Entropic elasticity of end adsorbed polymer chains: The spectrin network of red blood cells as C*-gel

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We use Monte Carlo methods to investigate the end-to-end distance distribution and entropic elasticity of self-avoiding walks in a three-dimensional half-space with both ends adsorbed on the limiting surface. The obtained distributions are well described by the Redner–des Cloizeaux (RdC) ansatz \(q(x) = Cx^\theta \exp(-Kx)\), \(x\) being the rescaled length. Using the recent solution of the junction affine model for networks of RdC springs we apply the results to the cytoskeleton of the red blood cell (RBC), a two-dimensional network of spectrin molecules which is attached to the inner surface of the erythrocyte membrane. The shear moduli predicted for a noninteracting surface are in close agreement with simulation results by Boal for a bead–spring model of the spectrin network. Moreover, we calculate stress–strain relations for finite deformations. In particular for a network which is fully adsorbed on the bilayer we find a strongly nonlinear elastic response. Our results suggest that the elastic properties of RBCs cannot be obtained within the usual Gaussian models and depend sensitively on the degree of adsorption of the spectrin network. © 1996 American Institute of Physics. [S0021-9606(96)51107-3]

INTRODUCTION

The structural rigidity and the elasticity of biological systems often have their origins in macromolecular networks. One important example is the membrane skeleton of the erythrocyte or red blood cell (RBC).\textsuperscript{1,2} This skeleton is a 2\(d\) network of spectrin tetramers tethered at their centers to the inner surface of the lipid bilayer of the RBC membrane by means of membrane proteins. The spectrin network is for the most part sixfold coordinated with a triangular connectivity. The molecular structure of the individual spectrin molecules is well known\textsuperscript{3} and the molecules themselves are water-soluble due to a large number of charged side groups. The corresponding tetramer units are flexible with a persistence length of the order of 20 \(\text{nm}\) and a contour length of approximately 200 \(\text{nm}\). The 2\(d\) lipid bilayer/spectrin network complex is responsible for the mechanical properties of the RBC. In particular, the lipid bilayer gives the RBC its resistance to area compression, whereas the spectrin network contributes to properties related to shear.

Networks of flexible macromolecules are conventionally modeled by a two-step process.\textsuperscript{4} The elastic properties of individual network strands are derived in the first step and the second step involves the construction and investigation of a network of noninteracting entropic springs. Phenomenological continuum models\textsuperscript{5,6} as well as computer simulations by Boal et al.\textsuperscript{7,8} of the RBC membrane follow the classical theories of rubber elasticity by describing the network strands in terms of random walks (RW). RWs have a Gaussian end-to-end distance distribution and, as a consequence, they behave as harmonic entropic springs.

Computer simulations of networks where the spectrin molecules are explicitly included as bead–spring chains can be used to test this approach. Petsch and Grest\textsuperscript{9} were interested in the properties of isolated skeletons and studied a bead–spring model of closed, self-avoiding tethered vesicles. Boal\textsuperscript{10} modeled the bilayer as an impenetrable surface on which the movements of the center beads of the strands were confined. He found that the behavior of these systems could not be explained by network models based on tethers or harmonic springs only.

The random walk model of flexible polymers from which the harmonic springs are derived is only appropriate for the description of chain conformations in a polymer melt or a theta solvent.\textsuperscript{11} In a good solvent individual flexible polymers are swollen due to the excluded volume effect and correspond to self-avoiding walks (SAW) on a lattice.\textsuperscript{11} The key to understanding the behavior of polymer networks in a dilute solution, equivalent to the vanishing of the external pressure in Boal’s simulations, is de Gennes’ c\(^*\) theorem.\textsuperscript{11} This theorem states that the networks retain an internal concentration of the order of the overlap concentration of the network strands. In the blob picture each strand of the net-

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work forms a blob of the size of an isolated chain. The blobs are closely packed, but the strands display single chain behavior inside one blob. As a consequence, the elastic properties of the network strands ought to be derived from a SAW rather than a RW model,\textsuperscript{12,13} while the interactions between neighboring chains can be reduced to an isotropic pressure which determines the equilibrium extension of the strands.

