Theorie polymerer Netzwerke
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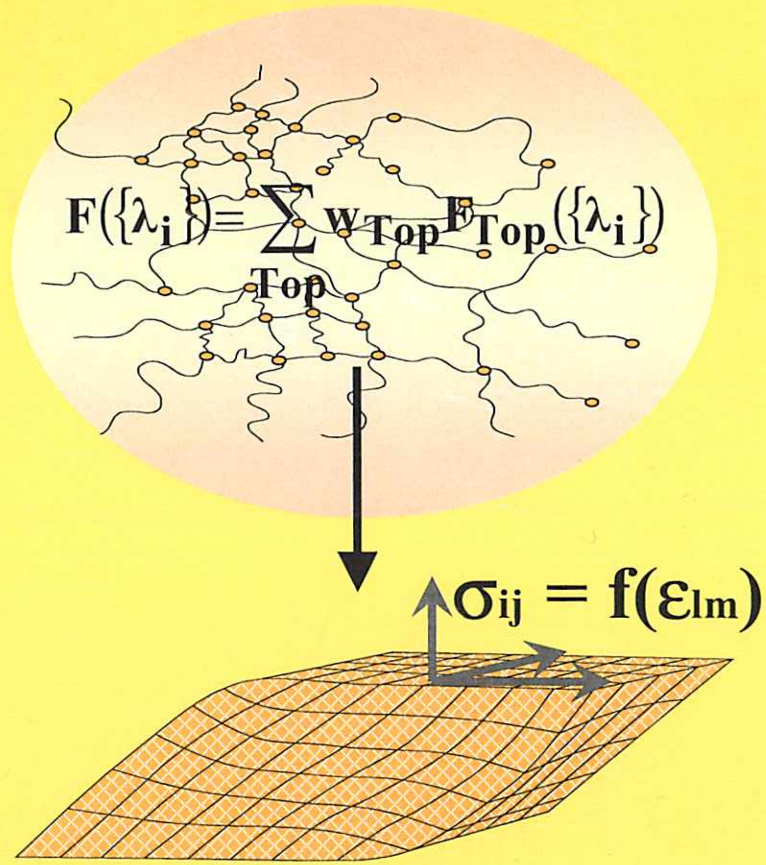


- Introduction:
  Basics „Formation of Networks“; Classical Phantom Network Models
- Statistics of free chains; Path-Integral formulation of polymer statistics; Feynman path integrals in quantum mechanics; Brownian motion and Wiener integrals
- Constrained polymer chains: topological constraints in 2 and 3 dimensions; gauge field formalism and entanglements
- Statistical mechanics with topological constraints: crosslinks and entanglements; Non-Gibbsian statistical mechanics for quenched systems (S.F. Edwards); Statístical mechanics of phantom networks (Deam-Edwards approach)
- Outlook:
  - Entanglements and Fillers in Networks: towards a constitutive law for real rubbers
  - State-of-Art (2013) concerning (FE) applications in engineering science and practice. Examples.

Some references:

Some basic references:

Freed, Karl F., *Functional Integrals and Polymer Statistics*, Advances in Chemical Physics XXII, 1-128 (1972)

Kleinert, Hagen, *Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets*, World Scientific Publishing (2009)

Deam, R.T., Edwards, S. F., *The Theory of Rubber Elasticity*, Philos. Trans. R. Soc. London, Ser. A 280, 317 (1976)

See also:

Stealing the Gold, A Celebration of the Pioneering Physics of Sam Edwards, Eds.: P. Goldbart, N. Goldenfeld, D. Sherrington, Oxford Univ. Press 2005

Some references:

Some reviews about physics and theories of polymer networks and filled elastomers (with many references to original papers):

G. Heinrich, E. Straube, G. Helmis, *Rubber Elasticity of Polymer Networks: Theories*, Advances in Polymer Science **85**, 33-87 (1988)

G. Heinrich, G. Helmis, T.A. Vilgis, *Polymere Netzwerke – Entwicklungsstand der molekular-statistischen Theorie*, Kautschuk u. Gummi, Kunststoffe 48, 689-702 (1995)

G. Heinrich, M. Klüppel, *Recent Advances in the Theory of Filler Networking in Elastomers*, Advances in Polymer Science **160**, 1-44 (2002)

G. Heinrich, M. Klüppel, T.A. Vilgis, *Reinforcement of Elastomers*, Current Opinion in Solid State & Materials Science **6**, 195-203 (2002)

M. Klüppel, *The Role of Disorder in Filler Reinforcement of Elastomers on Various Length Scales*, Advances in Polymer Science **164**, 1-86 (2003)

G. Heinrich, M. Klüppel, T.A. Vilgis, *Reinforcement Theories*, in Physical Properties of Polymer Handbook (Ed.: J. E. Mark), Springer 2006

T.A. Vilgis, G. Heinrich, G.; M. Klüppel, *Reinforcement of Polymer Nano-Composites: Theory, Experiments and Applications*, Cambridge University Press (2009), 222 pages

List of distributed pdfs concerning applications, FE-implementations and constitutive material laws of real rubbers based on the ‚Merseburg tube-model' and the ‚Hannover filler-flocculation-model' (Klüppel) of rubber elasticity:

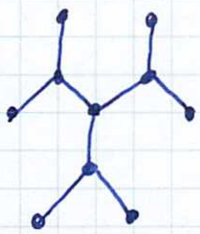
G. Heinrich, T. Vilgis, *Contribution of Entanglements to the Mechanical Properties of Filled Polymer Networks*, Macromolecules **26**, 1109-1119 (1993)

G. Heinrich, M. Kaliske, *Theoretical and Numerical Formulation of a Molecular Based Constitutive Tube-Model of Rubber Elasticity*, Computational and Theoretical Polymer Science **7**, 227-241 (1998)

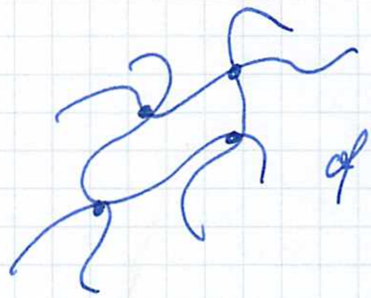
M. Kaliske, G. Heinrich, *An Extended Tube-Model for Rubber Elasticity: Statistical-Mechanical Theory and Finite Element Implementation* , Rubber Chemistry and Technology **72**, 602-632 (1999)

H. Lorenz, M. Klüppel, G. Heinrich, *Microstructure-based modelling and FE implementation of filler-induced stress softening and hysteresis of reinforced rubbers*, ZAMM - Journal of Applied Mathematics and Mechanics **92,** 608–631 (2012)

1. Basics – Formation of Networks – Percolation



Gelation of small polyfunctional units



Vulcanisation of long chains

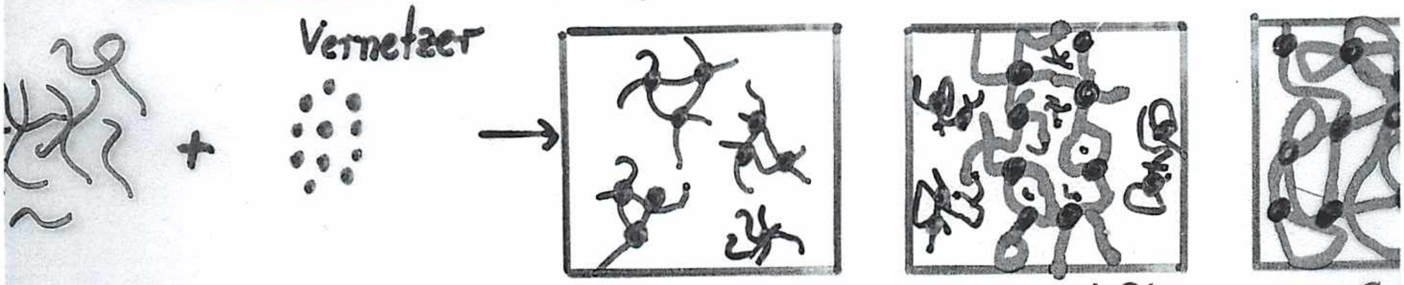
critical phenomenon $\hat{=}$ FS-theory (classical case)

charact. length: ξ mesh size

„Interspersion" - effects

affine transform. of length scales $\gtrsim \xi$ $\Leftarrow$ Swelling $\Rightarrow$ Disinterspersion, Loss of affinity

Statistische Mechanik von Systemen mit „eingefrorener" Topologie

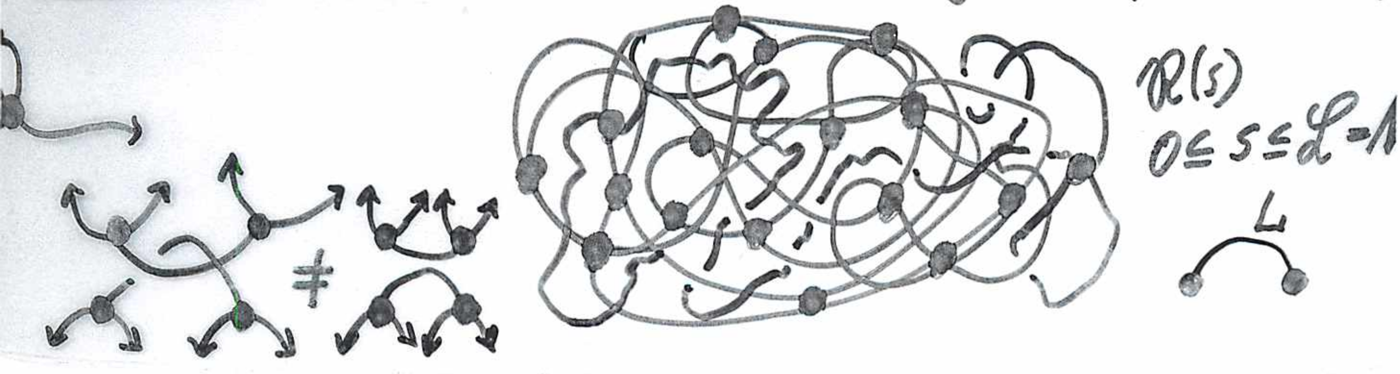


Sol | Sol-Gel-Phase | Gel
$p < p_c$ | $p = p_c$ | $p = 1$

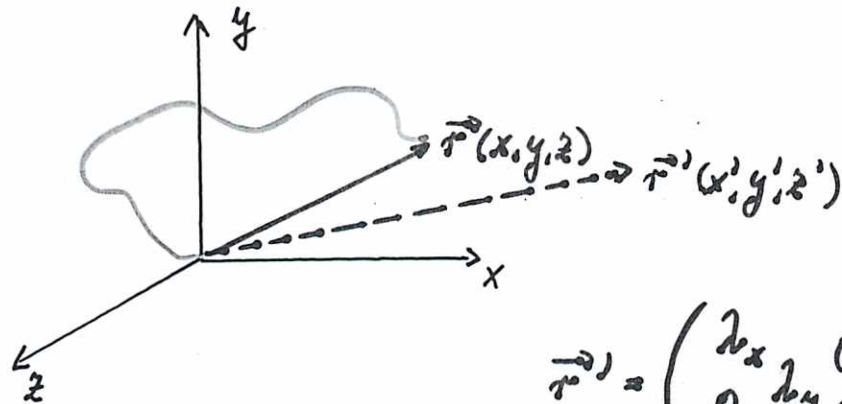
$\varepsilon = \left| \frac{p - p_c}{p_c} \right| \ll 1$

- krit. Phänomen
- Perkolation ; obere krit. Dim. $d_c = 6$
- Vulkanisation
  $\hat{=}$ Perkol. auf Bethe-Gitter („Mean-Field"-Approx.)
- Fraktale Strukturen

Statistische Mechanik von Behinderungen (quenched s



1. Phantomnetzwerk theorie: Basics



$$\vec{r}\,' = \begin{pmatrix} \lambda_x & & 0 \\ & \lambda_y & \\ 0 & & \lambda_z \end{pmatrix} \vec{r}$$

$$\lambda_x \lambda_y \lambda_z = 1$$

$$\lambda_x = \lambda = \frac{L}{L_0}, \quad \lambda_y = \lambda_z = \lambda^{-1/2}$$

(uniaxiale Deform)

– Entropie einer einzelnen Kette im undeformierten Zustand

$$s_0 = k \ln W(h)$$

$$W(h)\,dh = 4\pi h^2 \left(\frac{3}{2\pi n b^2}\right)^{3/2} \exp\left\{-\frac{3h^2}{2nb^2}\right\} dh$$

$$s_0 = C - 3kh^2/2nb^2 = C - \frac{3k}{2nb^2}(x^2+y^2+z^2)$$

– Zahl der Ketten im undeform. Zustand mit Enden im Volumenelement $dxdydz$

$$\frac{d\nu}{\nu} = \frac{\beta^3}{\pi^{3/2}} e^{-\beta^2(x^2+y^2+z^2)} dx\,dy\,dz, \quad \beta^2 = \frac{3}{2nb^2}$$

– Entropie pro Volumeneinheit des undeform. NW.

$$S_0 = \int s_0\, d\nu = \nu\left(C - \frac{3}{2}k\right)$$

- Entropie einer affin deform. Kette:

$$s = C - k\beta^2 (\lambda_x^2 x^2 + \lambda_y^2 y^2 + \lambda_z^2 z^2)$$

- Entropieänderung pro Volumeneinheit des NW:

$\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle = \frac{1}{3} n b^2$

$$\Delta S = S - S_0 = \frac{1}{2} \nu k (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

- Freie Energie:

$$\Delta F \hat{=} -T\Delta S = \frac{1}{2} \nu k T (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

$\Delta U = 0$

$\downarrow$ Flory

$$\Delta F = \frac{1}{2} \xi k T (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

ξ - cycle rank

perfektes NW d. Funktionalität f:

$$\xi = \nu - \mu = \frac{f-2}{f}\nu$$

Netzbogendichte — chemische Knotendichte

$f = 4$
$\mu = 4$
$\nu = 8$

$$\xi = \nu + 1 - \mu$$

- Spannungs-Dehnungs-Gesetz (uniaxiale Dehnung: $\lambda_x = \lambda$, $\lambda_y = \lambda_z = \lambda^{-1/2}$
trock. System

$$\sigma(\lambda) = \frac{\partial}{\partial\lambda}\Delta F = 2C_1(\lambda - \lambda^{-2})$$

$$2C_1 = \frac{\nu}{2} k T$$

- Experimentelles Verhalten:

$$\sigma = 2C_1(\lambda - \lambda^{-2}) + 2C_2(1 - \lambda^{-3})$$ Mooney-Rivlin-Gl.

