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COPOLYMER NETWORKS:
THE SPECTRUM OF SCALING DIMENSIONS

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Кополімерні сітки: спектр масштабних вимірностей

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Анотація. Досліджуються властивості перетинів зірок випадкових блукань та блукань із самоуниканням. Ми показуємо, як відповідні масштабні показники описують скейлінґ кополімерних сіток у розчині. Ці показники обчислюються на підставі ренормґрупового аналізу відповідного гамільтоніану Едвардса. Отриманий за допомогою теоретико-польової ренормалізації у третьому порядку теорії збурень спектр показників має цікаву властивість: всі показники є скейлінґовими вимірностями комозитних польових операторів, опуклість спектру дозволяє його мультифрактальну інтерпретацію а границя 2D не описується простою формулою, подібною до формули Каца.

Copolymer networks: the spectrum of scaling dimensions

Ch. von Ferber, Yu. Holovatch

Abstract. We explore the intersection properties of stars of random and self-avoiding walks. We show how the corresponding scaling exponents govern the scaling behavior of copolymer networks in solution. We derive and calculate these exponents from a renormaization group analysis of a corresponding Edwards Hamiltonian. Our 3rd order spectrum of exponents calculated by field theoretic renormalization shows remarkable features: All exponents are scaling dimensions of composite power of field operators, convexity of the spectrum allows for a multifractal interpretation, and the 2D limit has no simple Kac formula like structure.

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1. Introduction

Considerable effort is brought towards the understanding of copolymers in various contributions to this conference. Here we focus on the static scaling properties of copolymer networks in solution, as governed by scaling exponents. Recently there has been much interest in the relation of field theory and multifractals [1] and the associated multifractal dimension spectra [2,3] as well as non-intersecting random walks and their 2D conformal theory [4]. Our model of multicomponent polymer networks shows a common core of these topics and allows for a study of the interrelations. For polymer networks consisting of polymer chains of one species it has been shown, that the basic scaling exponents are connected with 'stars', polymer chains tied together at one core [5–7]. The number of configurations $\mathcal{Z}_{*f}$ of a polymer star with f arms of N monomers (see below) will scale for large N like

$$\mathcal{Z}_{*f} \sim N^{\gamma_f - 1} \sim (R/\ell)^{\eta_f - f\eta_2}. \tag{1}$$

The second part shows scaling with the size $R \sim N^{\nu}$ of the isolated coil of N monomers on some scale ℓ. The exponents $\nu = 3/4, 0.58(8)$ and $\gamma_1 = \gamma_2 = \gamma = 43/32, 1.16(0)$ for space dimensions $d = 2, 3$ are known in polymer theory [8]. The exponents γ_f have been calculated analytically in perturbation theory [6,7,9], and by exact methods in two dimensions [5].

At short distance two polymer stars will repel each other. In view of the language of field theory this is described in terms of a short distance expansion. One finds the following relation for the probability $P(r)$ to find the cores of two stars of f_1 and f_2 at short distance r [6]

$$P(r) \sim r^{\Theta} \ , \Theta = \eta_{f_1} + \eta_{f_2} - \eta_{f_1+f_2} > 0 \ . \tag{2}$$

This is compatible with the result, that the spectrum of polymer star exponents η_f is convex from below as function of f with $\eta_1 = 0$.

On the other hand a multifractal (MF) measure μ_x defined on the sites x of scale ℓ on some object of size R is characterized by the scaling of its moments averaged over all sites:

$$\langle \mu_x^k \rangle = \sum_x \mu_x^k \sim (R/\ell)^{y_f} \ . \tag{3}$$

From general inequalities for the moments of a probabitity distribution one may deduce that the spectrum of exponents y_f has to be convex from above.

