

# Analytical Estimation of Scaling Behavior for the Entanglement Complexity of a Bond Network

Gustavo A. Arteca<sup>†</sup>

Département de Chimie et Biochimie, Laurentian University, Ramsey Lake Road,  
Sudbury, Ontario, Canada P3E 2C6

Received September 27, 2001

Geometrical entanglements in a polymer network can be characterized in terms of the mean number of projected bond–bond crossings,  $\bar{N}$ . Here, we present an analytical method to study the dependence of  $\bar{N}$  on the number of bonds in the network,  $n$ . Our approach shows the occurrence of power-law scaling,  $\bar{N} \sim n^\beta$ . The estimated upper bound to the exponent for maximally compact networks,  $\beta \approx 1.38$ , agrees well with the values observed in simulations of transient networks in liquids and in the folding features of native states of globular proteins.

## INTRODUCTION

The instantaneous configuration of a bond network (e.g., a melt of polymer chains) is said to be *entangled* when it shows bond–bond crossings, or “overcrossings”, by rigid projection.<sup>1</sup> In this sense, a single rodlike polymer or clusters of polymer rods in the nematic phase are not entangled. In linear chains, entanglements are *transient*, as opposed to the *permanent* (or topological) entanglements found in knotted chains.<sup>2,3</sup> The nature and extent of these entanglements are important pieces of information toward understanding structural and dynamical properties of polymers, polymer melts, or transient networks.<sup>4</sup> There has been an effort to characterize these effects by using appropriate shape descriptors. In this work, we deal with some properties of a common geometrical descriptor of entanglement complexity, the *mean overcrossing number*,  $\bar{N}$ .<sup>1–3,5,6</sup> (For other descriptors used in the case of polymer knots, see refs 1c and 3a–c.) In particular, we present an analytical approach to study its dominant scaling behavior for bond networks with variable compactness.

For a given conformation, the mean overcrossing number  $\bar{N}$  is defined as the number of projected bond–bond crossings, averaged over all directions in space.<sup>5,6</sup> Whereas  $\bar{N}$  describes both the geometry and connectivity of a single conformer, the equilibrium organization of the network can be characterized in terms of the configurationally averaged descriptor,  $\langle \bar{N} \rangle$ . In knotted chains,  $\langle \bar{N} \rangle$  behaves as a “weak” invariant for knot type.<sup>2</sup> In single chains with transient entanglements,  $\langle \bar{N} \rangle$  varies with the conformational compactness. In bond networks, the behavior is similar. Whereas  $\langle \bar{N} \rangle = 0$  for an ensemble of parallel rods, an array of densely packed *nonparallel* rods is characterized by  $\langle \bar{N} \rangle \neq 0$ . That is, this measure of entanglement complexity distinguishes between networks in variable topologies and spatial organizations. In addition, it has recently been discovered that  $\langle \bar{N} \rangle$  provides a better discrimination between shape features compared to other descriptors of polymer size and entanglement complexity.<sup>7</sup>