Phänomenologie: $\Delta F = W(I_1, I_2, I_3) = \sum_{i=0}\sum_{j=0} C_{ij} (I_1 - 3)^i (I_2 - 3)^j$

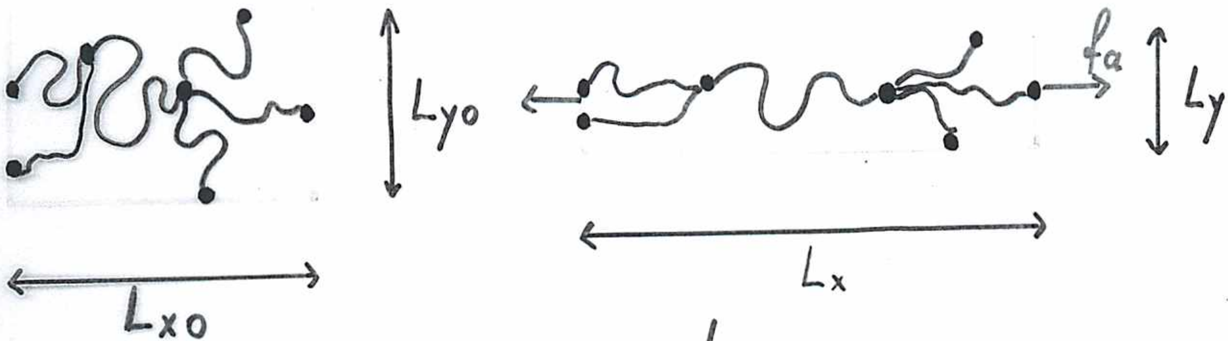
$I_1 = \lambda_x^2 + \lambda_y^2 + \lambda_z^2$, $I_2 = \lambda_x^2\lambda_y^2 + \lambda_x^2\lambda_z^2 + \lambda_y^2\lambda_z^2$

$I_3 = \lambda_x^2\lambda_y^2\lambda_z^2 \quad (=1)$

$2C_1 \equiv C_{10}$
$2C_2 \equiv C_{01}$

1. Das Phantomnetzwerk

Zusammenfassung



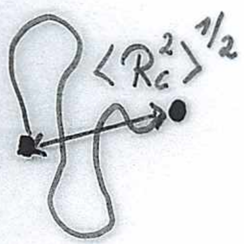
<u>Dehnung:</u> $\lambda_x = \frac{L_x}{L_{x0}} = \lambda$

$\lambda_y = \lambda_z = \lambda^{-1/2} \qquad (V = V_0)$

Änderung d. freien elastischen Energie

$$\Delta F = -T \Delta S(\lambda_x, \lambda_y, \lambda_z)$$

$$= \nu_c k_B T \left[\frac{1}{2} g \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 \right) - B \sum_{\mu = x,y,z} \ln \left(\eta^{1/2} \lambda_\mu \right) \right]$$



$g = \eta \cdot A$ Frontfaktor

$\eta^{1/2} = \frac{\langle R_c^2 \rangle_i^{1/2}}{\langle R_c^2 \rangle_0^{1/2}}$ „memory"-Faktor (= 1 „b

$A = 1$ od. $A = \frac{f-2}{f}$ Mikrostrukturfaktor

b) a)

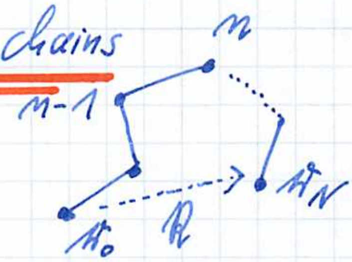
f = Funktionalität

<u>Spannung:</u>

$$\sigma(\lambda) = \frac{\partial}{\partial \lambda} \frac{\Delta F}{V} = 2C_1 \left(\lambda - \lambda^{-2} \right) + 2C_2 \left(1 - \lambda^{-3} \right)$$

Mooney-Rivlin

2. Statistics of free chains



Markov-chain: $p(\mathbf{r}_n - \mathbf{r}_{n-1})$ is probability to find segment n at $\mathbf{r}_n$, if segment $(n-1)$ is located at $\mathbf{r}_{n-1}$:

$$P_N(\mathbf{r}_N - \mathbf{r}_0) = \int \cdots \int p(\mathbf{r}_N - \mathbf{r}_{N-1})\, p(\mathbf{r}_{N-1} - \mathbf{r}_{N-2}) \cdots p(\mathbf{r}_1 - \mathbf{r}_0) \prod_{\alpha=1}^{N-1} d^3 r_\alpha \qquad (1)$$

Fourier transf. of p:

$$p_k = \frac{1}{(2\pi)^3} \int e^{-i\mathbf{k}\mathbf{r}}\, p(\mathbf{r})\, d^3 r \qquad \mathbf{r} \mathrel{\hat{=}} \mathbf{r}_N - \mathbf{r}_{N-1},\ \mathbf{r}_{N-1} - \mathbf{r}_{N-2},\ \vdots \qquad (2)$$

$$p(\mathbf{r}) = \int e^{i\mathbf{k}\mathbf{r}}\, p_k\, d^3 k \qquad \hat{=} \text{ bond probability} \qquad (3)$$

$\rightsquigarrow$

$$P_N(\mathbf{r}_N - \mathbf{r}_0) = \int \cdots \prod_{\alpha=0}^{N-1} d^3 k_\alpha \, \exp\left\{ i\mathbf{k}_{N-1}(\mathbf{r}_N - \mathbf{r}_{N-1}) + \cdots + i\mathbf{k}_0(\mathbf{r}_1 - \mathbf{r}_0) \right\} \cdot p_{k_{N-1}}\, p_{k_{N-2}} \cdots p_{k_0} \prod_{\beta=1}^{N-1} d^3 r_\beta \qquad (4)$$

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$$= (2\pi)^{3N} \int \cdots \prod_{\alpha=0}^{N-1} d^3k_\alpha \; \delta(k_{N-1}-k_{N-2})\,\delta(k_{N-2}-k_{N-3}) \cdots \delta(k_1-k_0)\, p_{k_{N-1}} \cdots p_{k_0} \cdot \qquad (5)$$

über k_0 integriert

$$\cdot \exp\{i(k_{N-1}\cdot r_N - k_0 r_0)\}$$

$$= (2\pi)^{3N} \int \cdots d^3k_1 \cdots d^3k_{N-1}\; \delta(k_{N-1}-k_{N-2}) \cdots \delta(k_2-k_1) \cdot p_{k_{N-1}} \cdots p_{k_1}^2\, e^{i(k_{N-1}\cdot r_N - k_1 r_0)}$$

etc.

$$= (2\pi)^{3N} \int d^3k_{N-1}\, p_{k_{N-1}}^N\, e^{i(k_{N-1} r_N - k_{N-1} r_0)}$$

$$\boxed{P_N(r_N - r_0) = (2\pi)^{3N} \int p_k^N\, e^{ik(r_N - r_0)}\, d^3k} \qquad (6)$$

Es gilt: $\int p(r)\, dr = 1$, $\qquad (7)$

From (6) with $R \equiv r_N - r_0$

$$P_N(R) = \int d^3k \exp\{ikR - N\cdot \log((2\pi)^3 p_k)\} \qquad (8)$$

If $N \gg 1$, approximation (k small)

$$p_k \approx \frac{1}{(2\pi)^3}\left[1 - \frac{\alpha}{2}k^2\right] \rightarrow (8) \qquad (*)$$

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$$p_N(\mathbf{R}) = \int d^3k \, \exp\{ i\mathbf{k}\mathbf{R} - N\alpha k^2/2 \}$$

$$\boxed{p_N(\mathbf{R}) = \frac{\exp\{-\mathbf{R}^2/2N\alpha\}}{(2\pi N\alpha)^{3/2}}} \qquad (9)$$

In case of freely-joined chain

bond probability $p(\mathbf{r}) = \frac{1}{4\pi l^2} \, \delta(|\mathbf{r}| - l)$ (10)

$$\int p(\mathbf{r}) d^3r = \frac{1}{4\pi l^2} \int_0^\infty \int_0^\pi \int_0^{2\pi} \delta(|\mathbf{r}| - l) \, r^2 \sin\vartheta \, d\vartheta \, d\varphi \, dr$$

$$= \frac{1}{4\pi l^2} \cdot 4\pi l^2 = 1 \qquad !$$

From (2) we obtain expression for α:

$$p_k = \frac{1}{(2\pi)^3} \int \left(1 - i\mathbf{k}\mathbf{r} - \frac{1}{2} (\mathbf{k}\mathbf{r})^2 \right) p(\mathbf{r}) \, d^3r$$

$$= \frac{1}{(2\pi)^3} \left[1 - \frac{1}{2} |\mathbf{k}|^2 \int \underbrace{d^3r}_{r^2 \sin\vartheta \, d\vartheta \, d\varphi \, dr} \, (r^2 \cdot \cos^2\vartheta) \, \frac{1}{4\pi l^2} \, \delta(r - l) \right]$$

$$= \frac{1}{(2\pi)^3} \left[1 - \frac{k^2}{2} \cdot \frac{2\pi \cdot l^2 \cdot l^2}{4\pi l^2} \underbrace{\int_0^\pi d\vartheta \, \cos^2\vartheta \cdot \sin\vartheta \, d\vartheta}_{2/3} \right.$$

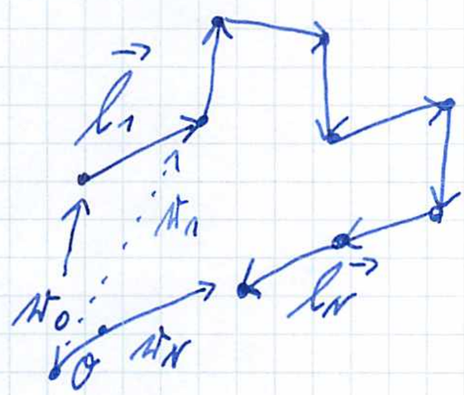
$$= \frac{1}{(2\pi)^3} \left[1 - \frac{k^2}{2} \cdot \frac{l^2}{3} \right] \curvearrowright^{(*)} \alpha = l^2/3$$

$l = \sqrt{3\alpha}$ effective step length.

$$\boxed{p_N(\vec{R}) = \left(\frac{3}{2\pi N l^2}\right)^{3/2} \exp\left\{-\frac{3}{2Nl^2}\vec{R}^2\right\}} \qquad (11)$$

$$\boxed{\langle \vec{R}^2 \rangle = \int \vec{R}^2 p_N(\vec{R})\, d^3\vec{R} = N l^2}$$

Partition Function and Distribution Functions as (Functional-) Path-Integrals



Gaussian segment length distribution !

$$p(r) \longrightarrow \tau(\vec{l}_i) = \left(\frac{3}{2\pi l^2}\right)^{3/2} \exp\left\{-\frac{3}{2}\frac{l_i^2}{l^2}\right\} \qquad (12)$$

$$i = 1, \dots, N$$

+ stiffness for stiff chains: $(12) \cdot \exp\left\{-\varepsilon \frac{(l_i - l_{i-1})^2}{2 l_i}\right\}$

$$\int d^3\vec{l}_i\, \tau(\vec{l}_i) = 1 \qquad (13)$$

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i) flexible chains: correlations between directions of bond vectors vanish, even if distance between bond vectors is small compared to contour length

$L = N \cdot l = l_1 + l_2 + l_3 + \dots + l_N$

ii) $N \gtrsim 20$: Gauss - approximation good.

$\Longrightarrow$ continuous chain: identical segments

$0 \leq s \leq L$ arc length

$\vec{r}(s) \hat{=}$ conformation of polymer $\hat{=}$ space curve

Zustandssumme / partition function / configurational integral
conformational

$$Z = \int \cdots \int d\{\vec{r}\} \left[\prod_{j=1}^{N} \tau(\vec{l}_j) \right]$$

$$\tau_i(\vec{l}_i) = \left(\frac{3}{2\pi l \cdot \Delta s_i} \right)^{3/2} \exp\left\{ -\frac{3 l_i^2}{2 \Delta s_i \cdot l} \right\} \qquad (14)$$

with $\sum_{i=1}^{N} \Delta s_i = L = N \cdot l$

Limes: $N \longrightarrow \infty$ but $\sum_i \Delta s_i = \text{const} = L$
$\max(\Delta s_i) \longrightarrow 0$

$$\prod_i \tau_i \longrightarrow \exp\left\{-\frac{3}{2l}\sum_i \frac{l_i^2}{\Delta s_i^2}\cdot\Delta s_i\right\}\exp\left\{-\varepsilon\sum_i \frac{(l_i-l_{i-1})^2}{2\Delta s_i^2}\Delta s_i\right\} \tag{15}$$

$\vec{l}_i = r_i - r_{i-1}$

$$\longrightarrow \exp\left\{-\frac{3}{2l}\int_0^L\left(\frac{\partial r(s)}{\partial s}\right)^2 ds\right\}\exp\left\{-\varepsilon\int_0^L \ddot{r}(s)^2\, ds\right\}$$

next steps without stiffness

$$p(r(s)) = \mathcal{N}\exp\left\{-\frac{3}{2l}\int_0^L \dot{r}^2(s)\right\} \qquad \dot{r} \equiv \frac{\partial r(s)}{\partial s}$$

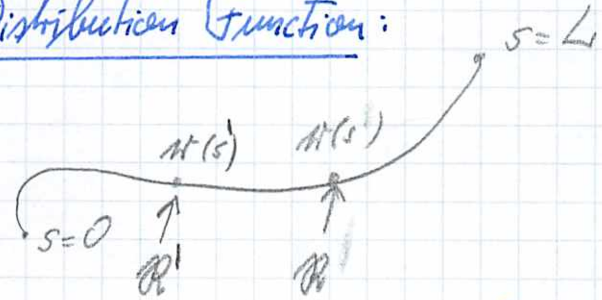
$$Z = \int \mathcal{D}[r(s)]\exp\left\{-\frac{3}{2l}\int_0^L ds\, \dot{r}^2(s)\right\} \tag{16}$$

$\delta[r(s)]$

$$\times \exp\left\{-\int_0^L ds\int_0^L ds'\, W(r(s)-r(s'))\right\}$$

Interactions

Reduced Distribution Function:



$$G(R,R'|ss') = \int \mathcal{D}[r(s)]\exp\left\{-\frac{3}{2l}\int_0^L \dot{r}^2(s)\, ds\right\}\cdot \tag{17}$$

$$\cdot\,\delta(R-r(s))\,\delta(R'-r(s')) = \int_{r(s)=R}^{r(s')=R'} \mathcal{D}[r(s)]\exp\{\dots\}$$

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$4\pi D = 2\pi l$
$2D = l$

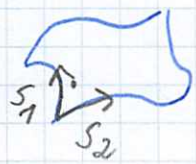
Pathintegral (Functionalintegral)

- limes of ordinary higher-dimensional integrals

$$d\{r_i\} = dr_1\, dr_2 \dots \rightarrow \mathcal{D}[r(s)]$$

$$1\ 2\ 3 \dots \rightarrow \text{contour variable } s$$

- membranes $\quad \mathcal{D}[r(\vec{s})] = \mathcal{D}[r(s_1, s_2)]$

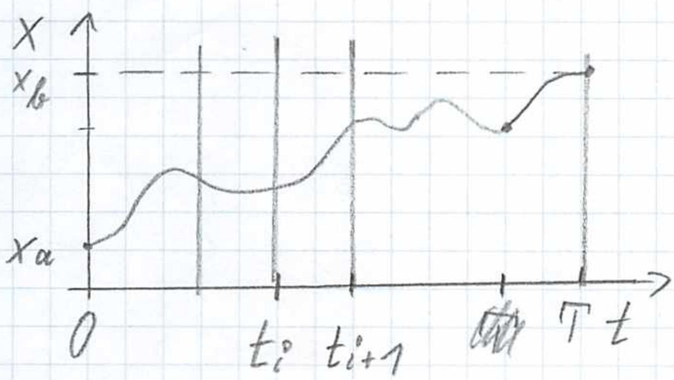


- Maß / Measure of integrals of Gauß'ian type well-known:

$$J = \int_{x(0)=x_a}^{x(T)=x_b} \mathcal{D}[x(t)] \exp\left\{-\frac{1}{2l}\int_0^T \dot{x}^2(t)\, dt\right\}$$

$$= \lim_{\substack{\varepsilon\to 0 \\ N\to\infty}} \Big\} N\cdot\varepsilon = T \quad A^N \int \dots \int dx_1 \dots dx_{N-1} \exp\left\{-\frac{1}{2l}\sum_{i=1}^{N} \varepsilon \left(\frac{x_i - x_{i-1}}{\varepsilon}\right)^2\right\}$$

$$\text{Maß} \quad A = \frac{1}{\sqrt{2\pi l \cdot \varepsilon}}$$



Prinzip

$$\int_{-\infty}^{+\infty} \exp\left\{-a(x-x')^2 - b(x-x'')^2\right\} dx$$

$$= \left(\frac{\pi}{a+b}\right)^{1/2} \exp\left\{-\frac{a\cdot b}{a+b}(x'-x'')^2\right\}$$

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Differential eq. of reduced distribution function

see: K.F. Freed, Adv. in Chemical Physics

Without Interaction [long-range] between segments

$$\left\{\frac{\partial}{\partial L} - \frac{l}{6}\nabla_R^2 + V(R)\right\} \underbrace{G(R,R';L0)}_{\text{Greenfunction}} = \delta(L)\,\delta^{(3)}(R-R') \qquad (18)$$

$$G(R,R';L0) = \int_{r(0)=R'}^{r(L)=R} \mathcal{D}[r(s)] \exp\left\{-\frac{3}{2l}\int_0^L \dot{r}(s)^2\,ds + \int_0^L V(r(s))\,ds\right\}$$

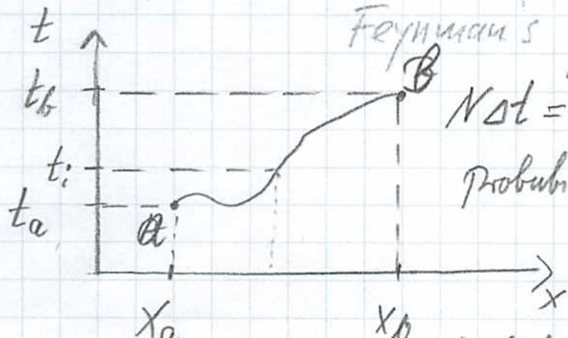
$$\boxed{P(R) \equiv G(R,0;L0) = \left(\frac{3}{2\pi l L}\right)^{3/2} e^{-\frac{3R^2}{2lL}}} \qquad (19)$$

$$\lim_{L\to 0} G(R,0;L0) = \delta(R) \qquad lL = \langle R^2\rangle$$

Analogous Schrödinger eq. in QM: $V(R)=0!$, $R'=0$

$$\left\{\frac{\hbar}{i}\frac{\partial}{\partial T} - \frac{\hbar^2}{2m}\nabla_R^2\right\} K(R,0;T) = \delta(R)\,\delta(T)$$

Feynman's path integral formulation of QM



$N\Delta t = t_b - t_a \equiv T$

Probability of transition $a \to b$

$$P(b,a) = |K(b|a)|^2$$

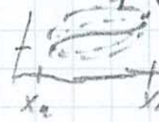
↳ Amplitude of transition

$$K(b|a) = \int_{x(t_a)=x_a}^{x(t_b)=x_b} e^{i/\hbar\, S[b,a]}\, \mathcal{D}x(t)$$

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{x}} - \frac{\partial L}{\partial x} = 0$$

Action: $S(b,a) = \int_{t_a}^{t_b} L(\dot{x}, x, t)\,dt$

$\frac{m}{2}\dot{x}^2 - V(x)$ Lagrangian → Euler-Lagrange (Lagrange 2) → $x_{klass.}(t)$



free moving particle:

$$K(b/a) = \sqrt{\frac{m}{2\pi i \hbar \underbrace{N\cdot\Delta t}_{T}}}\ \exp\left\{-\frac{m}{2i\hbar T}(x_b - x_a)^2\right\}$$

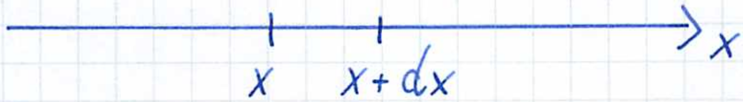
$$K(b/a) = \sum_n \psi_n(x_b)\,\psi_n^*(x_a)\, e^{-i/\hbar \cdot E_n (t_b - t_a)}$$

Spektraldarstellg.

