

Rigid Gaussian Chains I: the Scattering Function

C.M. Marques (*) and G.H. Fredrickson

Departments of Chemical Engineering and Materials, University of California,
Santa Barbara, CA 93106, USA

(Received 11 March 1997, received in final form 2 September 1997, accepted 4 September 1997)

PACS.36.20.Ey – Conformation (statistics and dynamics)

PACS.61.25.Hq – Macromolecular and polymer solutions; polymer melts; swelling

Abstract. — We study the scattering function of semiflexible polymer chains within the framework of a rigid Gaussian model for polymers first introduced by Harris and Hearst. The tractability of this model allows for a computation of the most relevant physical properties for any value of the chain rigidity. We also explore at the level of the Random Phase Approximation some of the bulk and surface behaviour of semidilute solutions of semiflexible polymers.

1. Introduction

The scattering function of a polymer chain is of central importance in theoretical and experimental studies of macromolecular systems. It is defined [1] as the average of coherent scattering between any two points \mathbf{R}_n and \mathbf{R}_m in the chain:

$$g(\mathbf{q}) = \frac{1}{N} \sum_{n,m}^N \langle \exp[i\mathbf{q} \cdot (\mathbf{R}_n - \mathbf{R}_m)] \rangle \quad (1)$$

where \mathbf{q} is the scattering vector and N the number of monomers in the chain. Light scattering, small-angle X-rays and neutron scattering, are nowadays routinely used [1, 2] to extract the average macromolecular dimensions from the low angle (or Guinier) region of the scattering curves: the radius of gyration $R_g^2 = 1/N^2 \sum_{n,m} \langle (\mathbf{R}_n - \mathbf{R}_m)^2 \rangle$ is given by the curvature of the scattering function in this region ($qR_g \ll 1$): $g(\mathbf{q}) = N(1 - q^2 R_g^2/3)$ [1]. The high angle (or asymptotic) decay provides information about the statistical distribution of monomers internal to a coil.

For a flexible, Gaussian chain described by a connected random walk, the structure factor (see Fig. 1) first calculated by Debye [3] and named after him reads

$$g_D(\mathbf{q}) = \frac{2N}{(qR_g^0)^4} (\exp[-(qR_g^0)^2] - 1 + (qR_g^0)^2). \quad (2)$$

(*) Author for correspondence (e-mail: marques@phoenix.princeton.edu)

Present Address: R.P.-CNRS, Complex Fluids Laboratory UMR166, Cranbury, NJ 08512, USA

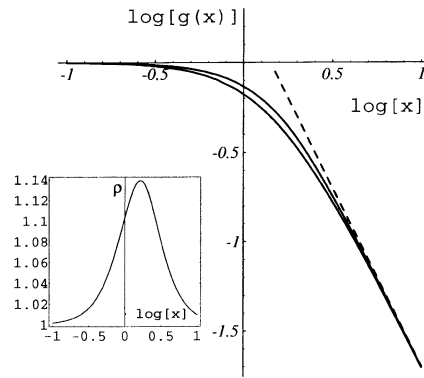


Fig. 1. — The Debye scattering function $g_D(qR_g)/N$ in a logarithm representation of $x = qR_g$ which underlines the function asymptotic behaviour. A Lorentzian approximant g_{app} and the ratio $\rho = g_D/g_{app}$ are also depicted.

The Gaussian radius of gyration scales like the square root of the polymerization index $R_g^0 = N^{1/2}b/\sqrt{6}$, with b the statistical segment length. The q^{-2} behaviour at large angles ($qR_g^0 \gg 1$) is the signature of random walk statistics for the segmental distribution of monomers.

The Debye function has been at the heart of theoretical developments in polymer science for the last three decades. It has been used for instance to calculate the scattering intensity of a semidilute polymer solution within the framework of the Random-Phase Approximation (R.P.A.) which accounts for excluded volume interactions [4] at the mean-field level. It also provides a route to computing both thermodynamic and dynamic quantities such as the osmotic pressure or the spectrum of dynamic light scattering. Extended Cahn-Hilliard theories, based on gradient expansions extracted from the scattering function, have been successfully used to describe inhomogeneous polymer systems: interfaces in polymer mixtures [5], polymer adsorption [6], wetting in polymer blends [7]... The Debye function is also central to the theoretical framework developed to describe weak microphase separation in diblock copolymer melts [8].

Surprisingly less attention has been paid to the development of an equivalently useful tool for correlation functions of semiflexible polymer chains, especially considering that actual polymers always possess some intrinsic rigidity. Such a tool must be able to continuously describe how the scattering function of a rigid polymer chain crosses over from the Debye function limit (Eq. (2)) of a purely flexible chain (zero intrinsic rigidity) to the scattering function of a rigid rod (infinite intrinsic rigidity) which is given by [9]

$$g_{rod}(\mathbf{q}) = \frac{2N}{qL} \int_0^{qL} dx \frac{\sin x}{x} - \frac{N}{(qL/2)^2} \sin[qL/2]^2. \quad (3)$$

The radius of gyration of a rod is related to the rod length $L = Nb$ by $R_g^{rod} = L/\sqrt{12}$. In the high q limit ($qL \gg 1$) one has $g_{rod} \simeq \pi/q$, the scattering signature of a one-dimensional object (see Fig. 2). We thus anticipate that a semiflexible chain exhibiting some local rigidity over a length $l_p b$ (see below for the definition of l_p) must at high enough diffusion vectors $ql_p b \sim 1$ crossover from a flexible $1/q^2$ to a rigid $1/q$ behaviour [10].

