

# Are polymer melts “ideal”?

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## Abstract

It is commonly accepted that in concentrated solutions or melts high-molecular weight polymers display random-walk conformational properties without long-range correlations between subsequent bonds. This absence of memory means, for instance, that the bond-bond correlation function,  $P(s)$ , of two bonds separated by  $s$  monomers along the chain should exponentially decay with  $s$ . Presenting numerical results and theoretical arguments for both monodisperse chains and self-assembled (essentially Flory size-distributed) equilibrium polymers we demonstrate that some long-range correlations remain due to self-interactions of the chains caused by the chain connectivity and the incompressibility of the melt. Suggesting a profound analogy with the well-known long-range velocity correlations in liquids we find, for instance,  $P(s)$  to decay algebraically as  $s^{-3/2}$ . Our study suggests a precise method for obtaining the statistical segment length  $b_e$  in a computer experiment.

*Key words:* Macromolecular and polymer solutions; polymer melts; swelling; Monte Carlo methods

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## 1. Introduction

Following Flory’s “ideality hypothesis” [1], one expects a macromolecule of size  $N$  (numbers of monomers per chain) in a melt (disordered polymeric dense phase) to follow Gaussian statistics [2,3]. The official justification of this mean-field result is that density fluctuations are small, hence, negligible. One immediate consequence is of course that the mean-squared size of a chain segment of curvilinear length  $s = m - n$  scales as

$$R^2(s) = \langle (\mathbf{r}_{m=n+s} - \mathbf{r}_n)^2 \rangle_n = b_e^2 s, \quad (1)$$

at least if the two monomers  $n$  and  $m$  are sufficiently separated along the chain backbone and local correlations may be neglected ( $s \gg 1$ ). Here,  $b_e$  denotes the statistical segment length [3] and  $\mathbf{r}_i$  the position

vector of monomer  $i$ . Obviously, the chain end-to-end distance is then  $R_e \equiv R(s = N) = b_e \sqrt{N}$ .

Recently, this cornerstone of polymer physics has been challenged both theoretically [4–6] and numerically [6,7] for three-dimensional melts and ultrathin films [5,7]. The physical idea behind the predicted long-rang intrachain correlations is related to the “segmental correlation hole” [2],  $\rho^*(s) \approx s/R(s)^d$ , of a typical chain segment of length  $s$  in  $d$  dimensions. Due to the overall incompressibility of the melt this is thought to set an entropic penalty  $\delta U(s) \approx \rho^*(s)/\rho$  ( $\rho$  being the total density) against bringing two adjacent chain segments together [5]. The swelling of the chains caused by this repulsion is most pronounced for small curvilinear distances where  $\delta U(s)$  is important but vanishes for large  $s$  (see Ref. [5] for logarithmic corrections relevant for ultrathin films,  $d \rightarrow 2^+$ ) at variance to the behaviour of dilute polymer chains in good solvent [2].

In  $d = 3$  dimensions, the segmental correlation hole effect is weak,  $\delta U(s) \propto 1/\sqrt{s}$ , and a standard

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one-loop perturbation calculation [6] can be readily performed following closely Edwards [3]. For instance, for the chain segment size this yields to leading order

$$1 - \frac{R^2(s)}{b_e^2 s} = \frac{\kappa_R}{\sqrt{s}} \text{ with } \kappa_R = \frac{\sqrt{24/\pi^3}}{\rho b_e^3} \quad (2)$$

if intermediate distances larger than the monomer ( $1 \ll s$ ) and smaller than the end-to-end distance ( $s \ll N$ ) are probed. The latter restriction avoids additional universal physics due to chain end effects and polydispersity which may be calculated in principle [6]. In the present study we do not focus on these effects. Note that the l.h.s. should be rigorously zero for an ideal chain with statistical segment length  $b_e$  while the r.h.s. is proportional to the perturbation potential  $\delta U(s)$ .

