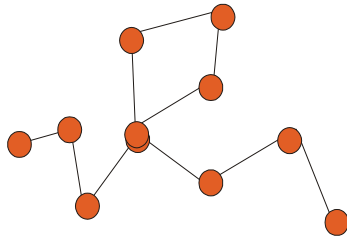


Long Range Correlations in Polymer Melt

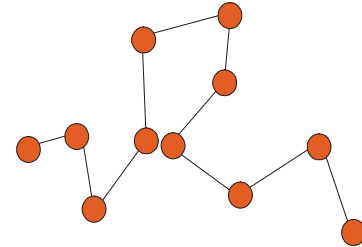
J.P. Wittmer, H.Meyer, J.Baschnagel,
A.Johner, S.Obukhov, L.Mattioni,
M.Muller, A.N.Semenov

ICS, Strasbourg, Florida and other places

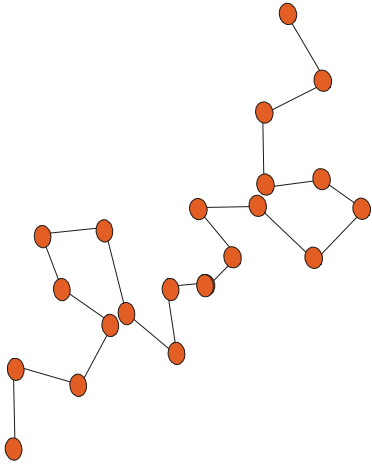
Supported by LEA



1. History
2. Theory
3. Simulation



History



It is commonly accepted that in concentrated solutions or melts high-molecular weight polymers display random-walk conformational properties without long range memory between subsequent bonds.

This has been anticipated already in the 1950s by Flory in his famous "ideality hypothesis".

The absence of memory (multiplicative loss of information along the chain) means that the correlation function,

$C(n)$, of two bonds separated by n monomers along the chain should exponentially decay with n . This is the standard basis

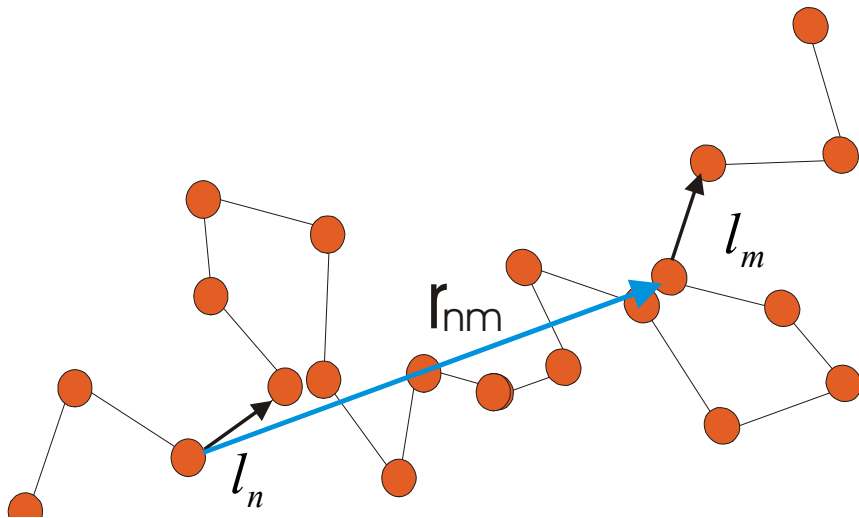
for defining an important experimental measure of chain stiffness, the persistence length.

Recent developments:

Non-Gaussian corrections to end-to-end distance (Johner, Semenov 2003)

Long range forces, Anti Casimir effect in a polymer melt (Obukhov, Semenov 2004-2005)

Single Chain



$$r^2 \approx S^{2\nu}$$

$$\langle l_n \bullet l_m \rangle = \langle \partial_n r_n \bullet \partial_m r_m \rangle = -\frac{1}{2} \partial_n \partial_m \langle r_{nm}^2 \rangle$$

$$\langle l_n \bullet l_m \rangle \approx S^{-\omega} \quad \omega = 2 - 2\nu \approx 0.824$$

