Structure factors for regular polymer gels and networks

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Structure factors, $P(q)$, for regular dendrimeric polymer gels and two-dimensional tetrafunctional networks are calculated. Since the low-q limit (q being the scattering wave number) region is uninteresting for these systems (the Guinier region yields gel and network overall sizes), this paper focuses on the intermediate q region, whereby the scattering radiation is probing sizes larger than single blocks but smaller than the whole macromolecule. Kratky plots [$q^2P(q)$vs q^2] are presented for starburst dendrimer gels with varying functionality and correlation range r (with respect to a reference block) and for "crumpled sheet" tetrafunctional networks with varying r. For regular networks, the structure factor has contributions from the various "lattice animals" that correspond to a chosen pair of correlated blocks. A simple method based on multivariate Gaussian distributions is used to express the mean square intermonomer distance $\langle r_{ij}^2 \rangle$ for not too complicated correlation diagrams ($r<4$).

INTRODUCTION

The structure factor for complicated structures such as gels or networks is needed in order to interpret scattering data from these systems. While a good deal of experimental data exist, only limited endeavors at modeling even regular systems are available[1–3] due to the complexity in describing such structures. Because the low-q region is uninteresting for large size gels and networks (Guinier plots yield the radius of gyration which is huge in these systems), our focus here will be on the intermediate-q region (Kratky plots).

Regular gels (the word gel is used here to refer to structures that are constructed through multifunctional polymerization without closed loops) such as "starburst dendrimers" have been modeled[4,5] using Gaussian statistics to describe interactions between monomers. A simple intermediate-q limit (q being the scattering wave number) expression for the structure factor $P(q)$ of a regular starburst dendrimer will be presented. Variations of the characteristically peaked Kratky plot [$q^2P(q)$vs q^2] show the effect of increased branching (represented by the functionality f) or range of correlations r (i.e., the number of intermediate blocks between a pair of correlated blocks beyond which correlations are neglected). Zimm plots could also have been used to observe trends in the intermediate-q region; however Kratky plots were chosen because they are more suitable for branched systems.

It is difficult to describe even regular networks (the word network is used here to describe structures that are cross linked starting from linear polymers and that can contain closed loops). Because of the large number of possible pathways (some involve linear chain portions while others involve closed loops) between a pair of correlated blocks, only two-dimensional structures will be considered here. These do not have to be planar, they can form a "crumpled sheet"[6] type of structure. The structure factor $P(q)$ for such a two-dimensional regular (on an "amorphous" lattice) tetrafunctional network has contributions from a variety of correlation diagrams (referred to as "lattice animals" following a common terminology in the field of computer simulation calculations on a lattice). The mean square intermonomer distance $\langle r_{ij}^2 \rangle$ between two monomers that belong to a pair of correlated units in the network will be worked out for a number of possible pathways using an old (mostly forgotten) method[7] based on multivariate Gaussian distributions that allows the "construction" of complicated looped structures starting from one single chain and introducing cross links judiciously. All possible pathways will be worked out up to $r=3$.

STRUCTURE FACTOR FOR REGULAR DENDRIMER GELS

Consider a regular dendrimer gel of infinite extent (in order to neglect end effects) and of functionality f [the number of blocks is multiplied by a factor $(f-1)$ between one generation and the next]. All blocks in the gel are assumed to be identical with n monomers (of segment length b) each. Consider a pair of blocks (reference block and correlated block as shown in Fig. 1) with r intermediate blocks in between. Because Gaussian correlations between two monomers i and j decay as $\exp(-\alpha\langle r_{ij}^2\rangle/b^2)$ where $\alpha=q^2b^2/6$, contributions are more important for short interdistances r_{ij}. For this reason (and for intermediate q values), correlations are assumed to become negligible beyond a given range r.

