Polymer adsorption on a fractal substrate

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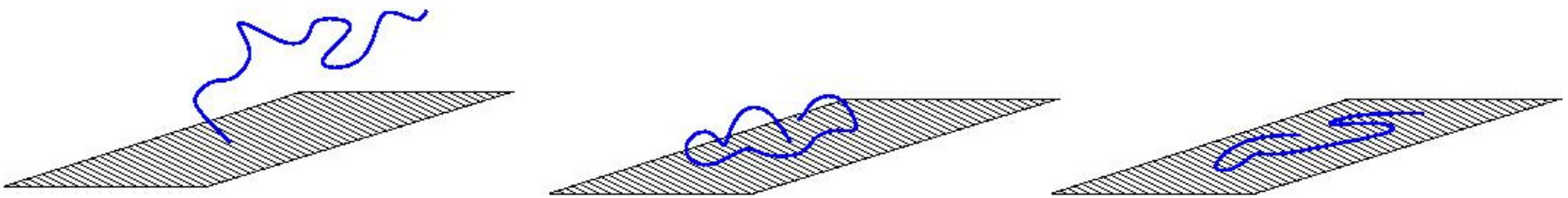
Adsorption transition



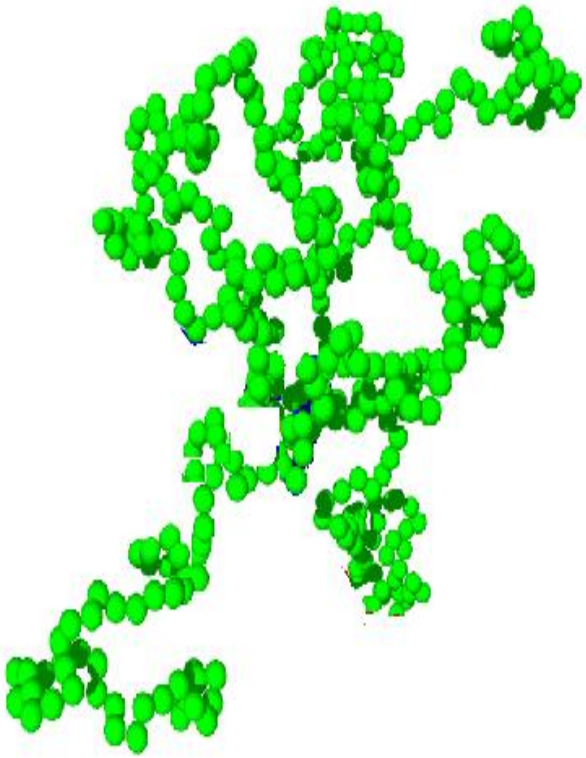
$T > T_A$ $T \sim T_A$ $T < T_A$

Averaged fraction of monomers N_s in contact with the surface:

$$\frac{\langle N_s \rangle}{N} \sim \begin{cases} N^{-1}, & T > T_A, \\ N^{\phi_s - 1}, & T = T_A, \\ const, & T < T_A. \end{cases}$$

$\phi_s = 0.496 \pm 0.005$ (R. Hegger and P. Grassberger, J. Phys. A **27**, 4069 (1994))
$T_A = 3.5006 \pm 0.0009$ (P. Grassberger, J. Phys. A **38**, 323 (2005))

Observables: Gyration radius



- Position vectors

$$\vec{R}_n = \{x_n^1, \ldots, x_n^d\}, \quad n = 1, \ldots, N.$$

- Gyration radius

$$R_g^2 = \frac{1}{2N^2} \sum_{i,j=1}^{N} \left(\vec{R}_i - \vec{R}_j\right)^2$$

- Scaling

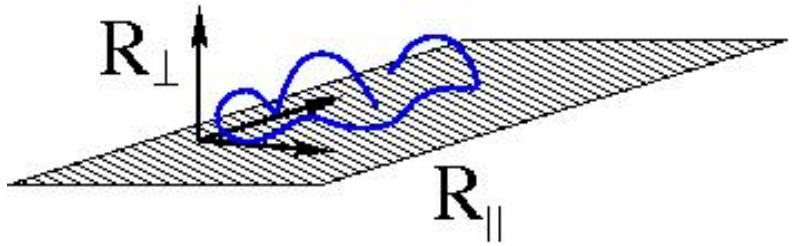
$$R_g^2 \sim N^{2\nu_d}$$

- Universality:

  $\nu_3 = 0.5887(6)$ (D. MacDonald, et al., J. Phys. A (2006))

  $\nu_2 = 3/4$ (B. Nienhuis, Phys. Rev. Lett. (1982))

