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The persistence length of polyelectrolyte chains

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Abstract. We present simulations of the basic model of weakly charged polyelectrolyte chains of variable intrinsic stiffness within the Debye–Hückel approximation. For intrinsically flexible chains the persistence length L_P shows a sublinear dependence on the screening length $r_D = 1/\kappa$ in strong contrast to all known analytical approaches which propose an effective exponent of either $y = 2$ or $y = 1$. The observed exponent y varies as a function of the system parameters. With increasing intrinsic stiffness the corresponding effective exponent y crosses over to values of up to 2 when the intrinsic persistence length L_0 exceeds the electrostatic one L_e. We find a pronounced minimum of L_P with increasing intrinsic stiffness due to a reduction of entropy. The concept of a unique persistence length is not applicable for these systems.

1. Introduction and model

The theoretical understanding of polyelectrolytes is weak compared to that of neutral polymers [1–3]. The long-ranged nature of the Coulomb interaction and the large number of degrees of freedom of the counterions cause severe problems for an analytical treatment. While theories mostly discuss dilute solutions, experiments typically are in the semi-dilute regime, where the chains strongly overlap. Furthermore, experiments as simulations face severe finite-size effects in the search for general asymptotic behaviour. In such a situation, computer simulations offer the possibility of building a bridge between basic models and experiment as they can test theoretical aspects as well as experimentally measurable quantities under well controlled conditions (see e.g. [4]).

In the first part of the present work [5], the aim is to test certain theoretical concepts for model systems. The question of whether the theories of Odijk [6] and Skolnick and Fixman [7] (for the rest of this paper referred to as OSF) remain valid for intrinsically flexible chains [8, 9] or whether several variational *ansatze* [10–12] give the right description is addressed in this work. The second part [13] extends these results towards intrinsically stiff systems.

The polymer is, as in the above papers, modelled by a random walk of N monomers, where every $(1/f)$th monomer is monovalently charged (f is the charge fraction). The screening of the counterions is accounted for by the Debye–Hückel (or Yukawa) potential V_{DH}. This is known to be a crude approximation [3, 14]. With $r_D = 1/\kappa$ being the screening length it reads

$$V_{DH} = \frac{q^2}{4\pi\epsilon\epsilon_0}\frac{\exp(-\kappa r)}{r} = \lambda_B k_B T \frac{\exp(-\kappa r)}{r} \tag{1}$$

where q is the charge per monomer and $\epsilon\epsilon_0$ is the dielectric constant of the solvent. $\lambda_B = q^2/4\pi\epsilon\epsilon_0 k_B T$ is the Bjerrum length which describes the strength of the bare Coulomb interaction and is about 7 Å in water.

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The intrinsic stiffness is varied using a cosine potential with variable amplitude to vary its strength. This gives the model Hamiltonian

$$\frac{H}{k_B T} = \sum_{i=1}^{N-1} a^p (\boldsymbol{b}_{i+1} \cdot \boldsymbol{b}_i) + \sum_{i=2}^{N} \sum_{j=1}^{i-1} \Theta(q_i q_j) \lambda_B \frac{\exp(-\kappa r_{ij})}{r_{ij}} \tag{2}$$

where $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$ is the distance between two monomers, $A = a^p$ defines the strength of the angular potential, k_B represents the Boltzmann constant and T the temperature. $\boldsymbol{b}_i = \boldsymbol{r}_{i+1} - \boldsymbol{r}_i$ is the bond vector. The bond length $b = |\boldsymbol{b}|$ is fixed to one, defining the unit length. The Bjerrum length λ_B is fixed to one, and the amplitude a of the angular potential to 2. By variation of p the intrinsic stiffness is tuned. This is a basic theoretical model and common starting point for analytical theories, which necessarily include assumptions. Variation of N, f and κ ($16 \leqslant N \leqslant 512$, $\frac{1}{256} \leqslant f \leqslant \frac{1}{4}$, $0.001 \leqslant \kappa \leqslant 0.48$) allows us to cover the whole experimentally relevant parameter space and to go even beyond experiment for flexible ($p = -\infty$) chains (equivalent molecular weight for a NaPSS–PS block copolymer up to 13 000 000 g mol^{-1}) [5]. The results on intrinsically stiff chains presented here are based on isolated chains of $N = 2049$ monomers with every sixteenth charged (i.e. 129 charges, as the first and the last monomer are charged). This parameter set is chosen as a good compromise between computational effort to equilibrate the systems examined and possible finite-size effects.

