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The effect of stiffness in wormlike micelles

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Abstract. The effect of stiffness in a 2D living polymer system is investigated by Monte-Carlo simulation in a canonical ensemble. As the flexibility decreases, the mean chain contour length $\langle L \rangle$ decreases and goes through a local maximum. The mean end to end square distance shows a non-monotonic behaviour due to the coil-to-rod transition and the decrease in chain contour length. Near the maximum of chain ordering in the bulk, the chain length distribution adapts itself to increase the configurational entropy. With the parameters used in this simulation, it seems that the effect of the stiffness for high stiffness is to decrease $\langle L \rangle$ as in the isotropic case, since the ordering decreases again.

PACS. 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 05.50.+q Lattice theory and statistics; Ising problems – 64.60.Cn Order–disorder transformations; statistical mechanics of model systems

Wormlike micelles can be seen as a system of linear aggregates in equilibrium that are able to break and recombine. The isotropic-nematic transition of cylindrical micelles has been studied analytically, numerically and experimentally [1–5].

The effect of the chain flexibility on the general properties of living polymers has not been studied numerically as the single varying parameter so far, although it influences greatly the behaviour of living polymers in, *e.g.*, a constrained geometry [6,7]. In all the cases found in the literature [4,8–10], the simulation is conducted in a grand canonical ensemble and the various interactions essentially varied through a change in temperature, so that the relative affinity of the monomers for each other and their density are not kept constant. The density plays a major role in living polymers systems [11,12], not only by changing the mean end to end square distance as in dead polymers systems of fixed contour length, but also by changing directly the contour length distribution.

Moreover, in most of the simulations carried out, non-binding attractive interactions between monomers are fixed [1,4] in order to take into account the role of interfacial tension. Hence, a phase separation into a dense and dilute phase may occur, increasing the complexity of the system.

That a grand-canonical simulation cannot give without ambiguity the physical origin of an order-disorder transition has been underlined in reference [4]. Typically, the disorientation of the chains because of increased flexibility is not alone responsible for the observed phase transition. One indeed observes a sharp drop in the mean chain length at the phase transition whatever the flexibility. As a conclusion, Milchev [4] suggested that the phase transition in a grand-canonical system is more closely connected to the creation of holes and the rapid change in polymer weight than to disorientation of long semi-flexible polymer chains. Hence, it is expected that a canonical simulation will show only the effect of chain stiffness, since both the binding energy and the monomer concentration are kept constant. This work could also lead to some reflections about other problems found in wormlike micelles or living polymers. The effect of charges in wormlike micelles has been studied theoretically taking into account only modification of the chain end energy [11], neglecting the effect on the persistence length. Also, certain natural system, like actin or tubulin, which under given conditions can also be modeled by living polymers, are rather stiff and are known to form more-or-less ordered systems [12].

This present study is limited to the two-dimensional case for the following reasons. First, the results should be compared with existing grand canonical simulations, mostly carried out on a square lattice. Secondly, an additional isotropic interaction between parallel monomers is necessary to stabilize an ordered phase [13] in three dimensions. The introduction of such an interaction would strongly increase the complexity of the system.

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The chosen order parameter is in general $\psi = \left|\frac{N_x - N_y}{N}\right|$ [1–4] where N_x and N_y are the fraction of bonds in the x and y direction and $N = N_x + N_y$. Thus the order parameter ψ is a measure of the ordering in the whole system. This quantity is subject to finite size effects which can be used to obtain critical exponent [9]. Another order parameter is the mean stiffness ζ of the chains, defined as $\zeta = \frac{1}{m}\sum_m \frac{\max(nx, ny)}{n}$, where nx and ny are the number of bonds in the x and y directions, respectively, of a chain of $n = nx + ny$ monomers. ζ is an average value taken over all m chains present in the system and, contrary to ψ, feels the effect of the finite size of the lattice only if the longest chains in the simulation span a distance of the order or greater than the linear system size. This is of course never the case in the present simulation. Both ψ and ζ are needed to describe precisely the system at the level of the chain (ζ) and at the level of the whole systems (ψ). Although tidely bound to each other, they do not always vary in the same way. For example, for a system of rods, $\zeta = 1$, but $\psi = 1$ if the rods are ordered and $\psi = 0$ if the system consists of an isotropically oriented solution of rods.

