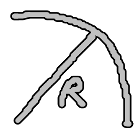
$$\boxed{E = \frac{1}{2} k_B T \int_0^{L_{tot}} ds\, A\, \beta^2} \quad (9.5), \quad \beta = \frac{d\hat{\underline{t}}}{ds}, \quad \hat{\underline{t}} = \frac{d\underline{r}}{ds}$$

... einfaches elastisches Stab-Modell

9.1.3 Persistenzlänge

- Zufallsweg-Konformationen?
- 90°-Krümmung:

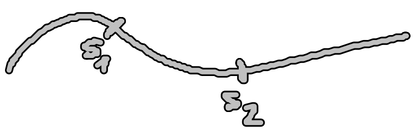


$$E = \frac{1}{2} k_B T A \underbrace{\frac{2\pi R}{4}}_{L_{tot}} \frac{1}{R^2} = \frac{\pi A}{4R} k_B T \quad (9.6)$$

$R \gg A \longrightarrow E \ll k_B T \longrightarrow L_{tot} \gg A \;\hat{=}$ Zufallskonfiguration

- Autokorrelationsfkt.:

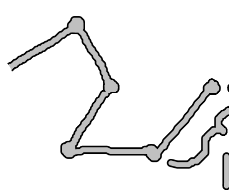
$$\langle \hat{\underline{t}}(s_1) \cdot \hat{\underline{t}}(s_2) \rangle \overset{\text{o.B.}}{=} e^{-\frac{|s_1 - s_2|}{A}} \quad (9.7)$$



"Richtung" bei s_1 und s_2 ist unkorreliert für $|s_1 - s_2| \gg A$

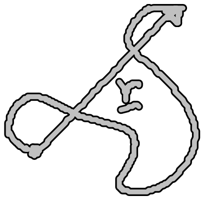
$\Longrightarrow \lambda, L_{tot} \gg A$: frei verbundenes Ketten-Modell

$\hat{=}$ Zufallsweg-Modell



$\boxed{L_{seg} = 2A}$ ... effektive Segmentlänge / Kuhnlänge $\Big\}$ phänomenolog. Parameter

L_{seg}? (i) $\langle \underline{r}^2 \rangle = \langle \underbrace{\int_0^{L_{tot}} ds_1\, \hat{\underline{t}}(s_1)} \cdot \underbrace{\int_0^{L_{tot}} ds_2\, \hat{\underline{t}}(s_2)} \rangle$



$$= \int_0^{L_{tot}} ds_1 \int_0^{L_{tot}} ds_2 \langle \hat{\underline{t}}(s_1)\cdot\hat{\underline{t}}(s_2)\rangle \overset{\text{o.B.}}{=} 2A L_{tot} \overset{!}{=} 2A L_{seg} N$$

$$\text{(ii)} \quad \langle \underline{r}^2\rangle = \sum_{i,j=1}^{N} \langle (L_{seg}\hat{\underline{t}}_i)\cdot(L_{seg}\hat{\underline{t}}_j)\rangle \underset{i\neq j}{\overset{\langle \hat{\underline{t}}_i \cdot \hat{\underline{t}}_j\rangle = 0}{=}} N(L_{seg})^2 \quad ||$$

$\Longrightarrow L_{seg} = 2A$!! qed

- DNS: $L_{seg} \approx 100\,nm \longrightarrow$ steifes, semiflexibles Polymer

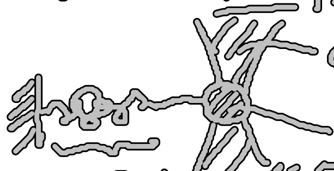
Polyäthylen: $L_{seg} \approx 1\,nm \longrightarrow$ flexibles Poly.

- entropische Ursprung von Gummi-Elastizität!

9.2 Makromoleküle unter Spannung

9.2.1. Kraft-Dehnungs-Kurve für DNS

- **Exp:**

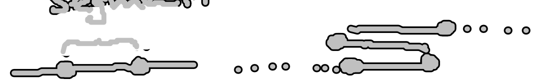


- Resultat: $z(f)$
- Berechnung?

9.2.2. 1D-frei verbundenes Ketten-Modell

$\longrightarrow$ Bereich A & B

- Zwei-Zustands-Modell:



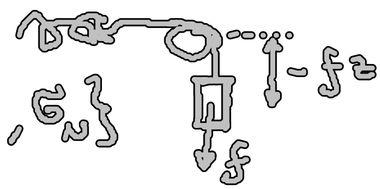
$$\Longrightarrow \text{Ausdehnung: } z = L_{seg}^{(1D)} \sum_{i=1}^{N} \sigma_i \qquad (9.8)$$

• Ensemble mit konst. Dehnkraft f:

f konjugiert zu z : $dE = f\,dz$

$$\longrightarrow \quad Z = \sum_\alpha e^{-(E_\alpha - f z)/k_B T} \quad , \text{ hier: } E_\alpha = 0$$

anders:



Wahrscheinlichkeit für Konfig.: $\{\sigma_1, \dots, \sigma_N\}$

$$P(\sigma_1, \dots, \sigma_N) = \frac{1}{Z}\, e^{f z / k_B T} \qquad (3.9)$$

$\longrightarrow$ mittlere Ausdehnung:

$$\langle z \rangle = \sum_{\{\sigma_i = \pm 1\}} P(\dots)\, z = k_B T \frac{d}{df} \ln Z$$

$$= k_B T \frac{d}{df} \ln \left[\sum_{\{\sigma_i = \pm 1\}} e^{f L_{seg}^{(10)} \sum_{i=1}^{N} \sigma_i / k_B T} \right]$$

