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# Change of the scaling behavior of the end-to-end square distance in a two-dimensional polydisperse system

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**Abstract.** The simulation of a two-dimensional, broadly polydisperse, living polymers system at high concentration reveals an unusual conformational behaviour for the longer chains. Unlike in three dimensions, the longer chains are not swollen but are squeezed by the smaller chains. This observation is discussed in terms of a two dimensional solvent- polymer mixture whose solvent particules are larger than the polymer monomers.

**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

The change in the chain dimension upon change in concentration, $\phi$, is a major topic in polymer physics, and has already been studied numerically to some extent [1–5]. The main effect observed is a change of the scaling exponent, $\nu$, relating the end-to-end square radius, $R_e^2(L)$, to the degree of polymerization, $L$.

Both in two and three dimensions, the value of $\nu$ interpolates from the value for a dilute self-avoiding walk ($\nu \cong 3/5$ in three dimensions and $\nu = 3/4$ in two dimensions) to the value for a Gaussian chain ($\nu = 1/2$).

However, some huge differences exist between two-dimensional and three-dimensional systems. Unlike the three-dimensional case, $\theta$-chains are not Gaussian in two dimensions: $\nu(\theta) = 4/7 > 1/2$ [6]. Two-dimensional Gaussian chains are simply globular ($\nu_g = 1/2 = 1/d$). In three dimensions, for a melt of monodisperse chains, the chains interpenetrate each other. A chain of $N$ monomers is swollen by smaller chains of $P$ monomers, provided that $N^{1/2} > P$ [7].

In a two-dimensional monodisperse system, the chains are non-interpenetrating, and the notion of blob seems to be no more valid at high concentrations [2]. Also, in a two-dimensional polydisperse system, no swelling of the larger chain by the smaller is observed [8–10]. The last result comes from the simulation of living polymers [11]. These polymers are particulary interesting as a case study for the simulation of a polydisperse system [12]. The chain length distribution $C(L)$ is broad and decays exponentially:

$$\begin{aligned} C(L) &\propto e^{-L|\langle L\rangle} \\ \langle L\rangle &\propto \phi^{1/2} e^{(E+1)/2kT} \end{aligned} \tag{1}$$

where $E$ is the energy between two bound monomers. The great amount of small chains for few long chains is an ideal case to study a possible swelling of the longer chains by the smaller. Moreover, the algorithm for the simulation, which is based on a binding and breaking of the chains, is able to simulate very dense systems [9,10,13–15]. A swelling of the longer chains by the smaller chains would lead to

$$\begin{aligned} R_e^2(L-1) &\sim (L-1)^{2\nu_{long}} \quad L > L^* \\ R_c^2(L-1) &\sim (L-1)^{2\nu_{short}} \quad L < L^* \end{aligned} \tag{2}$$

where $R_e^2(L)$ is the end-to-end mean square distance of a polymer of $L$ monomers ($L-1$ bonds). $L^*$ is a cross-over value at which the scaling regime changes. Swelling occurs if $\nu_{short} < \nu_{long}$.

In fact, $\nu_{short} > \nu_{long}$ is observed [10]: the asymptotic regime given by $\nu_{long}$ is seen for chain length $L \gg lp$, where $lp$ is the persistance length.

They are only a few numerical investigations on dense systems [13,14], and even fewer on two-dimensional dense systems [2,8,16]. Moreover, the chain lengths used were rather short. Here, however, the numerical experiment showing the absence of swelling in polydisperse systems was conducted for a chain length ranging from 1 to 250 monomers, and for concentration $\phi \leq 0.81$ [10]. A complete study of the dependence of $R_e^2$ on $L$ and $\phi$ using the same range of parameters leads to [17]:

$$R^2(L,\phi) = R^2(L,0)(1 - cL^{\varepsilon}\phi) \tag{3}$$

where $R^2(L,0)$ is the end-to-end square distance of a dilute self-avoiding walk of $L-1$ steps, $c$ is a numerical constant depending on the lattice type ($c = 0.21$ for the present square lattice) and $z = \gamma_{2d} - 1 = 0.34$.