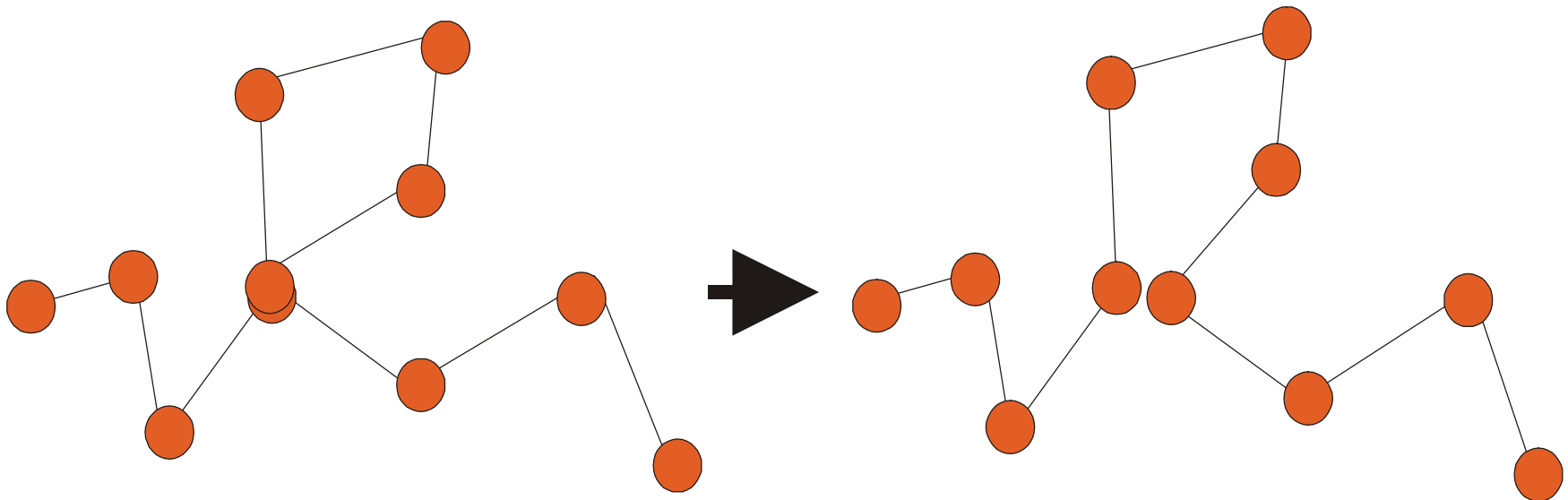
For Gaussian configuration

$$\langle l_n \bullet l_m \rangle = 0$$

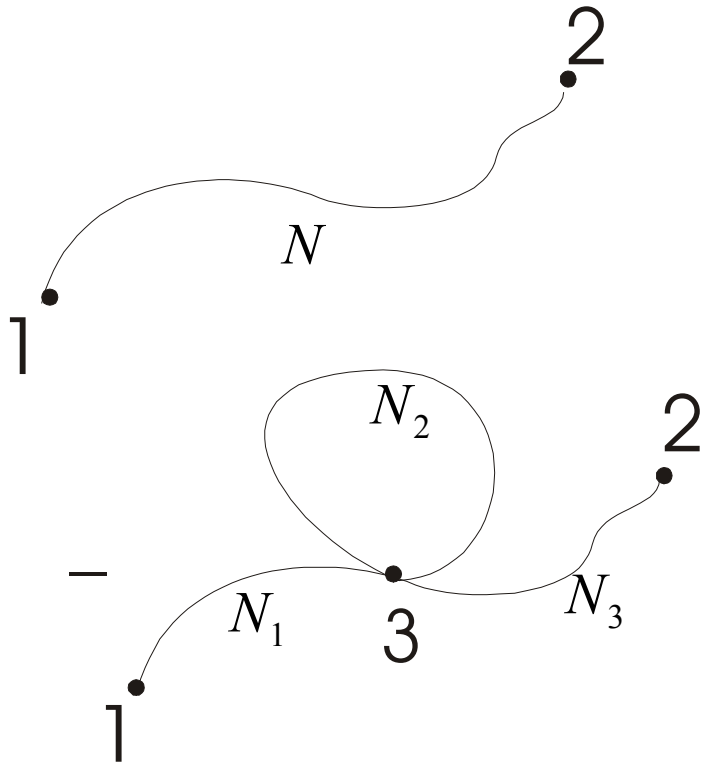
Configuration of a chain in a melt

If configuration of a single chain in a melt is Gaussian, than should be $N^{1/2}$ self intersections, what to do with them?

