SUPPLEMENTARY INFORMATION

for

Modelling and confocal microscopy of biopolymer mixtures in confined geometries

by Sophia Fransson, Niklas Lorén, Anne-Marie Hermansson, Orit Peleg, and Martin Kröger[1]

Spin–chain with variable bond length

Consider a one–dimensional (ring) chain of N consecutive segments (distances) and N nodes (Lennard-Jones particles), as shown in Figure 1 of the manuscript. The total chain length $L = gN$ we parameterize through g, i.e., g denotes mean distance between particles. Segment lengths are allowed to be in one of two possible states, either short (represented by spin state $\phi = 0$) or long ($\phi = 1$). Short segments have length unity, $b_0 = 1$ (and represent the gelatin phase, dark regions in the images), while $b_1 > g$ is the length of stretched segments (maltodextrin phase, light areas). Particles are not allowed to cross each other, and we consider only nearest neighbor interactions between particles. This corresponds to cutting the LJ interaction at a distance of twice the length of a short segment, $2b_0$. The configurational energy, $H(\{\phi\})$, of such a spin–chain in state $\{\phi\} \equiv \{\phi_1, \phi_2, \ldots, \phi_N\}$, representing the one–dimensional elastic LJ model, is a sum of elastic and LJ contributions,

$$H(\{\phi\}) = \sum_{i=1}^{N} \frac{k}{2} b_{\phi_i}^2 + U(\phi_i, \phi_{i+1}), \tag{1}$$

where $\phi_{N+1} = \phi_1$, as we are focusing on a ring chain without end effects. Particles surrounded by long segments ($\phi_i = 1$) are part of the low density phase and do not contribute to the LJ energy, $U(1,1) = U^{\mathrm{LJ}}(b_1) \approx 0$, while particles located at the interface between the high and low density phases ($\phi_i + \phi_{i+1} = 1$) have a lower LJ energy owing to their single short bond, $U(0,1) = U(1,0) = U^{\mathrm{LJ}}(b_0) \approx -1$. Finally, the energetically preferred state (from the point of view of the LJ potential) is $U(0,0) = U^{\mathrm{LJ}}(b_0) + U^{\mathrm{LJ}}(2b_0) \approx -1 - \alpha$, with positive nonzero but small α. Using $b_0 = 1$, one has $\alpha = 63/1024 \approx 0.03$. Having specified U, the hamiltonian (1) can be alteratively cast into the following form

$$H(\{\phi\}) = -(1+\alpha)N + \sum_{i=1}^{N} \left[\frac{k}{2} b_{\phi_i}^2 + \alpha(\phi_i + \phi_{i+1}) + (1-\alpha)\phi_i \phi_{i+1} \right] \tag{2}$$

In passing we note that if the same model is used to interpret the behavior of the two– or three–dimensional elastic LJ system, α might receive slightly larger values. Obviously, U is symmetric in its arguments, $U(\phi_i, \phi_{i+1}) = U(\phi_i + \phi_{i+1})$. With the Hamiltonian (1) and

[1] www.complexfluids.ethz.ch

values for b_0, b_1, α (and thus U) at hand, we would have completely specified the spin–chain model and can resolve its statistical behavior, i.e. temperature dependence assuming a canonical ensemble, via standard methods. However, we have not yet specified b_1, the length of stretched segments. This length is not a constant but its value depends on the actual spin state. It is fixed by the above–mentioned constraint of constant contour length, which reads $gN = b_1\Psi + b_0(N - \Psi)$, with the number of long bonds, Ψ.
To summarize, the spin–chain is defined by hamiltonian (2) with bond lengths

$$b_0 = 1, \qquad b_1 = 1 + \frac{(g-1)N}{\Psi}, \qquad \Psi \equiv \sum_{i=1}^{N} \phi_i. \tag{3}$$

The model can be solved numerically or analytically. It ultimately captures the competition between short range attraction (via the LJ interaction) and long range repulsion (via the constraint for b_1, Eq. 3, which is effective as long as k is nonzero) inherent in the elastic Lennard-Jones model. The model has parameters N, g, k, α, and temperature T, which enters by considering a canonical ensemble of such spin chains. To be specific, an average $\langle A \rangle$ for an observable $A(\{\phi\})$ in the canonical ensemble is calculated via a sum over all possible (2^N) spin states, denoted as $\{\phi\}$,

$$\langle A \rangle = \frac{1}{Z} \sum_{\{\phi\}} A \exp(-H/k_{\mathrm{B}}T), \tag{4}$$

where $Z \equiv \sum_{\{\phi\}} \exp(-H/k_{\mathrm{B}}T)$ is the partition sum. Averages such as $\langle \Psi \rangle$, the order parameter or mean size of inclusions are analytically obtained by derivatives of $\ln Z$ with respect to model parameters T, α, and k.