Observables: Gyration radius



Perpendicular component:

$$\langle R_{g\perp}^2 \rangle \sim \begin{cases} N^{2\nu_3} & T > T_A \\ (T - T_A)^{-\frac{2\nu_3}{\phi_s}} & T < T_A \end{cases}$$

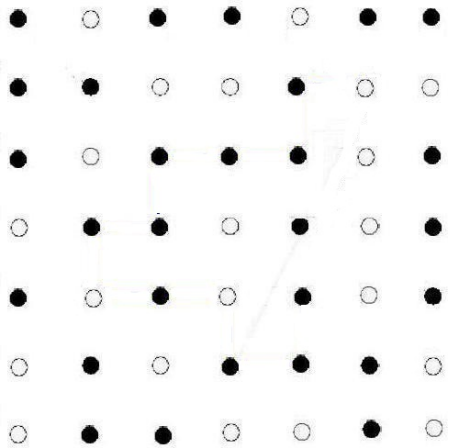
Parallel component:

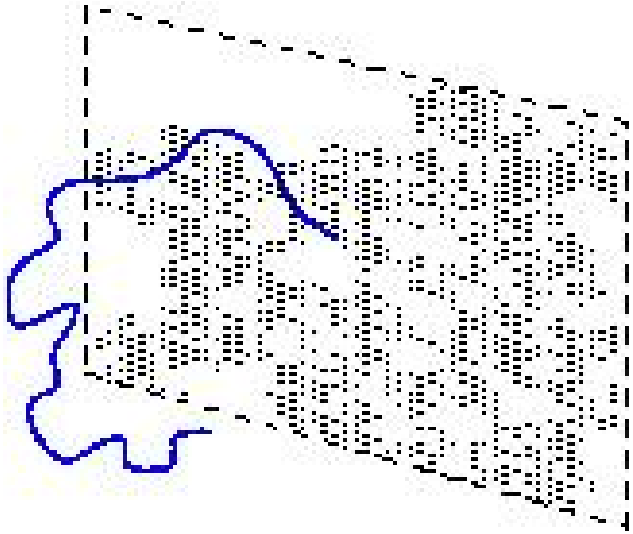
$$\langle R_{g||}^2 \rangle \sim \begin{cases} N^{2\nu_3} & T > T_A \\ N^{2\nu_2}(T - T_A)^{-\frac{2(\nu_2 - \nu_3)}{\phi_s}} & T < T_A \end{cases}$$

Scaling representation:

$$\langle R_{g\perp}^2 \rangle \sim N^{2\nu_3} H_\perp(N^{\phi_s}(T - T_A)) \qquad \langle R_{g||}^2 \rangle \sim N^{2\nu_3} H_{||}(N^{\phi_s}(T - T_A))$$

Polymers on disordered surface





- p – concentration of attractive lattice sites
- percolation cluster at critical concentration $p_c = 0.592$
- Fractal dimension of percolation cluster $d_s^{p_c} = 91/49 \simeq 1.89$
- Such surface is taken as $z = 0$-plane of 3-dimensional lattice

Pruned-enriched Rosenbluth method (PERM)

Adsorption energy of N-step chain:

$$E_N = N_s \varepsilon$$

Weight of Nth step:

$$W_N = \prod_{l=1}^{N} m_l \mathrm{e}^{\frac{-(E_l - E_{l-1})}{k_B T}}$$

m_l is number of possibilities to put lth monomer
We assume $\varepsilon / k_B = -1$
Control parameters: W_n^{max} W_n^{min} (P. Grassberger, Phys. Rev. E **56**, 3682 (1997).)

- $W_n < W_n^{min}$ – pruning with probability $1/2$, $W_n = 2W_n$
- $W_n > W_n^{max}$ – enrichment, $W_n = W_n/2$

Observables averaging

The configurational averaging for any observable O:

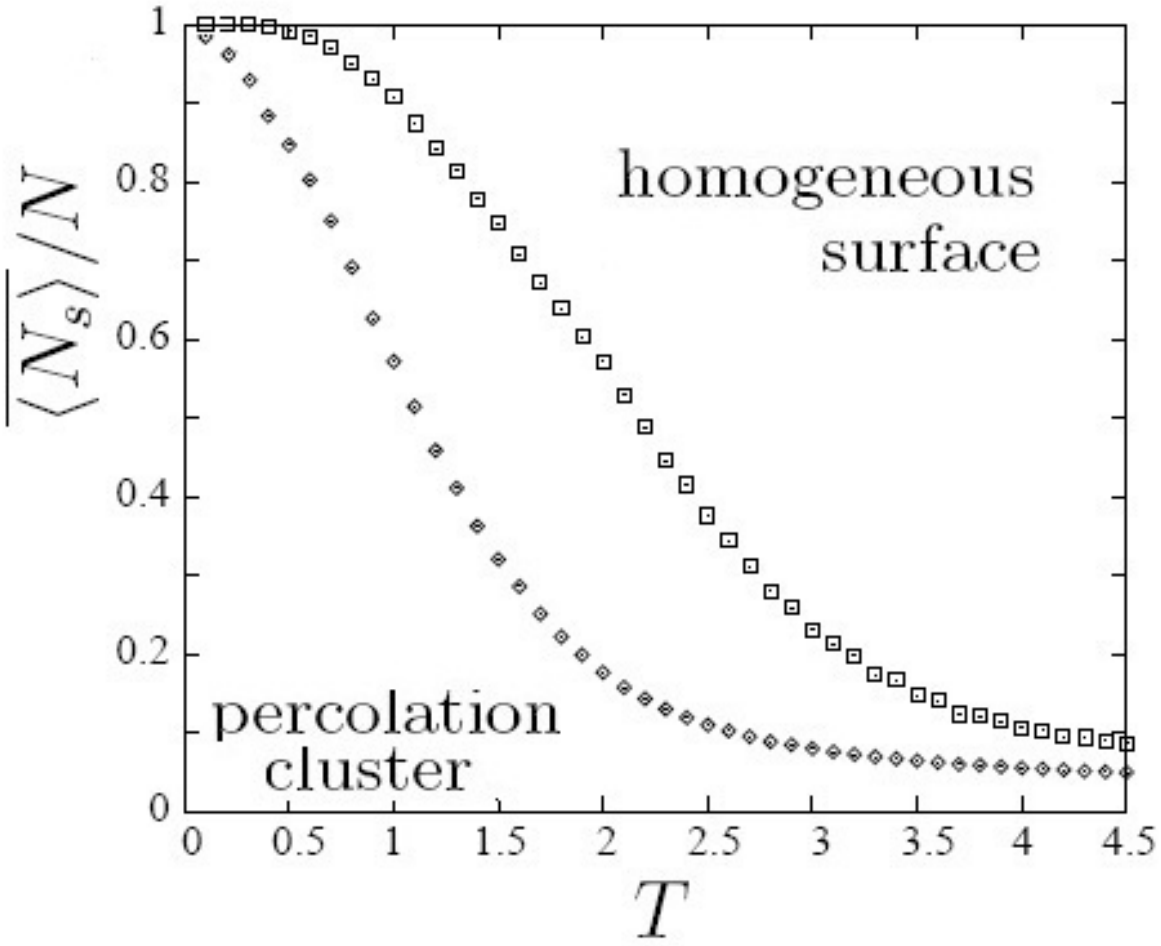
$$\langle O \rangle = \frac{\sum_{\text{conf}} W_N^{\text{conf}} O}{\sum_{\text{conf}} W_N^{\text{conf}}}, \tag{1}$$

The averaging over different realizations