The structure factor (for correlations with respect to a reference block) is defined as

$$P(q)=\left(\frac{1}{n^2}\right)\sum_{\text{blocks}}\sum_{i,j}\exp(-\alpha\langle r_{ij}^2\rangle/b^2),$$

where the first summation is over all correlated blocks, the index i runs over monomers that belong to the reference

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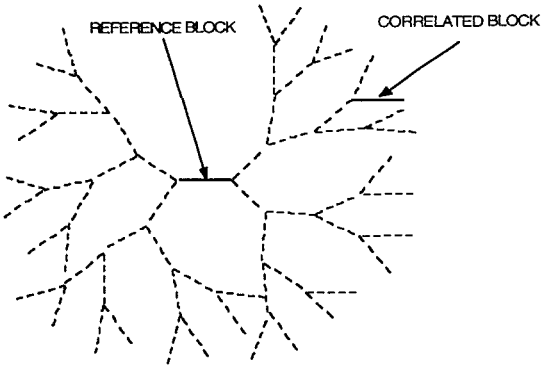

FIG. 1. Regular dendrimer gel.

block, and j runs over monomers that belong to the correlated block as shown in Fig. 1 (note that the correlated block is allowed to be the same as the reference block). $P(q)$ can be expressed as

$$P(q)=P_s(\alpha n)+2F^2(\alpha n)\sum_{k=2}^{r+2}(f-1)^{k-1}\times\exp[-\alpha n(k-2)],$$

where the single block structure and form factors have been defined (for Gaussian statistics) as

$$P_s(\alpha n)=\left(\frac{1}{n^2}\right)\sum_{i,j}^{n}\exp(-\alpha|i-j|)=\left(\frac{1}{n}\right)+\frac{2[\exp(-\alpha n)-1+\alpha n]}{(\alpha n)^2},$$

$$F(\alpha n)=\left(\frac{1}{n}\right)\sum_{i}^{n}\exp(-\alpha i)=\frac{[1-\exp(-\alpha n)]}{\alpha n}.$$

The summations can be performed to give

$$P(q)=P_s(\alpha n)+2F^2(\alpha n)[\exp[n\alpha]]\times\{\exp[-\alpha n(r+2)](f-1)^{r+2}-\exp(-\alpha n)\times(f-1)\}/\{\exp[-\alpha n](f-1)-1\}.$$

Note that $P(q=0)$ is equal to the total number of blocks $N_T=1+2[(f-1)^{r+2}-(f-1)]/(f-2)$. These expressions are valid in the intermediate-q region where $\alpha<1$ but $\alpha n(r+2)>1$. Figures 2(a) and 2(b) show the comparison of the peak height in Kratky plots, $(\alpha n)P(q)$vs(αn), for varying r and f. Figure 2(c) summarizes the variation of the Kratky plot peak position for fixed $f=4$ and increasing r.

