$, with⁹ $\nu \approx 0.588$ (in d = 3 dimensions) or v = 3/4 (d = 2). It was also shown that on intermediate length scales, the dependence of the scattering intensity S(q)on wave number q reflects the self-similar fractal structure of the polymer,⁸ $S(q) \propto q^{-1/\nu}$ (under good solvent conditions) or $S(q) \propto q^{-2}$ (Theta conditions or melts, respectively). Also the crossovers between these regimes when either the temperature distance from the Theta point or the concentration of the solution are varied have been investigated,⁴ and the length scales ruling these crossovers (i.e., diameter of "thermal blobs" or "concentration blobs," respectively) have been identified.¹⁻⁴

The behavior gets more complicated, however, when chain stiffness plays a prominent role: only when chain stiffness is essentially due to chain thickness, i.e., when the effective persistence length ℓ_p scales proportional to the lo-

cal chain diameter D the problem can still be reduced to a rescaled self-avoiding walk problem.^{10,11} However, when $\ell_p \gg D$, one finds (in d = 3) a double crossover, since then short chains behave like rigid rods (i.e., $R_g \propto N$ as long as $R_g < \ell_p$), and then a crossover to Gaussian randomwalk like coils occurs, while for $R_g \approx R_0$ (R_0 will be discussed below) a second crossover to swollen coils ($R_g \propto N^{\nu}$) starts. Also this behavior has been established in beautiful classical experiments,¹² as well as in recent simulations.^{11,13} The standard model for semiflexible worm-like chains, the Kratky-Porod model,¹⁴ can only describe the first crossover (from rods to Gaussian coils) but fails to account for the second crossover to swollen coils, due to its complete neglect of excluded volume effects. It turns out that this second crossover still is incompletely understood: while in the early experiments¹² it was suggested that this crossover occurs for $n_K = n_K^*$ with $n_K^* = 50$ Kuhn segments, independent of the persistence length, a Flory-type argument^{15, 1 $\overline{6}$} suggests that the crossover occurs for a polymer radius $R_0 \propto \ell_p^2/D$ (corresponding to $n_K^* \propto (\ell_p/D)^2$), while the simulations rather find¹³ $n_K^* \propto \ell_p^{1.5}$. Remember that a worm-like chain can be described as an equivalent freely jointed chain of n_k Kuhn segments of length $2\ell_p$ each.^{5,6} In view of an apparent conflict of the estimate¹² $n_K^* = 50$ with the Yamakawa-Stockmayer-Shimata theory^{16–19} for worm-like chains, the result $n_K^* = 50$ was considered as a very fundamental problem.^{20,21} However, Tsuboi et al.²¹ confirmed this estimate for another stiff polymer and concluded that the result $n_K^* = 50$ is compatible with the theory. We also note that in d = 2, there occurs a

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single crossover from rods to self-avoiding walks, any regime of Gaussian-like behavior is completely absent.^{13,22} We emphasize however, that the results of Refs. 11, 13, 15, and 16 imply that a universal number n_K^* (independent of ℓ_p) up to which the Kratky-Porod model holds in d = 3 does not exist.

It is then interesting to ask how chain stiffness shows up on intermediate length scales that can be probed via the scattering function S(q). If one disregards excluded volume¹ and bases the treatment on the Kratky-Porod model, one can show²³ that the rod-like behavior at large q leads to a scattering law proportional to q^{-1} , i.e. (in d = 3 dimensions),

$$N\ell_b q S(q) = \pi + \frac{2}{3} (q\ell_p)^{-1}, \quad N \to \infty,$$
 (1)

where we have assumed that the chain has a contour length $L = N\ell_b$, where ℓ_b is the bond length, while the persistence length⁶ is $\ell_p = (N/n_K)\ell_b/2$. While for Gaussian "phantom chains" (i.e., excluded volume interactions are completely neglected) the structure factor S(q) is readily found¹⁻⁶ in terms of the Debye function, and the only length that enters is the gyration radius $\langle R_g^2 \rangle^{1/2}$, choosing a normalization where S(q = 0) = 1,

$$S(q) = 2[\exp(-\zeta) - 1 + \zeta]/\zeta^2, \ \zeta = q^2 \langle R_g^2 \rangle = q^2 N \ell_b^2 / 6,$$
(2)

for semiflexible polymers the calculation of S(q) for chains with *N* finite is a formidable problem,^{24–39} even in the absence of excluded volume effects. However, including excluded volume effects in the description of scattering of semiflexible chains is even more an unsolved problem: existing phenomenological approaches require the adjustment of many empirical parameters.³⁷ It will be one of the tasks that will be addressed in the present paper, to investigate S(q) for semiflexible chains numerically in the presence of excluded volume interactions between the effective monomers, varying ℓ_p over a wide range.

In recent years also the behavior of macromolecules under the influence of stretching forces has found enormous interest (e.g., Refs. 40–56), in particular, for the study of biomacromolecules. Experimentally, this can be realized, e.g., by pulling at one end of a chain, that is anchored at a substrate with the other chain end, by optical or by magnetic tweezers or by the tip of an atomic force microscope^{42,46,48,49,52,55,56} but it is also conceivable to stretch polymers by the forces occurring when a polymer solution is exposed to strong shear flow^{57–59} or elongational flow.⁶⁰ It is difficult to carry out scattering experiments on such stretched chains and measure the structure factor (which then is anisotropic and has two relevant parts $S_{||}(q_{||})$, $S_{\perp}(q_{\perp})$ since the direction of the scattering vector \vec{q} relative to the stretch direction, either parallel, q_{\parallel} , or perpendicular, q_{\perp} , matters). But nevertheless a theoretical investigation of $S_{\parallel}(q_{\parallel})$, $S_{\perp}(q_{\perp})$ is worthwhile, it gives detailed insight into the local structure of stretched chains, including also chains under cylindrical confinement;61-63 this may help to understand problems such as transport of semiflexible polymers through porous materials, or channels in nanofluidic devices,⁶¹ etc. Thus, we shall also investigate the structure factor of stretched semiflexible chains, extending previous work on flexible chains.40,44

The outline of our paper is as follows: in Sec. II, we give a summary of the theoretical background, and in Sec. III we define our model and briefly recall the simulation methodology. In Sec. IV, we present our results for the structure factor S(q) of semiflexible chains, for both d = 2 and d = 3dimensions, in the absence of stretching forces. Section V describes the modifications of the structure factor due to stretching, while Sec. VI summarizes our conclusions. The calculation of the scattering function of random walk chains under constant pulling forces can be carried out analytically and is presented in the Appendix.

II. THEORETICAL BACKGROUND

A. Definitions

We consider here the scattering from a single polymer chain, describing the chain by a sequence of N + 1 (effective) monomers at positions \vec{r}_j , j = 1, 2, ..., N + 1, with N bond vectors $\vec{a}_j = \vec{r}_{j+1} - \vec{r}_j$. In the absence of stretching forces, the structure factor $S(\vec{q})$ does not depend on the direction of the scattering vector \vec{q} , and can be defined as S(q) $= \langle \sum_{j=1}^{N+1} \sum_{k=1}^{N+1} \exp[i\vec{q} \cdot (\vec{r}_j - \vec{r}_k)] \rangle / (N + 1)^2$, choosing a normalization for which $S(q \to 0) = 1$. When a stretching force is applied to one chain end in the +x-direction, the structure factor becomes anisotropic. In d = 3 dimensions, the conformations of chains still have axis-symmetric geometries, and we must distinguish between $S_{||}(q_{||})$, where \vec{q} is oriented in the x-direction parallel to the force, and $S_{\perp}(\vec{q}_{\perp})$, where \vec{q} is oriented perpendicular to it. So we define $\vec{r}_j = (x_j, y_j, z_j) = (x_j, \vec{\rho}_j)$ to obtain

$$S_{\parallel}(q_{\parallel}) = \frac{1}{(N+1)^2} \left\{ \left\langle \left[\sum_{j=1}^{N+1} \sin(q_{\parallel}x_j) \right]^2 \right\rangle + \left\langle \left[\sum_{j=1}^{N+1} \cos(q_{\parallel}x_j) \right]^2 \right\rangle \right\},$$
(3)

$$S_{\perp}(q_{\perp}) = \frac{1}{(N+1)^2} \left\{ \left\langle \left[\sum_{j=1}^{N+1} \sin(\vec{q}_{\perp} \cdot \vec{\rho}_j) \right]^2 \right\rangle + \left\langle \left[\sum_{j=1}^{N+1} \cos(\vec{q}_{\perp} \cdot \vec{\rho}_j) \right]^2 \right\rangle \right\}.$$
 (4)

In d = 2 dimensions, we have $\vec{r}_j = (x_j, y_j)$ and then $\vec{q}_{\perp} \cdot \vec{\rho}_j$ in Eq. (4) needs to be replaced simply by $q_{\perp}y_j$.

In this paper, we are not at all concerned with effects due to the local structure of (effective) monomers, such as chemical side groups, which show up at large q in the scattering from real chains.²⁹ We next define our notation for characteristic lengths of the chain. Assuming a rigidly fixed bond length ℓ_b between neighboring monomers along the chain, the contour length L is $L = N\ell_b$. The mean square endto-end distance (in the absence of stretching forces) simply is $\langle R^2 \rangle = \langle (\sum_{j=1}^N \vec{a}_j)^2 \rangle$. The mean square gyration radius is given by

$$\langle R_g^2 \rangle = \frac{1}{N+1} \left\langle \sum_{j=1}^{N+1} (\vec{r}_j - \vec{r}_{CM})^2 \right\rangle$$

= $\frac{1}{(N+1)^2} \left\langle \sum_{j=1}^{N+1} \sum_{k=j+1}^{N+1} (\vec{r}_j - \vec{r}_k)^2 \right\rangle,$ (5)

where $\vec{r}_{CM} = \sum_{j=1}^{N+1} \vec{r}_j / (N+1)$ is the center of mass position of the polymer.

In the presence of stretching forces, the chain takes a mean extension $\langle X \rangle$ and mean square extensions also become anisotropic,

$$\langle X \rangle = \left\langle \sum_{j=1}^{N} a_{jx} \right\rangle, \quad \langle X^2 \rangle = \left\langle \left(\sum_{j=1}^{N} a_{jx} \right)^2 \right\rangle, \tag{6}$$

$$\langle R_{\perp}^2 \rangle = \left\langle \left(\sum_{j=1}^N a_{jy} \right)^2 \right\rangle + \left\langle \left(\sum_{j=1}^N a_{jz} \right)^2 \right\rangle.$$
(7)

Equation (7) refers to the three-dimensional case, for d = 2 the second term in the right-hand side needs to be omitted. A related anisotropy applies to the gyration radius square, namely,

$$\left\langle R_{g,\parallel}^2 \right\rangle = \frac{1}{(N+1)^2} \left\langle \sum_{j=1}^{N+1} \sum_{k=j+1}^{N+1} (x_j - x_k)^2 \right\rangle,$$
 (8)

$$\langle R_{g,\perp}^2 \rangle = \frac{1}{(N+1)^2} \left\langle \sum_{j=1}^{N+1} \sum_{k=j+1}^{N+1} [(y_j - y_k)^2 + (z_j - z_k)^2] \right\rangle,$$
(9)

for d = 3, again the term $(z_j - z_k)^2$ simply is omitted in the case d = 2.

