Environmental Impact on DNA denaturation

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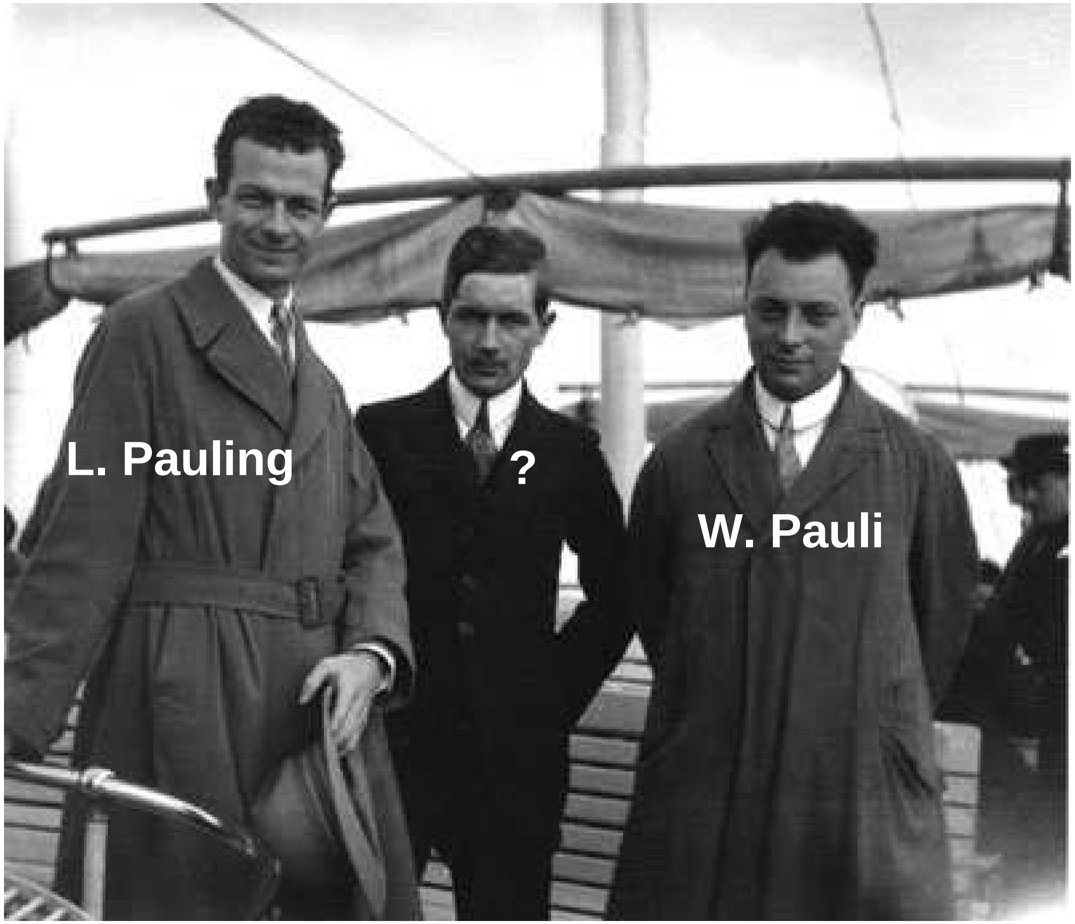
The Shape of Polymers



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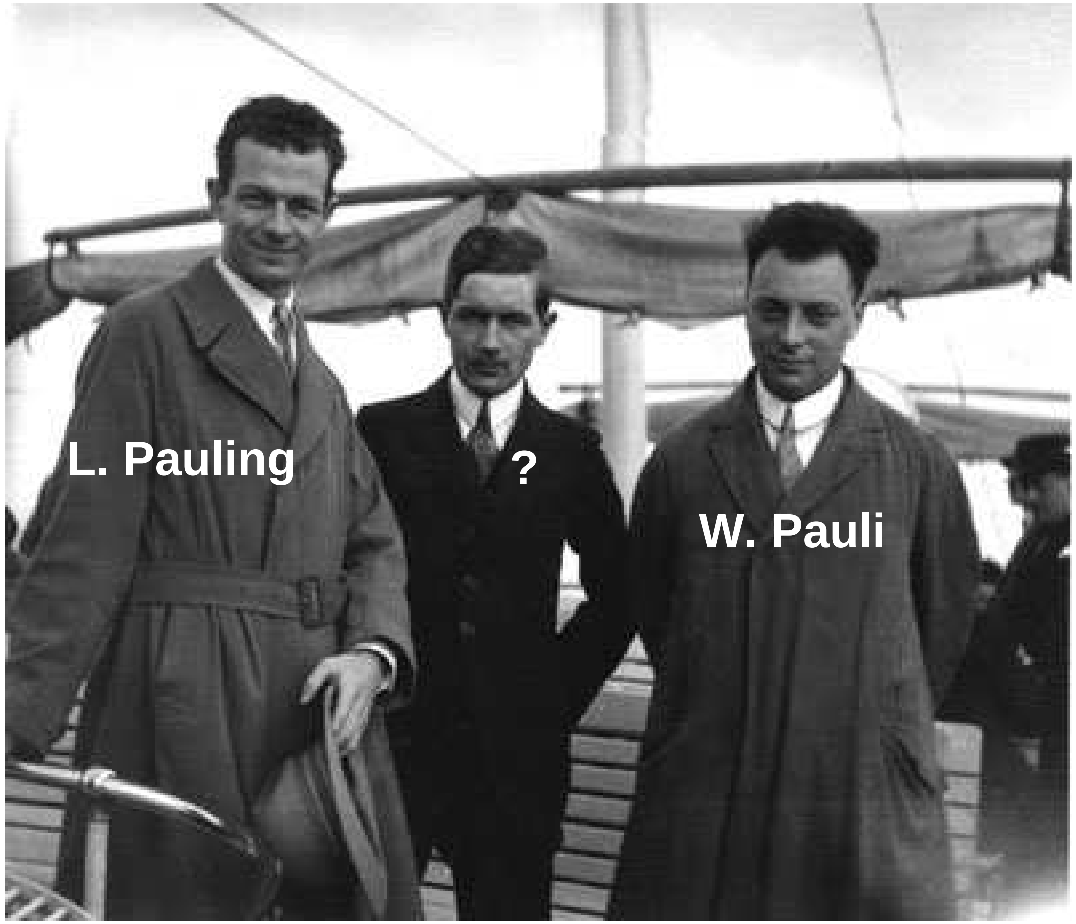

Über die Gestalt fadenförmiger Moleküle in Lösungen.

Von Werner Kuhn (Karlsruhe). (Eingegangen am 18. Mai 1934.)