The chains are simulated by a generalized off-lattice pivot algorithm which includes rotations of inner parts [15, 16]. (For more details see [5, 15, 16, 13].) The simulations started from two extreme conformations: the random walk and the totally stretched state. The runs are considered equilibrated when results coincide for the two sets. The program runs 576 independent polyelectrolyte chains in parallel giving 576 truly independent states. For local quantities which allow for an intrachain average the statistics is even better.

2. Flexible chains

We examined chain radii, charge–charge distances, structure factors, persistence lengths and scaling properties [5, 13]. Here we focus on the κ-dependence of the persistence length. The electrostatic blob diameter ξ [1] and the number of charges per blob g_e are calculated directly from our data to avoid unnecessary assumptions. From neutral chains one would expect a scaling of the chain radii with ξ. This however does not work out here. Obviously the persistence length L_P is not a simple linear function of ξ. As the persistence length defines a kind of stiff-chain-segment length, the chain dimensions should show a characteristic dependency on L_P. Therefore we investigate R_e plotting R_e^2/L_P^2 versus the number of persistence lengths per chain, which is the ratio of contour length L and L_P:

$$\frac{L}{L_P} = \frac{N\xi}{g_e L_P}.$$

L_P is the sum of the intrinsic part L_0, which within a blob picture equals ξ, and the electrostatic contribution L_e. All variational theories predict $L_e \sim 1/\kappa$. Explicitly for a blob picture Ha and Thirumalai give [11]

$$L_e \sim \frac{g_e}{\kappa} \sqrt{\frac{\lambda_B}{\xi}}. \tag{3}$$

The OSF theory [6, 7] predicts

$$L_e = \frac{\lambda_B}{4\kappa^2 A^2} \tag{4}$$

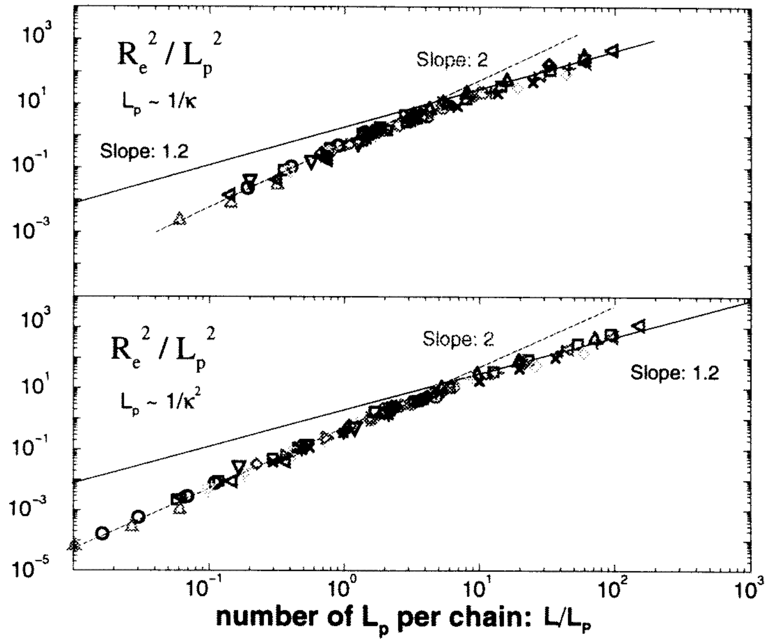

Figure 1. (a) A scaling plot obtained from the variational *ansatze*: R_e^2/L_P^2 versus L/L_P. L/L_P is the number of persistence lengths per chain, $L_e \sim 1/\kappa$. (b) A scaling plot obtained by the OSF approach: R_e^2/L_P^2 versus L/L_P. L/L_P is the number of persistence lengths per chain, $L_e \sim 1/\kappa^2$.

