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Scaling properties of dendrimers with long flexible branches

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Monte-Carlo computer simulation as well as theoretical estimate of the properties of dendrimers with long, flexible branches in good solvent were conducted. It was shown that such dendrimers demonstrate universal behavior independent on details of their internal building. In particular, there exist a critical dendrimer generation number $G_{cr}\approx 5$ that signifies the transfer from coil-type structure with properties similar to linear polymer coil to fractal structure (with fractal dimension $\varepsilon \approx 1.82$). Numerical simulations as well as theoretical estimate shows that both G_{cr} and ε (at $G > G_{cr}$) are independent on the number of spacers M in dendrimer branch and on dendrimer generation G (at $G > G_{cr}$).

Обсуждаются результати компьютерного моделирования методом Монте-Карло и теоретические оценки свойств дендримеров с длинными гибкими сегментами в растворителе. Показано, что такие дендримеры демонстрируют универсальное поведение независимо от деталей их внутреннего строения. Так, существует критический номер поколения $G_{cr}\approx 5$, при котором происходит переход от структуры типа клубок со свойствами, подобными свойствам линейных полимеров, к фрактальной структуре (фрактальная размерность $\varepsilon \approx 1.82$). Как численное моделированние, так и теоретические оценки показывают, что G_{cr} не зависит от числа звеньев M в одной ветви дендримера, а ε не зависит от M и поколения дендримера G (при $G > G_{cr}$).

Dendrimers are synthetic macromolecules with a tree-like branched structure. The schematic representation of 2^{nd} generation dendrimer on cubic lattice is given in Fig. 1. Researching dendrimers is a part of molecular nanoscience with the purpose of tailoring material properties at molecular level. A considerable number of researches were dedicated to computer simulation of dendrimer properties (see e.g.[1–3]). However length of dendrimer branches of the researched structures was restricted to several (up to seven) spacers, which led to the dependence of dendrimer scaling properties on the details of concrete model [2, 4]. The purpose of the present work is to conduct computer modeling of dendrimers with long flexible branches, containing a large number (up to fifty) of spacers. Such dendrimers, like linear polymers, are expected to obey universal scaling lows independently of details of their building. In the present work dendrimer properties are modeling by Monte-Carlo method using algorithms, described in the next section.

In the present work dendrimer chain is modeled by a random walk along the ribs of cubic lattice, the length of each rib taken equal to unity. Excluded volume interactions are modeled by prohibition to the dendrimer chain to visit the same lattice node more then once. According to [5] such model corresponds to a macromolecule in a good solvent where repulsion between its segments much exceeds the attraction. In the present work dendrimer modeling was realized via the following algorithms.

During the first step of dendrimer construction, two random chains (branches), containing M links each are built by consequent adding links, starting from central node. Each link is represented by one lattice rib while the end points of each link represent dendrimer beads (similar to those in bead-rode model [5]). Orientation of each newly grown link is randomly chosen from the available free positions to which new bead could be placed. Then, during the second step, two new child branches are built in the same way starting from the end beads of previously built parent chains. After G-steps, dendrimer of generation G is built. A schematic representation of 2nd generation dendrimer with $M = 4$ on cubic lattice is given in Fig. 1. All branches, obtained at k-th step of constructing given dendrimer constitute its k-th shell. The total number of dendrimer beads Ntot equals to $2^{G+1}M$. It is possible that at some moment branch gets stack, i.e. it has no place for further growth. In this case a limited number of tries, n_{tries}, to built given branch is made starting from the same end node of the parent branch. If even then the new branch can not be built, the entire structure is discarded and the growth procedure starts again from the central bead. To each dendrimer D_j, obtained by algorithm I, the statistical weight W_j is ascribed

$$W_j = \frac{1}{\prod_{\text{all branches of } D_j} n_{tries}} \qquad (1)$$

that is equal to probability to obtain given structure if each structure was discarded after first unsuccessful try to built new branch.

Average value of any macroscopic characteristic Z of dendrimers of given generation is determined as

$$\langle Z \rangle = \sum_j W_j Z_j / \sum_j W_j , \qquad (2)$$

where the summation is conducted over all obtained structures.

Let us note that there is no guarantee that conformations with the highest statistical weight W_j can be obtained by algorithm I. It is evident, that, due to exponential growth of number branches with shell number, outer shells of dendrimer D_j make greater contribution to its statistical weight than inner ones. On the other hand, algorithm I leaves more free space, available for growth, to inner shells, then to outer ones. In order to diminish given drawback, the following improvement of the described algorithm is proposed.

