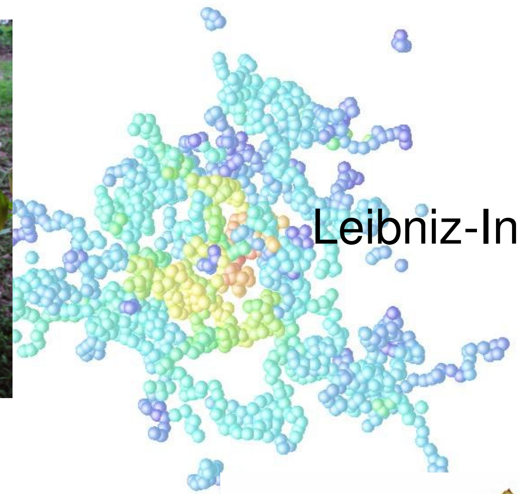
Eine kurze Geschichte der Polymerphysik von Naturkautschuk zu Nanostrukturen



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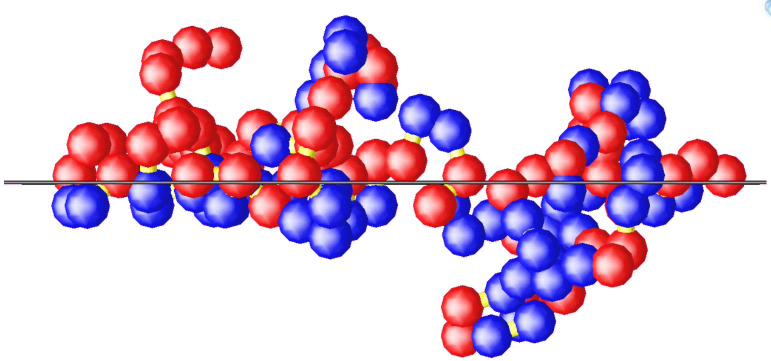

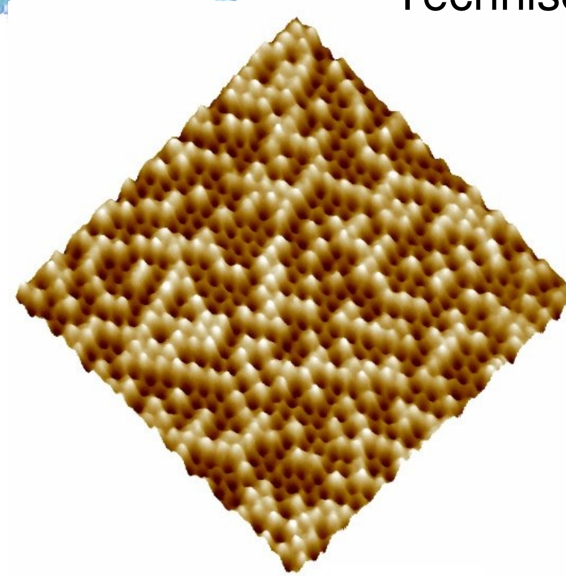

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Berlin, den 15.12. 2008

Charles Goodyear (1800 - 1860)

Hermann Staudinger (1881 - 1965)

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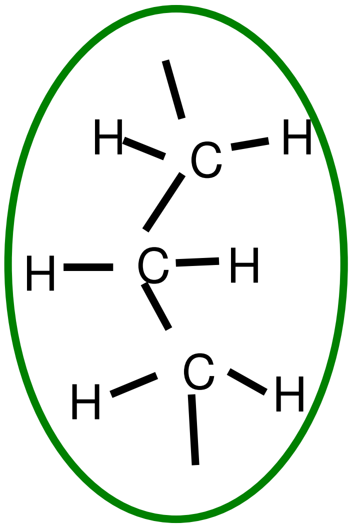
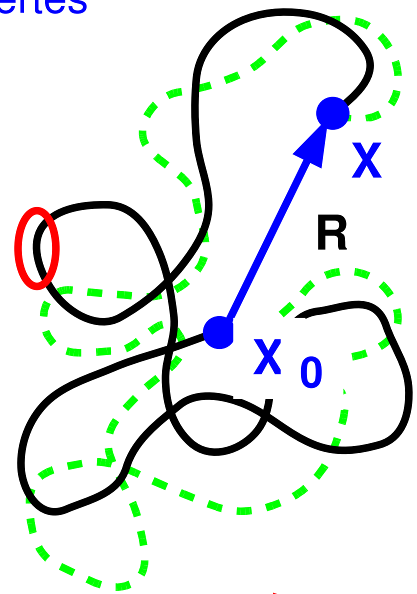
Konformationsentropie eines Polymers