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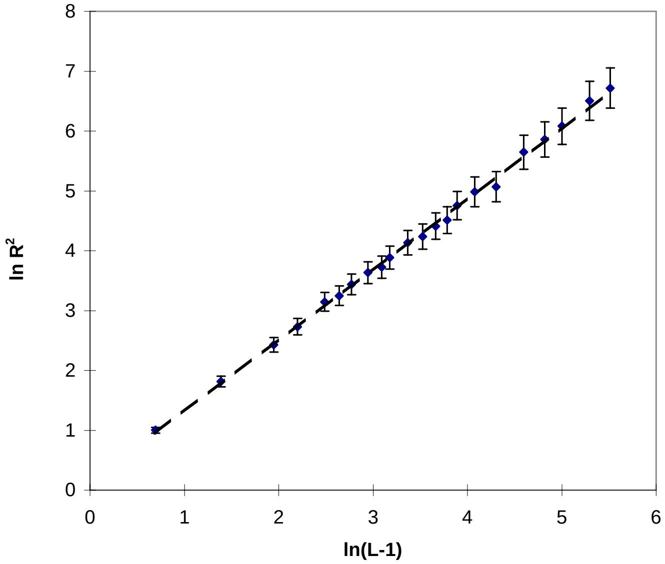

**Fig. 1.** Scaling plot of $R_e^2(L)$ as a function of $(L-1)$ at $\phi = 0.81$.

Equation (3) has only a physical meaning for $L^\varepsilon \phi \ll 1$. When this condition is no more valid, $R^2$ should have a different dependence on $L$ and $\phi$. From a practical point of view, the study of the chains for which $L^\varepsilon \phi \sim 1$ is a demanding computer task. The reasons are as follows: the motion of the chains are slowed down at high density, even if a reptation algorithm is chosen. This implies that a huge number of Monte-Carlo Steps (MCS) has to be taken between two independant configurations. Due to the quasi-exponential decaying distribution, a long chain of contour length $L$, so that $L^\varepsilon \phi \sim 1$, is a rare event. This implies that a huge number of configurations have to be sampled in order to have reliable statistics for those chains. The binding energy, $E$, should be chosen so that the mean chain length $\langle L \rangle$ is not too short. Except at too high value of $E$, the correlation between two configurations increases since, not only does the relaxation of longer chains take significantly longer, but the lifetime of a bond is increased. So, parameter values used in previous work have been retained.

An exhaustive description of the numerical procedure can be found in [10].

Simulations have been conducted using a living polymer system at concentrations of $\phi = 0.81$, $\phi = 0.9025$, $\phi = 0.9801$ and $\phi = 1$, and reduced binding energy $E/kT = 7.04$. Measurement of data were performed at intervals of 20000 MCS (instead of 2500 for lower concentrations [10]) to obtain independent data sets. In spite of the algorithm used, the system takes relatively long time to relax and generate uncorrelated states. This limitation comes from the very few number of free lattice sites available for the chain to move to [14]. At $\phi = 1$, only the binding and breaking process generates new configurations, but the relaxation of the system is not appreciably slower than at $\phi = 0.9801$.

For chain lengths $L$ between $L = 5$ and $L = 55$, the curve of $\ln(R_e^2)$ *versus* $\ln(L-1)$ displays a straight-line behaviour, and the corresponding values of the exponent, $\nu$, given by a least square fit are 0.58, 0.56, 0.53 and $0.5 \pm 0.01$ at concentrations $\phi = 0.81, 0.9025, 0.9801$ and 1, respectively. As for all other preceeding studies [1–5] the effective value of the exponent, $\nu$, decreases with increasing concentration. The same least square fit has been applied on chains ranging from length $L = 5$ to $L = 255$. At a concentration of $\phi = 0.81$, the correlation of the curve $\ln(R_e^2)$ *versus* $\ln(L-1)$ with a straight line remains very good, leading to an apparent exponent of $\nu = 0.59 \pm 0.02$ (Fig. 1). The value of $\nu$ remains the same regardless of the chain length investigated. The same holds at $\phi = 0.9025$, with $\nu = 0.59 \pm 0.02$. The slight change in the value of $\nu$ remains very small, and is still within the reported error range. However, at concentration of $\phi = 0.9801$, a least square fit over the same range of chain length, *i.e.*, $5 < L < 255$, gives a poorer correlation, yielding a value of $\nu = 0.63 \pm 0.04$. Both the poorer correlation and the unexpected high value of $\nu$ in comparison with that obtained for $\phi = 0.81$, suggest that $R_e^2(L)$ is not a simple or single power law function of $L - 1$. A snapshot of the system (Fig. 2) at a concentration $\phi = 0.9801$, indeed shows two kinds of chains: small globular chains and longer chains squeezed by the globular chains with an enteric extended conformation. The change of conformation appears for values of $L \sim 55$. Below this chain are globular, and above this, extended. An hypothesis is that the transition appears when the chain is so shrunk that its mean square end-to-end distance, $R^2(L, \phi)$, correspond to that of a globular (Gaussian) chain on a square lattice, $R^2_{Gauss}(L)$. Using the numerical values for a square lattice [17,18], and also using equation (3), the condition $R^2(L, \phi) = R^2_{Gauss}(L)$ is found numerically for $L = 53.6$, in good agreement with the value of $L = 55$. A characteristic squeezing size can, therefore, be defined, depending only on $L$. The data were then analyzed in terms of the two chain population (Fig. 3). The effective exponents are $\nu = 0.53 \pm 0.01$ for the globular chain (last square fit for $5 < L < 55$), and $\nu = 0.78 \pm 0.05$ (last square fit for $55 < L < 400$) for the enteric chains. The same happens at $\phi = 1$ (Fig. 4) where $\nu = 0.5 \pm 0.01$ for the globular chains, and $\nu = 0.85 \pm 0.05$ for the enteric chains. High values of $\nu$ in a simulation occurs often for chains of length $L \sim lp$. The chains are only made of a few basic elements, which are not necessarily monomers.