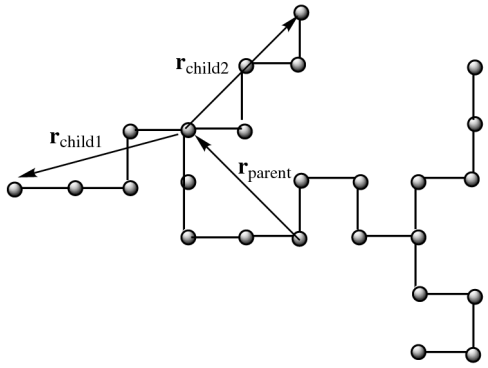

Fig. 1. A schematic representation of second-generation dendrimer on cubic lattice.

The idea of such algorithm is to "artificially" extend inner branches of dendrimer in order to allow more space for the outer ones. In the present work this idea is realized via regulating the two following parameters. The first regulated parameter is

$$K = \frac{\mathbf{r}_{child} \cdot \mathbf{r}_{parent}}{|\mathbf{r}_{parent}|}, \qquad (3)$$

where $\mathbf{r}_{child}$ is a vector connecting first and last beads of a branch from the given shell while $\mathbf{r}_{parent}$ is the same vector for the parent branch of the previous shell (see Fig. 1). In fact parameter K presents some kind of "effective stiffness" of dendrimer. Increase of K diminishes probability for the child chain turn backwards relative to its parent chain, thus leading to dendrimer swelling and allowing outer branches more space to grow. Let us note that parameter K has local character and does not apply on dendrimer requirements of spherical symmetry. As it will be shown below, this is important due to pronounced fractal structure of modeled dendrimers. Second regulated parameter is

$$R_{center} = \frac{1}{2}|r_{child1} - r_{child2}|, \qquad (4)$$

where $\mathbf{r}_{child1}$ and $\mathbf{r}_{child2}$ are two branches of a given shell originating from the same bead (see Fig. 1). Increase of R_{center} leads to separation in space of two branches points of the same shell with the smallest topological distance between them.

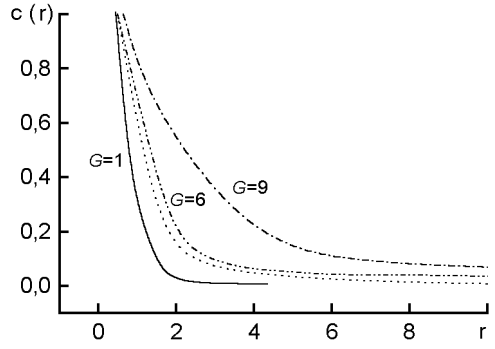

Fig. 2. The dependence of beads concentration c on the distance r from dendrimer center. Generation number for each curve is indicated in the figure.

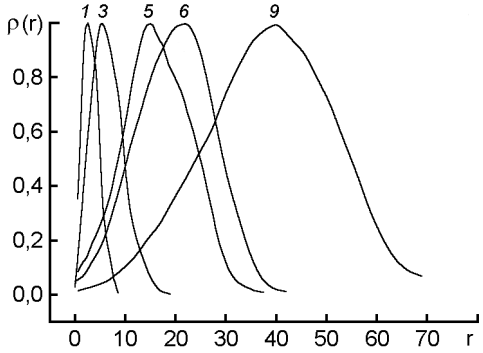

Fig. 3. The dependence of beads radial concentration ρ on the distance r from dendrimer center. Generation number for each curve is indicated in the figure.

In the present work parameters K and R_{center} for each branch were limited from below. The statistical weight (1) of obtained structures was calculated with account of stuck brunches as well as of discarded branches, that did not satisfy restrictions for K and R_{center}. In order to increase element of randomness, the lower limits of these parameters were chosen randomly for each branch. Both uniform and Gaussian random distributions with various dispersions were used for this purpose, then structures with maximal statistical weight were selected. Results with the best statistical weight were achieved by regulating parameter R_{center} only for the first and second shells and parameter K only for the rest of shells. The both described growth algorithms were used. Starting from the sixth generation, structures, obtained by algorithm II have larger statistical weight. Starting from the seventh generation, only algorithm II can provide further dendrimer growth. In the present work dendrimers with $M = 20$ were investigated. The results were averaged with account of statistical weight (1) over 1000 conformations for each dendrimer generation.

