Some Study on the Molecular and Multiscale Modelling of Liquid Crystals

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Banff International Research Station
November 30, 2017

Liquid crystals

- Liquid crystals (LCs) are matter in a state between liquids and crystals. [Wikipedia: Liquid crystal].
- Liquid crystals may flow like a liquid, but oriented in a crystal-like way.
- Nematic phase: the rod-shaped molecules have long-range directional order and are free to flow.
- We study different models (lattice-based Gay–Berne, Lebwohl–Lasher, Landau–de Gennes) of nematic liquid crystals in 1D and 2D, at zero temperature. And then, we focus on the multiscale model.

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Gay–Berne Model

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Multiscale Method

Gay–Berne Model

- The Gay–Berne (GB) model [GB81] is an off–lattice, pair potential model for nematic liquid crystals.
- An empirical coarse grained model to approximate the interaction between two rod–like molecules.
- The GB pair potential function depends on the positions and the orientations of molecules, $(\mathbf{x}, \mathbf{n}) \in \mathbb{R}^d \times \mathbb{S}^{d'}$.
- The standard GB pair potential between a pair of molecules i and j is,

$$U_{\mathrm{GB}}\left(\mathbf{n}_i, \mathbf{n}_j, \mathbf{r}\right) := 4\epsilon\left(\mathbf{n}_i, \mathbf{n}_j, \hat{\mathbf{r}}\right)\left(\left(q\left(\mathbf{n}_i, \mathbf{n}_j, \mathbf{r}\right)\right)^{12} - \left(q\left(\mathbf{n}_i, \mathbf{n}_j, \mathbf{r}\right)\right)^{6}\right). \tag{1}$$

- $\mathbf{r} := \mathbf{x}_i - \mathbf{x}_j$. $r := |\mathbf{r}|$. $\hat{\mathbf{r}} := \mathbf{r}/r$.
- $\epsilon\left(\mathbf{n}_i, \mathbf{n}_j, \hat{\mathbf{r}}\right)$ is an energetic term. $\left(q\left(\mathbf{n}_i, \mathbf{n}_j, \mathbf{r}\right)\right)^{12} - \left(q\left(\mathbf{n}_i, \mathbf{n}_j, \mathbf{r}\right)\right)^{6}$ is a Lennard–Jones type contribution.

Gay–Berne Model, Potential Energy Function

- Four parameters: μ, ν, κ', κ.
- The energy term is,

$$\epsilon\left(\mathbf{n}_i, \mathbf{n}_j, \hat{\mathbf{r}}\right) := \epsilon_0 \left(\epsilon_3\left(\mathbf{n}_i, \mathbf{n}_j, \hat{\mathbf{r}}\right)\right)^{\mu} \left(\epsilon_2\left(\mathbf{n}_i, \mathbf{n}_j\right)\right)^{\nu}. \tag{2}$$

-

$$\epsilon_3\left(\mathbf{n}_i, \mathbf{n}_j, \hat{\mathbf{r}}\right) := 1 - \frac{\chi'}{2}\left(\frac{\left(\mathbf{n}_i \cdot \hat{\mathbf{r}} + \mathbf{n}_j \cdot \hat{\mathbf{r}}\right)^2}{1 + \chi'\left(\mathbf{n}_i \cdot \mathbf{n}_j\right)} + \frac{\left(\mathbf{n}_i \cdot \hat{\mathbf{r}} - \mathbf{n}_j \cdot \hat{\mathbf{r}}\right)^2}{1 - \chi'\left(\mathbf{n}_i \cdot \mathbf{n}_j\right)}\right). \tag{3}$$

$$\chi' := \left(\left(\kappa'\right)^{1/\mu} - 1\right) / \left(\left(\kappa'\right)^{1/\mu} + 1\right), \tag{4}$$

and κ' is the well–depth ratio of the end–to–end and side–by–side configurations.

Gay–Berne Model, Potential Energy Function

- $$\epsilon_2\left(\mathbf{n}_i, \mathbf{n}_j\right) := \left(1 - \chi^2 \left(\mathbf{n}_i \cdot \mathbf{n}_j\right)^2\right)^{-1/2}, \tag{5}$$

and the shape anisotropy parameter χ is,

$$\chi := \frac{\kappa^2 - 1}{\kappa^2 + 1}, \tag{6}$$

and $\kappa := \sigma_e/\sigma_s$ is a measure of the molecular aspect ratio and σ_e σ_s are proportional to the length and width of the molecules respectively. ($\chi = 0$ for spherical particles, $\chi = 1$ for infinitely long rods, $\chi = -1$ for infinitely thin disks.)

Gay–Berne Model, Potential Energy Function

- The q term is,

$$q\left(\mathbf{n}_i, \mathbf{n}_j, \mathbf{r}\right) := \frac{\sigma_s}{r - \sigma\left(\mathbf{n}_i, \mathbf{n}_j, \hat{\mathbf{r}}\right) + \sigma_s}. \tag{7}$$

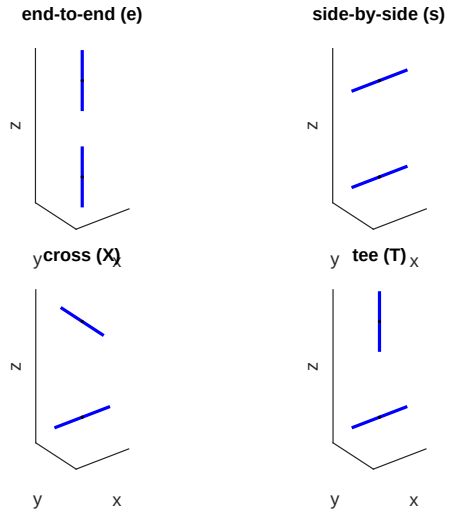
- We define σ_s as the width of the nematic molecules, and the shape parameter (range parameter) $\sigma\left(\mathbf{n}_i, \mathbf{n}_j, \hat{\mathbf{r}}\right)$ is the intermolecular separation at which the potential is zero,