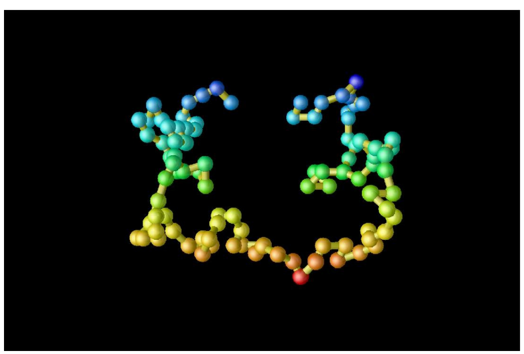
Vergröbertes Bild



Viele Konformationsalternativen ohne Energieaufwand

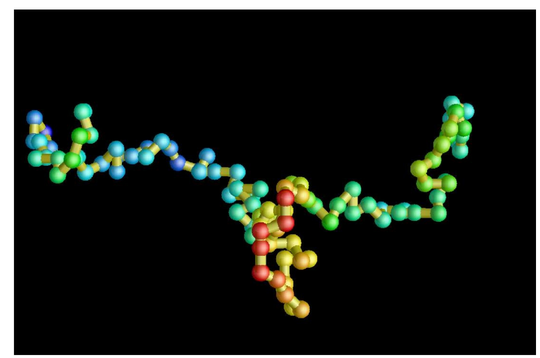
$$S = k \ln(\Sigma\, Wege)$$

effektive Segmentlänge l



Entropie wird reduziert

$$f = -T\,\nabla S(x)$$



Einfachstes Modell: Unkorrelierte Segmentorientierungen

$$\langle \vec{l}_k \vec{l}_m \rangle = l^2 \delta_{km} \longrightarrow \langle \vec{R}^2 \rangle = l^2 N$$ (Gauß-Knäuel)

allgemein: $R \sim N^{\nu}$

Zustandssumme und Schrödingergleichung

Was ist die Zustandssumme eines Kettenmoleküls?

Sir Sam F. Edwards

Wechselwirkungen

$$Z(\boldsymbol{x},\boldsymbol{x_0};N)=\int_{Pfade}\exp\{-\frac{1}{kT}\int_0^N ds\,V(\boldsymbol{r}(s))\}$$

Kettenzusammenhang (harmonisch)

$$Z=\int D[\boldsymbol{r}(s)]\exp\{-\frac{d}{2l^2}\int_0^N ds\left(\frac{d\boldsymbol{r}}{ds}\right)^2-\frac{1}{kT}\int_0^N ds\,V(\boldsymbol{r}(s))\}$$

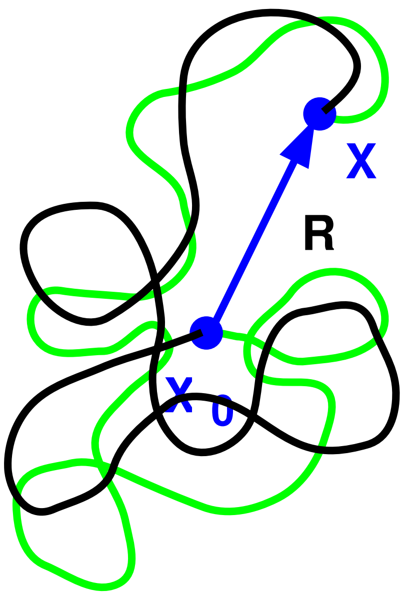
Segmentlänge

(Feynman)

Differentialgleichung für die Zustandssumme

$$\frac{\partial}{\partial N}Z(\boldsymbol{x},\boldsymbol{x_0};N)=\frac{l^2}{2d}\Delta_x Z(\boldsymbol{x},\boldsymbol{x_0};N)-\frac{1}{kT}V(\boldsymbol{x})\cdot Z(\boldsymbol{x},\boldsymbol{x_0};N)$$

$$\frac{\partial}{\partial N} Z(\boldsymbol{x},\boldsymbol{x_0};N) = \frac{l^2}{2d}\nabla_x Z(\boldsymbol{x},\boldsymbol{x_0};N) - \frac{V(\boldsymbol{x},s)}{kT}\cdot Z(\boldsymbol{x},\boldsymbol{x_0};N)$$

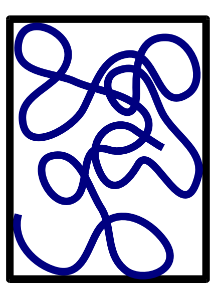


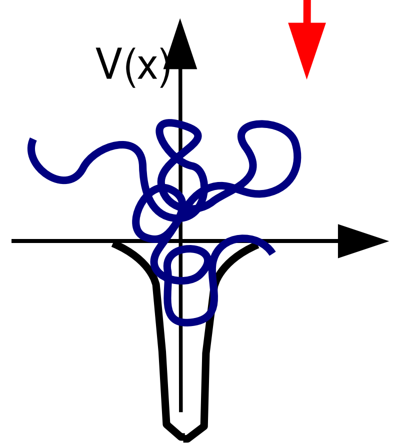
Homopolymer:

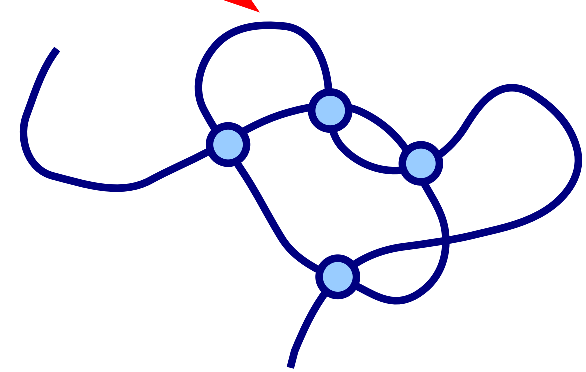
$$V(\boldsymbol{x},s) = V(\boldsymbol{x}) \rightarrow Z = \sum_q \exp\{-\lambda_q N\}\varphi_q(\boldsymbol{x})\varphi_q(\boldsymbol{x_0})$$

Ground State Dominance (GSD)

$$\boxed{\frac{l^2}{2\mathrm{d}}\Delta\varphi_q - \frac{1}{kT}V\varphi_q = \lambda_q\varphi_q}$$







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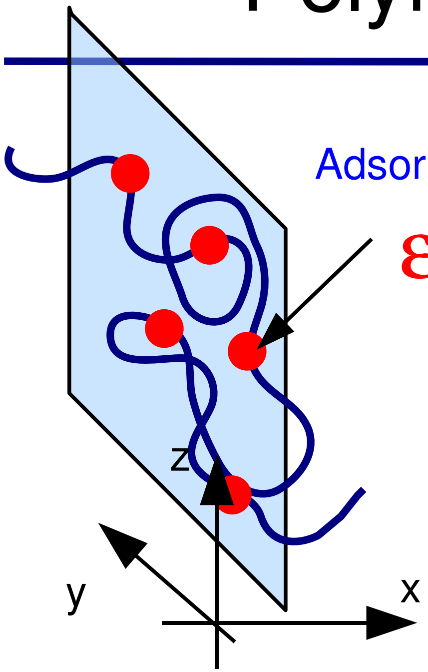
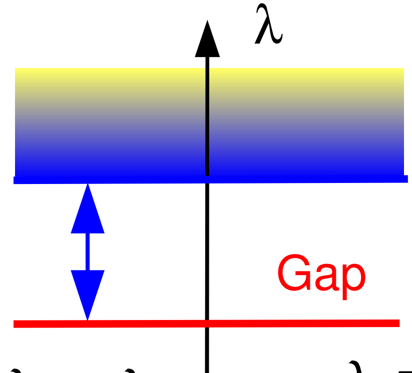
Polymere an Grenzflächen - Lokalisation



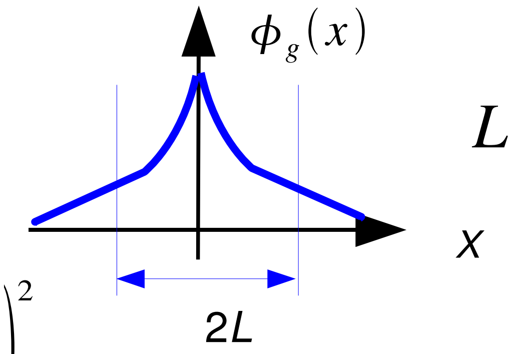
$V(x) = -\epsilon l \delta(x)$

Adsorptionsenergie pro Monomer



$\Delta\lambda = -\lambda_g$ $\qquad \lambda_g = -\frac{1}{2}\left(\frac{\epsilon}{kT}\right)^2$

Lokalisationslänge



$$L = \frac{kTl_x}{\epsilon}$$

GSD für $y = \Delta\lambda N \gg 1$ $\qquad Z = \sum_q \exp\{-\lambda_q N\}\varphi_q(\boldsymbol{x})\varphi_q(\boldsymbol{x_0})$

Adsorptionsübergang: $\boxed{\epsilon N^{1/2} \simeq kT}$

Freie Energie in GSD: $F \simeq N k T \lambda_g$

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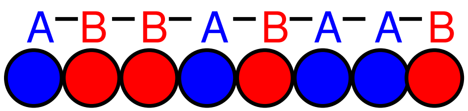
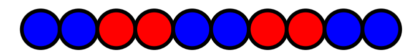
Kopolymere und Paulsche Fallen