where A is the distance between two charges along the contour of the chain. Khokhlov and Katchaturian [8] claim that after averaging over the transversal fluctuations of the flexible chains the same formalism applies to this 'renormalized' chain which is represented by a chain of blobs. Therefore, within the framework of a blob picture they formulate for L_P explicitly:

$$L_e \sim \frac{\lambda_B g_e^2}{\kappa^2 \xi^2}. \tag{5}$$

Figure 1 shows the corresponding scaling plots. There is no way to distinguish them. To explain this, it is necessary to divide the plots into two parts. For small X-values the plots show straight lines with slope two. This is the regime where the chains build up blob poles. The dependence on L_P cancels out. The end-to-end distance is proportional to the number of blobs times the blob diameter. For larger numbers of L_P per chain the behaviour crosses over to a regime of slope 1.2. This is a self-avoiding-walk regime where the dependence on L_P is explicit:

$$\frac{R_e^2}{L_P^2} \sim X^{6/5} = \frac{N^{6/5}\xi^{6/5}}{g_e^{6/5} L_P^{6/5}} \Rightarrow R_e^2 \sim \left(\frac{N\xi}{g_e}\right)^{6/5} L_P^{4/5}. \tag{6}$$

Here something should be seen, but the κ-dependence of R_e seems to be too weak, so no difference can be figured out. As result the demand remains to measure the persistence length directly.

A natural approach is the analysis of the bond-angle correlation function BAC defined via the scalar product of two normalized bond vectors:

$$\mathrm{BAC}(k) = \left\langle \frac{\boldsymbol{b}_j}{\|\boldsymbol{b}_j\|} \cdot \frac{\boldsymbol{b}_{j+k}}{\|\boldsymbol{b}_{j+k}\|} \right\rangle = \langle \cos[\phi(\boldsymbol{b}_j, \boldsymbol{b}_{j+k})] \rangle \tag{7}$$

where $\phi(\boldsymbol{b}_j, \boldsymbol{b}_{j+k})$ is the angle between the two bond vectors and $\langle \cdots \rangle$ indicates the average over all polymers.

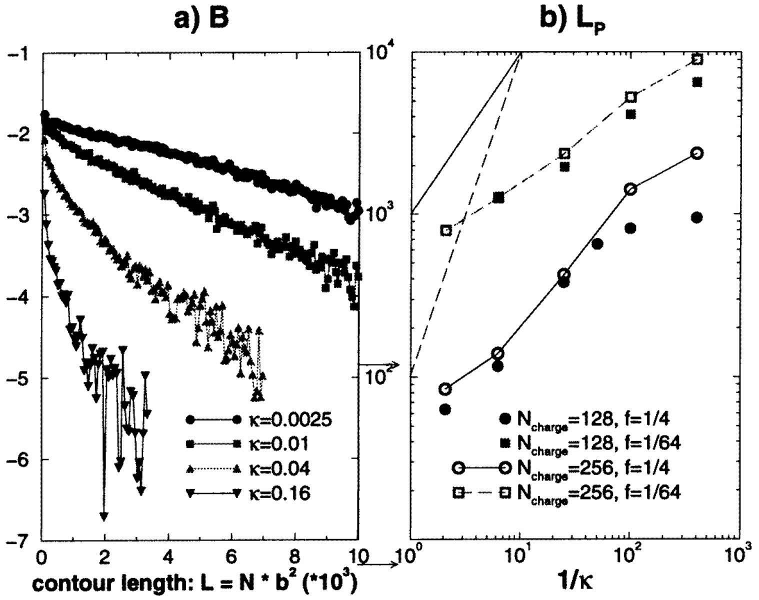

Figure 2. (a) The logarithm of the bond-angle correlation function for $N = 16\,384$, $f = \frac{1}{64}$ and the specified κ-values. (b) The persistence length based on ln(BAC) versus $1/\kappa$. The two lines in the upper left-hand corner indicate the slopes predicted by OSF (dashed) and the variational methods (solid). The model system should give the best description for weakly charged polyelectrolytes and therefore the upper curves.

Since the persistence length is defined as the decay contour length of all angular correlations, BAC should show—after some 'transient time' representing the inner part of the blob—an exponential decay, similar to the case of a wormlike chain for which the following applies:

$$\mathrm{BAC}(k) \sim \exp\left(-\frac{k}{L_P}\right) \tag{8}$$

giving

$$B(k) = \ln\langle \cos\phi(\boldsymbol{b}_j, \boldsymbol{b}_{j+k})\rangle \sim \ln\exp\left(-\frac{k}{L_P}\right) = -\frac{k}{L_P} \tag{9}$$

(see figure 2(a)).