The examples of dendrimer radial density and concentration profiles $\rho(R)$ and $c(R)$, that is the number and the concentration of dendrimer beads, found at distance R from the central bead, are presented in Figs. 2 and 3 correspondingly. It can be seen from the figures, that, although maximal concentration is achieved at $R = 0$, most of the beads are found at relatively large distance from the central one. At dendrimer generation $G < 5$, the radial density profiles have asymmetric shape similar to linear chains with excluded volume [5], with left slope essentially steeper then the right one. When dendrimer generation reaches five, shape of density profiles changes, becoming almost symmetric with right slope slightly steeper then the left one.

In order to investigate the described phenomena in more details, let us consider average distance $R_{end}(G)$ of the dendrimer endpoints to central bead (see Fig. 3). This characteristic interesting due to easy analogy with linear polymers of the length $L = MG$. Indeed, as it can be seen from Fig. 3., at $G < 5$, the dependence of R_{end} on G is close to that predicted by scaling theory for linear polymer of length $L = MG$ (see e.g. [5]):

$$R_{end}(G) = MG^{\nu}, \nu \approx 3/5 (G < 5). \qquad (5)$$

At $G > 5$ $R_{end}(G)$ is well approximated by the exponential dependence on G:

$$R_{end}(G) \sim R_{end}(G_{cr}) 2^{(G - G_{cr})\nu_{fract}}, \qquad (6)$$
$$\nu_{fract} \approx 0.53.$$

Such dependence can be explained by the fractal properties of dendrimers considered in the next subsection.

It can be expected that dendrimers possess fractal properties since, from the topological point of view, each dendrimer bead of k-th shell is a center of $G-k$ generation dendrimer. Indeed fractal properties of dendrimers with a small number of spacers between branching points were described in work [4] with fractal dimension ε close to 3. In the present work, as it can be seen from Fig. 4, dendrimers of generation G larger than critical value $G_{cr} = 5$ possess fractal properties with fractal dimension ε close to 1.82 on the scale larger than $R_{end}(G_{cr})$. It is natural to suppose that these properties are

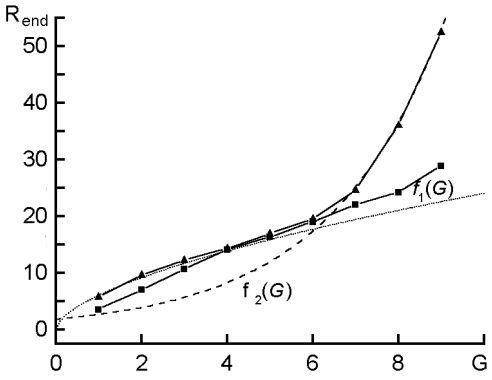

Fig. 4. The dependences of center-to-end distance R_{end} on dendrimer generation G (solid curve). The approximating functions are $f_1(G) = 20G^{0.6}$ (short dashes) and $f_2(G) = 17.5 \cdot 2^{(G-6)\cdot 0.53}$.

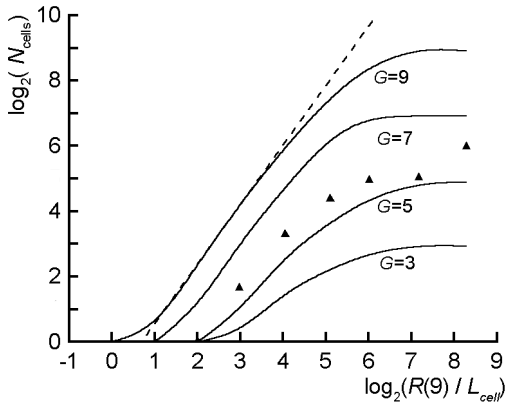

Fig. 5. The dependences of the number of filled cells on cell size (for branching points). Dendrimer generation is indicated in the figure. The linear fit for $G = 9$ is indicated by dashed line.

due to the fact that when system scaling is diminished by η times each dendrimer D_G of generation $G > G_{cr}$ is split into η^{ε} partially overlapping sub- of generation $G - \eta^{\varepsilon}$ that repeat structure of initial dendrimer. Central beads of new sub-dendrimers are separated in space via extension of their connecting branches. The process of splitting continues until sub-dendrimer generation reaches its minimal value G_{cr}. It can be easily seen that characteristic size $R(G) \sim R_{end}(G)$ of such system is of the order of $R(G_{cr})2^{(G - G_c)/\varepsilon}$, that well agrees with Eq.6. Thus, according to the results of numerical simulations, at $G < G_{cr} \approx 5$ dendrimers show structure similar to linear polymer coil with the same dependence of characteristic size on total number of beads while at $G > G_{cr}$ the transfer to fractal structure occurs. In the next subsection theoretical estimation is made of the dependence of ε and G_{cr} on dendrimer generation number G and spacer length M.