$$\sigma\left(\mathbf{n}_i, \mathbf{n}_j, \hat{\mathbf{r}}\right) := \sigma_s \left(1 - \frac{\chi}{2}\left(\frac{\left(\mathbf{n}_i \cdot \hat{\mathbf{r}} + \mathbf{n}_j \cdot \hat{\mathbf{r}}\right)^2}{1 + \chi\left(\mathbf{n}_i \cdot \mathbf{n}_j\right)} + \frac{\left(\mathbf{n}_i \cdot \hat{\mathbf{r}} - \mathbf{n}_j \cdot \hat{\mathbf{r}}\right)^2}{1 - \chi\left(\mathbf{n}_i \cdot \mathbf{n}_j\right)}\right)\right)^{-\frac{1}{2}}. \tag{8}$$

Important Configurations

- There are four orientations of particular significance and simplicity [LSP90]. We set $\mathbf{n}_i$ and $\mathbf{n}_j$ of them with $\mathbf{r} = d\sigma_s\hat{\mathbf{z}}$, and $d > 0$ is our new variable here.

type	$\mathbf{n}_i$	$\mathbf{n}_j$
end–to–end (e)	$\hat{\mathbf{z}}$	$\hat{\mathbf{z}}$
side–by–side (s)	$\hat{\mathbf{x}}$	$\hat{\mathbf{x}}$
cross (X)	$\hat{\mathbf{x}}$	$\hat{\mathbf{y}}$
tee (T)	$\hat{\mathbf{x}}$	$\hat{\mathbf{z}}$



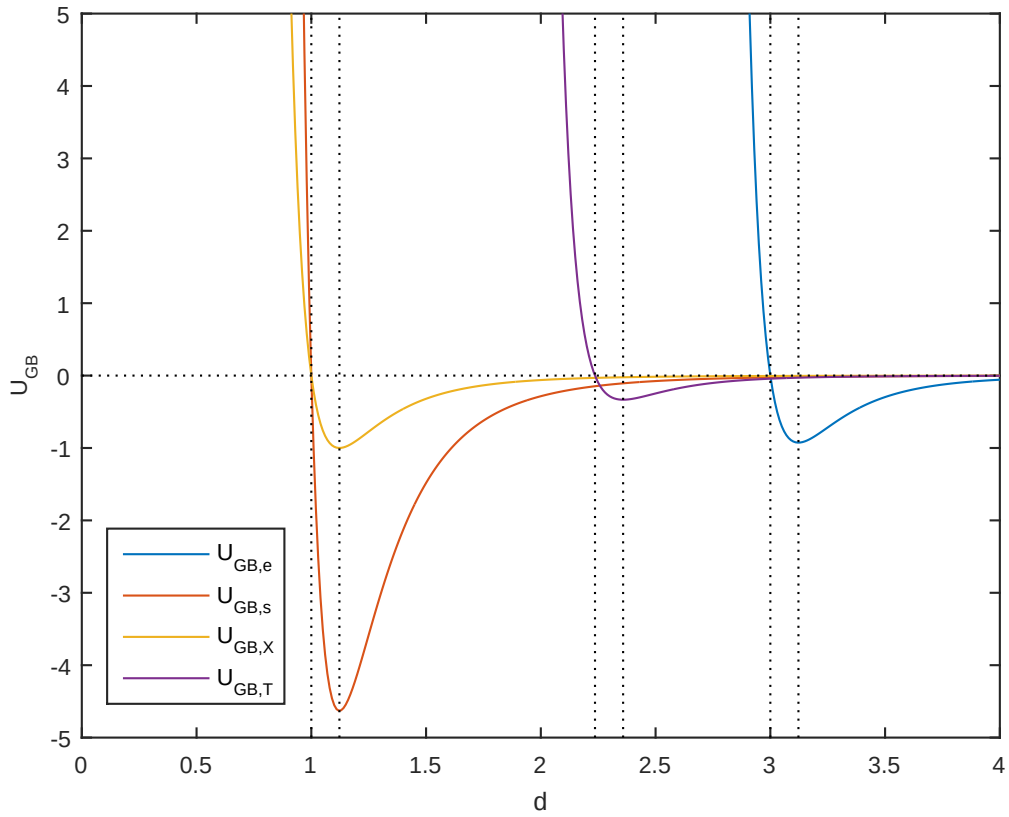
- Important in square lattice-based systems.
- For two of the orientations, the expressions are simple,

$$U_{\mathrm{GB},s}(d) = 4\epsilon_0\left(\tilde{d}^{-12} - \tilde{d}^{-6}\right)\left(1-\chi^2\right)^{-\nu/2}, \tag{9}$$

$$U_{\mathrm{GB},X}(d) = 4\epsilon_0\left(\tilde{d}^{-12} - \tilde{d}^{-6}\right). \tag{10}$$

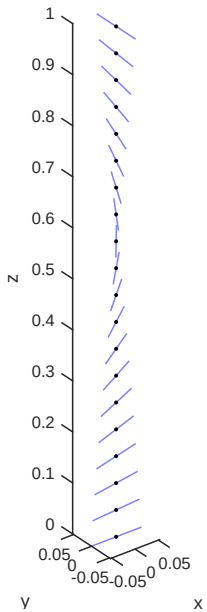
Important Configurations

- All the four pair energies are actually Lennard–Jones potential energies. We show for $(\mu, \nu, \kappa', \kappa) = (1, 3, 5, 3)$.