Although the SAW problem cannot be solved analytically, scaling arguments suggest that SAW chains behave as nonlinear entropic springs.\textsuperscript{15} In a previous paper\textsuperscript{14} we investigated the end-to-end distance distributions of SAWs in two and three dimensions by means of computer simulations. The principal result was that an ansatz proposed by Redner\textsuperscript{15} and des Cloizeaux\textsuperscript{16} (RdC) provides an excellent approximation to the data. Furthermore, one of the authors has shown that the elastic properties of a network of RdC springs can be estimated from the analytical solution of the classical junction affine model.\textsuperscript{17}

In the case of the spectrin network the situation is further complicated by the lipid bilayer whose presence has to be taken into account in the derivation of the chain elastic properties. Even though the spectrin tetramers are tethered to the bilayer at their center points in such a way as to allow the junction points of the network to rise from the surface, we consider as a first approximation chains where the endpoints are adsorbed. This allows us to treat the network of entropic springs in the second step as strictly two dimensional, as the interaction between two junction points would otherwise depend additionally on their distances \(z_1\) and \(z_2\) from the surface. We feel that this model faithfully represents the short range repulsive interaction which is characteristic of the excluded volume effect.

In the present paper, we report the results of Monte Carlo simulations of a SAW lattice model for polymers in a good solvent. In these simulations, we examined chains in a three dimensional half-space with both endpoints adsorbed onto the limiting surface. This is a standard model for adsorption onto an impenetrable, flat, two-dimensional surface.\textsuperscript{18–20} In general an attractive surface potential is in-sorption onto an impenetrable, flat, two-dimensional three dimensional half-space with both endpoints adsorbed good solvent. In these simulations, we examined chains in a range repulsive interaction which is characteristic of the ex-face. We feel that this model faithfully represents the short range repulsive interaction which is characteristic of the ex-face.

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The paper is organized as follows. In the theory section we first review established results for the scaling theory of polymers with particular emphasis on those aspects which are relevant to the end-to-end distance distribution. Subsequently, we discuss the solution of the junction affine model for RdC springs. In the following sections we present our simulation methods and results. We determine the complete end-to-end distance distribution and its reduced moments for end adsorbed chains. Both are of intrinsic interest, but the latter is the starting point for the the discussion of the chain and network elastic properties and the biological implications of our results. This is contained in the fifth section. The final section gives a brief conclusion.

**THEORY**

In this section we give a brief review of the theoretical background for the paper. We frequently refer to our previous article\textsuperscript{14} for details.

We focus on the end-to-end distance distribution \(p_N(r)\) of a \(N\)-step walk, where \(r\) is the vector linking the two ends of the chain. \(p_N(r)\) is expected to have the form\textsuperscript{11}

\[
p_N(r) = \frac{1}{R_N} q(x)
\]

with \(x=r/R_N\), and \(R_N^2 = \langle r^2 \rangle - N^2 \nu\) is the mean-square end-to-end distance. Equation (1) implies that \(R_N\) is the only relevant length scale, which only holds for \(N\gg1\). The total number of conformations of the chain is given by \(c_N \sim N^{N/2}\), where \(\gamma\) is a second critical exponent, independent of \(\nu\). For free chains\textsuperscript{16} one expects power-law behavior of the form \(q(x) \sim x^{\theta} \exp(-Kx^t)\) when the endpoints are close together (i.e., \(x \to 0\)). When the endpoints are far apart (\(x\gg1\)), the distribution is expected to decay as \(q(x) \sim x^{\theta} \exp(-Kx^t)\). The exponents \(t, g, \theta\) and \(\gamma\) can be expressed in terms of the more fundamental exponents \(\gamma\) and \(\nu\). It is important to note that they depend on the spatial dimension and may change if the polymer is constrained, for example, by a surface. Theoretical estimates of these exponents for the different cases considered here are summarized in Table I.

In 3\(d\) the exponents \(\gamma\) and \(\theta\) agree to within the error bars of current estimates, while in 2\(d\), where the values are known exactly, the difference of 1/6 is still quite small compared to \(\theta=11/24\). This led Redner\textsuperscript{15} and des Cloizeaux\textsuperscript{16} to conjecture that the expression

\[
q(x) = C x^{\theta} \exp(-Kx^t)
\]

should be a good approximation for the entire scaled end-to-end distance distribution using the theoretical values for \(t\) and \(\theta\) appropriate to the dimension. In the ansatz of Eq. (2) \(K\) and \(C\) are not additional parameters but are fixed by the requirements (a) that the end-to-end distance distribution is normalized and (b) that the the second moment of the end-to-end distribution was chosen as the scaling length [see Eqs.
TABLE I. Theoretical and numerical estimates of the exponents $\nu$, $\gamma$, $t$, and $\theta$ in the large-$N$ limit. The literature values for $t$ and $\theta$ were calculated from the current best estimates for $\nu$ and $\gamma$. The results in 2$d$ are considered exact.

