Supporting Information for "Harnessing entropy to enhance toughness in reversibly crosslinked polymer networks"

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SI. STRETCHED GAUSSIAN POLYMER BINDING

In this section, we consider the binding distribution for adding one reversible crosslink between two Gaussian polymers of N_1 and N_2 segments, having two of their endpoints fixed at the origin, while their other two endpoints are fixed at arbitrary coordinates.

Suppose that the first chain has its end fixed at \mathbf{R}_1 , and the other at \mathbf{R}_2 . The partition function for just one chain is

$$Q^{\circ}(N_i, \mathbf{R}_i) = \exp\left(-\frac{3(x_i^2 + y_i^2 + z_i^2)}{2N_i b^2}\right)$$
(S1)

where *i* is either 1 or 2, and $\mathbf{R}_i = (x_i, y_i, z_i)$ is the end-to-end vector for the polymer (such that $|\mathbf{R}_i| = \sqrt{x_i^2 + y_i^2 + z_i^2}$). Equivalently, we can express this as the product of two connected subchains of length n_i and $N_i - n_i$:

$$Q^{\circ}(N_i, \mathbf{R}_i) = \frac{1}{b^3} \left(\frac{3N_i}{2\pi n_i (N_i - n_i)} \right)^{3/2} \int_{\mathbf{R}'} w_i(\mathbf{R}') w_i'(\mathbf{R}_i | \mathbf{R}') \ d\mathbf{R}'.$$
(S2)

where

$$w_i(\mathbf{R}') = \exp\left(-\frac{3(x'^2 + y'^2 + z'^2)}{2n_i b^2}\right)$$
(S3)

$$w_i'(\mathbf{R}_i|\mathbf{R}') = \exp\left(-\frac{3((x_i - x')^2 + (y_i - y')^2 + (z_i - z')^2)}{2(N_i - n_i)b^2}\right)$$
(S4)

For both chains, the combined partition function is

$$Q_{free}(N_1, N_2, \mathbf{R}_1, \mathbf{R}_2) = Q^{\circ}(N_1, \mathbf{R}_1)Q^{\circ}(N_2, \mathbf{R}_2)$$
(S5)

$$= \exp\left(-\frac{3(x_1^2 + y_1^2 + z_1^2)}{2N_1b^2}\right) \exp\left(-\frac{3(x_2^2 + y_2^2 + z_2^2)}{2N_2b^2}\right)$$
(S6)

$$= \exp\left[-\frac{3}{2b^2}\left(\frac{|\mathbf{R}_1|^2}{N_1} + \frac{|\mathbf{R}_2|^2}{N_2}\right)\right]$$
(S7)

The partition function for the two chains when we place a link at position (n_1, n_2) is

$$Q_{bound}(n_1, n_2; N_1, N_2, \mathbf{R}_1, \mathbf{R}_2) = \frac{1}{b^6} \left(\frac{3}{2\pi}\right)^3 \left(\frac{N_1 N_2}{n_1 (N_1 - n_1) n_2 (N_2 - n_2)}\right)^{3/2} \\ \times \int_{\mathbf{R}'} w_1(\mathbf{R}') w_1'(\mathbf{R}_1 | \mathbf{R}') w_2(\mathbf{R}') w_2'(\mathbf{R}_2 | \mathbf{R}') \ d\mathbf{R}'$$
(S8)

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Just focusing on x, we must evaluate

$$\int_{-\infty}^{\infty} \exp\left\{-\frac{3}{2b^2}\left[\left(\frac{n_1+n_2}{n_1n_2}\right)x'^2 + \frac{(x_1-x')^2}{N_1-n_1} + \frac{(x_2-x')^2}{N_2-n_2}\right]\right\}\,dx'.$$
(S9)