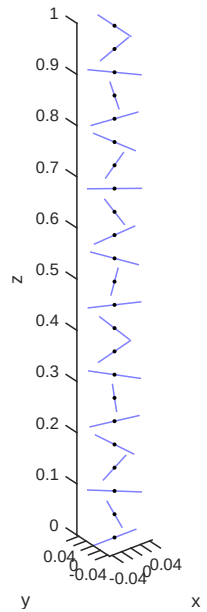


1D Simulation

- We setup one dimensional chain of molecules $(\mathbf{x}, \mathbf{n}) \in \mathbb{R}^1 \times \mathbb{S}^2$ with Dirichlet boundary condition and fixed positions. We find a phase transition by numerical experiments, which agrees with the analysis above.



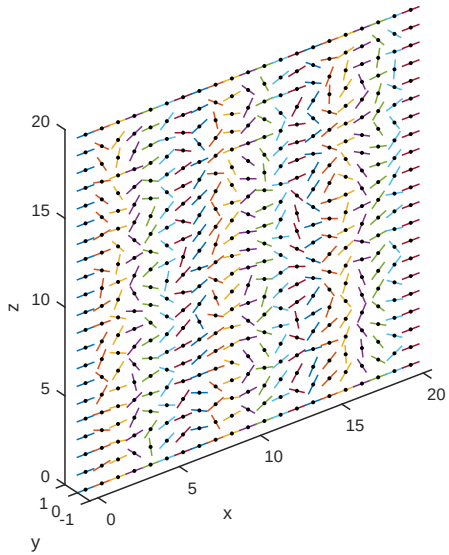
$\sigma_s = 1/20$, spacing = $1/19$, 's'.



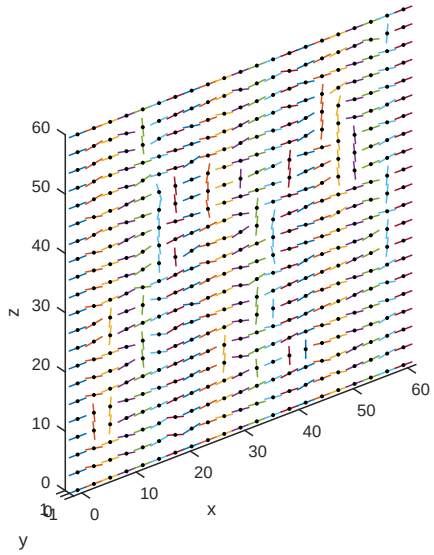
$\sigma_s = 1/20$, spacing = $1/22$, 'X'.

2D Simulation

- We setup two dimensional array of molecules $(\mathbf{x}, \mathbf{n}) \in \mathbb{R}^2 \times \mathbb{S}^2$ with Dirichlet boundary condition and fixed positions. The optimized configurations vary with the boundary conditions.



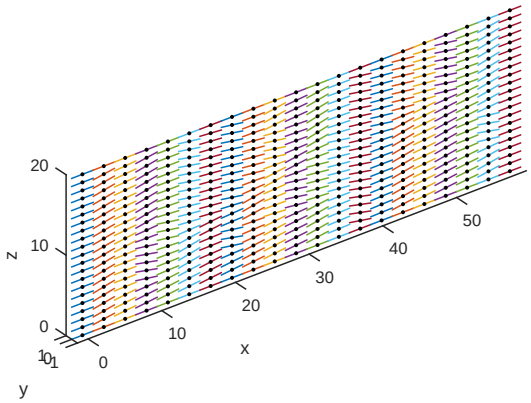
$\sigma_s = 1$,
#molecule: 21×21,
domain size: 20×20.

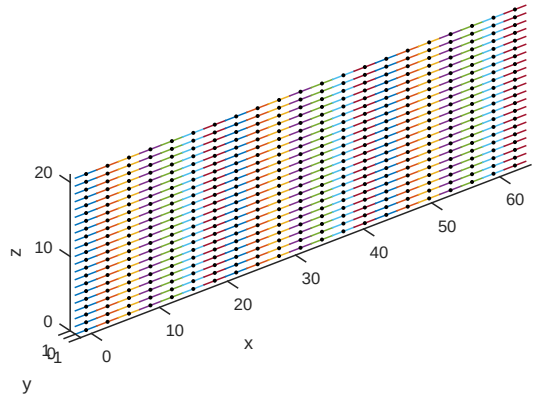


$\sigma_s = 1$,
#molecule: 21×21,
domain size: 60×60.

2D Simulation

- When we choose rectangular domains, the uniform boundary condition is able to give us aligned configurations.





$\sigma_s = 1$,
#molecule: 21×21,
domain size: 58×20.

$\sigma_s = 1$,
#molecule: 21×21,
domain size: 63×21.

- The optimized configuration has too much micro structures, so GB model are not compatible with the continuum methods.

Gay–Berne Model

Lebwohl–Lasher Model and Landau–de Gennes Model

Multiscale Method

Lebwohl–Lasher Model

- The Lebwohl–Lasher (LL) model [LL73] is a lattice–based, nearest neighbour, pair potential model for nematic liquid crystals.
- The LL pair potential function depends on the orientations of molecules, $\mathbf{n} \in \mathbb{S}^{d-1}$, when the positions are fixed and interaction ranges are determined.
- The LL pair potential energy is given by,

$$U_{\mathrm{LL}}\left(\mathbf{n}_i, \mathbf{n}_j\right) = L_{LL}\left(1 - \left(\mathbf{n}_i \cdot \mathbf{n}_j\right)^2\right). \tag{11}$$

  It prefers aligned configurations.
- L_{LL} is a measure of the strength of intermolecular interactions.

Landau–de Gennes Model

- The Landau–de Gennes (LdG) theory [dGP95] [LME12] [MPH13] is a continuum theory for nematic liquid crystals.
- LdG model is a variational theory with an associated energy functional, defined in terms of a macroscopic order parameter – the LdG Q–tensor.
- In d dimensional case, the LdG Q–tensor order parameter is a symmetric, traceless $d \times d$ matrix in the space $S_0 := \left\{ \mathbf{Q} \in \mathbb{R}^{d \times d} \mid \mathbf{Q} = \mathbf{Q}^\top, \mathrm{tr}\mathbf{Q} = 0 \right\}$.