Although ψ is the most natural choice for the order parameter, and was used in all of the preceding simulations to describe the ordering in the system of living polymers, it might be that a short-range ordering parameter would be more realistic [14,15]. The question remains to what extent the lattice influences the results. It seems that this question has never been discussed in previous simulational works, where the effect of stiffness was always studied on lattices [15,16]. On a two dimensional lattice, the order-disorder transition is clearly second order [9,17].

However, a two dimensional off-lattice simulation [18] on dead polymers suggests, not without ambiguities on the model used however, that the transition could be of the Kosterlitz-Thouless type.

Simulation procedure

The simulation procedure has been extensively described in reference [19]. The principal details are just recalled there for sake of clarity.

Only one monomer at a time may be present on a lattice site (excluded volume interaction between monomers). Those sites of the lattice which are not occupied by monomers are considered empty (vacancies) and contribute to the free volume of the system.

An energy $-V$ ($V > 0$) is set for the creation of a bond between monomers.

In the present study the ends of a given polymer chain are not allowed to bind together. This last condition avoids the formation of rings [10,17] which gives a different length distribution for even and odd chain length (in monomer units) with temperature.

This is not really a constraint if we consider micellar systems in which rings are not likely to occur [20].

A MCS (Monte-Carlo Step) is organised as follows:

(i) The chains are allowed to perform a reptation move. The slithering snake algorithm is very efficient in dense systems and allows fast relaxation, both of the chain conformation and system configuration.

(ii) A monomer is chosen at random. If the monomer happens to be at the end of a chain, an attempt is made to create a bond with another monomer which might be present on any one of the four neighbouring sites also chosen at random. If the end of another polymer is present on the chosen neighbouring site, the Metropolis algorithm [21] is applied, that is, a new bond is created if the value of a random number between 0 and 1 is smaller than $\min(1, \exp\left(\frac{-V}{K_B T}\right))$.

(iii) Finally, a monomer is chosen at random. If a bond on the right of the current monomer exists, it attempts to break, also according to the Metropolis rule.

During one MCS one carries out (ii)–(iii) as many times as there are monomers in the system. The order in which these sequences are carried out does not play any role.

A number of structural properties are sampled during the simulation: mean average values like the mean contour length $\langle L\rangle$ and the mean square end-to-end distance $\langle R_e^2\rangle$ (an average over all the chains), which can be estimated experimentally. The mean square end-to-end distance is the mean value of the square of the end-to-end distance taking into account the chains only; *i.e.*, a monomer is a chain without any bond and has a mean square end-to-end distance of zero. The simulations have been carried out on a 100×100 square lattice with periodic boundary conditions. The absence of finite-size effects was checked, and the breaking of the chain eliminates the non-ergodicity of the slithering snake algorithm [21,22]. Within the framework of this model, an extra energy cost $\sigma > 0$ is added for the creation of a kink either by binding or moving of the chain.

Typically, 2×10^5 MCS were necessary to achieve full equilibrium at the concentration $\phi = 0.5$ and parameter $V/K_B T = 7.4$ used in this simulation. It has been checked that the main preferential orientation of the chains near maximum value of ψ changes many times during the simulation, so that the set of data taken after equilibration were possibly uncorrelated. An accurate determination of the maximum of ψ, which would have needed a complete finite size scaling analysis, is however beyond the scope of this study.

Result and discussion

At the level of mean-field approximation (20) in the absence of closed rings, one can write the free energy for a system of linear chain as:

$$\frac{F}{k_B T} = \sum_L c(L,T)\left[\ln c(L,T) - (L-1)\frac{V}{k_B T}\right] \qquad (1)$$

where $c(L,T)$ is the molecular weight distribution for chain length L. Minimization of equation (1) with respect to $c(L,T)$, subject to the condition

$$\phi = \sum_{l} Lc(L,T) \tag{2}$$

with ϕ the density of the system yields

$$c(L,T) = \exp\left(-\left(\frac{V}{k_B T}+1\right)\right)\exp\left(-\frac{L}{\langle L\rangle}\right) \tag{3}$$

with

$$\langle L\rangle = \phi^{1/2}\exp\left(\left(\frac{V}{k_B T}+1\right)/2\right). \tag{4}$$

In the presence of stiffness, two cases have to be distinguished.

