SUPPORTING INFORMATION FOR:

Responsive Behavior of a Branched-Chain Polymer Network: a Molecular Dynamics Study

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On units

Describing a neutral mechanical system requires three independent base units, for which we may for instance choose *mass* $\mathcal{M}$, *length* $\mathcal{L}$, and *energy* $\mathcal{E}$. All other units can then be derived from these; for instance, force has units $\mathcal{E}/\mathcal{L}$, pressure has units $\mathcal{E}/\mathcal{L}^3$, and time has units $\mathcal{L}\sqrt{\mathcal{M}/\mathcal{E}}$. When describing real systems, we commonly pick SI-units, $\mathcal{M} = \text{kg}$, $\mathcal{L} = \text{m}$, and $\mathcal{E} = \text{J}$. Dealing with atomistic simulations, some derived units are often more convenient and hence widely used, such as length measured in nanometer, or energy in kilojoule per mol.

However, when dealing with generic coarse-grained simulations, which in principle could stand for a wide spectrum of real systems, it is not always necessary—nor even useful—to immediately commit to SI units and hence tie one's model to a very specific situation. Instead, it is more common to use base units that have a direct meaning within the framework of the generic model, such as a coarse-grained bead size σ or bond length b as the length unit, or the thermal energy $k_B T_r$ at room temperature as the energy unit. If need be, one can always later translate to "real" units by mapping σ or b to their corresponding (and system specific) numerical SI values. Note also that the mass unit (say, the bead mass) does not even have to be specified if one stays within the confines of equilibrium statistical mechanics, since the mass only enters dynamical observables. We will leave it at a generic $\mathcal{M}$ for the mass of each bead, which also gives a generic time unit $\tau = \mathcal{L}\sqrt{\mathcal{M}/\mathcal{E}} = \sigma\sqrt{\mathcal{M}/k_B T_r}$.

We follow this latter coarse-grained strategy in this paper. To suggest a possible mapping for those who wish to be more specific, we point out that $k_B T_r \approx 4.14 \times 10^{-21}\text{J} \approx 2.5\,\text{kJ/mol}$. And since we imagine an all-carbon backbone, with one coarse-grained bead representing a double carbon (-C–C-) unit, the length of a carbon bond (0.154 nm) together with the tetrahedral angle of approximately 109.5° gives a projected bond-length of 0.252 nm, which is essentially identical with the coarse grained bead size σ, and we will use this as our length unit—see Fig. S1.

Potentials

For our coarse grained model we need potentials to describe non-bonded interactions between beads, as well as bond- and angle-potentials (the latter to approximately tune a persistence length).
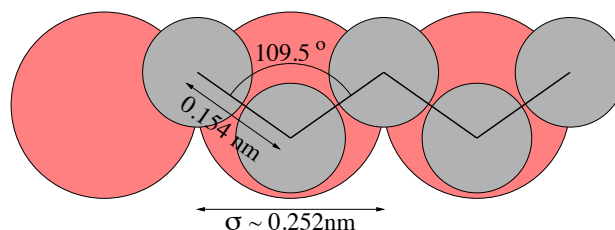

Fig. S1 Illustration of the coarse-grained mapping.

The nonbonded interactions U_{nb} are assumed to be pairwise additive and given by

$$U_{\text{nb}} = \sum_{i<j}^{N} U_{ij}(r_{ij}) , \qquad (1)$$

where U_{ij} is the interaction between bead i and j, separated by the distance r_{ij}, and the sum runs over all pairs of beads.

A soft repulsive interaction potential between all beads is established by using a truncated and shifted Lennard-Jones (LJ) potential,

$$U_{\text{LJ}}(r;\varepsilon) = \begin{cases} 4\varepsilon\left[\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^{6}\right] + \delta U & , r \leq R_c \\ 0 & , r > R_c \end{cases} . \qquad (2)$$

The constant shift δU ensures continuity at the cutoff, $U_{\text{LJ}}(R_c;\varepsilon) = 0$, and we choose $R_c = 2.5\,\sigma$. The depth of the potential minimum, ε, controls the effective hydrophobicity of the interaction: the more hydrophobic these residues are, the stronger their effective solvent-mediated attraction is, and hence the larger ε. Lorentz-Berthelot mixing rules are applied to describe the interaction energy between two dissimilar non-bonded beads.[1,2] Since the ratio of ε with respect to our principal energy scale $k_B T_r$ will occur very frequently, it is convenient to define the *scaled* interaction strength $\tilde{\varepsilon} = \varepsilon/k_B T_r$.

We link beads into chains via the standard FENE potential

$$U_{\text{FENE}}(r) = -\frac{1}{2}kr_\infty^2 \log\left[1 - \left(\frac{r}{r_\infty}\right)^2\right] , \qquad (3)$$

where $0 \leq r < r_\infty$, and we use the standard parameters $r_\infty = 1.5\,\sigma$, and $k = 30\,k_B T_r$.[3] Notice that for $r \ll r_\infty$ this is merely a harmonic

spring with stiffness k, but as r approaches r_∞, the spring constant increases, and the force diverges at $r = r_\infty$.

The polymer's bond length b is set by a competition between the Lennard-Jones repulsion and the FENE attraction, and so it slightly depends on ε. The resulting equation $\partial_r[U_{LJ}(r;\varepsilon) + U_{FENE}(r)] = 0$ cannot be solved analytically, but to a very good approximation, our choice of FENE parameters leads to

$$\frac{b(\varepsilon)}{\sigma} \approx 0.96 + 0.05\log(\tilde{\varepsilon}) . \tag{4}$$

To control the stiffness (and hence persistence length[4] ℓ_p) of a chain of beads, we introduce bending potentials of the form

$$U_{bend}(\vartheta) = -k_\vartheta\,(\hat{\mathbf{r}}_i \cdot \hat{\mathbf{r}}_{i+1}) = -k_\vartheta \cos\vartheta , \tag{5}$$

where $\hat{\mathbf{r}}_i$ and $\hat{\mathbf{r}}_{i+1}$ are two subsequent *unit-length* bond vectors along a chain, differing in orientation by an angle ϑ (with $\vartheta = 0$ being the stretched configuration). Calculating the bending energy of a circular ring made of many beads and comparing it to the continuum energy derived for a wormlike chain, it is easy to see that

$$\frac{k_\vartheta}{k_B T_r} = \frac{\ell_p}{b} . \tag{6}$$

Bearing in mind the special case of an all-carbon backbone with PEG side chains, recall that the persistence length of polyethylene is $\ell_p = 7.7\,\text{Å}$,[5] while that of PEG is $\ell_p = 3.75\,\text{Å}$.[6] Combining this with our mapping $\sigma = 2.5\,\text{Å}$, this leads to $\ell_p = 3.08\,\sigma$ for the backbone and about half as much, $\ell_p = 1.5\,\sigma$, for the side chains.

References

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