<table>
<thead>
<tr>
<th>Dimension</th>
<th>$\nu$</th>
<th>$\gamma$</th>
<th>$t$</th>
<th>$\theta$</th>
<th>$g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2$d$</td>
<td>0.75$^a$</td>
<td>43/3$^a$</td>
<td>4</td>
<td>11/24</td>
<td>5/8</td>
</tr>
<tr>
<td>3$d$</td>
<td>0.592(1)$^b$</td>
<td>1.162(2)$^c$</td>
<td>2.451(6)</td>
<td>0.274(4)</td>
<td>0.279(7)</td>
</tr>
<tr>
<td>3$d/2$</td>
<td>0.592(1)</td>
<td>−0.37(2)$^d$</td>
<td>2.451(6)</td>
<td>0.38(4)</td>
<td></td>
</tr>
</tbody>
</table>


$^d$References 21 and 22.

(8) and (9) in our previous paper$^{14}$ for the resulting expressions. Thus the RdC distribution is completely specified given values for $t$, $\theta$, and the spatial dimension $d$.

While for end adsorbed chains the exponent, $\nu$, is known to have the same value as in 3$d$, there is little information available on the end-to-end distance distribution in 2$d$. Power law behavior has, however, been established in the small distance limit$^{19}$ with an exponent $\theta_{d=2}=1+\gamma/1/4$. Here, $\gamma$ is the critical exponent for the number of conformations with this particular geometry.$^{18}$ In the large distance limit it is tempting to speculate that the distribution again follows the Fisher–Pincus law $q(x)\approx \exp(-[Kx]^1)$ with $K$ given by its value in 3$d$. However, this has to be checked by numerical simulation and it is one of the points addressed here. Previous simulations$^{19,21,22}$ concentrated on chains adsorbed onto the surface at one end only.

We are particularly interested in a study of the elastic properties of the system and this requires an expression for the entropic force, $f$, between the chain ends. The average force can be derived from the definition of the entropy $S(x)$ as a function of the end-to-end vector, $x$

$$s(x) = \log(q(x)) + \log(c_N)$$

(3) together with the relationship $f(x) = -(T/R_N)(d/dx)s(x)^4$.

Our study of the distribution $p_N(r)$ thus allows us to investigate the elastic properties of the polymer chain with little additional effort. For RdC springs Eq. (2) yields

$$f(x) = -\frac{T}{R_N}(\Theta x^{-1} - tK'r^{-1})$$

(4)

For SAW models $t$ and $\theta$ can be taken from Table IV and $K$ calculated from Eq. (8) in Ref. 14. The resulting spring equation is nonlinear and repulsive at short distances. In particular, the force is zero for a given finite distance between the endpoints, while it vanishes for RWS ($t=2$ and $\theta=0$) when both ends coincide. The differences are particularly marked in two dimensions.

We now estimate the elastic response of a network of entropic springs to a simple elongation of the form

$$\lambda = \begin{pmatrix} \lambda & 0 \\ 0 & \lambda^{-1} \end{pmatrix}$$

(5)

by considering the entropy change in an ensemble of network strands using the junction affine model.$^4$ Here, the system is taken to be incompressible due to the presence of the lipid bilayer. The model starts from a reference state with density $c^*$ where the strands are randomly oriented in space and have the same statistics as uncrosslinked chains. The stress-free original state of the network has a density $\lambda_0^d c^*$ of order $c^*$ where we assume a simple rescaling of the strand end-to-end vectors from $x$ to $\tilde{x}_0 x = \lambda_0 x$. $\lambda_0$ is a parameter of order one which has to be estimated independently. To obtain the response to the deformation of Eq. (5) we assume that each strand adapts to it by changing its end-to-end vector from its original value $\lambda_0 x$ to $\lambda_0 x$. The free energy of the strain then changes from $-T \log q(\lambda_0 x)$ to $-T \log q(\lambda_0 x)$. This expression has to be averaged over $q(x)$, the end-to-end distance distribution of the strands in the reference state. One advantage of the RdC distribution of Eq. (2) is that this scheme can be carried out analytically without further approximations. The shear modulus $\mu$ and the restoring force of a 2$d$ network of RdC springs for an elongation Eq. (5) is given by

$$\mu^{(2d)} = \frac{1}{4} \rho_{\text{strand}} T \left( \frac{2 + t + (2 + \theta)}{2} \right) \left( \lambda_0^d - \theta \right)$$