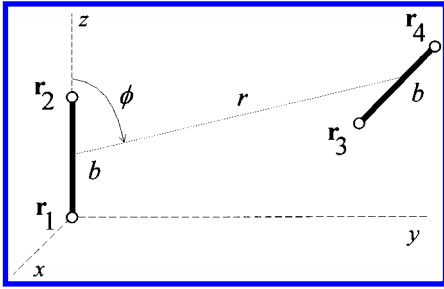
The averaged mean overcrossing number is known to follow a power law in terms of the number of bonds,  $n$ :  $\langle \bar{N} \rangle \sim n^\beta$ ,  $n \gg 1$ , where  $\beta$  is the so-called *entanglement scaling exponent*. Different estimates for the exponent  $\beta$  are known. Monte Carlo simulations yield an estimated lower bound  $\beta = 1.12 \pm 0.01$  for self-avoiding walks in a cubic lattice<sup>5</sup> and an effective exponent  $\beta = 1.33 \pm 0.03$  for medium-size off-lattice polygons with variable excluded volume.<sup>6</sup> The latter exponent agrees well with the value observed in experimental native states of globular proteins, which suggest  $\beta \approx 1.4$  for single-domain protein folds and  $\beta \approx 1.2$  for multidomain folds.<sup>6</sup> The notion of entanglement complexity has also been used to study the transient geometry and topology of a fluctuating network of hydrogen bonds in water.<sup>8</sup> In this case, the network appears in maximally compact configurations, and  $\langle \bar{N} \rangle$  is found to scale with number of molecules within a liquid cluster. Molecular dynamics simulations yield similar estimates for the scaling exponent ( $\beta = 1.44 \pm 0.04$  and  $1.25 \pm 0.06$ ) over a range of temperatures.<sup>8</sup> These values are consistent with the available analytical estimates, which include a rigorous bound  $\beta \leq 4/3$  for single-chain *knots* in canonical configurations<sup>3,9</sup> and a conjectured  $\beta < 1.4$  value for the effect of excluded volume in linear chains.<sup>10</sup> The upper bound  $\beta \leq 4/3$  is sharp, in the sense that it can be realized in particular classes of curves.<sup>3,9</sup> However, it is possible that the exponent has a lower value in polymer networks characterized by different topologies and densities.

A common entanglement exponent suggests an underlying principle in the organization of most bond networks. Below, we explore this principle by using an approach that combines a path-integral representation for overcrossings,<sup>11</sup> together with an averaged bond distribution.

## ESTIMATION OF THE AVERAGE ENTANGLEMENT COMPLEXITY

Consider the instantaneous configuration of an array of  $n$  linear bonds. Depending on its connectivity, we may find a single chain or a polymer network.<sup>1c,11</sup> In the case of a single chain, our approach will provide a measure of *self-entangle-*

<sup>†</sup> Corresponding author phone: +1-(705)675-1151, ext. 2117; fax: +1-(705)675-4844; e-mail: Gustavo@nickel.laurentian.ca.



**Figure 1.** Generic pair of two overcrossing bonds embedded in a cubic lattice. (The two segments are coplanar for  $\phi = 0$  and  $\phi = \pi$  and thus do not overcross for  $r \geq b$ .)

ment. In the case of a network, the degree of entanglement will depend on the length of the individual chains within the ensemble. These differences will reflect in the actual value for the entanglement complexity but not necessarily in a new scaling behavior with the number of bonds. In single chains or polymer networks, the overall entanglement complexity can be measured by an approach that reduces the former to contributions from *pairs of single bonds*. To this end, we now focus on the mean overcrossing number,  $\bar{N}_{\text{TOT}}$ , for the projected bond–bond crossings in the entire network. We take the  $i$ th bond as one linking “atoms”  $i$  and  $i + 1$ , numbered according to some convention. Let  $\bar{N}_{ij}$  be the mean number of projected crossings corresponding to the  $i$ th bond crossing the  $j$ th bond. Since  $\bar{N}_{ij} = \bar{N}_{ji}$ , the total (mean) number of overcrossings in the network is

$$\bar{N}_{\text{TOT}} = 2 \sum_i \sum_{j>i} \bar{N}_{ij} \quad (1)$$

Let  $\{\mathbf{r}_i\}$  be the position vectors for the “atoms” defining the bond network, measured from an arbitrary origin. (Note that  $\bar{N}_{\text{TOT}}$  is invariant under rigid translations and rotations.) Using the network connectivity and geometry, we can now write the mean overcrossing number in closed form by invoking a path-integral representation developed for the analysis of writhe and linking in closed curves<sup>12–14</sup> and extended recently for the study of overcrossings in lattice polygons<sup>15</sup> and networks.<sup>11</sup> Within this approach, the individual contribution of a pair of straight-line bonds to the mean overcrossing number,  $\bar{N}_{ij}$ , is given by<sup>11</sup>

$$\bar{N}_{ij} = \frac{1}{4\pi} \int_0^1 \int_0^1 \frac{|\dot{\gamma}_i(s) \times \dot{\gamma}_j(t) \cdot (\gamma_i(s) - \gamma_j(t))|}{\|\gamma_i(s) - \gamma_j(t)\|^3} ds dt \quad (2)$$

in terms of the bond vectors  $\gamma_i = \mathbf{r}_i + s(\mathbf{r}_{i+1} - \mathbf{r}_i)$ ,  $s \in [0,1]$ , and their parametric derivatives  $\dot{\gamma}_i = \partial \gamma_i / \partial s = (\mathbf{r}_{i+1} - \mathbf{r}_i)$ . As shown below, eqs 1 and 2 can be used to determine the approximate dependence of  $\langle \bar{N}_{\text{TOT}} \rangle$  on the number of bonds,  $n$ , in the network.