$\eta(s)$ - Konfigurationsfunktion ± 1

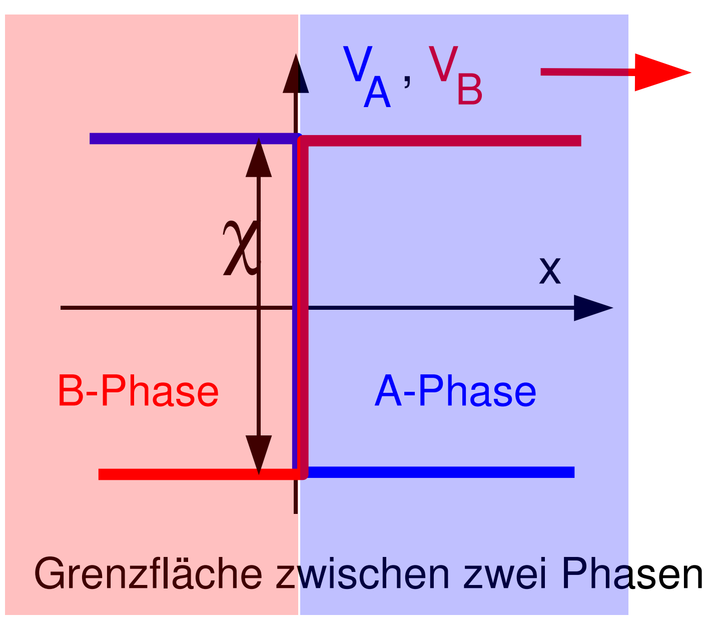


$\eta(s)=\eta(s-b)$ Alternierendes Kopolymer

$[\eta(s)\eta(t)]=\delta(s,t)$ Zufälliges Kopolymer

$$\frac{\partial}{\partial s} Z = \frac{l^2}{2d}\Delta_x Z - \boxed{V(\boldsymbol{x},s)\cdot Z}$$