(6)

$$F^{(2d)}(\lambda) = \rho_{\text{strand}} L_0 T \left( \frac{1 - \lambda^2}{\lambda + \lambda^2} \right) \left( \lambda_0^d - \theta \right)$$

$$\times \left( \frac{2 + \theta}{\lambda^2 + 1} \right) \left( \frac{\lambda^{-4} + 1}{2} \right) 2 F_1 \left( \frac{3}{2}; \frac{3}{2}, 1 + \frac{t}{2}, 1 - \lambda^4 \right)$$

$$- \frac{2}{\frac{3}{2}, \frac{3}{2}, 1, 1 - \lambda^4},$$

(7)

where $\rho_{\text{strand}}$ is the number density of elastically active network strands, $L_0$ the side length of the quadratic sample, and $2 F_1 (\alpha, \beta, \gamma, z)$ the hypergeometric function. The principal weakness of this ansatz lies in the affine change of the junction positions, since this assumption neglects fluctuations in the crosslink positions as well as the nonlinear character of the entropic springs.$^{17}$ This should not, however, lead to serious discrepancies for a system with the regular connectivity of the spectrin network, where the mean crosslink positions change in an affine manner for symmetry reasons.

METHODS

As in our previous paper$^{14}$ we used the dimerization method$^{25}$ to obtain equilibrated initial configurations and the pivot algorithm$^{24,25}$ for data production. The idea behind dimerization is to combine two SAWs of half the desired length. If this fails to yield a SAW both halves are discarded and another attempt is made. This algorithm is applied recursively down to a small initial length. When used to generate end adsorbed walks, two additional restrictions are imposed: The walk is prohibited from entering the half-space and the second endpoint has to be on the limiting surface. These constraints decrease the efficiency of the algorithm considerably. In the pivot algorithm$^{24,25}$ a single MC step consists of...
randomly choosing a point along the chain and applying a symmetry operation of the lattice (reflection or rotation) to the rest of the chain. The result is accepted, if no self-intersections occur. As pointed out by Madras and Sokal this leads to relatively short correlation times for global properties of the chain such as the end-to-end distance. Note that this is not the case for local quantities.

When the chains are end adsorbed, the endpoints are restricted to move on the 2d surface, while the rest of the chain is free to explore the 3d half-space. In order to simulate this situation we combined the pivot algorithm for 2d movement of the endpoints with the 3d version of a recent algorithm by Madras, Orlitsky, and Shepp for the study of walks with fixed endpoints. Madras et al. considered transformations that are applied to randomly chosen sections of the chain, leaving the positions of the endpoints unchanged. There are three classes of transformation: (1) inversion of the sequence of steps, (2) reflection, and (3) interchange of two sets of step coordinates. In general, the last two operations would break the chain, and they are therefore applicable only if the endpoints of the chosen segment fulfill certain conditions (for details see Ref. 26). Madras et al. were able to prove the ergodicity of the algorithm. While this property is certainly preserved in combination with the pivot algorithm, which is ergodic itself, we have no formal proof that it is not destroyed by restricting our walks to a halfspace. As an elementary check we verified that our algorithm does indeed generate all conformations of short walks ($N=5$ to 8).

Using this algorithm, we measured the end-to-end distance and the number of surface contacts. To ensure uncorrelated data we first performed short runs to determine the relaxation times for the measured quantities. For end adsorbed walks the relaxation times for the geometrical quantities were of the order of 100 MC steps, largely independent of the chain length $N$. However, in the calculation of the number of surface contacts, we found relaxation times roughly proportional to the chain length ($10N$ MC steps). In the production runs we took data every $10N$ MC steps, ensuring uncorrelated results for quantities such as the end-to-end distance and weakly correlated data for the number of surface contacts. We studied chains of length $N=10$, 20, 40, 60, 80, 100, 120, 160, 200, and 240 and in all cases we made $5\times 10^3$ measurements. To obtain better statistics in the histograms of the end-to-end distance distribution, the data was binned at an additional five intermediate time steps. For comparison we also generated data with the dimerization algorithm for $N=20$ and 40. In this case we generated $10^5$ data points, which are uncorrelated due to the nature of the algorithm.