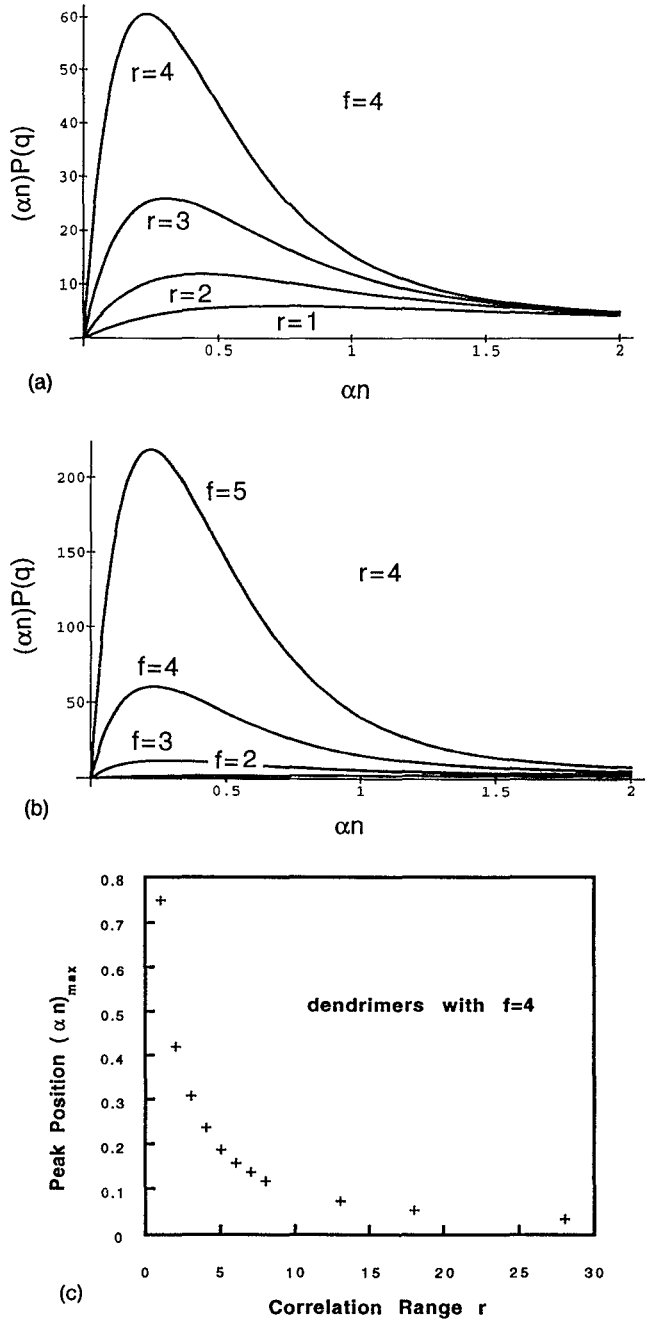

FIG. 2. (a) Kratky plot for a regular dendrimer gel for increasing correlation range r ($r=1,2,3,4$) and a fixed functionality $f=4$. The curves have been normalized to unity for $\alpha n=10$. (b) Kratky plot for a regular dendrimer gel for increasing functionality f ($f=3,4,5,6$) and a fixed correlation range $r=4$. The curves have been normalized to unity for $\alpha n=10$. (c) Variation of the position of the Kratky peak with the correlation range r for a fixed functionality $f=4$ in the case of a regular dendrimer.

MULTIVARIATE DISTRIBUTIONS FOR REGULAR NETWORKS

In order to calculate the contributions of the various correlation diagrams (lattice animals) for regular networks, a systematic method based on multivariate Gaussian distributions is used to construct such structures from linear polymer chains.

For the sake of clarity, a simple case involving correlations between two blocks (n monomers each) separated by three linear chain portions (n_1, n_2, and n_3 monomers, respectively) that are joined at the extremities of the two

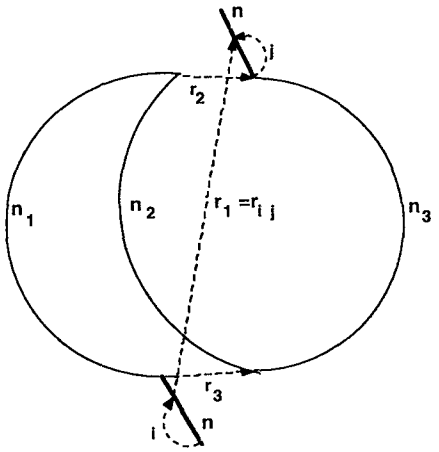

FIG. 3. Correlations between two blocks when their extremities are connected by three intermediate blocks of different lengths.

blocks (see Fig. 3) is considered here. This structure can be constructed using a long linear chain (with $2n+n_1+n_2+n_3$ monomers) that comprises two cross links (corresponding to $\mathbf{r}_2=0$ and $\mathbf{r}_3=0$ in Fig. 3). All segment lengths are assumed to be equal to b. The trivariate Gaussian distribution is given by

$$P(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\left(\frac{3}{2\pi b^2}\right)^{9/2}\Delta^{-3/2}\times\exp\left[-\left(\frac{3}{2b^2}\right)\sum_{\mu,\nu=1}^{3}\mathbf{r}_\mu D_{\mu\nu}\,\mathbf{r}_\nu\right],$$