A classical case is the observation of an apparent value of $\nu$ of the order unity for the coil globule transition in three dimensions [19]: the chain goes through a state where it is made of only a few sub-structures, and may not be long enough to obey an asymptotic behavior. In the present case, the question remains as to what the asymptotic value of $\nu$ could be for the longer chains.

The observed effect could be analyzed on the basis of a short chain/long chain binary mixture [20,21]. However, most of the available studies deal with short chains only, a few times smaller than the long chains. The present system, made of few long chains among many short chains,

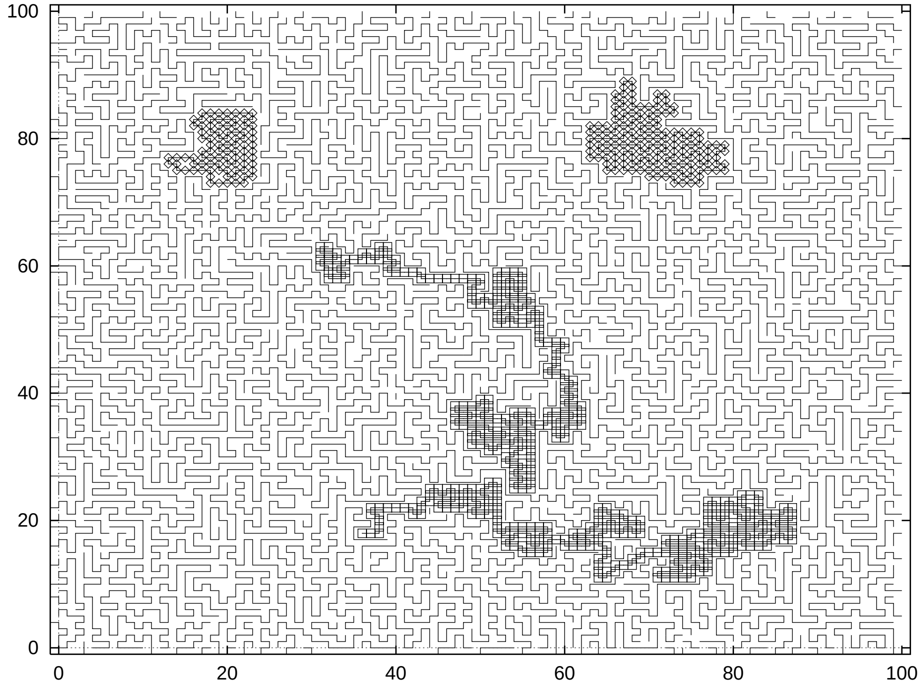

**Fig. 2.** Snapshot of the system for $\phi = 0.9801$ showing the conformation of two small chains (diamonds) and two long chains (squares) in the system.