(On the shape of thread−like molecules in solutions)

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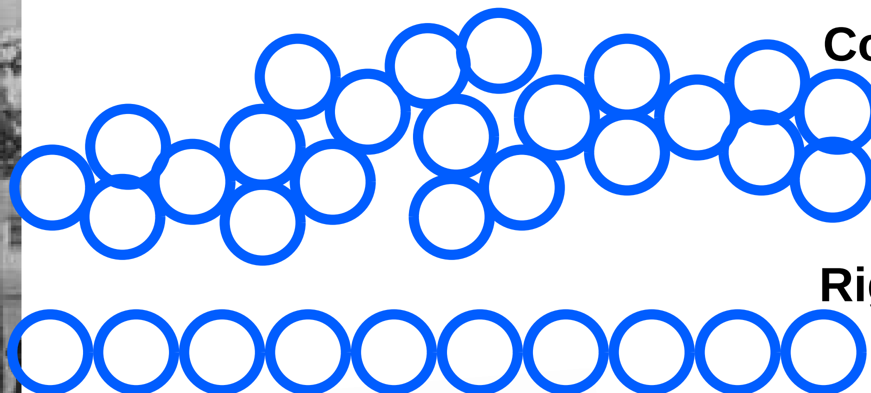
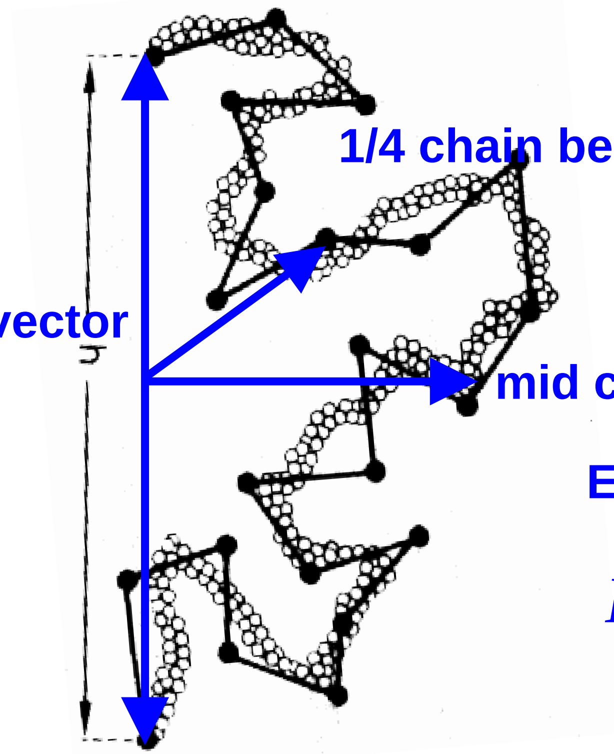
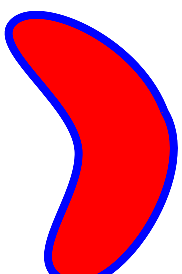






Estimated ratio 6 : 2.3 : 1

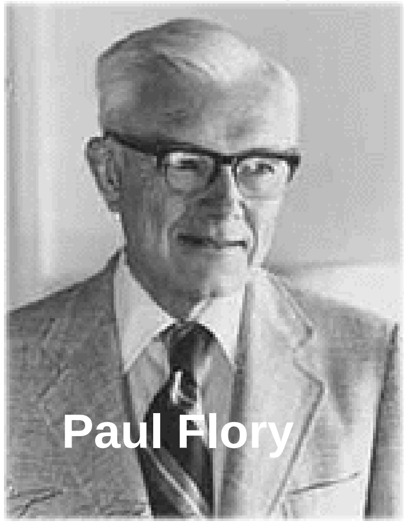
Estimated excluded volume effect:

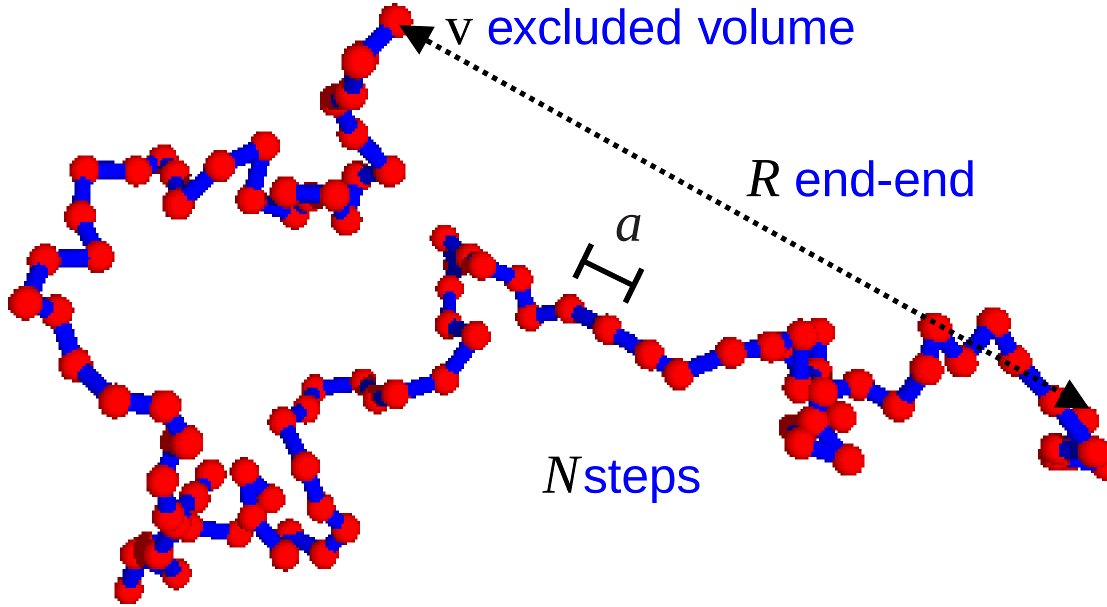
$$R \sim N^{1/2+\varepsilon} \qquad \varepsilon = 0.11$$

"Raumerfüllungseffekt"

Polymer

self−avoiding random walk





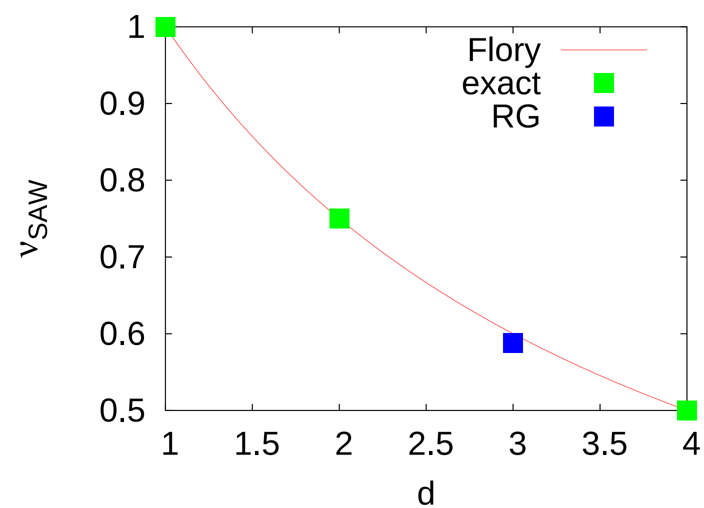
random walk $P(R) \sim e^{-\frac{R^2}{Na^2}}$

FLORY:

cloud of monomers $\rho \sim \frac{N}{R^d}$ that interact at overlap

$\rightarrow$ free Energy $\frac{1}{kT}\mathcal{F}(R) \sim \underbrace{\frac{R^2}{Na^2}}_{\text{elastic}} + \underbrace{N\mathrm{v}\frac{N}{R^d}}_{\text{overlap}}$