Testing the RdC ansatz is nontrivial as precise measurements of distributions themselves and not just mean values are required. While the moderate chain lengths investigated in this study are sufficient in view of the application of our results to spectrin, they clearly lie far from the asymptotic regime where the theoretical predictions for the exponent should hold. The following questions then arise: (i) Is the RdC expression Eq. (2) capable of describing data for finite-sized systems using chain length dependent exponents $\theta_N$ and $r_N$: (ii) How do these effective exponents depend on $N$?: (iii) Do $\theta_N$ and $r_N$ extrapolate to the theoretically predicted values in the limit $N\to\infty$?

In our previous paper we examined this scaling problem for free chains in $2d$ and $3d$. Two different methods were used to obtain $\theta_N$ and $r_N$. These were (a) a fit of the binned distributions to the RdC expression Eq. (2) with $\theta_N$ and $r_N$ as adjustable parameters and (b) a more indirect approach based on the reduced moments $\delta_{pq}$ of the chain end-to-end distributions, defined as

$$\delta_{pq} = \langle r^p \rangle / \langle r^q \rangle^{pq}.$$  

(8)

The advantage of the second method is that the moments can be measured with high precision as well as reliably extrapolated to chain lengths beyond those investigated in the simulations.

We found that the reduced moments for free chains scale with $N$ via

$$\delta_{pq}(N) = a_{pq} + b_{pq} / N^{\Delta_{pq}},$$  

(9)

where $a_{pq}$, $b_{pq}$, and the exponent $\Delta_{pq}$ all depend on the order of the moment. On the other hand, the reduced moments of the RdC distribution of Eq. (2) are given by

$$\delta_{pq} = \Gamma([\theta + d + p] / t) \Gamma([\theta + d] / t)^{p/q - 1} \times \Gamma([\theta + d + q] / t)^{-p/q}.$$  

(10)

Inverting this expression for two independent reduced moments (for example, $\delta_{p1}$ and $\delta_{p2}$) allows us to calculate the appropriate exponents $\theta$ and $r$. Thus using Eq. (9) we can estimate $\theta_N$ and $r_N$ for arbitrary $N$ and with some reliability in the limit $N\to\infty$. For a more detailed discussion of this method the reader is referred to Ref. 14.

**SIMULATION RESULTS**

We first present results of our study of the moments of the end-to-end distribution, which were calculated directly from the simulation data. We next examine the full distributions, $g(x)$, and we then test how well the RdC ansatz describes these results. In both cases we obtain the variation of the data with increasing chain-length and we extrapolate the results for $N\to\infty$.

Our results for the mean square end-to-end distance $\langle r^2 \rangle$ and the reduced moments $\delta_{pq}(N)$ are summarized in Table II. A comparison shows that the $\langle r^2 \rangle$ values for free 3d chains given in Ref. 14 are about 40% larger (for RWs $\langle r^2 \rangle_{3d}\approx 2 \langle r^2 \rangle_{3d} = 2 \langle r^2 \rangle_{2d}$). As for our previous results on free chains, the pivot and dimerization data for end adsorbed chains agree to within the statistical error. This consistency is a useful validation of our simulation methods.

Djordjevic et al. predicted the chain length dependence of $\langle r^2 \rangle$ for free chains in terms of two exponents, $\nu$ and $D$. Now theory suggests that $\nu$ should be the same for both $3d$ and $3d/2$: our best estimate for $\nu_{3d}$ is $0.592\pm 0.001$, which is consistent with our other results. We next estimated the lead-
ing correction-to-scaling exponent by setting $\nu$ to the best literature values quoted above, and fitting for $\Delta$. We obtained the following fits for the end adsorbed case:

$$\sqrt{\langle r^2 \rangle} = N^{0.592(1)}(0.82(1) - 0.99(5)N^{-0.86(4)}).$$  \hspace{1cm} (11)

As in the case of the free chains, this provided an excellent description of the data. For purposes of comparison we repeat our results for free $2d$ and $3d$ chains

$$\sqrt{\langle r^2 \rangle} = N^{0.75(0)(0.7701(9) + 0.37(2)N^{-0.79(3)}),}$$

$$\sqrt{\langle r^2 \rangle} = N^{0.592(1)1.15(2) - 0.175(7)N^{-0.54(10)}).}$$

We note that the correction term is particularly large when a surface is present, and that the correction exponent $\Delta$ is clearly affected by the presence of the surface.