The limited effort that has been put into the development of a tractable, useful expression for the scattering function of semiflexible polymer chains is in part due to the technical difficulties

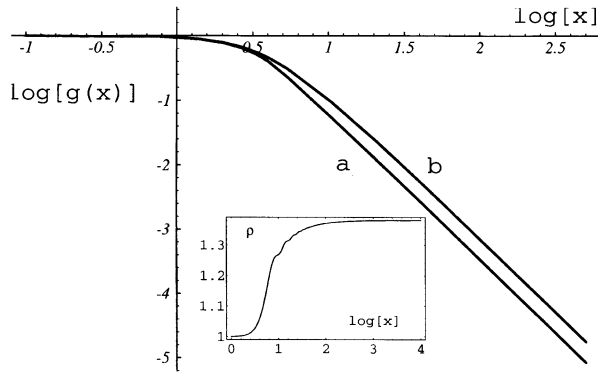


Fig. 2. — Comparison between (a) the scattering function of a rod of length L and (b) the scattering function of a breathing rod of same average length. Curves are plotted as a function of the reduced wavevector $x = qL$. The ratio of the two functions is also shown.

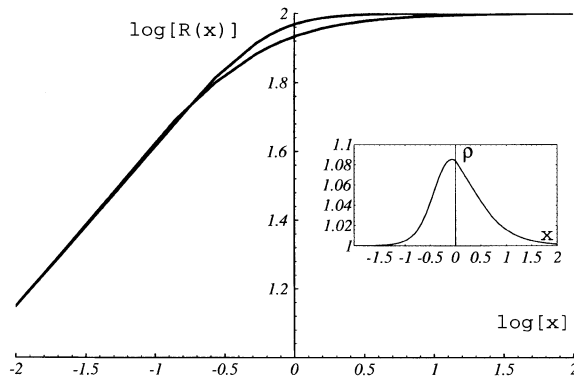


Fig. 3. — The variation of the average dimensions of a Kratky-Porod chain of 100 segments, as a function of ratio $x = l_p/N$. The correspondent quantity for a rigid Gaussian chain and the ratio $\rho = R_{KP}/R_{rg}$ are also shown.

associated with the mathematical model that is usually accepted as the best representation of an actual polymer chain possessing some rigidity, namely the Kratky-Porod (K-P) representation [11–13]. In the discrete version of this representation the polymer chain is described by a succession of bond vectors \mathbf{r}_i ; ($i = 1, \dots, N$) of fixed length $|\mathbf{r}_i| = b$ and correlations $\langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = b^2 \exp\{-|i-j|/l_p\}$. The chain bonds decorrelate (one also usually says that the chain loses the memory of its orientation) over a chemical persistence length l_p . The mean-squared end-to-end dimension $\mathbf{R} = \sum_{i=1}^N \mathbf{r}_i$ of the K-P chain is given by

$$\langle \mathbf{R}^2 \rangle = \sum_{i,j} \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = 2b^2 l_p^2 \left[\frac{N}{l_p} - 1 + \exp\left(-\frac{N}{l_p}\right) \right]. \tag{4}$$

When the persistence length is much larger than the chain contour length, $l_p \gg N$ (see Fig. 3), the chain dimensions approach the rod limit $R^2 = L^2(1 - N/(3l_p) + \dots)$. Gaussian chain

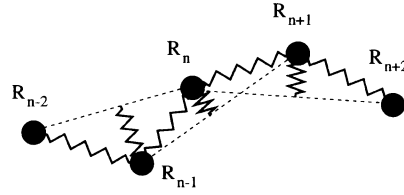


Fig. 4. — A sketch of the mechanical model associated with the Hamiltonian of a rigid Gaussian chain. The unusual extra springs ensure that three consecutive bonds tend to lie along a common direction.

dimensions are recovered for $l_p \ll N$ with a renormalized monomer size

$$R^2 = N(\sqrt{2l_p} b)^2(1 - l_p/N + \dots).$$

A more complete description of the statistics of a K-P chain, involving for instance the monomer probability distribution, cannot be achieved analytically, due to the technical difficulty of evaluating the K-P partition function under the constraint of a fixed bond length [14–16]. In this paper we revisit a Gaussian rigid chain model first introduced [17] by Harris and Hearst that allows for bond length fluctuations. Although some aspects of this model have been studied in the past [18–21], most authors have focused on the intrinsic aspects of the model, discussing for instance its adequacy as a representation of the K-P chain, and neglecting the actual usefulness of the model as a practical tool for further developments. Most of the statistically relevant quantities of this rigid Gaussian model can be explicitly evaluated, thus allowing for a detailed discussion of the crossover behaviour of the different physical quantities as the variation of the persistence length drives the chain from flexible to rigid. With the present paper we set the foundations for a more complete study of the implications of this model in other situations involving semiflexible chains like the structure of a grafted polymer layer and the phase behaviour of strongly and weakly separated diblock copolymers.