of disorder, i.e., over different constructed percolation clusters:

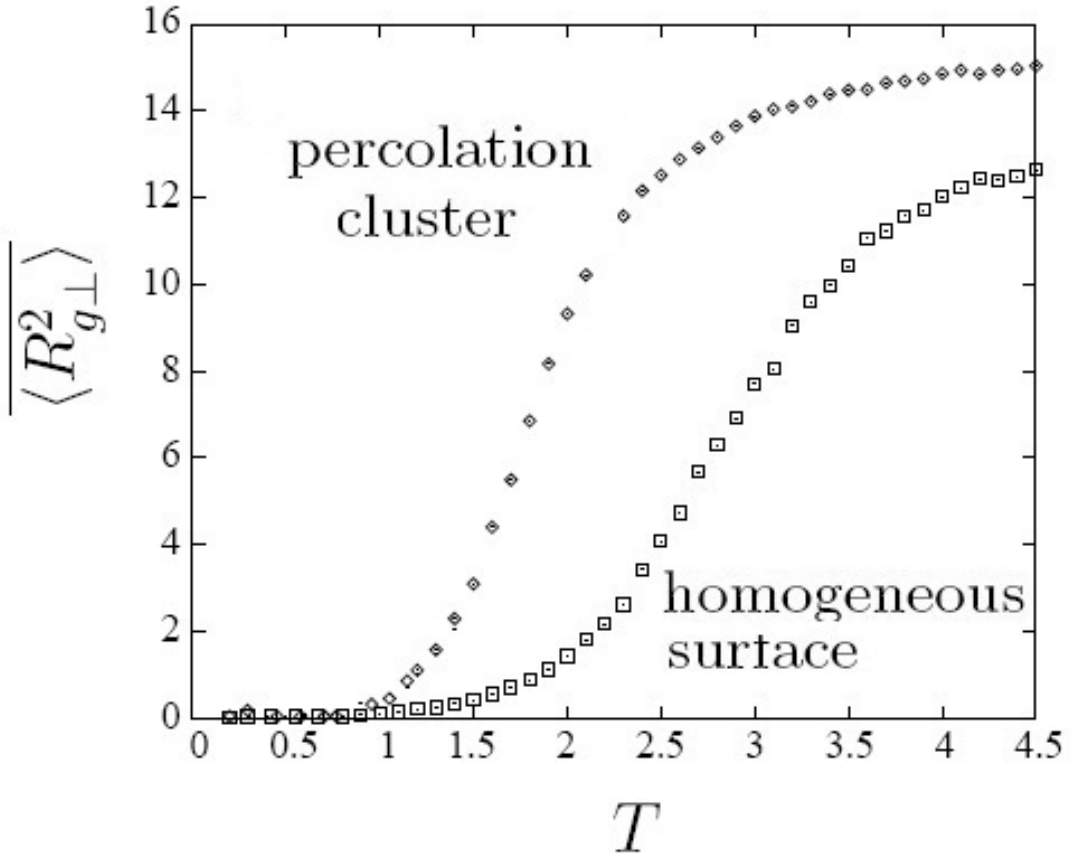
$$\overline{\langle O \rangle} = \frac{1}{M} \sum_{i=1}^{M} \langle O \rangle_i. \tag{2}$$