The pair contribution  $\bar{N}_{ij}$  adopts a simpler form if the bonds are embedded into a regular array. Since the scaling behavior is expected to be lattice invariant, we use here the simplest representation, i.e. a cubic lattice.<sup>11</sup> In terms of overcrossings, bonds in a cubic lattice can be grouped into two classes. Perpendicular bonds that are *not* coplanar do overcross. Parallel, coplanar, and collinear bonds do not. Consider two generic bonds, such as those in Figure 1. Depending on the angle  $\phi$ , these bonds produce overcrossings. Without loss of generality, let us suppose that the two

overcrossing segments have the same bond length  $b$ . Moreover, consider two perpendicular bonds, given as:  $\mathbf{r}_1 = (0,0,0)$ ,  $\mathbf{r}_{i+1} = (0,0,b)$ ,  $\mathbf{r}_j = (x_j, y_j, z_j)$ , and  $\mathbf{r}_{j+1} = (x_j + b, y_j, z_j)$ . The contribution of two such bonds to the mean overcrossings is known in closed form:<sup>11</sup>

$$\bar{N}_{ij} = \frac{1}{4\pi} |\arctan\{(z_j - b)x_j / y_j r_{i+1,j}\} - \arctan\{(z_j - b)(x_j + b) / y_j r_{i+1,j+1}\} + \arctan\{z_j(x_j + b) / y_j r_{i,j+1}\} - \arctan\{z_j x_j / y_j r_{i,j}\}| \quad (3)$$

Here  $r_{s,k} = \|\mathbf{r}_s - \mathbf{r}_k\|$  is the distance between the  $s$ th and  $k$ th “atoms”. We can now simplify further eq 3 by extracting the dominant terms expressed as a function of the  $r$  and  $\phi$  coordinates in Figure 1. These two coordinates contain sufficient information to characterize the *main* contributions to the overcrossing between two segments in a *cubic lattice*. If  $\phi = 0$ , the two bonds are coplanar and thus do not overcross. For  $\phi > 0$ , the mean overcrossing number decreases as  $r$  (the mean distance between the segments) increases. Equation 3 can be written in terms of  $r$  and  $\phi$  by assuming that  $r_{s,k} \approx r$  for sufficiently large  $y_j$  values. Using simple trigonometric relations for arctan, we get

$$\bar{N}_{ij} \approx \frac{1}{4\pi} \arctan \left\{ \left[ 1 + \frac{z_j^2 y_j^2 b^2 r^2}{(y_j^2 r^2 + z_j^2 x_j^2)^2} \right]^{-1} \frac{y_j b^2 r}{y_j^2 r^2 + z_j^2 x_j^2} \right\} \quad (4)$$

where the approximation  $x_{j+1}x_j \approx x_j^2$  is used to simplify the denominators. If we now invoke the angular relations  $y_j \approx r \sin \phi$  and  $z_j \approx r \cos \phi$ , the dominant term in eq 4 (corresponding to small  $x_j$  values) becomes

$$\bar{N}_{ij}(r, \phi) \approx \frac{1}{4\pi} \arctan[f(r, \phi)]$$

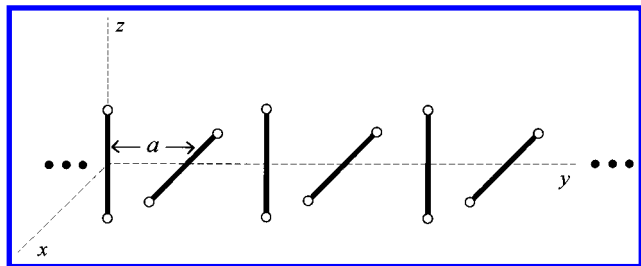
$$f(r, \phi) = \frac{b^2 \sin \phi}{r^2 \sin^2 \phi + b^2 \cos^2 \phi} \quad r \geq b \quad (5)$$