In absence of ordering, the distribution is given by [23]

$$c(L,T) = \mu^{(2-L)}c(1,T)^L(\mu\exp(V/K_B T))^{L-1} \times (1+(\mu-2)\exp(-\mu/K_B T))^{L-2} \tag{5}$$

where μ is the coordination number of the lattice.

By numerical integration, it is shown that $\langle L\rangle$ decreases with σ [23].

In the limit $\sigma \to 0$, a simple argument allows one to calculate directly the dependence of $\langle L\rangle$ on σ. The addition of a stiffness for the chain through the presence of a persistence length defined by $Lp = \sigma/K_B T$ leads to a free energy

$$\frac{F}{k_B T} = \sum_{L} c(L,T)\left[\ln c(L,T) - (L-1)\frac{F}{k_B T} + (L/Lp-1)\frac{\sigma}{k_B T}\right] \tag{6}$$

where the term $L/Lp - 1$ is the mean number of kinks in a chain of length L. Minimization of equation (1) with respect to $c(L,T)$, subject to the condition (2) leads to a similar expression for the mean chain length $\langle L_\sigma\rangle$ as (4):

$$\langle L_\sigma\rangle = \phi^{1/2}\exp\left(\left(\frac{V_\sigma}{k_B T}+1\right)/2\right) \tag{7}$$

with $V_\sigma = V - \sigma$.

Milchev [4] and Jaric and Benneman [13,14] have calculated that the effect of the stiffness enters the free energy in a two dimensional lattice as $K_B T \ln[2 + 4\exp(-\sigma/K_B T)]$. The insertion of this last expression developed in the limit $\sigma \to 0$ in equation (1) leads to the same result, equation (7).

In case of ordering, a term accounting for the orientational entropy loss of the micelles in the nematic phase must be added in equation (1). The ordering increases the contour length and $\langle L\rangle$ grows with σ [24]. There is, however, no simple relation between the parameter σ and the mean angle between a section of a micelle and the nematic director, so that the dependence of $\langle L\rangle$ on σ can not be explicitly given.

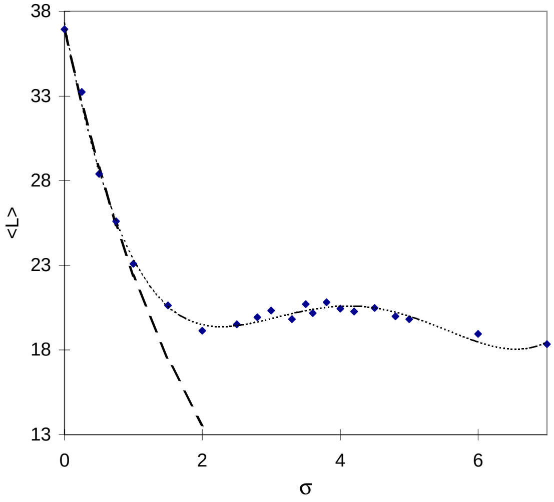

Fig. 1. Plot of the mean chain length $\langle L\rangle$ *versus* σ. The dashed line is a fit according to equation (7).

The dependence of the mean chain length $\langle L\rangle$ as a function of σ are plotted in Figure 1. The energetic cost of a kink in the chain decreases first the mean chain length $\langle L\rangle$ as σ increases [23].

Note that in reference [4], such a behaviour could not be observed: the influence of σ was reduced by increasing the temperature T (note that the relevant physical quantity here is $\sigma/K_B T$), which at the same time reduce also the effect of the binding energy so that the apparent behaviour is always the greater $\sigma/K_B T$, the greater the chain. In reference [1], the authors have shown a snapshot of a two-dimensional system of linear micelles at constant concentration and at various (but not too) different temperatures, so that they apparently did not notice the variation in $\langle L\rangle$. In Figure 1, the first part of the curve is well-fitted with an exponential function as a function of σ with the expected slope of -0.5 (Eq. (7)). The dependence of $\langle L\rangle$ on σ was studied in detail for $2 < \sigma < 5$ (Fig. 2). The chain length $\langle L\rangle$ goes through a local maximum for $\sigma \sim 3.5$ before decreasing again. This effect will be correlated with the evolution of other parameters later in this article.

The evolution of $\langle \mathrm{Re}^2\rangle$ depends both on the mean degree of polymerisation $\langle L\rangle$ of the chains and on the conformation of the chain, *i.e.*, coil or rodlike.