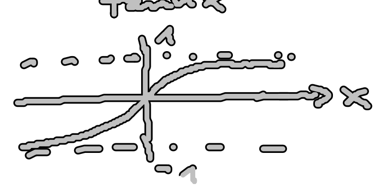
$$\Longrightarrow \langle z \rangle = k_B T \frac{d}{df} \ln \left[\left(\sum_{\sigma_1 = \pm 1} e^{f L_{seg}^{(10)} \sigma_1 / k_B T} \right) \times \dots \times \left(\sum_{\sigma_N = \pm 1} e^{f L_{seg}^{10} \sigma_N / k_B T} \right) \right]$$

$$= k_B T \frac{d}{df} \underbrace{\ln \left(e^{f L_{seg}^{(10)} / k_B T} + e^{-f L_{seg}^{(10)} / k_B T} \right)^N}_{N \ln(\dots)}$$

$$= \underbrace{N L_{seg}^{10}}_{L_{tot}} \frac{e^{(\dots)} - e^{-(\dots)}}{e^{(\dots)} + e^{-(\dots)}}$$

$$\Longrightarrow \boxed{\left\langle \frac{z}{L_{tot}} \right\rangle = \tanh \frac{f L_{seg}^{(10)}}{k_B T}} \qquad (3.10)$$

$\tanh x$



(i) $\langle z \rangle = \text{const.} \longrightarrow f \sim T \;\hat{=}\;$ entropische Effekt
(vgl. ideales Gas, osmot. Druck $p \sim T$)

(ii) $\langle z \rangle \longrightarrow L_{tot}$, $f \to \infty$

(iii) $\langle z \rangle = \frac{f}{k}$, $f \to 0$, $k = \frac{k_B T}{L_{tot} L_{seg}^{(0)}}$

$\tanh x \approx x$ ... Hookesche Relation

(iv) Vgl. mit Exp. $\longrightarrow L_{seg}^{(10)} \approx 35\,nm$

Qualitativ: o.k.

quantitativ: $10 \to 30$, kooperatives Ketten-Modell

(v) Analogie zu 1D Kette von unabhängigen Ising spins: $\uparrow\downarrow \;\hat{=}\; \sigma_i = \pm 1$

$f \;\hat{=}\; H$ ... Magnetfeld

$\langle z \rangle \;\hat{=}\; M = \langle \sigma_i \rangle$ ... magnetisches Moment

9.2.3 1D-Kooperatives Ketten-Modell

$\longrightarrow$ Kreid A & B

- Biege-Elastizität von DNS $\longrightarrow$ Ww der Segmente:

$E(\text{—}) < E(=)$

$\longrightarrow$ Ising-Modell: $\boxed{\text{Hamiltonian: } \frac{H}{k_B T} = -\gamma \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1}}$ (9.11)

mikroskop. Energie

"Ising" $\longrightarrow$ Ferromagnetismus

$\longrightarrow$ das Modellsystem der stat. Physik hier: N Segmente (Länge l): $\sigma_i = \underset{+1\ \ +1}{\bullet\!\!-\!\!\!-\!\!\bullet\!\!-\!\!\!-\!\!\bullet}$: $-\gamma k_B T$

$\underset{+1}{\overset{-1}{=}}$: $\gamma k_B T$ $\Big\}$ Ww-energie !!

l, γ ... phänomenolog. Parameter

$\alpha = \frac{fl}{k_B T}$

• Zustandssumme mit $f \neq 0$:

$$Z(\alpha) = \sum e^{-\frac{H - fz}{k_B T}} = \sum_{\{\sigma_i = \pm 1\}} \left[e^{\alpha \sum_{i=1}^{N} \sigma_i + \gamma \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1}} \right] \quad (9.12)$$

$$\Longrightarrow \langle z \rangle \underset{SM}{=} k_B T \frac{d}{df} \ln Z(f) = l \frac{d}{d\alpha} \ln Z(\alpha) \underset{TD}{=} -\frac{\partial F(T,f)}{\partial f} \quad (9.13)$$

mit $F(T,f) = -k_B T \ln Z(f)$

• $Z(\alpha)$? (H. Kramers & G. Wannier (1941): Ferromagnet)

Folien!

(vi) $f \sim \alpha \rightarrow 0$: $\sinh\alpha \approx \alpha$

$$\Longrightarrow \boxed{\langle z \rangle \approx \frac{1}{k} f \quad \text{mit } k = \frac{k_B T}{e^{2\gamma} l L_{tot}}} \quad (9.19) \quad (\text{vgl. } 9.2.2)$$

(vii) vgl. Fig. 9.4: $l e^{2\gamma} = 35\,nm$, $\gamma \gg 1$

$= L_{seg}^{(\approx 0)}$

• Sehr guter Fit: 3D - kooperatives Ketten-Modell

= elastisches Stab-Modell

$A = 51\,nm$

$\longrightarrow$ Erfolg des phänomenolog. Modells

$A \gg 2\,nm = \emptyset(DNS)$