We constructed $M = 1000$ clusters.

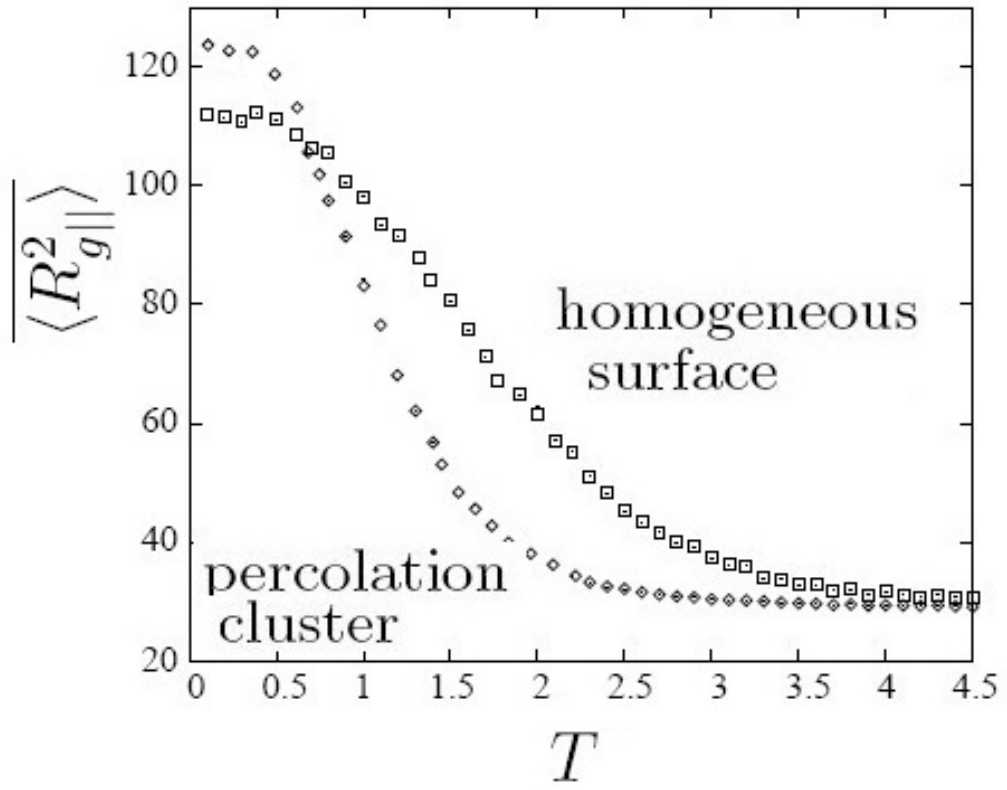
Fraction of adsorbed monomers



The thickness of adsorbed layer



The parallel component of gyration radius

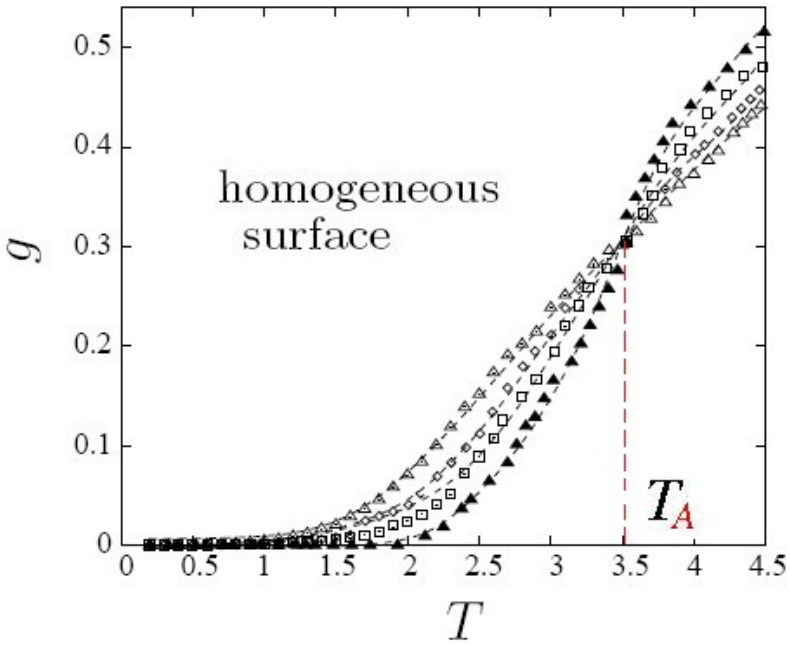


In adsorbed state ($T \ll T_A$): $\nu_2 = 0.742 \pm 0.006$, $\nu_2^{pc} = 0.772 \pm 0.006$.

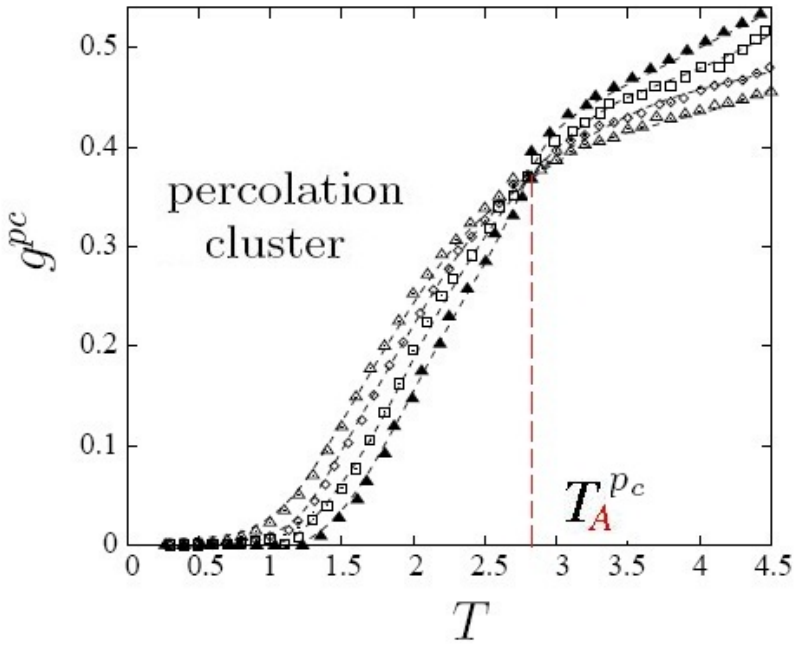
The size ratio

$$g \equiv \frac{\overline{\langle R^2_{g\perp} \rangle}}{\overline{\langle R^2_{g||} \rangle}} = \frac{H_\perp(N^\phi(T - T_A))}{H_{||}(N^\phi(T - T_A))}.$$

At the adsorption critical point ($T \to T_A$), this ratio becomes independent of N.



