ADSORPTION OF SEMIFLEXIBLE POLYMERS ON HOMOGENEOUS SURFACES

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ABSTRACT

We investigate the problem of adsorption of a single semiflexible polymer chain on to a planar, homogeneous surface using off-lattice Monte Carlosimulations. Adsorption characteristics were studied at different temperatures for chains of various stiffness. We have found that the stiffer chains adsorb more to the surface and the adsorption transition takes place at a higher temperature when compared to that of the flexible chains. As stiffness increases, the adsorption transition is found to be sharper. The computed persistence length is found to grow linearly with the bending energy above the transition temperature, however, it shows a power-law behavior in the adsorbed state. In the ground state, the parallel size of the stiffer chain is found to be much larger than that of the corresponding flexible polymer chain. The classical   scaling laws for the flexible chains were tested for the stiffer chains and   found that they are well obeyed, indicating that the universal properties of the chain measured over it's whole dimension are unaffected by the local stiffness of the chain.

O. Kratky, G. Porod. Rec. Trav. Shim. **68**, 1106 (1949)

Fatty Acids Properties

Many polymers are rigid to certain extent mainly due to electronic delocalisation and steric effects. Some important examples of such stiff chains can be found in biology, as actin filaments, microtubules, DNA and collagen. On a local length scale, the stiffness is very prominent and is expected to cause significant changes in the macromolecular properties. As an example, observe the change in the melting temperature of fatty acids that differ in the number of unsaturated bonds and chain length.

$C_{18}H_xO_2$
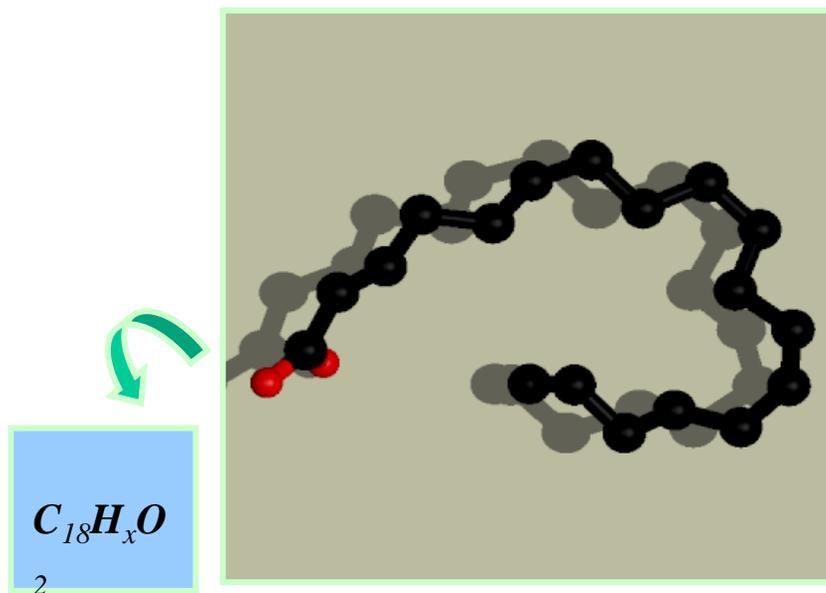
	%Oleic (1)	%Linoleic (2)	T_m/C
Olive	84.4	4.6	-6.0
Sunflower-seed	25.1	66.2	-17.0
Butterfat (Palmitic (0))			32

