## Variation of Interaction Zone Size For The Target Design of 2D supramolecular networks

Ł. Baran, W. Rżysko, D. Tarasewicz

June 6, 2021

## **1** Simulation details

In molecular dynamics simulations, all of the molecules has been treated as flat, rigid objects. To maintain the molecular geometry, we have used harmonic binding potentials:

$$u_{bb} = k_{bb}(r - \sigma_{bb})^2 \tag{1}$$

and

$$u_{ab} = k_{ab}(r-l)^2 \tag{2}$$

Likewise, all of the necessary angles has been preserved

$$u_{bb}(\theta_{bb}) = k_{\theta}(\theta_{bb} - \theta_{0,bb})^2 \tag{3}$$

and

$$u_{ab}(\theta_{ab}) = k_{\theta}(\theta_{ab} - \theta_{0,ab})^2 \tag{4}$$

The interparticle potential employed in our simulations was (12,6) Lennard-Jones potential, which has been appriopriately shifted to ensure its continuity, as well as the continuity of its derivative [1].

$$U_{SF} = \begin{cases} U_{LJ}(r) - U_{LJ}(r_{cut}) + U'_{LJ}(r_{cut})(r - r_{cut}) & r < r_{cut} \\ 0 & \text{otherwise} \end{cases}$$
(5)

where  $U_{LJ}(r) = 4\varepsilon_{kl}[(\sigma_{kl}/r)^{12} - (\sigma_{kl}/r)^6]$  and  $U'_{LJ}(r_{cut})$  is the first derivative of  $U_{LJ}(r)$  at  $r = r_{cut}$ .

The Lennard-Jones potential parameters,  $\sigma_b = \sigma$  and  $\varepsilon_{bb} = \varepsilon$  have been set to be the units of length and energy, respectively. The reduced time and temperature are equal to  $\tau^* = t\sqrt{\varepsilon/m\sigma^2}$  and  $T^* = kT/\varepsilon_{bb}$ , respectively. The number density has been defined as  $\rho^* = \frac{(X+A+B+C+D)*\sigma_b^2}{L_x*L_y}$ , where **X** and **A**-**D** are the numbers of segments in the backbone as shown in the Figure 1 a in the main text. As already mentioned, the segments diameters in the main framework were equal and set to  $\sigma_b = \sigma$  and the active sites were five times smaller  $\sigma_a = 0.2\sigma$ . The energies of the backbone-backbone and the backbone-active site interactions have been set to  $\varepsilon_{bb} = \varepsilon$  and  $\varepsilon_{aa} = 5.0\varepsilon$ , which means that the only attraction in the system is due to the association between active sites. This kind of screened interparticle interactions can reflect, for instance the behavior of this system in a solvent. However, we did not add any solvent molecules explicitly but we refer to our system as it would have an implicit solvent.

The backbone-site diameter and the energy of the backbone-site interactions have been set to  $\sigma_{ab} = (\sigma_a + \sigma_b)/2$  and  $\varepsilon_{ab} = \varepsilon$ , respectively. The cutoff distance of the interactions between two active sites has been set to  $r_{cut,aa} = 2\sigma_{aa} = 0.4\sigma$ , and  $r_{cut,ij} = \sigma_{ij}$ , where ij = ab, bb. This has been done in order to ensure that the only attraction in the system is due to the association between active sites, whereas the remaining are the soft-core interactions. The harmonic potential constants  $k_{ab} \equiv k_{bb}$  have been set to  $1000\varepsilon/\sigma^2$  and  $k_{\theta} = 1000\varepsilon/(rad)^2$ . Such high values of harmonic constants have been set to reduce the range of fluctuations and, in consequence, to maintain the rigidity of the assumed geometries.

All of the molecular dynamics simulations have been performed in the NVT ensemble, using LAMMPS simulation package [2, 3]. The velocity Verlet integration scheme has been used with the reduced time step of the order of  $t = 0.001\tau$ . The number of molecules varied from 2500 to 8100. However, one has to note that the total number of "atoms" varied depending on the molecular architecture. These numbers are sufficient for the most of the self-assembly systems, which is simultaneously large enough to form ordered networks and small enough to form those structures within a reasonable time frame.

The simulation scheme involved preliminary runs in the NPT ensemble to establish the desired density. Next, equilibration runs for  $5 \times 10^6$  times steps using Berendsen thermostat [4] with the damping constant equal to  $\tau_B = 10\tau$ have been performed. Further equilibration for  $5 \times 10^7$  as well as production runs have been performed using Nosé-Hoover chain algorithm [5], with the damping constant equal to  $\tau_{NH} = 10\tau$  and the number of chains set to  $N_{chain} = 3$ . Every system has been cooled down from temperatures where we did not observe any order, up to the point where self-assembled networks have been distinct. The temperature grid was set to  $\Delta T^* = 0.01$ .

## 2 Additional results



Figure 1: Fragment of the configuration for the model **R4\_M1** at  $\rho^* = 0.2$  and  $T^* = 0.40$  (a). Part b) shows how active sites assemble into Archimedean tesselation. Different polygons are marked by different colors to better pronounce the ordering. Centers of mass of the clusters of active sites calculated for the threshold distance  $r_{cl} = 1.35\sigma$  and for the models **R3\_M1** (c) and **R4\_M1** (d).