We also extrapolated our results for the reduced moments to the limit of infinite chain length using the ansatz Eq. (9). As in our previous study of $2d$ and $3d$ chains our data are well described by this form, if we use different exponents for the individual moments. The best-fit parameters $a_{pq}$ and $\Delta_{pq}$ from Eq. (9) are tabulated in Table II. These extrapolations are more precise than for $\langle r^2 \rangle$, as the reduced moments do not depend on the leading exponent $\nu$. As was the case for free chains there is a regularity in the exponents. They appear to be largely independent of $q$ and their values were found to decrease with $p$ in approximately equidistant steps.

The full distribution functions were obtained by binning the end-to-end distance data into a histogram. Figure 1 shows superpositions of the resulting scaled end-to-end distance distributions (averaged over angles) for end adsorbed chains of length $N=80$, 160, and 240, demonstrating that $R_N$ is the only relevant length scale. We see small but systematic variations with chain length close to the maxima of the distributions. This is expected from finite-size considerations.

The solid lines in these figures show the RdC scaling function Eq. (2), using the theoretical values for the exponents $t$ and $\theta$ (Table I). The figure indicates that this function gives a good description of the behavior of our simulation results although there are clearly systematic differences.

We first test whether the RdC ansatz can give a better description of our data by using the exponents $t_{pq}$ and $\theta_{pq}$ as parameters and fitting to the different size-dependent distributions. The dotted line in Fig. 1 shows the fitted RdC distribution for $N=120$: The agreement with the data seems excellent. This is a reassuring test of the overall appropriateness of the ansatz, although—being an approximation—the RdC form is rejected by the statistical $\chi^2$ criterion.

As a second test Table II shows reduced moments for end ad-

![FIG. 1. Scaled end-to-end distance distribution for 3d/2-end adsorbed walks. We show data for chainlength $N=80$ (\(\circ\)), $N=120$ (\(\cdot\)), $N=240$ (\(\square\)) as well as RdC distributions for the theoretically expected exponents from Table I (---) and the effective exponents for $N=120$ from Table III (--).](image)
TABLE III. Effective exponents $\theta_N$ and $t_N$ obtained by fitting the complete end-to-end distance distribution to Redner–des Cloizeaux functions [Eq. (2)]. The final row gives the result of a simple $1/N$ extrapolation to $N \to \infty$.  

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\theta_N$</th>
<th>$t_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.278(4)</td>
<td>2.784(5)</td>
</tr>
<tr>
<td>60</td>
<td>0.397(4)</td>
<td>2.512(5)</td>
</tr>
<tr>
<td>80</td>
<td>0.381(4)</td>
<td>2.454(4)</td>
</tr>
<tr>
<td>100</td>
<td>0.349(3)</td>
<td>2.452(4)</td>
</tr>
<tr>
<td>120</td>
<td>0.333(3)</td>
<td>2.447(4)</td>
</tr>
<tr>
<td>160</td>
<td>0.310(3)</td>
<td>2.465(4)</td>
</tr>
<tr>
<td>200</td>
<td>0.316(3)</td>
<td>2.448(4)</td>
</tr>
<tr>
<td>240</td>
<td>0.315(3)</td>
<td>2.442(4)</td>
</tr>
<tr>
<td>Extrap.</td>
<td>0.274(8)</td>
<td>2.445(7)</td>
</tr>
</tbody>
</table>

TABLE IV. Best estimates of the exponent $\nu$ (from $\langle r^2 \rangle/N$) and the optimal asymptotic parameters $t$ and $\theta$ for a RdC model (from Fig. 2) for end adsorbed SAWs in a 3$d$ half-space. The result for 2$d$ and 3$d$ SAWs are from Ref. 14.

<table>
<thead>
<tr>
<th>Dimension</th>
<th>$\nu$</th>
<th>$t$</th>
<th>$\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2$d$</td>
<td>0.750(2)</td>
<td>4.05(5)</td>
<td>0.49(1)</td>
</tr>
<tr>
<td>3$d$</td>
<td>0.592(3)</td>
<td>2.39(3)</td>
<td>0.29(4)</td>
</tr>
<tr>
<td>3$d$/2</td>
<td>0.594(2)</td>
<td>2.33(4)</td>
<td>0.33(3)</td>
</tr>
</tbody>
</table>

Absorbed polymers, as calculated from Eq. (10) using the fitted RdC exponents for chains of length 60, 120, and 240. The agreement with the measured moments is excellent. The fitted exponents for end adsorbed polymers of all chain lengths (Table III) are included in Fig. 2. Although they appear to lie on a line, it is not clear as to how they can best be extrapolated towards $N \to \infty$. Better extrapolation is possible if we use the measured values for the reduced moments.