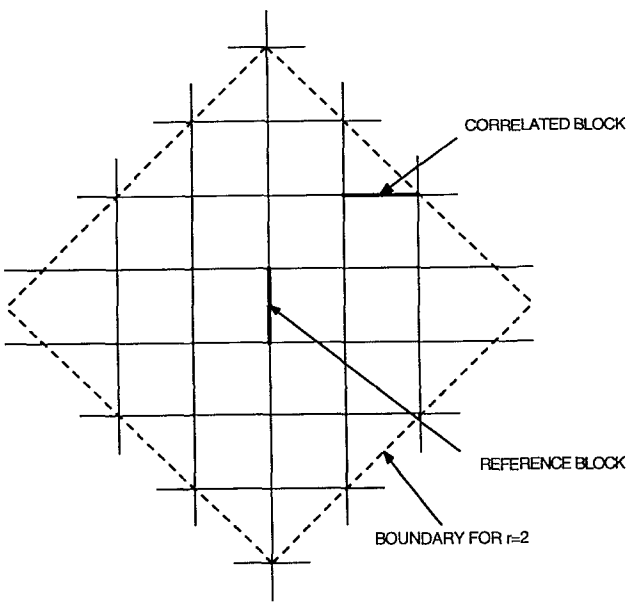

FIG. 4. Correlations around a chosen reference block in a regular tetrafunctional network. The region of interest within the considered boundary depends on the correlation range r.

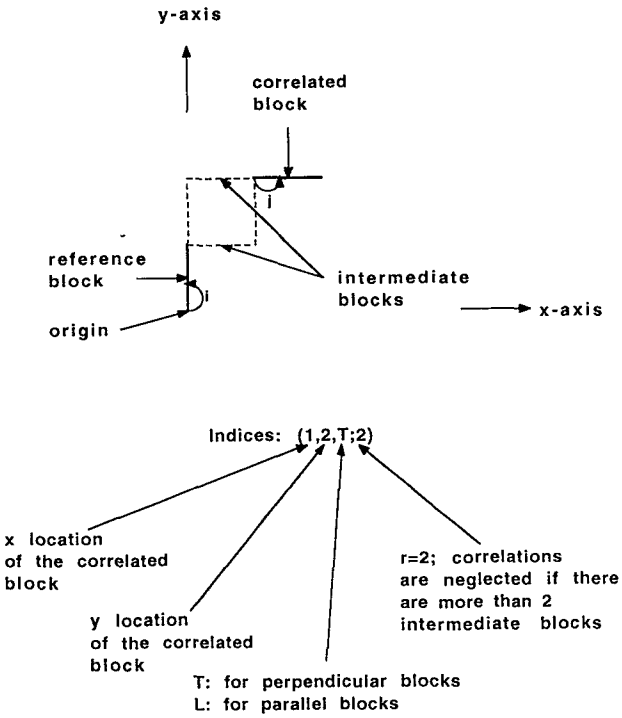

FIG. 5. Indexing scheme for regular 2D tetrafunctional networks.

where $\mathbf{r}_1=\mathbf{r}_{ij}$, Δ is the determinant of the correlation matrix, $\mathbf{C}$, $\mathbf{D}$ is its inverse ($\mathbf{D}=\mathbf{C}^{-1}$), and the nine elements of $\mathbf{C}$ are given by: $C_{\mu\nu}=\langle\mathbf{r}_\mu\cdot\mathbf{r}_\nu\rangle/b^2$ with $\{\mu,\nu=1,3\}$. The formation of the two cross links (by setting $\mathbf{r}_2=\mathbf{r}_3=0$) leaves a univariate Gaussian distribution:

$$P(\mathbf{r}_1)=P(\mathbf{r}_1,0,0)\Big/\int d^3r_1P(\mathbf{r}_1,0,0)$$
$$=(3/2\pi b^2)^{3/2}D_{11}^{3/2}\exp[-(3/2b^2)\,D_{11}\mathbf{r}_1^2].$$

The average mean square distance between two monomers i and j that belong to the blocks of length n is therefore given by

$$\langle r_{ij}^2\rangle/b^2=1/D_{11}.$$

In the specific case considered here (Fig. 3)

TABLE I. Case of a regular two-dimensional (2D) tetrafunctional network for $r=1$. List of the various coefficients $s_{ij}=\langle r_{ij}^2\rangle/b^2$ where $\langle r_{ij}^2\rangle$ is the mean square interdistance between two i and j monomers that belong to two different blocks, b is the monomer segment length and n is the number of monomers per block.