The gyration radii describe the scattering at small \vec{q} . In the absence of stretching forces

$$S(q) = 1 - q^2 \langle R_g^2 \rangle / d, \quad q \to 0, \tag{10}$$

while if stretching forces are present, one finds instead

$$S_{\parallel}(q_{\parallel}) = 1 - q_{\parallel}^2 \langle R_{g,\parallel}^2 \rangle, \quad q \to 0, \tag{11}$$

$$S_{\perp}(q_{\perp}) = 1 - q_{\perp}^2 \langle R_{g,\perp}^2 \rangle / (d-1), \quad q \to 0.$$
 (12)

In addition to the limit $q \to 0$, also the limiting behavior of $S(q \to \infty)$ is trivially known: then all interference terms in S(q) average to zero, and only the terms j = k contribute to the double sum. Hence, we obtain $S(q \to \infty) = 1/(N + 1)$, $S_{\parallel}(q_{\parallel} \to \infty) = S_{\perp}(q_{\perp} \to \infty) = 1/(N + 1)$, irrespective of the value of the persistence length ℓ_p , the value of an applied force *f*, etc.

We emphasize, however, that there is no general definition for the persistence length ℓ_p that would be both universally valid and practically useful.^{10,11,13} The definition of textbooks^{6,64} via the asymptotic decay of the bond vector orientational correlation (for $N \rightarrow \infty$),

$$\langle \cos \theta(s) \rangle \equiv \langle \vec{a}_j \cdot \vec{a}_{j+s} \rangle / \langle \vec{a}_j \cdot \vec{a}_j \rangle \propto \exp(-s\ell_b/\ell_p),$$

$$s \to \infty \quad (13)$$

makes sense only for Gaussian PHANTOM chains. It is not applicable to real polymers under ANY CIRCUMSTANCES, since the asymptotic decay of $\langle \cos \theta(s) \rangle$ with the "chemical distance" $s\ell_b$ along the chain always is a power-law decay. In fact, for $\ell_p \ll s\ell_b \ll L$ one has^{10,11,13,65–68}

$$\langle \cos \theta(s) \rangle \propto s^{-\beta},$$
 (14)

where $\beta = 3/2$ both in melts^{65,66} and for chains in dilute solution under Theta conditions.^{10,67} For good solvent conditions, one finds the scaling law^{10,68}

$$\beta = 2(1 - \nu), \tag{15}$$

which yields $\beta = 0.825$ (d = 3) and $\beta = 1/2$ (d = 2), respectively. In simple cases, such as the semiflexible self-avoiding walk model studied in Ref. 13 and further investigated here, one can rather use an analog of Eq. (13) but for short chemical distances,

$$\langle \cos \theta(s) \rangle = \exp(-s\ell_b/\ell_p), \quad 0 \le s \le \ell_p/\ell_b.$$
 (16)

Equation (16) is useful for the simple model that will be studied here, namely, the self-avoiding walk (SAW) on square and simple cubic lattices with an energy penalty ϵ_b for "bond bending" (i.e., kinks of the SAW by 90°), serving as a convenient parameter to control the persistence length. Since for $\epsilon_b/k_BT < 2$ the power law, Eq. (14), already starts to set in even for small *s* of order unity, we use in practice an alternative definition,

$$\ell_p/\ell_b = -1/\ln(\langle\cos\theta(1)\rangle),\tag{17}$$

which is equivalent to Eq. (16), if Eq. (16) holds over a more extended range of s. Unfortunately, Eq. (17) is not straightforwardly applicable for chemically realistic models (such as alkane chains when ℓ_b means a bond between two successive carbon atoms, but the all-trans state corresponds to a zigzag configuration with a nonzero bond angle $\theta(1)$). It is also not useful for coarse-grained models of polymers with complex architecture, such as bottle-brush polymers.^{10,11} Thus, we emphasize that for our model Eq. (17) is a practically useful definition, while for real polymers studied experimentally the estimation of ℓ_p is a delicate problem. The same caveat applies for the Kuhn length ℓ_K , which is $\ell_K = 2\ell_p$ for wormlike chains, but the latter does not apply in solutions, as stated above. In dense melts, $\ell_K/\ell_b = 6\langle R_g^2 \rangle/(\ell_b^2 N)$ is supposed to hold, but due to local interactions with neighboring monomers in a dense environment it is not obvious that ℓ_K for a melt is a relevant parameter for a chain under good solvent conditions.

Thus, it is a clear advantage of our model calculations that via Eqs. (16) and (17) accurate direct estimates of ℓ_p are possible, unlike in experiment. These estimates for ℓ_p are given in Table I.

TABLE I. Values of persistence lengths ℓ_p/ℓ_b for semiflexible chains in d = 2 and d = 3, estimated by Eq. (17), and the crossover length N^* between the intermediate Gaussian regime and the SAW regime in d = 3, estimated empirically from Fig. 7(b) of Ref. 13 ($N^* = N^{\text{rod}} = 2\ell_p/\ell_b$ in d = 2) for various values of q_b .

q_b	0.005	0.01	0.02	0.03	0.05	0.10	0.20	0.40	1.0
$\ell_p/\ell_b \ (d=2)$	118.22	59.44	30.02	20.21	12.35	6.46	3.50	2.00	1.06
$\ell_p/\ell_b \ (d=3)$	51.52	26.08	13.35	9.10	5.70	3.12	1.18	1.12	0.67
$N^* (d = 3)$	36000	9000	1850	700	180	41	11		

B. Theoretical predictions for the scattering function of single polymers in good solvents in the absence of stretching forces

The classical result for the scattering from Gaussian chains is the Debye function¹⁻⁴

$$S_{\text{Debye}}(q) = \frac{2}{q^2 \langle R_g^2 \rangle} \left\{ 1 - \frac{1}{q^2 \langle R_g^2 \rangle} \left[1 - \exp\left(-q^2 \langle R_g^2 \rangle\right) \right] \right\}.$$
(18)

For large q this reduces to $S_{\text{Debye}}(q) \approx 2/(q^2 \langle R_g^2 \rangle)$, reflecting the random-walk like fractal structure of a Gaussian coil, $S_{\text{Debye}}(q) \propto q^{-1/\nu_{MF}}$ with $\nu_{MF} = 1/2$. Equation (18) does not tell how large q can be in order for this power law to be still observable. For semiflexible Gaussian chains, the contour length $L = N\ell_b$ can be written as $L = n_p\ell_p$ and the mean square end-to-end distance and gyration radius are^{14,69}

$$\frac{\langle R^2 \rangle}{2\ell_p L} = 1 - \frac{1}{n_p} [1 - \exp(-n_p)], \tag{19}$$

$$\frac{6\langle R_g^2 \rangle}{2\ell_p L} = 1 - \frac{3}{n_p} + \frac{6}{n_p^2} - \frac{6}{n_p^3} [1 - \exp(-n_p)].$$
(20)

From Eqs. (19) and (20), one can clearly recognize that Gaussian behavior of the radii is only seen if the number n_p of persistence lengths that fit to a given contour length of the chain is large, $n_p \gg 1$ (for n_p of order unity, a crossover to rod-like behavior occurs). Since q^{-1} is also a length scale, one concludes that the Gaussian coil behavior reflected in Eq. (18) also implies that a scale q^{-1} requires that a subchain with this gyration radius contains many persistence lengths as well, i.e., Eq. (18) can only hold for

$$q\ell_p \ll 1. \tag{21}$$

In the regime

$$\ell_p^{-1} \ll q \ll \ell_b^{-1},\tag{22}$$

the scattering function resembles the scattering function of a rigid rod of length $L_{\rm rod}$,⁷⁰

$$S_{\rm rod}(q) = \frac{2}{qL_{\rm rod}} \left[\int_0^{qL_{\rm rod}} dx \frac{\sin x}{x} - \frac{1 - \cos(qL_{\rm rod})}{qL_{\rm rod}} \right],\tag{23}$$

which for large q varies like

$$S_{\rm rod}(q \to \infty) = \pi/(q L_{\rm rod}).$$
 (24)

Equations (23) and (24) refer to a rigid rod on which the scattering centers are uniformly and continuously distributed. In the lattice model studied here, the scattering centers are the subsequent lattice sites along the rod. For a rod of length $L_{\rm rod}$, there are $L_{\rm rod} + 1$ such centers,⁷¹

$$S_{\rm rod}(q) = \frac{1}{L_{\rm rod} + 1} \left[-1 + \frac{2}{L_{\rm rod} + 1} \sum_{k=0}^{L_{\rm rod}} (L_{\rm rod} + 1 - k) \frac{\sin qk}{qk} \right],$$
$$q < \pi. \quad (25)$$

Both Eqs. (23) and (25) have a smooth crossover from $S_{\rm rod}(q) = 1 - q^2 \langle R_g^2 \rangle_{\rm rod}/3$ with $\langle R_g^2 \rangle_{\rm rod} = L_{\rm rod}^2/12$ to the 1/q power law (Eq. (24)). Of course, on the lattice consideration of $q > \pi$ does not make sense, distances of a lattice spacing and less are not meaningful.

While for a Gaussian coil no direction of \vec{q} is singled out, for a rod it makes sense to consider also the special case where the wave vector \vec{q} is oriented along the rod. Then one rather obtains, $q_{||}$ being the component of \vec{q} parallel to the axis of the rod⁵⁷

$$S_{\rm rod}(q_{\parallel}) = \frac{2}{(q_{\parallel}L_{\rm rod})^2} [1 - \cos(q_{\parallel}L_{\rm rod})].$$
(26)

Equation (26) leads to an oscillatory decay since $\cos(q_{\parallel}L_{\rm rod})$ = 1 for $q_{\parallel}^{(k)} = k(2\pi/L_{\rm rod}), k = 0, 1, 2, \dots, L_{\rm rod}$, and $S_{\rm rod}(q_{\parallel})$ hence has zeros for all $q_{\parallel}^{(k)}, k = 1, 2, \dots, L_{\rm rod}$.