2. The Rigid Gaussian Chain

In the model employed here, which is closely related to the Harris-Hearst model [17], we describe the polymer chain by a succession of bond vectors \mathbf{r}_i and associate the following Hamiltonian

$$H(\{\mathbf{r}_i\}) = \frac{3}{2a^2} \sum_{n=1}^N \mathbf{r}_n^2 + \frac{3}{2a^2} \alpha \sum_{n=2}^N (\mathbf{r}_n - \mathbf{r}_{n-1})^2 \quad (5)$$

with the allowed chain configurations (all energies being expressed in units of $k_B T$). When $\alpha = 0$ this Hamiltonian describes a purely flexible Gaussian chain, corresponding to a mechanic model where each of the chain points \mathbf{R}_i ; $i = 0, 1, \dots, N$ is connected to its neighbours by a harmonic spring of constant $3/a^2$. The introduction of the second term on the right hand side of equation (5) corresponds to the addition of extra harmonic springs of constant $12\alpha/a^2$ exerting a force that tends to align the points along the chain (see Fig. 4). Because we allow for length variations of the bond vectors, the partition function of this “rigid Gaussian” chain

can be straightforwardly evaluated from

$$Z(a, x) = \int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp\left\{-\frac{1}{2} \sum_{n,m} M_{nm} \mathbf{r}_n \cdot \mathbf{r}_m\right\} = (2\pi)^{3N/2} (\det \mathbf{M})^{-3/2} \tag{6}$$

with M_{nm} the elements of the $N \times N$ matrix

$$\mathbf{M} \equiv \frac{3}{a^2} \begin{pmatrix} 1 + \alpha & -\alpha & 0 & 0 & \dots & 0 \\ -\alpha & 1 + 2\alpha & -\alpha & 0 & \dots & 0 \\ 0 & -\alpha & 1 + 2\alpha & -\alpha & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & \dots & & -\alpha & 1 + 2\alpha & -\alpha & 0 \\ 0 & \dots & & 0 & -\alpha & 1 + 2\alpha & -\alpha \\ 0 & \dots & & 0 & 0 & -\alpha & 1 + \alpha \end{pmatrix} \tag{7}$$

It is a well known property of the Gaussian form (6) that the pair correlation function between two given bonds \mathbf{r}_n and \mathbf{r}_m is simply related to the nm element of the inverse matrix \mathbf{M}^{-1} . A recursive calculation of the elements of this matrix gives for $m \geq n$

$$\begin{aligned} \langle \mathbf{r}_n \cdot \mathbf{r}_m \rangle = 3M_{n,m}^{-1} &= a^2 \tanh\left(\frac{1}{2l_p}\right) \frac{\exp\left(-\frac{m-n}{l_p}\right)}{1 - \exp\left(-\frac{2N}{l_p}\right)} \\ &\times \left[1 + \exp\left(-\frac{2n-1}{l_p}\right)\right] \left[1 + \exp\left(-\frac{2N-2m+1}{l_p}\right)\right] \end{aligned} \tag{8}$$

where the persistence length l_p is related to the Hamiltonian parameter α by

$$l_p^{-1} = -\log \frac{1 + 2\alpha - \sqrt{1 + 4\alpha}}{2\alpha} \simeq \begin{cases} -\log \alpha & \alpha \rightarrow 0 \\ 1/\sqrt{\alpha} & \alpha \rightarrow \infty \end{cases} \tag{9}$$

Equation (8) holds for matrix elements $m \geq n$. For elements such that $n \geq m$ the permutation $n \rightleftharpoons m$ should be applied. The bond pair correlations as given by (8) are functions of the microscopic parameter a . For flexible polymers ($l_p = 0$), a is the typical fluctuating length of a bond: $\langle \mathbf{r}_n \cdot \mathbf{r}_m \rangle = a^2 \delta_{nm}$. Because the length of each bond in a Gaussian chain is a fluctuating quantity, one needs some prescription to determine which quantity in the model should be associated the statistical segment length b . This is usually done by simply associating the segment length b to the average fluctuating length of the bonds: $a^2 = 1/N \sum_n \langle \mathbf{r}_n^2 \rangle = b^2$, with an associated contour length $L = Nb$. By applying the same prescription to the rigid Gaussian chain, one obtains a relation between the microscopic parameter a , the persistence length of the chain l_p and the statistical segment length b . In the mechanical picture of a rigid chain composed of two types of springs, this amounts to tuning the spring constants such that *i*) l_p is the average chemical length over which bond correlations decay and *ii*) the average bond length is a fixed quantity b . Rewriting the bond correlations as a function of the persistence length l_p and the segment length b leads to

$$\begin{aligned} \langle \mathbf{r}_n \cdot \mathbf{r}_m \rangle &= b^2 \frac{N \sinh\left(\frac{1}{l_p}\right)}{1 + N \coth\left(\frac{N}{l_p}\right) \sinh\left(\frac{1}{l_p}\right)} \frac{1}{1 - \exp\left(-\frac{2N}{l_p}\right)} \exp\left(-\frac{m-n}{l_p}\right) \\ &\times \left[1 + \exp\left(-\frac{2n-1}{l_p}\right)\right] \left[1 + \exp\left(-\frac{2N-2m+1}{l_p}\right)\right]. \end{aligned} \tag{10}$$