The integrand can be written as

$$\exp\left\{-\frac{3}{2b^2}\left[\left(\frac{n_1+n_2}{n_1n_2}\right)x'^2 + \frac{(x_1-x')^2}{N_1-n_1} + \frac{(x_2-x')^2}{N_2-n_2}\right]\right\}$$
(S10)

$$= \exp\left\{-\frac{3}{2b^2}\left[\left(\frac{n_1+n_2}{n_1n_2}\right)x'^2 + \frac{x_1^2 - 2x'x_1 + x'^2}{N_1 - n_1} + \frac{x_2^2 - 2x'x_2 + x'^2}{N_2 - n_2}\right]\right\}$$
(S11)

$$= \exp\left[-\frac{1}{2b^2}\left(\frac{1}{N_1 - n_1} + \frac{2}{N_2 - n_2}\right)\right] \times \exp\left\{-\frac{3}{2b^2}\left[\left(\frac{n_1 + n_2}{n_1 n_2}\right)x'^2 + \frac{-2x'x_1 + x'^2}{N_1 - n_1} + \frac{-2x'x_2 + x'^2}{N_2 - n_2}\right]\right\}$$
(S12)

The first factor depends only on x_1 and x_2 , so it can be factored out of the integral over x', leaving behind the second factor:

$$\exp\left\{-\frac{3}{2b^2}\left[\left(\frac{n_1+n_2}{n_1n_2}\right)x'^2 + \frac{-2x'x_1+x'^2}{N_1-n_1} + \frac{-2x'x_2+x'^2}{N_2-n_2}\right]\right\}$$
(S13)

$$= \exp\left\{-\frac{3}{2b^2}\left(\frac{n_1+n_2}{n_1n_2} + \frac{N_1-n_1+N_2-n_2}{(N_1-n_1)(N_2-n_2)}\right)x'^2 + \frac{3}{b^2}\left(\frac{x_1}{N_1-n_1} + \frac{x_2}{N_2-n_2}\right)x'\right\}$$
(S14)

We must then integrate this over x':

$$\int_{-\infty}^{\infty} \exp\left\{-\frac{3\mathcal{A}}{2b^2}x'^2 + \frac{3}{b^2}\left(\frac{x_1}{N_1 - n_1} + \frac{x_2}{N_2 - n_2}\right)x'\right\}dx'$$
$$= \sqrt{\frac{\pi}{\mathcal{A}}} \exp\left[\frac{3}{2\mathcal{A}b^2}\left(\frac{x_1}{N_1 - n_1} + \frac{x_2}{N_2 - n_2}\right)^2\right]$$
where $\mathcal{A} = \left(\frac{1}{n_1} + \frac{1}{n_2} + \frac{1}{N_1 - n_1} + \frac{1}{N_2 - n_2}\right)$ (S15)

Performing this integral over y' and z' leads to

$$\begin{aligned} Q_{bound}(n_1, n_2; N_1, N_2, \mathbf{R}_1, \mathbf{R}_2) &= \frac{1}{b^3} \left(\frac{3}{2\pi}\right)^{3/2} \left(\frac{N_1 N_2}{\mathcal{A} n_1 (N_1 - n_1) n_2 (N_2 - n_2)}\right)^{3/2} \\ &\times \exp\left[-\frac{3}{2b^2} \left(\frac{|\mathbf{R}_1|^2}{N_1 - n_1} + \frac{|\mathbf{R}_2|^2}{N_2 - n_2}\right)\right] \\ &\times \exp\left\{\frac{3}{2\mathcal{A}b^2} \left[\left(\frac{x_1}{N_1 - n_1} + \frac{x_2}{N_2 - n_2}\right)^2 + \left(\frac{y_1}{N_1 - n_1} + \frac{y_2}{N_2 - n_2}\right)^2 + \left(\frac{z_1}{N_1 - n_1} + \frac{z_2}{N_2 - n_2}\right)^2\right]\right\} \end{aligned}$$