As expected, coplanar bonds do not overcross for  $r \geq b$  (i.e.,  $\bar{N}_{ij}(r, 0) = 0$ ). Similarly, the contribution to the overcrossings maximizes for  $\bar{N}_{ij}(b, \pi/2)$ .

Equations 1 and 5 allow us to estimate the total mean number of overcrossings in terms of the *radial distribution of segments*. We proceed as follows. First, we divide the network into two sets of  $n/2$  mutually perpendicular segments, i.e., a total of  $n^2/4$  segment pairs contributing to overcrossings. Within a given conformation, the spatial distribution of bonds is characterized by a set of  $\{\bar{N}_{ij}(r, \phi)\}$  values. In contrast, the *configurationally averaged* total mean overcrossing number,  $\langle \bar{N}_{\text{TOT}} \rangle$ , can be expressed in terms of two averaged properties: (a)  $g^{(3D)}(r)$ , the distribution function for pairs of  $(i, j)$  segments separated by a distance  $r$  within the interior of an  $n$ -bond cluster; (b)  $\langle \bar{N}_{ij}(r, \phi) \rangle_\phi$ , the angular mean (over  $\phi \in [0, 2\pi]$ ) for the contribution to the total mean overcrossing number of a single pair of bonds separated by a distance  $r$ . Using these two quantities, and considering that there are  $n^2/4$  of such possible bond pairs, we write

$$\langle \bar{N}_{\text{TOT}} \rangle = 2 \sum_i \sum_{j>i} \langle \bar{N}_{ij} \rangle \approx \frac{n^2}{2} \int g^{(3D)}(r) r^2 \langle \bar{N}_{ij}(r, \phi) \rangle_\phi dr \quad (6)$$

If we estimate a minimum distance for two neighbor segments as  $r_{\text{min}} \approx b$ , then the  $g^{(3D)}(r)$  distribution in eq 6 is



**Figure 2.** Example of a one-dimensional regular chain of isolated bonds of length  $b$ , separated by a distance  $a$ . First-neighbor bonds are perpendicular, whereas second neighbors are parallel. The mean overcrossing number of the network scales linearly with the bond number.

normalized as  $\int_b^R r^2 g^{(3D)}(r) dr = 1$ , where the  $R$  distance is a diameter spanning the interior of the cluster. For a maximally compact cluster, we have  $R \approx n^{1/3}b$ .

#### ASYMPTOTIC BEHAVIOR OF ENTANGLEMENTS IN VARIOUS NETWORKS

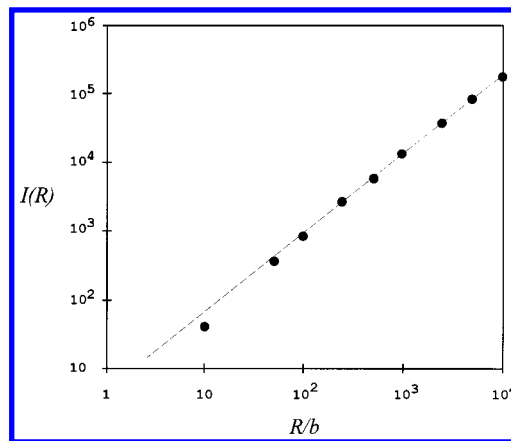
First, we can test the above approach in a simple array. Consider a regular chain of isolated bonds of length  $b$ , separated by a distance  $a \gtrsim b$  and displaced along the  $y$  direction. Further, suppose that the  $y$ -displaced bonds alternate in being parallel to the  $x$  and the  $z$  axes, as indicated in Figure 2. In other words, each bond is perpendicular to (i.e., overcrosses) its first neighbors, third neighbors, etc. This network represents a regular conformation for which the entanglements are numerically known to scale linearly with the number of segments; i.e.,  $\beta = 1$ .<sup>16</sup> In this array, the angular average in eq 6 can be omitted. Consequently, we have