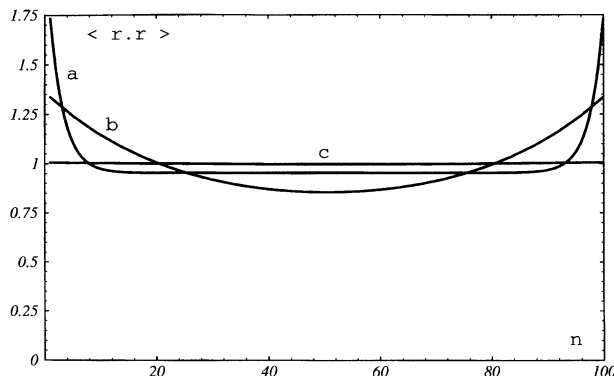


Fig. 5. — The variation of the amplitude of bond correlations along a chain of 100 segments. Bonds at the ends of the chain fluctuate more than bonds in the middle. This difference extends from the ends over a chemical length of order of the persistence length l_p . (a) $l_p = 5$; (b) $l_p = 50$, (c) $l_p = 500$.

An interesting feature of these correlations is the variation of the amplitude of bond fluctuations along the chain (see Fig. 5). The magnitude of bond fluctuations is larger at the chain extremities and then decays over a distance l_p to the value in the middle of the chain. This aspect has as been regarded by other authors [18–20] as a drawback of the rigid Gaussian model, and somewhat artificially corrected by inserting two extra springs with different spring constants at the chain extremities. We consider this feature as a legitimate and interesting one; moreover, it is plausible that actual semiflexible chains exhibit end-chain effects.

The average distance between two monomers n and m in the chain can be calculated from the bond correlation function (10). One obtains ($m > n$)

$$\begin{aligned} \langle (\mathbf{R}_m - \mathbf{R}_n)^2 \rangle &= \sum_{i,j=n+1}^m \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = \\ &= b^2 \frac{N \sinh\left(\frac{1}{l_p}\right)}{1 + N \coth\left(\frac{N}{l_p}\right) \sinh\left(\frac{1}{l_p}\right)} \left[(m-n) \coth\left(\frac{1}{2l_p}\right) \right. \\ &+ \frac{1}{4} \frac{1}{\sinh\left(\frac{N}{l_p}\right)} \frac{1}{\sinh^2\left(\frac{1}{2l_p}\right)} \left[\cosh\left(\frac{N-2m}{l_p}\right) + \cosh\left(\frac{N-2n}{l_p}\right) \right. \\ &\left. \left. + 2 \cosh\left(\frac{N+m-n}{l_p}\right) - 2 \cosh\left(\frac{N-m-n}{l_p}\right) - 2 \cosh\left(\frac{N}{l_p}\right) \right] \right]. \quad (11) \end{aligned}$$

In particular, the fluctuating value of the end-to-end vector is

$$\langle \mathbf{R}^2 \rangle = Na^2 = Nb^2 \frac{N \sinh\left(\frac{1}{l_p}\right)}{1 + N \coth\left(\frac{N}{l_p}\right) \sinh\left(\frac{1}{l_p}\right)} \coth\left(\frac{1}{2l_p}\right). \quad (12)$$

Figure 2 compares the end-to-end vector of a K-P chain (4) with the end-to-end vector of a rigid Gaussian chain (12). They have exactly the same asymptotic values in the limit of small ($1 \ll l_p \ll N$) and large persistence lengths $l_p \gg N$. Deviations from the small persistence length limit of both results agree up to first order in l_p/N . There is a less good agreement between the two expressions in the limit where the persistence length is large ($N \ll l_p$), the

radius of the rigid Gaussian chain being given by $R^2 = L^2(1 - 1/6(N/l_p)^2 + \dots)$. This is due to the different physical picture of both chains in the limit of large rigidities. A K-P chain with a persistence length much larger than its contour length can be viewed as a rigid rod with a small bending flexibility. A rigid Gaussian chain with a very large persistence length is a “breathing rod”, with average breathing dimensions (*i.e.*, contour length fluctuations) comparable to the associated contour length. The breathing rod has also some bending flexibility. This difference between the two models will also emerge later in the limiting forms for the scattering functions. Note that equation (12) correctly crosses over from the K-P result at small l_p to the Gaussian limit where l_p vanishes.