When transfer from "coil" to "fractal" state occurs at $G = G_{cr}$, 2^{nd} shell branching points of dendrimer become centers of new sub-dendrimers of generation $G_{cr} - 1$. Such transfer is accompanied by extension of branches that connect 2^{nd} shell branching points with central bead and corresponding total free energy increase $F_+(G)$. On the other hand, concentration of beads in each sub-dendrimer decreases, as compared to initial dendrimer, that leads to the total free energy decrease $F_-(G)$. It is evident that transfer from "coil" to "fractal" state occurs at the value of G when $F_+(G)$ and $F_-(G)$ become comparable. The part of free energy $F_{coil}(G)$, connected with the inner degrees of freedom of a dendrimer can be estimated as that of linear polymer, containing $2^G M$ links and placed into the cavity with linear size $R(G) \sim R_{end}(G)$ determined by Eq. 5. Such estimate gives (see e.g. [5]):

$$F_{coil}(G) \sim 2^G M \left(\frac{2^G M}{R(G)^3}\right)^{\frac{1}{3\nu - 1}}. \qquad (7)$$

Then free energy decrease due to transfer to fractal structure is

$$F_-(G) = F_{coil}(G) - 2F_{coil}(G-1) \sim \qquad (8)$$

$$\sim \frac{1}{2}\left(\frac{2^G}{G}\right)^{\frac{3\nu}{3\nu-1}} \approx \frac{1}{2}\left(\frac{2^G}{G}\right)^{2.25}.$$

The free energy increase $F_+(G)$ is due to space separation of the second shell branching points. $F_+(G)$ can be estimated as that for a linear polymer chain with excluded volume, containing $2M$ beads and extended to the distance $2R(G-1)$ (measured in the units elementary link length). Then estimate of $F_+(G)$, obtained from linear polymer scaling properties (see e.g. [5]) gives:

$$F_+(G) \sim R(G)^2/(2M)^{2\nu} = (G/2)^2. \qquad (9)$$

Thus $F_+(G)$ and $F_-(G)$ become comparable at

$$G_{cr} \sim 2^{\frac{3\nu}{9\nu-2}G_{cr}} \approx 2^{0.52G_{cr}}. \qquad (10)$$

From Eq.(10) follows transfer from "coil" to fractal" state occurs at critical dendrimer generation $G_{cr} \approx 5$ in full accordance with numerical results. Moreover, Eq.(10) predicts that the number of critical generation G_{cr} is independent on the num-

ber of links in the branch M. Indeed, preliminary simulations with $M = 30$ and 50 show the same transfer from "coil" to fractal" state at "critical" generation $G_{cr} \approx 5$.

In order to check the dependence of fractal dimension ε on M the free energy of the system should be estimated with account of interpenetration of different sub-dendrimers. Let us consider sub-dendrimer of generation $Q + 1$ with characteristic size $L(Q + 1)$ that is split into two smaller sub-dendrimers of generation Q and characteristic size $L(Q)$. Sub-dendrimer of generation $Q + 1$ can from geometrical point of view be considered as a spheres of the radius $R(Q + 1)$ equal to $L(Q + 1)/2$ while the smaller sub-dendrimers of generation Q presents two overlapping spheres of radii equal to $L(Q)/2$ and distance between their centers equal to $2R_{center}$, so that $L(Q + 1) = L(Q) + 2R_{center}$. Considering the shape of sub-dendrimers to be spherical, one easily finds the volume $V_{intersec}$ of overlapping area:

$$\frac{V_{intersec}(Q)}{V(Q)} = 1 + \frac{R^3_{center}}{2R^3(Q)} - \frac{3}{2}\frac{R_{center}}{R(Q)}. \quad (11)$$

Thus, similar to the way it was made in subsection 3.2.1., sub-dendrimers of generation Q can be associated with linear polymer chains with the same number of links, placed into the cavities of the radii $R(Q)$. Then free energy of the system can be estimated as

$$F_{fract}(Q) \sim \left(\frac{R_{center}}{(2M)^{\nu}}\right)^2 + \left(\frac{2^Q M}{R^{1/\nu}}\right)^{\frac{3\nu}{3\nu-1}} + \left(\frac{2^Q M}{R^{1/\nu}}\right)^{\frac{3\nu}{3\nu-1}} \frac{V_{intersec}}{V}. \quad (12)$$

Here first term corresponds to free energy increase due to space-separation of sub-dendrimers, 2^{nd} term corresponds to their internal energy and 3^{rd} term corresponds to interaction of sub-dendrimers with each-other.