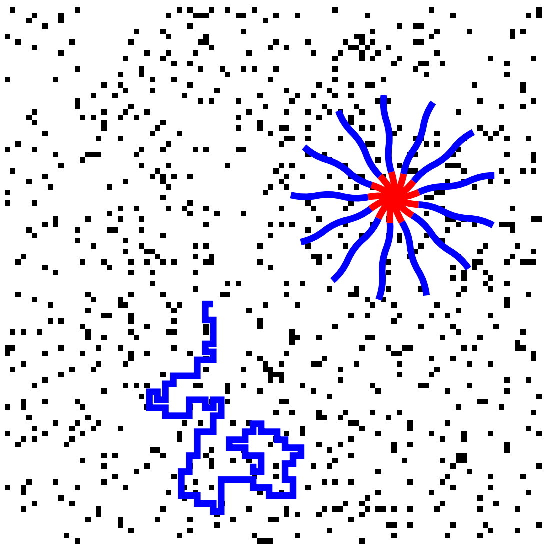
minimize: $R \sim N^{\frac{3}{d+2}} = N^{\nu_{\mathrm{Flory}}}$



Models for disordered and correlated environments

A. Weak disorder, $c_{\rm perc} < c \leq 1$

uncorrelated



universality unchanged

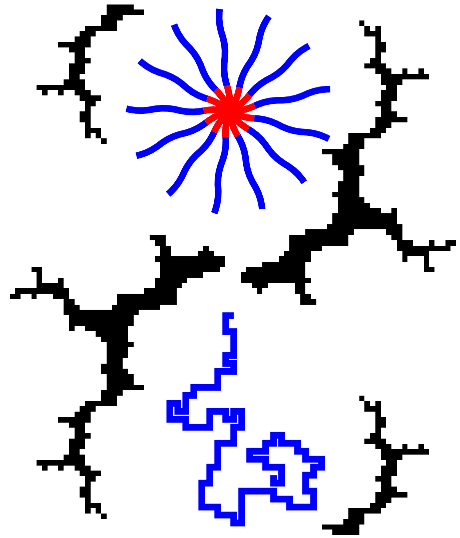
$$4 - d = \varepsilon$$

$$\nu^{\rm saw} = 1/2 + \varepsilon/16$$

Kim '82

long range correlated

$$g(R) \sim R^{-a}$$



universality may change

$$4 - a = \delta \leq \varepsilon/2$$

$$\nu = \nu^{\rm saw} = 1/2 + \varepsilon/16,$$

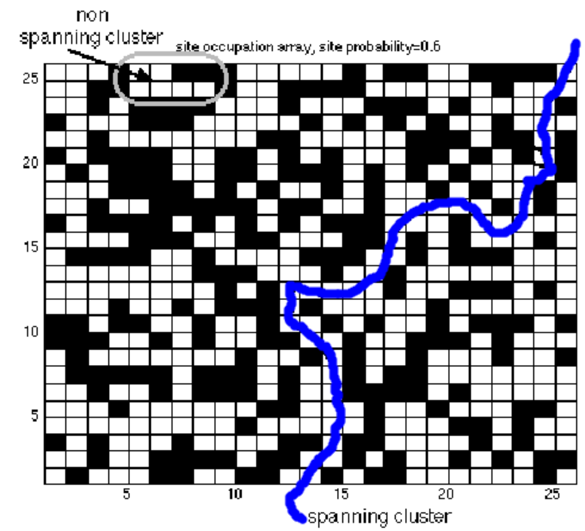
$$\varepsilon/2 \leq \delta \leq \varepsilon:\ \nu = 1/2 + \delta/8.$$

Weinrib, Halperin '83

V. Blavats'ka, CvF, Yu Holovatch '01,'06

B. Strong disorder, $c = c_{\rm perc}$

incipient percolation cluster



universality and upper crit. dim. change

$$6 - d = \varepsilon > 0$$

$$\nu = 1/2 + \varepsilon/42,$$

Y. Meir, A. B. Harris'89,

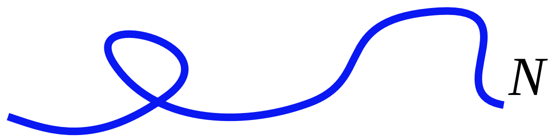
CvF, V. Blavats'ka, R. Folk, Yu Holovatch'04

O. Stenull, H.-K. Janssen '07

Partition function

Number of Configurations

- linear chain



- Radius

$$\langle (r_N - r_1)^2 \rangle \sim N^{2\nu}$$

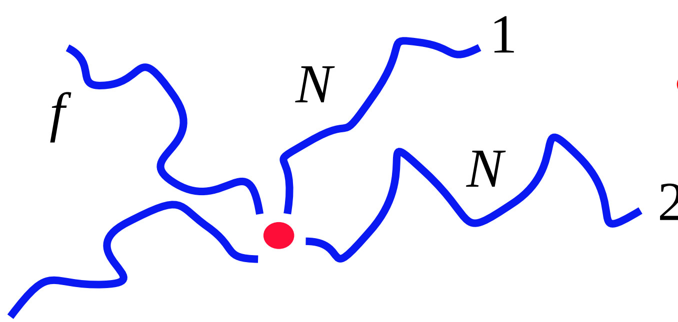
- Partition function

$$\mathcal{Z}_1(N) \sim z^N N^{\gamma - 1}$$

fugacity z

- star polymer

f arms, length N

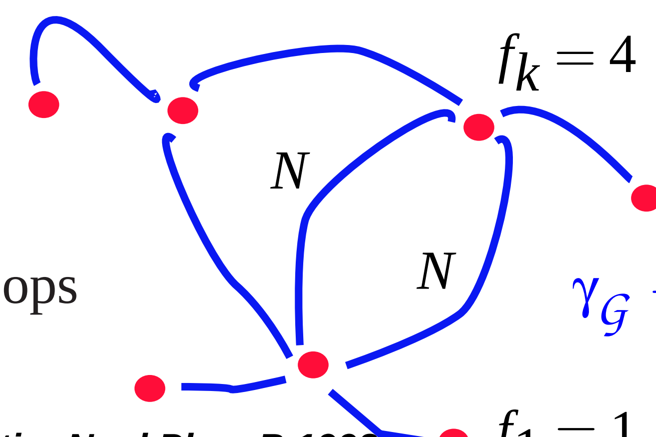


- Family of exponents γ_f

$$\mathcal{Z}_f(N) \sim z^{fN} N^{(\gamma_f - 1)}$$

- network

F chains, $L_{\mathcal{G}}$ loops



$$\mathcal{Z}_{\mathcal{G}}(N) \sim z^{FN} N^{\gamma_{\mathcal{G}} - 1}$$

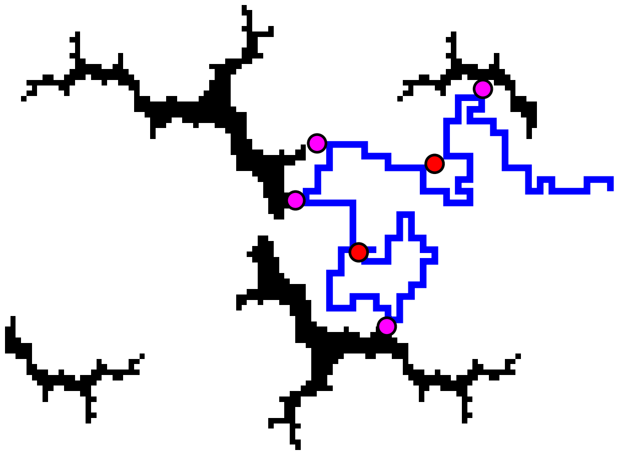
- linear combination

$$\gamma_{\mathcal{G}} - 1 = -d\nu L_{\mathcal{G}} + \sum_k \left(\gamma_{f_k} - 1 - \frac{f_k}{2}(\gamma - 1) \right)$$