The determinant of \mathbf{M} can also be calculated recursively, leading to the partition function

$$Z(l_p) = \left(\frac{2\pi b^2}{3}\right)^{3N/2} \left[\frac{2N \sinh^2\left(\frac{1}{l_p}\right)}{1 + N \coth\left(\frac{N}{l_p}\right) \sinh\left(\frac{1}{l_p}\right)} \right]^{3N/2} \times \left[2 \tanh\left(\frac{1}{2l_p}\right) \sinh\left(\frac{N}{l_p}\right) \right]^{-3/2}. \tag{13}$$

In the limit of zero rigidity one gets the usual Gaussian partition function $Z = (2\pi b^2/3)^{3N/2}$. For persistence lengths larger than unity but small compared to the chain contour length one has $Z \simeq (2\pi b^2/3)^{3N/2} (2/l_p)^{3N/2}$: the increasing rigidity reduces by a factor of $\sqrt{2/l_p}$ the available phase space of each degree of freedom. Note that this is different from $Z = (2\pi l_p b^2/3)^{3N/2}$, the result that one would get for the partition function of N/l_p freely hinged monomers of length $\sqrt{l_p} b$. When the rigidity is very large (with $l_p \gg N$) the partition function reduces to $Z \simeq (2\pi b^2/3)^{3N/2} (2N/l_p^2)^{3N/2}$, a further decrease of $\sqrt{N/l_p}$ in the available phase space of each degree of freedom.

The scattering function of the rigid Gaussian chain g_{rg} can now be easily evaluated by using another well known property of the quadratic form (6), relating the average of the phase factors $\langle \exp[i\mathbf{q} \cdot (\mathbf{R}_n - \mathbf{R}_m)] \rangle$ with the fluctuating average value of the vector $(\mathbf{R}_n - \mathbf{R}_m)$:

$$g_{rg}(\mathbf{q}) = \frac{1}{N} \sum_{n,m} \exp \left[-\frac{\mathbf{q}^2 \langle (\mathbf{R}_n - \mathbf{R}_m)^2 \rangle}{6} \right]. \tag{14}$$

The scattering function (14) is plotted in Figure 6 for a value of the persistence length much smaller than the length of the chain. As expected, three different regimes can be observed. In the small wavevector domain $qR_g \ll 1$ the scattering function exhibits the usual parabolic shape from which the radius of gyration of the chain $R_g^2 = N2l_p b^2/6$ can be extracted. At intermediate wavevectors $R_g \gg q^{-1} \gg l_p$ the random orientation statistics of segments separated by a chemical distance larger than the persistence length dominates the scattering intensity and gives the characteristic q^{-2} scaling. For even larger wavevectors $q^{-1} \ll l_p$, the stiff nature of segments smaller than l_p forces the scattering function to decay with the typical scaling for rods q^{-1} . In this limit, however, the fluctuations of the bond lengths cause an increase of the scattering amplitude with respect to the scattering amplitude of normal, non-breathing rods. To see this, we consider the limit where the persistence length is much larger than the chain length. In this regime, we find a simplified expression for the scattering function of a breathing rod

$$g_{rod}^{rg}(\mathbf{q}) = \frac{1}{N} \sum_{n,m} \exp \left[-\frac{q^2(n-m)^2}{6} \right] = N \left[\frac{\sqrt{6\pi}}{qL} \operatorname{erf} \left[\frac{qL}{\sqrt{6}} \right] - \frac{1 - \exp \left[-\frac{q^2 L^2}{6} \right]}{\frac{q^2 L^2}{6}} \right] \tag{15}$$

from which one can extract a radius of gyration that agrees exactly with the radius of gyration

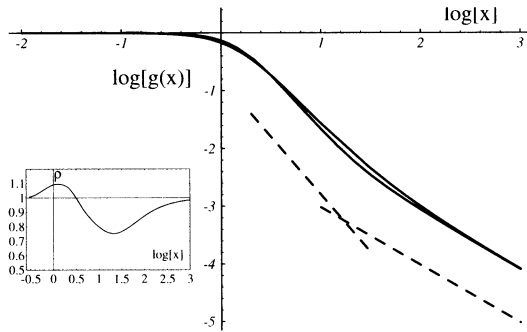


Fig. 6. — Scattering function of a rigid Gaussian chain with a persistence length much smaller than its contour length $l_p/N = 0.001$ as a function of the reduced wavevector $x = qR_g$. Two lines of slopes -2 and -1 have been included as guides for the eye. The approximant of the scattering function and the ratio of both functions have also been included. The scattering function is smaller than its approximant in the region of less good agreement.

of a normal rod. However, in the limit of large wavevectors (see Fig. 2), the scattering amplitude of a breathing rod is a factor of $\sqrt{6/\pi}$ larger than the scattering amplitude of a normal rod.

In practice, computation of the scattering function of a rigid Gaussian chain only requires one numerical step to perform the double summation (or the double integral) of equation (14). Also, the calculation can be performed for any value of the chain length or rigidity, in contrast to previously available scattering functions restricted either [22] to the first few cumulants of equation (14), or to infinite chain lengths [23].