Solution methods There are at least three basic methods which can be applied to calculate the partion sum Z and free energy $F = -k_{\mathrm{B}} \ln Z$ of the spin chain.

A) **Direct summation**

Direct summation of (4) over 2^N states can be performed exactly and quickly for given model parameters up to $N \approx 20$ on a modern processor. For much larger N, one must resort to Metropolis Monte Carlo or other numerical schemes or to the analytic solution.

B) **Metropolis Monte Carlo**

In a Metropolis Monte Carlo simulation, one (i) randomly assigns values $\phi_i \in \{0, 1\}$ to N spins, (ii) calculates energy $H = H(\{\phi\})$ – according to (1) with (3) – for the spin state, (iii) randomly selects a spin $j \in 1, \ldots, N$, flips it ($\phi'_j = 1 - \phi_j$), and calculates $H' = H(\{\phi'\})$ for the modified state, (iv) accepts the modified state with probability $\min(1, \exp[(H - H')/k_{\mathrm{B}}T])$, and finally continues with (ii) until the statistical error of the observable of interest reaches a desired small value.

C) **Analytical solution (transfer matrix method)**

In order to calculate the partition sum one can consider Ψ, defined in (3), as a constant, and introduce a corresponding Lagrange parameter, Λ. The Hamiltonian (1) is supplemented by a term $\Lambda(\Psi - \sum_i \phi_i)$, and then written as $H_\Psi = \sum_i h_\Psi(\phi_i, \phi_{i+1})$, where one can read off h_Ψ. With the four components $T_{\mu,\nu} \equiv \exp\{-h_\Psi(\mu,\nu)/k_\mathrm{B}T\}$ of matrix $\mathbf{T}$, the partition sum becomes $Z = \sum_{\Psi=1}^{N} Z_\Psi$ with $Z_\Psi = \mathrm{tr}(\mathbf{T}^N) = \lambda_+^N + \lambda_-^N$, where λ_+ and λ_- are the smallest and largest eigenvalue of $\mathbf{T}$, respectively. The Lagrange parameter is determined by $\partial\lambda/\partial\Lambda = 0$ which yields $\Lambda = 1$.

D) **Analytic solution in the thermodynamic limit (large N)**

For large N, the partition sum is well approximated by $Z \approx \lambda_+^N$.

E) **Mean–field approximation**

Within a mean–field approximation, we may replace the term $\phi_i\phi_{i+1}$ in (2) by $\phi_i\langle\phi\rangle$, and Ψ by $N\langle\phi\rangle$ in order to essentially remove the Lagrange parameter and to reduce the problem to a single–spin problem.

Derived quantities, model predictions To provide a rough impression, some of the highly degenerate energetically preferred configurations of this spin–chain model are shown in Tab. 1 of the manuscript. Importantly, the model allows to calculate the mean number of (low density, maltodextrin) inclusions from half the number of interfacial bonds using the observable $A = \frac{1}{2}\sum_i \delta_{\phi_1+\phi_{i+1},1}$ in (4), where δ_{ij} is the Kronecker symbol. We also have access to the total size of inclusions, using $A = \sum_i \phi_i b_{\phi_i}$, or to the total thickness of high density regions (which corresponds to the thickness of filaments in higher dimensions) via $A = \sum_i (1-\phi_i) b_0$. For the spin–chain model, the number of filaments equals the number of inclusions so that we can deduce the mean number and mean size of a low density (maltodextrin) inclusion, in particular. Moreover, we can calculate the order parameter (amount of gelatin) defined previously for the elastic LJ model, as it had been defined as the fraction of particles with at least one neighbor at close distance (b_0). In two dimensions, the order parameter quantifies the fraction of clustered particles. The order parameter, denoted as Φ and bound to the interval $[0, 1]$, is most conveniently calculated by $A = 1 - \frac{1}{N}\sum_i \delta_{\phi_i+\phi_{i+1},2}$, i.e. by the complementary fraction of particles that belong to the low density phase. Such particles are attached with two long springs, giving rise to the form of the Kronecker symbol in this expression. The size (length fraction) of the high density region (gelatin area fraction), Φ_0, is obtained from the order parameter via $\Phi_0 \equiv b_0\Phi/g$. In summary, quick access is gained to all statistical properties of the spin–chain model, which provides a simplified description of some of the main features of the one–dimensional elastic LJ system. A qualitative impression is provided by the exact results (employing exact enumeration) for $N = 20$ presented in Fig. 2 of the manuscript. For the reason of completeness, Fig. 10 shows results obtained via Monte Carlo, for $N = 100$.