Schäfer,vF,Lehr,Duplantier Nucl.Phys.B 1992

Long−range correlated medium

- self−avoidance u_0
- disorder



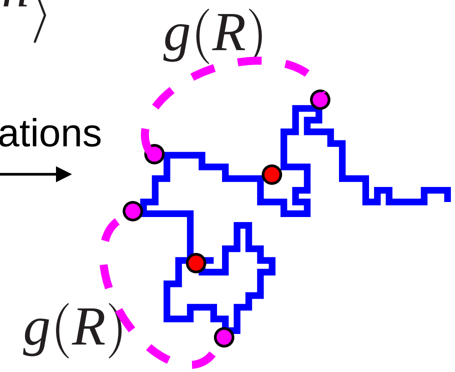
Replica

$$\langle \ln Z \rangle = \lim_{n\to 0}\frac{1}{n}\langle Z^n \rangle$$

average disorder configurations →

Weinrib, Halperin '83

- long−range coupling



$$g(R) \sim R^{-a}$$

$$\widehat{g}(k) \sim v_0 + w_0 |k|^{a-d}$$

$$\mathcal{L}_{LR} = \sum_{\alpha,\beta=1}^{n} \int \mathrm{d}^d x \mathrm{d}^d y\, g(|x-y|)\vec{\phi}_\alpha^2(x)\vec{\phi}_\beta^2(y)$$

n-replicated $O(m)$-symmetric m-vector $\vec{\phi}$ model

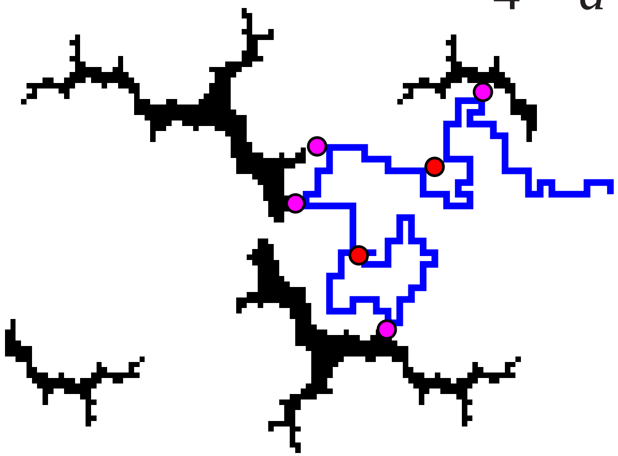
$n, m \to 0$:

$$\mathcal{L}(\vec{\phi}) = \sum_k \sum_\alpha^n \frac{1}{2}(\mu_0^2 + k^2)(\vec{\phi}_k^\alpha)^2 + \frac{u_0+v_0}{4!}\sum_\alpha^n \sum_{\{k\}'}(\vec{\phi}_{k_1}^\alpha \vec{\phi}_{k_2}^\alpha)(\vec{\phi}_{k_3}^\alpha \vec{\phi}_{k_4}^\alpha)$$
$$+\frac{w_0}{4!}\sum_{\alpha\beta}^n \sum_{\{k\}''} |k|^{a-d} (\vec{\phi}_{k_1}^\alpha \vec{\phi}_{k_2}^\alpha)(\vec{\phi}_{k_3}^\beta \vec{\phi}_{k_4}^\beta).$$

ε-δ expansion

● self–avoidance u_0
● disorder w_0

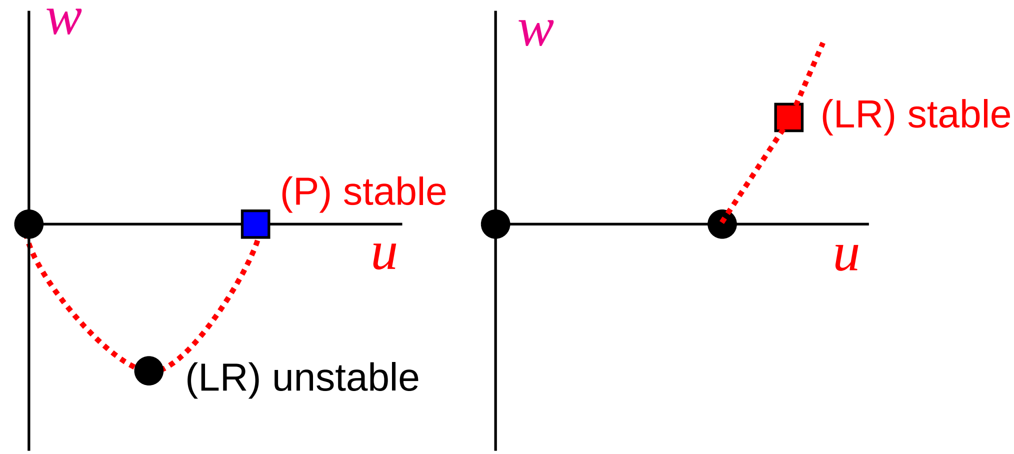
$$4 - d = \varepsilon$$



$$g(R) \sim R^{-a} \qquad 4 - a = \delta$$

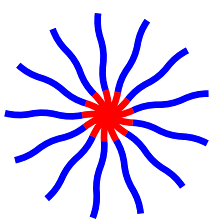
$$\widehat{g}(k) \sim v_0 + w_0 |k|^{a-d}$$

Renormalization group flow



$$\delta \leq \varepsilon/2 \qquad \varepsilon/2 \leq \delta \leq \varepsilon$$

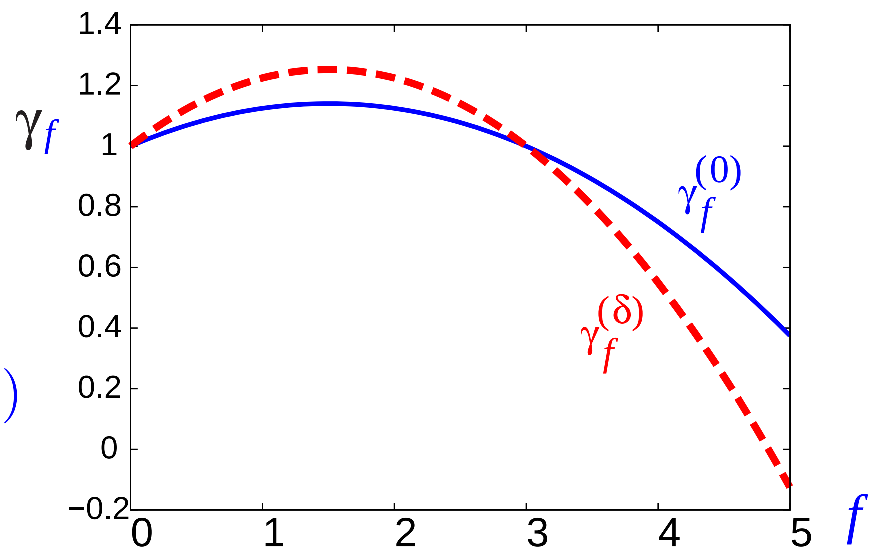
Blavat'ska, CvF, Holovatch PRE (2001)