Indices	s_{ij}
(0,1,T;1)	$n-i+j$
(1,0,L;1)	$(-i^2-2ij-j^2+2in+2jn+3n^2)/4n$
(1,1,T;1)	$2n-i+j$
(0,1,L;1)	$n-i+j$
(0,2,T;1)	$2n-i+j$
(1,1,L;1)	$2n-i+j$

TABLE II. Case of a regular 2D tetrafunctional network for $r=2$.

Indices	s_{ij}
(0,1,T;2)	$(-i^2+2ij-j^2-2in+2jn+3n^2)/4n$
(1,0,L;2)	$(-i^2-2ij-j^2+2in+2jn+3n^2)/4n$
(1,1,T;2)	$(-i^2+4jn+4n^2)/4n$
(2,0,L;2)	$(-i^2-2ij-j^2+2in+2jn+8n^2)/6n$
(2,1,T;2)	$-i+j+3n$
(0,1,L;2)	$-i+j+n$
(0,2,T;2)	$(-j^2-4in+2jn+7n^2)/4n$
(1,1,L;2)	$-(4i^2+2ij+4j^2+in-11jn-14n^2)/15n$
(1,2,T;2)	$-i+j+2n$
(2,1,L;2)	$-i+j+3n$
(0,2,L;2)	$-i+j+2n$
(0,3,T;2)	$-i+j+3n$
(1,2,L;2)	$-i+j+2n$
(0,3,L;2)	$-i+j+3n$

TABLE III. Case of a regular 2D tetrafunctional network for $r=3$.

Indices	s_{ij}
(0,1,T;3)	$(-32i^2+9ij-23j^2-28in+83jn+60n^2)/92n$
(1,0,L;3)	$(-16i^2-32ij-16j^2+32in+32jn+33n^2)/56n$
(1,1,T;3)	$(-16i^2+8ij-15j^2+42jn+49n^2)/56n$
(2,0,L;3)	$(-4i^2-2ij-4j^2+5in+5jn+20n^2)/15n$
(2,1,T;3)	$i/5+j-4i^2/15n+7n/5$
(3,0,L;3)	$-(i+j-5n)(i+j+3n)/8n$
(3,1,T;3)	$j-i^2/8n+2n$
(0,1,L;3)	$(-20i^2+8ij-20j^2-8in+40jn+28n^2)/48n$
(0,2,T;3)	$(-15i^2+8ij-16j^2-20in+24jn+68n^2)/56n$
(1,1,L;3)	$-(4i^2+2ij+4j^2+in-11jn-14n^2)/15n$
(1,2,T;3)	$(-15i^2+2ij-15j^2-10in+38jn+73n^2)/56n$
(2,1,L;3)	$(-14i^2-4ij-14j^2+4in+28jn+58n^2)/48n$
(2,2,T;3)	$-i+j+12n/5$
(3,1,L;3)	$-i+j+4n$
(0,2,L;3)	$-i+j+2n$
(0,3,T;3)	$-i+j/3-4j^2/15n+7n/3$
(1,2,L;3)	$(-15i^2-2ij-15j^2-12in+44jn+76n^2)/56n$
(1,3,T;3)	$-i+j+12n/5$
(2,2,L;3)	$(-15i+15j+36n)/15$
(0,3,L;3)	$-i+j+3n$
(0,4,T;3)	$-i+j+4n$
(1,3,L;3)	$(-15i+15j+36n)/15$
(0,4,L;3)	$-i+j+4n$

$$C_{11}=(n-i+j+n_1+n_2+n_3),\quad C_{12}=C_{21}=(n_2+n_3),$$

$$C_{13}=C_{31}=(n_1+n_2),\quad C_{22}=(n_2+n_3),$$

$$C_{23}=C_{32}=n_2,\quad C_{33}=(n_1+n_2)$$

and therefore

$$\langle r_{ij}^2\rangle=b^2[(-i+j+n)(n_1n_2+n_1n_3+n_2n_3)+n_1n_2n_3]/(n_1n_2+n_1n_3+n_2n_3).$$