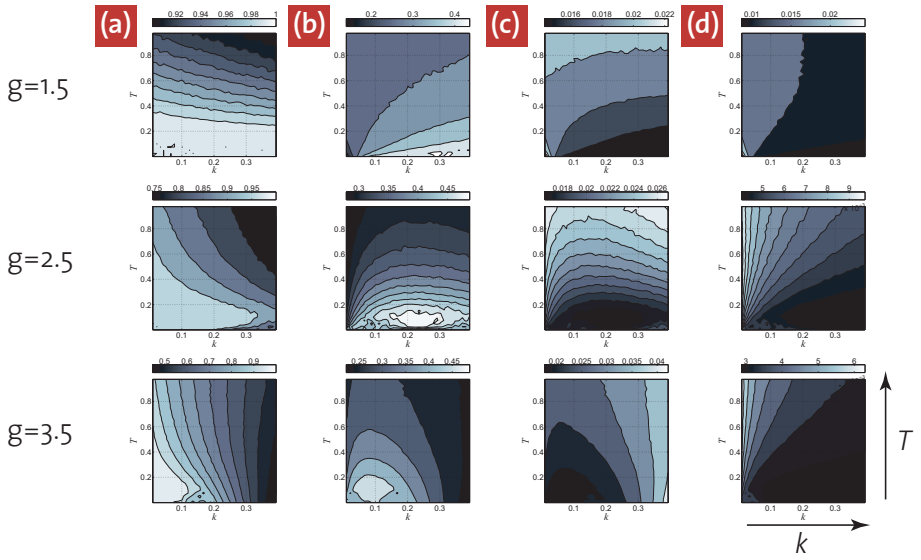

Figure 10: Results for the spin–chain with variable bond length, made of $N = 100$ spins, obtained via Metropolis Monte Carlo with $50,000$ spin flip attempts for each (g, k, T) triple. Figure shown for comparison with the exact result for $N = 20$, cf. Fig. 2 of the manuscript. Phase diagrams in the k–T plane for the spin–chain with $N = 100$ spins (bonds), and $\alpha = 0.03$, for three different choices (arranged in rows) of the total contour length $L = gN$ of the chain. (a) order parameter Φ, (b) number of inclusions (divided by N, the number of spins or "bonds"), (c) mean size of inclusions divided by length L of the spin–chain (or "radius" of confinement), (d) mean thickness of filaments divided by L. Grayscale bars, different for each individual plot, are drawn *above* the plots.

It is worthwhile mentioning that a given pair of values for the size and number of inclusions (at given system size $\sim N$) can be realized for various combinations of the system parameters of g, k and T. On the other hand, there are regions in the phase diagram where the elastic LJ model does not predict this kind of a microphase–separated state of circular inclusions. The phase behavior of the elastic LJ is more rich, as we have learned from previous studies. It is only in the case of small g's (as already discussed), and relatively low temperatures, and relatively low spring coefficients, that a highly ordered, non–filamentous, phase is observed. With increasing temperature, the size and number of inclusions can still be measured, but the variance of these values increases with temperature, as follows from the spin–chain model. The spin–chain model leaves us with some characteristic behavior which helps to interpret the results and to rate the meaning of the ELJ parameters chosen in

the comparisons with experiments.

Extensions Above, we have considered a ring–chain of spins, i.e., a one–dimensional chain with periodic boundary conditions. This setting can be released to study the effect of boundary conditions to the expense of an additional model parameter. Solution method B) can be basically overtaken without modification, while analytical calculations (methods A and C–E) become more tedious, when the periodic boundary condition is released.

Online tool An interactive application evaluating the spin–chain with variable bond length using methods A) for $N \leq 20$ and B) for $N > 20$ is permanently available online at http://www.complexfluids.ethz.ch/fransson.html . The website furthermore reports the histogram of inclusion sizes, as they are obtained by weighting each of the recognized inclusions by the Boltzmann weight of their spin state.