In this paper, Eq. (2) is checked numerically by means of a well-studied lattice Monte Carlo approach [8] and used to extract a precise value for the statistical segment size  $b_e$  for asymptotically long chains (cf. Figs. 1 and 2). We compare melts containing only monodisperse chains with systems of equilibrium polymers (EP) [9,10] where the self-assembled chains (no closed loops being allowed) have an annealed size-distribution of (essentially) Flory type. Finally, a striking demonstration of the intrachain correlations is obtained by the power-law decay of the bond-bond correlation function (cf. Fig. 3). We begin our discussion by briefly describing the numerical algorithms which allow to sample dense melts containing the large chain sizes needed ( $N \gg 1000$ ) for a clear-cut test of the theory.

## 2. Computational questions

For both monodisperse and equilibrium polymer systems we compare data obtained with the three dimensional bond-fluctuation model (BFM) [8] where each monomer occupies the eight sites of a unit cell of a simple cubic lattice. In all cases presented here cubic periodic simulation boxes of linear size  $L = 256$  containing  $2^{20}$  monomers have been used. These large systems are needed to suppress finite size effects, especially for EP [10]. The monomer number relates to a number density  $\rho = 0.5/8$  where half of the lattice sites are occupied (volume fraction 0.5). It has been shown that for this density the BFM has a low compressibility which is comparable to real experimental melts [8]. The chain monomers are connected by (at most two saturated)

bonds. In monodisperse systems adjacent monomers are permanently linked together (at least if only local moves through phase space are considered). EP, on the other hand, have a finite and constant scission energy  $E$  attributed to each bond (independent of density, chain length and position of the bond) which has to be paid whenever the bond between two monomers is broken. (Apart from this finite scission energy for EP all our systems are perfectly athermal. We set  $k_B T = 1$  and all length scales will be given below in units of the lattice constant.) Standard Metropolis Monte Carlo is used to break and recombine the chains. Branching and formation of closed rings are explicitly forbidden, such that only linear chains are present.

The monodisperse systems have been equilibrated using a mix of local, slithering snake and double pivot moves [8]. This allows to generate ensembles containing about  $10^3$  independent configurations with chain length up to  $N = 4096$  monomers. We have sampled EP systems with scission energies up to  $E = 15$ , the largest energy corresponding to a mean chain length  $\langle N \rangle \approx 6011$ . For EP only local hopping moves are needed in order to sample independent configurations since the breaking and recombination of chains reduces the relaxation times dramatically, at least for large scission-recombination attempt frequencies. In fact, all EP systems presented here have been sampled within four months while the  $N = 4096$  sample of monodisperse chains alone required about three years on the same XEON processor. EP are therefore very interesting from the computational point of view and allow for an efficient test of predictions applying to both system classes.

## 3. Numerical results

We now demonstrate numerically the long-rang intramolecular correlations predicted by theory. Data for both monodisperse and equilibrium polymers (open symbols) are presented. As one expects, the size-distribution of polymers is found irrelevant for small segments,  $s \ll \langle N \rangle$ . Note that averages are taken over all possible pairs of monomers ( $n, m = n + s$ ) and, hence, the statistics deteriorates for large  $s$ . For clarity and to focus the discussion on internal correlations without chain end effects, data points for large  $s$  have been omitted for most of the indicated samples. For our flexible BFM chains already small curvilinear distances of about  $s \approx 10$