This is exactly what is observed (see Fig. 3): $\langle \mathrm{Re}^2\rangle$ first decreases slightly with σ due to the decrease in $\langle L\rangle$ and afterward increases strongly due both to the transition from a coil to a rod and to the increase in $\langle L\rangle$. At higher value of σ however, when the chains are already stiff and rod-like, the effect of σ is only to reduce $\langle L\rangle$, so that $\langle \mathrm{Re}^2\rangle$ decreases again.

The difference in chain contour length is not large and a scaling law should be checked over at least one order of magnitude. An exponent ν_{eff} is nevertheless defined

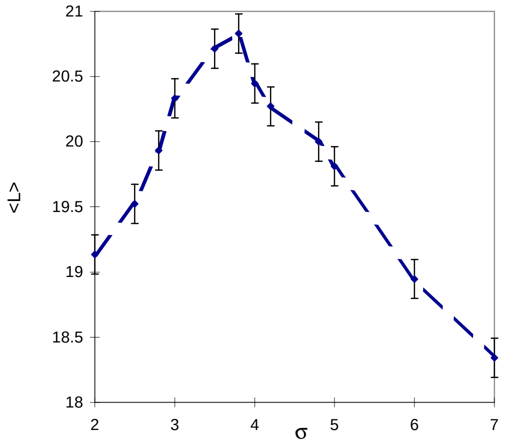

Fig. 2. Plot of the mean chain length $\langle L\rangle$ *versus* σ in presence of ordering.

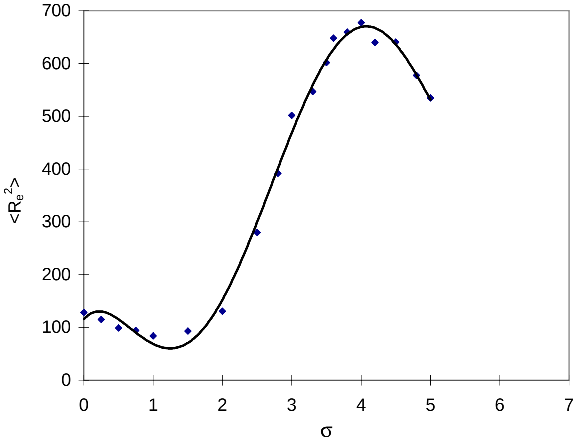

Fig. 3. Plot of the mean chain end-to-end square distance $\langle \mathrm{Re}^2\rangle$ *versus* σ.

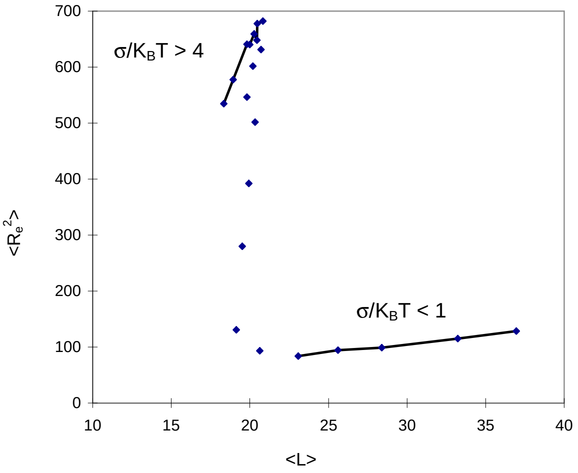

Fig. 4. Plot of the mean chain end-to-end square distance $\langle \mathrm{Re}^2\rangle$ *versus* $\langle L\rangle$.

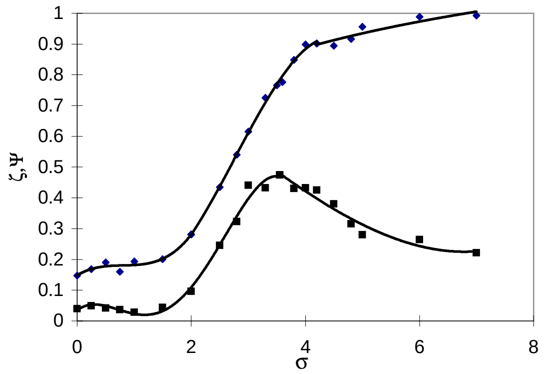

Fig. 5. Plot of the ordering parameter ζ (upper curve) and ψ (lower curve) as a function of σ.

by $\langle \mathrm{Re}^2\rangle \sim \langle L\rangle^{2\nu_{\mathit{eff}}}$. This enables, for example, the coil-to-rod transition to be checked by measuring the apparent exponent using the same data as for Figures 1 and 3. The dependence of $\langle \mathrm{Re}^2\rangle$ on $\langle L\rangle$ is divided in three main regions (Fig. 4).