When we consider the scattering from semiflexible Gaussian chains, we expect a smooth crossover between the Debye function, $S_{\text{Debye}}(q)$ and the rod scattering, Eq. (23), similar to the smooth crossovers from rods to Gaussian coils, as for the radii (Eqs. (19) and (20)). It turns out that this is a formidable problem, and no simple explicit formula exists, despite the fact that excluded volume effects still are neglected.^{17–21,23–33,35,37–39} Kholodenko³² derived an interpolation formula which describes the two limiting cases of Gaussian coils and rigid rods exactly, and which is expected to show only small deviations from the exact result in the intermediate crossover regime. His result has the form

$$S(q) = \frac{2}{x} \left[I_1(x) - \frac{1}{x} I_2(x) \right], \quad x = 3L/2\ell_p, \tag{27}$$

where $I_n(x) = \int_0^x dz z^{n-1} f(z)$, and the function f(z) is given by

$$f(z) = \begin{cases} \frac{1}{E} \frac{\sinh(Ez)}{\sinh z} & q \le \frac{3}{2\ell_p}, \\ \frac{1}{\hat{E}} \frac{\sin(\hat{E}z)}{\sinh z} & q > \frac{3}{2\ell_p} \end{cases}$$
(28)

with

$$E = \left[1 - \left(\frac{2q\ell_p}{3}\right)^2\right]^{1/2}, \quad \hat{E} = \left[\left(\frac{2q\ell_p}{3}\right)^2 - 1\right]^{1/2}.$$
(29)

In addition, Stepanow³⁵ has developed a systematic expansion of the scattering function in terms of the solution for the quantum rigid rotator problem, which converges fast if L/ℓ_p is not too large. Note that the opposite limit, $L/\ell_p \rightarrow \infty$, has already been considered by des Cloizeaux²³ (Eq. (1)). This expansion (as well as equivalent representations written as continued fractions³³) can only be evaluated numerically.⁷²

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However, a few qualitative statements can be made on the structure factor S(q) in the representation of a Kratky plot, qLS(q) plotted vs. Lq. Equations (23)–(25) imply a monotonous increase from the straight line qLS ($q \approx 0$) = qL towards the plateau value qLS ($q \gg 2\pi/L$) $= \pi$ for simple rigid rods, while for semiflexible polymers this Kratky plot exhibits a maximum. We may crudely approximate S(q)by its leading terms

$$qLS(q) \approx qL - \frac{1}{3}(qL)^3 \frac{\langle R_g^2 \rangle}{L^2},$$
 (30)

$$q_{\max} = 1/\sqrt{\langle R_g^2 \rangle}, \quad q_{\max} LS(q_{\max}) = \frac{2}{3}L/\sqrt{\langle R_g^2 \rangle},$$
 (31)

i.e., from Eqs. (20) and (30) we immediately find, for $n_p \gg 1$,

$$q_{\max} = \sqrt{3/(\ell_p L)}$$
 , $q_{\max} LS(q_{\max}) = \frac{2}{\sqrt{3}} \sqrt{L/\ell_p}.$

(32)

Using the full Debye function one finds a different prefactor, $q_{\text{max}} \approx \sqrt{6.4/(\ell_p L)}$, but the general scaling behavior is still given by Eq. (32). Thus, when *L* is known (as in simulations) for semiflexible Gaussian chains finding the coordinates of the maximum in the Kratky plot allows a straightforward estimation of the persistence length ℓ_p .

Considering now excluded volume effects, we emphasize that Eq. (31) still is valid, while Eq. (32) no longer holds. In particular, in Ref. 13 it was shown that in d = 2 the Kratky-Porod model¹⁴ of semiflexible chains, on which Eqs. (19), (20) and (27)–(29) are based, has no validity whatsoever: rather around $n_p = 1$ a smooth crossover from the rigid rod behavior to the behavior of two-dimensional self-avoiding walks occurs. Thus, we expect similarly instead of Eq. (20) that (recall $n_p = L/\ell_p$)

$$\frac{\langle R_g^2 \rangle}{\ell_p L} = f(n_p), \quad \text{with} \quad f(n_p < 1) = n_p, \tag{33}$$

as in Eq. (20), but

$$f(n_p \gg 1) = C_g^s n_p^{2\nu_2 - 1}, \quad \nu_2 = 3/4,$$
 (34)

 C_g^s being (for $\ell_p/\ell_b \gg 1$) a non-universal constant. Equations (33) and (34) hence imply in d = 2,

$$\left\langle R_g^2 \right\rangle = C_g^s \ell_p^{1/2} L^{3/2}, \quad L \to \infty, \tag{35}$$

in full analogy to the result for fully flexible chains,

$$\langle R_g^2 \rangle = C_g^f \ell_b^{1/2} L^{3/2}, \quad L \to \infty$$
 (36)

with C_g^f another non-universal constant. Similar relations hold¹³ for $\langle R^2 \rangle$,

$$\langle R^2 \rangle = C_e^f \ell_b^{1/2} L^{3/2}$$
 (flexible),

$$\langle R^2 \rangle = C_e^s \ell_p^{1/2} L^{3/2}$$
 (semiflexible) (37)

with C_e^f and C_e^s other (non-universal) constants for flexible and semiflexible chains, respectively. The ratios C_e^f/C_g^f and C_e^s/C_g^s are expected to be universal, however (for Gaussian chains $\langle R^2 \rangle / \langle R_g^2 \rangle = 6$), for both flexible and semiflexible chains.

In d = 3 dimensions, however, the end-to-end distance $\langle R^2 \rangle$ of semiflexible chains with excluded volume is considerably more involved.¹³ Two successive crossovers occur: for $n_p \approx 1$ from rods to Gaussian coils, while excluded volume effects become prominent for

$$n_p > n_p^*, \quad n_p^* \propto (\ell_p/D)^{\zeta}, \tag{38}$$

where we have introduced the chain diameter *D* as another characteristic length that may be needed in general (while in our model $D = \ell_b$, however), and ζ is an exponent that is not yet known precisely. Arguments based on Flory theory yield^{13,15,16} $\zeta = 2$, while Monte Carlo results rather suggested¹³ $\zeta \approx 1.5$. We recall that in d = 3 Flory arguments are not¹ exact, implying^{3,9} $\nu = 3/5$ instead of $\nu = 0.588$. A similar double crossover from rods to first Gaussian coils and then to d = 3 self-avoiding walks is expected to be visible in $\langle R_g^2 \rangle$, too. If we could rely on Flory theory, we would predict from these considerations that

$$\langle R_g^2 \rangle / (\ell_p L) = C_g^s (n_p / n_p^*)^{2\nu - 1}, \quad n_p > n_p^*$$
 (39)

and hence (using the Flory value $\nu = 3/5$),

$$\langle R_g^2 \rangle = C_g^s L^{6/5} (\ell_p D)^{2/5} .$$
 (40)

From $q_{\text{max}} = (\sqrt{C_g^s}L^{3/5}(\ell_p D)^{1/5})^{-1}$ the persistence length ℓ_p can be inferred, provided C_g^s has been determined. However, if $\ell_p \gg \ell_b$ and $D = \ell_b$, in the regime $1 < n_p < n_p^*$ Gaussian statistics for the gyration radius is still applicable, and hence Eq. (32) applies.

C. The structure factor in the presence of stretching forces

For Gaussian chains under stretch, where a force *f* is applied at a chain at one end in the +x-direction, the other end being fixed at the coordinate origin, the structure factor $S(\vec{q})$ has been derived by Benoit *et al.*⁴⁰ as follows $\{\vec{q} = (q_x, q_y, q_z) \text{ with } q_{||} = q_x \text{ and } q_{\perp} = \sqrt{q_y^2 + q_z^2}\},\$

$$S_{\parallel}(q_{\parallel}) = 2Re\left\{\frac{\exp(-X_{\parallel}) - 1 + X_{\parallel}}{X_{\parallel}^2}\right\},\tag{41}$$

$$S_{\perp}(q_{\perp}) = 2 \frac{\exp(-X_{\perp}) - 1 + X_{\perp}}{X_{\perp}^2},$$
 (42)

where $X_{\perp} = q_{\perp}^2 (\langle R^2 \rangle_0 / 6 \lambda_{\perp}^{-2})$, with $\langle R^2 \rangle_0$ the mean-square end-to-end distance of the chain in the absence of any force (f = 0), and λ_{\perp} describes the modification of the Gaussian distribution in the transverse directions (*y* and *z*-direction, for d = 3). The quantity X_{\parallel} is complex (therefore, the real part of Eq. (41) is taken) and is given by

$$X_{\parallel} = \frac{q_{\parallel}^2 \langle R^2 \rangle_0}{6\lambda_{\parallel}^{-2}} + i \langle X \rangle q_{\parallel}, \qquad (43)$$

where $\lambda_{||}$ describes the modification of the Gaussian distribution in the *x*-direction (parallel to the force). Benoit *et al.*⁴⁰ explicitly state that their result is restricted to deformations of small amplitudes and do not specify how λ_{\perp} , $\lambda_{||}$ are related to the applied force. However, considering the small *q* expansion of Eqs. (41) and (42) one can relate these parameters to the mean square gyration radius components of the chain, since for $X_{\perp} \ll 1$,

$$S(q_{\perp}) = 1 - q_{\perp}^2 \frac{\langle R^2 \rangle_0}{18\lambda_{\perp}^{-2}} = 1 - q_{\perp}^2 \langle R_{g,\perp}^2 \rangle /2,$$
(44)

where in the last step Eq. (12) was used. Hence, we conclude (note that $\langle R_g^2 \rangle_0 = \langle R^2 \rangle_0/6$ for Gaussian chains) that λ_{\perp}^2 $= (3/2) \langle R_{g,\perp}^2 \rangle / \langle R_g^2 \rangle_0 = (\langle R_{gy}^2 \rangle + \langle R_{gz}^2 \rangle) / (\langle R_{gy}^2 \rangle_0 + \langle R_{gz}^2 \rangle_0)$, as expected. Similarly, Eq. (41) yields for $q_{\parallel} \rightarrow 0$, also using Eq. (11),

$$S(q_{\parallel}) = 1 - q_{\parallel}^2 \left(\frac{\langle R^2 \rangle_0}{18\lambda_{\parallel}^{-2}} + \frac{\langle X \rangle^2}{12} \right) = 1 - q_{\parallel}^2 \langle R_{g,\parallel}^2 \rangle, \quad (45)$$

and hence we see that $\lambda_{||}$ in $X_{||}$ can be expressed in terms of the gyration radius component $\langle R_{g,||}^2 \rangle$ of the stretched chain and the extension $\langle X \rangle$. However, since from the work of Benoit *et al.*⁴⁰ it is not clear that Eqs. (41) and (42) are applicable for conditions where $\langle X \rangle / L$ is not very small, we hence rederived Eqs. (41) and (42) by an independent method, which is more transparent with respect to the basic assumptions that are made. This derivation is presented in the Appendix, and it shows that $S(q_{||})$ can be cast into the form

$$S(q_{\parallel}) = \frac{1}{(N+1)^2} \sum_{i,j} \exp\left[-\frac{1}{2}q_{\parallel}^2 (\langle X^2 \rangle - \langle X \rangle^2) \frac{|i-j|}{N}\right] \\ \times \cos\left(q_{\parallel} \frac{|i-j|\langle X \rangle}{N}\right), \tag{46}$$

which is equivalent to Eq. (41) but with a somewhat different expression for $X_{||}$, namely,

$$X_{\parallel} = \frac{1}{2} q_{\parallel}^2 (\langle X^2 \rangle - \langle X \rangle^2) + i q_{\parallel} \langle X \rangle.$$
⁽⁴⁷⁾

It is interesting to note that Eqs. (41) and (46) can be given a very simple physical interpretation: with respect to the correlation in stretching direction, the stretched polymers is equivalent to a harmonic one-dimensional "crystal" (which at nonzero temperature lacks long range order, of course) of length $Na = \langle X \rangle$, *a* being the "lattice spacing" of the crystal.