Dimensionless LdG Model

- Take the reference domain $\tilde{\Omega} := [0,1] \times [0, a_r]$.
- $\tilde{x} := x/L$ is the dimensionless coordinate.
- $\tilde{\mathbf{Q}}(\tilde{x}) := \mathbf{Q}(x)/s_0$ is the Q–tensor of order 1.
- The total energy can be written in terms of dimensionless variables [LME12],

$$\frac{1}{s_0^2 L_{el}} \mathbf{I}_{LdG}(\mathbf{Q})$$

$$= \int_{\tilde{\Omega}} \left(\left|\tilde{\nabla} \tilde{Q}_{11}\right|^2 + \left|\tilde{\nabla} \tilde{Q}_{12}\right|^2 + \frac{1}{\tilde{\epsilon}^2} \left(\tilde{Q}_{11}^2 + \tilde{Q}_{12}^2 - 1 \right)^2 \right) \mathrm{d}\tilde{x}, \quad (12)$$

$$=: E_{el} + E_b. \quad (13)$$

It prefers smooth configurations.

Gay–Berne Model

Lebwohl–Lasher Model and Landau–de Gennes Model

Multiscale Method

Multiscale Method

- Idea: Continuum models are efficient at smooth regions while discretization models are accurate near singularities.
- We study the combination of LdG (continuum) model and the LL (discretization) model.
- Key problem: How does LL model converge to LdG model? What is the relationship between them?
- We try to implement them numerically on 2D square lattice / mesh.

Multiscale Method, Abstract Setting

Let X be a Hilbert space,

- Original problem:

$$\min_{u \in X} E(u),$$

  or find $u \in X$, s.t. $\langle \delta E(u), v \rangle = 0$, $\forall v \in X$.

- Approximation problem:

$$\min_{u_N \in X_N} E_N(u_N),$$

  or find $u_N \in X_N$, s.t. $\langle \delta E_N(u_N), v_N \rangle = 0$, $\forall v_N \in X_N$. N is the DoF.

We hope $u_N \to u$.

Multiscale Method, A Priori Analysis

Inverse function theorem (IFT)

- Suppose E_N has Lipschitz continuous Hessian,

$$\left\|\delta^2 E_N(u) - \delta^2 E_N(v)\right\|_{L\left(X_N, X_N^*\right)} \leq M\|u-v\|_{X_N}. \tag{14}$$

- $\exists$ constants $c, r_N > 0$, such that, $2Mr_N c^{-2} < 1$, and

$$\left\langle \delta^2 E_N(\Pi_N u)\, v, v\right\rangle \geq c\|v\|_{X_N}^2, \quad \left\|\delta E_N(\Pi_N u)\right\|_{X_N^*} \leq r_N. \tag{15}$$

- Then $\exists! u_N \in X_N$ s.t. $\delta E_N(u_N) = 0$, and

$$\|u_N - \Pi_N u\|_{X_N} \leq 2r_N/c = 2\frac{\text{consistency error}}{\text{stability constant}}, \tag{16}$$

$$\left\langle \delta^2 E_N(u_N)\, v, v\right\rangle \geq \left(1 - 2Mr_N c^{-2}\right) c\|v\|_{X_N}^2. \tag{17}$$

For a consistent numerical method, $r_N \to 0$, while the mismatch of models would introduce dominant error for r_N.

Matching Energies

- To reduce consistent error numerically: $E(u) = E_N(u_N)$.
- Determine the coefficients s_0, L_{el}, ϵ in LdG model corresponding to a fixed LL model $L_{LL} = 1$.
- In order to connect the LdG model with the LL model, we let $\tilde{Q}(\mathbf{n}) = 2\mathbf{n} \otimes \mathbf{n} - \mathbf{I}_2$. This is NOT unique in inducing $\tilde{Q}$ from $\mathbf{n}$.
- We have,

$$E_{LL} = L_{LL} \sum_{i \sim j} \left(1 - (\mathbf{n}_i \cdot \mathbf{n}_j)^2\right) =: L_{LL} E, \tag{18}$$

$$E_{LdG} = s_0^2 \left(L_{el} E_{el} + \frac{L^2 E_b}{\epsilon^2}\right), \tag{19}$$

L: discretization parameter, L_{LL}, s_0, L_{el}, ϵ: potential parameters.

Smooth Boundary and Singularity

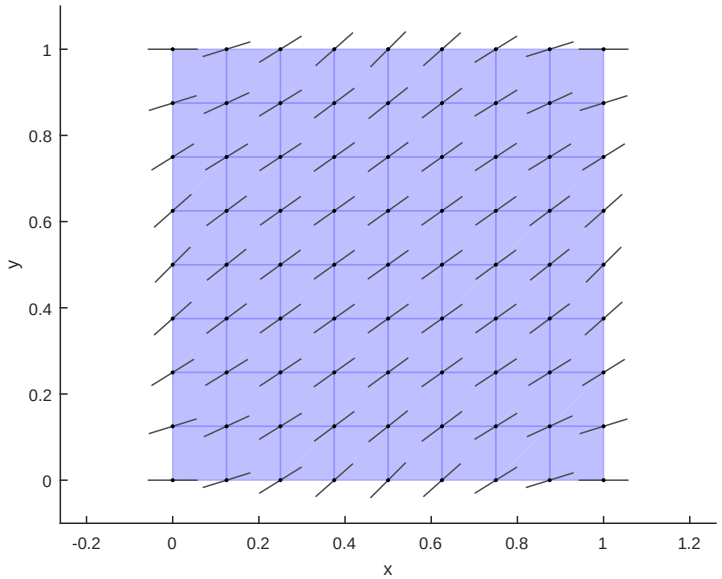
- For both LL and LdG model in 2D with $\mathbf{n} = (\cos\theta, \sin\theta)$.
- Sine boundary condition, which is smooth.