2. Theory

We model the copolymer network by a fixed number f of polymer chains of different species linked at their endpoints. For each chain $a = 1, \dots, f$ the configuration may be given by a path $r^a(s), 0 \leq s \leq S_a$ in d-dimensional space with a length parameter S_a. Then, the statistics of the f polymers in solution with self and mutual excluded volume interactions u_{ab} is described by an Edwards-Hamiltonian:

$$\begin{aligned} \mathcal{H} &= \sum_{a=1}^{f} \int_0^{S_a} \mathrm{d}s_a \left(\frac{\mathrm{d}r^a(s_a)}{\mathrm{d}s_a} \right)^2 + \\ & \sum_{a,b=1}^{f} \frac{u_{ab}}{2} \int_0^{S_a} \mathrm{d}s_a \int_0^{S_b} \mathrm{d}s_b \delta^d(r^a(s_a) - r^b(s_b)). \end{aligned} \tag{4}$$

Let us explicitely give the partition sum for a 'star'-network, f chains constrained to have one common endpoint in terms of a path integral:

$$\mathcal{Z}_{*f} = \int \mathcal{D}\{r^a\} \exp[-\mathcal{H}] \prod_{b=2}^{f} \delta(r^b(0) - r^1(0)) \tag{5}$$

For more general networks additional products of δ-functions are introduced to fix the topology of the network. For $\mathcal{Z}_{*f}$ we expect scaling analogous to (1) but with new exponents when allowing for more then one polymer species. To make the perturbation theory in u_{ab} of $\mathcal{Z}_{*f}$ well defined, a cut-off s_0 may be introduced, such that all simultaneous integrals $\int \mathrm{d}s_a \mathrm{d}s'_a$ will be cut off by the condition $|s_a - s'_a| \geq s_0$. This in turn allows to give a meaning to the above introduced number of monomes N as $N_a = S_a/s_a$ in this model.

We apply RG theory to make use of the scaling symmetry of the systems in the asymptotic limit to extract the universal content and at the same time remove divergences which occur for the evaluation of the bare functions in this limit [11]. We pass from the theory in terms of the initial bare variables to a renormalized theory. Then, for instance the bare couplings u_{ab} are given in terms of their renormalized dimensionless counterparts g_{ab} by

$$u_{ab} = \kappa^{4-d} Z_{ab} g_{ab} \ . \tag{6}$$

The renormalized couplings g_{ab} depend on the scale parameter κ. Thus the renormalization Z - factors also depend implicitly on κ. This dependence defines the RG functions:

$$\kappa \frac{\mathrm{d}}{\mathrm{d}\kappa} g_{aa} = \beta_{aa}(g_{aa}); \qquad \kappa \frac{\mathrm{d}}{\mathrm{d}\kappa} g_{ab} = \beta_{ab}(g_{aa}, g_{bb}, g_{ab}).$$

. In a study devoted to ternary polymer solutions the RG flow given by the above defined β-functions has been calculated [10,12] to third loop order. The equations for the fixed points of the β-functions were found to have the following nontrivial solutions: $\beta_{aa}(g^*_{\rm S}) = 0$ and for $a \neq b$: $\beta_{ab}(0,0,g^*_{\rm G}) = 0$, $\beta_{ab}(g^*_{\rm S},0,g^*_{\rm U}) = 0$, $\beta_{ab}(0,g^*_{\rm S},g^*_{\rm U}) = 0$, $\beta_{ab}(g^*_{\rm S},g^*_{\rm S},g^*_{\rm S}) = 0$, corresponding to all combinations of interacting and non-interacting chains.

Here, we evaluate the exponents for two general arrangements of the fixed point matrix. We describe polymer stars made of f_1 chains of species 1 and $f_2 = f - f_1$ chains of species 2. Either both species are non self-interacting, case 'G', or species 1 self-interacts and species 2 does not, case 'U':

$$
\begin{aligned}
\eta^G_{f_1 f_2} &\equiv \eta_{*f}(g_{ab} = 0 \text{ if } a,b \leq f_1 \text{ or } a,b > f_1;\ \text{else } g_{ab} = g^*_{\rm G}) \ , && (7)\\
\eta^U_{f_1 f_2} &\equiv \eta_{*f}(g_{ab} = g^*_{\rm S} \text{ if } a,b \leq f_1; g_{ab} = 0 \text{ if } a,b > f_1; && (8)\\
&\qquad \text{else } g_{ab} = g^*_{\rm U}). && (9)
\end{aligned}
$$

For $f_2 = 0$ this includes the homo-polymer star with $\eta_f = \eta^U_{f,0}$ in eq.(1).

