Patchy particles at a hard wall: Orientation-dependent bonding

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Patchy colloids

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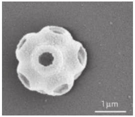

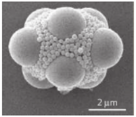

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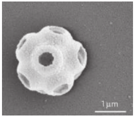

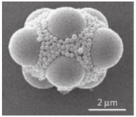

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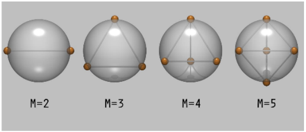

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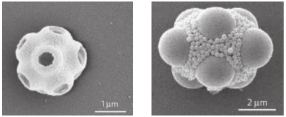

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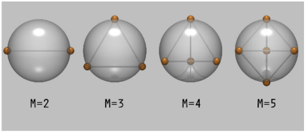

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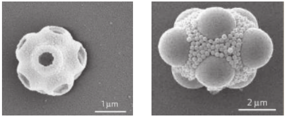

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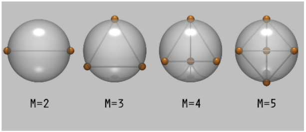


- The bulk phase behaviour of this model has been extensively studied by both simulation and theory – mostly Werteim's thermodynamic perturbation theory (TPT).

- But TPT cannot account for the orienting effects of surfaces [e.g., Gnan *et al.*, J. Chem. Phys. **137**, 084704 (2012)] – it averages over the directionality of interpatch interactions. How do we fix this?

The model we simulate

- The interparticle pair potential is the sum of HS repulsion between cores and attraction between surface patches:

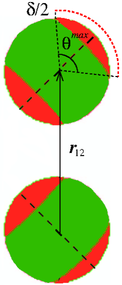
$$u(\mathbf{r}_i, \hat{\mathbf{r}}_j) = u_{HS}(\mathbf{r}_{ij}) + \sum_{\alpha,\beta=1}^{2} V_{ij,\alpha\beta}$$

- Bol-Kern-Frenkel potential:

$$V_{12,\alpha\beta}(\mathbf{r}_{12}, \hat{\mathbf{r}}_{\alpha 1}, \hat{\mathbf{r}}_{\beta 2}) = V^{SW}_{\alpha\beta}(r_{12}) G(\hat{\mathbf{r}}_{12}, \hat{\mathbf{r}}_{\alpha 1}, \hat{\mathbf{r}}_{\beta 2})$$

$$G(\hat{\mathbf{r}}_{12}, \hat{\mathbf{r}}_{\alpha 1}, \hat{\mathbf{r}}_{\beta 2}) = \begin{cases} 1 & \begin{cases}\text{if} & \hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{\alpha 1} > \cos\theta^{max}_{\alpha\beta} \\ \text{and} & -\hat{\mathbf{r}}_{12} \cdot \hat{\mathbf{r}}_{\beta 2} > \cos\theta^{max}_{\alpha\beta}\end{cases} \\ 0 & \text{otherwise.} \end{cases}$$

$$V^{SW}_{\alpha\beta}(x) = \begin{cases} \infty & \text{if} \quad x < \sigma \\ -\epsilon_{\alpha\beta} & \text{if} \quad \sigma < x < \sigma + \delta_{\alpha\beta} \\ 0 & \text{otherwise,} \end{cases}$$



How we fix the theory

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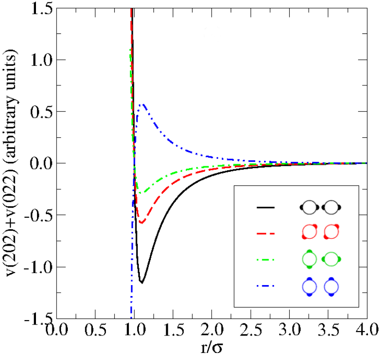
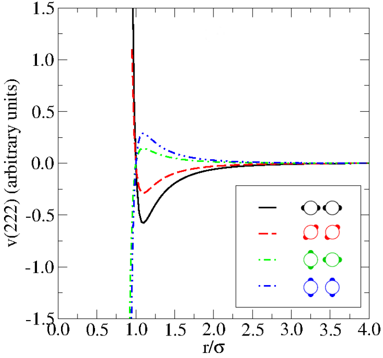
- Particles with one patch at either pole want to lie parallel to an impenetrable wall.
- Do the theory as if the model contained an effective orientation-dependent potential that favours pole-to.pole alignment.