Figure 2: Fragment of the configurations for the model **R2\_M2** at  $\rho^* = 0.4$  and  $T^* = 0.45$  (a). Snapshots for the model **R3\_M2** at  $\rho^* = 0.2$  and  $T^* = 0.40$  (b) and at  $\rho^* = 0.4$  and  $T^* = 0.45$  (c). Parts d-f) display configurations for the models **R2-R4\_M2** at  $\rho^* = 0.12$  and  $T^* = 0.35$ 



Figure 3: Fragments of the configurations for the models **R3\_M3** (a) and **R4\_M3** (b) at  $\rho^* = 0.4$  and  $T^* = 0.45$ . Snapshots for the model **R3\_M4** at  $\rho^* = 0.5$  and  $T^* = 0.56$  (c) and at  $\rho^* = 0.5$  and  $T^* = 0.5$  (d).



Figure 4: The configurations for the models **R2\_M5** at  $\rho^* = 0.2$  and  $T^* = 0.4$ (a) and **R4\_M5** at  $\rho^* = 0.2$  and  $T^* = 0.4$  (b). Part c) shows the snapshot for the model **R4\_M5** at  $\rho^* = 0.4$  and  $T^* = 0.45$ . Schematically drawn association paths are shown on the right-hand side of the panels (a-c). The distribution of the association number for the models **R2-R4\_M5** recorded at  $\rho^* = 0.2$  and  $T^* = 0.4$  (open symbols) and at  $\rho^* = 0.4$  and  $T^* = 0.45$  (filled symbols) (d).



Figure 5: Fragment of the configurations for model **R2\_M5** in  $\rho^* = 0.4$ , at  $T^* = 0.45$  (a). Snapshots for model **R3\_M5** in  $\rho^* = 0.2$ , at  $T^* = 0.40$  (b) and in  $\rho^* = 0.4$ , at  $T^* = 0.45$  (c). Parts d-f) display configurations for models **R2-R4\_M5** in  $\rho^* = 0.1$ , at  $T^* = 0.35$ 



Figure 6: Fragments of the configurations for the model **R3\_M2** at  $\rho^* = 0.2$ and  $T^* = 0.25$  for  $l = 0.36\sigma$  (a), and at  $\rho^* = 0.2$  and  $T^* = 0.50$  for  $l = 0.44\sigma$ (b), and at  $\rho^* = 0.4$  and  $T^* = 0.65$  for  $l = 0.44\sigma$  (c). Snapshots for the model **R4\_M2** at  $\rho^* = 0.2$  and  $T^* = 0.25$  for  $l = 0.36\sigma$  (d), at  $\rho^* = 0.2$  and  $T^* = 0.50$ for  $l = 0.44\sigma$  (e), and at  $\rho^* = 0.4$  and  $T^* = 0.65$  for  $l = 0.44\sigma$  (f)



Figure 7: Configurations for the model **R2\_M5** at  $\rho^* = 0.2$  and  $T^* = 0.3$  for  $l = 0.36\sigma$  (a), at  $\rho^* = 0.2$  and  $T^* = 0.5$  for  $l = 0.44\sigma$  (b), and at  $\rho^* = 0.4$  and  $T^* = 0.65$  for  $l = 0.44\sigma$ . Part d) shows the distribution of the association number for the models **R2-R4\_M5** at density  $\rho^* = 0.2$  and  $T^* = 0.30$  (open symbols,  $l = 0.36\sigma$ ) and at  $T^* = 0.50$  for  $l = 0.44\sigma$  (filled symbols).



Figure 8: Configurations for the model **R3\_M5** at  $\rho^* = 0.2$  abnd  $T^* = 0.3$  for  $l = 0.36\sigma$  (a), at  $\rho^* = 0.2$  and  $T^* = 0.50$  for  $l = 0.44\sigma$  (b), and at  $\rho^* = 0.4$  and  $T^* = 0.65$  for  $l = 0.44\sigma$  (c). Snapshots for the model **R4\_M5** at  $\rho^* = 0.2$  and  $T^* = 0.3$  for  $l = 0.36\sigma$  (d), at  $\rho^* = 0.2$  and  $T^* = 0.50$  for  $l = 0.44\sigma$  (e), and at  $\rho^* = 0.44\sigma$  (f)

## References

- S. Toxvaerd and J. C. Dyre, "Communication: Shifted forces in molecular dynamics," *The Journal of Chemical Physics*, vol. 134, no. 8, p. 081102, 2011.
- [2] Steve Plimpton et. al., "Large-scale atomic/molecular massively parallel simulator." lammps.sandia.gov, 1995. [Online; accessed 29-April-2019].
- [3] S. Plimpton, "Fast parallel algorithms for short-range molecular dynamics," *Journal of Computational Physics*, vol. 117, no. 1, pp. 1 – 19, 1995.
- [4] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, and J. R. Haak, "Molecular dynamics with coupling to an external bath," *The Journal of Chemical Physics*, vol. 81, no. 8, pp. 3684–3690, 1984.
- [5] G. J. Martyna, M. L. Klein, and M. Tuckerman, "Nosé-hoover chains: The canonical ensemble via continuous dynamics," *The Journal of Chemical Physics*, vol. 97, no. 4, pp. 2635–2643, 1992.