

APPENDIX 1: PARTIALLY BOUND LINEAR POLYMER

Assume a polymer of length $L=l_0N_T$ where l_0 is the length of the fundamental unit (monomer) of the polymer and N_T is the number of fundamental units in the polymer. Further assume that there is a binding site at one end of each monomer that can attach within (or between) different molecules. Finally, assume a) that p is the probability that any particular binding site is *not* attached at any time and b) that the states of the binding sites are not correlated. Our interest is to determine the number N_m of segments of length $L_m=l_0m$ that are *not* attached to other molecules for a polymer with $N_T \gg 1$.

This problem is a specific case of studying *runs* in a Bernoulli process. The general theory of runs is quite complicated and is still in development [35]. In order to facilitate our work, we will derive the necessary relationship and then test it against numerically generated data. With the assumption that the binding of different sites is not correlated, an immediate observation is that the probability of k consecutive sites being unbound is p^k . Defining N_1 as the number of free segments of length l_0 with the subscript 1 representing free segments, we immediately define: $N_m = N_1 p^{m-1}$, so that the number of segments of each length appears in the same relative proportion as the probability of their occurrence. To determine N_1 we use the observation that there are two transitions (01) and (10) that define the ends of each segment. There are pN_T sites unbound and $(1-p)N_T$ sites bound. If we know that site m is bound, the probability that the next site ($m+1$) is unbound is p . Similarly, if m is unbound, the probability that the previous site is bound is $(1-p)$. Hence, the total number of transitions is $(1-p)N_T p + pN_T(1-p) = 2p(1-p)N_T$. To complete the derivation, we note that the total number of unbound segments N is the sum of the N_m as:

$$N = \sum_{m=1}^{N_T} N_m = \sum_{m=1}^{N_T} N_1 p^{m-1} = \frac{N_1}{p} \sum_{m=1}^{N_T} p^m = \frac{N_1}{p} \frac{p(1-p^{N_T})}{1-p} = N_1 \frac{1-p^{N_T}}{1-p} \quad \text{Equation A1}$$

where the summation is resolved as a geometric series. Since the total number of transitions is twice the number of segments, it is immediate that $N_1 = N_T p(1-p)^2 / (1-p^{N_T})$ and, finally:

$$N_m = \left(\frac{(1-p)^2 p^m}{1-p^{N_T}} \right) N_T \quad \text{Equation A2}$$

We tested this prediction of the number of unbound segments of length $L_m = ml_0$ by comparison to Bernoulli runs data generated using the function `gsl_ran_bernoulli` from the GNU Scientific Library (Free Software Foundation, Inc., 51 Franklin Street, Fifth Floor, Boston, MA 02110-1301). As examples for $N_T = 500000000$, 1) for $p = 0.999$, regression between the numerically simulated and the predicted numbers of unbound segments gave $N_{m\text{PREDICTED}} = 0.9825 * N_{m\text{CALCULATED}}$; $r^2 = 0.9943$ 2) for $p = 0.9$ the prediction was $N_{m\text{PREDICTED}} = 0.9998 * N_{m\text{CALCULATED}}$; $r^2 = 1$. These are typical results where p is close to 1. Small values of N_T resulted in scatter of the numerical simulation away from the predicted values.

APPENDIX 2: STRETCHED EXPONENTIAL APPROXIMATION FOR RELAXATION OF PARTIALLY BOUND LINEAR POLYMER

Given a length distribution ($L_m = ml_0$, $N_m = N_1 p^{m-1}$, $0 < p < 1$, $m = 1, 2, \dots, N_T$) and a relaxation function $\Psi(t, L_m)$ associated with each length L_m , an approximation for the relaxation function $\phi(t)$ of the system with this distribution of lengths is:

$$\phi(t) = \frac{\sum_{m=1}^{N_T} N_m}{\sum_{m=1}^{N_T} N_m} \Psi(t, L_m) = \frac{(1-p)}{(1-p^{N_T})p} \sum_{m=1}^{N_T} p^m \Psi(t, L_m) \quad \text{Equation A3}$$