All systems lead to the same answer: the effective exponent y of the κ-dependence of the persistence length for flexible systems is continuously varying and smaller than one (see figure 2(b)):

$$L_P \sim \frac{1}{\kappa^y} \qquad y < 1. \tag{10}$$

No unique power law can be derived, even if finite-size effects and the statistical errors of the data are taken into account. This result is in strong contrast to all known analytical results! Recently, a new field theoretical approach was suggested pointing towards a sublinear behaviour [17]. The common tendency with our data is encouraging; however, no mapping of the data has been possible so far.

To examine the chain conformation in detail at all length scales we calculate the spherically averaged structure factor $S(q)$:

$$S(q) = \left\langle \frac{1}{N} \left| \sum_{i<j}^{N} \exp(\mathrm{i}\boldsymbol{q} \cdot (\boldsymbol{r}_i - \boldsymbol{r}_j)) \right|^2 \right\rangle . \tag{11}$$

The structure factor reveals all the former results. The chain conformation varies between SAW and almost rodlike behaviour ($R_G \sim N^{0.58} - N^{0.92}$). $S(q)$ along the first main axis of gyration shows κ- and f-dependent oscillations that are typical for rods. Perpendicular to that axis, the chain conformation is similar to the spherically averaged quantity. There is definitively no random-walk behaviour as claimed by several analytical approaches (see e.g. [8]). Viewing a polyelectrolyte chain in an extremely oversimplified way as a random walk composed of rodlike segments of length L_P shows that there has to be a kink between two regions of different slopes in $S(q)$. Using this kink to derive a measure for the persistence length, again the sublinear behaviour is regained. So all former results are recovered, impressively showing the overall consistency of the present analysis.

3. Stiff chains

Intrinsic stiffness is introduced (see equation (2)) to study the development of the κ-dependence of the electrostatic persistence length L_e and to get further insight in the chain structure. L_P is again deduced from the BAC. As L_P is the sum of L_0 and L_e, L_0 has to be calculated from simulations on neutral chains first. Then the analysis of the κ-dependence of L_e is straightforward [13].

We demonstrate the crossover from the sublinear behaviour of intrinsically flexible chains to exponents larger than one for intrinsically rather stiff systems for $p = 2, 5, 7, 9$ (see figure 3). $p = 2$ causes a rather small intrinsic persistence length and therefore the κ-dependence of L_e is completely analogous to flexible polyelectrolytes ([5]). For $p = 5, 7, 9$, L_0 crosses over from being smaller to becoming comparable and then larger than L_e. In this region the effective exponent y crosses the value of one towards two which is the limit of the original analytical treatment [6, 7]. As L_e is smaller for larger κ, the crossover depends strongly on the screening. Our data reproduce the variational results [10–12] for $L_e \sim L_0$.

Our results underline the strong coupling between the chain conformation and the electrostatic effects destroying the basic assumption of the OSF approach and its extensions (see e.g. [8, 9]) for flexible systems. Only if $L_0 \gg L_e$ do the exponents approach the OSF value $y = 2$. In this case the intrinsic stiffness is so dominating that the influence of the electrostatic contribution on the conformation is very small. In this sense we cover the whole parameter space towards very stiff polymers and find the expected behaviour.

Much more striking is the behaviour of the whole persistence length L_P, as taken from the long-range decay of BAC. L_P shows a pronounced minimum as a function of L_0 (see figure 4) [13]. This means that increasing the intrinsic stiffness and thereby increasing the end-to-end distance causes a reduction of the persistence length! It is obvious from our data that the entropic part of the free energy is underestimated by all known analytical approaches