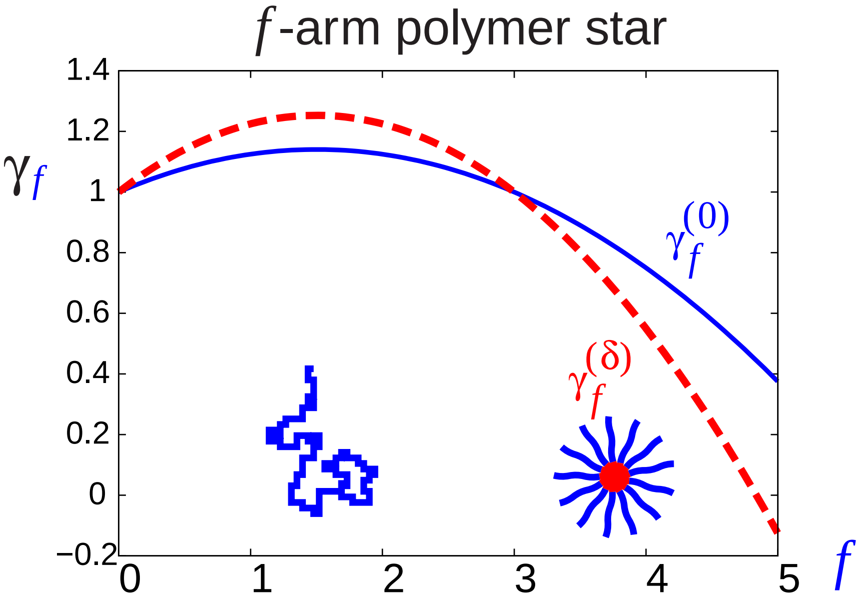
f-arm polymer star

● Partition function

$$\mathcal{Z}_f(N) \sim z^{fN} N^{(\gamma_f - 1)}$$



Static separation

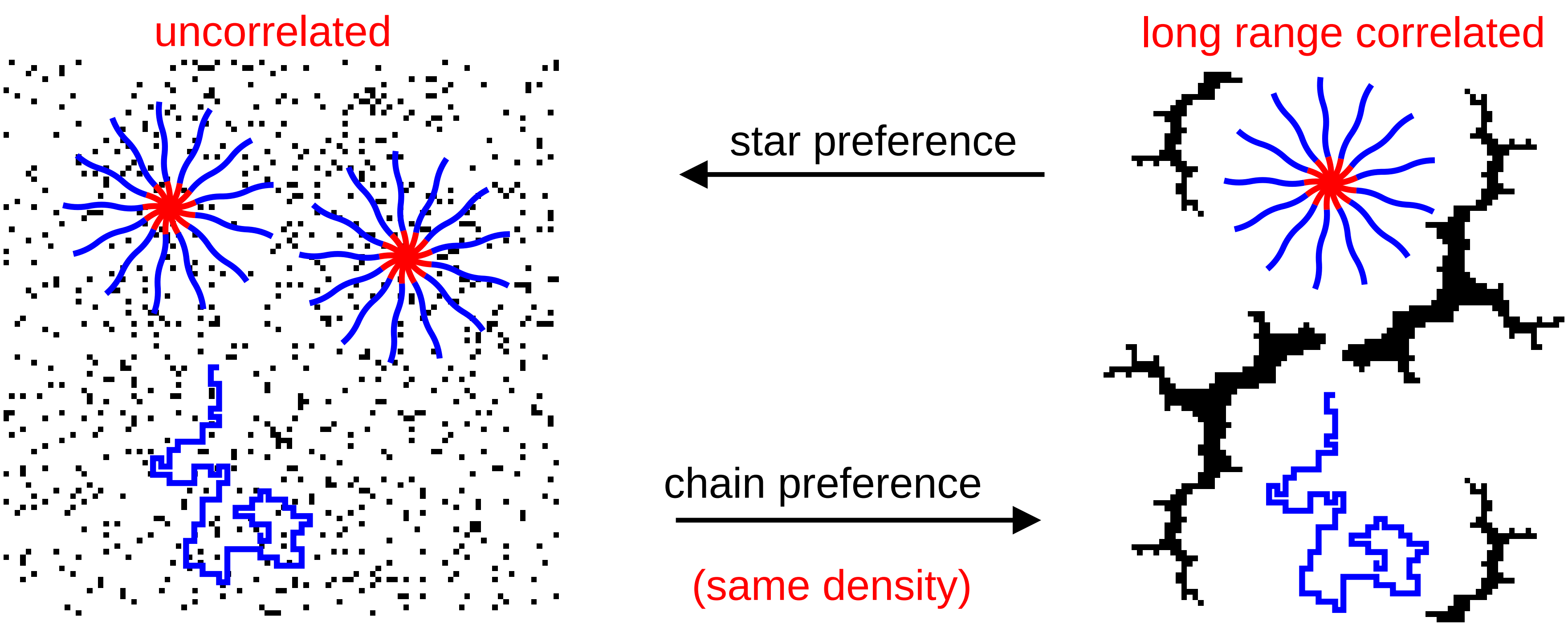


Partition function

$$Z_{*f}(N) \propto e^{\mu f N} N^{\gamma_f} - 1$$

Free energy

$$\mathcal{F} = -\mu f N - (\gamma_f - 1)$$



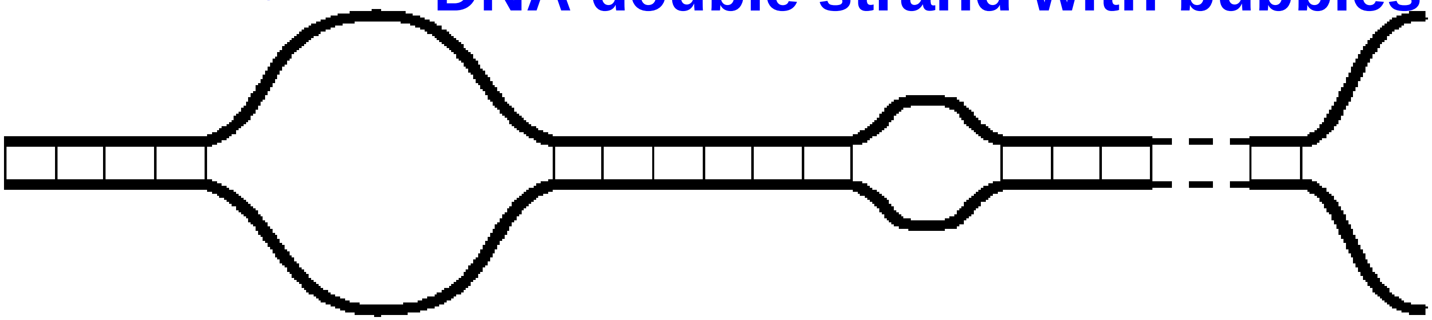
Blavat'ska, vF, Holovatch, PRE (2006)

DNA denaturation

Poland, Scheraga (1966)

ℓ

DNA double strand with bubbles



Competition between binding energy and configurational loop entropy

$$\mathcal{Z} = 1/(1-UV) \qquad V = \sum_k \omega^k z^k, \qquad U = \sum_k z^k s^k k^{-c}, \qquad \text{critical} \quad z_c = 1/s$$