$$V_{eff}(\mathbf{r}_{ij}, \omega_i, \omega_j) = v(202) + v(022) + v(222)$$





The fix in more detail

- These are spherical harmonic expansion coefficients:

$$v(l_1 l_2 l) = \sum_{m_1, m_2, m} v(l_1 l_2 l; r_{ij}) C(l_1 l_2 l : m_1 m_2 m) Y_{l_1 m_1}(\omega_i) Y_{l_2 m_2}(\omega_j) Y^*_{lm}(\omega_{ij})$$

- Use truncated and shifted generalised Lennard-Jones r-dependence:

$$v(l_1 l_2 l; r_{ij}) = \begin{cases} \infty \quad \text{if } r_{ij} < \sigma \\ \epsilon_{l_1 l_2 l} \left[\left(\frac{\sigma}{r_{ij}} \right)^{24} - \left(\frac{\sigma}{r_{ij}} \right)^{n} \right] - \epsilon_{l_1 l_2 l} \left[\left(\frac{\sigma}{r_{max}} \right)^{24} - \left(\frac{\sigma}{r_{max}} \right)^{n} \right] & \text{if } \sigma \leq r_{ij} < r_{max} \\ 0 \quad \text{if } r_{ij} \geq r_{max} \end{cases}$$

- Potential parameters used:

$\cos\theta^{max}$	δ/σ	$\epsilon_{202}/\varepsilon = \epsilon_{022}/\varepsilon$	$\epsilon_{222}/\varepsilon$	n
0.895	0.119	0.6	0.6	4

Only free parameter is cutoff ("range") r_{max}.

Theory for particles with 2 identical patches at hard wall I

Helmholtz free energy (FE) functional is sum of three contributions:

$$\mathcal{F}\left[\rho(z), \hat{f}(z,\theta)\right] = \mathcal{F}_{id}\left[\rho(z), \hat{f}(z,\theta)\right] + \mathcal{F}_{hs+b}\left[\rho(z), X(z)\right] + \mathcal{F}_{MF}\left[\rho(z), \hat{f}(z,\theta)\right]$$

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- Translational + rotational entropy of ideal system (exact):

$$\mathcal{F}_{id}\left[\rho(\mathbf{r})\right] = k_B T \int d\mathbf{r}\, \rho(\mathbf{r}) \left\{\ln\left[\Lambda^3 \rho(\mathbf{r})\right] - 1\right\} + k_B T \int dz\, d\omega\, \rho(z)\hat{f}(z,\theta) \log\left[4\pi \hat{f}(z,\theta)\right]$$

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$$\mathcal{F}_{hs+b}\left[\rho(z)\right] = \int dz\,\rho(z)\Phi_{hs+b}\left(\overline{\rho}(z)\right)$$

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- Effective potential contribution, in MF approximation:

$$\mathcal{F}_{MF}\left[\rho(z),\eta(z)\right]=\frac{1}{2}\int dz_i dz_j\,\rho(z_i)\left[\overline{v}(202;|z_i-z_j|)\eta(z_i)+\overline{v}(022;|z_i-z_j|)\eta(z_j)\right]\rho(z_j)$$
$$+\frac{1}{2}\int dz_i dz_j\,\rho(z_i)\eta(z_i)\overline{v}(222;|z_i-z_j|)\rho(z_j)\eta(z_j)$$

Theory for particles with 2 identical patches at hard wall II

- Minimise grand-canonical potential:

$$\frac{\Omega\left[\rho(z),\hat{f}(z,\theta)\right]}{A} = \mathcal{F}\left[\rho(z),\hat{f}(z,\theta)\right] + \int dz\,\left[V_{ext}(z)-\mu\right]\rho(z)$$

$$\frac{\delta\Omega\left[\rho(z),\hat{f}(z,\theta)\right]}{\delta\rho(z)} = 0 \Leftrightarrow \frac{\delta\mathcal{F}\left[\rho(z),\hat{f}(z,\theta)\right]}{\delta\rho(z)} = \mu - V_{ext}(z)$$

$$\frac{\delta\Omega\left[\rho(z),\hat{f}(z,\theta)\right]}{\delta\hat{f}(z,\theta)} = \lambda$$