In summary, this method consists in forming the correlation diagram using one single chain and choosing judiciously the location of cross links. All elements of the correlation matrix $\mathbf{C}$ need to be calculated so that the first element (recall that $\mathbf{r}_1=\mathbf{r}_{ij}$) of its inverse, $D_{11}=\Delta_{11}/\Delta$ (where Δ_{11} is the cofactor of element C_{11} and Δ is the determinant of $\mathbf{C}$) is obtained, therefore yielding $\langle r_{ij}^2\rangle/b^2=\Delta/\Delta_{11}$. In order to simplify the notation, $\langle r_{ij}^2\rangle/b^2$ will be called s_{ij}. This procedure will be used in the next section to calculate the s_{ij} terms for many lattice animals needed in the modeling of regular networks.

STRUCTURE FACTOR FOR REGULAR TETRAFUNCTIONAL POLYMER NETWORKS

Consider a regular two-dimensional polymer network with an infinitely extended structure of blocks comprising n monomers each. Starting from an arbitrarily chosen reference block, our aim is to express all possible correlations with all other blocks within a correlation range r (see Fig. 4). For a fixed r, a number of correlation diagrams (lattice animals) have to be worked out using the method described in the previous section. For simplicity the correlation range is divided into four quadrants and only the upper right quadrant is considered explicitly. The other three are accounted for by including a degree of degeneracy, d, for each lattice animal (i.e., how many times it occurs). An indexing scheme has been chosen to represent the various correlation diagrams. As shown in Fig. 5, the first two indices represent the coordinates of the bottom left extremity of the correlated block, the third index keeps track of whether the two correlated blocks are parallel (L) or perpendicular (T), while the last index is the correlation range r.

For a fixed correlation range r, the structure factor (representing correlations between all correlated blocks within r and the reference block) is given by

$$P(q)=P_s(\alpha n)+d\sum_{\substack{\text{lattice}\\ \text{animals}}}(1/n^2)\sum_{i,j}\exp(-\alpha s_{ij}),$$

where the first summation is taken over all the various lattice animals within the considered range and the second over one is over all monomers in each block and where the s_{ij} values are given in Tables I–III. As before $P_s(\alpha n)$ is the single block structure factor and $P(q)$ is normalized as $P(q=0)=N_T$. The i,j summations are performed numerically.

When zero or one intermediate block is allowed between the pair of blocks under consideration ($r=1$), there are six possible lattice animals [see Fig. 6(a)] of which only one, with indices (1,0,L;1), involves loop interactions. For $r=2$, there are 14 possible lattice animals [see Fig. 6(b)] that involve either bi- or trivariate distributions. The case $r=3$ contains 23 correlation diagrams [see Figs. 6(c) and 6(d)] some of which involve up to six variate distributions. In some cases, in order to construct the desired lattice animal [such as for (1,0,L;3), for example], one has toconsider fictitious chain portions (say, of length n_1) between specific cross links and take the limit $n_1\to\infty$ in the