Entropic contributions of the loop:

Kafri,Mukamel,Peliti EPJB (2002)

- Graph $\mathcal{G}$ $\qquad \mathcal{Z}_{\mathcal{G}}(N) \sim z^{4N} N^{\gamma_{\mathcal{G}}-1} \qquad \gamma_{\mathcal{G}} - 1 = -d\nu + 2(\gamma_3 - 1) - 2(\gamma - 1)$

- loop $\quad \ell << N: \quad \mathcal{Z}_{\mathcal{G}}(N,\ell) \sim \left(z^{2\ell}\ell^{-c}\right)\left(z^{2N}N^{\gamma-1}\right) \qquad c = d\nu - 2(\gamma_3 - 1) + 3(\gamma - 1)$

short chain expansion ***CvF NucPhB (1997)***

- loop exponent c determines phase transition:

$c \leq 1$:none, $1 < c \leq 2$: 2nd, $2 < c$: 1st order

Incomplete History of the loop exponent in the Poland–Scheraga model

c determines phase transition: $c \leq 1$:none, $1 < c \leq 2$: 2nd, $2 < c$: 1st order

1966 Poland Scheraga JCP

Random walk loop

$$c = \frac{1}{2}d$$

$$d = 3$$

$$c = 1.5$$

1966 M Fisher JCP

Self avoiding walk loop

$$c = d\nu_{\text{SAW}}$$

$$c = 1.8$$

2000 Kafri Mukamel Peliti

$$c = d\nu - 2(\gamma_3 - 1) + 3(\gamma_1 - 1)$$

$$c = 3(0.588) - 2(0.05) + 3(0.15) = 2.11$$

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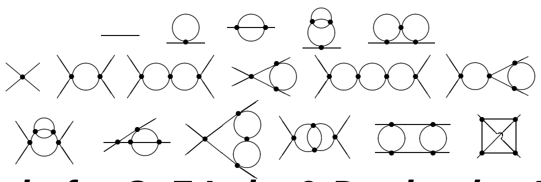
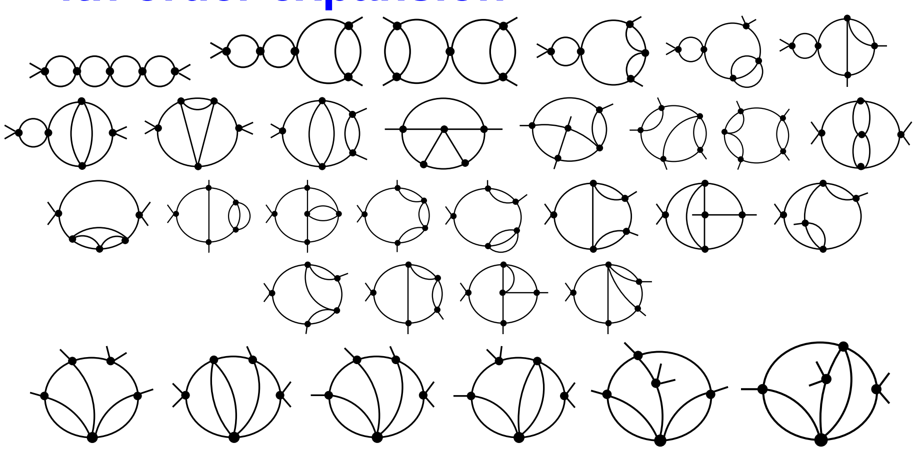


Schafer CvF Lehr & Duplantier 1992

4th order expansion



c=2.15

V.Schulte−Frohlinde,Y.Holovatch,CvF,A.Blumen, Phys. Lett. A 2004

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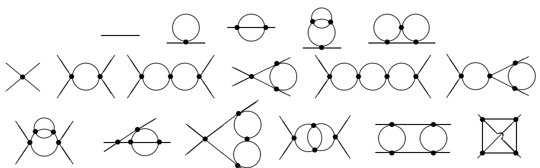

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4th order expansion

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DNA denaturation in correlated disorder

- loop exponent

$$c = d\nu - 2(\gamma_3 - 1) + 3(\gamma_1 - 1)$$

LR disorder ($a = 2.3$)

$$c = 3(0.68) - 2(-0.3) + 3(0.38) = 3.78$$

c=3.78

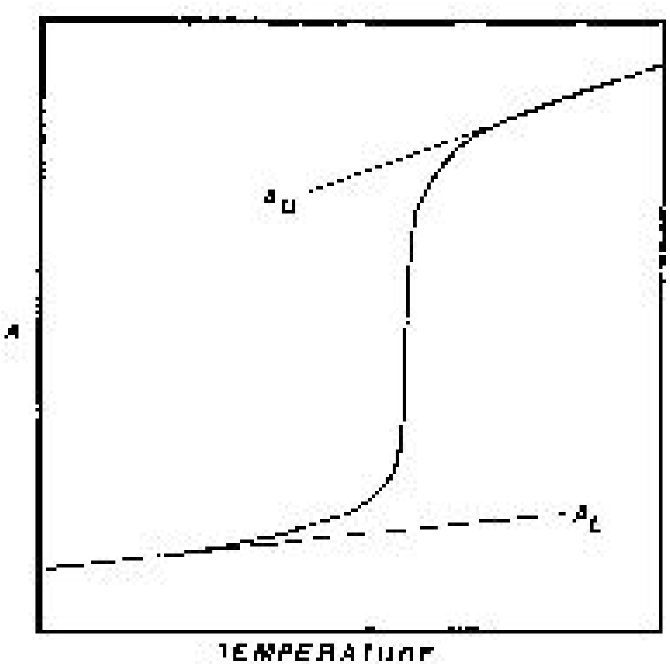
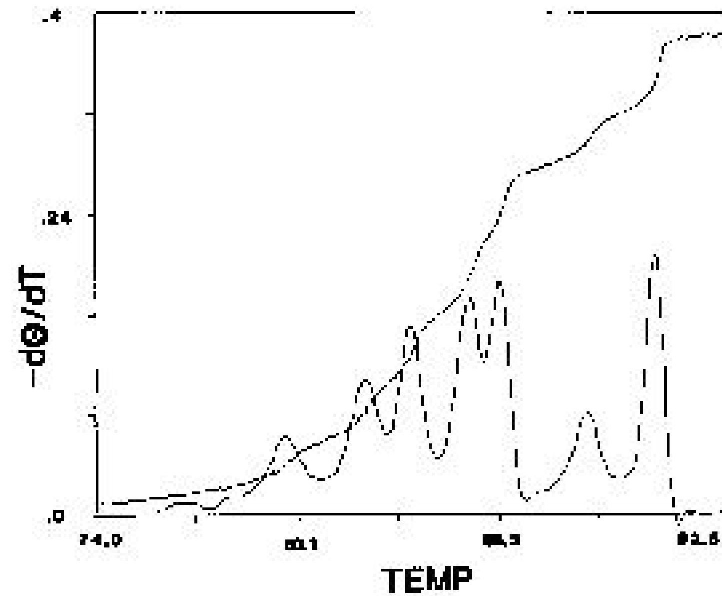
- correlated disorder shifts the transition to 1st order.