	T_m/C
Myristic (C_{14})	54
Palmitic (C_{16})	62
Stearic (C_{18})	69

STIFFNESS
CHAIN LENGTH

→ **ADSORPTION PROPERTIES**

NUMERICAL MODEL

We have considered a polymer chain confined in a unit box with peridic boundary conditions in the *x-y* domain. The polymer chain is represented by a *pearl-necklace* model containing *N* beads of diameter σ. The stiffness of the polymer chain is introduced through the bending potential U_B. Monomers units interact with an impenetrable planar surface (z=0) with adsortion energy ε < 0.
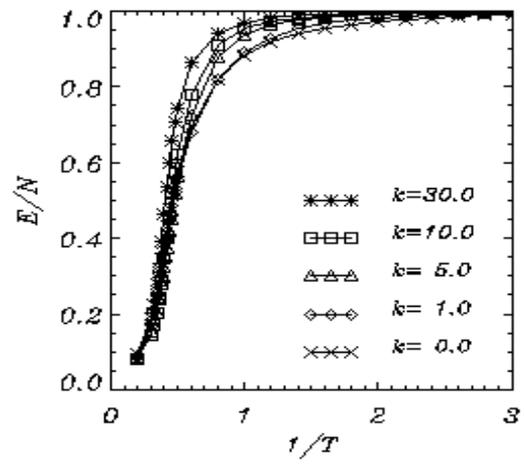
• **Metropolis MC algorithm**

$$U = U_A + U_B + U_{steric}$$

$$U_A = n_c \varepsilon$$

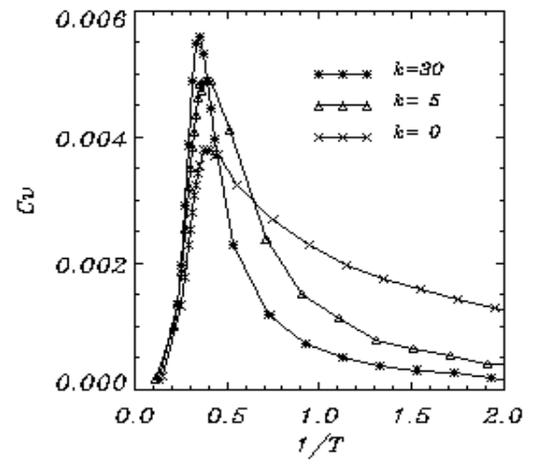$$U_B = \sum_{\theta} \kappa (1 + \cos\theta)^2$$

$$U_{steric} = \sum_{i,j=1}^{N} V(r_{ij})$$

$$T \equiv \frac{k_B T}{|\varepsilon|}$$

T_C (N,k)
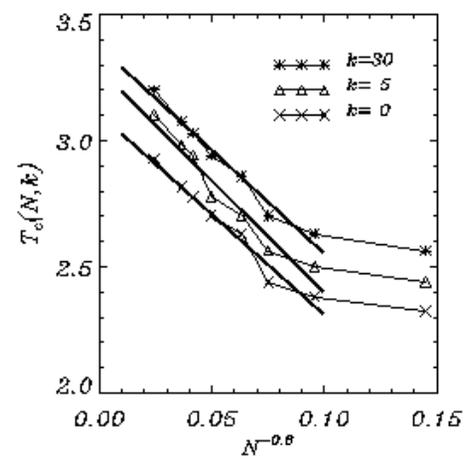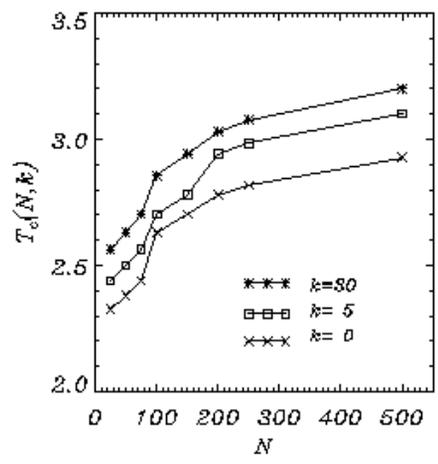
Average adsorption energy per monomer as a function of the Temperature for selected values of the stiffness parameter κ