For $\sigma/K_BT \le 1$, the chains are not rigid and the effect of σ is essentially to reduce $\langle L\rangle$ as discussed for Figure 1. The apparent exponent is $\nu_{\mathit{eff}} = 0.5 \pm 0.05$, *i.e.*, the exponent expected for a melt of segregated chains. This apparent value is below the value of the exponent in the θ regime $\nu_\theta = 4/7$ that we would expect as lower boundary value. In an earlier study [19], we have observed a similar behaviour when the change of $\langle L\rangle$ is made through a change of concentration. In that case, the growth of the end-to-end square distance with $\langle L\rangle$ was lowered by the effect of the increasing density which reduce the end to end square distance. In the present case, the reduction of $\langle L\rangle$ through an increased rigidity also has an effect on the end-to-end square distance. The increased rigidity of the chain tends to increase the end-to-end square distance, so that the end-to-end square distance decreases more slowly with decreasing $\langle L\rangle$, or conversely that the end-to-end square distance scales with $\langle L\rangle$ with an apparently lower exponent. For $\sigma/K_BT \ge 4$, the chains are rod-like, and the apparent exponent is $\nu_{\mathit{eff}} = 1 \pm 0.05$. Here again, the effect of σ is restricted to a reduction of $\langle L\rangle$. The end-to-end square distance is very sensitive to a change in $\langle L\rangle$: $\langle \mathrm{Re}^2\rangle \sim \langle L\rangle^2$, so that a variation of 10% leads to a change of $\sim$ 20% in $\langle \mathrm{Re}^2\rangle$. The intermediate regime, $1 < \sigma/K_BT < 4$, shows a very high dependence of $\langle \mathrm{Re}^2\rangle$ on $\langle L\rangle$, but it is not well fitted by any simple function. In this regime, the effect of σ is essentially to induce the coil to rod transition.

The increase in stiffness as a function of σ is also clearly seen on the curve ζ as a function of σ (Fig. 5). ζ starts from a value slightly above zero at $\sigma = 0$ and reaches asymptotically the value of 1 for $\sigma > 5$. The nonzero value of ζ at $\sigma = 0$ comes from the presence of chains with contour length smaller than or of the order of the persistence length lp induced by the excluded volume interaction. In this 2D lattice model, $lp \sim 4$ [19]. The ordering in the bulk is given by the curve Ψ as a function of σ (Fig. 5). The ordering increases first with increasing chain stiffness, goes through a maximum for $\sigma \sim 3.5$ and decreases slowly. It is also for this value of σ that $\langle L \rangle$ reaches a local maximum. The growth of $\langle L \rangle$ seems to be correlated with a nematic ordering, in agreement with analytical predictions [24].

The snapshots of the system at $\sigma = 0$, $\sigma = 3.5$ and $\sigma = 7$ (Figs. 6a, 6b, 6c) illustrate the behaviour of the system. At $\sigma = 0$, the system is clearly isotrop whereas at $\sigma = 3.5$, large domains of ordered chains are observed, the chains being rod-like. The further increase of σ does not change the chain conformation (the chains are already rod-like) but reduces the mean contour chain length, so that at $\sigma = 7$ an isotropic system of small rods is observed.

The chain contour length distribution at $\sigma = 3.5$ and $\sigma = 7$ are plotted in Figure 7. The effect of the stiffness is to modify the Schultz-Zimm like distribution observed in living polymers systems [25]. As observed in the absence of order [24], the number of monomers is below the amount of dimers and trimers. Only the classical mean-field exponential remains for $L > 2$, without the appearance of the typical shoulder in the distribution due to a different behaviour for the chain smaller than a blob size [25,26]. The particularities of the molecular weight distribution in two dimensions [25] are also found in three dimensions [27], so that the same modification of the molecular weigth distribution with stiffness are likely to occur in three dimensions (see also [1] for the use of two-dimensional simulations and extension of the results to the three dimensional case). It is worth noting that at the maximum of ordering and local maximum of $\langle L \rangle$ ($\sigma = 3.5$) and beyond, the distribution is still of the form given in absence of ordering.