Paulsche Falle



$$V(x,s)=\eta(s)\cdot\chi\cdot T(x)$$

Renormierung:
Homopolymer aus Diblöcken

Störungsrechnung

$$\epsilon \sim -\chi^2 b^2$$

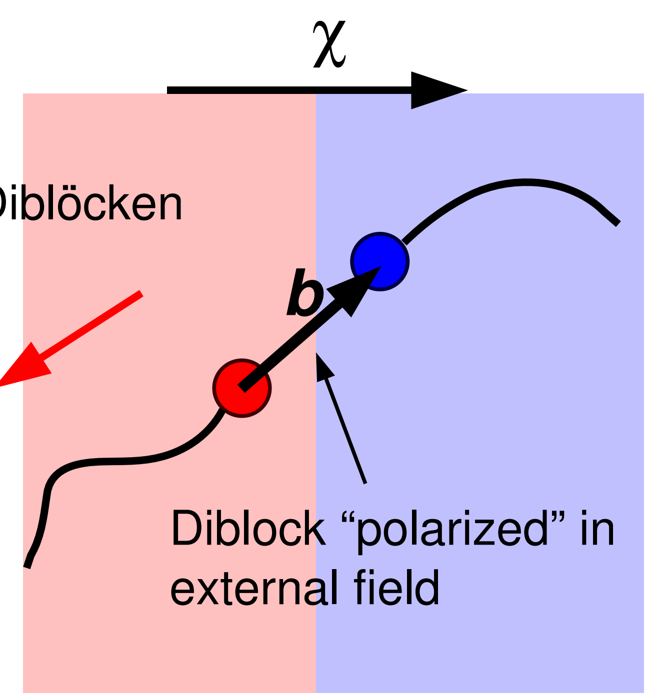


Abbildung auf Problem der Adsorption an durchdringbaren Grenzflächen

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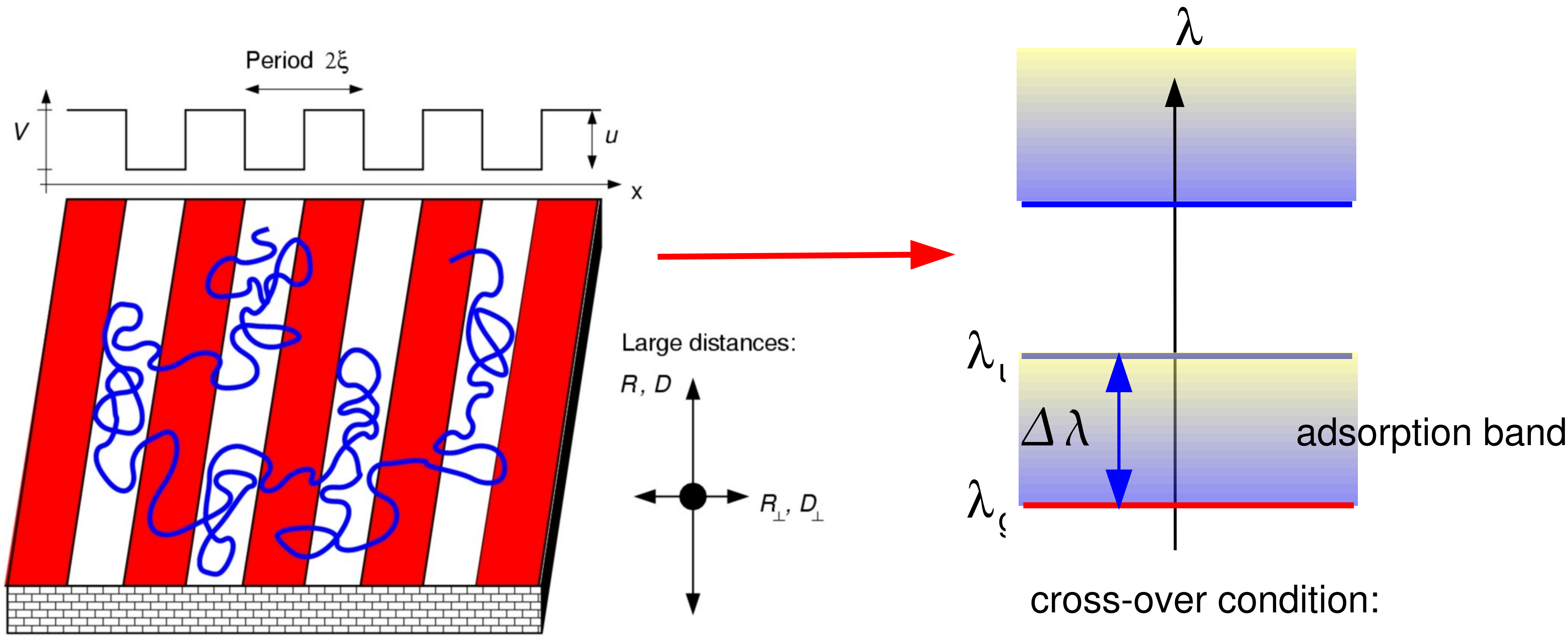
Polymers in nano-structured environments



Kronig Penney model

(Copolymers adsorb at Interfaces)

$$V(x) = -\sum_k \epsilon\, l\, \delta(x - k\,\xi)$$

kT = 1

cross-over condition:

$N\,\Delta\lambda \ll 1$ Chain is localized in in one trap

$N\,\Delta\lambda \gg 1$ Chain bridges many traps

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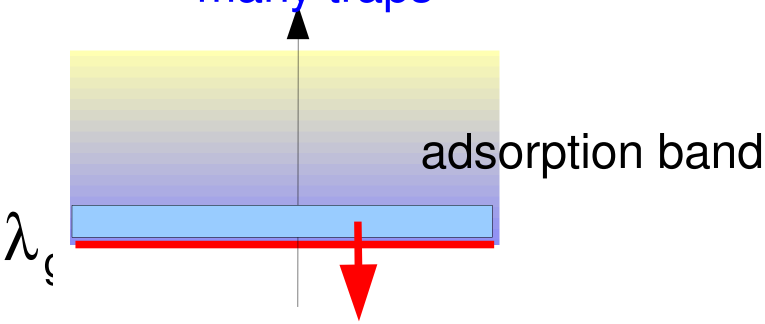
Effective chain properties

$N\,\Delta\lambda \gg 1$

Chain bridges many traps



Analogy

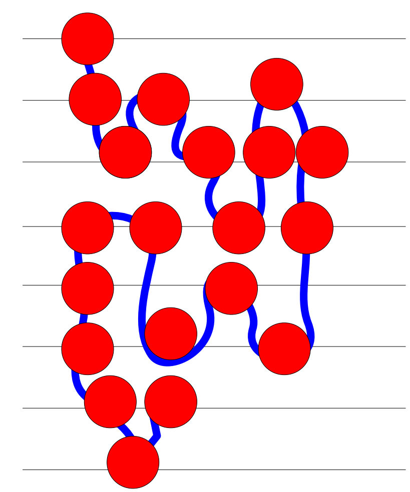
$1/l_{eff}^2$ — effective mass of a Schrödinger particle m_{eff}

Expansion of the dispersion relation for: $\lambda \simeq \lambda_g$

$$G(x,x';N) \simeq \left(2\pi l_{eff}^2 N\right)^{-1/2} \exp\left\{-\frac{1}{2 l_{eff}^2}(x-x')^2\right\}$$

with the effective statistical segment length:

$$\left(\frac{l_{eff}}{l}\right)^2 = \begin{cases} \frac{1}{2}(\epsilon\xi)^2 \exp(-\epsilon\xi/2) & \epsilon\xi \gg 1 \\ 1 & \epsilon\xi \ll 1 \end{cases}$$