Writing the Hamiltonian of the one-dimensional chain $as^{73,74}$

$$\mathcal{H} = \frac{1}{2} \sum_{\ell} \left[\frac{\pi_{\ell}^2}{m} + mc^2 \frac{(x_{\ell+1} - x_{\ell} - a)^2}{a^2} \right],$$
(48)

where point particles of mass *m* have positions x_{ℓ} and conjugate momenta π_{ℓ} . The spring potential coupling neighboring particles is expressed by the sound velocity *c*. At T = 0, particles are localized at positions $x_n^{(0)} = x_0^{(0)} + na$, n = 0, 1, ..., N. So it makes sense to consider displacements relative to the ground state, $u_n = x_n - x_n^{(0)} = x_n - na$, putting $x_0^{(0)}$ at the origin. Due to the harmonic character of this "crystal," one can calculate the mean square displacements easily to find (for periodic boundary conditions) that $\langle (u_n - u_0)^2 \rangle = na^2k_BT/(mc^2) = n\delta^2$, where δ characterizes the local displacement for two neighboring particles. Applying the formula also for the end-to-end distance of a chain without periodic boundary conditions, $\langle (u_N - u_0)^2 \rangle = N\delta^2$, one immedi-

ately finds that $S(q_{||})$ for the harmonic chain yields the above expressions of $S(q_{||})$, since $X = x_N - x_0 = Na + u_N - u_0$, $\langle X \rangle = Na$, and $\langle X^2 \rangle = N^2 a^2 + N\delta^2 = \langle X \rangle^2 + N\delta^2$. This consideration also emphasizes that a condition $\langle X \rangle \ll L = N\ell_b$ in fact is not required for the validity of Eqs. (41)–(47).

For the unstretched case ($\langle X \rangle = 0$) Eqs. (41)–(47) reduce to Eq. (18), as it should be. We recall that according to the Kratky-Porod model simple approximations for the extension $\langle X \rangle$ of a chain as a function of the force can be derived (see Ref. 13 for a review), namely,

$$\frac{f\ell_p}{k_BT} = \frac{3}{4}\frac{\langle X \rangle}{L} + \frac{1}{8(1-\langle X \rangle/L)^2} - \frac{1}{8}, \quad d = 2$$
(49)

and

$$\frac{f\ell_p}{k_BT} = \frac{3}{4}\frac{\langle X \rangle}{L} + \frac{1}{4(1-\langle X \rangle/L)^2} - \frac{1}{4}, \quad d = 3.$$
(50)

Equations (49) and (50) imply in the linear response regime, where $\langle X \rangle \propto f$, that

$$\frac{f\ell_p}{k_BT} = \frac{d}{2}\frac{\langle X\rangle}{L}\,.$$
(51)

However, from linear response one can show generally that

$$\langle X \rangle = f \langle X^2 \rangle_0 / (k_B T) = f \langle R^2 \rangle_0 / (dk_B T),$$
 (52)

where $\langle R^2 \rangle_0$ is the mean square end-to-end distance in the absence of forces. Equations (51) and (52) are compatible with each other for Gaussian semiflexible chains, for which $\langle R^2 \rangle_0$ = $2\ell_p L$ (Eq. (19)), but are incompatible in the presence of excluded volume forces. In this case, one observes a crossover from the linear response regime, as described by Eq. (52) together with Eq. (37) for d = 2 and a result analogous to Eq. (50), namely,

$$\langle R^2 \rangle = C_e^s L^{6/5} (\ell_p D)^{2/5}, \quad d = 3 \text{ (using } \nu \approx 3/5),$$
 (53)

to the "Pincus blob"⁴¹ regime, a power law for the extension versus force relation

$$\langle X \rangle / L \propto (f \ell_p / k_B T)^{1/\nu - 1} \,. \tag{54}$$

While in d = 2, Eq. (52) holds up to $\langle X \rangle / L$ of order unity, where saturation ($\langle X \rangle / L \rightarrow 1$ for large enough *f*) sets in, in *d* = 3 the validity of Eq. (52) is much more restricted, namely,¹³

$$\xi_p \equiv k_B T/f > R_0 \propto \ell_p^2/D.$$
(55)

For stronger forces (corresponding to $\xi_p < R_0$) the Kratky-Porod results, Eqs. (49) and (50), are expected to become valid. In the Pincus blob regime, also nontrivial power laws for the fluctuations $\langle X^2 \rangle - \langle X \rangle^2$ and the transverse linear dimensions are predicted⁵⁴

$$\langle X^2 \rangle - \langle X \rangle^2 \propto \langle R_\perp^2 \rangle \propto (f \ell_p / k_B T)^{1/\nu - 2}.$$
 (56)

Since we are not aware of any treatment of the structure factor of the Kratky-Porod model under stretch, we shall use Eqs. (41) and (42) also for semiflexible chains (but using the numerical results for $\langle X \rangle$ and $\langle X^2 \rangle - \langle X \rangle^2$, $\langle R_{g,\perp}^2 \rangle$, rather than theoretical predictions).

III. MODEL AND SIMULATION TECHNIQUE

Our model is the standard SAW on the square and simple cubic lattices, effective monomers being described by occupied lattice sites, connected by bonds. Each site can be taken only once, and thus we realize the excluded volume interaction. The lattice spacing henceforth is our unit of length, $\ell_b = 1$. We introduce an energy ϵ_b for any kink the walk takes (by an angle of $\pm 90^\circ$). Any such kink introduces hence a factor $q_b = \exp(-\epsilon_b/k_BT)$ to the statistical weight of the walk.

In the presence of a force *f* coupling to the extension *X* of the chain in x-direction, the statistical weight gets another factor b^X , with $b = \exp(f/k_B T)$. Then the partition function of a SAW with *N* bonds (i.e., N + 1 effective monomers) and N_{bend} local kinks becomes

$$Z_{N,N_{\text{bend}}}(q_b, b) = \sum_{\text{config.}} C(N, N_{\text{bend}}, X) q_b^{N_{\text{bend}}} b^X.$$
(57)

By the pruned-enriched Rosenbluth method, it is possible to obtain estimates of the partition function and quantities derived from it (e.g., $\langle X \rangle$, $\langle X^2 \rangle$) and additional averages such as S(q), using chain lengths up to $N = 25\,600$. Both the chain stiffness and the force *f* have been varied over a wide range; for $q_b = 1$, one has fully flexible self-avoiding random walks, while for $q_b = 0.005$ the persistence length (computed from Eq. (17)) is of the order of 120 in d = 2 and 52 in d = 3 (Table I lists our corresponding estimates). For technical details on the implementation of the algorithm, we refer to the literature.¹³

IV. THE SCATTERING FUNCTION OF UNSTRETCHED CHAINS

We start with our data for the mean square gyration radius $\langle R_g^2 \rangle$, normalized by the square of the Kuhn length ℓ_K = $2\ell_p$, plotted vs. the number of Kuhn segments $n_K = L/\ell_K$ = $N\ell_b/(2\ell_p)$, Fig. 1(a) since this was the representation chosen for the experimental data of Norisuye and Fujita,¹² reproduced in Fig. 1(b). Both diagrams show the same range of abscissa ($30 \le n_K \le 3000$) and ordinate ($5 < \langle R_g^2 \rangle/(2\ell_p)^2$ < 1000). The similarity between simulation and experiment is striking. Since only the regime of rather large n_K is shown,



FIG. 1. (a) Log-log plot of normalized gyration radius square $\langle R_g^2 \rangle / (2\ell_p)^2$ versus the number of Kuhn segments, for the range $30 \le n_K \le 3000$, for chains of widely varying stiffness, and comparison to corresponding experimental data (b), taken from Norisuye and Fujita.¹² The full straight line is the Kratky-Porod model, Eq. (20).

the crossover from rods to Gaussian chains is not included (the full straight line represents the Gaussian chain behavior, as described by Eq. (20) for $n_K = (1/2)n_p \gg 1$). Equation (20) works for very stiff chains and not too large n_K , while for large n_K systematic deviations occur, which can be attributed to excluded volume effects. Both the simulation and the experiment include data for widely varying persistence lengths (in the experiment, this could only be achieved by combining data for chemically different polymers in this plot). From their results (see Fig. 1(b)), the experimentalists concluded that the excluded volume effects set in for $n_K > 50$, irrespective of the precise value of the persistence length.

However, this latter conclusion needs to be questioned: in fact, for large n_K the data do not superimpose in this representation for different choices of ℓ_p , indicating that the behavior is more complicated. To elucidate this, we take out the leading power law in the Gaussian coil regime, plotting $\langle R_g^2 \rangle / (\ell_p L)$ versus n_K over the full range (Fig. 2(a)). Nice scaling behavior occurs with respect to the crossover from rigid rods to Gaussian coils; in this regime, Eq. (20) works in d = 3. However, now one can see rather clearly that the crossover from Gaussian coils to SAWs does not scale in this representation:



FIG. 2. (a) Log-log plot of $\langle R_g^2 \rangle / (2\ell_p L)$ versus n_K for d = 3, and including data for widely varying persistence lengths. Note that the worm-like chain result, WLC (Eq. (20)), describes correctly the crossover from rods to coils, but not the onset of excluded volume effects. (b) Same as (a), but choosing $N/N^*(q_b)$ as an abscissa variable ($N^*(q_b)$ was already estimated for a similar scaling plot for the mean square end-to-end distance (cf. Fig. 7(b) of Ref. 13). Here $L = N\ell_b$.



FIG. 3. Log-log plot of $\langle R_g^2 \rangle / (2\ell_p L)$ versus n_K for d = 2, including data for widely varying persistence lengths. Note that in d = 2 there occurs a direct crossover from rods to SAWs, an intermediate Gaussian regime in absent.

rather for large n_K the curves "splay out," the larger ℓ_p the longer the data follow Eq. (20), before an onset of excluded volume effects occur. This behavior has already been studied in Ref. 13 with respect to the end-to-end distance. Empirically, it was found that scaling N with N*, where $N^* \propto \ell_p^{2.5}$ rather than $N^* = \ell_p$, Figure 2(b) shows that a master curve results as an envelope of the curves for individual ℓ_p . We also recall, that Flory arguments predict $N^* \propto \ell_p^3$, cf. Eq. (38) and the subsequent discussion. The data in Fig. 2 are fully analogous to our data on the end-to-end distance that were discussed recently in Ref. 13. In d = 2, however, the behavior is clearly simpler (Fig. 3): there occurs a single crossover from rods to d = 2 SAWs, and a regime where the Kratky-Porod worm-like chain model presents a faithful description of the data is absent. These results for $\langle R_a^2 \rangle$ confirm our earlier analogous findings¹³ for $\langle R^2 \rangle$.