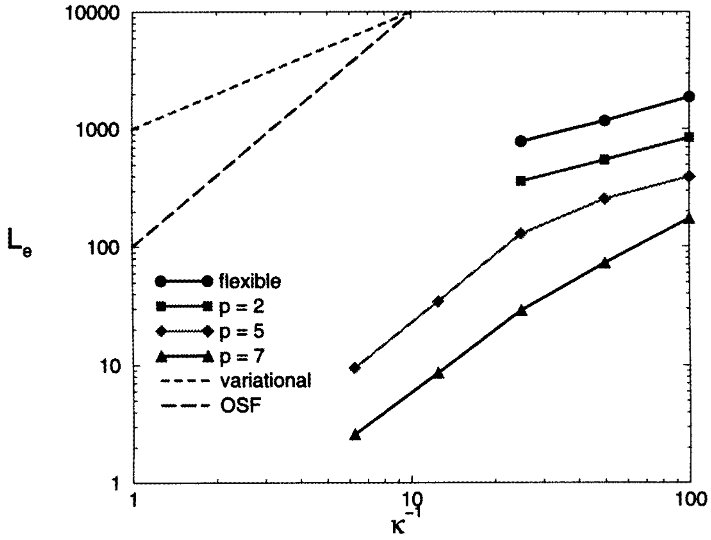

Figure 3. The electrostatic persistence length as a function of $1/\kappa$ for several p-values.

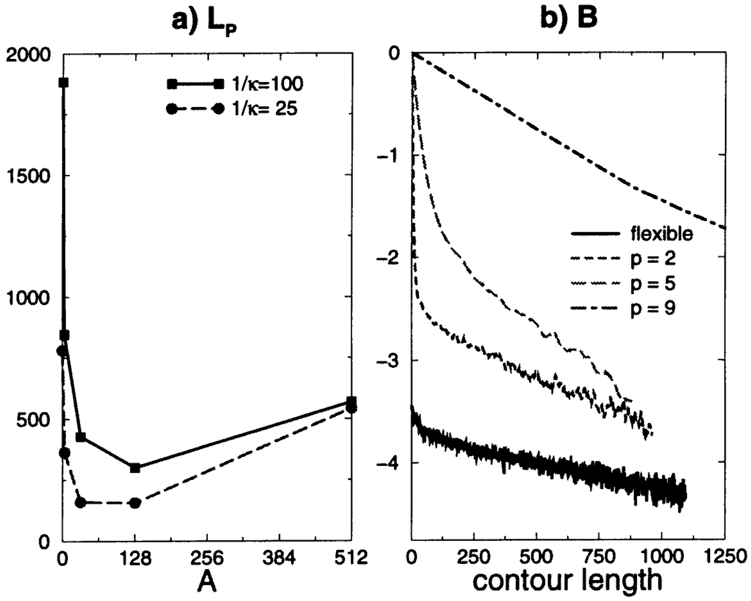

Figure 4. (a) The persistence length as a function of the intrinsic stiffness. (b) $B(k) = \ln(\mathrm{BAC})$ for $\kappa = 0.01$ and several p-values.

for flexible systems for (at least) all relevant chain lengths. The onset of intrinsic stiffness destroys a large amount of the entropy of the neutral chains in between the charges. This is demonstrated by the strong increase of the distance between two adjacent charges [15] and snapshots of typical configurations [16]. The data demonstrate that the system is governed

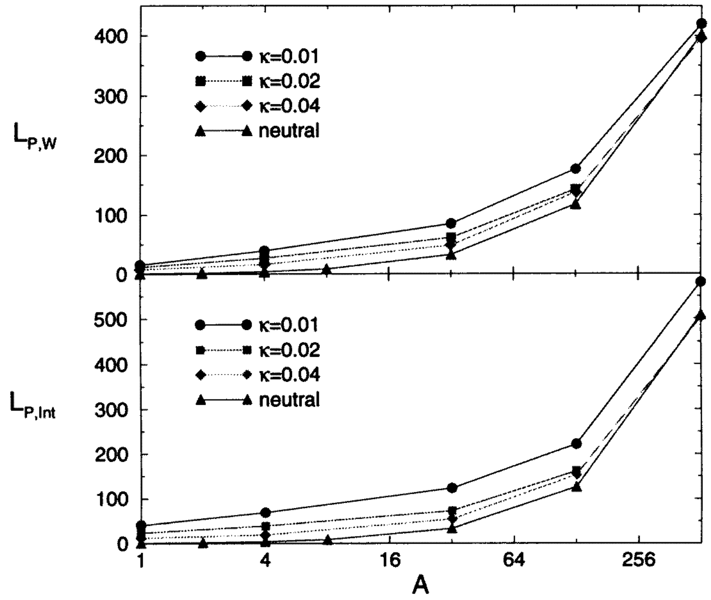

Figure 5. (a) L_P calculated with the wormlike chain formalism. (b) L_P calculated by integrating the bond-angle correlation function.

by two distinct length scales, as figure 4 shows. Due to this the bending rigidity becomes length scale dependent.