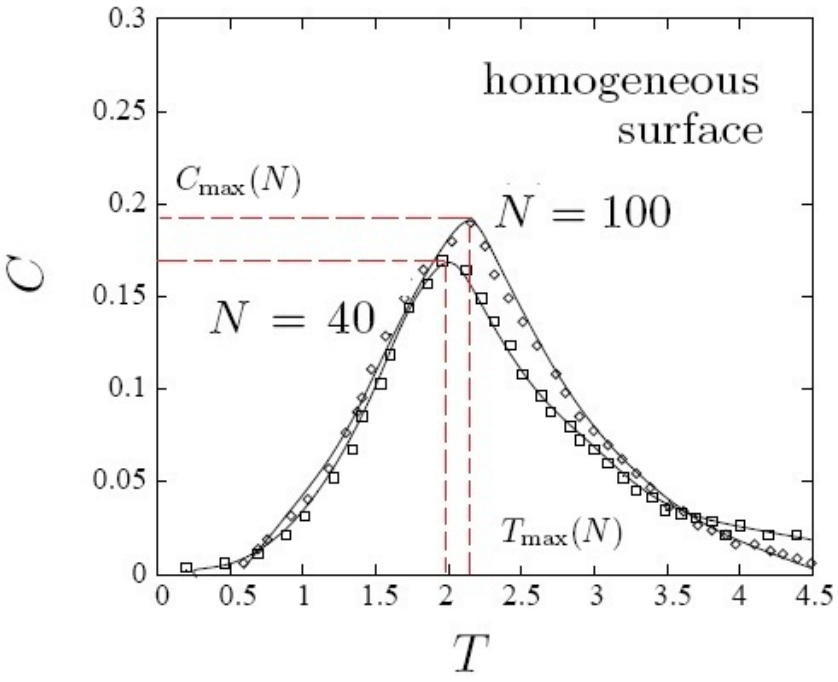
$T_A = 3.5 \pm 0.1$

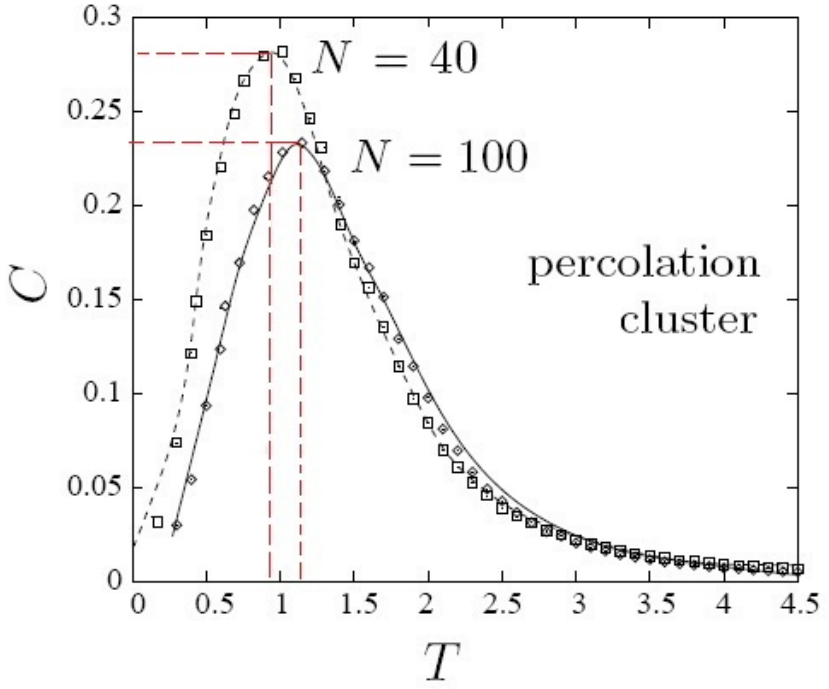


$T_A{}^{pc} = 2.7 \pm 0.1.$

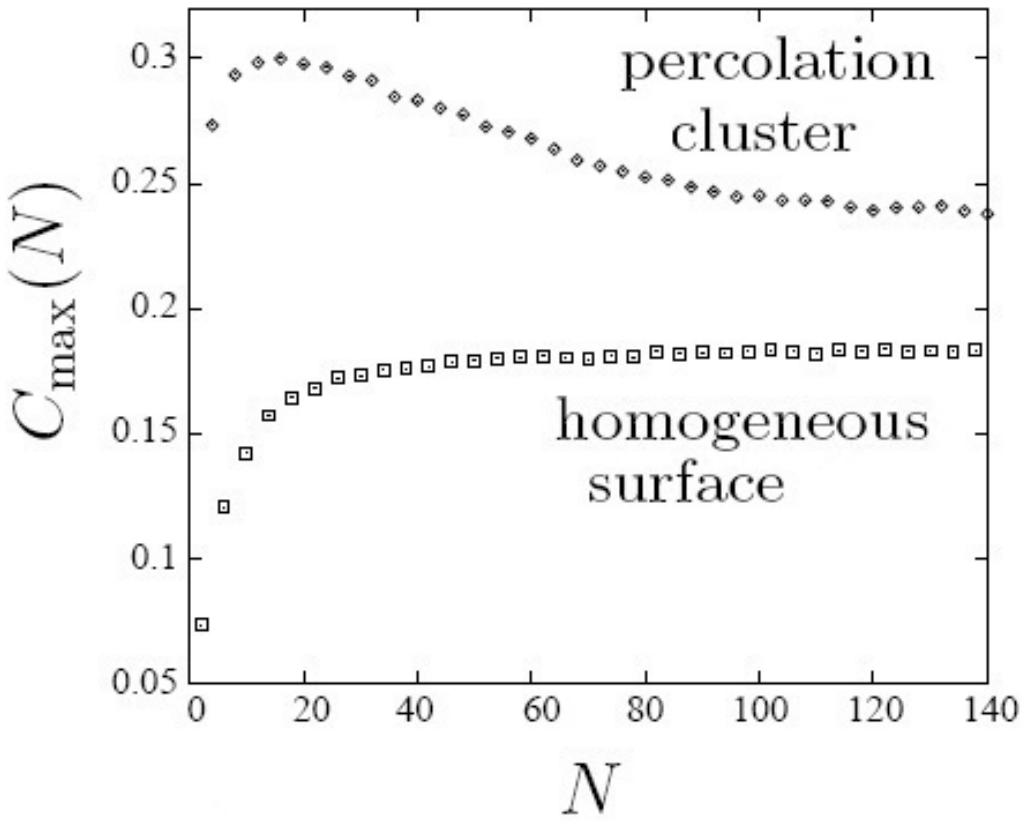
Heat capacity

$$C(T) = \frac{1}{NT^2}\left(\overline{\langle N_s^2\rangle} - \overline{\langle N_s\rangle^2}\right).$$



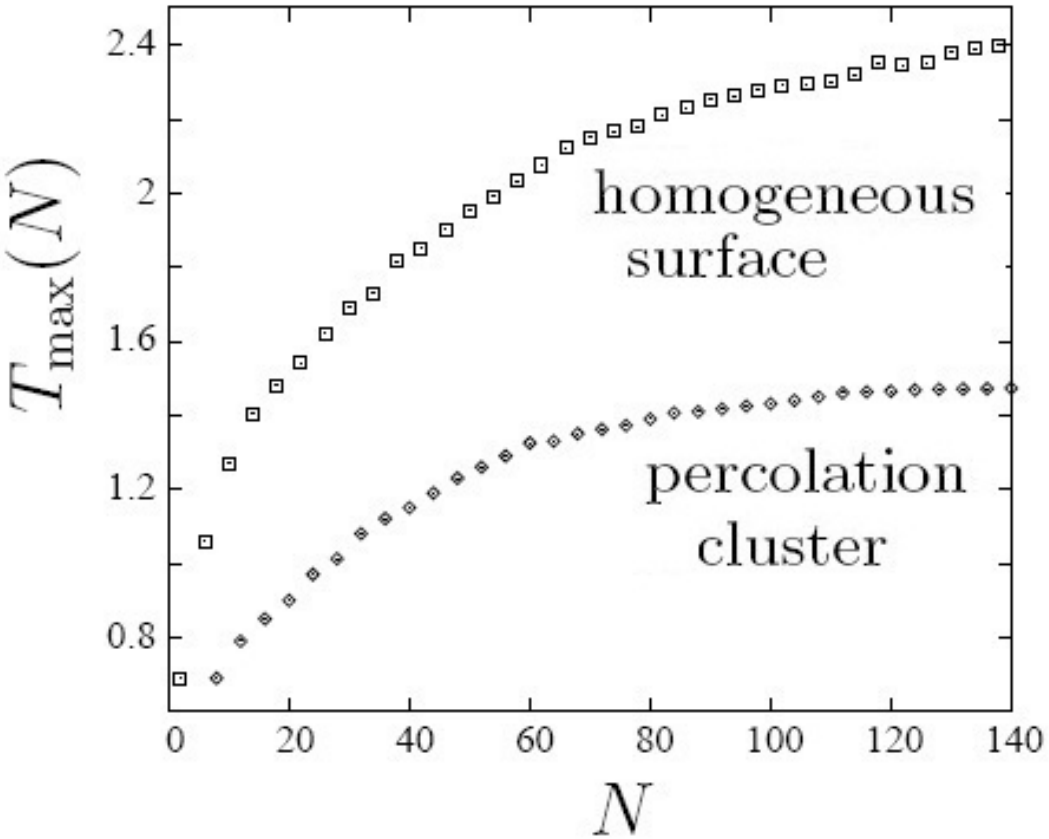


Analysis of the “heights” of heat capacity curves



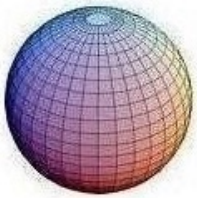
In the vicinity of transition point: $C_{\max}(T) \sim N^{2\phi_s - 1}$
We receive: $\phi_s = 0.509 \pm 0.009$, $\phi_s^{pc} = 0.425 \pm 0.009$.

Analysis of the maxima of heat capacity curves



The finite-size deviation takes place: $T_{\max}(N) - T_A \sim N^{-\phi_s}$.
We receive: $T_A = 3.47 \pm 0.02$, $T_A{}^{p_c} = 2.64 \pm 0.02$.