Specific heat of the chain for *N=100* and different rigidities
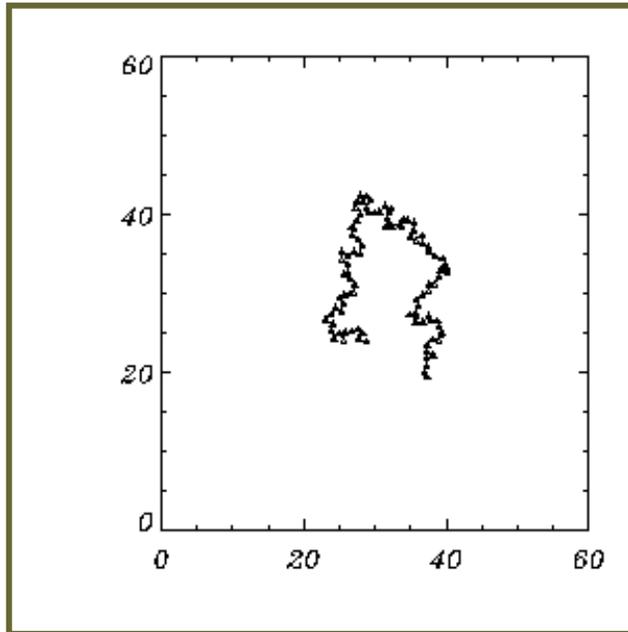
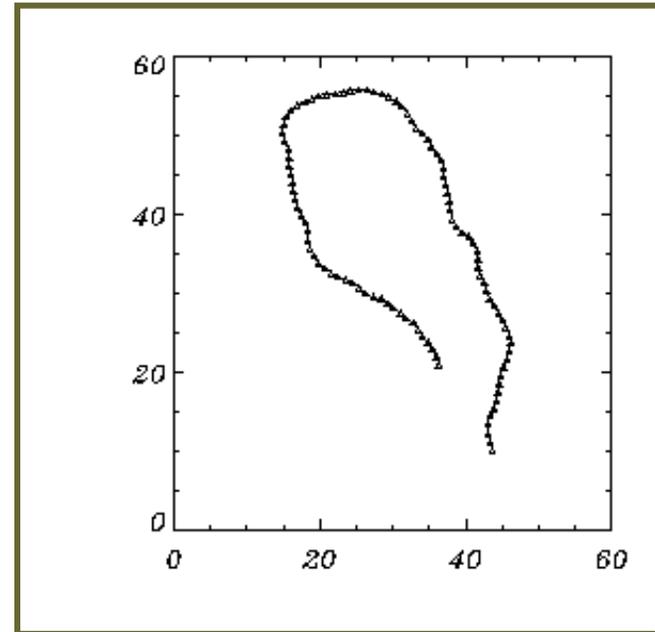Determination of the transition temperatures

$$Tc(N,\kappa) \approx N^{-\phi}$$

$$Tc(\infty,\kappa)$$

Critical adsorption temperatures for infinite chain length $\phi=0.59$ is the critical cross-over exponent.
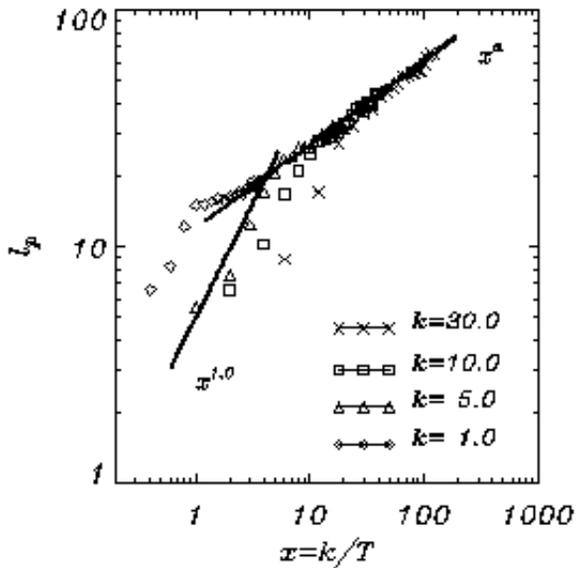
POLYMER ADSORBED ON THE SURFACE (TOP VIEW)