Figure 4 shows some of our raw data for the structure factor S(q). For small q, one recognizes the Guinier regime, $S(q) \approx \exp(-q^2 \langle R_g^2 \rangle/3) \approx 1 - q^2 \langle R_g^2 \rangle/3$, and then a crossover occurs to the power law of SAWs or of Gaussian chains (the latter is seen clearly only for d = 3 and very stiff chains). At large q and stiff chains, the expected q^{-1} behavior is in fact compatible with the data.

It turns out that an analysis of S(q) in the form of Kratky plots (Eq. (30)) is more illuminating, cf. Fig. 5: The location

of the maximum in the Kratky plot, as discussed in Eqs. (31) and (32), is easily identified, and it shows the expected scaling with L/ℓ_p both in d = 3 and in d = 2 (Fig. 6). In d = 3, with increasing L/ℓ_p a crossover from Gaussian behavior to SAW behavior occurs. Our data also confirm that for rather stiff chains in d = 3 both the Kholodenko and the Stepanow theories describe S(q) very accurately. Note that Fig. 5(b) refers to rather short chains, for which strong effects due to excluded volume interactions are not yet expected, and hence the good agreement with the theories is not surprising.

Another issue of interest is the behavior qLS(q) in the rigid rod limit, where one clearly notes the approach to π (Fig. 5). Can we then use S(q) in this region, applying the des Cloizeaux formula (Eq. (1)) to extract quantitatively reliable estimates for the persistence length ℓ_p from a plot of qLS(q) versus 1/q? Figure 7 suggests that although a regime occurs where the variation is linear in $(q\ell_p)^{-1}$, the coefficient of this linear variation is inconsistent with the des Cloizeaux result. We have no final answer to offer to explain this discrepancy; we suspect that in the regime where q^{-1} and ℓ_p are of the same order, the discreteness of our lattice model (opposed to the Kratky-Porod continuum model) might matter.

V. RESULTS FOR THE SCATTERING FROM STRETCHED CHAINS

While for unstretched chains it is only $\langle R_g^2 \rangle$ as a measure of the linear dimension of the whole chain matters (Figs. 1– 3), for chains under the action of stretching forces anisotropy of the chain conformation comes into play. However, from the small *q* expansion of Eqs. (3) and (4) one can show straightforwardly that $S_{||}(q_{||})$ yields information on $\langle R_{g,||}^2 \rangle$ and $S_{\perp}(q_{\perp})$ on $\langle R_{g,\perp}^2 \rangle$ cf. Eqs. (11) and (12). Since for larger $q_{||}$ where also the extension $\langle X \rangle$ of the chain along the direction of the force enters the description of the scattering, we begin by describing these linear dimensions and their variation as a function of the force *f* (for a more detailed discussion and related results, we refer the reader to Ref. 13).

Figure 8 shows typical data of $\langle R_{g,\perp}^2 \rangle$ versus $f \ell_p / k_B T$, both for rather flexible chains ($q_b = 0.4$) and for rather stiff chains



FIG. 4. Structure factor S(q) plotted q, on log-log- scales, for d = 2 (a) and d = 3 (b); only data for $L = 25\,600$ are shown, but many different choices of the stiffness parameter q_b are included. The straight lines indicate the rod-like behavior at large q (slope = -1) and the SAW behavior for flexible chains (slope $= -1/\nu$). Also the slope expected in the Gaussian regime is included (slope = -2). Only data up to $q = \pi$ have been included (larger q cannot be studied due to the lattice character of our model).



FIG. 5. (a) Rescaled structure factor qLS(q) plotted against Lq for d = 3 and $L = 25\,600$, including 5 choices of the stiffness. The result for Gaussian chains (Debye function) and for continuous rigid rods (for which $qLS(q) \rightarrow \pi$ for large q. cf. Eq. (24)) are included for comparison. Also predictions obtained from the formulas proposed by Kholodenko (Eqs. (27)–(29)) are shown. (b) Rescaled structure factor qLS(q) plotted against $q\ell_p$ for d = 3 and for L = 400, including both the predictions due to Stepanow³⁴ and Kholodenko (Eqs. (27)–(29)), which are essentially indistinguishable on the scale of the figure. (c) Same as (b), but for 3 different choices of L for $q_b = 0.005$.

 $(q_b = 0.01 \text{ in } d = 2, q_b = 0.05 \text{ in } d = 3$, respectively). We recognize three regimes: for very small forces $\langle R_{g,\perp}^2 \rangle \approx \langle R_{g,\perp}^2 \rangle_0$, the unperturbed value in the absence of forces. In this linear response regime, the force orients the coil without deforming it. Then a regime occurs where $\langle R_{g,\perp}^2 \rangle$ decreases according to a power law, namely, Eq. (56). This power law holds in the regime where the radius of the Pincus blob, $\xi_p = k_B T/f$, is smaller than the unperturbed radius, but much larger than the persistence length ℓ_p itself. Thus, this is the analog of

the "Pincus blob" law that yields another power law for the extension vs. force curve, Eq. (54). The physical picture invoked here for the chain is an elastic string of Pincus blobs, $\langle R_{g,\perp}^2 \rangle$ describing the transverse mean square displacement of this string. As one can see from Fig. 8, the data indeed are compatible with the predicted power law in d = 2, and in d = 3 at least for the flexible chains. For stiff chains in d = 3, the regime where Eq. (56) holds is more restricted, since the Kratky-Porod regime has a more extended regime of



FIG. 6. Log-log plot of the inverse position of the maximum in the Kratky plot, $(\ell_p q_{max})^{-1}$, versus the rescaled contour length L/ℓ_p , for d = 2 (a) and d = 3 (b). The full straight line included in (a) is described by the equation $0.19(L/\ell_p)^{3/4}$. In case (b), two straight lines with slope $\nu = 1/2$ and $\nu = 0.588$ are included, to illustrate the crossover. In both cases the persistence length ℓ_p is varied over a wide range, and the contour lengths chosen are L = 400, 1600, 6400, and 25 600, as indicated.



FIG. 7. Plot of qLS(q) versus $(qL_p)^{-1}$, for d = 2 (a) and d = 3 (b). All data are for $L = 25\,600$ only, and many different choices of q_b , as indicated. In each case, two straight lines are shown: the result of des Cloizeaux,²³ Eq. (1), $qLS(q) = \pi + (2/3)(q\ell_p)^{-1}$, and empirical fits, $qLS(q) = \pi + 2.35(q\ell_p)^{-1}$ for d = 2 and $qLS(q) = \pi + 1.9(q\ell_p)^{-1}$ for d = 3, respectively.

validity, effects due to Pincus blobs can only be detected in a regime $\langle R_{g,\perp}^2 \rangle_0^{1/2} > \xi_p > R^* \propto \ell_p^2/D$, cf. Eq. (55).¹³ Therefore, we have not included very stiff chains in Fig. 8(b) (for $q_b = 0.005$, leading to $\ell_p \approx 52\ell_b$, excluded volume effects, which also lead to the existence of Pincus blobs, could even for chains as long as $N = 25\,600$ hardly be detected in the chain linear dimensions in the absence of a force, cf. Figs. 1–3). So this failure to detect Pincus blobs for very stiff long chains in d = 3 dimensions is hardly surprising (although Eq. (56) ultimately will become valid as $N \to \infty$, irrespective how large ℓ_p is).

It is also interesting to analyze the behavior for large forces, for $f\ell_p/k_BT > 1$. At first sight, one might expect another power law with a large exponent. However, a closer look reveals a slight but systematic curvature, and a plot versus $f\ell_p/k_BT$ on a linear rather than a logarithmic scale reveals that this apparent power law is nothing but the onset of an exponential decay (Figs. 8(c) and 8(d)): indeed, already from the partition function, Eq. (57) we recognize that for large forces the chains will be stretched out almost completely like rigid rods, and the few remaining kinks are suppressed exponentially when $f\ell_p/k_BT \gg 1$.



FIG. 8. Log-log plot of $\langle R_{g,\perp}^2 \rangle / \langle R_{g,\perp}^2 \rangle_0$ versus $f\ell_p/k_BT$, for d = 2 (a) and for d = 3 (b), using $L = N\ell_b = 25\,600$ in both cases, for two choices of q_b . In parts (c) and (d) the same data as in (a) (b) for large $f\ell_p/k_BT$ are reploted choosing a linear scale for $f\ell_p/k_BT$, to show that the behavior is compatible with an exponential decay in d = 3.



FIG. 9. Log-log plot of the relative extension $\langle X \rangle / L$ versus the scaled force $f\ell_p/k_BT$ for $L = 25\,600$ in d = 2 (a) and d = 3 (b), for the same choices of q_b as shown in Fig. 8. The straight lines indicate the linear response regime and the Pincus-blob regime, respectively (Eq. (54)). In neither case has the Kratky-Porod model (curves labeled as K-P-model, cf. Eqs. (49) and (50)) a well-defined regime of validity (this is expected since for large $f\ell_p/k_BT$ the approach to saturation, $\langle X \rangle / L \rightarrow 1$, is exponentially fast rather than proportional to $(k_B T / f\ell_p)^{1/2}$, cf. Fig. 8).

For completeness, we show the corresponding simulation data for the relative extension $\langle X \rangle / L$ vs. $f \ell_p / k_B T$ in Figs. 9 and 10 present the corresponding data for the longitudinal component $\langle R_{g,\parallel}^2 \rangle / L^2$ of the gyration radius in the direction of the force. While for very small forces, one expects a nonzero plateau (unlike $\langle X \rangle / L$, which vanishes as $f \rightarrow 0$), corresponding to the gyration radius square component of an unstretched chain, for large *f* another plateau means that the chain has been stretched out fully to a rod of length *L*. In between these two plateaus, the Pincus blob behavior is seen rather clearly, for the flexible chains.

