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Notes

Shape of Self-Avoiding Walks in Two Dimensions

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The common understanding of equilibrium properties of polymers is largely based on ensemble averages. Even in experiments on a single molecule level, usually mean values are investigated.[1,2] Averaging over an ensemble of self-avoiding polymers gives an appearance of spherical symmetry. Theoretically, however, the path of a single self-avoiding walk turned out to be highly asymmetric.[3,4] Aronovitz and Nelson defined a rotationally invariant quantity Δ_2 that characterizes the average asphericity of the molecules and showed that it is a universal constant for long chain polymers.[3] However, experimentally such asphericity of polymers was hardly investigated so far, since experiments on the single molecule level are required. A first attempt was made very recently by Haber et al., who investigated the shape of fluorescently labeled DNA molecules in solution.[5]

In this note we investigate DNA adsorbed to fluid cationic supported membranes, which presents a model system for polymers in two dimensions, as we showed earlier.[6,7] DNA preparations can be made which exhibit equilibrium properties where DNA is strongly swollen. In particular, the scaling laws for self-avoiding polymers in two dimensions, i.e., the scaling of the radius of gyration, the self-diffusion coefficient, and rotational relaxation time, were found in striking agreement with theory. Because of reduced dimensionality, the self-avoidance of the chain is determined by steric repulsion between the chain segments, and electrostatic interactions are negligible. In the following we analyze individual shapes of fluorescently labeled DNA molecules on cationic supported membranes and show that another universal aspect, the average asphericity, can be determined with this model system and is found to be in good agreement with the value predicted by renormalization group theory[3] and Monte Carlo simulations.[8]

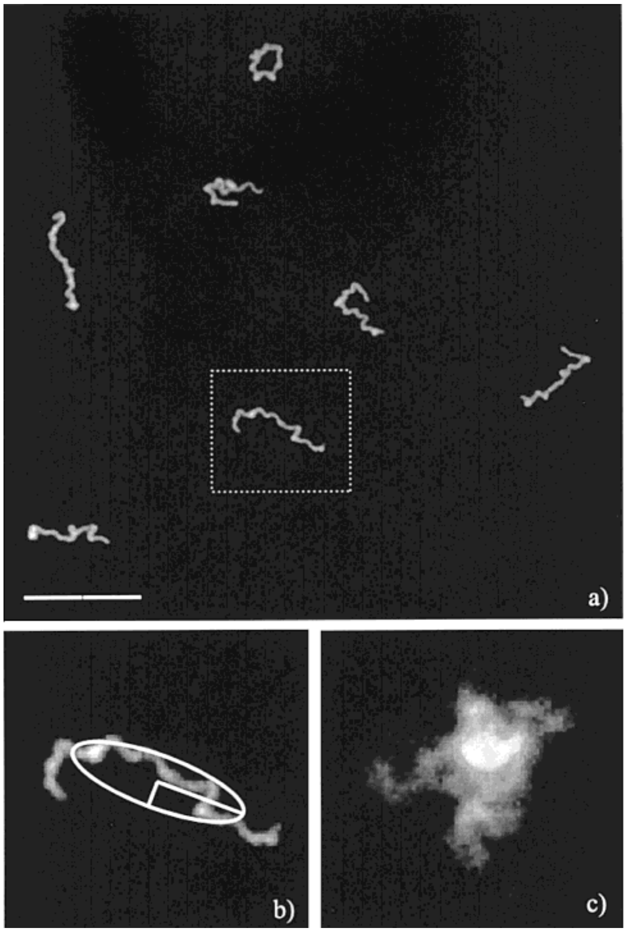

Figure 1. (a) Typical fluorescence micrographs of λ-DNAs bound to a fluid glass-supported lipid membrane. (b) Enlargement of the framed molecule in (a). The tensor of the radius of gyration is represented by its corresponding ellipse. (c) Superposition of 14 snapshots from a freely diffusing molecule at time intervals of 30 s yields a symmetric mass distribution (bar represents 10 μm).

In our experiment a few λ-phage DNA molecules are electrostatically adsorbed to a fluid membrane containing 10% cationic lipid. The supported membranes were prepared as previously reported on glass cover slides.[9] Fluorescence images of a typical population as shown in Figure 1 are taken using an inverted microscope and a cooled CCD camera (Micromax, Princeton Instruments, USA). Typically frames of 2 s exposure were taken and analyzed by image processing (IP-Lab, Scanalytics). The quantity that shall interest us in the following is the normalized second moment of the fluorescence intensity distribution

$$M_{ij} = \frac{1}{I_0}\sum_{i,j}(r_i - R_{\mathrm{cm}i})(r_j - R_{\mathrm{cm}j})I_{ij} \tag{1}$$

where $I_{i,j}$ is the fluorescence intensity of the pixel $[i,j]$, R_{cm} is the coordinate of the center of mass, and I_0 is the total fluorescence intensity. In Figure 1b an enlargement of one single molecule from Figure 1a is shown with an ellipse representing the shape tensor overlaid.