ψ_n Eigenfunction
E_n Eigenvalues

of Hamiltonian

Reminder: Brownian Motion and Wiener-Integral



time t : number of particles between x, $x+dx$: $c(x,t)\,dx$
(no interaction)

particle current $j(x,t)$: Brownian particles crossing x per time unit in direction of increasing x.

$$j(x,t) = -D\,\frac{\partial c}{\partial x} \qquad (\sim \text{gradient of concentr.}) \qquad (R1)$$

$$D = kT/\zeta \qquad \text{diffusion coefficient}$$

eq. of continuity (conservation of particle number):

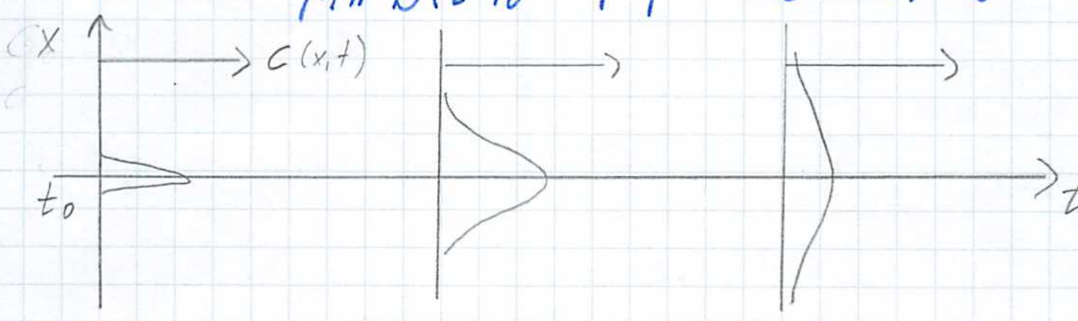
$$\partial c/\partial t = -\partial j/\partial x \qquad (R2)$$

$$\rightsquigarrow \boxed{\partial c/\partial t = D\,\frac{\partial^2 c}{\partial x^2}} \qquad \text{diffusion eq.} \qquad (R3)$$

$$t = t_0 \longleftrightarrow x = x_0, \text{ i.e. } c(x,t_0) = \delta(x-x_0) \qquad (R4)$$

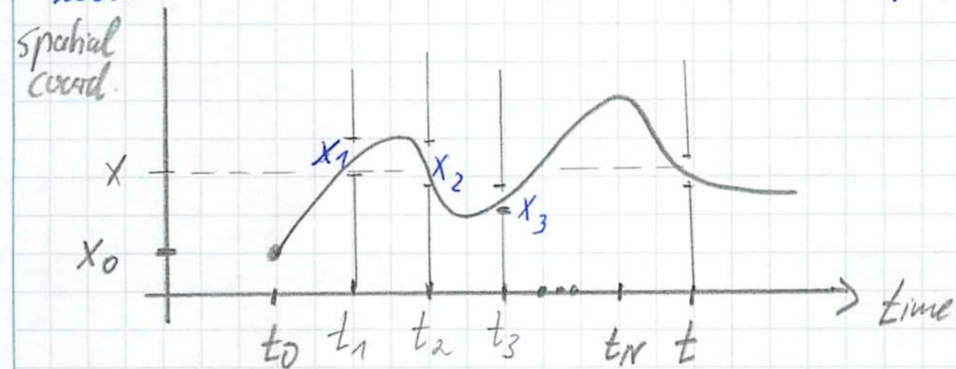
solution: Greenfunction $t \geq t_0$

$$G_0(x,t) = \frac{1}{\sqrt{4\pi D(t-t_0)}}\exp\left\{-\frac{(x-x_0)^2}{4D(t-t_0)}\right\} \qquad (R5)$$



broadening!

<u>Now</u>: intervall $(t_0, t) \longrightarrow$ $N+1$ steps of "length" ε



<u>Probability for</u> $x_1, x_2, x_3, \ldots x_N, x$ at times
$t_1, t_2, t_3, \ldots t_N, t$:

$$\sim \left(4\pi D\cdot\varepsilon\right)^{-\frac{(N+1)}{2}} \cdot \exp\left\{-\frac{1}{4D\varepsilon}\sum_{j=0}^{N}\left(x_{j+1}-x_j\right)^2\right\} \prod_{j=1}^{N+1} dx_j \qquad (R6)$$

$x_{N+1} \equiv x$

limes $\varepsilon \rightarrow 0,\ N \longrightarrow \infty\ ;\ (N+1)\cdot\varepsilon = t - t_0$

Probability for a special Path $x(\tau)$ from x_0 (at time t_0) to x (at time t)

$$\frac{1}{\varepsilon}\sum_{j=0}^{N}\left(x_{j+1}-x_j\right)^2 \Longrightarrow \int_{t_0}^{t}\left(\frac{dx(\tau)}{d\tau}\right)^2 d\tau \qquad (R7)$$

$$p\left(x(\tau)\right) \sim \exp\left\{-\frac{1}{4D}\int_{t_0}^{t}\left(\frac{dx}{d\tau}\right)^2 d\tau\right\} \qquad (R8)$$

<u>Propagator</u>:

Measure

$$\lim_{\substack{\varepsilon\to 0\\ N\to\infty}} \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \ldots \int_{-\infty}^{+\infty} dx_N \left(4\pi\varepsilon D\right)^{-\frac{(N+1)}{2}} \Longrightarrow \int \mathcal{D}\left[x(\tau)\right] \qquad (R9)$$

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$$G_0(x,x_0;t,t_0) \equiv G_0(x,t) =$$

$$= \int_{x_0,t_0}^{x,t} \mathcal{D}[x(\tau)] \exp\left\{-\frac{1}{4D}\int_{t_0}^{t}\left(\frac{dx}{d\tau}\right)^2 d\tau\right\}$$

$$\int_{-\infty}^{+\infty} \exp\left\{-a(x-x')^2 - b(x-x'')^2\right\} dx$$

$$= \left(\frac{\pi}{a+b}\right)^{1/2} \exp\left\{-\frac{a\cdot b}{a+b}(x'-x'')^2\right\}$$

$x'=x_0,\ x''=x_2,\ x=x_1$ $\wedge$ Integr. über x_1

usw. " " x_2

$\vdots$

" " x_N

$$= \left(4\pi D(t-t_0)\right)^{-1/2} \exp\left\{-\frac{(x-x_0)^2}{4D(t-t_0)}\right\} \qquad (R10)$$

Now: Brownian Motion in media where Brownian Particle (BP) can be vanish (Vernichtet) with probab. $A(x,t)$ per time unit

"annihilation"

$$j(x,t) = -D\frac{\partial c}{\partial x}$$

balance (continuity eq.): $\dfrac{\partial c}{\partial t} = -\dfrac{\partial j}{\partial x} - A\cdot c$

$$\curvearrowright \boxed{\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - Ac} \qquad (R11)$$

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Propagator: $G_A(x,t)$ (solution of (R11)) ?

with $G_A(x,t_0) = \delta(x-x_0)$

$\downarrow$

Wiener-Integral:

Path:

Probability that BP "survives" path $x(\tau)$ (i.e. will not be adsorbed):

$$P[x(\tau)] = \exp\left\{-\int_{t_0}^{t} A(x(\tau),\tau)\, d\tau\right\} \qquad (R12)$$

The propagator is sum (weighted) over all trajectories from $x_0\,(t_0)$ to $x(t)$:

$$\boxed{G_A(x,t) = \int_{x_0,t_0}^{x,t} \exp\left\{-\frac{1}{4D}\int_{t_0}^{t}\left(\frac{dx}{d\tau}\right)^2 d\tau - \int_{t_0}^{t} A(x(\tau),\tau)\, d\tau\right\} \mathcal{D}[x(\tau)]} \qquad (R13)$$

$t > t_0$

Def.: $G_A(x,t\,|\,x_0,t_0) = G_A(x,t) \qquad t > t_0$

$G_A(x,t\,|\,x_0,t_0) = 0 \qquad t < t_0 \qquad (R14)$

$$\left[\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2} + A(x,t)\right] G_A(x,t\,|\,x_0,t_0) = \delta(x-x_0)\,\delta(t-t_0)$$

t beliebig, $G_A = 0$ for $t < t_0$

Free moving Brownian Particle:

$$\left[\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2}\right] G_0(x,t\,|\,x_0,t_0) = \delta(x-x_0)\,\delta(t-t_0) \qquad (R15)$$

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↷ Integral eqn.:

$$G_A(x,t\,|\,x_0,t_0) = G_0(x,t\,|\,x_0,t_0) - \qquad (R\,16)$$

$$- \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} G_0(x,t\,|\,x',t')\,A(x',t')\,G_A(x',t'\,|\,x_0,t_0)\,dx'dt'$$

Proof: $\hat{\partial}_{t,xx} \equiv \frac{\partial}{\partial t} - D\frac{\partial^2}{\partial x^2} \;\hat{=}\;$ Operator

$\hat{\partial}_{t,xx} \circ (R\,16)$

↷

$$\hat{\partial}_{t,xx}\,G_A(x,t\,|\,x_0,t_0) = \hat{\partial}_{t,xx}\,G_0(x,t\,|\,x_0,t_0) -$$

$$- \iint \hat{\partial}_{t,xx}\,G_0(x,t\,|\,x',t')\,A(x',t')\,G_A(x',t'\,|\,x_0t_0)\,dx'dt'$$

$\Downarrow$ (R 15)

$$= \delta(x-x_0)\,\delta(t-t_0) - \iint \delta(x-x')\,\delta(t-t')\cdot A(x',t')\circ$$
$$\circ\, G_A(x',t'\,|\,x_0,t_0)$$

$$= \delta(x-x_0)\,\delta(t-t_0) - A(x,t)\,G_A(x,t\,|\,x_0,t_0)$$

↷ $$\left(\hat{\partial}_{t,xx} + A\right) G_A(x,t\,|\,x_0,t_0) = \delta\,\delta \qquad ✓$$

Example Harmonic Potential

→ Polymers:

$$A(x,\tau) = \alpha x^2 \quad , \quad \alpha > 0 \ \wedge \ \text{const.} \tag{20}$$

Solve the Differenzial-eq. or Integral-eq.

Or another method (for quadratic exponentials) of importance:

$$G_A(x,t \mid x_0,t_0) = \int_{x_0,t_0}^{x,t} \exp\{-S\}\, \mathcal{D}[x(\tau)] \tag{21}$$

$$S = \text{„Action / Wirkung"} \overset{!}{=} \int_{t_0}^{t} L(x,\dot{x})\, d\tau \tag{22}$$

$$L = \frac{1}{4D}\left(\frac{dx}{d\tau}\right)^2 + \alpha x^2 \quad , \quad \text{Mechanics: } L = \frac{m}{2}\dot{x}^2 - \frac{m}{2}\omega^2 x^2 \tag{23}$$

Hamilton principle: $S \rightarrow \min$ for classical path; follows from Euler-Lagrange-Equation (Lagrange II)

$$\frac{\partial L}{\partial x} - \frac{d}{d\tau}\frac{\partial L}{\partial \dot{x}} = 0 \qquad 2\alpha x - \frac{d}{d\tau}\frac{1}{4D}\cdot 2\dot{x} = 0 \tag{24}$$

$$4D\alpha x - \ddot{x} = 0$$

$$\ddot{x} = 4\alpha D x$$

$$d^2x/d\tau^2 = 4\alpha D x \qquad x(t_0) = x_0 \tag{25}$$

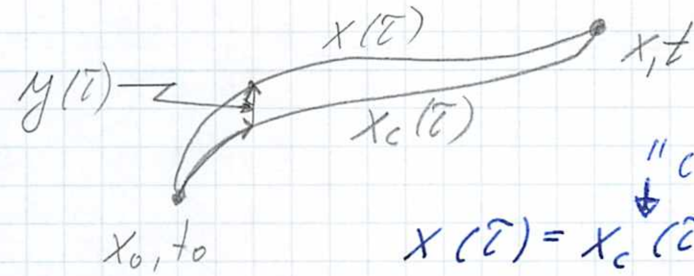
$$x(t) = x$$

↓ mathem. exercise!

analog: $\ddot{x} + \omega^2 x = 0$

Solution:

$$x_c(\tau) = x_0 \cosh\left[\sqrt{4\alpha D}\,(\tau - t_0)\right] + \frac{x - x_0\cosh\left(\sqrt{4\alpha D}\,(t-t_0)\right)}{\sinh\left(\sqrt{4\alpha D}\,(t-t_0)\right)} \cdot \sinh\left(\sqrt{4\alpha D}\,(\tau - t_0)\right) \tag{26}$$



"classical path" ↓ ↑ deviations of "quantum" paths from classical path

$$x(\tau) = x_c(\tau) + y(\tau) \qquad (27)$$

$$y(t_0) = 0, \quad y(t) = 0$$

Eq. (27) into Eq (22) gives (partial integration)

$$S = \underbrace{\sqrt{\frac{\alpha}{4D}}\; \frac{(x_0^2 + x^2)\cosh\sqrt{4\alpha D}\,(t-t_0) - 2x_0 x}{\sinh\sqrt{4\alpha D}\,(t-t_0)}}_{\hat{=}\, S_c} \qquad (28)$$

$$+ \int_{t_0}^{t} \left[\frac{1}{4D}\left(\frac{dy}{d\tau}\right)^2 + \alpha y^2\right] d\tau$$

$$S = S_c + \int_{t_0}^{t} \text{"} \quad \text{"} \qquad (29)$$

Propagator Eq. (21)

$$G_A(x,t\,|\,x_0,t_0) \underset{0,t}{=} f(t-t_0)\, e^{-S_c} \qquad (30)$$

$$f(t-t_0) \equiv \int_{0,t_0} \exp\left\{-\int_{t_0}^{t} \left[\frac{1}{4D}\left(\frac{dy}{d\tau}\right)^2 + \alpha y^2\right]\right\} \mathcal{D}[y(\tau)] \qquad (31)$$

Fourier-series:

$$y(\tau) = \sum_{n=1}^{\infty} a_n \sin\left(n\pi \frac{\tau - t_0}{t - t_0}\right), \quad a_n \text{ reell} \qquad (32)$$

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NR: (32) $\curvearrowright$

$$dy/d\tau = \sum_n a_n \frac{n\pi}{t-t_0} \cos\left(n\pi \frac{\tau - t_0}{t-t_0}\right)$$

$$\alpha y^2 = \alpha \sum_n \sum_{n'} a_n a_{n'} \sin\left(n\pi \frac{\tau-t_0}{t-t_0}\right) \cdot \sin\left(n'\pi \frac{\tau-t_0}{t-t_0}\right)$$

$\vdots$

$$\int_{t_0}^{t} d\tau \, \sin(\dots)\sin(\dots) = \qquad \pi\frac{\tau-t_0}{t-t_0} \stackrel{!}{\equiv} x$$

$$= \frac{t-t_0}{\pi} \int_0^{\pi} dx \sin(nx)\sin(n'x)$$

$$= \frac{t-t_0}{\pi} \delta_{nn'} \underbrace{\int_0^{\pi} \sin^2(nx)dx}_{\pi/2} = \frac{t-t_0}{2}\delta_{nn'}$$

usw.