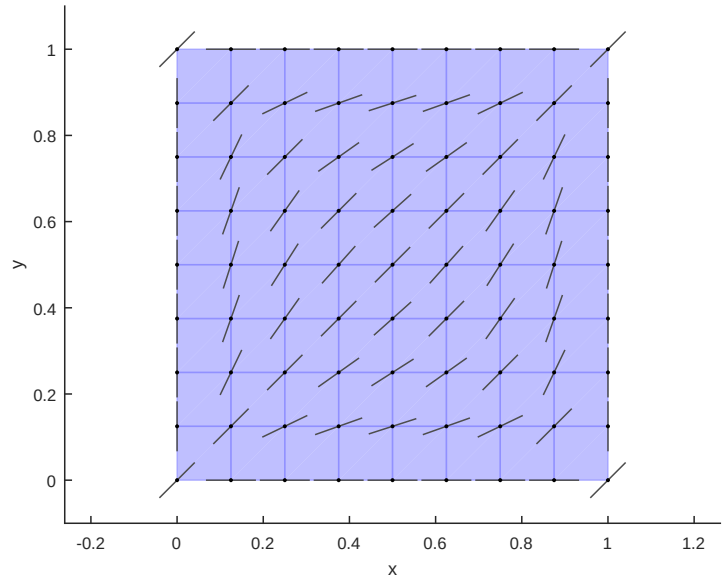
$$\theta(x,0) = \theta(x,1) = \alpha \sin(\pi x), \quad \theta(0,y) = \theta(1,y) = \alpha \sin(\pi y). \tag{20}$$

- Orthogonal boundary condition, with singularities [LME12].

$$\theta(x,0) = \theta(x,1) = 0, \quad \theta(0,y) = \theta(1,y) = \pi/2. \tag{21}$$

- They behave differently.





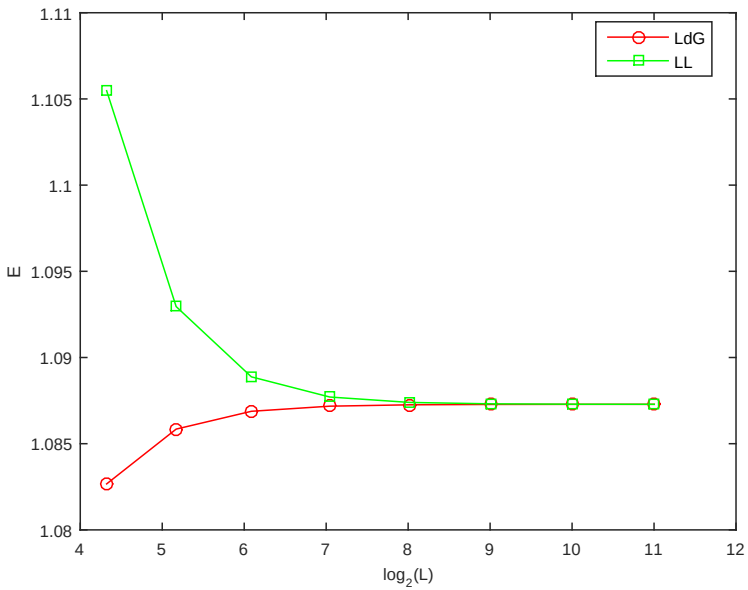
Matching Result

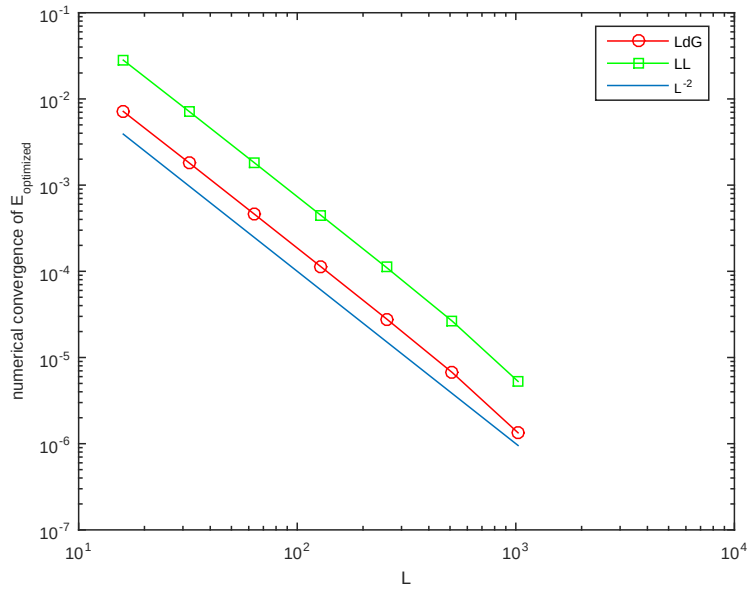
- The energies E, E_b, E_{el} is sensitive to the type of boundary conditions.
- For all the cases, $E_b \ll E \sim E_{el}$.
- When converting the discretization method to the continuum method, we let, $\tilde{Q}(\mathbf{n}) = 2\mathbf{n} \otimes \mathbf{n} - \frac{\mathbf{I}}{2}$, so the integrand in the bulk energy, $\left(\tilde{Q}_{11}^2 + \tilde{Q}_{12}^2 - 1\right)^2$, is exactly zero at the molecule mesh grid, and the integral is a small number.
- We set $\epsilon = \infty$, $L_{el} = 1$, and $s_0 = 1/2$.