We conclude this section by discussing the treatment of experimental scattering data obtained from rigid chains. In a typical situation one obtains the scattered intensity $I(\mathbf{q})$, a function that is proportional to the scattering function $g(\mathbf{q})$ defined in (1). If the large q region is well defined, one can extract the persistence length $l_p b$ by plotting the function $q^2 I(q)$ and fitting the linear asymptotic region to the straight line $q^2 I(q) \simeq Cte(2/3 + ql_p b \pi)$ [23] with the two fitting parameters Cte and $l_p b$. Note that because of the breathing factor the rigid Gaussian chain has in this regime an offset of $\sqrt{6/\pi}$. An alternative, perhaps more informative representation of the data is illustrated in Figure 7 for our rigid Gaussian function. From the experimental data, this representation would be obtained by first normalizing the scattered intensity to unity at zero wavevector. From the low wavevector region one can extract a value for the radius of gyration R_g and define a dimensionless wavevector $X = qR_g$. One plots then the quantity $X^2 I(X)/I(X=0)$ in a double logarithmic plot. This extends considerably the crossover region from the Guinier regime to the high wavevector regime. The intersection of the asymptotic linear regime with the X -axis defines a point $X = X_c$ which reveals the number of segments in the chain, N/l_p . For the rigid Gaussian chain one has $N/l_p = 2\pi/X_c^2$, while for the usual Kratky-Porod chain one has instead $N/l_p = \pi^2/(3X_c^2)$.

3. Some Simple Applications

For the purposes of calculating the static, bulk or surface polymer properties one often approximates the Debye structure factor by the Lorentzian form

$$g_D(q) \simeq \frac{N}{1 + (qR_g^0)^2/2} \quad (16)$$

which never deviates more than 15% from the actual Debye function over the entire q -range

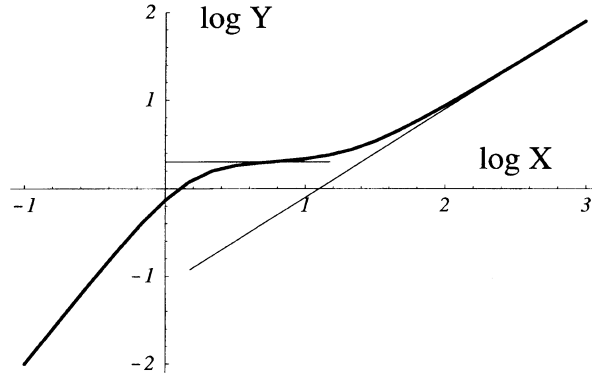


Fig. 7. — An useful representation for experimental data. One first normalizes the scattering function by its value at the origin and the wavevector by the radius of gyration. One then draws the double logarithmic plot of $Y = X^2 I(X)/I(X=0)$, where $X = qR_g$ is the normalized wavevector. The number of persistence lengths in the chain N/l_p is then given by the intersection of the large wavevector asymptotic line with the X -axis. In this particular case one has $N/l_p = 1000$. Note also that in this representation the inflexion point is at the height $Y = 2$.

(see Fig. 1). This single-chain scattering function can be used as input to compute collective correlations within the R.P.A. framework [24]. For instance, the scattering function of concentration fluctuations in a semidilute polymer solution is given by

$$\frac{1}{g_{sd}(q)} = \frac{1}{g_0(q)} + vc \quad (17)$$

where c is the polymer concentration, v is a microscopic parameter measuring the strength of volume excluded interactions and $g_0(q)$ is an appropriate single-chain scattering function (here $g_0 = g_D$). In good solvents $v \sim b^3$. Using the Lorentzian approximant (16) and defining the screening length $\xi^{-2} = 12vc/b^2 + 12/(N^2b^2) = \xi_b^{-2} + 2(R_g^0)^{-2}$ one gets [4]

$$g_{sd}(q) = \frac{12\xi^2}{b^2} \frac{1}{1 + q^2\xi^2}. \quad (18)$$

Note that the screening length ξ accounts at the R.P.A. level for finite-size corrections to the screening length ξ_b of a semidilute solution of infinitely long polymers.

To enlighten the role of the screening length one can for instance study the one and three dimensional inverse Fourier transform of the scattering function $g_{sd}(q)$. The three dimensional inverse transform is related to $g(r)$, the pair correlation function of the polymer solution

$$g(r) = c \int_0^\infty \frac{4\pi q^2 dq}{(2\pi)^3} \frac{\sin qr}{qr} \frac{12\xi^2}{b^2} \frac{1}{1 + q^2\xi^2} = \frac{3c}{\pi b^2 r} \exp\left[-\frac{r}{\xi}\right] \quad (19)$$

which has the form of a Yukawa potential with a distance cutoff ξ . The one dimensional inverse Fourier transform is related to the average concentration profile of a polymer solution in the neighbourhood of an attractive or repulsive surface with a weak surface potential $U(z) = \frac{b^2}{6} \gamma \delta(z)$:

$$c(z) = c_b \left[1 + \frac{b^2}{6} \gamma \int_0^\infty \frac{dq_z}{\pi} \cos q_z z \frac{12\xi^2}{b^2} \frac{1}{1 + q_z^2 \xi^2} \right] = c_b \left[1 + \gamma \xi \exp\left[-\frac{|z|}{\xi}\right] \right]. \quad (20)$$