Figure 11 shows typical data for $S_{\perp}(q_{\perp})$ vs. q_{\perp} and Fig. 12 the corresponding data for $S_{\parallel}(q_{\parallel})$ vs. q_{\parallel} , focusing again on those selected values of q_b that were used in Figs. 8–10. As expected from Eq. (42), the perpendicular structure factor is similar to the case without stretching force; the plateau at small q, where $S_{\perp}(q_{\perp})$ deviates only very little from unity, gets more extended with increasing f, reflecting the decrease of $\langle R_{g,\perp}^2 \rangle$ with f (Fig. 8). This decrease is more pronounced for stiff chains than for flexible chains at the same value of f, since the proper control variable is not f/k_BT but rather $f\ell_p/k_BT$. While the power law-like decay of $S_{\perp}(q_{\perp})$ with q_{\perp} for flexible chains can be observed until $S_{\perp}(q_{\perp})$ has decayed up to $S_{\perp}(q_{\perp}) \approx 10^{-4}$ as b < 1.5, for stiff chains it extends only to $S_{\perp}(q_{\perp}) \approx 10^{-3}$ in d = 3 and $S_{\perp}(q_{\perp}) \approx 10^{-2}$ in d = 2, respectively. As expected, the theory of Benoit *et al.*⁴⁰ can only be applied if $q_{\perp}\ell_p \ll 1$, and when $\langle R_{g,\perp}^2 \rangle$ exceeds ℓ_p^2 only by few orders of magnitudes, the applicability of Eq. (42) is correspondingly restricted. In fact, noting that, for $q_b = 0.05$, $\ell_p/\ell_b \approx 5.9$, we conclude that b = 1.5means $f\ell_p/k_BT \approx 2.4$, and Fig. 8 shows that in this case indeed $\langle R_{g,\perp}^2 \rangle$ is about an order of magnitude smaller than for f = 0. Approximating a stiff chain as a sequence of rods of length ℓ_p such that $n_p \ell_p = N \ell_b$, and stating that at large q_{\perp} interference effects of different rods can be neglected, one would expect that for $q_\perp \ell_p \approx 1$ one obtains a scattering of the order of $S_{\perp}(q_{\perp}) \approx n_{p}^{-1}$, independent of q_{\perp} . This (admittedly rough) argument would qualitatively explain the systematic increase of the plateau S(q)in Fig. 5 and $S_{\perp}(q_{\perp})$ in Fig. 11 with increasing chain stiffness.

Even more interesting is the behavior of $S_{||}(q_{||})$, Fig. 12. The rapid increase of $\langle R_{g,||}^2 \rangle$ with increasing stretching force has the consequence that $S_{||}(q_{||})$ deviates from unity for smaller and smaller $q_{||}$. While for small f just a shoulder develops, before (at large $q_{||}$) the behavior is similar to that of $S_{\perp}(q_{\perp})$, for large f pronounced oscillations develop. As found by Pierleoni *et al.*⁴⁴ for fully flexible chains under stretch, this behavior can be attributed to the fact that the chain behaves as an elastically stretched string. We shall discuss this



FIG. 10. Log-log plot of the parallel component $\langle R_{g,\parallel}^2 \rangle / L^2$ versus $f \ell_p / k_B T$, for the same parameters as in Figs. 8 and 9. Straight lines indicate the Pincus blob regime. Part (a) refers to d = 2, part (b) to d = 3.



FIG. 11. Log-log plot of the structure factor $S_{\perp}(q_{\perp})$ versus q_{\perp} for d = 3 and two choices of the stiffness parameter q_b , $q_b = 0.4$ (a) and $q_b = 0.05$ (b), and also for d = 2 and two choices of q_b , namely, $q_b = 0.4$ (c) and $q_b = 0.01$ (d). In each case several choices of $b = \exp(f/k_B T)$ are included, as indicated. Chain length is $L = 25\,600$ throughout.



FIG. 12. Log-log plot of the structure factor $S_{||}(q_{||})$ versus $q_{||}$ for d = 3 and two choices of the stiffness parameter q_b , $q_b = 0.4$ (a) and $q_b = 0.05$ (b), and also for d = 2 and two choices of q_b , namely, $q_b = 0.4$ (c) and $q_b = 0.01$ (d). In each case several choices of $b = \exp(f/k_B T)$ are included. Chain length is L = 25600 throughout.



FIG. 13. Log-log plot of $q_{\perp}^2 S_{\perp}(q_{\perp})$ versus q_{\perp} for d = 3 and two choices of the stiffness parameter q_b , $q_b = 0.4$ (a) and $q_b = 0.05$ (b), and also for d = 2 and two choices of q_b , namely, $q_b = 0.4$ (c) and $q_b = 0.01$ (d). The curves are the Debye function, Eq. (42) with $X_{\perp} = \frac{3}{2}q_{\perp}^2 \langle R_{g,\perp}^2 \rangle$ in d = 3, and $X_{\perp} = 3q_{\perp}^2 \langle R_{g,\perp}^2 \rangle$ in d = 2. In each case several choices of $b = \exp(f/k_BT)$ are included. Chain length is $L = 25\,600$ throughout.

behavior in more detail below. Here, we only note that the maxima of these oscillations decay according to a power law, similar to the power law of $S_{\perp}(q_{\perp})$ in the intermediate range of q_{\perp} . The minima of $S_{\parallel}(q_{\parallel})$, as well as $S_{\parallel}(q_{\parallel})$ itself at larger values of q_{\parallel} where the oscillations of q_{\parallel} have decayed, show a slow further decrease with q_{\parallel} . While for very large $q_{\parallel} = q_{\perp}$ but not very strong stretching (b < 1.5) we have $S_{\parallel}(q_{\parallel})$ is not the case for stiff chains: $S_{\parallel}(q_{\parallel}) \ll S_{\perp}(q_{\perp})$ for $q_{\parallel} = q_{\perp}$ then.

In order to understand these results more quantitatively, we first report $S_{\perp}(q_{\perp})$ in form $q_{\perp}^2 S_{\perp}(q_{\perp})$ versus q_{\perp} and compare to the Debye function, Eq. (42), but using $\langle R_{g,\perp}^2 \rangle$ from the simulation (rather than any theoretical prediction for it). Figure 13 shows that the Debye function works surprisingly well: for d = 3 the slope $2 - 1/\nu$ indicating non-Gaussian behavior is seen for $q_b = 0.4$ only for weak stretching (b = 1.001 and 1.003), while for larger stretching forces a horizontal part in the plot $q_{\perp}^2 S_{\perp}(q)$ has developed. Also in d = 2 the excluded volume regime, where the slope $2 - 1/\nu$ is compatible with the data, is pronounced only for rather flexible chains ($q_b = 0.4$, Fig. 13(c)), while for stiff chains in d = 2 ($q_b = 0.01$) excluded volume effects show up in $S_{\perp}(q_{\perp})$ only for extremely weak stretching (such as b = 1.0001, i.e., $f/k_BT = 10^{-4}$). For stronger stretched semiflexible chains in d = 2, the Debye function describes the data for small q_{\perp} (q_{\perp} $\leq 10^{-2}$), but then a crossover to $S_{\perp}(q_{\perp}) \approx const$ and hence $q_{\perp}^2 S_{\perp}(q_{\perp}) \propto q_{\perp}^2$ sets in.

The behavior of $S_{\parallel}(q_{\parallel})$ when plotted in the form $q_{\parallel}^2 S_{\parallel}(q)$ vs. q_{\parallel} is particularly striking (Fig. 14). Again excluded vol-

ume effects (described by a slope $2 - 1/\nu$ again) are pronounced only for very small forces. For somewhat larger forces (e.g., for $b \ge 1.070$ for $q_b = 0.4$ and for $b \ge 1.015$ for q_b = 0.05 in d = 3, and in d = 2 for $b \ge 1.015$ for $q_b = 0.4$, and for $b \ge 1.005$ for $q_b = 0.01$), the oscillatory behavior of the structure factor, described by the Debye function with complex $X_{||}$ (Eq. (41)), sets in. To interpret this behavior in more detail, we write $X_{||} = a + ic$, where $a = q_{||}^2 (\langle X^2 \rangle - \langle X \rangle^2)/2$ and $c = q_{||} \langle X \rangle$, to rewrite Eq. (42) as follows:

 $S_{\parallel}(q_{\parallel})$

$$=2\frac{\exp(-a)[(a^2-c^2)\cos c - 2ac\sin c] + a^3 + ac^2 + c^2 - a^2}{(a^2+c^2)^2}.$$
(58)

There are two distinct parts, an exponentially damped oscillatory part and a "background part" which survives when the oscillatory part has died out. For $a \gg 1$, this background part can be written as (for large stretching there is a regime where $a^2 \ll c^2$)

$$S_{\parallel}(q_{\parallel}) \approx \frac{2a}{c^2} = \frac{\langle X^2 \rangle}{\langle X \rangle^2} - 1.$$
 (59)

When the oscillations have died out, there is a flat part of $S_{||}(q_{||})$, independent of $q_{||}, S_{||}(q_{||})$ hence measures the relative fluctuation in the length of the strongly stretched polymer.

We now consider the oscillatory part of Eq. (58). Since we are in a regime where $a^2 \ll c^2$, the maxima are reached when $\cos c = -1$ and when $a \ll 1$ and hence $\exp(-a) \approx 1$



FIG. 14. Log-log plot of $q_{\parallel}^2 S_{\parallel}(q_{\parallel})$ versus q_{\parallel} for d = 3 and two choices of the stiffness parameter q_b , namely, $q_b = 0.4$ (a) and $q_B = 0.05$ (b), and also for d = 2 and two choices of $q_b = 0.4$ (c) and $q_b = 0.01$ (d). The curves are the Debye function, Eq. (58) with complex $X_{\parallel} = q_{\parallel}^2 (\langle X^2 \rangle - \langle X \rangle^2)/2 + i q_{\parallel} \langle X \rangle$, and the straight line shows the excluded volume power law (slope $= 2 - 1/\nu$). In each case several choices of $b = \exp(f/k_B T)$ are included. Chain length is L = 25600 throughout.



FIG. 15. Log-log plot of $q_{\perp}^2 S_{\perp}(q_{\perp})$ versus q_{\perp} in d = 3 dimensions for $q_b = 0.2$ (a), 0.1 (b), 0.03 (c), and 0.01 (d), for several choices of the force parameter $b = \exp(f/k_B T)$, as indicated. The curves are the Debye function, Eq. (42) with $X_{\perp} = \frac{3}{2}q_{\perp}^2 \langle R_{g,\perp}^2 \rangle$. When the data settle down at a horizontal plateau, it yields an estimate of $4/(3\langle R_{g,\perp}^2 \rangle)$.



FIG. 16. Log-log plot of $q_{\perp}^2 S_{\perp}(q_{\perp})$ versus q_{\perp} in d = 2 dimensions for $q_b = 0.2$ (a), 0.1 (b), 0.05 (c), and 0.03 (d), for several choices of the force parameter $b = \exp(f/k_B T)$, as indicated. The curves are the Debye function, Eq. (42) with $X_{\perp} = 3q_{\perp}^2 \langle R_{g,\perp}^2 \rangle$, and the straight line shows the excluded volume power law (slope = $2 - 1/\nu$). From the Debye plateau $2/(3\langle R_{g,\perp}^2 \rangle)$ can be extracted.

we have

$$S_{\parallel}^{\max}(q_{\parallel}) \approx \frac{4}{c^2} = \frac{4}{q_{\parallel}^2 \langle X \rangle^2}, \quad q_{\parallel} \langle X \rangle = (2m+1)\pi,$$

$$m = 0, 1, \dots, \tag{60}$$

and $q_{\parallel}^2 S_{\parallel}^{\text{max}} \approx \text{ const}$, as observed from Eq. (58), and the simulation.