Substituting Eq.(11) into Eq.(12) and minimizing the free energy (12) with respect to R one obtains

$$\frac{r_{center}(Q)}{R(Q)} = \frac{2}{3\nu + 2} \approx 0.53 \quad (13)$$

and

$$\lambda = \frac{L(Q)}{L(Q-1)} = \frac{r_{center}(Q) + R(Q)}{R(Q)} \approx 1.53. \quad (14)$$

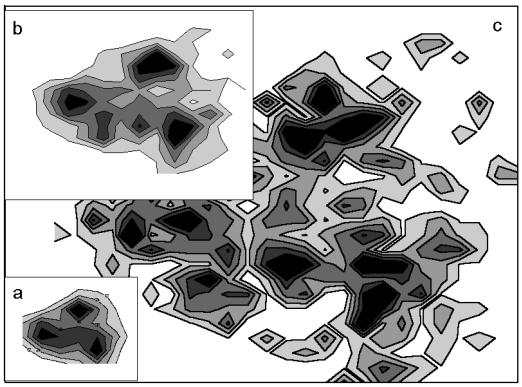

Fig. 6. Snapshots of concentration distribution of the same 9^{th} generation dendrimer. The spatial scale L of density averaging is increased by 2 times for snapshots *a*, *b* and *c* consequently. Black areas relate to concentrations six time higher than ht-grey ones.

Now the fractal dimension of the system can be estimated using the fact that as the scaling L of fractal system diminishes by λ times, the number of filled cubic cells with rib length L increases twice.

$$\left(\frac{L(Q)}{L(Q-1)}\right)^{\varepsilon} = 2. \quad (15)$$

Substituting Eq.14 into Eq.15, one obtains $\varepsilon \approx 1.62$ that is close to obtained numerically value $\varepsilon \approx 1.82$. As it follows from Eqs.(14), (15), the fractal dimension ε of a dendrimer is independent on G and M (at $G > G_{cr}$).

It is interesting to note that, as it follows from Eqs. (13–15), the best coincidence of theoretically and numerically obtained fractal dimension values is achieved at critical index value $\nu_{fract} \approx 0.54$ slightly smaller critical index value $\nu \approx 0.54$ of liner polymer chains. On the other hand, as it follows from Eq.6, the following equality is met:

$$R(G) \sim N_{tot}(G)^{\nu_{fract}}, \ \nu_{fract} = 0.54. \quad (16)$$

Thus, it can be supposed that all properties of dendrimer at $G > G_{cr}$ are determined by the single characteristic size $N_{tot}(G)^{\nu_{fract}}$ and critical index ν_{fract} plays for dendrimers the same role as critical index value ν for linear polymers.

In conclusions, Monte-Carlo computer simulation as well as theoretical estimate of the properties of dendrimers with long, flexible branches in good solvent were conducted. It was shown that such dendrimers demonstrate universal behavior independent on details of their internal building. In par-

ticular, there exist a critical dendrimer generation number $G_{cr} \approx 5$ that signifies the transfer from coil-type structure with properties similar to linear polymer coil to fractal structure (with fractal dimension $\varepsilon \approx 1.82$). Numerical simulations as well as theoretical estimate shows that both G_{cr} and ε (at $G > G_{cr}$) are independent on the number of spacers M in dendrimer branch and on dendrimer generation G (at $G > G_{cr}$). It was shown that both in "coil" and "fractal" states dendrimers possess universal scaling properties, the dependence of dendrimer's characteristic size on its generation number being determined by Eqs.(5), (6). In particular, it was shown that dendrimer in fractal state is split into sub-dendrimers that interact with each other in the same way as parts of a linear polymer chain (blobs) with the same number of links, but with critical index $\nu_{fract} \approx 0.54$ slightly smaller than that for linear polymers ($\nu \approx 0.6$).

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Скейлінгові властивості дендримерів з довгими гнучкими сегментами

М.Ратнер

Обговорюються результати комп'ютерного моделювання методом Монте-Карло і теоретичного оцінювання властивостей дендримерів з довгими гнучкими сегментами у розчиннику. Показано, що такі дендримери демонструють універсальну поведінку незалежно від деталей внутрішньої будови. Так, існує критичний номер покоління $G_{cr} \approx 5$, за якого відбувається перехід від ланцюгового типу структури з властивостями, подібними до лінійних полімерів, до фрактальної структури (фрактальна розмірність $\varepsilon \approx 1.82$). Як числове моделювання, так і теоретичні оцінки демонструють, що G_{cr} не залежить від кількості ланок M в одній гілці дендримеру, а ε не залежить від M і покоління дендримеру G при $G > G_{cr}$.