$\kappa = 0$

$\kappa = 10$

Persistence Length on the adsorbed state
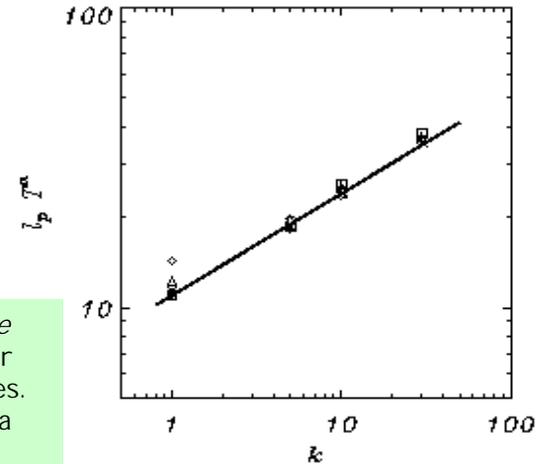
$$\langle u(r)\cdot u(0)\rangle = \exp(-r/l_p)$$

Free energy of a polymer chain subject to a bending moment

$$A(R) = \frac{3}{2}\frac{k_B T}{N\sigma^2}R^2 + \frac{\kappa}{R} + \frac{1}{2}\upsilon k_B T \frac{N^2}{R^3}$$

At low **T**, *(large persistence length)* the excluded volume is neglected in front of the other terms. By minimizing A(R) :

$$l_p \approx \left(\frac{\kappa}{k_B T}\right)^{1/3}$$

Persistence length as a function of κ/T. The solid lines indicate the two observed regimes above and below the adsorption transition.

Scaling of the persistence length. The symbols refer to different Temperatures. α=**0.35**. The solid line as a slope of **1/3**.

Scaling of the *averaged adsorbed energy* with the persistence length. In the figure we present the case for *N=100.*
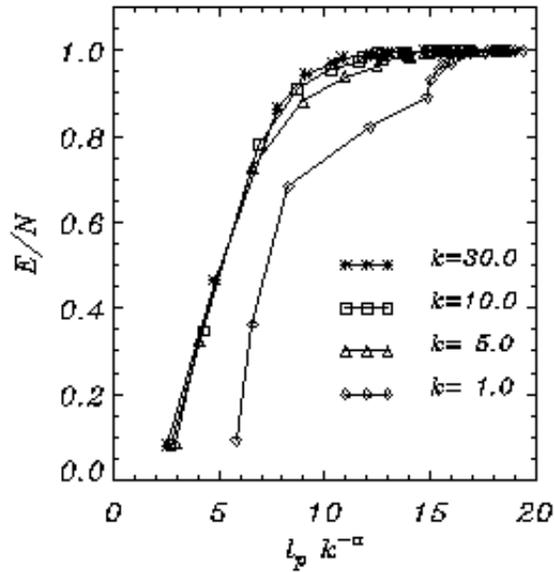
As the persistence length *lp* increases, the semiflexible chain can be seen as an ideal chain *(v=1/2)* consisting in *N/lp* segments of size *lp*. In the figure the straight line has a slope of 0.5