Knowing the distribution also enables the calculation of the contribution of the mean-field configurational entropy [4] $\varDelta S/K_BT = -\sum_L C(L)\ln(C(L))$ that is plotted as a function of σ in Figure 8. This entropy is not the total entropy of the system, since the interchain ordering in the system is not taken into account. It also doesn't include the contribution due to the various conformations a chain of a given length could take. It is defined as the entropy related to the distribution of the monomers in clusters (living polymers) of different sizes. The configurational entropy decreases first with increasing stiffness signalling the disappearance of the longer chains and the repartition of the monomers in smaller chains. The entropy stops its decrease for $\sigma \sim 2$ and increases a bit with a maximum near $\sigma = 3.5$, a value for which the local ordering parameter $\varPsi$ takes its maximum value. Hence the loss of entropy due to the ordering of the stiff chains in the system is, at least partially, counterbalanced by this increases in configurational entropy.

Another entropic contribution of interest is given by the mixing of rigid and flexible bonds $\varDelta S_f/K_BT = -(f\ln(f) + (1-f)\ln(1-f))$ (Fig. 9), where f is the total fraction of adjacent flexible bonds (or kinks). This definition of the flexibility is different than in [4] and is the one suitable for the calculation of $\varDelta S_f$. In [4], where the IMS model is used, the monomers possess two dangling ends. The overlap of two dangling ends of two different monomers defines a bond between the monomers.

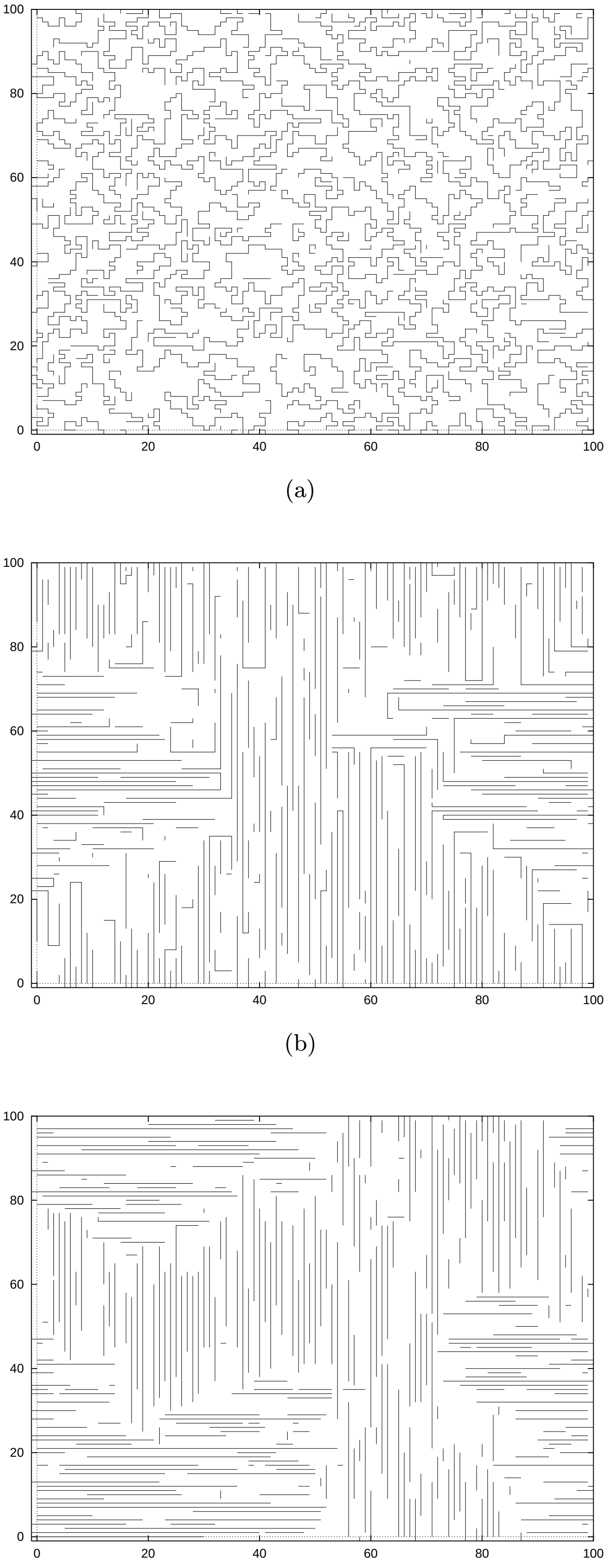

Fig. 6. Snapshot of the system at (a) $\sigma = 0$, (b) $\sigma = 3.5$ and (c) $\sigma = 7$.