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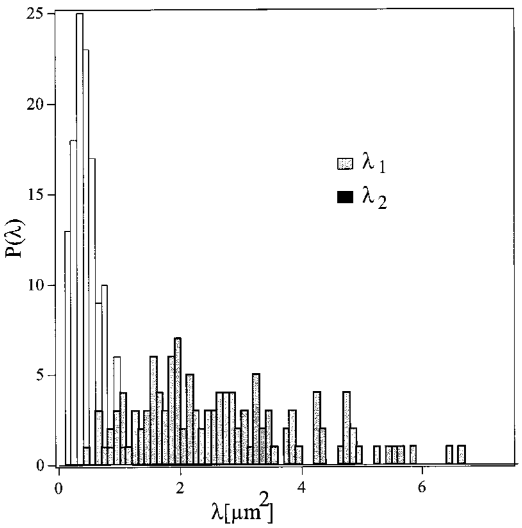

Figure 2. Probability distribution of the eigenvalues λ of the tensor of the radius of gyration derived from 124 molecules. The average eigenvalues are $\langle\lambda_1\rangle = 2.7\ \mu m^2$ and $\langle\lambda_2\rangle = 0.5\ \mu m^2$.

The tensor M_{ij} is a measure of the size and the shape of the polymer: First, the trace of M defines the radius of gyration, $R_G{}^2 = \mathrm{tr}(M)$, and hence polymer's size. Note that what generally is known as the radius of gyration is the ensemble average (or the time average) of tr(M). For demonstration we show in Figure 1c the superposition of 14 frames with a time delay $\delta t = 30$ s, i.e., a time average over random configurations of one freely diffusing DNA. We see a symmetric shape with the mean-square radius of gyration $\langle(R_G)^2\rangle = 3.2 \pm 0.3\ \mu m^2$. On the other hand, each individual snapshot provides a tensor M with generally two unequal principal axes, $l_{1,2} = \sqrt{\lambda_{1,2}}$, which are given by the eigenvalues

$$\lambda_{1,2} = \frac{1}{2}\mathrm{tr}(M_{ij}) \pm \frac{1}{2}[\mathrm{tr}(M_{ij})^2 - 4\ \det(M_{ij})] \qquad (2)$$

The index 1 and 2 denote the major and the minor principal axis, respectively. Figure 2 shows the measured distribution of λ_1 and λ_2, which reflects the anisotropy of the individual polymer shapes. The average values of the major and minor eigenvalue are $\langle\lambda_1\rangle = 2.70 \pm 1.5\ \mu m^2$ and $\langle\lambda_2\rangle = 0.46 \pm 0.22\ \mu m^2$. The large standard deviations arise from the considerable width of the distribution. The normalized eigenvalues $\langle\lambda_1\rangle/\langle R_G{}^2\rangle = 0.84$ and $\langle\lambda_2\rangle/\langle R_G{}^2\rangle = 0.14$ can be compared to the Monte Carlo simulations of self-avoiding walks by Bishop et al.[8] The simulated values $\langle\lambda_1\rangle/\langle R_G{}^2\rangle_{MC} = 0.87$ and $\langle\lambda_2\rangle/\langle R_G{}^2\rangle_{MC} = 0.13$ are in good agreement with our experiment. Note that the experimental aspect ratio, i.e., the molecule's anisotropy $\langle\lambda_1\rangle/\langle\lambda_2\rangle = 6$ as well as the simulated one $\langle\lambda_1\rangle/\langle\lambda_2\rangle_{MC} = 6.7$ for self-avoiding walks, is larger than the simulated aspect ratio for Gaussian random walks $\langle\lambda_1\rangle/\langle\lambda_2\rangle = 5.2$.[8] Thus, the excluded volume makes the chain appear more aspherical.

In analytical treatment rotationally invariant quantities are of interest, which likewise characterize the polymer shape:[3]

$$\Delta_2 = \frac{\langle(\lambda_1 - \lambda_2)^2\rangle}{\langle(\lambda_1 + \lambda_2)^2\rangle} \qquad (3)$$

Δ_2 is a measure of the asymmetry, which turns out to be a universal constant $\Delta_2 = 0.59$ in a first-order ϵ-expansion, whereby the index 2 indicates that this is the value obtained in two dimensions.[3] Experiment shows $\Delta_2 = 0.61$ in remarkable agreement with the theoretical value. Using Monte Carlo simulations, Bishop et al. obtained $\Delta_2 = 0.62$.[8]

A more difficult task is to calculate the distribution of eigenvalues. For a random walk Rundick and Gaspari show that a χ^2-distribution depicts a good approximation for the distribution of eigenvalues.[10] To our knowledge for self-avoiding chains no analytic prediction exists. However, the data shown in Figure 2 are in qualitative agreement with Monte Carlo simulation for self-avoiding walks in two dimensions.[11] Interestingly, the aspect ratio of the eigenvalues with maximal likelihood $\lambda_1^{\max}/\lambda_2^{\max} = 6.1$ is close to the universal ratio of the above average ratios.

Our experiments using DNA as a model for a self-avoiding polymer show that in two dimensions a highly anisotropic shape is adopted. The average anisotropy agrees remarkably well with predictions about the shape anisotropy of polymers with excluded-volume interaction. Although the average asphericity is only slightly influenced by the self-avoidance of the chain, the probability distributions clearly disagree with a random walk model and hence indicate an excluded-volume effect. In this paper we have not discussed the dynamical aspects of polymer shape changes. These were partly described in our previous work, where we showed that the rotational relaxation of the gyration tensor follows the predicted dynamic scaling.[7]

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