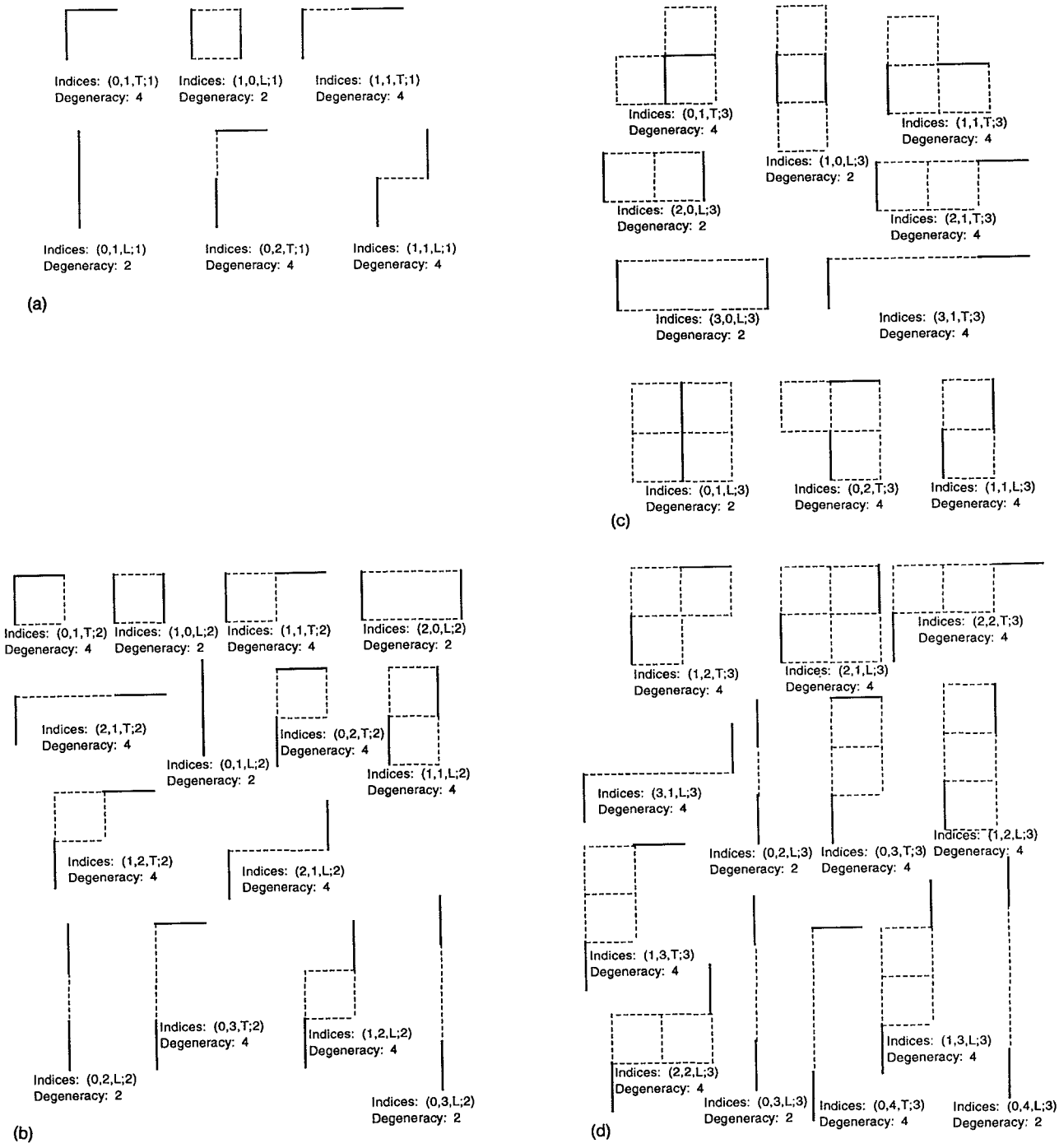

FIG. 6. Various lattice animals representing correlations with respect to the reference block for a regular 2D tetrafunctional network (a) when $r=1$, (b) when $r=2$, (c) and (d) when $r=3$.

result for $s_{ij}=\langle r_{ij}^2\rangle/b^2$. For example, in Fig. 3, taking $n_1\to\infty$ gives the correlation diagram for two blocks (of n monomers) grafted at diametrically opposite points of a ring (comprising n_2+n_3 monomers) so that $\langle r_{ij}^2\rangle=b^2[(-i+j+n)(n_2+n_3)+n_2n_3]/(n_2+n_3)$. Kratky plots are presented in Fig. 7(a).

DISCUSSION

Comparing the Kratky plots for regular dendrimers [Figs. 2(a), 2(b)] and regular networks [Fig. 7(a)], one can observe that for a fixed functionality f, the presence of correlations involving closed loops increases the peak height and width. Increasing f further enhances this peak. As shown in Fig. 7(b), loop interactions cannot be neglected in the calculation of network correlations. This figure represents Kratly plots for $r=1$ when the only looped interaction $(1,0,L;1)$ is either included or replaced by its equivalent one $(1,1,T;1)$ when the loop interaction is "opened up." One can observe a difference of 8% in the peak height of the Kratky plot for this case $(r=1)$.