As a result, the end-to-end distance between the ends of a polymer chain is slightly changed:



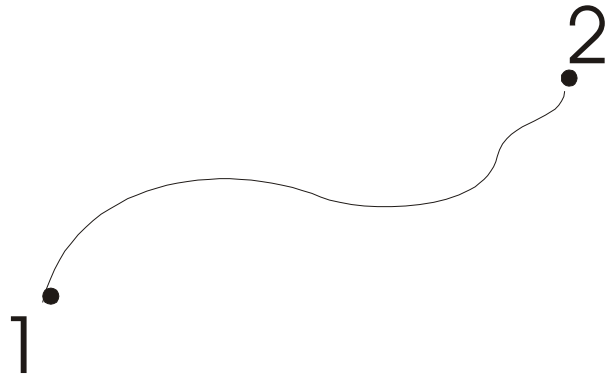
Single chain perturbed



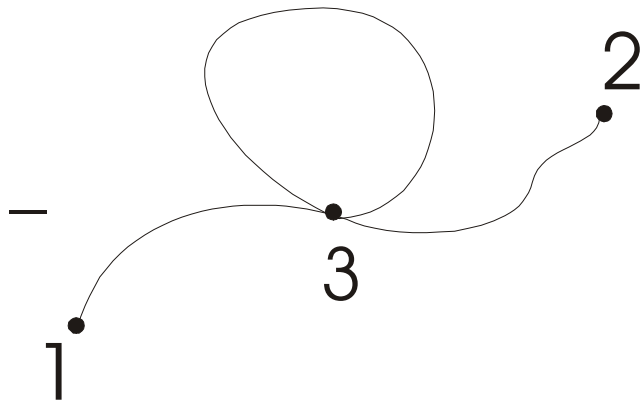
$$G_N(x_1, x_2) = \frac{1}{(2\pi N)^{d/2}} e^{-\frac{x^2}{2N}}$$

$$G^1_N(x_1, x_2) = \int d^d x_3 \sum_{N_1+N_2+N_3=N} G_{N_1}(x_1, x_3) G_{N_2}(x_3, x_3) G_{N_3}(x_3, x_2)$$

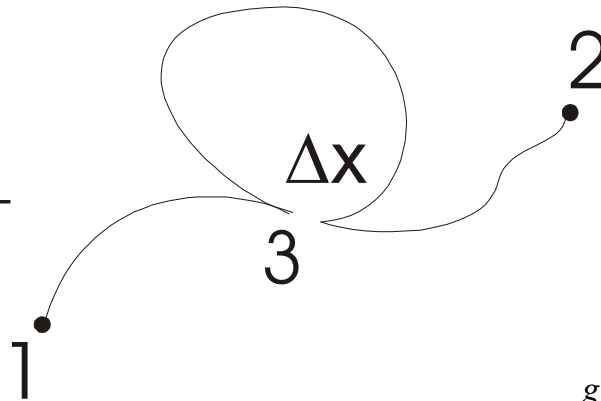
Single chain in a melt.



$$G_N(x_1, x_2) = \frac{1}{(2\pi N)^{d/2}} e^{-\frac{x^2}{2N}}$$



+



$$g \rightarrow g \left(1 - e^{\vec{\Delta x} \cdot \vec{\nabla}} \right) \approx \frac{g}{6} \overline{(\Delta x)^2} \nabla^2$$

$$G_N^1(x_1, x_2) = -g \int d^d x_3 \sum_{N_1+N_2+N_3=N} G_{N_1}(x_1, x_3) G_{N_2}(x_3, x_3) G_{N_3}(x_3, x_2) +$$

$$+ g \int d^d x_3 \sum_{N_1+N_2+N_3=N} G_{N_1}(x_1, x_3) G_{N_2}(x_3, x_3 + \Delta x) G_{N_3}(x_3 + \Delta x, x_2)$$