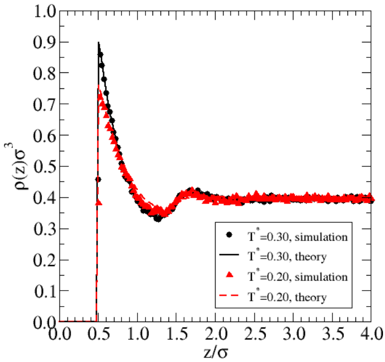
- Outputs are number density profile $\rho(z)$, fraction of unbonded sites $X(z)$, and orientational order parameter profile $\eta(z)$:

$$\eta(z) = \int P_2(\cos\theta)\hat{f}(z,\theta)\,d\omega$$

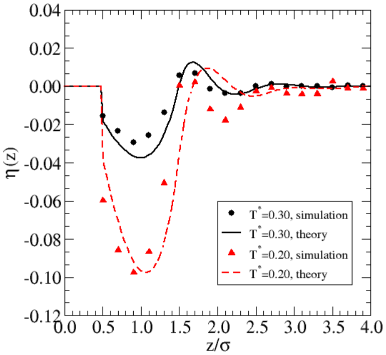
Simulations

- Standard NVT MC of $N = 10800$ particles enclosed in a cubic box of edge length 30σ ($\rho_{bulk}\sigma^3 = 0.4$).
- Periodic boundary conditions along directions x and y, two hard walls at $z = \pm 15\sigma$.
- Elementary roto-translational moves consist of a random translation of at most $\pm 0.05\sigma$ and a random rotation of at most ± 0.1 rad.
- Temperatures from $k_B T/\varepsilon = 0.30$ down to $k_B T/\varepsilon = 0.08$.
- Number of MC steps (one step = N attempts to move a particle) increased progressively from 10^6 to 10^7 on lowering the temperature. No difficulty equilibrating.

Density



Order parameter



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Results: density and order parameter profiles, $T^* = 0.15$

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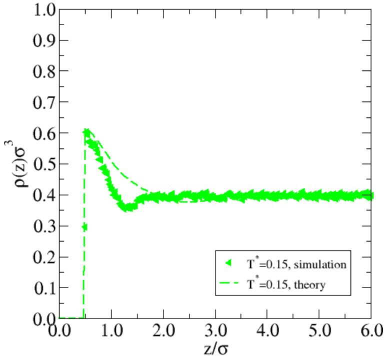

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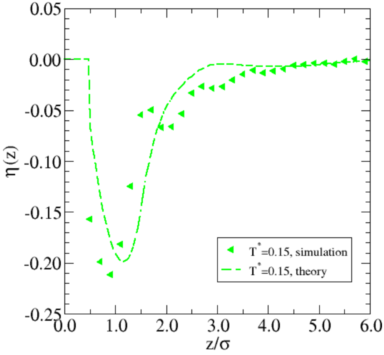

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Results: density and order parameter profiles, $T^* = 0.12$

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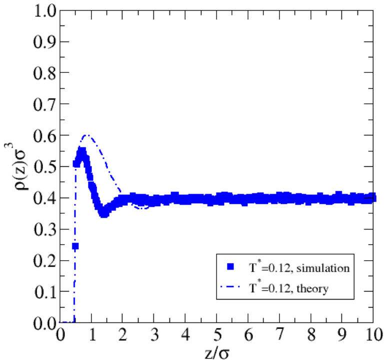
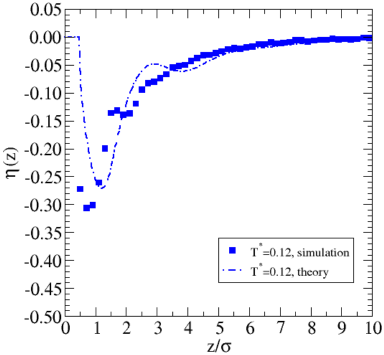