$$E_{LL} = E. \quad E_{LdG} = E_{el}/4. \tag{22}$$

Finite Energy

- For sine boundary condition case,

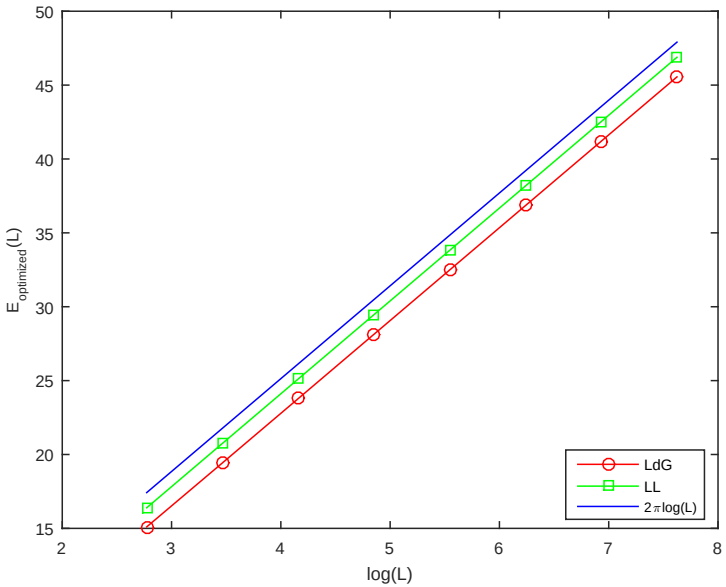


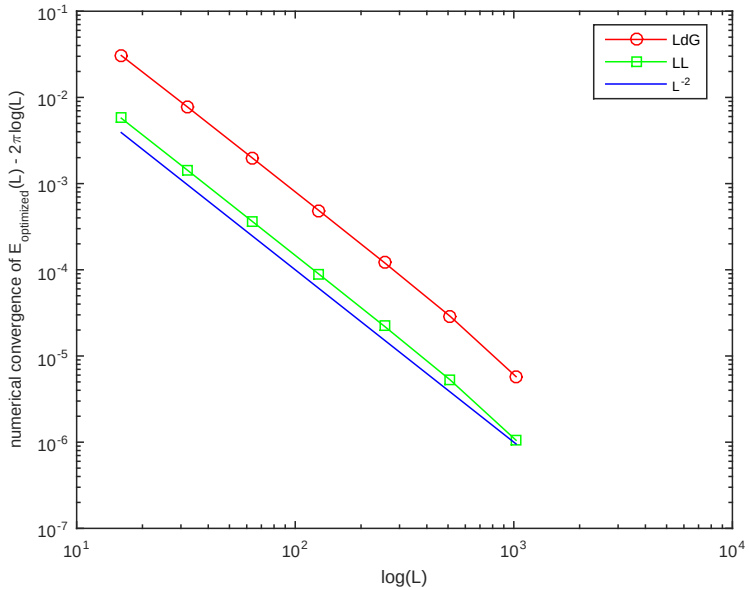


- L : element number (LdG) / molecule number (LL) in each direction.
- The matching coefficients are good.

Logarithmic Energy

- For the orthogonal boundary condition case, we have $E_{LL} \sim 2\pi \log L + \text{const}$, $E_{LdG} \sim 2\pi \log L + \text{const}$ numerically. This is well known as the singularity energy.





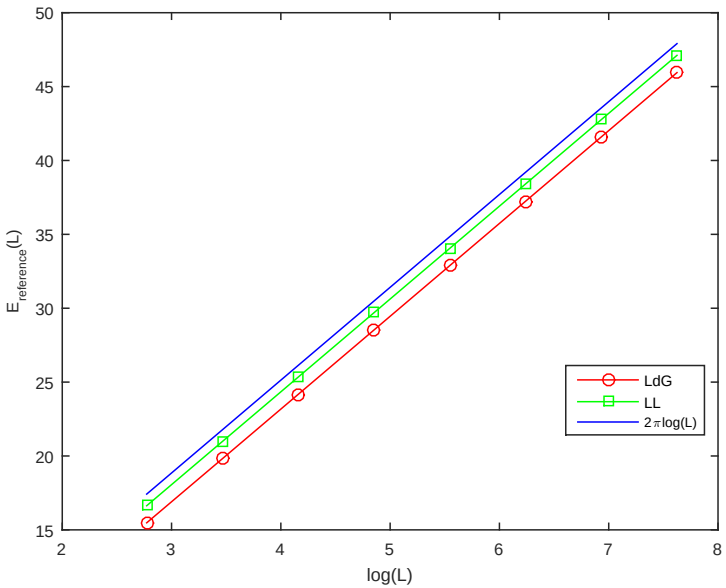
- How to define a well-posed reference energy is a problem (energy difference with respect to some reference configuration).

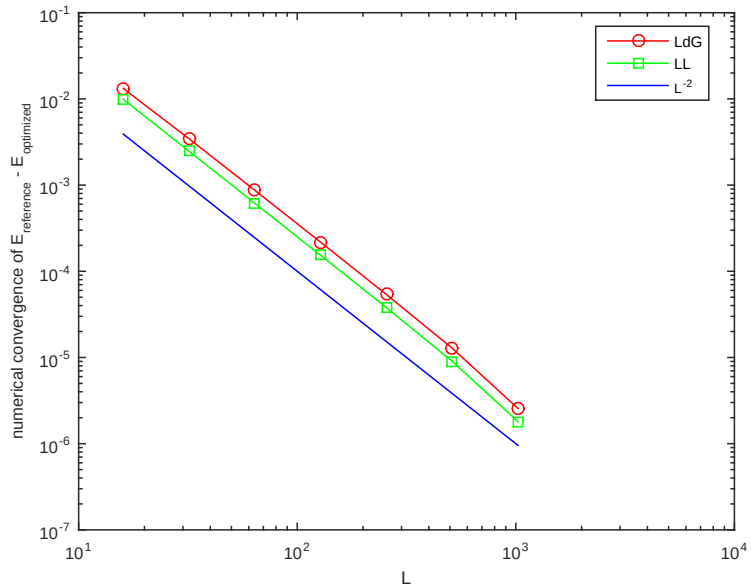
Reference Configuration

- On the domain $[0, D_1] \times [0, D_2]$, and for each on $\mathbf{x} = (x_1, x_2)$, we set the direction of this molecule in the reference configuration to be,

$$\mathbf{n} = \operatorname{atan2}\left(\min\left(x_2, D_2 - x_2\right), \min\left(x_1, D_1 - x_1\right)\right). \tag{23}$$