$$\left\langle R^2 \right\rangle^{1/2} = l_p \left(\frac{N}{l_p} \right)^v \approx l_p^{1-v}$$
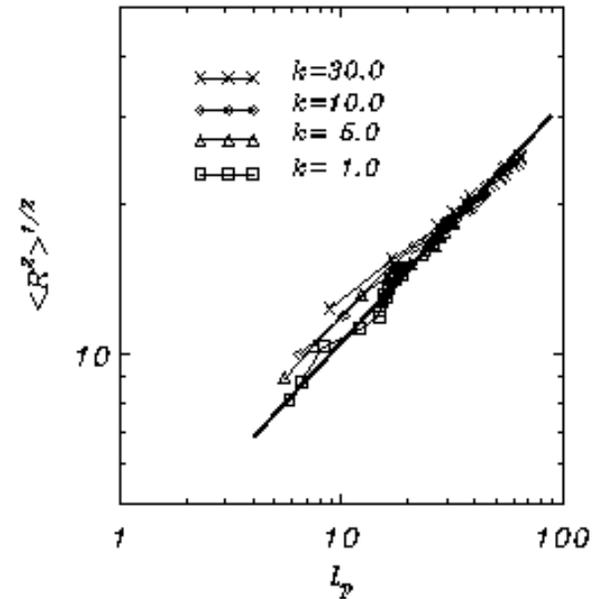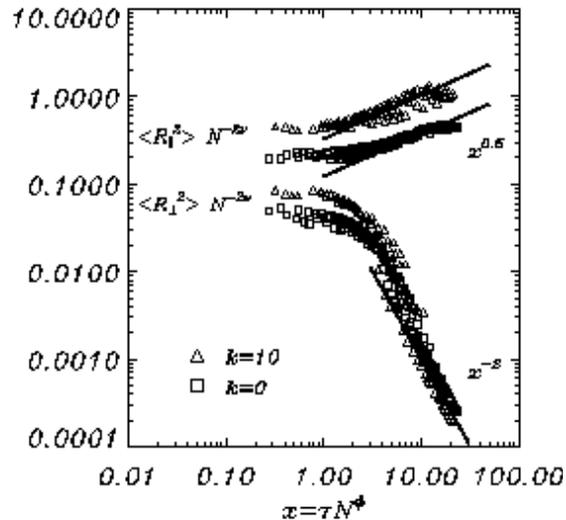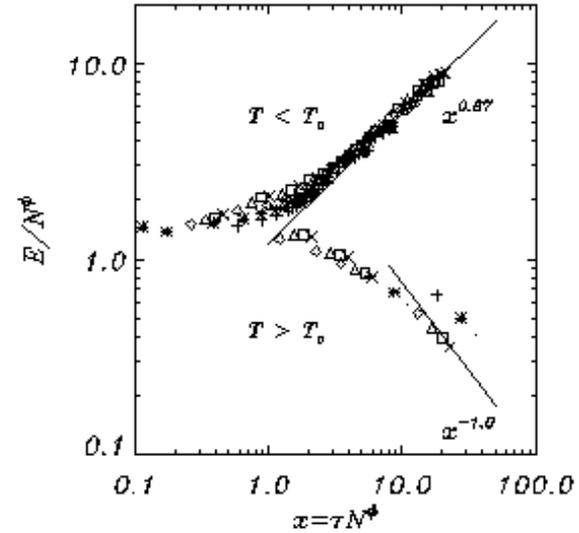
SCALING ANALYSIS

$$E_N / N^\phi = h(\tau N^\phi)$$

$$h(x) \, \alpha \begin{cases} x^{-1}, & x \to \infty \\ const., & x \to 0 \\ |x|^{(1-\phi)/\phi} & x \to -\infty \end{cases}$$

$$\tau = \frac{T - T_c(\infty, \kappa)}{T_c(\infty, \kappa)}$$

$$\left\langle R_\perp^2 \right\rangle = N^{2\nu} f_\perp^2(\tau N^\phi)$$

$$\left\langle R_\parallel^2 \right\rangle = N^{2\nu} f_\parallel^2(\tau N^\phi)$$

$$f_\perp(x) \approx |x|^{-\nu/\phi} \qquad x \to -\infty$$

$$f_\parallel(x) \approx |x|^{(\nu_{d=2} - \nu)/\phi}$$

CONCLUSIONS

ADSORPTION INCREASES WITH CHAIN LENGHT AND STIFFNESS.

THE PERSISTENCE LENGTH FOLLOWS THE KRATKY-POROD MODEL BELOW Tc, BUT CHANGES UPON ADSORPTION.

THE ADSORPTION ENERGY AND CHARACTERISTIC POLYMER SIZE OBEY THE CLASSICAL SCALING LAWS WITH A CROSSOVER EXPONENT $\phi=0.59$.