When we compare these results to the scattering from rigid rods, however, Eq. (26) predicts maxima that are undamped and minima that are zero, so for increasing $q_{||}$ the oscillations continue forever. However, this is a result for a rod of strictly fixed length $L_{\rm rod}$. The polymer under strong stretch (with $1 - \langle X \rangle / L \ll 1$) is only similar to a rod of fluctuating length, and this fact is borne out by $S_{||}(q_{||})$ at large $q_{||}$ (Eq. (59)).

The success of the Debye function, Eqs. (41) and (58) for the description of the scattering from strongly stretched chains in both d = 2 and d = 3 dimensions is very remarkable, since it is derived from Gaussian chain statistics,⁴⁰ and we have seen that in d = 2 in the absence of stretching forces Gaussian statistics does not work, irrespective of chain stiffness.

At the end of this section, we emphasize that the examples given for the success of the Debye function for stretched chains, as derived by Benoit *et al.*,⁴⁰ are not accidental, but typical for a wide range of chain stiffnesses. As an example, we show further data for $S_{\perp}(q_{\perp})$ in both d = 2 and d = 3 and various other choices of q_b in Figs. 15 and 16. Whenever the plots indicate a well-defined plateau, one can extract an

estimate of $\langle R_{g,\perp}^2 \rangle$ from it (the actual values of $\langle R_{g,\perp}^2 \rangle$ that were independently estimated were used to predict the Debye functions as shown in Figs. 15 and 16). As has been shown already in Fig. 8, the radii $\langle R_{g,\perp}^2 \rangle$ do have a broad regime of forces f/k_BT where excluded volume effects ("Pincus blob" – behavior) prevail, so the success of the Debye function must not be over-emphasized, it does not mean that the chain conformation follow Gaussian statistics.

VI. CONCLUSIONS

In this paper, we have presented a comparative simulation study of the single-chain structure factor S(q) for variable stiffness of the macromolecules in both d = 2 and d= 3 dimensions, both for coils in equilibrium in dilute solution under good solvent conditions, and for polymers under the influence of a stretching force. Characteristic linear dimensions of the macromolecules that are needed in the theoretical interpretation of S(q), have in our Monte Carlo simulation always been estimated directly and hence independently, such as the mean square gyration radius $\langle R_{\rho}^2 \rangle$ and the persistence length ℓ_p . In the presence of stretching forces, the extension $\langle X \rangle$ in the direction of the force (as well as fluctuations $\langle X^2 \rangle - \langle X \rangle^2$, and components of the gyration radius $\langle R_{g_{\parallel}}^2 \rangle$ and $\langle R_{g_{\parallel}}^2 \rangle$ have been obtained as well. The simulations are performed for the strictly monodisperse case, the number of bonds N and hence also the contour length $L = N\ell_b$ of the chain molecules are known input parameters of the simulation. In this respect, a more definite interpretation of the

outcome of the simulations can be expected, than for corresponding experiments (where polydispersity is a problem, and often the average contour length is not a priori known but is obtained from fitting suitable experimental data). However, the drawback of our Monte Carlo simulations on a lattice is the highly idealized character of our coarse-grained model, the self-avoiding walk with additional energy penalty for kinks. Nevertheless, the comparison between our simulation results for the mean square gyration radius versus the number of "Kuhn segments" n_K with corresponding experimental data (Fig. 1) is very encouraging: one notes a striking similarity between simulation and experiment, and also the same range of dimensionless variables $(n_K \text{ and } \langle R_g^2 \rangle / (2\ell_p)^2)$ is obtained. The simulation has the bonus that directly single-chain properties are obtained (no extrapolation as a function of the concentration c of the solution towards $c \rightarrow 0$ is required and the stiffness is easily controlled by changing the energy parameter ϵ_b/k_BT that describes the cost of making a kink). In experiment, stiffness can only be widely varied by combining data for polymers with different chemical structure.

From our data, we have confirmed the conclusion that in d = 2 a direct crossover occurs from rod-like behavior to selfavoiding walks, with a scaling $\langle R_g^2 \rangle \propto \ell_p^{1/2} L^{3/2}$, without the existence of any intermediate regime with Gaussian behavior (Fig. 3). In d = 3, however, such an intermediate regime has been found, Fig. 2, for $1 \ll n_K \ll n_K^* \propto (\ell_p/D)^{\zeta}$, where *D* is the local chain diameter and the exponent ζ is in the range 1.5 $\leq \zeta \leq 2$. Thus, there is no universal value n_K^* where excluded volume effects set in, but rather $n_K^* \to \infty$ for $\ell_p/D \to \infty$.

In the equilibrium structure factor S(q), in the absence of stretching forces, correspondingly several regimes can be distinguished. For small enough q, the standard Guinier behavior always occurs, which contains the information on $\langle R_a^2 \rangle$, of course. For d = 2, one then always has the excluded volume regime (for long enough chains), $S(q) \propto q^{-4/3}$, and possibly (for rather stiff chains) a crossover to rod-like behavior (S(q)) $\propto q^{-1}$) sets in gradually. A Gaussian behavior $S(q) \propto q^{-2}$ is never seen, unlike the case d = 3, where this behavior does become visible for very stiff chains (before for still larger q the rod-like behavior starts). The excluded volume power law, $S(q) \propto q^{-1/\nu}$ with $\nu \approx 0.588$, is only visible for not very stiff chains (if chain lengths $L \le 25\,600$ are analyzed, as done here: if $L \to \infty$, this power law would emerge for any finite value of the persistence length). This pattern of behavior (Fig. 4) could have been *a priori* expected, but we also show via Kratky plots (qLS(q) vs. qL) that for semiflexible chains in d = 3 the expressions derived by Kholodenko and by Stepanow provide a quantitatively accurate description. For large q this quantity qLS(q) settles down at π , unlike the behavior predicted for flexible chains (the Debye function predicts qLS(q)) $\propto q^{-1}$ for large q). However, the onset of the plateau occurs gradually in the decade $1 < q\ell_p < 10$; thus the onset of the plateau allows an estimation of ℓ_p only somewhat roughly. The peak position of the Kratky plot (Figs. 5 and 6) reflects the theoretically expected scaling of the gyration radius with L and ℓ_p , even though in the Kratky plot (Fig. 5) direct evidence for excluded volume effects seem to be minor.

Des Cloizeaux²³ derived $LqS(q) = \pi + \text{const}(q\ell_p)^{-1}$ from the Kratky-Porod model for $L \to \infty$ with the constant being 2/3 (Eq. (1)). Unfortunately, this result is at variance with our numerical results (Fig. 7). The reason for this problem is still not clear.

Turning to the behavior of chains under the influence of stretching forces, we have shown that for weak forces, where linear response holds, excluded volume effects invalidate the Kratky-Porod model completely in d = 2 dimensions, and one typically observes a broad range of forces where the extension versus force relation is a power law, and also $\langle R_{g\perp}^2 \rangle$, $\langle X^2 \rangle - \langle X \rangle^2$ scale like $(f\ell_p/k_BT)^{1/\nu-2}$ in this "Pincus blob" regime. In d = 3, dimensions, however, a Pincus blob regime also exists, but its observability is restricted. For large k_BT/f , however, the (continuum) Kratky-Porod descriptions is not valid for our discrete lattice model either: then $\langle R_{g\perp}^2 \rangle$ and $\langle X^2 \rangle - \langle X \rangle^2$ decrease like exp $(-f/k_BT)$ for $f/k_BT \gg 1$.

Although the excluded volume effects show up clearly in the chain extensions and gyration radii components, Benoit's extension of the Debye formula to stretched chains⁴⁰ is surprisingly accurate for both the transverse ($S_{\perp}(q_{\perp})$) and parallel parts ($S_{\parallel}(q_{\parallel})$) of the structure factor. The oscillatory behavior of $S_{\parallel}(q_{\parallel})$ for strongly stretched chains shows that their conformations resemble a string of elastically coupled particles. Thus, if measurable, the structure factor of stretched chains would add valuable information on their conformations.

As we have emphasized in our paper, the statistical mechanics of semiflexible polymers has been a longstanding and controversial problem of polymer science. The subject is of great relevance for biopolymers, but also of broad interest in material science. We expect that the present study will be useful both for the interpretation of experiments and stimulate further theoretical studies, such as of the interplay between solvent quality and chain stiffness.

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APPENDIX: SCATTERING FUNCTION OF RANDOM WALK CHAINS UNDER CONSTANT PULLING FORCE

The paper by Benoit *et al.*⁴⁰ uses the distribution function of the end-to-end vector of a Gaussian chain of |i - j| repeat units for the calculation of the single chain scattering function. The result is the well-known Debye function.

Following an idea from Doi's book,⁷⁵ one can derive the diffusion equation yielding the end-to-end vector distribution in the following way. Assume a stepwise Markov growth of

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the chain

$$P(\vec{R}, N) = \sum_{i} P(\vec{R} - \vec{l}_{i}, N - 1) p(\vec{l}_{i}).$$
(A1)

The sum over "i" goes over an isotropic bond vector set, i.e., both $\vec{l_i}$ and $-\vec{l_i}$ are members of the set.

Expanding the right side to first order in N and to second order in \vec{R} yields

$$P(\vec{R} - \vec{l}_i, N - 1) = P(\vec{R}, N) - \frac{\partial P}{\partial N} - \sum_{\alpha=1}^{3} \frac{\partial P}{\partial R_{\alpha}} l_{i,\alpha}$$
$$+ \frac{1}{2} \sum_{\alpha=1}^{3} \sum_{\beta=1}^{3} \frac{\partial^2 P}{\partial R_{\alpha} \partial R_{\beta}} l_{i,\alpha} l_{i,\beta} + \dots$$
(A2)

Averaging the derivatives with respect to R_{α} with a symmetric bond probability $p(\vec{l}_i)$ (in the simplest case this is just one over the number of bonds) gives zero for the first derivative and $\delta_{\alpha\beta}l^2/3$ for the second term, resulting in the diffusion equation $\partial P/\partial N = l^2 \nabla^2 P/6$. Solving this for a bulk chain gives the well-known result for the end-to-end vector distribution

$$P(\vec{R}, N) = (2\pi N l^2 / 3)^{-3/2} \exp\left(-\frac{3R^2}{2N l^2}\right).$$
 (A3)

The Debye function is derived by averaging with this probability.⁴⁰

The derivation above is useful as a starting point for calculating the scattering function for a pulled chain. Then the bond probabilities are not symmetric. For our model

$$p_0 = \frac{b}{b^2 + 4b + 1},\tag{A4}$$

$$p_{+} = \frac{b^{2}}{b^{2} + 4b + 1},$$

$$p_{-} = \frac{1}{b^{2} + 4b + 1}$$
(A5)

for moves perpendicular to the pulling direction, in +X direction and in -X direction, respectively, where $b = \exp(fl/k_BT)$ with l = 1 is used as in the main text. When we now expand Eq. (A2) and perform the average over the bond probabilities, we obtain

$$\frac{\partial P}{\partial N} = -(p_{+} - p_{-})l\frac{\partial P}{\partial X} + p_{0}l^{2}\left(\frac{\partial^{2} P}{\partial Y^{2}} + \frac{\partial^{2} P}{\partial Z^{2}}\right) + \frac{p_{+} + p_{-}}{2}l^{2}\frac{\partial^{2} P}{\partial X^{2}}.$$
(A6)