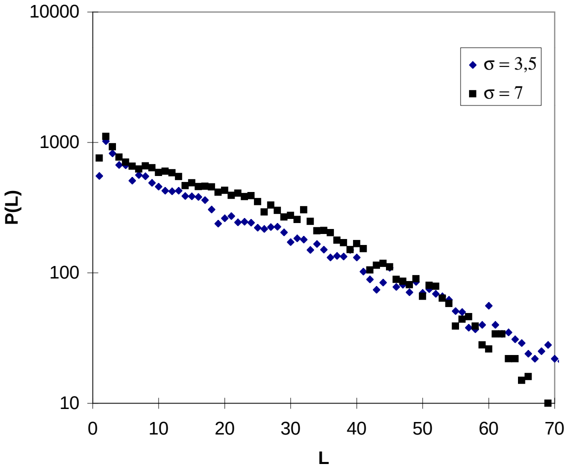

Fig. 7. Semi-logarithmic plot of the chain length distribution for $\sigma = 3.5$ (lower curve) and $\sigma = 7$ (upper curve).

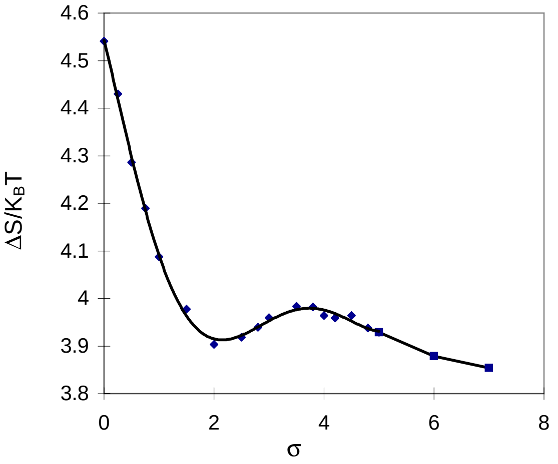

Fig. 8. Plot of the configurational entropy ΔS *versus* σ.

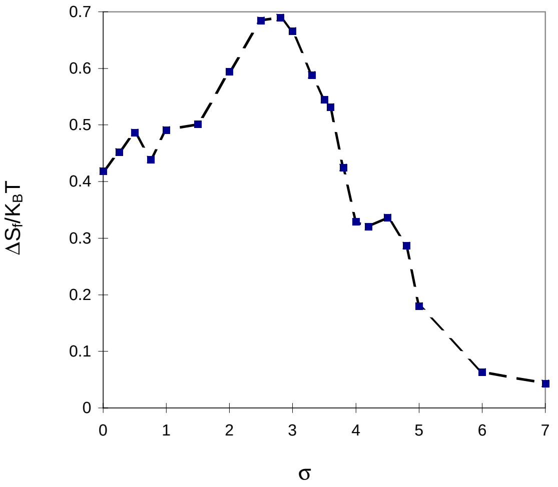

Fig. 9. Plot of ΔS *versus* σ.

The parameter σ acts directly on each monomer by defining the probability of having parallel or perpendicular dangling ends. The flexibility is defined per monomer through the relative position of the dangling ends to each other, independently of the fact that a bond between monomers exists or not. In the IMS model, a polymer of L monomers has $L + 1$ bonds taken into account in the flexibility calculation, each polymer end having a dangling end whose orientation depend on σ. It means also that f depends not only on σ but also strongly on $\langle L \rangle$ in general since *e.g.* chains of length $L = 1$ without bonds contribute to f. In the present work, the flexibility is defined strictly by the relative orientation of adjacent bonds in a polymer of L monomers that contains $L - 1$ bonds.