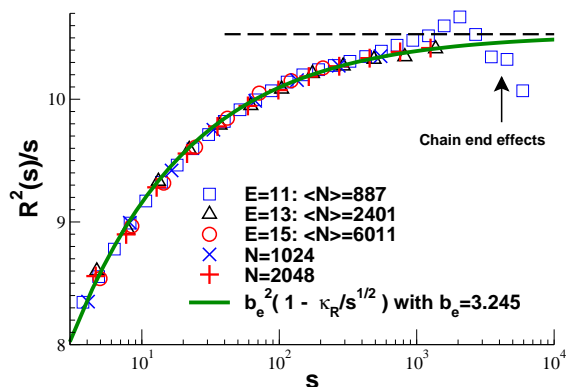


Fig. 1. Curvilinear distance  $R^2(s)/s$  for monodisperse chains and equilibrium polymers (EP) obtained by Monte Carlo simulation of the bond-fluctuation model (BFM) vs. curvilinear distance  $s$ . We use log-linear coordinates to emphasize the power-law swelling over several orders of magnitude of  $s$ . The data points approach the asymptotic behaviour from below, i.e. the chains are swollen, as predicted by Eq. (2). Provided  $s \ll \langle N \rangle$ , both system classes are identical. For larger  $s$  intricate chain end effects become relevant — especially for the polydisperse EP as indicated for the scission energy  $E = 11$  — which are out of the scope of this study. The averages are taken for all possible monomer pairs ( $n, m = n + s$ ). The statistics deteriorates, hence, for large  $s$ .

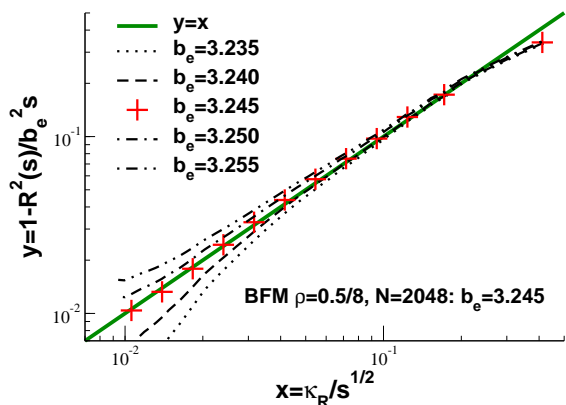


Fig. 2. Replot of the segment size  $R(s)$ , as suggested by Eq. (2), for monodisperse chains of length  $N = 2048$  for different trial statistical segment lengths, as indicated. The bold line for the value  $b_e \approx 3.245$  shows that the correction is indeed proportional to the correlation hole,  $1/\sqrt{s}$ . This procedure is very sensitive to the value chosen and allows for a precise determination. The same  $b_e$  allows to collapse data points from all systems (not shown) if  $s \ll \langle N \rangle$  and  $100 \ll \langle N \rangle$ .

are well fitted by the theory, provided the *total* chain length is large,  $\langle N \rangle \gg 10^3$ .

The size  $R(s)$  of curvilinear chain segments of length  $s$ , as defined in Eq. (1), is presented in Figs. 1 and 2. The first figure clearly shows that the chains are swollen. As predicted, the asymptotic

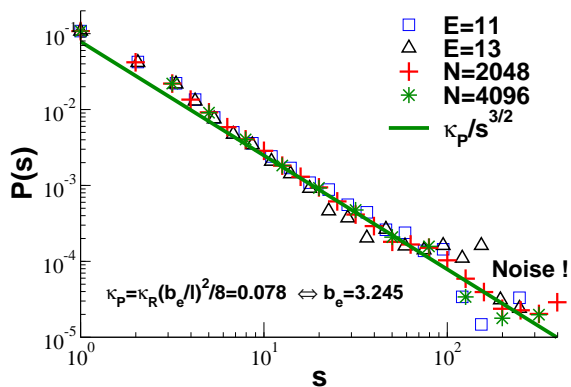


Fig. 3. The bond-bond correlation function  $P(s)$  for both system classes considered (at number density  $\rho = 0.5/8$ ) as a function of the curvilinear distance  $s$ . Provided that  $1 \ll s \ll \langle N \rangle$ , all data sets collapse on the power-law slope (bold line) predicted by Eq. (4). The coefficient  $\kappa_P$  indicated is consistent with a statistical segment length  $b_e \approx 3.245 \pm 0.005$ .

Gaussian behaviour  $R^2(s)/s \rightarrow b_e^2$  (dashed line) is approached from below and the deviation decays as  $\delta U(s) \propto 1/\sqrt{s}$  (bold line). (The more intricate non-monotonous behaviour for large  $s$  for both system classes, especially for EP, is indicated for one example with scission energy  $E = 11$ .)