$$\curvearrowright \int_{t_0}^{t}\left(\frac{1}{4D}\left(\frac{dy}{d\tau}\right)^2 + \alpha y^2\right)d\tau = \frac{t-t_0}{2}\sum_{n=1}^{\infty}\left[\frac{1}{4D}\left(\frac{n\pi}{t-t_0}\right)^2 + \alpha\right]\cdot a_n^2 \qquad (33)$$

$$\curvearrowright f(t-t_0) = F' \prod_{n=1}^{\infty} \int_{-\infty}^{+\infty} da_n \exp\left\{-\frac{1}{2}(t-t_0)\cdot\left[\frac{1}{4D}\left(\frac{n\pi}{t-t_0}\right)^2 + \alpha\right]a_n^2\right\} \qquad (34)$$

$\downarrow$ ~ Jacobi-Determinante d. Transf.. Unabh. v. α

$$= F' \prod_{n=1}^{\infty}\left\{\frac{1}{4D}\left(\frac{n\pi}{t-t_0}\right)^2 + \alpha\right\}^{-1/2}\left(\frac{2\pi}{t-t_0}\right)^{1/2}$$

$$= F \underbrace{\prod_{n=1}^{\infty}\left\{1 + 4\alpha D\left(\frac{t-t_0}{n\pi}\right)^2\right\}^{-1/2}}_{} \qquad (35)$$

$\downarrow$

F subsummiert weitere α-unabh. Faktoren.

$$\left\{\frac{\sinh (t-t_0)\sqrt{4\alpha D}}{(t-t_0)\sqrt{4\alpha D}}\right\}^{-1/2} \longrightarrow 1 \text{ für } \alpha = 0$$

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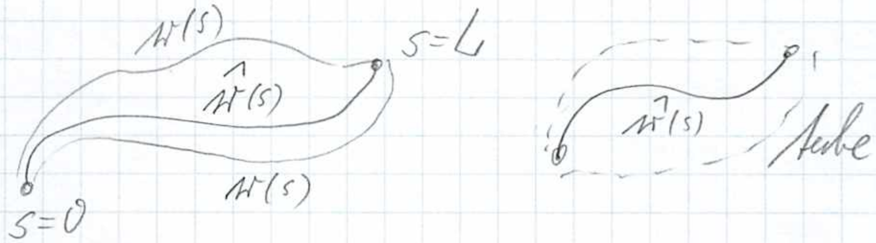
$\lim \alpha \to 0$ gives $G_0(x, x_0 | t, t_0)$, i.e.

$$F = \left(4\pi D(t-t_0)\right)^{-1/2} \qquad (36)$$

$$\boxed{\begin{aligned} G_A(x,t|x_0,t_0) &= \left\{\pi \sqrt{\frac{4D}{\alpha}} \sinh \sqrt{4\alpha D}\,(t-t_0)\right\}^{-1/2} \cdot \\ &\cdot \exp\left\{-\sqrt{\frac{\alpha}{4D}} \, \frac{(x_0^2+x^2)\cosh\sqrt{4\alpha D}\,(t-t_0) - 2xx_0}{\sinh\sqrt{4\alpha D}\,(t-t_0)}\right\} \end{aligned}} \qquad (37)$$

polymers

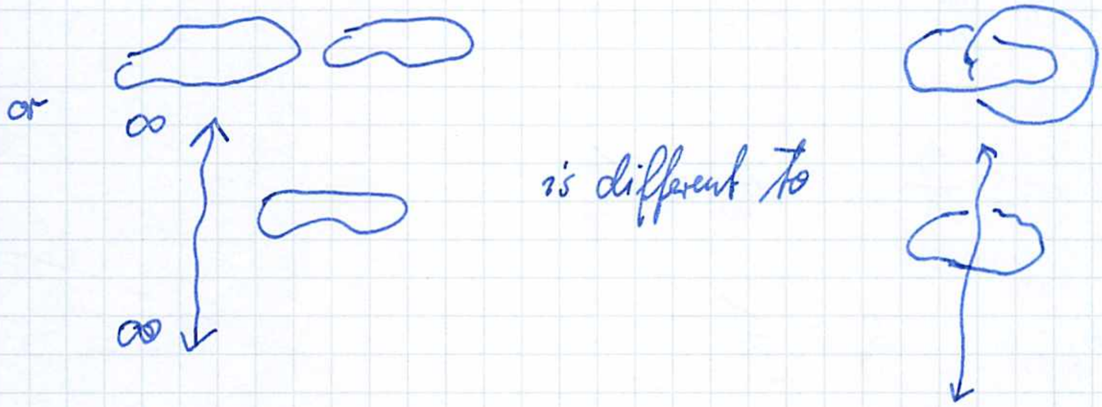


constraints of conformations: $\sim \alpha\left(r(s) - \hat{r}(s)\right)^2$

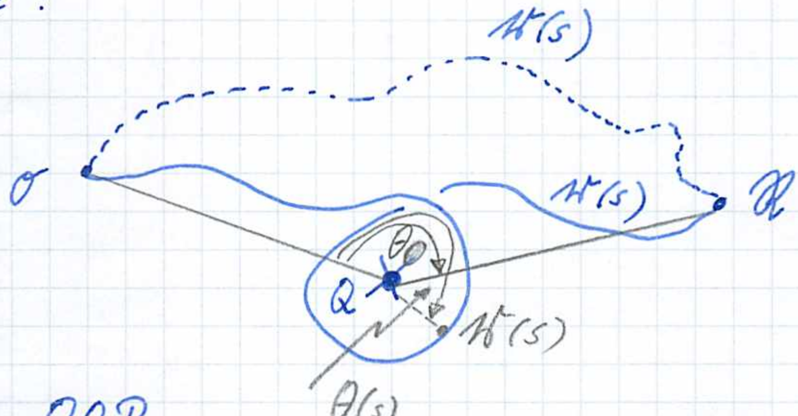
$$\int \mathcal{D}[r(s)] \exp\left\{-\frac{3}{2l}\int_0^L \left(\frac{\partial r(s)}{\partial s}\right)^2 ds - \alpha \int_0^L ds\left(r^2 - 2\hat{r}\,r\right)\right\}$$

3. Constrained polymer chains

3.1. Topological constraints in 2 dimensions



2d - case :



$\theta_0 = \measuredangle\, OQR$

For ------ $r(s)$: $$\int_0^L \frac{d\theta(s)}{ds}\, ds = \int_0^L \dot{\theta}(s)\, ds = \theta_0 \qquad (1)$$

For ∼∼ $r(s)$: $$\int_0^L \dot{\theta}(s)\, ds = \theta_0 + 2\pi m = \nu \qquad (2)$$

when m entanglements

→ reduced distrib. function / statistical weight / Greenfunction

$$G_\nu(R, 0; L) = \int_{r(0)=0}^{r(L)=R} \mathcal{D}[r(s)] \exp\left\{-\frac{3}{2l}\int_0^L \dot{r}^2(s)\, ds\right\} \cdot \delta\left[\nu - \int_0^L \dot{\theta}(s)\, ds\right] \qquad (3)$$

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$x = \rho \cdot \cos\theta$ $\qquad x^2 + y^2 = \rho^2$

$y = \rho \cdot \sin\theta$

$dx = \cos\theta \, d\rho - \sin\theta \cdot \rho \cdot d\theta$

$dy = \sin\theta \, d\rho + \cos\theta \, \rho \cdot d\theta$

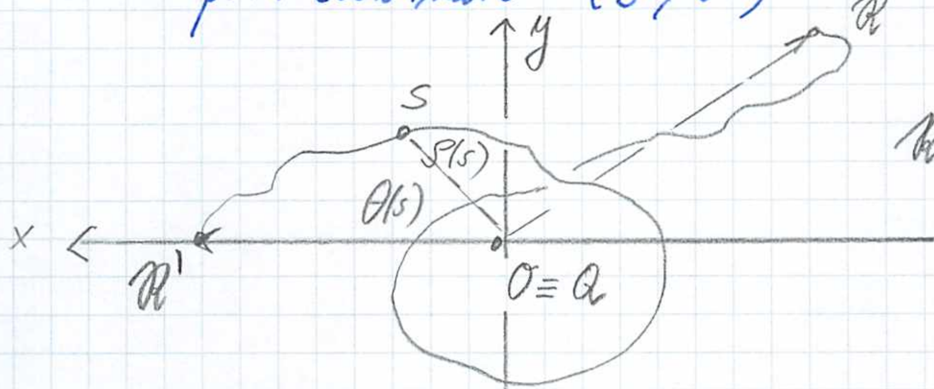
$x \cdot dy = \rho \cdot \sin\theta \cdot \cos\theta \, d\rho + \rho^2 \cdot \cos^2\theta \, d\theta$

$-y \, dx = -\rho \cdot \sin\theta \cos\theta \, d\rho + \rho^2 \sin^2\theta \, d\theta$

$x dy - y dx = \rho^2 (\underbrace{\sin^2\theta + \cos^2\theta}) \, d\theta$

$d\theta = \dfrac{x dy - y dx}{\rho^2} \overset{1}{=} \dfrac{x dy - y dx}{x^2 + y^2}$

Now: Origin of coord. system in Q
polar coordinates (ρ, θ)



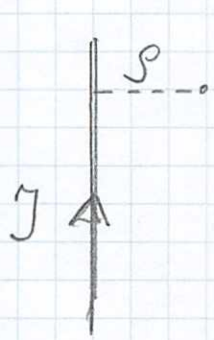
$\mathcal{R} = \mathcal{R}'' - \mathcal{R}'$

$x = \rho \cdot \cos\theta$
$y = \rho \cdot \sin\theta$ $\qquad d\mathbf{r} = (dx, dy)$

$$\curvearrowright \; d\theta = \frac{x\,dy - y\,dx}{x^2 + y^2} = \mathcal{A} \cdot d\mathbf{r} \qquad (4)$$

$$\mathcal{A} = \frac{1}{x^2 + y^2} \left(-y, +x \right)$$

$$\dot{\theta} = \frac{d\theta}{ds} = \mathcal{A} \cdot \frac{d\mathbf{r}}{ds} = \mathcal{A} \cdot \dot{\mathbf{r}} \qquad (5)$$



$\vec{H} = \frac{I}{2\pi} \frac{1}{\rho} \vec{e}_\varphi$ $\qquad \mathcal{A} = \frac{1}{x^2 + y^2} (-y, x)$ cartesian coordinates

Polarcoord. $A_\rho = 0$, $A_\varphi = \frac{1}{\rho}$

$\mathcal{A} \mathrel{\hat{=}} \vec{H}$ if $I/2\pi = 1$

$$\delta(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\lambda \cdot x} \, d\lambda$$

$\curvearrowright$ (3)

$$G_{\mathcal{R}}(\mathcal{R}, 0; L) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\lambda \, e^{i\lambda\theta} \underbrace{\int_{\mathbf{r}(0)=0}^{\mathbf{r}(L)=\mathcal{R}} \mathcal{D}[\mathbf{r}(s)] \exp\left\{ -\frac{3}{2l} \int_0^L \left(\dot{\mathbf{r}}(s)^2 + i\lambda \frac{2l}{3} (\mathcal{A}\dot{\mathbf{r}}) \right) ds \right\}}_{G_\lambda} \qquad (6)$$

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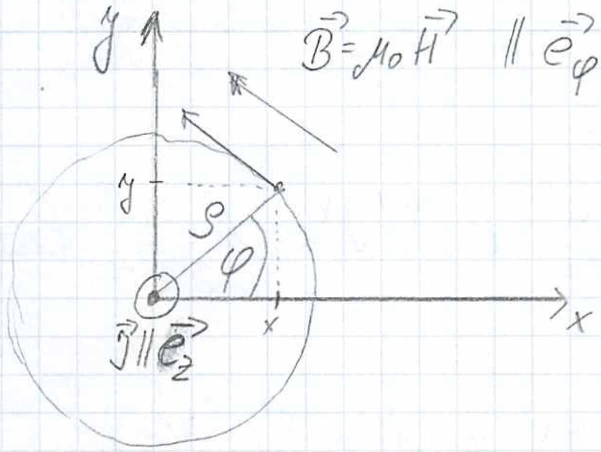
E



$\vec{B} = \mu_0 \vec{H} \parallel \vec{e}_\varphi$

Vektorpotential eines Leiters

$$\vec{H} = \frac{J}{2\pi\rho}\vec{e}_\varphi = \frac{J}{2\pi}\frac{-\sin\varphi\,\vec{e}_x + \cos\varphi\,\vec{e}_y}{\sqrt{x^2+y^2}} = \frac{J}{2\pi}\frac{-y\,\vec{e}_x + x\,\vec{e}_y}{\sqrt{x^2+y^2}}$$

gut geraten: $\vec{A} = -\frac{\mu_0 J}{4\pi} \cdot \ln(x^2+y^2) \cdot \vec{z}$

$\vec{B} = \mathrm{rot}\,\vec{A}$

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$$G_{\vartheta} = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\lambda\, e^{i\lambda\vartheta}\, G_{\lambda}(R,0;L) \qquad (7)$$

$(\dot{r}^2 + i\frac{2l}{3}\lambda\, \mathfrak{A}\dot{r})$ corresponds Lagrange-Function of a charged particle in the field with vectorpotential $\sim \mathfrak{A}$.

The inhomog. "Schrödinger-Eq." gives the Propagator function

$$\left\{\frac{\partial}{\partial L} - \frac{l}{6}\left(\nabla_R\left(\nabla_R - 2i\lambda\mathfrak{A}\right)\right) - \frac{\lambda^2 l^2}{9}\mathfrak{A}^2\right\} G_{\lambda} = \delta(L)\,\delta(R) \qquad (8)$$

or

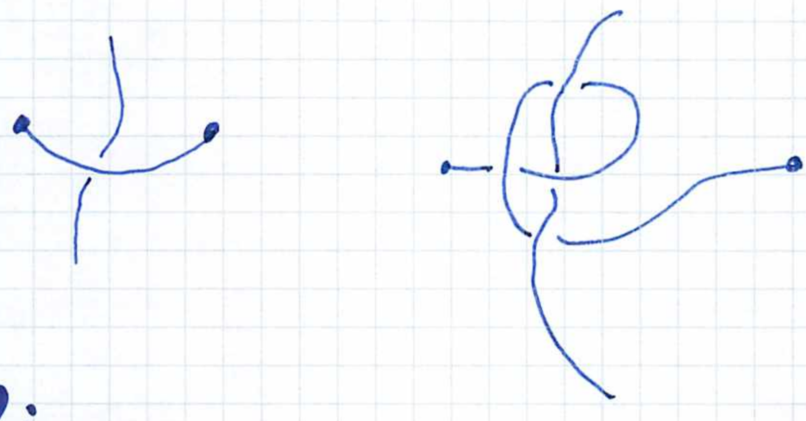
$$\left\{\frac{\partial}{\partial s} - \frac{l}{6}\left(\nabla_R - i\lambda\mathfrak{A}\right)^2\right\} G_{\lambda}(R,R';ss') = \delta(s-s')\,\delta(R-R') \qquad (9)$$

<u>Solution</u>: Edwards 1967/68

$$\boxed{\begin{aligned} G_{\vartheta}(R,R') &= \frac{1}{2\pi}\sum_m \delta(\vartheta - 2\pi m - \Theta_0)\,\cdot \\ &\cdot \int_{-\infty}^{+\infty} d\lambda\, \exp\left\{i\lambda(\Theta_0 + 2\pi m) - \frac{R^2+R'^2}{lL}\right\} I_{|\lambda|}\left(\frac{2RR'}{lL}\right) \end{aligned}} \qquad (10)$$

Problem:

Invariants often not "eindeutig". Gleich für verschieden topologisch nichtäquivalente Fälle, z.B.:



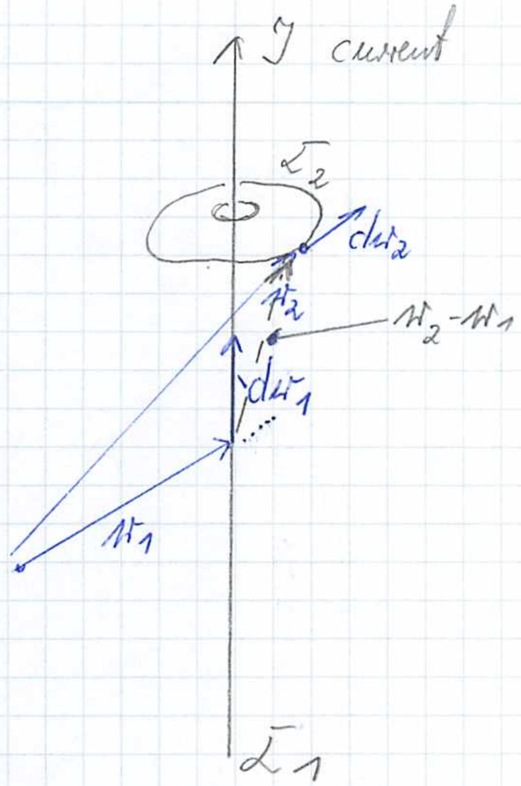
3.2:

3d-∞ case: Topol. invariants

$$I_{12} = I\{r_1(s), r_2(s)\} = \frac{1}{4\pi} \oint_{C_1} \oint_{C_2} dr_1 \times dr_2 \, \frac{r_1 - r_2}{|r_1 - r_2|^3} \qquad (11)$$

$$= \frac{1}{4\pi} \oint \oint ds_1 \, ds_2 \, \left(\dot{r}_1(s_1) \times \dot{r}_2(s_2) \right) \nabla \frac{1}{|r_{12}|^3}$$

Explanation comes easily from electrodynamics!