Figure 2 shows estimates of $t_N$ and $\theta_N$ obtained by simultaneously inverting Eq. (10) for two different combinations of reduced moments $\delta_{21}/\delta_{32}$ and $\delta_{21}/\delta_{52}$. The moments were calculated from fits using Eq. (9): The grey bands reflect the error bars on the resulting estimates of the moments. These regions have a typical width of $\pm 0.01$ for both $t$ and $\theta$. Also plotted are points representing the $t_N$ and $\theta_N$ obtained by directly fitting the RdC ansatz to the end-to-end distributions. Two estimation methods are in quite good agreement.

Thus at sufficiently large $N$, the RdC ansatz Eq. (2) provides an excellent description of the end-to-end distance distribution [and via Eq. (4) also of the elastic properties] of 2$d$, 3$d$, and 3$d$/2 SAWs. The optimal exponents $\theta_N$ and $t_N$ are chain length dependent and close to the theoretical predictions (Table I). Concerning the asymptotic behavior Fig. 2 indicates an effect similar to what we observed in Ref. 14 for 3$d$ SAWs (Table IV): The optimal $t = 2.33 \pm 0.04$ for an description of the asymptotic distribution of 3$d$/2 SAWs by the RdC ansatz Eq. (2) appears to be smaller than the theoretically expected value of 2.445. The values for $\theta$ agree within the margins of error.

ELASTIC PROPERTIES AND BIOLOGICAL IMPLICATIONS

We now use Eq. (4) to examine how the elastic properties of the chains depend on their degree of adsorption. Figure 3 shows the stress–strain relations in 2$d$($T \ll \epsilon$) and 3$d$/2($T \gg \epsilon$), along with the law obtained from the Gaussian random walk (RW) approach (dashed line).

For SAWs the relation is nonlinear and repulsive at short distances. In particular, the stress is zero for a finite separation of the endpoints, while for RWs it vanishes when both ends are at the same point. These differences between RWs and SAWs are most noticeable in 2$d$, i.e., for polymer chains
which are completely adsorbed on the surface. Note that the scaled stress–strain relations for 2d and 3d/2 RWs are identical.

In general, force-elongation relations for single chains can serve as input into network simulations such as those of Boal et al. Here, we use the solution of the junction affine model for RdC springs to estimate how the properties of the individual springs translate into the elastic response of a 2d network. To allow a comparison with Boal’s simulations, we have to determine the parameter \( \lambda_0 \) in Eqs. (6) and (7). His data suggest \( \langle r^2 \rangle_{\text{str}} = 1.65 \langle r^2 \rangle_{\text{str}} \). If we use Eq. (11) to determine the universal ratio \( \langle r^2 \rangle_{3d} \langle r^2 \rangle_{3d/2} = 1.97 \), we obtain \( \lambda_0 = \sqrt{\langle r^2 \rangle_{\text{str}} / \langle r^2 \rangle_{3d/2}} = 1.8 \). An evaluation of Eq. (6) for the estimated asymptotic values of \( t \) and \( \theta \) from Table IV yields the following estimate for the shear modulus of a surface tethered two dimensional network:

\[
\mu_{3d/2} = 4.6 \rho_{\text{str}} k_B T. \tag{12}
\]

In order to convert to Boal’s units, we need to express \( \rho_{\text{str}} \) in terms of the chain contour length \( l_c \). For his bead–spring model this yields \( \beta \mu_{\text{str}} l_c^2 = 1.77 \times 4.6 N^{0.8} \beta \mu_{\text{str}} l_c \). Figure 4 shows a graph of \( \beta \mu_{\text{str}} l_c^2 \) vs \( N \). The black dots indicate the shear moduli measured by Boal and our estimates are represented by the solid line. The agreement for the last three points (\( N = 10, 14, 20 \)) is excellent, though the measured moduli for the shorter chains with \( N = 4, 6, 8 \) are too high. On the basis of all six data points Boal proposed that \( \beta \mu_{\text{str}} l_c^2 = 36 N^{0.3} \) (the dashed line in Fig. 4). A possible explanation for this discrepancy is that the asymptotic behavior for the strand lengths considered in Boal’s simulations is obscured by strong finite-size effects. In order to understand the nature of such finite-size effects, we used Eq. (6) to calculate shear moduli from the effective exponents \( i_\nu \) and \( \beta_\nu \) listed in Table III (the gray dots in Fig. 4). As expected, the calculated moduli follow our prediction closely for large \( N \). The \( N = 40 \) and \( N = 60 \) data points, however, show a similar crossover as seen in Boal’s data. This makes us confident that the deviations for \( N = 4, 6, 8 \) are indeed finite-size effects.