With the assumption that $\Psi(t, L_m) = \exp(-at/L_m)$ the relaxation function for the mixture

is: $\phi(t) = \frac{(1-p)}{(1-p^{N_T})p} \sum_{m=1}^{N_T} p^m \exp(-at/(ml_0))$. We used a special-purpose EXCEL

(Microsoft Corp, Redmond, WA) program to generate numerical data for $a=1$, $l_0=1$ and $p=(0.999, 0.99, 0.9, 0.7, 0.5, 0.3)$ using the first 44 terms of the summation. (Note that truncating the sum of the exact relaxation function to the terms less than 44 results in $p^{44} \exp(-t/44) = (0.94, 0.63, 0.01, 1.5e^{-7}, 5.6e^{-14}, 9.6e^{-24})$ and $(1.3e^{-10}, 9e^{-11}, 1.3e^{-11}, 2e^{-17}, 7.6e^{-24}, 1.3e^{-33})$ for the six levels examined at $t=1$ and $t=1000$, respectively. Forty four terms were sufficient to the current study.)

These data were fit using a stretched exponential function $\exp(-((t/\tau_{KWW})^\beta))$ by transforming the ordinate as $\ln(t)$ and the abscissa as $\ln(\ln(\phi(t)))$. The transformed data were fit using linear regression in EXCEL and the linear regression coefficients were back-transformed into the original $t-\phi$ space (Table A1). The first 44 terms of the relaxation function $\phi(t)$ were very well approximated (transform-space r^2 of 0.998 and 0.992 for p of 0.999 and 0.3, respectively) by the stretched exponential for $0 < t < 1000$. Note that the model contains a wider distribution of unbound lengths as the unbound probability, p , increases toward unity and that, the effect the length distribution is primarily reflected in the values of τ_{KWW} (Table 2.1). The exponent β remains relatively stable (coefficient of variation less than 0.1) for the range of parameters examined, suggesting that it represents a factor other than polydispersity in the constrained motion model.

The results for the numerical simulation of polymer binding (Table A1) make it possible to consider the theoretical number of free versus bound sites in cartilage. First, comparing the curve fit results to the simulations in Table 1 and assuming that all relaxation originates from constrained motion, τ_{KWW} of 7.6 ± 1.0 seconds suggests that there is about an 80%-90% probability of binding or 10-20% of the potential bonds are unconstrained. The second observation regarding Table 2 is that β is not strongly dependent upon the probability of a segment being unbound, p . The observed decrease in τ_{KWW} with increasing p suggests that increasing the probability of each segment being bound results in a faster relaxation: because the molecules cannot move as far, relaxation proceeds more quickly. The relaxation time, τ_{KWW} , is shorter when bonds are more permanent, so the relaxation tends toward that of an elastic solid. The observation that

changes in p strongly affect τ_{KWW} suggests that a structural feature relating to molecular length dominates relaxation time. This is consistent with the results of polymer dynamics which relate stress relaxation to the autocorrelation of polymer bond vectors [14].

We further examined Equation A3 where it was assumed that $\Psi(t, L_m)$ was the reptation relaxation function (Equation 1). With this assumption, the stretched exponential function again fit the resulting relaxation function very well for a broad range of parameters (data not shown) demonstrating that the assumption that the segments relax stress following an exponential (Debye) function was not necessary for the stretched exponential to fit the data accurately.

p	r^2	τ_{KWW}	β
0.999	0.998	707.865	0.685
0.990	0.998	69.418	0.612
0.900	0.997	6.222	0.585
0.700	0.996	2.078	0.600
0.500	0.994	1.260	0.621
0.300	0.992	0.927	0.655

Table A1. The sticky relaxation model is well-fit by the KWW model. Fit of stretched exponential ($\exp(-((t/\tau_{KWW})^\beta))$) to numerically generated data from Equation 5 with $a=1$, $L_m=m$. These data in conjunction with the observation that short-term (~ 0.1 -100 s) cartilage stress-relaxation is described by the stretched exponential model (Table 1, Figure 5) motivated us to test the sticky model on experimental data (Figure 6).