To write the binding partition function in terms of $n = n_1 + n_2$, we must consider all permutations of binding positions (n_1, n_2) that lead to n. For notational simplicity, we restrict to the case where $N_1 = N_2 = N$. Both n_1 and n_2 must be between 1 and N - 1 (as segment N along each chain is now designated a permanent crosslink with a fixed position). The total binding partition function for a linker bound to $n_1 + n_2 = n$ is the sum over all valid permutations of (n_1, n_2) :

$$Q_{poly,b}(n; N, \mathbf{R}_1, \mathbf{R}_2) = \sum_{m=A}^{B} Q_{bound}(m, n-m; N, N, \mathbf{R}_1, \mathbf{R}_2)$$
(S16)

where

$$A = \max(n - N + 1, 1)$$
(S17)

$$B = \min(n - 1, N - 1).$$
(S18)

The binding free energy for attaching a reversible linker with $n_1 + n_2 = n$ is then computed as normal by $G_{poly,b}(n; N, \mathbf{R}_1, \mathbf{R}_2) = -kT \ln Q_{poly,b}(n; N, \mathbf{R}_1, \mathbf{R}_2).$

	Polymer Segment	Permanent Crosslink	Reversible Crosslink	Bind Sites A1/A2	Bind Sites B1/B2
Polymer Segment	$\epsilon=1,\sigma=1$	$\epsilon = 1, \sigma = 1$	$\epsilon = 1, \sigma = 1$	$\epsilon = 1, \sigma = R_b + 0.5$	$\epsilon = 1, \sigma = R_b + 0.5$
Permanent Crosslink		$\epsilon = 1, \sigma = 1$	$\epsilon = 1, \sigma = 1$	$\epsilon = 1, \sigma = R_b + 0.5$	$\epsilon = 1, \sigma = R_b + 0.5$
Reversible Crosslink			$\epsilon=1,\sigma=1$	$\epsilon = 1, \sigma = R_b + 0.5$	$\epsilon = 1, \sigma = R_b + 0.5$
Bind Sites A1/A2				$\epsilon = 1, \sigma = 2R_{b,rep}$	(none)
Bind Sites B1/B2					$\epsilon = 1, \sigma = 2R_{b,rep}$

TABLE I. Inverse power law potential parameters for the intermolecular interactions in the system. Units of measure are \mathcal{E} for ϵ , \mathcal{D} for σ .

SII. MOLECULAR DYNAMICS SIMULATION DETAILS

Our coarse-grained molecular dynamics simulation consists of two bead-spring polymers, each with N = 100segments, bound together by a permanent crosslink bead at segment 50. The position of the permanent crosslink is fixed to the origin of the simulation box, while the polymer chains are allowed to fluctuate. The box boundaries are periodic in all three dimensions, though the size of the box is set to be large enough that the polymer chains do not interact with their periodic images. Simulation parameters and quantities are all given in terms of fundamental model units of distance \mathcal{D} , energy \mathcal{E} (taken to be the thermal unit kT), mass \mathcal{M} , and time $\tau = \sqrt{\mathcal{M}\mathcal{D}^2/\mathcal{E}}$. Calculations were carried out using the HOOMD-Blue molecular dynamics package (v2.1.1).^{1,2} All systems are integrated using a time step size of $dt = 0.001\tau$.

The beads (segments) comprising the polymer chains are held together by strong harmonic bonds, with the bonding potential

$$U_{bond}(r) = \frac{1}{2}k_{bond}(r - r_0)^2$$
(S19)

where r is the separation distance between the two beads on a given timestep in the simulation, and r_0 is the bond rest length. We choose $k_{bond} = 5000 \mathcal{E}/\mathcal{D}^2$, and $r_0 = 0.85\mathcal{D}$. The bond between polymer segment 50 on each chain, and the permanent crosslink bead, has $k_{bond} = 1000 \mathcal{E}/\mathcal{D}^2$ with the same r_0 . This is because the bead for the permanent crosslink is intended to represent a structure somewhat larger than a single polymer segment. The smaller k_{bond} for the two permanent crosslink bonds is therefore a coarse-grained implementation of this flexibility/extensibility (as opposed to using multiple bound sub-beads). It affects the quantitative results of the simulations, but not the qualitative trends for reversible crosslink binding. The "helper linkers" used in Figure 7 (main text) are identical to the permanent crosslink bead, and are attached to their two neighbour polymers segments by the same type of harmonic bond.