Shape of adsorbed polymer chain



$\lambda_1 = \lambda_2$

$A_2 = 0$

$\lambda_1 \neq 0, \lambda_2 = 0$

$A_2 = 1$

- Gyration tensor

$$Q_{ij} = \frac{1}{2N^2} \sum_{n,m=1}^{N} (R_n^i - R_m^i)(R_n^j - R_m^j), \quad i,j = 1,\ldots,d$$

- Eigenvalues measure the shape
- Asphericity

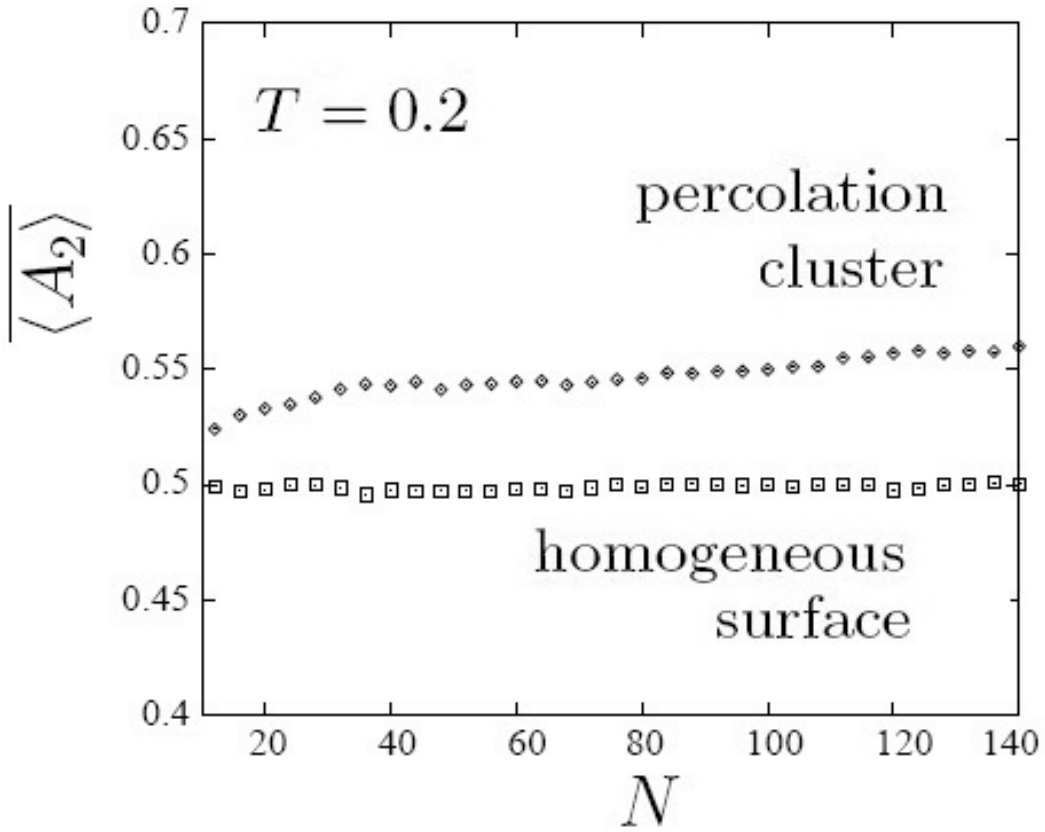
$$A_d = \frac{1}{d(d-1)} \sum_{i=1}^{d} \frac{(\lambda_i - \overline{\lambda})^2}{\overline{\lambda}^2} = \frac{d}{d-1} \frac{\mathrm{Tr}\,\hat{\mathbf{Q}}^2}{(\mathrm{Tr}\,\mathbf{Q})^2}$$

Mean eigenvalue $\overline{\lambda} \equiv \frac{1}{N} \sum_{i=1}^{d} \lambda_i = \frac{1}{N} \mathrm{Tr}\mathbf{Q}$

Moment of inertia tensor $\hat{\mathbf{Q}} \equiv \mathbf{Q} - \mathrm{Tr}\mathbf{Q}\,\mathbf{I}$

- $\langle A_2 \rangle = 0.501 \pm 0.003$ (M. Bishop, J. Chem. Phys. **88**, (1988))

Asphericity in adsorbed state



We receive: $\langle A_2 \rangle = 0.502 \pm 0.006$, $\overline{\langle A_2^{pc} \rangle} = 0.571 \pm 0.006$.

Conclusions

- The adsorption of flexible polymer macromolecules on attractive percolation cluster with fractal dimension $d_s^{pc} = 91/49$ is studied
- The estimates for the surface crossover exponent and for the adsorption transition temperature: $\phi_s^{pc} = 0.425 \pm 0.009$ $T_A^{p_c} = 2.64 \pm 0.02$.
- The adsorption is diminished, when a fractal dimension of the surface is smaller than that of a plain Euclidean surface
- The increasing of a shape anisotropy in an adsorbed state comparing with plain surface is found.