  $\operatorname{atan2}(Y, X)$ is the argument of the point (X, Y).
- We have $E_{reference}(L) \sim 2\pi \log(L) + \text{const.}$





- The reference configuration is good. The relative energy $E_{reference} - E_{optimized}$ is finite.

Blending Method

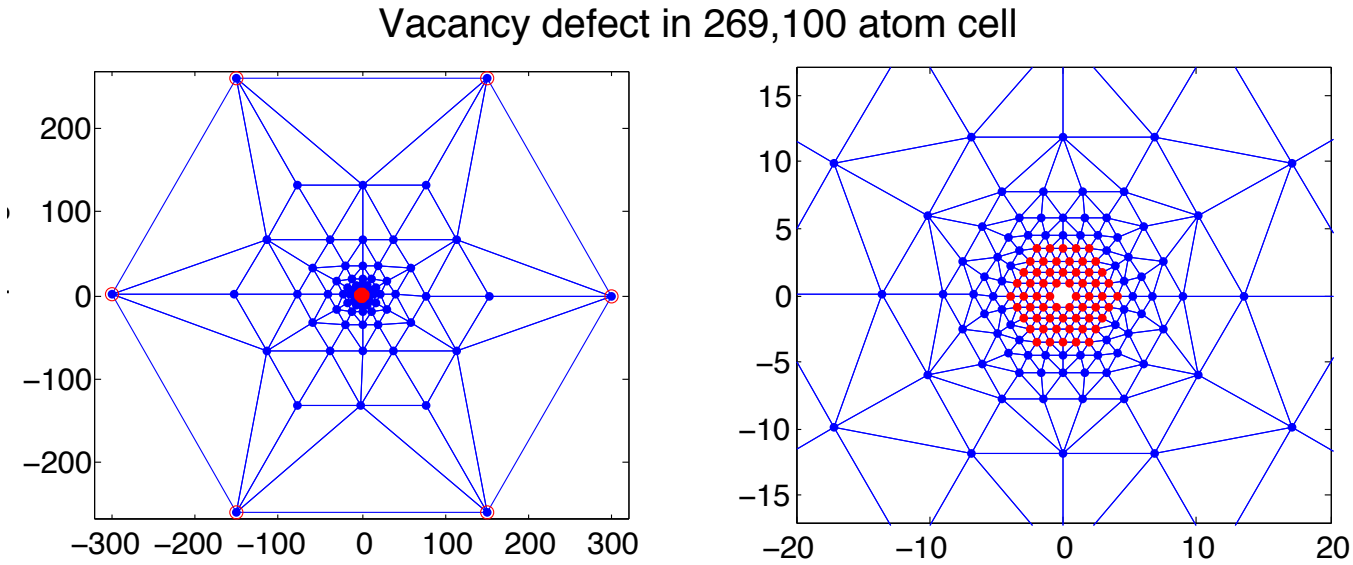
- Blending method is based on formulations which allow the superposition of different mechanical models [Dhi98].
- The blending function $\beta : \Omega \rightarrow [0, 1]$ is a weight function defined on the whole region Ω.
- The blending energy is,

$$E_{blending} = \int_{\Omega} \beta(x)\, I_{LdG}(x)\, \mathrm{d}x + \sum_{j \sim k} \left(1 - \bar{\beta}_{jk}\right) U_{LL}(n_j, n_k). \tag{24}$$

  We denote the continuum energy density by I_{LdG} and denote the pair potential energy by U_{LL}. We choose $\bar{\beta}_{jk}$ as an average of β on the bond $j \sim k$.
- We find the optimal configuration by minimizing the (relative) blending energy.

Blending Method in Atomistic\Continuum Coupling

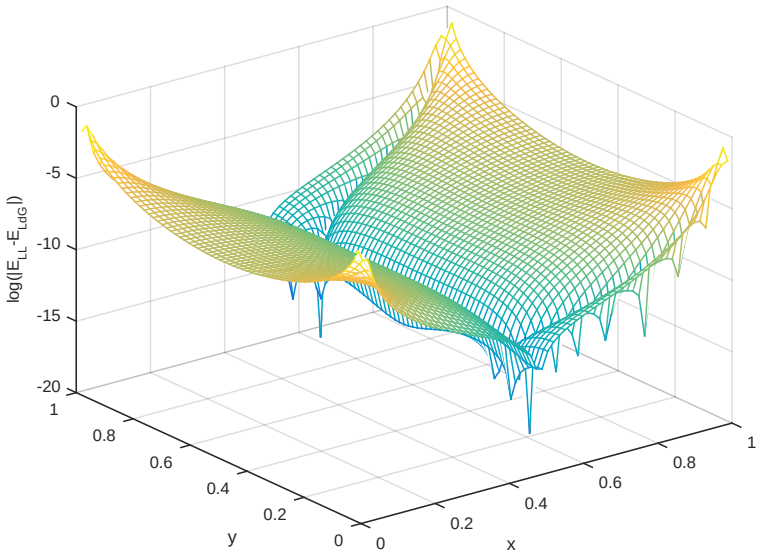
- A\C coupling for solid crystals:

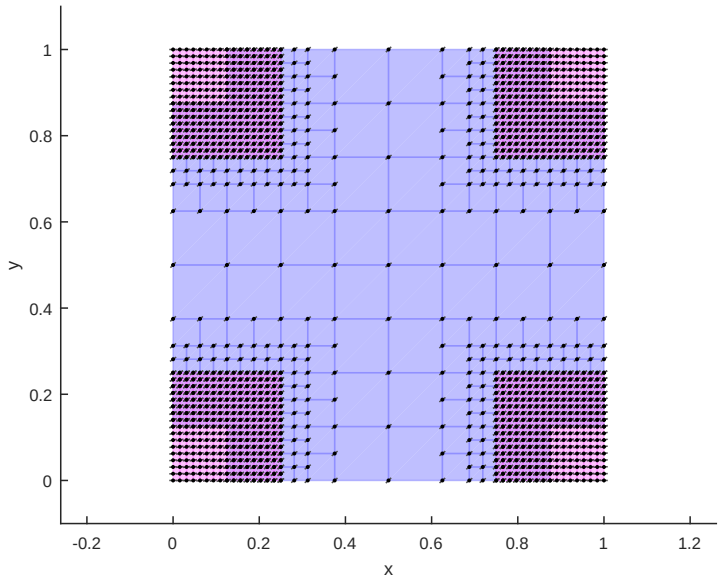


- Ghost forces appear on the interface, which contribute a constant to the consistency error. Blending method is a choice to reduce the ghost forces.
- BQCE: dominant error is $N^{\frac{1}{2}-\frac{2}{d}}$. [Li, et. al. 2016]
- BGFC: dominant error is $N^{-\frac{1}{2}-\frac{1}{d}}$ for P1 finite element and $N^{-\frac{1}{2}-\frac{2}{d}}$ for P2 finite element, which is optimal for coupling with Cauchy-Born continuum model. [Ortner, Zhang, 2016].

Graded Mesh and Blending Method

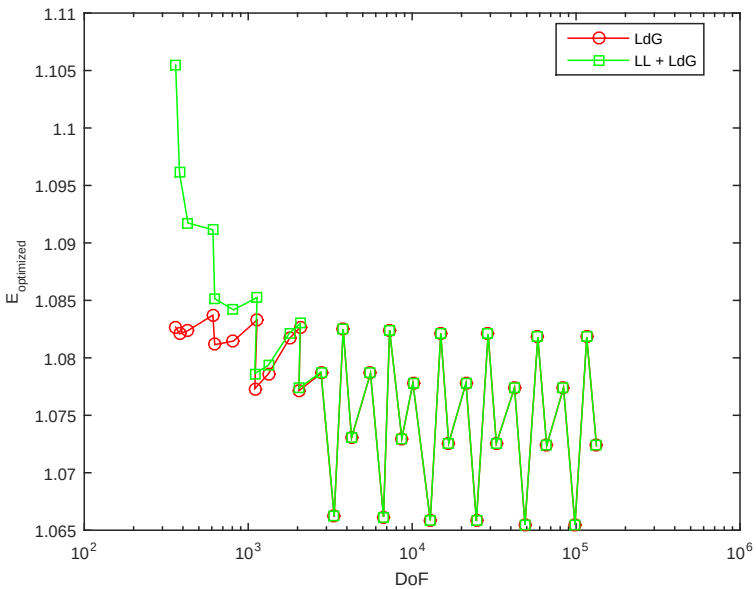
- We implement blending method (LL + LdG) for 2D problems.
- We construct graded meshes which are fine near the singularities and are coarse far away from the corners.

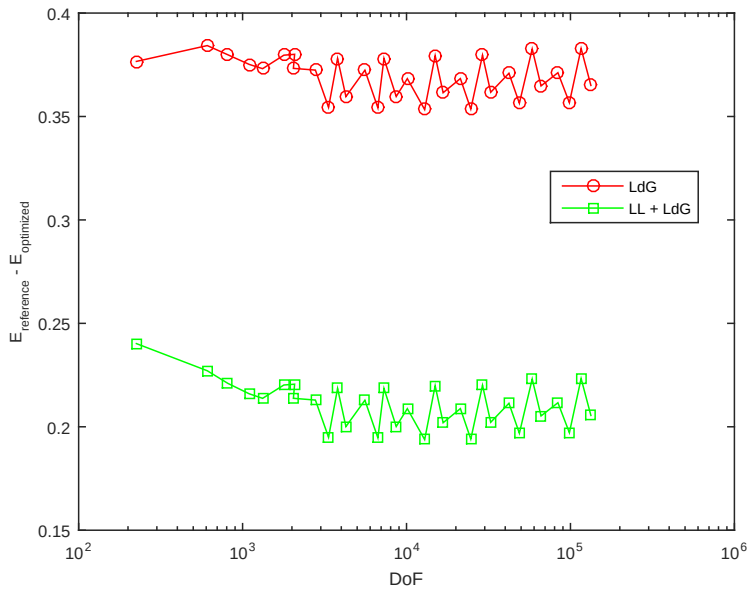




Energy on Graded Mesh

- For sine boundary condition, when we use the graded mesh, the optimized energy has a zigzag-shape for meshes with different sizes. The same phenomenon appears for the relative energy for orthogonal boundary condition.





- The zigzag-shape of the energy is the numerical artifact, which is due to the mesh we use, since it appears when solving Poisson equations on such meshes.

Summary

Future Work:

- Modify the mesh to get a better convergence.

Remained Questions:

- What is the thermodynamic limit for a molecular model for liquid crystal with defects?
- Is the (existing) continuum model the limit of some molecular model with respect to some small parameter?
- For liquid crystal, is there any nontrivial phenomena (e.g., defects) which can be discovered by molecular model but not by continuum model?

Thank you!

Any Question?

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