Scaling variable: $E = \epsilon\xi/l$

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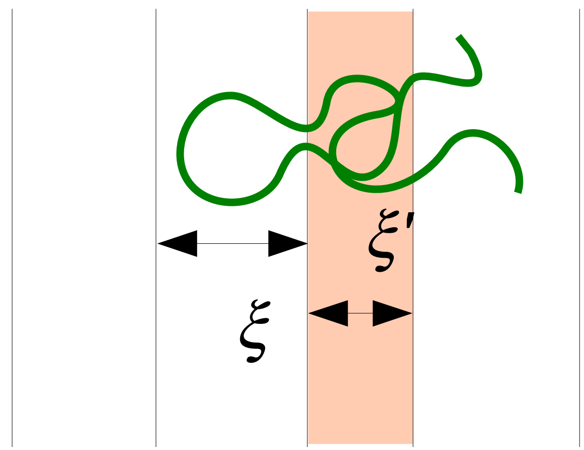
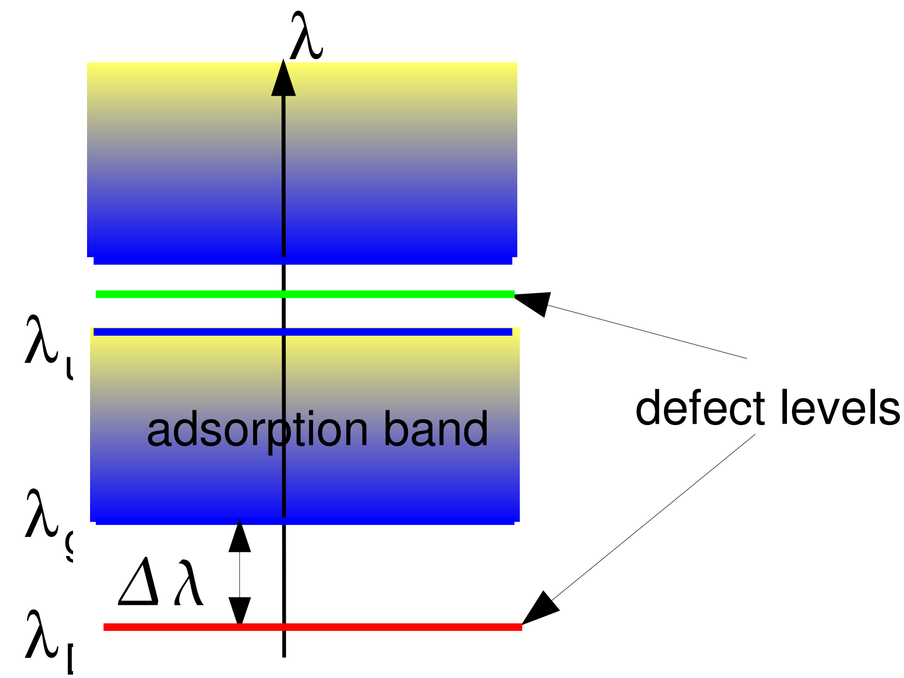
Defects and Localization





Localization length L:

$$L/\xi \simeq \frac{2}{\Delta\xi \cdot \epsilon}$$

for $\Delta\xi\varepsilon << 1$

localization condition: $L^2 \simeq N_L l_{eff}^2$

$$N_L \begin{cases} \dfrac{1}{2(\epsilon\Delta\xi)^2} & \epsilon\xi \ll 1 \\[2ex] \dfrac{8}{(\epsilon\Delta\xi)^2}\dfrac{1}{\xi^2\epsilon^2}\exp(\epsilon\xi/2) & \epsilon\xi \gg 1 \end{cases}$$

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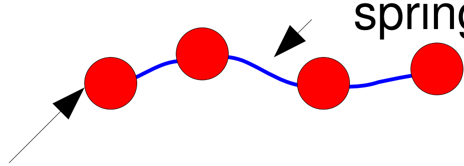
Dynamics

Bead-spring-model

spring constant $k_0 = \frac{3kT}{l^2}$



friction constant μ_0

Langevin equation of motion

$$\mu_0 \frac{dx_k}{dt} + k_0 M_{kl} x_l = \xi_k$$

Exactly solvable problem!