V Blavats'ka,Y Holovatch,CvF, tbp

Plan

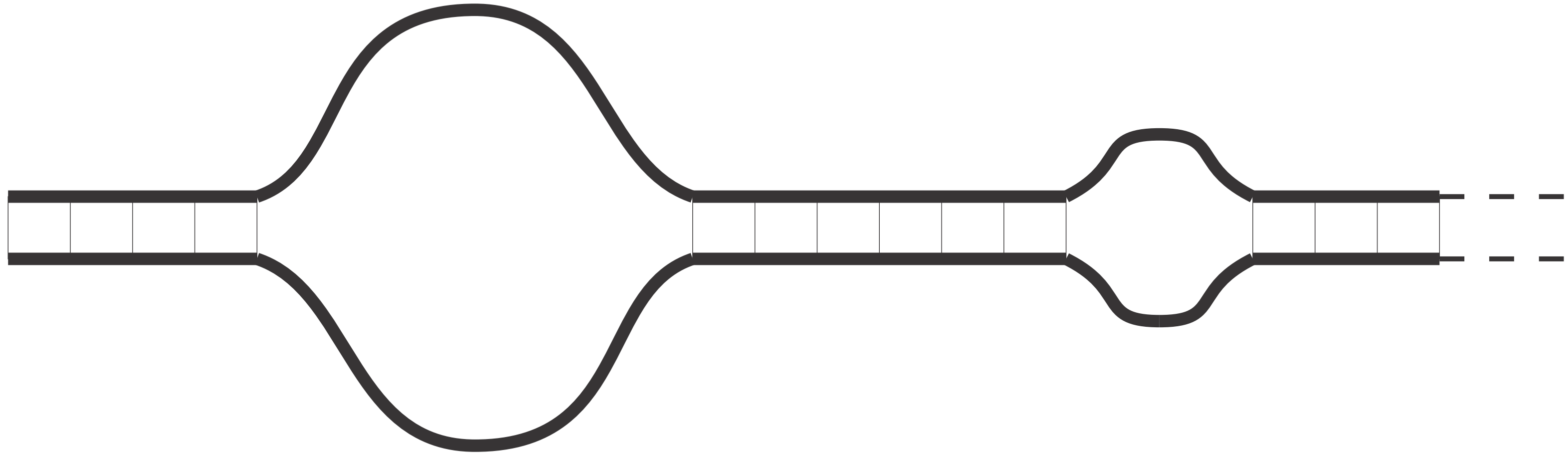
- Object/Phenomenon
- Model(s)
- Poland-Scheraga/Fisher description
- Scaling laws for homogeneous polymer networks
- Effect of heterogeneity
- Effect of long-range correlated disorder
- Conclusions and outlook

Thermal denaturation of DNA molecules

Typical plots of absorbance vs. temperature demonstrating the denaturation of
R.M. Wartel, A.S. Benight. Phys. Reports **126** *(1985) 67-107*

Models



Schematic representation of the Poland-Scheraga model *D. Poland, H.A. Sch*
J. Chem. Phys. **45** *(1966) 1456; 1464*

Scaling laws for polymer networks

For a network $\mathcal{G}$ of N chains of lengths $\ell_1, \ell_2, \ldots, \ell_N$ $(\sum \ell_i = L)$ tied together:

$$\mathcal{Z} \sim \mu^L L^{\gamma_{\mathcal{G}}-1} g\Big(\frac{\ell_1}{L}, \frac{\ell_2}{L}, \ldots, \frac{\ell_N}{L}\Big)$$

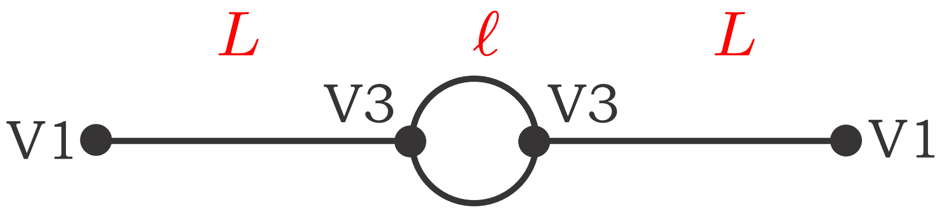
with the scaling exponent:

$$\gamma_{\mathcal{G}} = 1 - d\nu\mathcal{L} + \sum_{f\geq 1} n_f \sigma_f .$$

B. Duplantier. Phys. Rev. Lett. **57** *(1986) 941; L. Schäfer, C. von Ferber, U.*
B. Duplantier. Nucl. Phys. B **374** *(1992) 473.*

Scaling laws for polymer networks

For the network relevant in the DNA denaturation context:



the partition function in the limit $\ell << L$ factorises to:

$$Z_{\mathcal{G}} \sim \mu^{\ell} \ell^{-c} \mu^{L} L^{\gamma-1}, \quad c = d\nu - 2\sigma_3.$$

Y. Kafri, D. Mukamel, L. Peliti. Phys. Rev. Lett. **85** *(2000) 4988.*

Scaling laws for copolymer networks

For a network $\mathcal{G}$ of chains of size R tied together at vertices of orders n_s:

$$\mathcal{Z}(\mathcal{G}) \sim R^{\eta_{\mathcal{G}} - f_1 \eta_2},$$

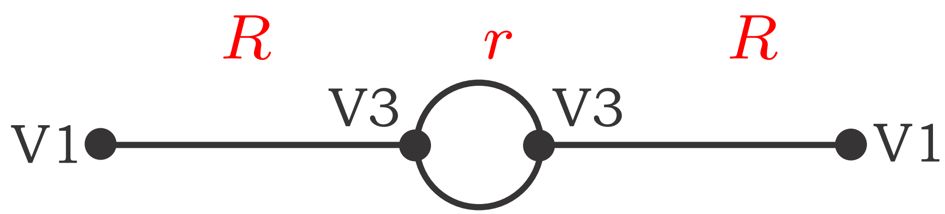
with the scaling exponent:

$$\eta_{\mathcal{G}} = -d\nu\mathcal{L} + \sum_s n_s \eta(s).$$

C. von Ferber, Yu. Holovatch. Europhys. Lett. **39** *(1997) 31; Phys. Rev. E* **56** *(*
6370.

Scaling laws for copolymer networks

For the network relevant in the DNA denaturation context:



the partition function in the limit $r << R$ factorises to:

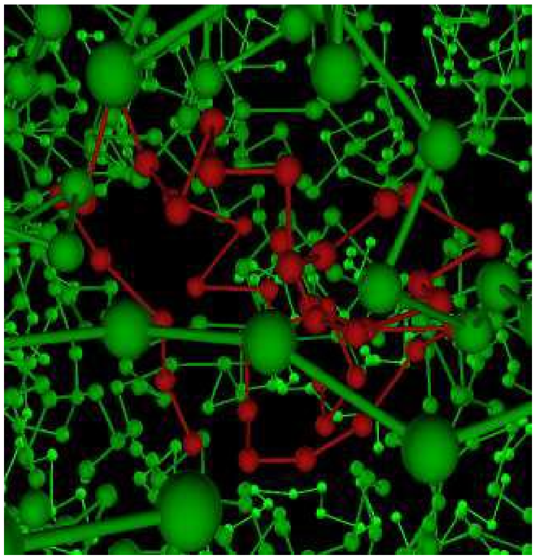
$$Z_{\mathcal{G}} \sim R^{-\eta_2} Z_{\mathsf{loop}}(r), \quad Z_{\mathsf{loop}}(r) \sim r^{-c/\nu} \sim \ell^{-c}.$$