Results

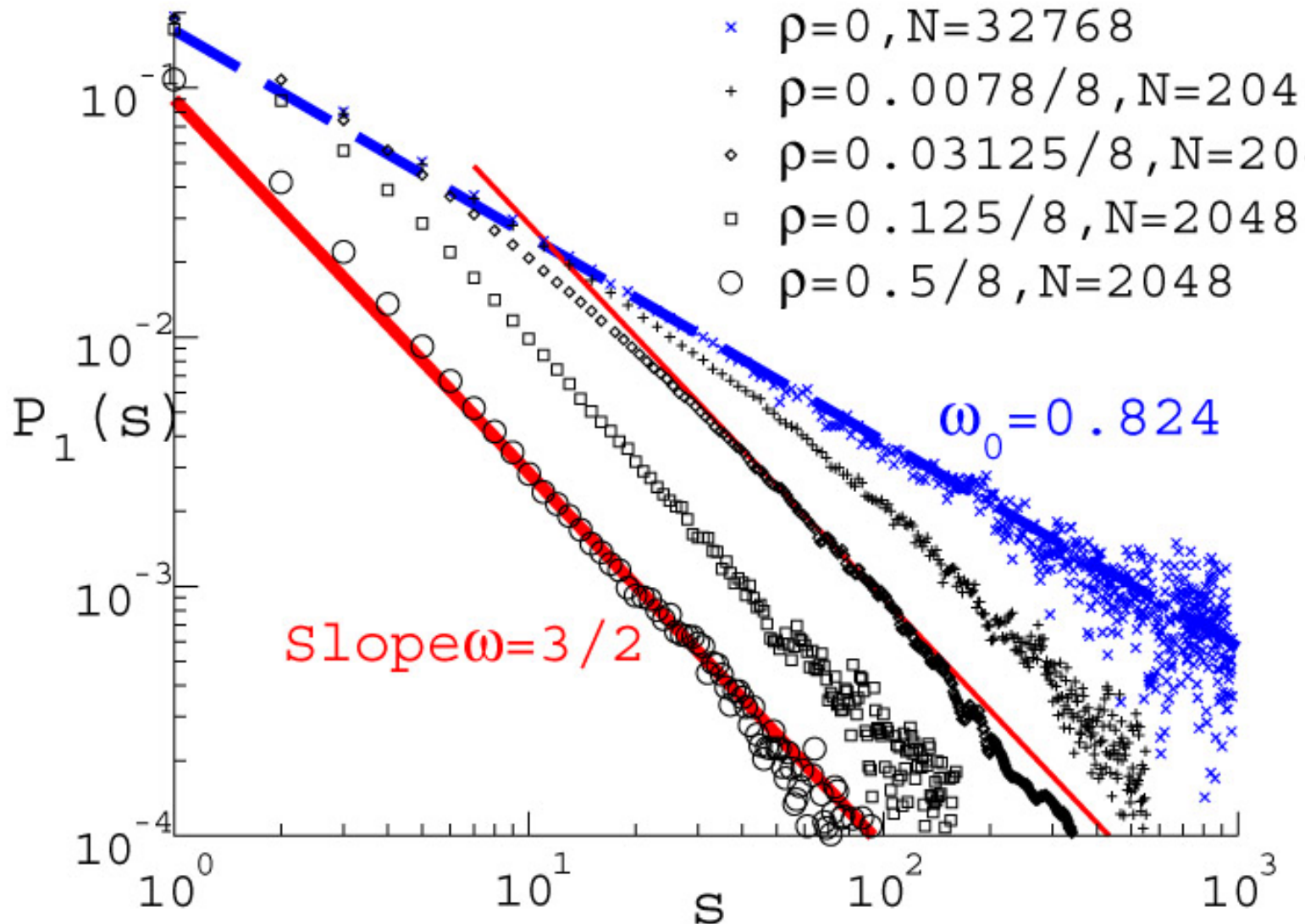
For bond-bond correlations:

$$P_1(s) = \langle l_n \bullet l_m \rangle = c_a s^{-3/2} \quad c_a = \frac{\sqrt{6/\pi^3}}{4\rho l^3}$$

For distance between monomers:

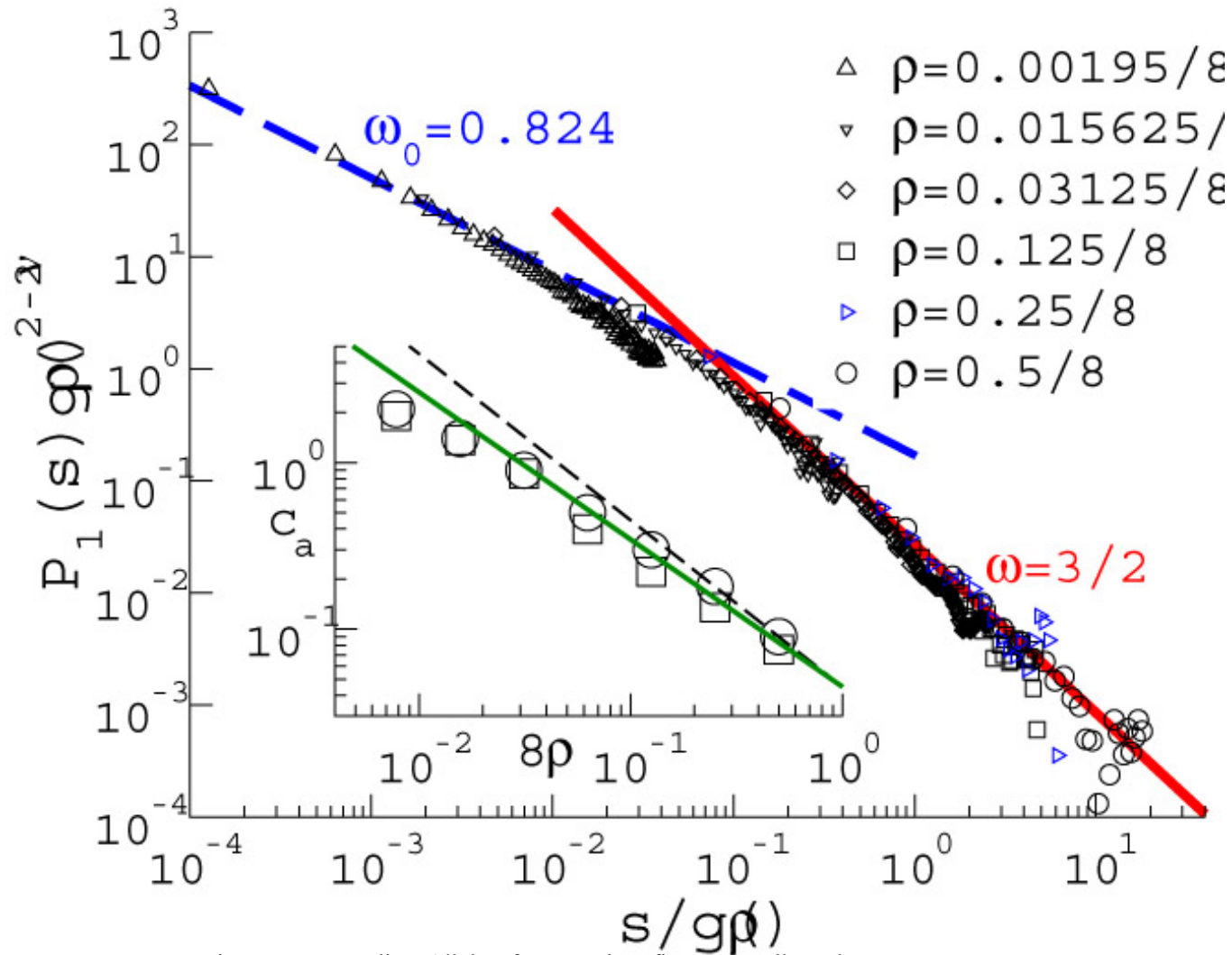
$$r^2(s) = b^2 - as^{1/2} \quad a = 8c_a l^2$$

Numerical results 1



Bond-bond correlation function for different densities. The two power law slopes are indicated by blue and red lines. The crossover corresponds to the number monomers per density blob.

Numerical results 2



Density crossover scaling. All data from previous figure are collapsed on a master plot. The insert showing the dependence of the amplitude of the correlations on the density. The prediction for the melt regime is indicated by bold line. No adjustable parameters.

Summary

- We have shown that long range correlations in polymer melts exist due to both chain compressibility and connectivity.
- Most striking effect – the the power law asymptote for the bond-bond correlation function.
- Non monotonous behavior (hump) in Kratky plot due to non-Gaussian corrections.
- Revision of standard operational definition of persistent length.
- Profound analogy with the well-known long range (algebraic) velocity correlations in liquids and granular materials