$$\bar{N}_{\text{TOT}} \approx \frac{n^2}{2} \int_a^{na} g^{(1D)}(y) \bar{N}_{ij}(|y|, \pi/2) dy \quad (7)$$

where  $g^{(1D)}$  is normalized as  $\int_a^R g^{(1D)}(y) dy \approx 1$ , for  $a \gtrsim b$  and  $R \approx na$ , the span for the above network. For  $n \gg 1$ , this array has a constant pair distribution probability:  $g^{(1D)} \approx 1/na$ . Moreover, we can accurately write  $\bar{N}_{ij}(|y|, \pi/2) \approx (4\pi)^{-1} \arctan(b^2/y^2) \approx b^2/4\pi y^2$ , for  $r \geq a \gtrsim b$ . Finally, by replacing these expressions in eq 7, we obtain a scaling law  $N_{\text{TOT}} \sim n(1 + O(n^{-1}))$  that agrees with the numerical results for regular configurations.<sup>16</sup> This result corresponds strictly to an infinite array, yet it describes also the leading behavior for a linear finite-size network. In this latter case, the pair distribution vanishes at long distances; its normalized form becomes then  $g^{(1D)} \approx 2(na)^{-2}(R - |y|)$ . When using eq 7 again with the modified distribution, we obtain  $\bar{N}_{\text{TOT}} \sim n(1 + O(n^{-1} \ln n))$ .

We can now apply this approach to 3D bond networks. As in the previous example, we expect a constant pair distribution of segments in a dense 3D array, for bond–bond distances between  $b$  and  $R \approx n^{1/3}b$ . This includes also the case of a single chain in the collapsed polymer regime, as it is characterized by the same size-scaling exponent,  $\nu = 1/3$ . With the normalization condition invoked before, we have  $g^{(3D)} \approx 3/nb^3$ , for large  $n$ . In general, for a network in a regime of compactness characterized by a size-scaling exponent  $\nu$  (i.e.,  $R \approx n^\nu b$ ), we expect<sup>17</sup>

$$g^{(3D)}(r) \approx (\nu nb^{1/\nu})^{-1} r^{-3+(1/\nu)} \quad (8)$$



**Figure 3.** Apparent power-law scaling for the integral  $I(R)$  as a function of the network size  $R$ , for clusters with a size-scaling exponent  $\nu = 1/3$ . The cluster diameter  $R$  is measured in units of  $b = 1$ . Within the range  $10^2 \leq R \leq 10^4$ , this behavior yields an effective scaling exponent  $\beta \approx 1.38 \pm 0.01$  for the mean overcrossing number.

Equation 8 includes the case of polymer chains in the ideal, or “ $\theta$ ”, regime ( $\nu = 1/2$ ), as well as chains in a poor solvent ( $\nu \approx 3/5$ ).<sup>17,18</sup> To use eq 6, we first note that one can accurately write  $\arctan|f(r, \phi)| \approx |f(r, \phi)|$ , for  $\phi \approx [0, 2\pi]$  and all  $r$  distances inside the cluster. Accordingly, the angular average for the overcrossing of two segments separated by  $r$  becomes

$$\begin{aligned} \langle \bar{N}_{ij}(r, \phi) \rangle_\phi &\approx (2\pi^2)^{-1} \int_0^{\pi/2} f(r, \phi) d\phi \\ &= \frac{b^2}{4\pi^2 r(r^2 - b^2)^{1/2}} \ln \frac{r + (r^2 - b^2)^{1/2}}{r - (r^2 - b^2)^{1/2}} \end{aligned} \quad (9)$$