Cf.: *E. Carlon, M. Baiesi. Phys. Rev. E* **70** *(2004) 066118.*

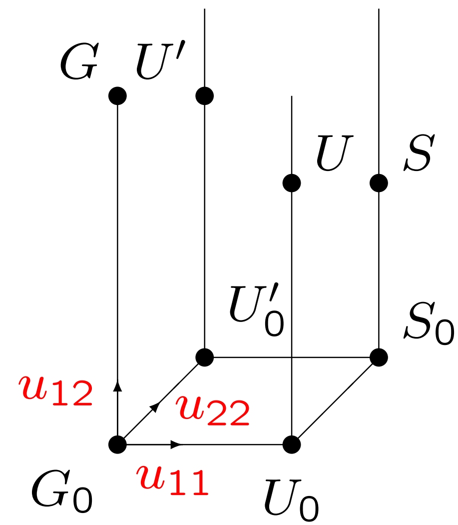
Ternary solution

Two species of polymers, with interactions u_{11}, u_{22}, u_{12} (L. Schäfer, U. Le
Kappeler'91, C. von Ferber, Yu.H.'97):

$$\mathcal{L}\{\phi_b, \mu_b\} \sim \int \mathrm{d}^d r \, u_{11}\phi_1^2(r)\phi_1^2(r) + u_{22}\phi_2^2(r)\phi_2^2(r) + u_{12}\phi_1^2(r)\phi_2^2(r).$$



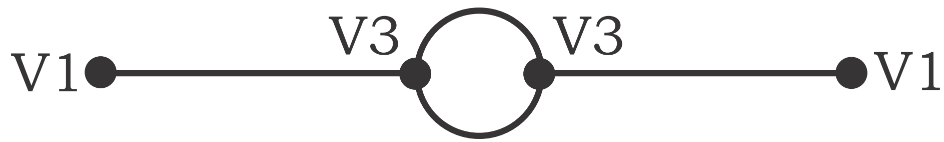
u_{11}: ●-●; u_{22}: ●-●; u_{12}: ●-●



Fixed points (FPs) of tern
polymer solution.

The FP S with $u^*_{11} = u^*_{22} = u^*_{12} = u^*_{\mathrm{SAW}}$ is stable $\Rightarrow$ scaling exponents do not c

c-exponents

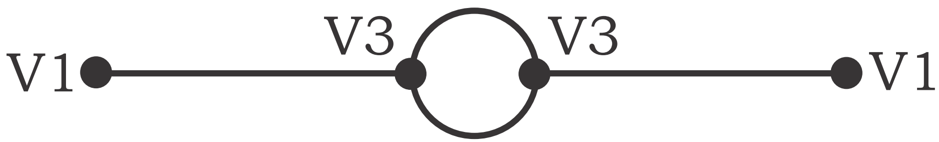


e.g. SAW-SAW-SAW $c = \nu_{\mathrm{SAW}}(3\eta_{20} + d - 2\eta^{S}_{21})$:

$$c = 2 + 1/8\,\varepsilon + \frac{5}{256}\,\varepsilon^2 + \left(-\frac{87}{4096} + \frac{3}{512}\,\zeta\,(3)\right)\varepsilon^3 +$$
$$\left(-\frac{3547}{262144} + \frac{903}{16384}\,\zeta\,(3) + \frac{1}{20480}\,\pi^4 - \frac{1815}{2048}\,\zeta\,(5)\right)\varepsilon^4$$

Using: *V. Schulte-Frohlinde, Yu. H., C. von Ferber, A. Blumen. Phys. Lett.*
(2004) 335.

c-exponents for heterogeneous strands

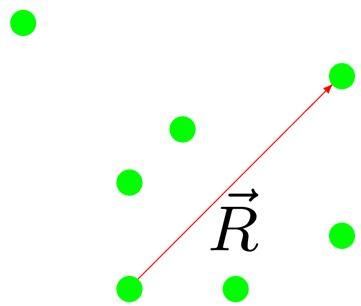


- SAW-RW-SAW $c = \nu_{\mathsf{RW}}(\eta_{20} + d - 2\eta^{U}_{12}) = 2.16$;
- RW-SAW-RW $c = \nu_{\mathsf{SAW}}(d - 2\eta^{U}_{21}) = 2.92$;
- RW-RW-RW $c = \nu_{\mathsf{RW}}(d - 2\eta^{G}_{21}) = 2.5$;
- SAW-SAW-SAW $c = \nu_{\mathsf{SAW}}(3\eta_{20} + d - 2\eta^{S}_{21}) = 2.13$.

The heterogeneity of the network drives the transition further to the 1st order r
c increases.

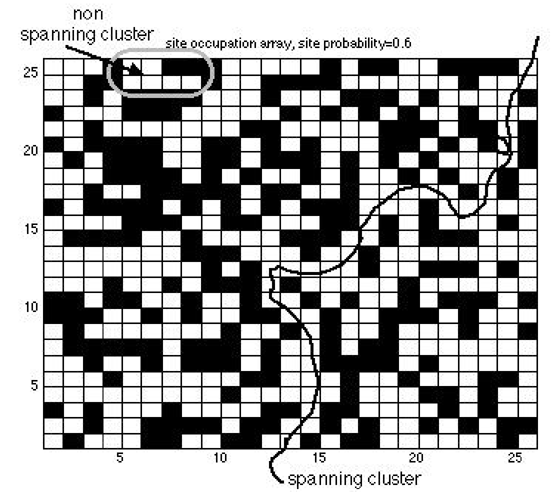
Influence of crowded environment

A. Weak disorder, $c_{\text{perc}} < c \leq 1$



$$g(R) \sim R^{-a}, \quad R \to \infty$$

B. Strong disorder, $c = c$



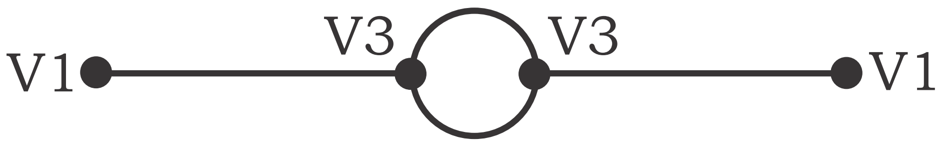
$\delta \leq \varepsilon/2$ $(\varepsilon = 4 - d,\ \delta = 4 - a)$:
$\nu = \nu^{\text{saw}} = 1/2 + \varepsilon/16$,

$\varepsilon/2 \leq \delta \leq \varepsilon$: $\nu = 1/2 + \delta/8$.
V. Blavats'ka *et al.*'01

$\epsilon > 0$ $(\epsilon = 6 - d)$:
$\nu = 1/2 + \epsilon/42$,

Y. Meir, A. B. Harris'89
C. von Ferber *et al.*'04

c-exponents for DNA in long-range correlated disc



e.g. SAW-SAW-SAW

$$c \simeq 2 - \varepsilon/2 + 5\delta/4\,,$$

$d = 3$, $a = 2.3$:

$$c \simeq 3.63.$$

Presence of crowded environment drives the transition further to the 1st order r
c increases.

Thank you.

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Supported in part by
European Commission
Research Directorate General
Human Resources and Mobility
MARIE CURIE ACTIONS