Computationally,  $R(s)$  is an important quantity since it allows for the precise determination of the statistical segment length  $b_e$  by extrapolation to asymptotically large segment sizes by means of the one parameter fit suggested by Eq. (2). The bold line indicated corresponds to  $b_e = 3.245$  which nicely fits the data over several decades in  $s$ . Note that a systematic *underestimation* of the true statistical segment length would be obtained by taking simply the largest  $R^2(s)/s \approx 3.23^2$  value available, say, for monodisperse chains of length  $N = 2048$ . A better representation for performing the fit is to plot  $R^2(s)/s$  vs.  $1/\sqrt{s}$  in linear coordinates (not shown). This has the disadvantage that data points with  $s \gg 10$  are less visible. A much more precise representation is given in Fig. 2 where we plot in logarithmic coordinates for different trial values of  $b_e$  the l.h.s. vs. the r.h.s. of Eq. (2), i.e. the non-Gaussian deviations against the depth of the segmental correlation hole. Since both sides of the relation must be identical (neglecting higher order perturbation corrections) the fit value should yield a data collapse on the bisection line (bold line). Note that our best value yields a collapse over more than an order of magnitude *without* curvature.

An even more striking violation of Flory's ide-

ality hypothesis may be obtained by computing the bond-bond correlation function,  $P(s) = \langle \mathbf{l}_{m=n+s} \cdot \mathbf{l}_n \rangle_n / l^2$ . Here,  $\mathbf{l}_i = \mathbf{r}_{i+1} - \mathbf{r}_i$  denotes the bond vector between two adjacent monomers  $i$  and  $i + 1$  and  $l(\rho = 0.5/8) \approx 2.634$ , the (mean-squared) bond length. It can be shown that  $P(s)$  must decay exponentially if no long-rang memory effects were present due to the multiplicative loss of information transferred recursively along the chain [1]. The bond-bond correlation function is in fact the second derivative of  $R^2(s)$  with respect to  $s$

$$P(s) l^2 = -\frac{1}{2} \frac{d^2}{ds^2} R^2(s), \quad (3)$$

hence, it allows us to probe the non-Gaussian corrections directly without the trivial ideal contribution [6]. (We remember that the velocity correlation function of a fluid is similarly related to the second derivative with respect to time of the mean-square displacement.) This relation together with Eq. (2) immediately yields an algebraical decay

$$P(s) = \frac{\kappa_P}{s^{3/2}} \text{ with } \kappa_P = \kappa_R (b_e/l)^2 / 8 \quad (4)$$

of the bond-bond correlation function for dense solutions and melts, rather than the exponential cut-off expected from Flory's hypothesis.<sup>1</sup> This prediction is perfectly confirmed by the data collapse presented in Fig. 3 for both system classes. In principle,  $b_e$  may also be measured from the power-law amplitude, however, to less accuracy than the previous method (Fig. 2).

#### 4. Conclusion

In this study we have challenged the famous ideality hypothesis suggested half a century ago by Flory. Testing recent theoretical predictions [5,6] by means of extensive lattice Monte Carlo simulations [8] of linear polymer melts having either a quenched and monodisperse or an annealed size-distribution we provide strong evidence that long-range correlations exist in dense polymer melts which tend to swell the

<sup>1</sup> Interestingly, the scaling of the bond-bond correlation function is related to the long-time power-law correlations of the velocity-correlation function found in dense fluids nearly forty years ago [11]. Albeit the *constraints* which cause the self-interactions are different (momentum conservation for fluid particles, incompressibility for polymer chains) the weight with which this constraints increase the stiffness of the random walker is in both cases proportional to the return probability,  $1/s^{d/2}$ , of a random walker in  $d$  dimensions.

chains. Their most striking effect is the power-law asymptote for the bond-bond correlation function suggesting a profound analogy with the well-known long-range velocity correlations in liquids [11]. We finally emphasize that our results rely on *generic* physics which should apply to all polymer melts containing *long* and preferentially *flexible* chains.

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