Bio - Savart'sches Gesetz

$$d\vec{H} = \frac{I}{4\pi} \frac{1}{|r_2 - r_1|^3} \, dr_1 \times (r_2 - r_1)$$

$$\vec{H}(r_2) = \oint_{\mathcal{L}_1} d\vec{H} = \frac{I}{4\pi} \oint_{\mathcal{L}_1} \frac{1}{|r_2 - r_1|^3} \, dr_1 \times (r_2 - r_1)$$

4. Maxwell - Eq.: $\quad \mathrm{rot}\, H = \vec{j}$ local

$$\oint_{\mathcal{L}_2} \vec{H}(r_2)\, dr_2 = \pm I \cdot n \qquad n \text{ ganz}$$

$$= \frac{I}{4\pi} \oint_{\mathcal{L}_1} \oint_{\mathcal{L}_2} \frac{[dr_1 \times (r_2 - r_1)]\, dr_2}{|r_2 - r_1|^3}$$

$$(a \times b)\, c = (c \times a) \cdot b$$

$$\rightsquigarrow \boxed{\begin{gathered}\frac{1}{4\pi} \oint_{\mathcal{L}_1} \oint_{\mathcal{L}_2} (d\mathbf{r}_2 \times d\mathbf{r}_1) \frac{\mathbf{r}_2 - \mathbf{r}_1}{|\mathbf{r}_2 - \mathbf{r}_1|^3} = m \\[1em] I(\mathbf{r}_1, \mathbf{r}_2) = m\end{gathered}} \qquad (12)$$

Edwards'sche Invariante

Einschub!

Eichfeldformulierung d. topol. Verschlaufungen von Polym

1. Einführung:

$s \mathrel{\hat=}$ Bogenlänge

statistisches Gewicht f. Konfiguration (random walk):

$$(1)\quad G_0(r, r_0; 0L) = \int_{r(0)=r_0}^{r(L)=r} \mathcal{D}r(s) \exp\left\{-\int_0^L \mathcal{L}_0(\dot r; r)\, ds\right\} \quad ''$$

$$\dot r \equiv \partial r(s)/\partial s$$

$$(2)\quad \mathcal{L}_0 = \frac{d}{2l}\dot r^2 = \frac{3}{2l}\dot r^2 \quad (d=3)$$ freier random walk

$$(3)\quad p \equiv \partial\mathcal{L}_0/\partial \dot r,$$ Hamiltonf.: $H = H(p, r) = p\dot r - \mathcal{L}_0$

$$(4)\quad \left\{\frac{\partial}{\partial L} - H(-\nabla, r)\right\} G_0(r; r_0) = \delta(L)\,\delta(r - r_0)$$

„Schrödinger"-Gl.

$$(5)\quad \left\{\partial/\partial L - l/6\, \nabla_r^2\right\} G_0 = \delta\delta$$

$$(6)\quad G_0(r; r_0; 0L) = \left(\frac{3}{2\pi l L}\right)^{3/2} \exp\left\{-\frac{3}{2lL}(r - r_0)^2\right\}$$

$$(7)\quad \langle (r - r_0)^2 \rangle = lL = Nl^2$$

Gauß'sche Invariante $\quad I_{\alpha\beta}=0 \qquad I_{\alpha\beta}=1 \qquad I_{\alpha\beta}=2 \qquad I_{\alpha\beta}=0$

(8) $I_{\alpha\beta} = I\{C_\alpha, C_\beta\} = \frac{1}{4\pi}\oint_{C_\alpha}\oint_{C_\beta} \dot{\mathbf{r}}_\alpha(s_\alpha)\times\dot{\mathbf{r}}_\beta(s_\beta)\,\nabla\frac{1}{|\mathbf{r}_\alpha-\mathbf{r}_\beta|}\, d$

(9) $I_{\alpha\beta} = \oint_{C_\alpha} \mathfrak{a}(\mathbf{r}_\alpha)\,d\mathbf{r}_\alpha = \oint_{C_\alpha} \mathfrak{a}(\mathbf{r}_\alpha)\,\dot{\mathbf{r}}_\alpha\,ds_\alpha$

(10) Vektorfeld: $\mathfrak{a}(\mathbf{r}_\alpha) = \frac{1}{4\pi}\oint_{C_\beta} d\mathbf{r}_\beta \times \nabla\frac{1}{|\mathbf{r}_\alpha-\mathbf{r}_\beta|}$

C_β „magn. Flußlinie" $\rightarrow$ $\mathfrak{a}(\mathbf{r}_\alpha)$ „magn. Vektorpotentia

Symmetrietransform.: (isotope) Deform. von C_β so, daß

(11) $C_\beta \to C_\beta' \wedge I_{\alpha\beta}\to I_{\alpha\beta}' = I_{\alpha\beta}$, dann

(12) $\mathfrak{a}(\mathbf{r}_\alpha) \to \mathfrak{a}'(\mathbf{r}_\alpha) = \mathfrak{a}(\mathbf{r}_\alpha) + \nabla\Omega(\mathbf{r}_\alpha)$

„lokale Eichtransf. d. Vektorpot. in d. E-Dynamik"

(13) $C_\beta \bigcirc \curvearrowright \nabla\mathfrak{a} = 0$

Erhaltung d. Windungszahl m:

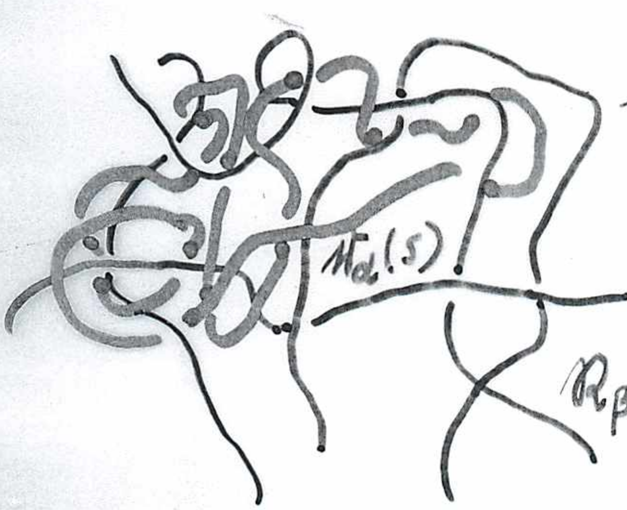
"Kopplungskonstante"

$$\delta[I_{\alpha\beta} - m] = \frac{1}{2\pi}\int_{-\pi}^{+\pi} dg \, \exp\{ig(I_{\alpha\beta} - m)\}$$

(14) $$= \frac{1}{2\pi}\int_{-\pi}^{+\pi} dg \, \exp\{ig(\oint_{C_\alpha} \mathfrak{a} \, d\mathfrak{r}_\alpha - m)\}$$

Wilson loop integral

2. Behinderung durch Verschlaufung als Eichfeldtheorie:



Spaghetti-Hintergrund

Eigenschaft:

$F_{\alpha\beta} = F[\{\mathfrak{r}_\alpha(s)\}, \{\mathfrak{R}_\beta$

(15) Konfigurationsmittelwert: $\langle F \rangle = \frac{1}{Z(0)} \frac{\partial}{\partial \lambda} Z(\lambda, L, m)$

(16) $$Z(\lambda, L, m) = \frac{1}{2\pi}\int_{-\pi}^{+\pi} dg \, e^{-igm} \tilde{Z}(\lambda, L, g)$$

$$\tilde{Z}(\lambda, L, g) = \int \mathcal{D}\mathbf{r}_\alpha \, \mathcal{D}\mathbf{R}_\beta \; \delta[\mathbf{r}_\alpha(0) - \mathbf{r}_\alpha(L_\alpha)] \, \delta[\mathbf{R}_\beta(0) - \mathbf{R}_\beta$$

$$\cdot e^{ig I_{\alpha\beta}} \cdot \exp\left\{ -\frac{3}{2\ell} \int_0^{L_\alpha} \dot{\mathbf{r}}_\alpha^2(s) \, ds - \frac{3}{2\ell} \int_0^{L_\beta} \dot{\mathbf{R}}_\beta^2(s) \, d\right.$$

$$\cdot \exp\left(\lambda F[\{\mathbf{r}_\alpha\}, \{\mathbf{R}_\beta\}]\right)$$

$\longrightarrow$ Mittelung über Hintergrund $\mathbf{R}_\beta(s)$

$$\langle e^{ig I_{\alpha\beta}} \rangle_{\{\mathbf{R}_\beta\}} \simeq \exp\left\{ -\frac{1}{2} g^2 \langle I_{\alpha\beta}^2 \rangle_{\{\mathbf{R}_\beta\}} \right\}$$

explizite Form:

$\rightarrow F\{\mathbf{r}\} = \delta[\mathbf{r}(s) - \mathbf{R}]$, $\rho(\mathbf{R}) = \int_0^L ds \, \langle \delta(\mathbf{r}(s) - \mathbf{R}) \rangle$

Raumpunkt

mittl. Dichte d. Monomere d.
d. Länge L.

Greenfunktion

$\rightarrow \frac{3}{2g\ell^2} \int d^3x$

$$G(\mathbf{R}, s, L, g) \sim \int \mathcal{D}\mathbf{a} \, \delta(\nabla \mathbf{a}) \exp\{-\mathcal{L}[\mathbf{a}]\} \cdot$$

$$\cdot K(\mathbf{R}, s; [\mathbf{a}]) K(\mathbf{R}, s; [-\mathbf{a}]$$

Propagator:

$$K(\mathbf{r}, s; [\mathbf{a}]) \sim \int_0^s \mathcal{D}\mathbf{r}(s')\, \delta[\mathbf{r}(s) - \mathbf{r}(0) - \mathbf{r}] \exp\left\{-\int_0^s ds \cdot \left[\tfrac{3}{2\ell}\dot{\mathbf{r}}^2(s') - ig\,\mathbf{a}\dot{\mathbf{r}}\right]\right\}$$

(19)

(20) $$\left\{\frac{\partial}{\partial s} - \frac{\ell}{6}\underbrace{(\nabla_{\mathbf{r}} - ig\,\mathbf{a})}_{\text{minimale Kopplung}}{}^2\right\} K(\mathbf{r}, s; [\mathbf{a}]) = 0$$

T $$\lim_{s \to 0} K = \delta(\mathbf{r})$$

$$\left\{\mu - \frac{\ell}{6}(\nabla - ig\,\mathbf{a})^2\right\}\hat{K} = \delta(\mathbf{r})$$

(21) $$\hat{K}(\mathbf{r}, \mu; [\mathbf{a}]) = \int_0^\infty ds\, e^{-\mu s} K(\mathbf{r}, s; [\mathbf{a}])$$

Start $\psi^*(0)$ > Komplexe stochastische Felder

Ende $\psi^*(\mathbf{r})$

(22) $$\hat{K} = \mathcal{N}^{-1}\int \mathcal{D}\psi^*(\mathbf{r})\,\mathcal{D}\psi(\mathbf{r})\,\psi^*(0)\psi(\mathbf{r})\, e^{-\mathcal{L}}$$

$$\equiv \langle \psi^*(0)\psi(\mathbf{r})\rangle_{[\psi]}$$

(23) $$\mathcal{L}[\psi] = -\frac{1}{2}\int d^3\mathbf{r}\, \psi^*(\mathbf{r})\left[\frac{\ell}{6}(\nabla - ig\,\mathbf{a})^2 - \mu\right]\psi(\mathbf{r})$$

Damit Laplace-Tr. von G:

$$\hat{G}(\mathfrak{R},\mu,L,g) = \lim_{J\to 0}\lim_{n\to 0}\frac{\delta}{\delta J(\mathbf{r})}\frac{\delta}{\delta J(0)}\cdot$$

$$\frac{\int \mathcal{D}\mathfrak{a}\,\delta(\nabla\mathfrak{a})\prod_{i=1}^{n}\int\mathcal{D}\psi_i\,\mathcal{D}\psi_i^{*}\exp(-\mathcal{L}_{tot}(J))}{\int \mathcal{D}\mathfrak{a}\,\delta(\nabla\mathfrak{a})\prod_{i=1}^{n}\int\mathcal{D}\psi_i\,\mathcal{D}\psi_i^{*}\exp(-\mathcal{L}_{tot}(0))}$$

$$\mathcal{L}_{tot}(J) = \int d^3\mathbf{r}\left\{\frac{3}{2gl^2}(\nabla\times\mathfrak{a})^2 + \frac{1}{2}\mu|\psi_i|^2 + \frac{l}{12}|(\nabla - ig\mathfrak{a})\psi_i|^2 \ldots\right.$$

$\downarrow$ invariant ggüber $\mathfrak{a}' \to \mathfrak{a} + \nabla\Lambda(\mathbf{r})$

$\psi_i' \to \psi_i e^{i\Lambda(\mathbf{r})}$, $\psi_i^{*'} \to \psi_i^{*} e^{-i\ldots}$

„excluded volume"-Ww.: $\mathcal{L}_{tot} = \cdots + v|\psi_i|^4$, $v>0$

$\Downarrow$ renormal. QED Lagrangian

$\downarrow$

Polymer als „Self avoiding walk" $\longrightarrow$ Krit. Phänomen

$\tau \left(\hat{=} \frac{T-T_c}{T_c}\right) = 1/N$

obere Krit. Dim.: $d_c = 4$

Damit Laplace-Tr. von G:

$$\hat{G}(\mathbf{r},\mu,L,g) = \lim_{J\to 0}\lim_{m\to 0}\frac{\delta}{\delta J(\mathbf{r})}\frac{\delta}{\delta J(0)}\cdot$$

$$(24)\quad \frac{\int \mathcal{D}\mathbf{a}\,\delta(\nabla\mathbf{a})\prod_{i=1}^{m}\int \mathcal{D}\psi_i\,\mathcal{D}\psi_i^*\exp(-\mathcal{L}_{tot}(J))}{\int \mathcal{D}\mathbf{a}\,\delta(\nabla\mathbf{a})\prod_{i=1}^{m}\int \mathcal{D}\psi_i\,\mathcal{D}\psi_i^*\exp(-\mathcal{L}_{tot}(0))}$$

$$(25)\quad \mathcal{L}_{tot}(J) = \int d\mathbf{r}^3\left\{\frac{3}{2g\ell^2}(\nabla\times\mathbf{a})^2 + \frac{1}{2}\mu|\psi_i|^2 + \frac{\ell}{12}|(\nabla - ig\mathbf{a})\psi_i|^2 - J|\psi_i|^2\right\}$$

$\downarrow$ invariant ggüber $\mathbf{a}' \to \mathbf{a} + \nabla\Lambda(\mathbf{r})$

$\psi_i' \to \psi_i e^{i\Lambda(\mathbf{r})}$, $\psi_i^{*\prime} \to \psi_i^* e^{-i\Lambda(\mathbf{r})}$

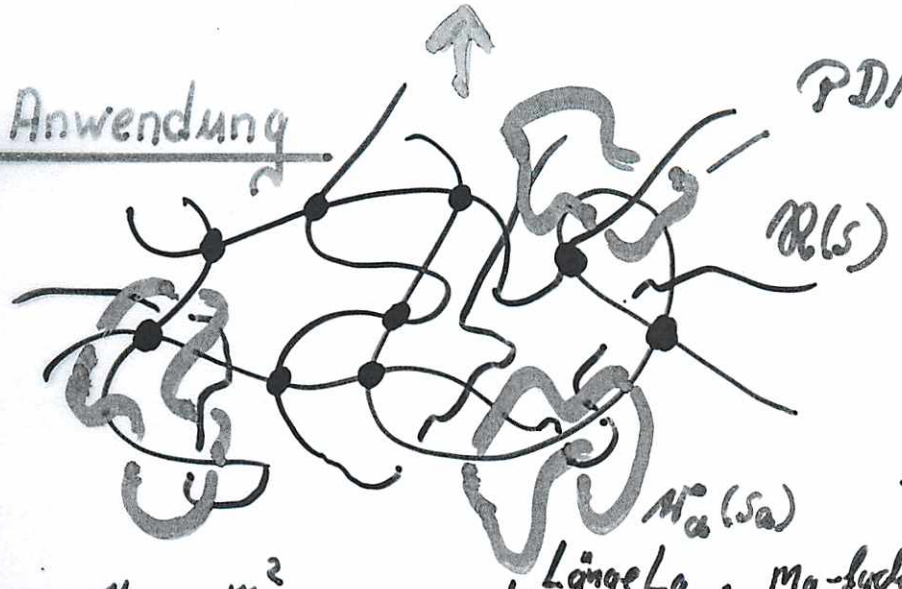
+ „excluded volume"-Ww.: $\mathcal{L}_{tot} = \dots + v|\psi_i|^4$, $v>0$

$\Downarrow$ renormal. QED Lagrangian

Polymer als „Self avoiding walk" $\longrightarrow$ Krit. Phänomen

3. Anwendung

PDMS - Cyclen



statistisches Netzwerk mit eingebauten Cy[clen]

Länge L_α, m_α-fach verschlauft.

$$p(m) = \left(\frac{1}{\pi \overline{m^2}}\right)^{1/2} e^{-\frac{m^2}{\overline{m^2}}}$$

Wahrsch. f. m-fache Verschl. mit Netzmatrix

Deformation des Systems

E-Modul?