Order parameter



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Results: density and order parameter profiles, $T^* = 0.11$

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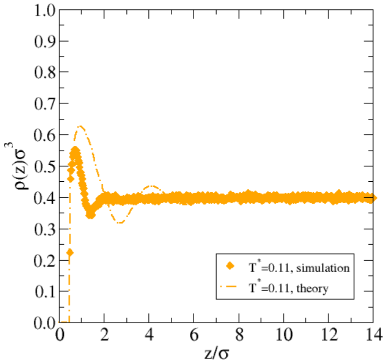
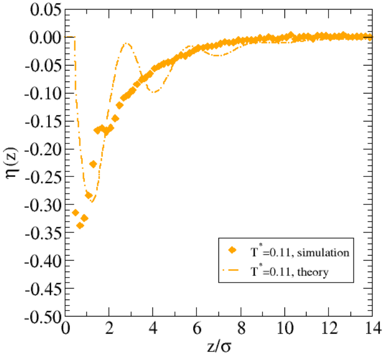


Order parameter



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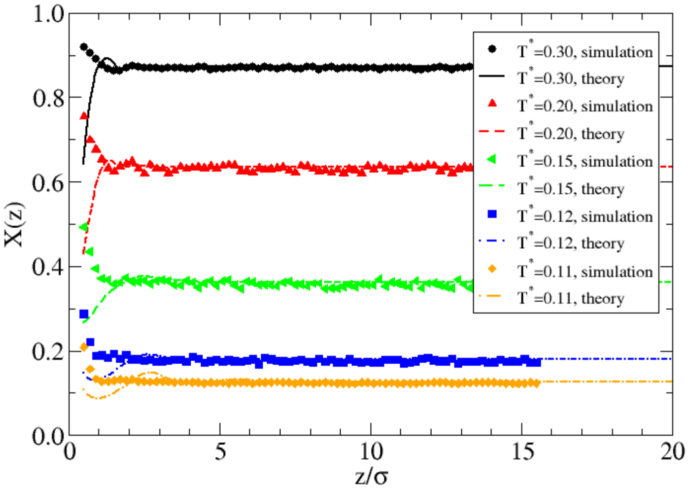
Results: profiles of fraction of unbonded patches



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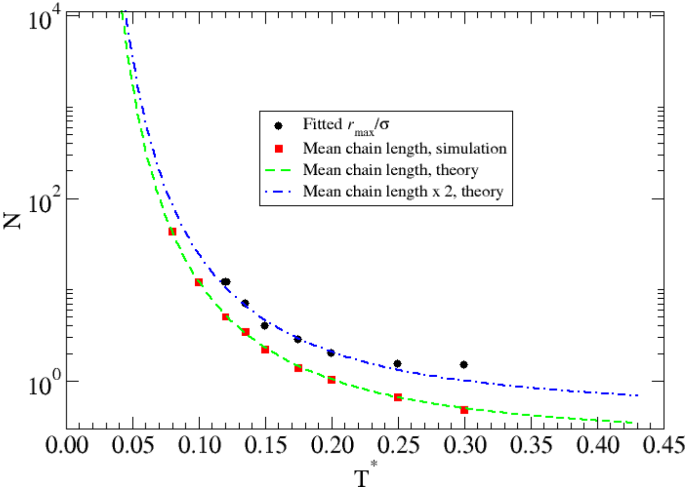
Results: r_{max} and mean chain length *vs* T



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- The theory is unable to predict the weaker bonding at the wall,
- Other patch configurations could be modelled.

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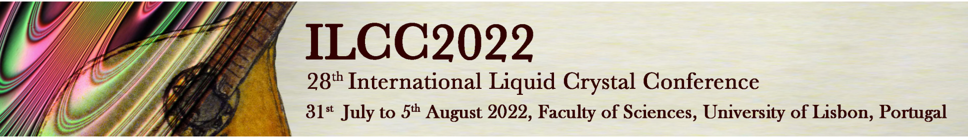

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- Confined Liquid Crystals
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- Mathematical Modelling, Symmetry and Topology
- Novel Applications