Connectivity (Rouse) matrix:

$$M = \begin{pmatrix} 1 & -1 & 0 & 0 \\ -1 & 2 & -1 & 0 \\ 0 & -1 & 2 & -1 \\ 0 & 0 & -1 & 1 \end{pmatrix}$$

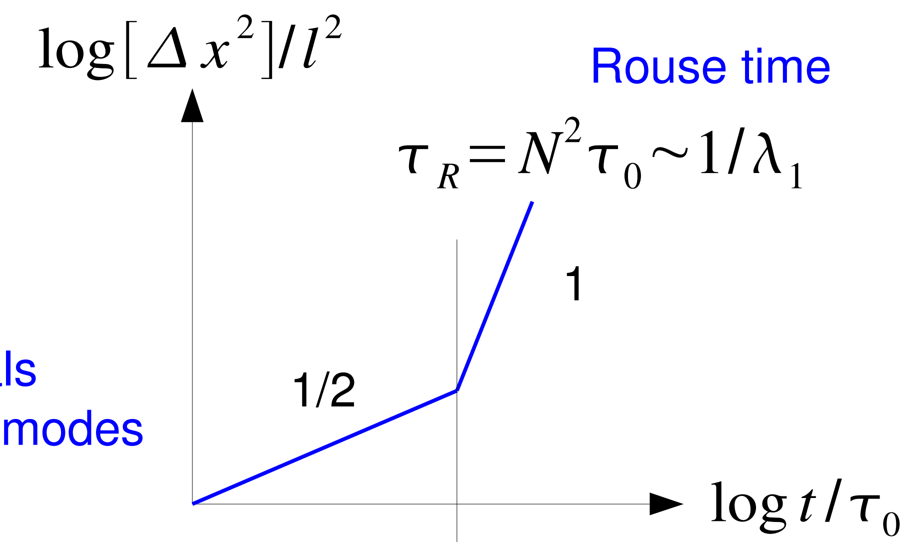
Average mean square displacement of all monomers

$$\left[\Delta x^2\right] = \frac{2\,l^2}{N}\, Tr\, \frac{1}{M}\left(1 - e^{-Mt/\tau_0}\right)$$

$$\tau_0 = \frac{k_0}{\mu_0}$$

Rouse time

$$\tau_R = N^2 \tau_0 \sim 1/\lambda_1$$



But:

Boundary conditions/inhomogeneous potentials
lead to coupling of the coordinates and eigen-modes

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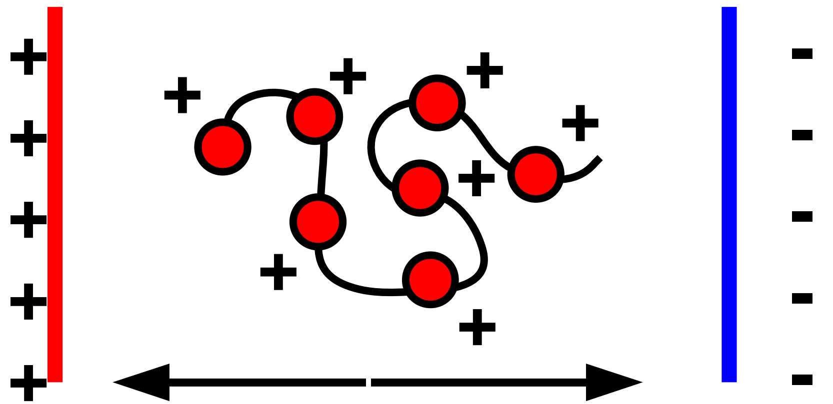
Dynamics in nano-structured arrays

Homogeneously charged chain in external field



$F_\mu \sim N$ $\quad$ $F_E \sim N$

drift velocity does **not** depend on ***N***

Chain diffusion in homogeneous space

$$\mu_0 \frac{dx_k}{dt} + M_{kl} x_l = \xi_k$$

internal forces only: $\sum_k M_{kl} = 0$

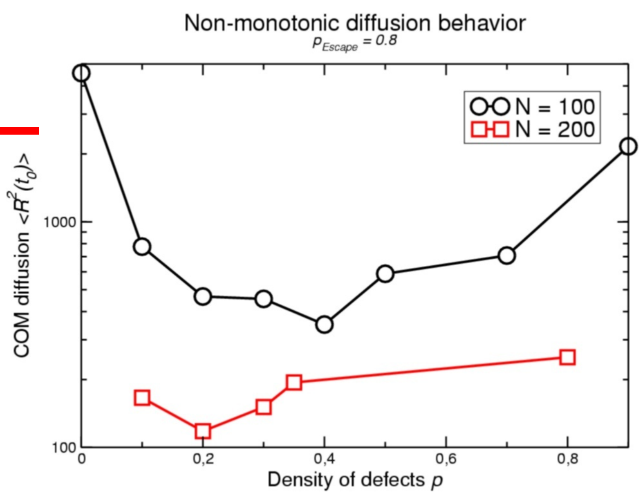
Center of mass:

$$S = \sum_k \frac{x_k}{N}$$

$$D_S = \frac{D_0}{N}$$

$$\mu_S = \mu_0 N$$

Computer simulation of chain diffusion in disordered nano-arrays:



$\mu_S(N)$

non-linear?