Each polymer segment (besides segment 50) has a binding site attached to it via a harmonic bond with $k = 5000 \mathcal{E}/\mathcal{D}^2$, and $r_0 = 0.4\mathcal{D}$ (henceforth called " r_b "). The binding sites on the first polymer chain are distinguished as type "A1", while those on the second polymer chain are defined as "A2".

Reversible crosslink particles may also be added to the simulation box if desired. These particles are composed of a single bead with two antipodal binding sites, one of type "B1" and the other of type "B2". The binding sites are attached to their host bead by harmonic bonds with $k = 5000 \mathcal{E}/\mathcal{D}^2$, and $r_0 = 0.4\mathcal{D}$. The two binding sites on each reversible linker are held at an angle of π relative to each other by a strong angle potential of the form

$$U_{angle}(\theta) = \frac{1}{2} k_{angle} (\theta - \pi)^2.$$
(S20)

Here θ is the angle between the two binding sites, $k_{angle} = 100 \mathcal{E}/\text{rad}^2$ is the strength of the angular potential, and π is the rest angle.

All non-bonded polymer segments, binding sites, the permanent crosslink, and any reversible crosslinks interact with each other via a Lennard-Jones-like inverse power law potential,

$$U_{int}(r) = 4\epsilon \left(\frac{\sigma}{r}\right)^{12} \text{ for } r < r_{cut}$$

= 0 otherwise. (S21)

Here, ϵ is the strength of the potential, σ is the width, and $r_{cut} = 3.0\mathcal{D}$ is the cut-off radius. The parameters of the potential for each pair of bead types in the system are given in Table I. The effective radius of a binding sites is given by $R_b = 0.1\mathcal{D}$.

$$U_{bind}(r) = -\epsilon_{bind} \exp\left[-\frac{1}{2} \left(\frac{r}{\sigma_{bind}}\right)^2\right] \text{ for } r < r_{cut}$$

= 0 otherwise. (S22)

The binding strength is tuned by ϵ_{bind} , and the binding range is set by the binding site radius, $\sigma_{bind} = 2R_b \mathcal{D}$.

With these ingredients in place, reversible crosslinks can form one or two bonds with the polymer chains. The strength of binding is tuned by ϵ_{bind} . The repulsion of binding sites of like type prevents, for example, two polymer segment binding sites from potentially attaching to a single reversible crosslink binding site. By virtue of separating the binding sites on the two polymers into two distinct categories, reversible crosslinks may also only form a link between a segment on polymer chain 1, and another segment on polymer chain 2.

For a given choice of ϵ_{bind} , the *effective* attraction strength between binding sites is actually weaker than $U_{bind}(r)$, because the binding sites are attached to their host beads. As noted in Table I, the host beads interact with other host beads, and also non-bonded binding sites, via an inverse power law potential. Thus, the effective attraction strength between two binding sites is the sum of the Gaussian potential $U_{bind}(r)$, plus the sum of the repulsive contributions from the inverse power law potentials. The effective depth of the potential energy well for two binding sites can be calculated analytically by

$$\epsilon_{bind,eff} = \min \left| U_{bind}(r - 2r_b) + U_{int,host/host}(r) + 2U_{int,host/binder}(r - r_b) \right|$$
(S23)

The three terms here correspond to, in order: the attractive Gaussian potential between the two binding sites; the inverse power law repulsion between the two host beads of the binding sites; and two factors of the inverse power law repulsion between a host and a binding site. The quantity r is the distance between the two host beads, and r_b is the length of the bond connecting a binding site to its host bead, noted above.