[Zust]andsint. d. verschlauften Cyclen:

$$Z(\{m_\alpha\}) \approx \oint \left(\prod_\alpha \mathcal{D}N(s_\alpha)\right) \exp\left\{-\sum_\alpha \frac{3}{2l} \int_0^{L_\alpha} \dot{N}_\alpha^2(s_\alpha)\, ds_\alpha\right\} \prod_\alpha$$

Windungszahl

$$\delta_\alpha = \left\langle \delta\left(I_\alpha(N_\alpha(s_\alpha), \mathcal{R}(s)) - m_\alpha\right)\right\rangle_{\{\mathcal{R}(s)\}}$$

$$= \frac{1}{2\pi} \int dg_\alpha\, e^{i g_\alpha m_\alpha} \left\langle e^{-i g_\alpha I_\alpha}\right\rangle_{\{\mathcal{R}(s)\}}$$

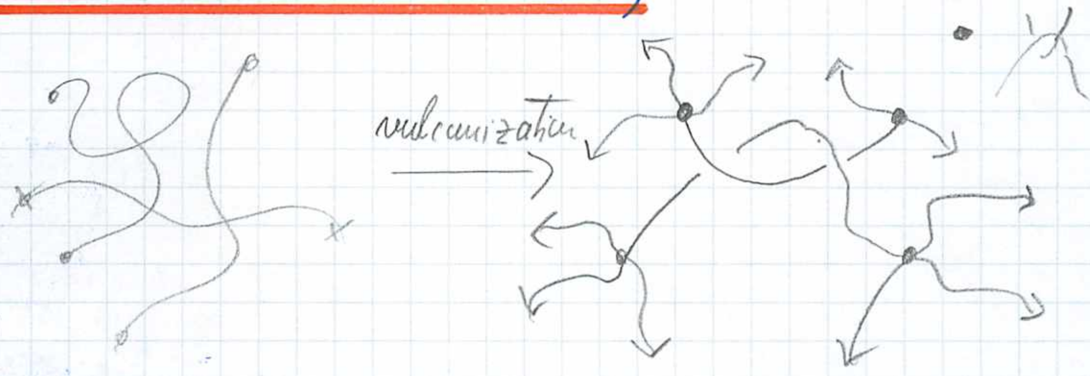
[Beitr]ag zum Elastizitätsmodul:

$$E_c \simeq \frac{\overline{m^2}}{\sqrt{\tilde{n}_s \tilde{n}_s^{\,2}}} \frac{\nu_{cyclen}}{N_s} k_B T$$

4. Statistische Mechanik mit topol. Behinderungen

[topological constraints]

4.1. Introduction (S.F. Edwards)



special topology: „m"

probability, to realize (vulcanization) topology m:

instantaneous crosslinking in thermody. equil. (T, p const.)

$$p_m = \exp\left[-\frac{(F_m - F_0)}{kT}\right] \tag{1}$$

F_m — (Gibbs) free energy of topology "m" -system

F_0 — free energy if all possible topologies can be realized

$$\sum_m p_m = 1 \curvearrowright \sum_m e^{-F_m/kT} = e^{-F_0/kT} \tag{2}$$

$\{1/kT \equiv \beta\}$

Macroscopically observable free energy of the material (network)

$$\tilde{F} \doteq \sum_m p_m F_m = \frac{\sum_m e^{-\beta F_m} \cdot F_m}{e^{-\beta F_0}} = \frac{-\frac{\partial}{\partial\beta}\sum_m e^{-\beta F_m}}{e^{-\beta F_0}}$$

$$= \frac{\left(-\frac{\partial}{\partial\beta}\right) e^{-\beta F_0}}{e^{-\beta F_0}} = \underline{\underline{F_0}} \tag{3}$$

Change of free energy:

$$\Delta F_m = \tilde{F}_m - F_m$$

e.g. $\underset{\approx}{\lambda}$ $\underset{\approx}{\lambda} = 1$

for given topology

$\underset{\approx}{\lambda} \hat{=}$ strain of network

$\lambda_x = \frac{L}{L_0}$

$$\boxed{\Delta \tilde{F} = \sum_m p_m \, \Delta F_m} \qquad (4)$$

annealed system (m not fixed): $\Delta F_0 = \Delta \left(\sum_m p_m F_m \right)$

Calculation of $\tilde{F} = \sum_m p_m \tilde{F}_m$ using modified Gibbs formula:

Usual Gibbs-eq.: $Z = e^{-F_0/kT} = \int d\Omega \, e^{-H_0/kT}$

H_0 = Hamiltonian with not fixed constraints

$\int d\Omega \hat{=}$ integration phase space

To calculate $\tilde{F}$ we consider $n+1$ copies of the sample with topology m (rubber network)

undeformed system ($\tilde{F} = F_0$) n deformed systems ($\tilde{F} \neq F_0$)

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Definition:

$$\boxed{Z(n) = \sum_m \exp\left\{-\frac{F_m}{kT_0} - n\,\frac{\tilde{F}_m}{kT}\right\}} \qquad (5)$$

F_m free energy of "0"-system : preparation (vulc.) T_0, p_0, etc

$\tilde{F}_m$ free energy of "m-systems" under new conditions (T, p, deformed λ)

$$\curvearrowright\; Z(n) = \sum_m \underbrace{\int e^{-\frac{H_m}{kT_0}}\, d\Omega}_{e^{-F_m/kT_0}} \cdot \underbrace{\tilde{\int} e^{-H_m/kT}\, d\Omega \;\ldots\; \tilde{\int} e^{-H_m/kT}\, d\Omega}_{n \text{ times}} \qquad (6)$$

H_m is Hamiltonian with constraint topology "m"

$\tilde{\int}\ldots$ integr. under new (stretched) conditions!

$$\curvearrowright\; \boxed{Z(n) = \sum_m \int d\Omega_{(0)} \prod_{\alpha=1}^{n} d\Omega_{(\alpha)}\, \exp\left[-\frac{H_m^{(0)}}{kT_0} - \frac{H_m^{(\alpha)}}{kT}\right]} \qquad (7)$$

Aus (5) $\curvearrowright$

$$\frac{\partial Z(n)}{\partial n} = -\sum_m \frac{\tilde{F}_m}{kT} \exp\left\{-\frac{F_m}{kT_0} - \frac{n\tilde{F}_m}{kT}\right\}$$

$$\left.\frac{\partial Z(n)}{\partial n}\right|_{n=0} = -\sum_m \frac{\tilde{F}_m}{kT} \exp\left\{-\frac{F_m}{kT_0}\right\} \underset{\uparrow (1)}{=} -\sum_m \frac{\tilde{F}_m}{kT} \cdot p_m\, e^{-\frac{F_0}{kT_0}}$$

$$\left.\frac{\partial Z(n)}{\partial n}\right|_{n=0} \underbrace{e^{+F_0/kT_0}}_{\substack{(5),(2)\\ \frac{1}{Z(n=0)}}} = -\sum_m p_m \frac{\tilde{F}_m}{kT}$$

$$\rightsquigarrow \quad \frac{\left.\frac{\partial Z(n)}{\partial n}\right|_{n=0}}{Z(n=0)} = -\frac{\tilde{F}(\underset{\approx}{\lambda})}{kT}$$

$$\boxed{\tilde{F}(\underset{\approx}{\lambda}) = -kT \lim_{n\to 0}\frac{d}{dn}\left(\ln Z(n)\right)} \qquad (8)$$

Via calculation of $Z(n)$ we find the free energy $\tilde{F}$ of an amorphous system with molecular constraints that are formed under equilibrium condition.

$\Longrightarrow$ Applic. to rubber networks.

Note: Replika-Trick:

$$\log x = \lim_{n\to 0}\frac{d}{dn} x^n = \lim_{n\to 0}\frac{d}{dn} e^{n\cdot\log x}$$

$$= \lim_{n\to 0}\frac{d}{dn}\left(1 + n\cdot\log x + O(n^2)\right) = \log x$$

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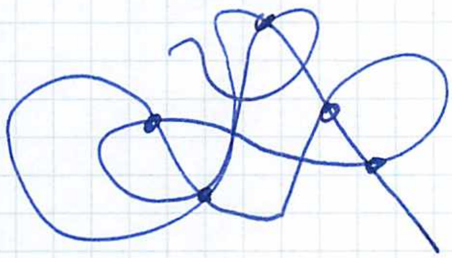
4.2 Model for Phantom Chain Network

(Deam, Edwards)



M chemical crosslinks

N primary chains of length L'

V volume

$L = N \cdot L'$

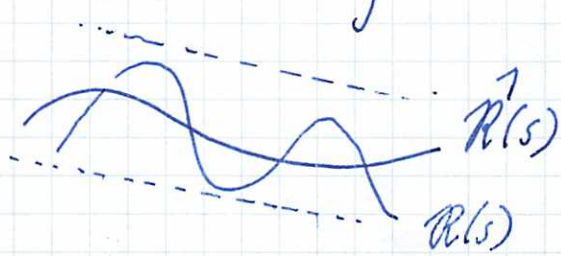
! $\hat{=}$ Network = one giant chain of contour length L

Phantom chain : $\mathcal{R}(s)$

Topology of the Network:

$$\mathcal{T} = \{ \mathcal{T}_{\text{crosslinks}}, \mathcal{T}_{\text{constraints/entangl.}} \}$$

$$= \{ \{s_i, s_i'\}, \hat{\mathcal{R}}(s) \} \qquad i = 1, \dots M$$



Probability density for realization of $\mathcal{T}$:

$$d w_{\mathcal{T}} = p\left(\hat{\mathcal{R}}(s)\right)\left(\mathcal{D}_{\{s_i, s_i'\}}\left(\hat{\mathcal{R}}(s)\right)\right) \cdot \prod_i \tfrac{1}{2}\, ds_i\, ds_i' \qquad (9)$$

$$p\left(\hat{\mathcal{R}}(s)\right) = \mathcal{N}' \exp\left\{ -\frac{3}{2l} \int_0^L \dot{\hat{\mathcal{R}}}(s)^2\, ds \right\}$$

$$\mathcal{D}_{\{s_i, s_i'\}}\left(\hat{\mathcal{R}}(s)\right) \equiv \mathcal{D}\hat{\mathcal{R}}(s) \prod_{i=1}^{M} \delta^{(3)}\left(\hat{\mathcal{R}}(s_i) - \hat{\mathcal{R}}(s_i')\right) \qquad (10)$$

$$\int_0^L \int_0^L \int \mathcal{D}\hat{\mathcal{R}}(s) \dots \Rightarrow \int d w_{\mathcal{T}} = 1 \quad \sim \mathcal{N}' \qquad (11)$$

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Statistical weight of an actual network chain conformation

$\underline{R}(s)$ in the deformed network with the average (affine changed) conformation $\underset{\approx}{\lambda} \hat{R}(s)$:

$$p\left(R(s) \,|\, \hat{R}(s)\right) = \mathcal{N}'' \exp\{-H/kT\} \qquad (12)$$

$$H/kT = \frac{3}{2l}\int_0^L \dot{R}(s)^2\, ds + \sum_{\mu = x,y,z} \int_0^L w_\mu^2 \left(R_\mu(s) - \lambda_\mu \hat{R}(s)\right)^2 ds \qquad (13)$$

strength of topol. constraints in stretching directions.

~ tube diameter $d_0^2 \equiv \langle (R(s) - \hat{R}(s))^2 \rangle$ (14)

$$d_0^2 = l^{1/2} / w \qquad (15)$$

$$d_\mu^2 = l^{1/2} / w_\mu$$

$d_\mu = d_0 (\lambda_\mu^*)^\delta$ ~ | deviations from Neo-Hookean law! Engineering Applic.

$\lambda_\mu^* = \lambda_\mu^\beta$ β: constraint release parameter $0 \le \beta \le 1$

$\delta = 1/2$ tube deformation (non-affine)

$d_0/l = K(f)\,(n_s l^3)^{-1/2}$ $n_s = \frac{N \cdot L}{l \cdot V} = \frac{L}{l V}$ segment number density

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$\tilde{n}_s = n_s l^3$ — 

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Elastic free energy:

$$F(\underset{\approx}{\lambda}) = \sum_{\mathcal{J}} w_{\mathcal{J}}\, F_{\mathcal{J}}(\underset{\approx}{\lambda}) \qquad (16)$$

$$F_{\mathcal{J}}(\underset{\approx}{\lambda}) = -kT \log Z_{\mathcal{J}}(\underset{\approx}{\lambda})$$

$$Z_{\mathcal{J}} = e^{-F_{\mathcal{J}}/kT} = \int_{(\lambda)} e^{-H/kT} \left(\vartheta_{\{s_i; s_i'\}}(\vec{R}(s))\right) \qquad (17)$$

$$\doteq Z(\vec{R}, \{s_i; s_i'\})$$

With (9)-(11):

$$F(\underset{\approx}{\lambda}) = -kT \int_0^L \int_0^L \int p(\vec{R}(s)) \cdot$$

$$\cdot \log\left[\int_{(\lambda)} e^{-H/kT} \left(\vartheta_{\{s_i; s_i'\}}(\vec{R}(s))\right)\right] \cdot \qquad (18)$$

$$\cdot \left(\vartheta_{\{s_i; s_i'\}}(\vec{R}(s))\right) \prod_{i=1}^{M} \frac{1}{2}\, ds_i\, ds_i'$$

Replica - trick: $A^n = 1 + n \cdot \log A + \mathcal{O}(n^2)$

$$\log A = \lim_{n \to 0} \frac{d}{dn} A^n \qquad (19)$$

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With (19) we perform averaging in (18) not over $\log Z_\tau$.