Equation to be solved:

$$\mu_0 \frac{dx_k}{dt} + M_{kl} x_l = \xi_k + f_k(x_k)$$

Example: $f_k(x_k) = A \sin(q\, x_k)$

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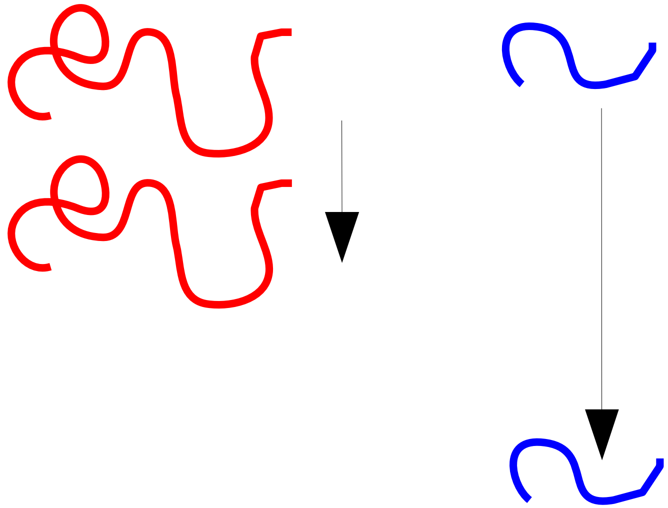
Electrophoresis in 1D Defect Structures

Non-linear molecular friction $\mu_S(N)$

+

distribution of chain lengths $P(N)$

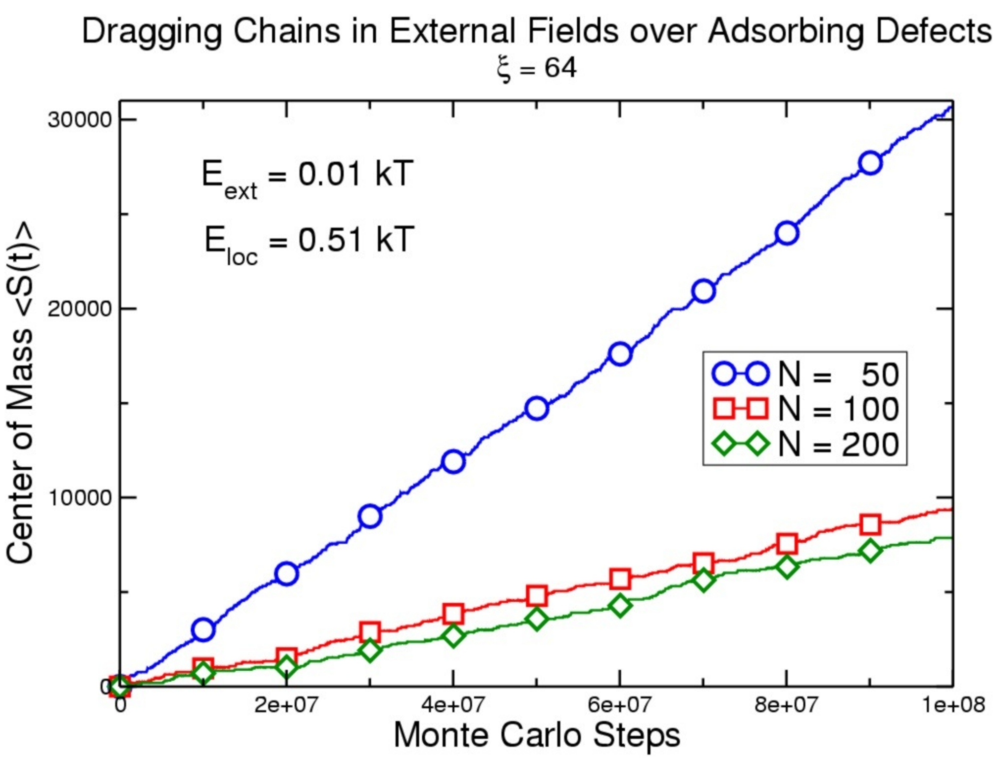


typical Displacement Pattern after time *t*

"Finger print" of *P(N)*

Electrophoretic Efect

Monte Carlo simulation (1D BFM)
regular distributed traps



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Zusammenfassung

Polymersysteme zeigen universelle Eigenschaften – Einzelne Moleküle können als kleine thermodynamische Objekte betrachtet werden (Konformationsentropie)

Die mathematische Beschreibung führt auf Analogien in der Quantenmechanik und in der statistischen Feldtheorie

Dynamische Beschreibung von Polymerketten führt auf stochastische DGL's. Randbedingungen und inhomogene Potentiale führen zu nichtlinearen Problemen - mit vielen Anwendungsbereichen.