In addition to the calculation of shear moduli, our theory allows us to discuss the elastic response to finite elongations [Eq. (7)]. The results for \( \lambda_0 = 1.8 \) are shown in Fig. 5. For consistency and in the absence of a more accurate estimate we have used the 3d/2 SAW value for both RW and 2d SAW networks. Figure 5 is qualitatively very similar to Fig. 3 except that the elastic response for a network vanishes for the undeformed sample (\( \lambda = 1 \)). Note that the result for networks does upto finite strand length effects not depend on the persistence length of a single strand. The requirement is that \( \lambda_0 \), defined as the ratio of the strand extension in equilibrium and to the unstrained state, does not depend on \( N \).

The stress–strain curves in Fig. 5 lead to three important conclusions for the spectrin network in red blood cells (RBCs):

1. The elastic properties of RBCs should depend sensitively on the degree of adsorption of the spectrin network between the tether points.
2. The deviations from a Gaussian model are particularly marked for fully adsorbed networks.
3. The deviations increase with the deformation of the cell. For small strains around \( \lambda = 1 \) the results for 2d SAWs and RWs differ by a factor of \( 1.8 \lambda^2 \) while for \( \lambda = 2 \) the elastic response of the 2d SAW network is almost \( 4 \lambda^2 \) times stronger. This result might point to an explanation of the discrepancies between flicker and deformation measurements of the shear modulus for RBCs.

**SUMMARY AND CONCLUSION**

In this paper we have investigated SAWs on a semi-infinite cubic lattice in three dimensions which have both endpoints adsorbed on the limiting surface. We obtained precise measurements of both the reduced moments of the end-to-end distance distributions and of the complete distributions themselves, for chain lengths up to \( N = 240 \). We observed that the reduced moments scale with chain length \( N \) via \( (a + b N^{-\delta_\nu}) \), where the exponents depend on the degree of the moment. We also found that the full distribution is well described using the ansatz of Redner and des Cloizeaux (RdC) Eq. (2) with effective exponents that extrapolate close but not quite to the theoretically expected values.
We used the RdC expression Eq. (4) to compare the elastic properties of both end adsorbed and fully adsorbed SAWs to those of RWs. We note that current models of the elastic properties of the spectrin network in red blood cells assume Gaussian chains, i.e., RWs. There is, however, little reason to believe that water constitutes a theta solvent for a highly charged macromolecule such as spectrin. Our results suggest that for flexible polymers in a good solvent the Gaussian approach is poor at best, and allow to quantify the modification of the elastic properties due to the excluded volume effects within the chains. Moreover, we find that in contrast to Gaussian chains the elasticity of SAWs can be strongly influenced by interactions with the surface. The nonlinearity of the elastic response is particularly marked for chains which are completely adsorbed on the surface.

Our theory for the spectrin network is based on de Gennes’ e*-theorem. For networks with an internal concentration of the order of the overlap concentration of the network strands the latter show single chain behavior. Multichain interactions affect the elastic properties only indirectly by determining the equilibrium width of the network strands. We derived stress–strain relations for two dimensional networks consisting of RWs, 2d SAWs and end adsorbed 3d/2 SAWs within the junction affine approximation. Our ansatz is supported by the close agreement between our prediction for the 3d/2 case and the shear moduli measured by Boal in simulations of a bead–spring model for the spectrin network. In fact, we have argued that for the smaller strand lengths investigated in these simulations finite size effects obscure the asymptotic behavior. Our results suggest that the elastic properties of a red blood cell should sensitively depend on the degree of adsorption of the spectrin network. The question in which manner these differences could be used by a cell in order to control its shape and elastic properties by changing the bilayer–spectrin interaction will be addressed in a future publication.