Averaging over Z_τ^n

$$\langle \log A \rangle = \langle \lim \frac{d}{dn} A^n \rangle = \lim \frac{d}{dn} \langle A^n \rangle \quad !$$

↷

$$\overline{F}(\underset{\sim}{\lambda}) = \frac{d}{dn} F(n) \Big|_{n=0} \qquad (20)$$

$$= -kT \frac{d}{dn} \log Z(n) \Big|_{n=0} \qquad (\hat{=}\ \text{Gl. } (8))$$

$$Z(n) = \int \mathcal{D}\hat{R}(s)\, p(\hat{R}(s)) \left[\int_{(\lambda)} \mathcal{D}R(s)\, e^{-H/kT} \right]^n \cdot \qquad (21)$$

$$\cdot \prod_i^M \int_0^L \int_0^L \left[\delta(\hat{R}(s_i) - \hat{R}(s_i')) \left(\delta(R(s_i) - R(s_i')) \right)^n \right]^{\frac{1}{2} ds_i ds_i'}$$

$n+1$ Replika-Systeme

super-vectors:

$\{R^{(\alpha)}\} = \{R^{(0)}, R^{(1)}, \dots R^{(n)}\}$

$\alpha = 0, 1, \dots, n$

$R^{(0)} \equiv \hat{R}$

$R^{(1)}, \dots R^{(n)} \equiv R$

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$$Z(n) = \int \mathcal{D}R^{(0)}_{(s)} \prod_{\alpha=1}^{n} \int_{(\lambda)} \mathcal{D}R^{(\alpha)}_{(s)} \exp\left\{-\sum_{\alpha=0}^{n} H^{(\alpha)}/kT\right\}$$

$$\prod_{i=1}^{M} \iint_0^L \prod_{\alpha=0}^{n} \delta\left(R^{(\alpha)}_{(s_i)} - R^{(\alpha)}_{(s_i')}\right) \tfrac{1}{2}\, ds_i\, ds_i' \qquad (22)$$

With

$$\frac{H^{(\alpha=0)}}{kT} = \frac{3}{2l} \int_0^L \dot{R}^{(0)\,2}_{(s)}\, ds$$

$$\frac{H^{(\alpha\neq 0)}}{kT} = \frac{3}{2l} \int_0^L \dot{R}^{2\,(\alpha)}_{(s)}\, ds + \sum_{\mu=x,y,z} w_\mu^2 \int_0^L r^{(\alpha)\,2}_{\mu(s)}\, ds \qquad (23)$$

$$\underset{\substack{\uparrow \\ \alpha\neq 0}}{r^{(\alpha)}_{\mu(s)}} = R^{(\alpha)}_\mu(s) - \lambda_\mu R^{(0)}_{\mu(s)}$$

Now „chemical potential" μ for M cross-links ~~(knots)~~:

In (22)

$$\prod_{i=1}^{M} \ldots \delta(\ldots) = \Big[\underbrace{\int_0^L\int_0^L \prod_{\alpha=0}^{n} \delta\left(R^{(\alpha)}_{(s)} - R^{(\alpha)}_{(s')}\right) \frac{ds\,ds'}{2}}_{A}\Big]^M \qquad (24)$$

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$$A^M = \frac{1}{2\pi i}\oint \frac{M!}{\mu^{M+1}}\, e^{\mu A}\, d\mu$$

Für jede analytische Funktion gilt:

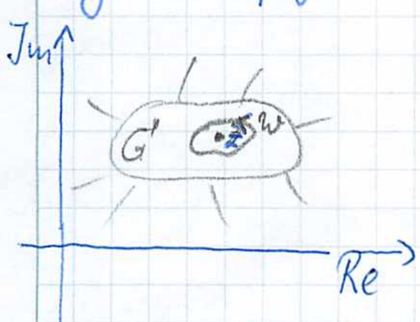
(*) $$\boxed{\frac{d^n f(z)}{dz^n} = \frac{n!}{2\pi i}\oint_w \frac{f(\xi)\,d\xi}{(\xi - z)^{n+1}}}$$

hier: $f(\xi) = e^{A\xi}$

$\rightsquigarrow f(z) = e^{Az}$

$\rightsquigarrow d^n f(z)/dz^n \Big|_{z=0} = \frac{d^n}{dz^n} e^{Az}\Big|_{z=0} = A^n$

Gl. (*) folgt aus der Cauchy'schen Integralformel:



$f(z)$ ist analyt. Funktion im Gebiet G und w ein geschlossener, in G verlaufender Weg, der den Punkt $G = z$ im mathem. positiven Sinne umläuft:

$$\boxed{f(z) = \frac{1}{2\pi i}\oint_w \frac{f(\xi)\,d\xi}{\xi - z}}$$

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$$A^M = \frac{1}{2\pi i}\oint \frac{M!}{\mu^{M+1}} e^{\mu A} d\mu \qquad \text{pole integration}$$

$$Z(n) = \frac{M!}{2\pi i}\oint d\mu \int\cdots\int\left(\prod_{\alpha=0}^{n} d\mathcal{R}^{(\alpha)}_{(s)}\right) \exp\left\{-\frac{H'}{kT} - (M+1)\ln\mu\right\} \quad (25)$$

$$H'/kT = \sum_{\alpha=0}^{n} \frac{H^{(\alpha)}}{kT} - \mu\int_0^L\int_0^L \prod_{\alpha=0}^{n} \delta\left(\mathcal{R}^{(\alpha)}_{(s)} - \mathcal{R}^{(\alpha)}_{(s')}\right)\frac{ds\,ds'}{2} \quad (26)$$

In the following:

- no constraints from entanglements : $\omega_\mu^2 = 0$
- ~~late~~ only crosslinks : effective constraints $\sim \omega_\mu^2$
  where ω_μ will not depend on λ_μ.
- final theory : $\hat{\omega}_\mu^2 = \omega_M^2 + \omega_\mu^2$
  $\downarrow$
  depends on λ_μ

additional terms in free energy of def. beyond Neo-Hooke

Expression (25) is still too complicated to do integrations via the Greens function method because of the non-local form of the potential and also the $n+1$ differential equations for the Greens functions are coupled.

Difficulty may be surmounted by doing an Unitary Transform on the $(n+1)$ $\mathcal{R}^{(\alpha)}$ coordinates: $\mathcal{R}^{(\alpha)} \xrightarrow{UT} \underset{\sim}{X}^{(\alpha)}_{(s)}$

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The UT has the property that the expression for $Z(n)$ is unchanged, we just replace $R^{(\alpha)}(s)$ by $\underset{\sim}{X}^{(\alpha)}(s)$.

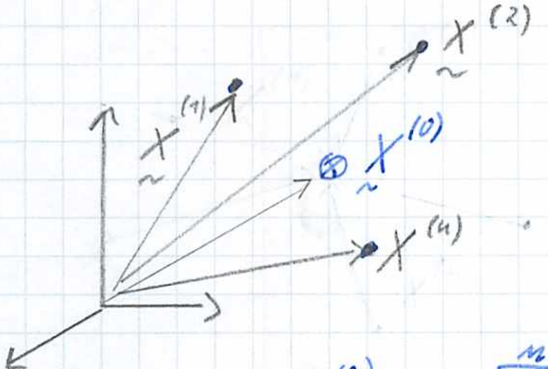
The Jacobian of a UT is unity and lengths are preserved. !

The UT is chosen to separate out the "centre of mass" of the $n+1$ systems from the other variables. The "centre of mass" variable is $\underset{\sim}{X}^{(0)}$: !

1. $$X_\mu^{(\beta)}(s) = \sum_{\alpha=0}^{n} \left(T_\mu\right)_\alpha^\beta R_\mu^{(\alpha)}(s) \qquad \mu = x,y,z = 1,2,3 \quad \alpha,\beta = 1 \ldots n \tag{27}$$

see: Deam, R; Edwards, S.F. ~~Proc. R. Soc. 19~~ Phil. Transactions of the Royal Soc. of London Series A, 280, 317-53 (1976)

2.



$$X_\mu^{(0)} = \frac{R_\mu^{(0)} + \lambda_\mu \sum_{\alpha=1}^{n} R_\mu^{(\alpha)}}{\left(1 + n\lambda_\mu^2\right)^{1/2}} \tag{28}$$

e.g.: $\lambda_\mu = 1$, $n = 1$ $\quad a, b \longrightarrow \tilde{a}, \tilde{b}$

$$\tilde{a} = \frac{a+b}{\sqrt{2}}, \quad \tilde{b} = \frac{a-b}{\sqrt{2}}$$

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$\underset{\approx}{T}$: matrix of rotation in the "n+1"-system (replica-space)

$$\det \underset{\approx}{T} = 1 \quad , \quad T_\alpha^{\ \beta} = \left[T_\alpha^{\ \beta} \right]^{-1} \quad , \quad \sum_{\beta=0}^{n} \left| T_{\beta_\mu}^{\alpha} \right|^2 = 1$$

etc.
see Deam / Edw.

Lengths are preserved:

$$\sum_{\alpha=0}^{n} \dot{R}_\mu^{(\alpha)2} = \sum_{\beta=0}^{n} \dot{X}_\mu^{(\beta)2} \tag{29}$$

$$\sum_{\alpha=1}^{n} r_\mu^{(\alpha)2} = \sum_{\beta=1}^{n} X_\mu^{(\beta)2}$$

$$\prod_{\alpha=0}^{n} \delta\left(R^{(\alpha)}_{(s)} - R^{(\alpha)}_{(s')} \right) = \prod_{\beta=0}^{n} \delta\left(\underset{\sim}{X}^{(\beta)}_{(s)} - \underset{\sim}{X}^{(\beta)}_{(s')} \right)$$

$$\left(T_\mu \right)^{\alpha\beta} = \frac{1}{\sqrt{1+n\lambda_\mu^2}} \left\| \begin{matrix} 1 & \lambda_\mu & \cdots & \lambda_\mu & \lambda_\mu \\ 0 & t^{11} & \cdots & t^{1\,n-1} & \frac{(1+n\lambda_\mu^2)^{1/2}}{n^{1/2}} \\ \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdots & \cdot & \cdot \\ 0 & t^{n-1\,1} & \cdots & t^{n-1\,n-1} & \frac{(1+n\lambda_\mu^2)^{1/2}}{n^{1/2}} \\ \lambda_\mu n^{1/2} & -\frac{1}{n^{1/2}} & \cdots & -\frac{1}{n^{1/2}} & -\frac{1}{n^{1/2}} \end{matrix} \right\|$$

$$t^{\alpha\beta} = \frac{(1+n\lambda_\mu^2)^{1/2}}{n^{1/2}} e^{2\pi i \alpha\cdot\beta/n} \tag{30}$$

$\updownarrow$

$\alpha, \beta = 1, \ldots, n-1$

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$\Uparrow$ Physiker muß auch intuitive Ideen erzeugen!

Now: Introduction of a local "Ersatz-Potential"

$$\mu \int_0^L ds \int_0^L ds' \prod_{\alpha=0}^{n} \delta\left(X^{(\alpha)}_{(s)} - X^{(\alpha)}_{(s')}\right) \simeq \sum_{\mu} \sum_{\alpha=1}^{n} - \frac{l}{6} \omega_{\mu}^{2} \int_0^L X^{(\alpha)\,2}_{\mu(s)}\, ds \quad (31)$$

$\downarrow$ this term is modelled by harmonic potential terms coming from all the $X^{(\alpha)}$-variables except the centre of mass variable

$$Z(n) = \frac{M!}{2\pi i} \oint \frac{d\mu}{\mu} \int_{V^{(0)}} \cdots \int_{V^{(n)}} \exp\left\{ - \sum_{\alpha=0}^{n} \left(\frac{H^{(\alpha)}}{kT} \right) + Q - (M+1) \ln \mu \right\} \prod_{\alpha=0}^{n} \mathcal{D} \underset{\sim}{X}^{(\alpha)}_{(s)} \quad (32)$$

with

$$H^{(\alpha=0)}/kT = \frac{3}{2l} \int_0^L \dot{\underset{\sim}{X}}^{(0)\,2}_{(s)}\, ds$$

$$H^{(\alpha\neq 0)}/kT = \frac{3}{2l} \int_0^L \dot{\underset{\sim}{X}}^{(\alpha)\,2}_{(s)}\, ds + \sum_{\mu} \frac{l}{6} \omega_{\mu}^{2} \int_0^L X^{(\alpha)\,2}_{\mu(s)}\, ds \quad (33)$$

$$Q = \mu \int_0^L ds \int_0^L ds' \prod_{\alpha=0}^{n} \delta\left(\underset{\sim}{X}^{(\alpha)}_{(s)} - \underset{\sim}{X}^{(\alpha)}_{(s')}\right) + \frac{l}{6} \sum_{\mu} \sum_{\alpha=1}^{n} \omega_{\mu}^{2} \int_0^L X^{(\alpha)\,2}_{\mu(s)}\, ds \quad (34)$$

Feynman's variational principle: / Bogoljubov inequality (?)

Q replaced by constant C: $Q \to C + Q - C$

$$e^{Q} = e^{C} e^{Q-C}$$

Bogoliubov inequality

Computing the free energy is an intractable problem for all but the simplest models in statistical physics. A powerful approximation method is mean field theory, which is a variational method based on the Bogoliubov inequality. This inequality can be formulated as follows.

Suppose we replace the real Hamiltonian H of the model by a trial Hamiltonian $\tilde{H}$, which has different interactions and may depend on extra parameters that are not present in the original model. If we choose this trial Hamiltonian such that

$$\left\langle\tilde{H}\right\rangle = \langle H\rangle$$

where both averages are taken with respect to the canonical distribution defined by the trial Hamiltonian $\tilde{H}$, then

$$A \leq \tilde{A}$$

where A is the free energy of the original Hamiltonian and $\tilde{A}$ is the free energy of the trial Hamiltonian. By including a large number of parameters in the trial Hamiltonian and minimizing the free energy we can expect to get a close approximation to the exact free energy.

The Bogoliubov inequality is often formulated in a sightly different but equivalent way. If we write the Hamiltonian as:

$$H = H_0 + \Delta H$$

where H_0 is exactly solvable, then we can apply the above inequality by defining

$$\tilde{H} = H_0 + \langle\Delta H\rangle_0$$

Here we have defined $\langle X\rangle_0$ to be the average of X over the canonical ensemble defined by H_0. Since $\tilde{H}$ defined this way differs from H_0 by a constant, we have in general

$$\langle X\rangle_0 = \langle X\rangle$$

Therefore

$$\left\langle\tilde{H}\right\rangle = \langle H_0 + \langle\Delta H\rangle\rangle = \langle H\rangle$$

And thus the inequality

$$A \leq \tilde{A}$$

holds. The free energy $\tilde{A}$ is the free energy of the model defined by H_0 plus $\langle\Delta H\rangle$. This means that

$$\tilde{A} = \langle H_0\rangle_0 - TS_0 + \langle\Delta H\rangle_0 = \langle H\rangle_0 - TS_0$$

and thus:

$$A \leq \langle H\rangle_0 - TS_0$$

Proof

For a classical model we can prove the Bogoliubov inequality as follows. We denote the canonical probability distributions for the Hamiltonian and the trial Hamiltonian by P_r and $\tilde{P}_r$, respectively. The inequality:

$$\sum_r \tilde{P}_r \log\left(\tilde{P}_r\right) \geq \sum_r \tilde{P}_r \log\left(P_r\right)$$

then holds. To see this, consider the difference between the left hand side and the right hand side. We can write this as:

$$\sum_r \tilde{P}_r \log\left(\frac{\tilde{P}_r}{P_r}\right)$$

Since

$$\log(x) \geq 1 - \frac{1}{x}$$

it follows that:

$$\sum_r \tilde{P}_r \log\left(\frac{\tilde{P}_r}{P_r}\right) \geq \sum_r \left(\tilde{P}_r - P_r\right) = 0$$

where in the last step we have used that both probability distributions are normalized to 1.

We can write the inequality as:

$$\left\langle \log\left(\tilde{P}_r\right)\right\rangle \geq \left\langle \log\left(P_r\right)\right\rangle$$

where the averages are taken with respect to $\tilde{P}_r$. If we now substitute in here the expressions for the probability distributions:

$$P_r = \frac{\exp\left[-\beta H(r)\right]}{Z}$$

and

$$\tilde{P}_r = \frac{\exp\left[-\beta \tilde{H}(r)\right]}{\tilde{Z}}$$

we get:

$$\left\langle -\beta\tilde{H} - \log\left(\tilde{Z}\right)\right\rangle \geq \left\langle -\beta H - \log\left(Z\right)\right\rangle$$

Since the averages of H and $\tilde{H}$ are, by assumption, identical we have:

$$A \leq \tilde{A}$$

Here we have used that the partition functions are constants with respect to taking averages and that the free energy is proportional to minus the logarithm of the partition function.