After initialisation, all systems are equilibrated in the NVT ensemble with Langevin dynamics for between 1×10^7 and 1×10^8 time steps. System statistics are then recorded within the same ensemble over 1×10^8 time steps (at intervals of 1×10^4 time steps).

SIII. LATTICE SCFT NETWORK DETAILS

Each bridge *i* in the SCFT model is represented as a random walk with a fixed number of steps N_i (which may be different for each bridge). The force along a bridge is approximated with the ideal chain model,

$$F_i(L_i) = \frac{2\langle L_i \rangle kT}{N_i b^2},\tag{S24}$$

where b = 1 is the width of a monomer (equal to the lattice unit size 1 here), $\langle L_i \rangle$ is the average end-to-end distance of the bridge extracted directly from the SCFT calculation, and kT is the energy unit (set to unity in the model). As L_i of each bridge changes during each strain step, the force $F_i(L_i)$ of the bridge changes according to Eq. S24. The bridge is instantaneously and irreversibly cut when $F_i(L_i)$ exceeds F^* , a model parameter representing the threshold force for breaking the connection between a bridge and a node. The cut is performed randomly from either of the two nodes the bridge is attached to. The bridge then remains in the system, connected to the second node, for all subsequent strain steps.

The full protocol for carrying out a strain experiment in our coarse-grained SCFT model is as follows:

- 1. Define a polymer network. This consists of choosing: the number of bridges in the system, the number of segments in each bridge, how the bridge ends are connected together via nodes, and the initial width and height of the network.
- 2. Use the lattice SCFT approach to approximate the equilibrium distribution of polymer conformations and node positions for the current system size.
- 3. Compute the force F_i along each bridge *i* via Eq. S24.
- 4. Cut each bridge that is bearing a force greater than F^* .
- 5. Perform a strain step, in which the width of the network is increased by two lattice units (2b).

6. Repeat Steps 2 - 5 until the desired final strain is reached.

A square network initially of 50×50 lattice units in size is employed in our calculations, with 283 bridges and 190 nodes. Of these nodes, 20 are defined as left-hand boundary nodes, and another 20 as right-hand boundary nodes; the remaining nodes are "free". The boundary nodes are spatially fixed, and initially placed at a width of 50 lattice units apart from each other in the system. (Their positions in the vertical axis of the lattice are random.) They thus represent the scenario of the polymer network being suspended between two boundary plates. The total width of the system is varied by changing the spacing between the left-hand and right-hand boundary nodes. Note that the boundaries of the network are invisible to the polymer bridges and free nodes.

The polymer bridges are randomly connected to the boundary and free nodes in the system such that: each node has either two or three connections; and no two given nodes are connected by two bridges. In the system considered in the main text, only four out of the 190 nodes have two connections, while the remaining nodes have three connections. The "coordination number" of three employed here is arbitrary, and can obviously be changed as desired.

The free nodes are assigned random initial positions within the 50×50 system, so that each bridge *i* has an initial length $L_{i,\text{init}}$. The number of segments N_i in each bridge is determined based on $L_{i,\text{init}}$, by enforcing that the initial tension in each bridge is (2/3)kT/b using Eq. S24. This initial tension can be changed or heterogenised, and represents a network pre-stress. For bridges where Eq. S24 yields an N_i that is less than 30 segments, the bridge length is set to 30. As such, the network studied here has a heterogeneous pre-stress.

¹J. A. Anderson, C. D. Lorenz, and A. Travesset, Journal of Computational Physics 227, 5342 (2008).

²J. Glaser, T. D. Nguyen, J. A. Anderson, P. Lui, F. Spiga, J. A. Millan, D. C. Morse, and S. C. Glotzer, Computer Physics Communications **192**, 97 (2015).