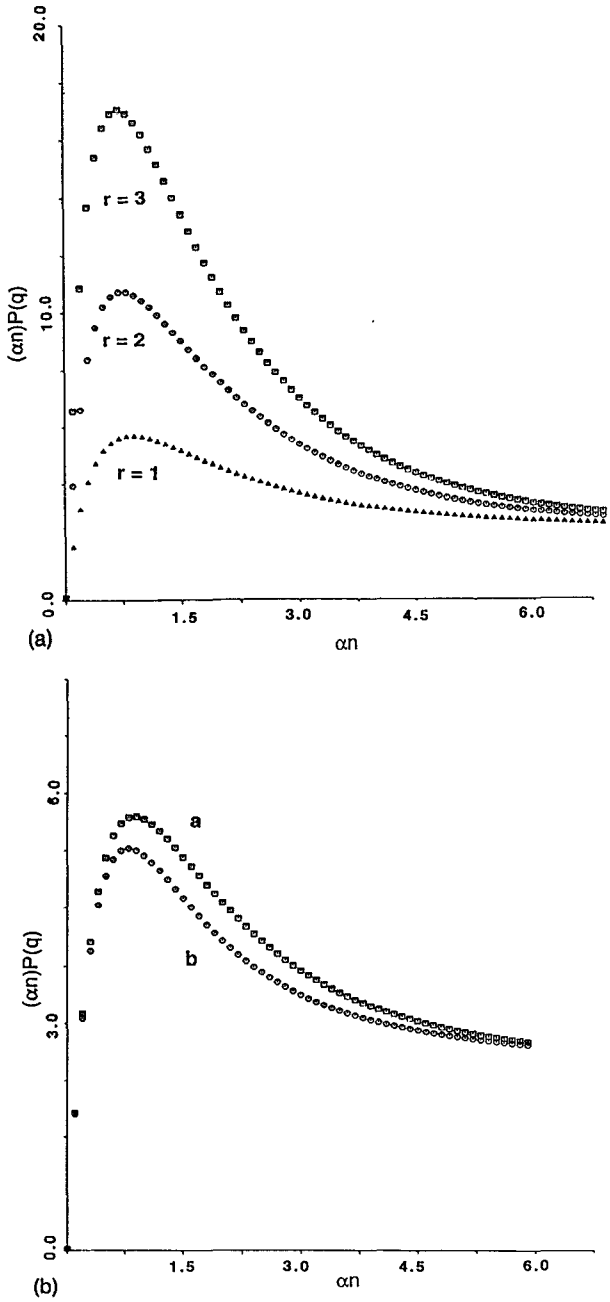

FIG. 7. (a) Kratky plot for a regular 2D tetrafunctional network with increasing correlation range r ($r=1,2,3$). (b) Kratky plot for a regular 2D tetrafunctional network for a correlation range $r=1$ when the only loop interaction $(1,0,L;1)$ is included [curve (a)] or replaced by its equivalent $(1,1,T;1)$ nonlooped interaction [curve (b)].

Fits of the high-q part of the Kratly plot for regular networks to the form $(\alpha n)P(q)=A+B/(\alpha n)$ yields an asympotic value $A=2$ for the three cases considered [see Fig. 7(a)] and the following values for the slope: $B=4.37$, 5.17, and 6.20 for $r=1$, 2, and 3, respectively. It is hoped that such empirical laws, when developed for more realistic three-dimensional networks, will be useful for the evaluation of experimental data. One could, eventually, estimate average cross link density and functionality.

Recently Benoit *et al.*[8] have derived general expressions for B/A in the high-q expansion $(\alpha n)P(q)=A+B/(\alpha n)$ for irregular gels without looped structures. Their results correspond to the case $r=0$ whereby correlations between two blocks are neglected except if these two blocks are neighbors.

In the approach used here to express the structure factor for regular gels and networks, only "topological neighbors" were considered. The existence of "spatial neighbors" (i.e., monomers that are physically close to each other but are separated by long chain contours) has been neglected. In an intermediate-q description, one can think of each block as surrounded by a correlation range beyond which two monomers do not feel each other.

The two-dimensional crumpled sheet description of regular networks presented here could serve as a basis for the modeling of more realistic three-dimensional structures.

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