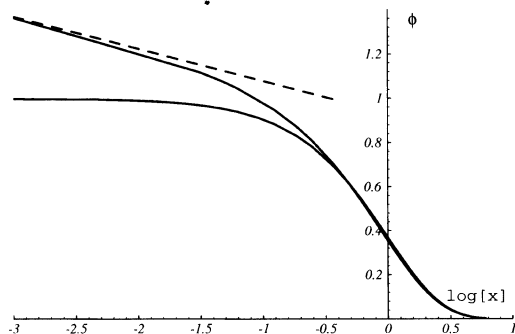


Fig. 8. — Comparison between the responses of a semidilute solution of semiflexible polymers and a semidilute solution of flexible polymers to weak surface fields. The curves are plotted for solutions with the same correlation length as a function of the reduced variable $x = z/\xi$. An enhancement of the response of semiflexible polymers is observed at distances shorter than the persistence length (here $l_p/\xi = 0.1$).

In the above expression z is the coordinate measured normal to the surface and c_b is the bulk polymer concentration far from the wall. The polymer concentration is enhanced or depleted over a distance ξ close to the wall according to the sign of γ , a measure of the polymer-wall affinity.

In the case of a rigid Gaussian chain with a persistence length smaller than the contour length of the chain, a convenient approximant for the single-chain structure factor can be written as

$$g_0(q) \simeq \frac{N}{1 + \frac{q^2 N 2l_p b^2}{12(1+q l_p b \sqrt{\pi/6})}}. \quad (21)$$

This particular form represents the actual scattering function with an accuracy better than 20% over the entire q range (see Fig. 6). If the goal is to more closely approximate the K-P chain model, one might further correct for the excess of large q scattering amplitude by replacing the coefficient $\sqrt{\pi/6}$ in (21) by the non-breathing rod coefficient $\pi/6$. In any case, a R.P.A. scattering function accounting for excluded volume effects in semidilute solutions of semiflexible polymers chains can be calculated from (17):

$$g(q) \simeq \frac{12\xi_r^2}{l_p^2 b^2} \frac{1}{1 + \frac{q^2 \xi_r^2}{1+q l_p b \sqrt{\pi/6}}}. \quad (22)$$

The correlation length of a semidilute solution of semiflexible chains is larger by a factor of l_p than the correlation length of a semidilute solution of flexible polymers at the same concentration: $\xi_r^2 \simeq l_p \xi_b^2$ [25]. The different asymptotic behaviour of the scattering form (21) implies also that the real space response of the solution to an external field is also modified on distances smaller than $l_p b$. Both the pair correlation function and the adsorbed/depleted polymer profile depart significantly from their flexible counterparts. The expressions of the three and one dimensional inverse Fourier transforms of the scattering function (21) are, however, rather cumbersome, so we only present in Figure 8 a comparison of the surface response of flexible and semiflexible polymer solutions with the same correlation length (which implies different monomer concentrations). For distances from the wall larger than the correlation length $x \gg \xi$, both profiles decay over a length ξ . The profiles are also similar in the intermediate

distance range $\pi l_p b \ll z \ll \xi$. For smaller distances however the semiflexible profile diverges logarithmically as

$$c(z) \simeq c_b \gamma \xi \left[\left(1 - \frac{|z|}{\xi}\right) - \frac{2l_p b}{\pi \xi} \left(\frac{1}{2} + C + \log \frac{|z|}{\xi}\right) \right] \quad (23)$$

where $C = 0.577\dots$ is the Euler constant. Increasing the local rigidity of the polymer chains enhances the response of the solution to a surface field. This can be understood as a reduction in the entropic price that one needs to pay in order to align longer chain segments in the surface field. Indeed, the enhancement of polymer adsorption is expressed by the second term in the rhs of equation (23) that carries the signature of a rod-like response, as can perhaps more explicitly be seen from the small z expression ($z \ll \xi$) for the correlation function of a semidilute solution of semiflexible chains (the equivalent of expression (19))

$$g(r) \simeq \frac{3c}{\pi b^2} \left[\frac{1}{r} + \frac{2l_p b}{\pi} \frac{1}{r^2} \right]. \quad (24)$$

The r^{-2} decay of the second term in the r.h.s. of equation is the typical scaling form of the monomer-monomer correlation function of infinitely long rods. For rods with a finite length L the correlation function can be obtained by inverse Fourier transforming the scattering function (3):

$$g(r) = \begin{cases} \frac{c}{b r^2} \left(1 - \frac{r}{L}\right) & r \leq L \\ 0 & r > L \end{cases}. \quad (25)$$

The corresponding one dimensional response to a surface field $U(z) = \frac{b^2}{6} \gamma \delta(z)$ also diverges logarithmically at the wall

$$c(z) = \begin{cases} c_b \left[1 + \frac{\gamma b}{6} \left(\frac{|z|}{L} - 1 + \log \frac{|z|}{L}\right) \right] & z \leq L \\ c_b & z > L \end{cases} \quad (26)$$

further confirming the origin of the logarithmic surface enhancement.