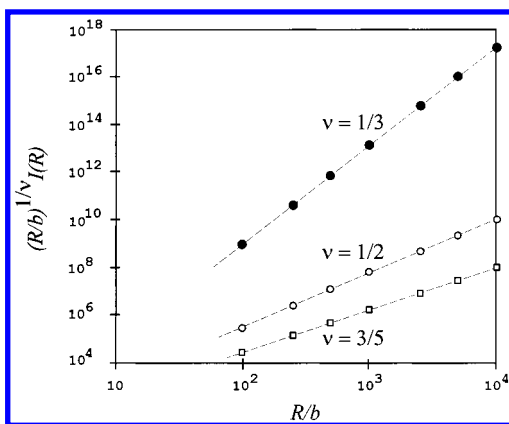
As required,  $\langle \bar{N}_{ij}(r, \phi) \rangle_\phi$  maximizes for  $r \ll b$  (where  $\langle \bar{N}_{ij}(b, \phi) \rangle_\phi \approx 1/4\pi^2$ ) and vanishes at long distances (where  $\langle \bar{N}_{ij}(r, \phi) \rangle_\phi \approx (b^2 \ln r)/2\pi^2 r^2$ , for  $r \rightarrow \infty$ ). Finally, when replacing in eq 6, we obtain an approximate analytical expression for the total mean overcrossing number:

$$\begin{aligned} \langle \bar{N}_{\text{TOT}} \rangle &\approx \frac{b^{2-(2/\nu)}}{8\pi^2 \nu} R^{1/\nu} I(R) \\ I(R) &= \int_b^R \frac{r^{-2+(1/\nu)}}{(r^2 - b^2)^{1/2}} \ln \frac{r + (r^2 - b^2)^{1/2}}{r - (r^2 - b^2)^{1/2}} dr \end{aligned} \quad (10)$$

Our hypothesis is that eq 10 resembles a power law  $b^{2-(2/\nu)} R^{1/\nu} I(R) \approx (R/b)^\beta \sim (n^\nu)^\beta = n^\beta$ , for different size-scaling exponents  $\nu$ , when analyzed within a range of  $n$  values similar to those found in the numerical experiments. To compare properly with the usual estimations for the exponent  $\beta$ , we have performed fittings of the form  $\ln \langle \bar{N}_{\text{TOT}} \rangle$  vs  $\ln n$ .

Figure 3 shows the numerical results for a dense bond network ( $\nu = 1/3$ ), where  $I(R)$  has been computed by Romberg integration for  $10^2 \leq R \leq 10^4$ . (Here,  $R$  is in units of  $b = 1$ .) In the case  $\nu = 1/3$  and for very large  $R$  values, the integral in eq 10 would have a logarithmic term leading to a scaling law  $\langle \bar{N}_{\text{TOT}} \rangle \sim n^{4/3} \ln n$ . However, when using the usual fitting (i.e.,  $\ln I$  vs  $\ln R$ ), the results in Figure 3 do mimic an accurate power law  $\ln I(R) = (1.156 \pm 0.019) \ln R + (1.48 \pm 0.13)$ , with 95% confidence intervals. This fitting produces an “effective” entanglement scaling exponent  $\beta = 1 + \nu(1.156 \pm 0.019) = 1.385 \pm 0.006$ . This value is





**Figure 4.** Apparent scaling behavior for the configurationally averaged total mean overcrossing number  $\langle \bar{N}_{TOT} \rangle$  as a function of the network size  $R$ , for networks with different size-scaling exponents  $\nu$ . ( $R$  measured in units of  $b = 1$ .) The depicted fittings yield effective entanglement exponents  $\beta$  ranging between 1.1 and 1.4.

in close agreement with the estimates obtained from computer simulations of other compact systems, e.g. liquid networks<sup>8</sup> and small globular polymers,<sup>6</sup> which were analyzed in a similar fashion. In the case of water clusters,<sup>8</sup> the fitting was performed with a cell of ca.  $10^3$  water molecules; this ensemble is commensurable with the present one, where the network is enclosed in a sphere with radius  $R/b > 10^3$ . For water clusters, the “melt” corresponds to fluctuating ensembles of separated hydrogen-bonded “chains”, each with an approximate mean length of 11 O–H bonds.<sup>8</sup>