For $p_+ = p_- = p_0$, this reduces to the normal diffusion equation. This equation has to be solved with the boundary conditions

$$P(\vec{R}, 0) = \delta(\vec{R}),$$

$$P(\vec{R}, N) \to 0 \quad \text{for} \quad R \to \infty.$$
(A7)

Let us define $D_{\perp} = 2p_0 l^2$, $D_{||} = (p_+ + p_-)l^2$, and $v = (p_+ - p_-)l$, so we have

$$\frac{\partial P}{\partial N} = -v \frac{\partial P}{\partial X} + \frac{1}{2} D_{\perp} \left(\frac{\partial^2 P}{\partial Y^2} + \frac{\partial^2 P}{\partial Z^2} \right) + \frac{1}{2} D_{\parallel} \frac{\partial^2 P}{\partial X^2}.$$
(A8)

These are three diffusion processes in the three Cartesian directions, X is parallel to the force, Y and Z are perpendicular. The solutions for the perpendicular directions are the same as for the force-free case. For the parallel direction, we have an altered diffusion coefficient and a drift part to the process, i.e., a Gaussian diffusion around a deterministic drift. The complete solution to Eq. (A8) is, therefore, given by

$$P(X, Y, Z, N) = \frac{1}{2\pi N D_{\perp}} \frac{1}{\sqrt{2\pi N D_{\parallel}}} e^{-\frac{Y^2 + Z^2}{2N D_{\perp}}} e^{-\frac{(x - vN)^2}{2N D_{\parallel}}}.$$
(A9)

For $p_0 = p_+ = p_- = 1/6$, we obtain back the force free solution. To calculate the scattering function, we follow the procedure employed in the calculation of the Debye function in the force free case.

 $S(\vec{q}) = \frac{1}{N^2} \sum_{i,j} \langle e^{i\vec{q}\cdot\vec{r}_{ij}} \rangle$ can be calculated assuming a continuous chain model (i.e., only look at distances much larger than $\ell = 1$) so that the distribution for the \vec{r}_{ij} is given by the above Gaussian distribution

$$S(\vec{q}) = \frac{1}{N^2} \sum_{i,j} \int d^3 \vec{r}_{ij} P(\vec{r}_{ij}, |i-j|) e^{i\vec{q} \cdot \vec{r}_{ij}}, \qquad (A10)$$

where we have $P(\vec{r}_{ij}, |i - j|) = P_Y(Y, |i - j|)P_Z(Z, |i - j|)P_X(X, |i - j|)$ and P_Y and P_Z have the same functional form and all P_i are normalized to one individually.

1. Scattering in the perpendicular direction

$$\begin{split} S(\vec{q}_{\perp}) &= \frac{1}{N^2} \sum_{i,j} \int dY \int dZ P_Y(Y, |i-j|) \\ &\times P_Z(Z, |i-j|) e^{i \vec{q}_{\perp} \cdot \vec{\rho}_{ij}}, \end{split} \tag{A11}$$

where $\rho_{ij} = Y \hat{e}_Y + Z \hat{e}_Z$. So we have to evaluate

$$S(q_Y, q_Z) = \frac{1}{N^2} \sum_{i,j} \int dY \frac{1}{\sqrt{2\pi |i - j| D_\perp}} e^{-\frac{Y^2}{2|i - j| D_\perp}} e^{iq_Y Y}$$
$$\int dZ \frac{1}{\sqrt{2\pi |i - j| D_\perp}} e^{-\frac{Z^2}{2|i - j| D_\perp}} e^{iq_Z Z}$$
(A12)

resulting in

$$S(q_{\perp}) = \frac{1}{N^2} \sum_{i,j} e^{-\frac{q_{\perp}^2 D_{\perp} |i-j|}{2}}.$$
 (A13)

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This is evaluated by a continuum approximation for the two sums, $\sum_i \to \int_0^N du$ and $\sum_j \to \int_0^N dv$ which finally yields

$$S(q_{\perp}) = \frac{4}{Nq_{\perp}^2 D_{\perp}} + \frac{8}{N^2 q_{\perp}^4 D_{\perp}^2} (e^{-\frac{q_{\perp}^2 D_{\perp} N}{2}} - 1).$$
(A14)

2. Scattering in the parallel direction

$$S(q_{\parallel}) = \frac{1}{N^2} \sum_{i,j} \int dX \frac{1}{\sqrt{2\pi |i-j|D_{\parallel}}} e^{-\frac{(x-v|i-j|D_{\parallel})^2}{2|i-j|D_{\parallel}}} e^{iq_{\parallel}X},$$
(A15)

which now results in

$$S(q_{\parallel}) = \frac{1}{N^2} \sum_{i,j} e^{-\frac{q_{\parallel} D_{\parallel} |i-j|}{2}} \cos(q_{\parallel} v |i-j|) \,. \tag{A16}$$

Performing the final calculation again in the continuum approximation gives

$$S(q_{\parallel}) = \frac{4}{N} \frac{D_{\parallel} q_{\parallel}^{2}}{q_{\parallel}^{4} D_{\parallel}^{2} + 4v^{2} q_{\parallel}^{2}} + \frac{8}{N^{2}} \frac{q_{\parallel}^{4} D_{\parallel}^{2} - 4v^{2} q_{\parallel}^{2}}{(q_{\parallel}^{4} D_{\parallel}^{2} + 4v^{2} q_{\parallel}^{2})^{2}} (e^{-\frac{q_{\parallel}^{2} D_{\parallel} N}{2}} \cos(Nvq_{\parallel}) - 1) - \frac{32}{N^{2}} \frac{q_{\parallel}^{3} D_{\parallel} v}{(q_{\parallel}^{4} D_{\parallel}^{2} + 4v^{2} q_{\parallel}^{2})^{2}} e^{-\frac{q_{\parallel}^{2} D_{\parallel} N}{2}} \sin(Nvq_{\parallel}).$$
(A17)

This result determines our scattering functions with parameters depending on the applied force f, so these equations contain no free parameters. Both functions reduce to the Debye function for the force free isotropic case (v = 0, $D_{\perp} = D_{\parallel}$ $= l^2/3$) as it should be, because the scattering function does then not depend on the direction of the scattering vector.

For fitting purposes, it might yield better results to replace some of the quantities by average values determined in the simulation. For the Y and the Z components simple Gaussian statistics holds, $\langle Y \rangle = \langle Z \rangle = 0$,

$$\langle Y^2 \rangle = \langle Z^2 \rangle = N D_\perp,$$
 (A18)

$$\langle R_{g,Y}^2 \rangle = \langle R_{g,Z}^2 \rangle = \frac{ND_{\perp}}{6}$$
 (A19)

but in the force direction we get from Eq. (A9) the moments of the end-to-end distance

$$\langle X \rangle = Nv, \quad \langle X^2 \rangle = N^2 v^2 + ND_{\parallel},$$
 (A20)

$$\langle \Delta X^2 \rangle = N D_{\parallel}, \quad \langle R_{g,X}^2 \rangle = \frac{N D_{\parallel}}{6} + \frac{D_{\parallel} N^2 v^2}{12}.$$
 (A21)

Rewriting the scattering functions in terms of $\langle R_{e,\perp}^2 \rangle$ yields

$$S(q_{\perp}) = \frac{4}{3q_{\perp}^2 \langle R_{g,\perp}^2 \rangle} + \frac{8}{\left[3q_{\perp}^2 \langle R_{g,\perp}^2 \rangle\right]^2} (e^{-\frac{3q_{\perp}^2 \langle R_{g,\perp}^2 \rangle}{2}} - 1).$$
(A22)

This is the Debye function with the appropriate prefactors, because for $\langle R_{g,\perp}^2 \rangle = 2/3 \langle R_g^2 \rangle$ it reduces to Eq. (18). For the scattering parallel to the pulling direction

$$S(q_{\parallel}) = 4 \frac{q_{\parallel} \langle \Delta X^{2} \rangle}{q_{\parallel}^{4} \langle \Delta X^{2} \rangle^{2} + 4q_{\parallel}^{2} \langle X \rangle^{2}} + 8 \frac{q_{\parallel}^{4} \langle \Delta X^{2} \rangle^{2} - 4q_{\parallel}^{2} \langle X \rangle^{2}}{(q_{\parallel}^{4} \langle \Delta X^{2} \rangle^{2} + 4q_{\parallel}^{2} \langle X \rangle^{2})^{2}} (e^{-\frac{q_{\parallel}^{2} \langle \Delta X^{2} \rangle}{2}} \cos(q_{\parallel} \langle X \rangle) - 1) - 32 \frac{q_{\parallel}^{3} \langle \Delta X^{2} \rangle \langle X \rangle}{(q_{\parallel}^{4} \langle \Delta X^{2} \rangle^{2} + 4q_{\parallel}^{2} \langle X \rangle^{2})^{2}} e^{-\frac{q_{\parallel}^{2} \langle \Delta X^{2} \rangle}{2}} \sin(q_{\parallel} \langle X \rangle).$$
(A23)

This gives the same formula as Eq. (58) when $X_{||}$ in Eq. (41) is written by $X_{||} = a + ic$ with $a = q_{||}^2 \langle \Delta X^2 \rangle / 2$, and $c = q_{||} \langle X \rangle$. For $\langle X \rangle = 0$ and $\langle \Delta X^2 \rangle = \langle X^2 \rangle = 6 \langle R_{g,X}^2 \rangle$ $= 2 \langle R_g^2 \rangle$ this again reduces to the Debye function, Eq. (18).

3. Scattering in d = 2

Both scattering functions as calculated in Eqs. (A14) and (A17) remain formally unchanged. However, the probabilities for the single steps change to

$$p_{0} = \frac{b}{b^{2} + 2b + 1}$$

$$p_{+} = \frac{b^{2}}{b^{2} + 2b + 1}$$

$$p_{-} = \frac{1}{b^{2} + 2b + 1}.$$
(A24)

The parallel and perpendicular diffusion coefficients as well as the drift velocity still have the same functional dependence on these probabilities. However, introducing the chain extensions into Eqs. (A14) and (A17) for d = 2 changes the prediction Eq. (A22) for the perpendicular scattering to

$$S(q_{\perp}) = \frac{2}{3q_{\perp}^2 \langle R_{g,\perp}^2 \rangle} + \frac{2}{(3q_{\perp}^2 \langle R_{g,\perp}^2 \rangle)^2} (e^{-3q_{\perp}^2 \langle R_{g,\perp}^2 \rangle} - 1),$$
(A25)

whereas it leaves Eq. (A23) unchanged. Taking $X_{\perp} = 3q_{\perp}^2 \langle R_{g,\perp}^2 \rangle$, the expression of Eq. (A25) has the same form as Eq. (42).

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