3. Results

We give the results for the exponents in $\varepsilon = 4-d$-expansion. We have also performed a fixed $d = 3$ RG analysis. The corresponding more lengthy expressions may be found in [12]:

$$
\begin{aligned}
\eta^G_{f_1 f_2}(\varepsilon) &= -f_1 f_2 \frac{\varepsilon}{2} + f_1 f_2 (f_2 - 3 + f_1) \times \\
&\quad \left[\frac{\varepsilon^2}{8} - \left(f_1 + f_2 + 3\,\zeta(3) - 3\right)\frac{\varepsilon^3}{16}\right]. && (10)\\
\eta^U_{f_1 f_2}(\varepsilon) &= f_1 \left(1 - f_1 - 3 f_2\right)\frac{\varepsilon}{8} + f_1 \left(25 - 33 f_1 + 8 {f_1}^2 - \right.\\
&\quad \left. 91 f_2 + 42 f_1 f_2 + 18 {f_2}^2\right)\frac{\varepsilon^2}{256} + f_1 \left[577 - \right.\\
&\quad 969 f_1 + 456 {f_1}^2 - 64 {f_1}^3 - 2463 f_2 + 2290 f_1 f_2 \\
&\quad -492 {f_1}^2 f_2 + 1050 {f_2}^2 - 504 f_1 {f_2}^2 - 108 {f_2}^3 + \\
&\quad \left(936 f_1 - 712 - 224 {f_1}^2 + 2652 f_2 - \right.\\
&\quad \left.\left. 1188 f_1 f_2 - 540 {f_2}^2\right)\zeta(3)\right]\frac{\varepsilon^3}{4096} && (11)
\end{aligned}
$$

Here $\zeta(3) \simeq 1.202$ is the value of the Riemann ζ-function. With these exponents we can describe the scaling behavior of polymer stars and networks of two components, generalizing the relation for single component networks [6]. In the notation of (1) we find for the number of configurations of a network $\mathcal{G}$ of F_1 and F_2 chains of species 1 and 2

$$
\begin{aligned}
\mathcal{Z}_{\mathcal{G}} &\sim (R/\ell)^{\eta_{\mathcal{G}} - F_1\eta_{20} - F_2\eta_{02}} && (12)\\
&\quad \text{,with } \eta_{\mathcal{G}} = -dL + \sum_{f_1+f_2\geq 1} N_{f_1 f_2}\eta_{f_1 f_2},
\end{aligned}
$$

where L is the number of Loops and $N_{f_1 f_2}$ the number of vertices with f_1 and f_2 arms of species 1 and 2 in the network $\mathcal{G}$. To receive an appropriate scaling law we assume the network to be built of chains which for both species will have a coil radius R when isolated.

4. Conclusions

Does the data answer the question of convexity? A close study of the resummed values reveals, that for fixed f_1 both $\eta^{\rm G}_{f_1 f_2}$ and $\eta^{\rm U}_{f_1 f_2}$ are convex from above as function of f_2, thus yielding 'MF statistics' [12]. The relation to a MF spectral function for $f_1 = 1,2$ has been pointed out in [2], it is analysed in close detail in view of the new data and FT formulation in a separate publication [12]. On the other hand also copolymer stars repel each other, the corresponding convexity from below shows up e.g. along the diagonal values η_{ff} as function of f. The general relation $\eta_{f_1 f_2} + \eta_{f'_1 f'_2} \geq \eta_{f_1+f'_1, f_2+f'_2}$ is always fulfilled. Thus we find no contradiction between the two features of our set of exponents.

The 2D exponents for polymer stars have been shown to belong to a Kac series of exponents of conformal FT with $\gamma_f - 1 = (4 + 27f - 9f^2)/64$ [5]. There are strong indications that this is the case also for stars of f only mutually avoiding walks (MAW) with $\eta^{\rm MAW}_f = (1-4f^2)/12$ [4]. In view of our results though, such a simple 2nd order polynomial seems not to describe the 2D limit of general copolymer star exponents. Thus, the copolymer generalization of the MAW star adds another problem, for which a rigorous formulation in terms of an exactly solvable 2D model is yet to be found.

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