For  $\nu > 1/3$ , the integral  $I(R)$  deviates from power-law behavior. However, as shown in Figure 4, the function  $R^{1/\nu} I(R)$  can still be represented accurately with a single scaling exponent over the same range of  $R$  values. When fitting the function in the case of ideal chains ( $\nu = 1/2$ ), we get  $s \approx 2.27 \pm 0.03$ , which leads to  $\beta = 1.13 \pm 0.02$ . In a network with self-avoiding chains ( $\nu \approx 3/5$ ), we get  $s = 1.77 \pm 0.02$ , which leads to  $\beta = 1.06 \pm 0.01$ . In this latter case, the main contribution to  $\langle \bar{N}_{TOT} \rangle$  corresponds to the regime of short distances ( $r \gtrsim b$ ) and *not* to the large  $R$  values. The present estimate of  $\beta \approx 1.1$  for  $\nu = 1/2$  and  $\nu = 3/5$  is in agreement with the results from Monte Carlo simulations of random walks and self-avoiding walks in the cubic lattice<sup>4</sup> and in the continuum.<sup>5</sup> (The data in Figure 4 give also  $\beta = 1.38 \pm 0.01$  for  $\nu = 1/3$ .)

We have checked the robustness of the above estimates by using other pair distribution functions. In a compact system with finite size, the distribution of distances is not constant but eventually vanishes for large  $R$  values. We have repeated the above analysis with two other such model distributions. When using  $g^{(3D)} \approx A(R - r)$  (subject to the usual normalization), we obtain  $\beta = 1.38 \pm 0.01$ , for  $\nu = 1/3$ . Similarly, a model distribution given by  $g^{(3D)} \approx A \exp(-r^2/R^2)$  leads to  $\beta = 1.39 \pm 0.01$  for a compact network. These results suggest that the effective scaling behavior depends mostly on the dominant behavior of  $g^{(3D)}$  for relatively short bond–bond distances.

## CONCLUSIONS

The present approach provides a simple explanation for the apparent scaling behavior observed in computer experiments of entangled polymers and polymer networks. The

behavior appears as a *balance* between the distribution of bonds in space and the long-distance decay of the contribution of a pair of bonds to the total mean overcrossing number. It also appears that differences in the scaling of  $\langle \bar{N}_{TOT} \rangle$  for random systems are mainly associated with changes in the pair distribution function  $g^{(3D)}(r)$  rather than with the details of the average overcrossing pattern of the bond pairs.

We estimate an *effective* scaling exponent  $\beta$  between 1.1 and 1.4, depending on the network (or chain) compactness. These results emerge from a fitting of  $\ln \langle \bar{N}_{TOT} \rangle$  vs  $\ln n$  in a finite network. These values can be compared with the numerical estimates observed in realistic networks, but they do not provide rigorous bound to the exponent  $\beta$  in the limit of an infinitely large system. Nevertheless, considering that fittings such as those in Figure 3 tend to overestimate critical exponents, our result of  $\beta \approx 1.4$  for a compact network is consistent with the analytical bound of  $\beta \leq 4/3$  for knotted polygons.<sup>3,8</sup>

Interestingly, our results indicate that polymer chains and networks in the collapsed regime are characterized by a larger exponent ( $\beta \approx 1.4$ ). This finding is consistent with differences in self-entanglement for small- and medium-size globular proteins. The native states of small globular proteins are found in the scaling regime for collapsed polymers and characterized by  $\nu \approx 0.33$  and  $\beta \approx 1.4$ .<sup>6</sup> In contrast, medium-size globular proteins ( $n > 300$ ) adopt less compact shapes ( $\nu \approx 0.4$ ) and are characterized by a smaller entanglement exponent ( $\beta \approx 1.2$ ).<sup>6</sup>

The present approach allows one to study separately the effects of topology and compactness on geometrical entanglements. Whereas the network compactness is reflected in the distribution function  $g^{(3D)}(r)$ , different network topologies will give rise to distinct patterns of  $\{\bar{N}_{i,j}\}$  values. Thus, the method can be useful for exploring the behavior of anisotropic networks, where the angular averaging of pair contributions to the overcrossing number (eq 9) would not be applicable. These problems include systems such as polymers under geometrical confinement,<sup>18</sup> where chain entanglements exhibit unusual behaviors (e.g., maxima in terms of the applied pressure), depending on chain length and flexibility.<sup>19</sup>

## ACKNOWLEDGMENT

I thank Prof. D. Ronis (McGill University) for discussions. This work was supported by grants from the NSERC (Canada) and the Canada Research Chairs Program.