We can easily generalize this proof to the case of quantum mechanical models. We denote the eigenstates of $\tilde{H}$ by $|r\rangle$. We denote the diagonal components of the density matrices for the canonical distributions for H and $\tilde{H}$ in this basis as:

$$P_r = \left\langle r\left|\frac{\exp\left[-\beta H\right]}{Z}\right|r\right\rangle$$

and

$$\left\langle r\left|\frac{\exp\left[-\beta \tilde{H}\right]}{\tilde{Z}}\right|r\right\rangle = \frac{\exp\left(-\beta \tilde{E}_r\right)}{\tilde{Z}}$$

$$\tilde{P}_r = \left\langle r \left| \frac{\exp\left[-\beta \tilde{H}\right]}{\tilde{Z}} \right| r \right\rangle = \frac{\exp\left(-\beta \tilde{E}_r\right)}{\tilde{Z}}$$

where the $\tilde{E}_r$ are the eigenvalues of $\tilde{H}$

We assume again that the averages of H and $\tilde{H}$ in the canonical ensemble defined by $\tilde{H}$ are the same:

$$\left\langle \tilde{H} \right\rangle = \langle H \rangle$$

where

$$\langle H \rangle = \sum_r \tilde{P}_r \langle r | H | r \rangle$$

The inequality

$$\sum_r \tilde{P}_r \log\left(\tilde{P}_r\right) \geq \sum_r \tilde{P}_r \log\left(P_r\right)$$

still holds as both the P_r and the $\tilde{P}_r$ sum to 1. On the l.h.s. we can replace:

$$\log\left(\tilde{P}_r\right) = -\beta \tilde{E}_r - \log\left(\tilde{Z}\right)$$

On the right hand side we can use the inequality

$$\langle \exp(X) \rangle_r \geq \exp\left(\langle X \rangle_r\right)$$

where we have introduced the notation

$$\langle Y \rangle_r \equiv \langle r | Y | r \rangle$$

for the expectation value of the operator Y in the state r. See here for a proof. Taking the logarithm of this inequality gives:

$$\log\left[\langle \exp(X) \rangle_r\right] \geq \langle X \rangle_r$$

This allows us to write:

$$\log\left(P_r\right) = \log\left[\langle \exp\left(-\beta H - \log(Z)\right) \rangle_r\right] \geq \langle -\beta H - \log(Z) \rangle_r$$

The fact that the averages of H and $\tilde{H}$ are the same then leads to the same conclusion as in the classical case:

$$A \leq \tilde{A}$$

$$\langle e^{Q-C} \rangle \geq 1 + \langle Q - C \rangle$$

↪ optimal (best) value of C: $\quad C = \langle Q \rangle$ (35)

This value defines <u>lower border</u> for $\underline{\mathcal{Z}(n)}$
<u>upper</u> " " $\underline{F(\underset{\sim}{\lambda})}$

$M \gg 1$

$$\mathcal{Z}(n) \geq \frac{1}{2\pi i} \oint d\mu \underbrace{\int\int \cdots \int}_{\tilde{V}} \prod_{\alpha=0}^{n} G_\alpha \exp\left\{ - C - \overset{\approx M}{(M+1)} \ln \mu - M \cdot \ln M \right\} \cdot d^3\underset{\sim}{X}_0^{(\alpha)} d^3 X_L^{(\alpha)} \quad (36)$$

$$C = \mu \left\langle \int_0^L ds \int_0^L ds' \prod_{\alpha=0}^{n} \delta\left(\underset{\sim}{X}^{(\alpha)}_{(s)} - \underset{\sim}{X}^{(\alpha)}_{(s')} \right) + \right. \left. + \left\langle \frac{\ell}{6} \sum_{\mu=1,2,3} \sum_{\alpha=1}^{n} \omega_\mu^2 \int_0^L \underset{\sim}{X}^{(\alpha)\,2}_{(s)} ds \right\rangle \quad (37)$$

<u>Now</u>: ⟶ Greenfunction G_α later

$\oint d\mu \cdots$ <u>Sattelpunktmethode / Method of Steepest descent</u>

$$\frac{\partial}{\partial \mu} \left\{ \mu \langle \cdots \delta \cdots \rangle - M \ln \mu \right\} \Big|_{\mu = \mu_s} = 0 \quad (38)$$

Method of steepest descent

From Wikipedia, the free encyclopedia

In mathematics, the **method of steepest descent** or **stationary phase method** or **saddle-point method** is an extension of Laplace's method for approximating an integral, where one deforms a contour integral in the complex plane to pass near a stationary point (saddle point), in roughly the direction of steepest descent or stationary phase. The saddle-point approximation is used with integrals in the complex plane, whereas Laplace's method is used with real integrals.

The integral to be estimated is often of the form

$$\int_C f(z)e^{\lambda g(z)}dz$$

where C is a contour and λ is large. One version of the method of steepest descent deforms the contour of integration so that it passes through a zero of the derivative $g'(z)$ in such a way that on the contour g is (approximately) real and has a maximum at the zero.

The method of steepest descent was first published by Debye (1909), who used it to estimate Bessel functions and pointed out that it occurred in the unpublished note Riemann (1863) about hypergeometric functions. The contour of steepest descent has a minimax property, see Fedoryuk (2001). Siegel (1932) described some other unpublished notes of Riemann, where he used this method to derive the Riemann-Siegel formula.

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$$\curvearrowright \quad \langle \ldots \delta \ldots \rangle - \frac{M}{\mu_s} = 0$$

$$\mu_s = M / \langle \ldots \delta \rangle$$

(36), (37)

$$\curvearrowright \exp\left\{ -\mu_s \langle \ldots \delta \ldots \rangle + \langle \ldots X^2_{\ldots} \rangle - M \ln \mu_s \right\}$$

$$= e^{-M} \, e^{\langle \ldots X^2 \ldots \rangle} \, e^{\ln \mu_s^{-M}} \longrightarrow e^{\ln \left(\frac{\langle \ldots \delta \ldots \rangle}{M} \right)^M}$$

$$= \frac{e^{-M}}{M^M} \, e^{\langle \ldots X^2 \ldots \rangle} \langle \ldots \delta \ldots \rangle^M$$

$$\curvearrowright \quad Z(n) \geq \underset{\tilde{V}}{\iint \ldots \int} \prod_{\alpha=0}^{m} G_\alpha \, e^{\langle \ldots X^2 \ldots \rangle} \langle \ldots \delta \ldots \rangle^M \qquad (39)$$

see (33)

$$G_0 \left(\underset{\sim}{X}^{(0)}, \underset{\sim}{X}^{(0)\prime}; s s' \right) = \int_{\underset{\sim}{X}^{(0)}_{(s)} = \underset{\sim}{X}^{(0)}}^{\underset{\sim}{X}^{(0)}_{(s')} = X^{(0)\prime}} \mathcal{D} \underset{\sim}{X}^{(0)}_{(s)} \exp\left\{ - \frac{H^{(0)}}{kT} \right\} \qquad (40)$$

$$G_{\alpha (\neq 0)} = \int_{\underset{\sim}{X}^{(\alpha)}_{(s)} = \underset{\sim}{X}^{(\alpha)}}^{\underset{\sim}{X}^{(\alpha)}_{(s')} = \underset{\sim}{X}^{(\alpha)\prime}} \mathcal{D} \underset{\sim}{X}^{(\alpha)}_{(s)} \exp\left\{ - \frac{H^{(\alpha \neq 0)}}{kT} \right\} \qquad (41)$$

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We have: see section about Greenfunctions / Path Integrals.

$$\alpha = 0: \quad \left\{ \frac{\partial}{\partial s} - \frac{l}{6} \nabla^2_{X^{(0)}} \right\} G_0 = \delta(X^{(0)} - X^{(0)'})\, \delta(s-s') \qquad (42)$$

$$\alpha \neq 0: \quad \left\{ \frac{\partial}{\partial s} - \frac{l}{6} \nabla^2_{X(\alpha \neq 0)} + \underbrace{\frac{l}{6} \sum_\mu \omega_\mu^2 X_\mu^{(\alpha)2}}_{\text{harmonic oscillator!}} \right\} G_\alpha = \delta(X^{(\alpha)} - X^{(\alpha)'}) \cdot \delta(s-s') \qquad (43)$$

•) The solution for $G_{\alpha(\neq 0)}$ are:

$$G_{\alpha(\neq 0)} = \sum_n \prod_{\mu=x,y,z} \left(\frac{\omega_\mu}{2\pi} \right)^{1/2} He_n(X_\mu^{(\alpha)})\, He_n(X_\mu^{(\alpha)'}) \cdot \exp\left\{ -\frac{l}{3} \omega_\mu \left(n + \frac{1}{2}\right) L \right\} \qquad (44)$$

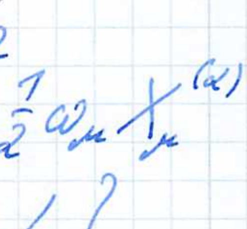
He_n is the n-th order Hermite Polynomial (see books)

For large L the $n=0$ eigenfunction dominates the expansion. ("ground" state)

$$G_{\alpha(\neq 0)} = \prod_\mu \left(\frac{\omega_\mu}{2\pi} \right)^{1/2} \exp\left\{ -\frac{1}{2} \omega_\mu X_\mu^{(\alpha)2} - \frac{1}{2} \omega_\mu X_\mu^{(\alpha)'2} - \frac{l}{6} \sum_\mu \omega_\mu \cdot L \right\} \qquad (45)$$

•) The solution for G_0 is the diffusion equation inside a box

$$\prod_\mu (1 + n\lambda_\mu^2)^{1/2} \underbrace{XYZ}_{V_0} = V_R(\underset{\approx}{\lambda}) \qquad (46)$$



"Replica-Box"

"junction gas" model for inhomog. networks ~ $\lim_{n \to 0}$ "Thermodyn. in $V_R(\underset{\approx}{\lambda})$"

Adresse: Hohe Str. 6, 01069 Dresden, Kontakt: (0351) 4658-0, ipf@ipfdd.de, www.ipfdd.de

The choice of Boundary Conditions $\Leftrightarrow$ good approximation leads to

! $$G_{(0)}\left(\underset{\sim}{X}^{(0)}, \underset{\sim}{X}^{(0)'}; s, s'\right) = \frac{L}{l \prod_{\mu} \left(1 + n_{\mu}^2\right)^{1/2} V} + \tag{47}$$

$$+ \left(\frac{3}{2\pi l\,|s-s'|}\right)^{3/2} \exp\left\{ -\frac{3}{2l} \frac{\left(\underset{\sim}{X}^{(0)} - \underset{\sim}{X}^{(0)'}\right)^2}{|s-s'|} \right\}$$

First term: constant part due to mean density of chains.
Second ": due to the enhanced probability of finding a single chain.

Solution (47) comes about through taking cyclic boundary conditions. Choice of boundary conditions is made ~~to~~ so to ensure the constant density of polymer
(would arise if the true molecular force were put into calculations — however this would require first mathematical technique to deal with the "liquid" state).
Choice of cyclic boundary conditions allows the calculation to proceed with the uniform density condition.

Final solution

$$\mathcal{Z}(n) \geq \exp\left\{(M-1)\log\prod_\mu (1+n\lambda_\mu^2)^{-1/2}\left(\frac{\omega_\mu}{2\pi}\right)^{M/2} - \sum_\mu \frac{n\,l\,L\,\omega_\mu}{12}\right\} \qquad (48)$$

(20)

$$\boxed{F \leq kT\left\{\frac{M}{2}\sum_\mu \lambda_\mu^2 - M\sum_\mu \log\left(\frac{\omega_\mu}{2\pi}\right)\right\}} \qquad (49)$$

Best value for ω_μ $\longrightarrow$ minimising the exponent in (48):

$$\frac{\partial}{\partial\omega_\mu}\left\{(M-1)\ \dots\ \right\} = 0$$

Remark: $\hat{\omega}_\mu^2 = \omega_\mu^2 + \omega_\mu^2(\lambda_\mu)$!
entang!. $\checkmark$

gives $\boxed{\omega_\mu = \dfrac{6M}{lL}}$ (independent of λ_μ) (50)

"radius" of "tube" due to presence of crosslinks is proportional to the <u>number of crosslinks per unit length</u>.

-) Note: functionality $f=4$ here

In general :

... $M \to M\cdot g(f)$
see Introduction

G. Heinrich 1980 : Bemerkungen zum E-Model stoch. vernetzter Netzwerke der Funkt. f
Z. f. phys. Chem. 261, 188 (1980)

-) Cyclic bound. cond. $\longleftrightarrow$ constant density condition $\longleftrightarrow$ constant volume constraint $\curvearrowright$ $\dfrac{F}{F_{el}} = \dfrac{M}{2}\sum_\mu \lambda_\mu^2$ and $\lambda_x\lambda_y\lambda_z = \dfrac{V}{V_0} = 1$

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Notes and Remarks:

Scattering function

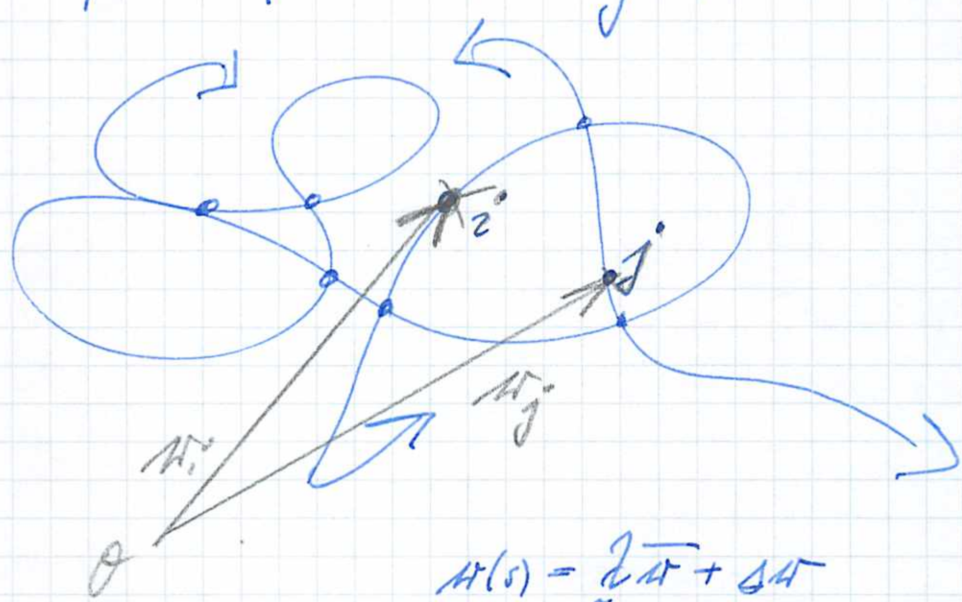
e.g.: n^0-scattering

$$S(k) = \frac{1}{N^2}\left\langle \sum_{i,j} \exp\{ik(r_i - r_j)\} \right\rangle$$

Network $\hat{=}$ one long chain of N monomers (segments) cross-linked to itself M times

k - scattering vector !

r_i, r_j - positions of the ith and jth monomer



$r(s) = \underset{\approx}{\lambda} \bar{r} + \Delta r$

$\langle \ldots \rangle$ conformational average according Philosophy of Deam / Edwards (1976) see:
M. Warner, S.F. Edwards, J. Phys. A vol 11 (8) 1649 - 1655 (1978)

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$\Rightarrow$ $S_m(k) \hat{=}$ scattering function due to the system with topology "m" must be averaged!

$m \hat{=} \{s_i, s_i'; i = 1, \dots M\}$

$$S_m(k) = \frac{1}{N^2} \frac{\sum_{ij} \int_{\sim} d\Omega_m \, e^{-\beta H} \exp[ik(r_i - r_j)]}{\int_{\sim} d\Omega_m \, e^{-\beta H}}$$

$\sim \hat{=}$ (λ) deformed system; i.e. phase/conformational integral is over strained volume.

Define

$$\phi_k = \frac{1}{N^2} \sum_{ij} e^{ik(r_i - r_j)}$$

$\curvearrowright$

$$S_m(k) = \frac{\partial}{\partial p} \log \left(\int_{\sim} d\Omega_m \, e^{-\beta H + p\phi_k} \right) \Big|_{p=0}$$

$$\equiv \frac{\partial}{\partial p} \underbrace{F(p,k)}_{} \Big|_{p=0}$$

"free energy" resulting from a Hamiltonian with sources $p\phi_k$ in it.

This is akin to the propagator formulation in Quantum Field Theory where source fields are put into the Lagrangian and where the propagator can be written as

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$$\frac{\delta}{\delta\phi}\frac{\delta}{\delta\phi^*}\mathcal{Z}[\phi,\phi^*]\Big|_{\phi=\phi^*=0}$$

$$\mathcal{Z}=\int\delta\psi\,\exp\left\{\int\mathcal{L}[\psi,\phi]\right\}$$

↷ On averaging (topologies "m") the scatt. function $S(k)$ becomes: $S(k)=\langle S_m(k)\rangle_m$

$$S(k)=\frac{\partial}{\partial p}\Big|_{p=0}\frac{\sum_m\int d\Omega_m\, e^{-\beta' H}F(p,k)}{\sum_m\int d\Omega_m\, e^{-\beta' H}}$$

$$=-\frac{\partial}{\partial p}\Big|_{p=0}\frac{\partial}{\partial n}\Big|_{n=0}\log\Big(\sum_m\int d\Omega_m\exp\big(-\beta' H-nF(p,k)\big)\Big)$$

Replica trick:

$$e^{-nF(p,k)}=\Big(\int_\sim d\Omega_m\, e^{-\beta' H-p\phi_k}\Big)^n$$

$$=\int_\sim\prod_{\alpha=1}^{n}d\Omega_m^{(\alpha)}\, e^{-\beta\sum_{\alpha=1}^{n}H^{(\alpha)}-p\sum_{\alpha=1}^{n}\phi_k^{(\alpha)}}$$