$\Delta Sf/K_BT$ has a maximum near $\sigma = 2.5$ (corresponding also to the maximum of ζ), a smaller value of σ than for the maximum of Ψ, and $\Delta S/K_BT$, and the local maximum of $\langle L \rangle$.

Various system sizes have been used in simulations to check the effect of the finite size of the simulation box. There is a very slight increase of $\langle L \rangle$ with the box size at high σ. Although the lattice is known to increases the chain orientation, the present work shows that the ordering disappears at very high σ. Hence, the lattice nature and finite size effects play against the present results, so that we can be confident to their reliability.

Conclusion

As for geometrical constraints like the presence of walls [7] or obstacles [28], the stiffness decreases the mean contour length.

The increase in stiffness causes a local ordering, but the decrease in the chain contour length leads to an isotropic system of stiff short rods so that the ordering in the system goes through a maximum as a function of the chain stiffness. This ordering of the rod-like polydisperse system and the appearance of an isotropic phase of rod should lead to interesting corresponding rheological behaviours [29]. The chain length distribution adapts itself near the maximum of ordering in the bulk increasing the configurational entropy.

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References

1. Y. Bohbot, A. Ben Shaul, R. Granek, W.M. Gelbart, J. Chem. Phys. **103**, (1995).
2. P. Van der Schoot, M.E. Cates, Langmuir **10**, 670 (1994).
3. P. Van der Schoot, J. Chem. Phys. **104**, 1130 (1996).
4. A. Milchev, Polymer **34**, 362 (1993).
5. J-F Benet, D.C. Roux, J. Rheol. **39**, 725 (1995).
6. V. Schmitt, F. Lequeux, C.M. Marques, J. Phys. II France **3**, 891 (1993)
7. Y. Rouault, A. Milchev, Macromol. Theor. Simul. **6**, 1177 (1997).
8. G.I. Menon, R. Pandit, M. Barma, Europhys. Lett. **24**, 253 (1993).
9. A.Milchev, D.P. Landau, Phys. Rev. E **52**, 6431 (1995).
10. G.F. Tuthill, M.V. Jaric, Phys. Rev. B **31**, 2981 (1985).
11. S.A. Safran, P.A. Pincus, M.E. Cates, F.C. MacKintosh, J. Phys. France **51**, 503 (1990).
12. J. Kas, H. Strey, J.X. Tang, D. Finger, R. Ezzel, E. Sackmann, P.A. Janmey, Biophys. J. **70**, 609 (1996).
13. M.V. Jaric, K.H. Benneman, Phys. Lett. A **95**, 127 (1983).
14. M.V. Jaric, K.H. Benneman, Phys. Rev. A **27**, 1228 (1983).
15. Comment made by P. Van der Schoot.
16. Comment made by an unknown referee.
17. G.F. Tuthill, J. Chem. Phys. **90**, 5869-5872 (1989).
18. M. Dijkstra, D. Frenkel, Phys. Rev. E **50**, 349 (1994).
19. Y. Rouault J. Phys. II France **6**, 1301 (1996).
20. M.E. Cates, S.J. Candau, J. Phys.-Cond. **2**, 6869 (1990).
21. K. Binder, D.W. Heermann, *Monte-Carlo Simulation in Statitical Physics* (Springer-Verlag, Berlin, 1992); K. Kremer, K. Binder, Computer Physics Reports **7**, 259-312 (1988).
22. N. Madras, A.D. Sokal, J. Stat. Phys. **50**, 109 (1988).
23. W. Carl, Y. Rouault, Macromol. Theor. Simul. (to be published).
24. P. Van der Schoot, M.E. Cates, Europhys. Lett. **25**, 515 (1994); P. Van der Schoot, J. Phys. II France **5**, 243 (1995).
25. Y. Rouault, A. Milchev, Phys. Rev. E **55**, 2020 (1997).
26. L. Schäfer, Phys. Rev. B **46**, 6061 (1992).
27. The excess monomers has been observed in Y. Rouault, A. Milchev, Phys. Rev. E **51**, 5905 (1995) for a two dimensional system. A recent work confirms this observation and the presence of a Schultz-Zimm like distribution in a three dimensional system (J. Wittmer, A. Milchev, M.E. Cates, manuscript submitted).
28. Y. Rouault, Eur. Phys. J. B (to be published).
29. M. Doi, S.F. Edwards in *The theory of polymer dynamics* (Oxford University Press, 1986), Chap. 10.