## REFERENCES AND NOTES

- (1) (a) Arteca, G. A.; Mezey, P. G. *Biopolymers* **1992**, 32, 1609. (b) Arteca, G. A. *Biopolymers* **1993**, 33, 1829. (c) Orlandini, E.; Tesi, M. C.; Whittington, S. G. *J. Phys. A* **2000**, 33, L181.
- (2) (a) Stasiak, A.; Katritch, V.; Bednar, J.; Michoud, D.; Dubochet J. *Nature* **1996**, 384, 122. (b) Katritch, V.; Bednar, J.; Michoud, D.; Scharein, R. G.; Dubochet, J.; Stasiak, A. *Nature* **1996**, 384, 142. (c) Vologodskii, A. V.; Crisona, N. J.; Laurie, B.; Pieranski, P.; Katritch, V.; Dubochet, J.; Stasiak, A. *J. Mol. Biol.* **1998**, 278, 1.
- (3) (a) Diaio, Y.; Ernst, C. *Topol. Its Appl.* **1998**, 90, 1. (b) Buck, G.; Simon, J. *Topol. Its Appl.* **1999**, 91, 245. (c) Dai, X.; Diaio, Y. *J. Knot Theory Its Ramif.* **2000**, 9, 713.
- (4) Everaers, R.; Kremer, K. *Macromol. Symp.* **1995**, 93, 53.
- (5) Orlandini, E.; Tesi, M. C.; Whittington, S. G.; Sumners, D. W.; Janse van Rensburg, E. J. *J. Phys. A* **1994**, 27, L333.
- (6) (a) Arteca, G. A. *Phys. Rev. E* **1994**, 49, 2417. (b) Arteca, G. A. *Phys. Rev. E* **1995**, 51, 2600.
- (7) Huang, J.-Y.; Lai, P.-Y. *Phys. Rev. E* **2001**, 63, 021506.

- (8) Arteca, G. A.; Cachau, R. E.; Veluri, K. *Chem. Phys. Lett.* **2000**, 319, 719.
- (9) (a) Cantarella, J.; Kuser, R. B.; Sullivan, J. M. *Nature* **1998**, 392, 237. (b) Buck, G. *Nature* **1998**, 392, 238.
- (10) (a) Kholodenko, A. L.; Rolfsen, D. P. *J. Phys. A* **1996**, 29, 5677. (b) Kholodenko, A. L.; Vilgis, T. A. *Phys. Rep.* **1998**, 298, 251.
- (11) Arteca, G. A. *J. Chem. Inf. Comput. Sci.* **1999**, 39, 550.
- (12) Arnol'd, V. I. *Sel. Math. Sov.* **1986**, 5, 327.
- (13) Freedman, M. E.; He, Z.-X. *Ann. Math.* **1991**, 134, 189.
- (14) Ozol'-Kalnin, V. G. *Pis'ma Zh. Eksp. Teor. Fiz.* **1994**, 59, 535; *JETP Lett.* **1994**, 59, 565.
- (15) Arteca, G. A.; Caughill, D. I. *Can. J. Chem.* **1998**, 76, 1402.
- (16) Arteca, G. A. *Can. J. Chem.* **1995**, 73, 241.
- (17) Strobl, G. *The Physics of Polymers*; Springer: Berlin, 1996.
- (18) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1985.
- (19) (a) Arteca, G. A. *Macromol. Theory Simul.* **1999**, 8, 137. (b) Edvinsson, T.; Elvingson, C.; Arteca, G. A. *Macromol. Theory Simul.* **2000**, 9, 398. (c) Arteca, G. A.; Edvinsson, T.; Elvingson, C. *Phys. Chem. Chem. Phys.* **2001**, 3, 3737.

CI010338S