In experiments this effect normally is not observed, because one needs models to extract a persistence length from the data. Usually, the Kratky–Porod model [18] describing wormlike chains is used to calculate L_P from the end-to-end distance [19]. Use of this expression misses the importance of different length scales. Figure 5 demonstrates this by showing the persistence length calculated from our data using the wormlike chain formalism. The striking minimum has vanished. Even calculating L_P from its most direct geometric definition [20] or, similarly, integrating the bond-angle correlation function does not reproduce the minimum, because these two methods mix the two different length scales (see figure 5), so the information on the two different length scales is lost. It is not sufficient to use one number L_P to describe the main features of the chain conformation.

4. Conclusions

We present extensive, systematic simulations to examine the behaviour of single weakly charged polyelectrolyte chains under variation of the intrinsic stiffness.

For flexible chains a crossover from blob pole behaviour to a SAW structure is found. None of the known analytic *ansatze* are able to describe the chain conformation and the sublinear κ-dependence of the electrostatic persistence length L_e correctly: $L_e \sim \kappa^{-y}$; $y = y(\kappa, f) < 1$!

Introducing intrinsic stiffness shows that the parameter space is split in three regions: as long as the intrinsic persistence length L_0 is small, y is smaller than one. When L_0 becomes comparable with L_e the exponent reflects the variational prediction $y = 1$. Only if $L_0 \gg L_e$ can the OSF value $y = 2$ be recovered. In this case the electrostatic interaction and the chain conformation are almost completely decoupled.

The whole persistence length L_P is characterized by a pronounced minimum as a function of L_0 caused by a subtle interplay of the intrinsic and the electrostatic contributions. The stretching on small and medium length scales due to the intrinsic stiffness causes a decrease of L_e that is much faster than the corresponding increase of L_0. This introduces a second relevant length scale. By this mechanism the influence of the Debye–Hückel potential and thereby of L_e is reduced significantly. Experiments need to measure length-scale- or q-dependent quantities to obtain this detailed information. Using 'simple' models leads to a loss of important knowledge on the chain structure. Equivalently, theory has to take this effect into account and cannot claim that just one length scale represented by one value for L_P describes the whole chain conformation.

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References

[1] de Gennes P 1979 *Scaling Concepts in Polymer Physics* (Ithaca, NY: Cornell University Press)
[2] Barrat J L and Joanny J F 1995 *Adv. Chem. Phys.* **94** 1
[3] Stevens M and Kremer K 1995 *J. Chem. Phys.* **103** 1669
See additionally:
Stevens M and Kremer K 1993 *Phys. Rev. Lett.* **71** 2228; 1993 *Macromolecules* **26** 4717
[4] Kremer K, Dünweg B and Stevens M 1995 *Monte Carlo and Molecular Dynamics Simulation in Polymer Science* ed K Binder (Oxford: Oxford University Press)
[5] Micka U and Kremer K 1996 *Phys. Rev.* E **54** 2653
[6] Odijk T 1977 *J. Polym. Sci., Polym. Phys. Edn* **15** 477
[7] Skolnick J and Fixman M 1977 *Macromolecules* **10** 944
[8] Khokhlov A R and Katchaturian K A 1982 *Polymer* **23** 1742
[9] Li H and Witten T 1995 *Macromolecules* **28** 5921
[10] Barrat J L and Joanny J F 1993 *Europhys. Lett.* **24** 333
[11] Ha B Y and Thirumalai D 1995 *Macromolecules* **28** 577
[12] Bratko D and Dawson K A 1993 *J. Chem. Phys.* **99** 5352
[13] Micka U and Kremer K 1996 *Europhys. Lett.* submitted
[14] Stevens M and Kremer K 1996 *J. Physique* II (6 November)
[15] Micka U and Kremer K 1996 to be published
[16] Micka U 1996 *PhD Thesis* Rheinische Friedrich-Wilhelms-Universität zu Bonn
[17] Liu A J, Rudnick J and Levine A 1996 *Preprint*
[18] Kratky O and Porod G 1949 *Rec. Trav. Chim.* **68** 1106
[19] Doi M and Edwards S F 1986 *The Theory of Polymer Dynamics* (Oxford: Oxford University Press)
[20] Christos G A and Carnie S L 1989 *J. Chem. Phys.* **91** 439