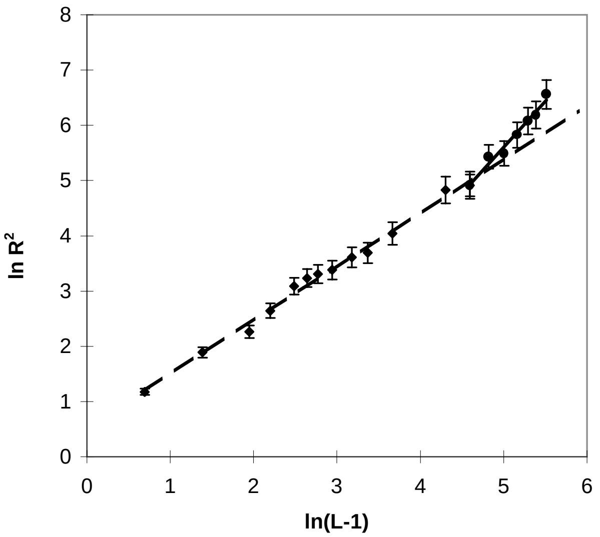

**Fig. 3.** Scaling plot of $R_e^2(L)$ as a function of $(L-1)$ at $\phi = 0.9801$.

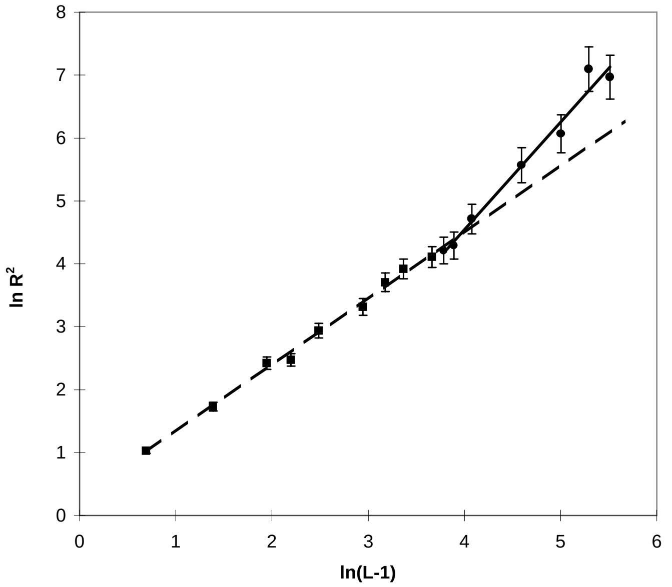

**Fig. 4.** Scaling plot of $R_e^2(L)$ as a function of $(L-1)$ at $\phi = 1$.

has to be compared with polymer/solvent systems [22–24]. For two-dimensional systems, a molecular dynamics simulation [23], showing the effect of the ratio $\sigma_s/\sigma_c$ on the chain radius, is enlightening ($\sigma_s$ and $\sigma_c$ being the solvent and monomer radius, respectively). For $\sigma_s/\sigma_c > 1$, the radius of the polymer chain increases with $\sigma_s/\sigma_c$. In this present work, the small globular chains can be seen as the solvent molecules with a radius $\sigma_s$ necessary greater than $\sigma_c$ (a single lattice site). Hence, the longer chains can be considered as dilute chains in a polydisperse solvent with solvent molecules much larger in size than the monomers. It is suggested that the physical origin of this chain extension is due to packing considerations, with the chain filling the space between solvent molecules [23]. A similar explanation can be given in the present case. This result can also be seen as a generalization to two-dimensions of an observation made on the conformation of a free chain in a dense frozen melt [25]: the free probe chains are stretched through bottlenecks into neighboring wells, with their dimension depending directly on the blob size of the frozen chains.

In order to ensure a gapless packing, the smaller chains fractionate the longer chains into sub-units so that the long chains fill the gaps. These sub-units, like the smaller chains, are similar to disc-like objects whose size distribution influences the packing density [26]. Indeed, it has been observed that in a system of two-dimensional monodisperse dense system, the chains are packed in triangular layers [2], this being the densest packing in two-dimensions.

Moreover, the enteric conformation, made of globular parts of the chain bound to each other instead of one single globule for a chain, is also one of the means to reduce the loss of entropy for shrunk chains. The longer chains with an enteric conformation, are considered as dilute so far. If, however, $E$ is so great that a majority of chains have a contour length greater than the squeezing length ($L > 55$ for the square lattice), they will interact with each other and their behaviour should be described by scaling laws for the semi-dilute regime, with the "monomer" being renormalized by an aggregate containing as many monomers as in the squeezing length.

## Conclusion

The present work shows the appearance of an enteric extended conformation for the longer chain in a two-dimensional polydisperse system. This squeezing of the longer chains by the shorter chains must not be confused with a swelling, as in three dimensions, but is related to a phenomenon similar to the swelling of monodisperse chains in the presence of solvent molecules greater than the monomer size.

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