4. Summary

In the present paper we discussed the effect of chain rigidity on the behaviour of semiflexible polymers. Revisiting a model first introduced [17] by Harris and Hearst we exactly calculated the relevant physical properties for polymer chains with an arbitrary persistence length. In particular, we show that the scattering function of the chains described by this model has the appropriate q^{-1} scaling form for scattering vectors larger than the inverse persistence length. Moreover, in the limit of a very large rigidity, when the persistence length is much larger than the contour size, we show that these Gaussian rigid chains can be pictured as “breathing rods”, a class of straight objects with length fluctuations. Such fluctuations give rise to an increase of the scattering amplitude with respect to the scattering amplitude of normal, non-breathing rods.

Because actual polymers always possess some intrinsic rigidity, the scattering function must always exhibit a q^{-1} regime for wavevectors larger than the inverse persistence length (but smaller than the inverse monomer size, where the form of the scattering function is determined by the detailed monomer structure). With a convenient approximant for the scattering function that correctly mimics this asymptotic q^{-1} scaling it is possible to study the bulk and surface behaviour of semidilute solutions of semiflexible polymer chains in the framework of the Random Phase Approximation. We showed for instance that the bulk monomer-monomer

correlation function crosses over at distances of order l_p from the usual $1/r$ dependence to a $1/r^2$ rod-like scaling. Interestingly, the rigidity of the chains also causes an enhancement in the response of the polymer solution to a surface field.

The tractability of the Harris and Hearst model for gaussian rigid chains allows for a number of applications to various polymer problems, beyond the scattering results reported in this paper. Work in progress concerns grafted layers of semiflexible polymers as well as strongly and weakly segregated diblock copolymers with arbitrary rigidity.

Acknowledgments

We would like to thank D. Wu and D. Morse for many fruitful discussions. This work was partially supported by a CNRS and NATO fellowships. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the ACS, for support of this research (#29306-AC7).

References

- [1] Higgins J.S. and Benoit C.H., *Polymers and neutron scattering* (Oxford University Press, New York, 1994).
- [2] des Cloizeaux J. and Jannink G., *Les Polymères en Solution* (Les éditions de Physique, Les Ulis, 1987).
- [3] Debye P., *J. Phys. Colloid Chem.* **51** (1947) 18.
- [4] Doi M. and Edwards S.F., *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).
- [5] Broseta D., Fredrickson G.H., Helfand H. and Leibler L., *Macromol.* **23** (1990) 183.
- [6] de Gennes P.G., *Macromol.* **14** (1981) 1637.
- [7] Jones R. and Kramer E.J., *Polymer* **34** (1993) 115.
- [8] Leibler L., *Macromol.* **13** (1980) 1602.
- [9] Berne B.J. and Pecora R., *Dynamic Light Scattering* (John Wiley and Sons, Inc., New York 1976).
- [10] Denkinger P. and Burchard W., *J. Polym. Sci.* **29** (1991) 589.
- [11] Kratky O and Porod G., *Rec. Trav. chim. Pays-Bas* **68** (1949) 1106.
- [12] Norisuye T., Murakama H. and Fujita H., *Macromol.* **1** (1978) 966.
- [13] Wilhelm J. and Frey E., *Phys. Rev. Lett.* **77** (1996) 2581.
- [14] Gupta A.M. and Edwards S.F., *J. Chem. Phys.* **98** (1993) 1588.
- [15] Bhattacharjee S.M. and Muthukumar M., *J. Chem. Phys.* **86** (1987) 411.
- [16] Kholodenko A.L., *J. Chem. Soc. Faraday Trans.* **91** (1995) 2473.
- [17] Harris R.A. and Hearst J.E., *J. Chem. Phys.* **44** (1966) 2595.
- [18] Ha B.-Y. and Thirumalai D., *J. Chem. Phys.* **103** (1995) 9408.
- [19] Lagowski J.B., Noolandi J. and Nickel B., *J. Chem. Phys.* **95** (1991) 1266.
- [20] Winkler R.G., Reineker P. and Harnau L., *J. Chem. Phys.* **101** (1994) 8119.
- [21] Papadopoulos O. and Thomchick J., *J. Phys. A: Math. Gen.* **7** (1977) 1115.
- [22] Heine S., Kratky O., Porod G. and Schmitz J.P., *Makromol. Chem.* **44** (1961) 682.
- [23] des Cloizeaux J., *Macromol.* **6** (1973) 403.
- [24] de Gennes P.G., *Scaling Concepts in Polymer Physics* (Cornell, Ithaca, 1979), Chap. II.
- [25] Schaefer D.W, Joanny J.F. and Pincus P., *Macromol.* **13** (1980) 1280.