

London (dispersion) forces: longer separations, always attractive

Fluctuating dipole – fluctuating dipole model:

● elst. field $E \propto 1/r^3$

● induced dipole $\mu_{\text{ind}} \propto E$

● energy $u(r) \propto \mu E \propto 1/r^6$ (negative = attractive)

Repulsion at shorter separations:

A, B, C are positive constants

$$u(r) \propto e^{-Br}$$

Total: exp-6

also Buckingham, Born–Mayer(–Huggins), Tosi-Fumi, ... :

$$u(r) = Ae^{-Br} - \frac{C}{r^6}$$

Component of *any* atom–atom interaction

NB: “ \propto ” = “is proportional to”

Repulsive forces approximated:

$$Ae^{-Br} \rightarrow \frac{A'}{r^{12}}$$

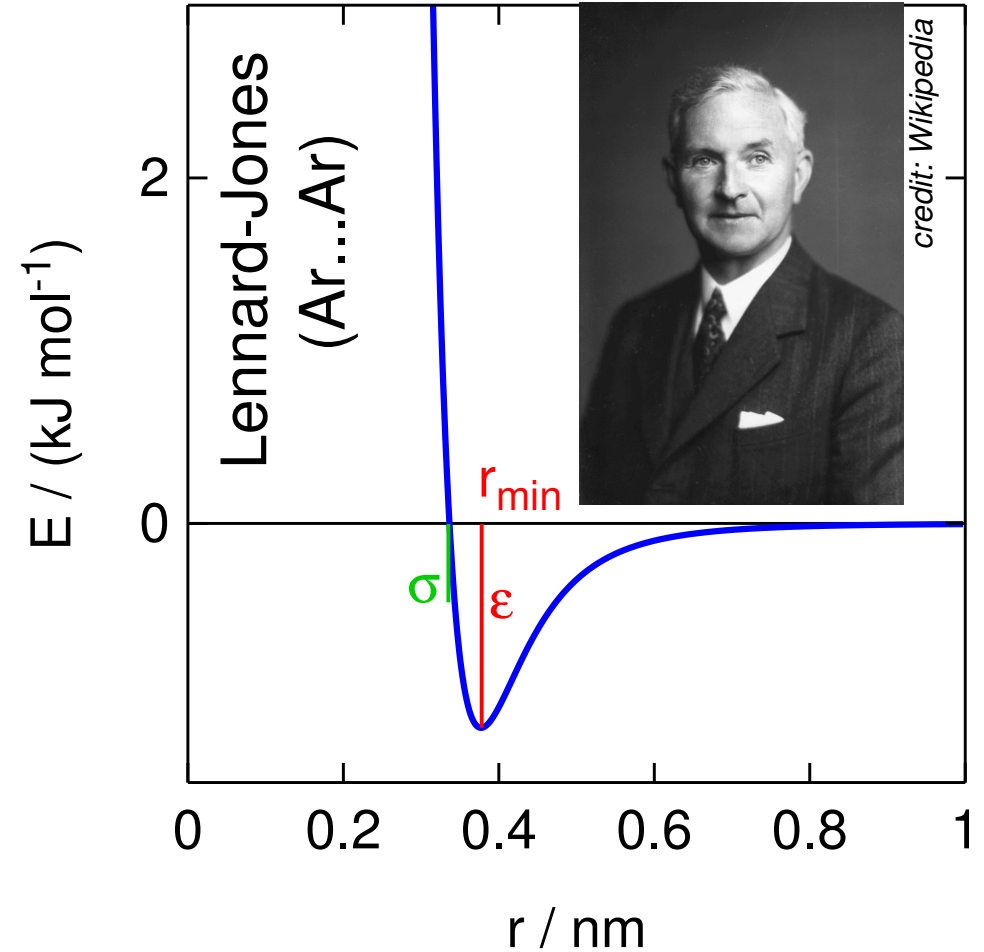
● Common formula:

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

$$E_{\min} = -\epsilon, r_{\min} = 2^{1/6}\sigma$$

● Optional formula:

$$u(r) = E_{\min} \left[2 \left(\frac{r_{\min}}{r} \right)^6 - \left(\frac{r_{\min}}{r} \right)^{12} \right]$$



... e.g., Ar

Approximation of **pair additivity**, accuracy $\approx 90\%$

$$E_{\text{pot}} = \sum_{ij} u(r_{ij})$$

Better:

$$E_{\text{pot}} = \sum_{ij} u(r_{ij}) + \sum_{ijk} u_3(r_{ij}, r_{ik}, r_{jk})$$

where

$$u_3(r_{ij}, r_{ik}, r_{jk}) = u(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) - u(r_{ij}) - u(r_{ik}) - u(r_{jk})$$

- charge–charge (ions)

$$U = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$

- partial charges:

such charges placed at nuclei so that their electric field approximates well the real one

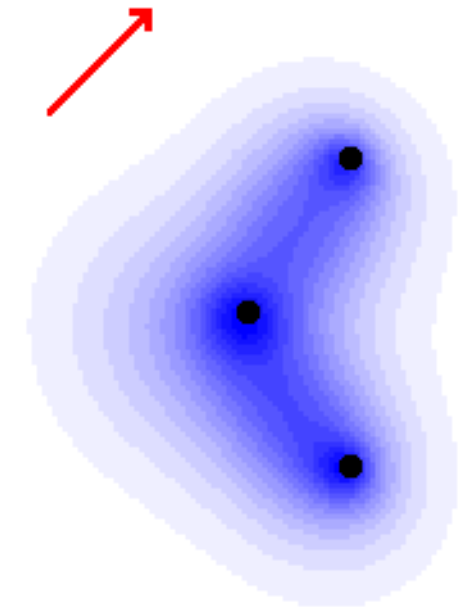
- dipole moment

$$\vec{\mu} = \sum_i q_i \vec{r}_i$$

- polarizability (el. field induces a dipole)

$$\vec{\mu}_{\text{ind}} = \alpha \vec{E}$$

(is not pair additive)



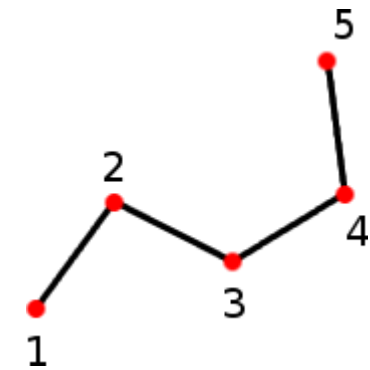
Force field

Force field = PES as a sum of contributions, comprises their functional forms and tables of parameters

Small molecules: rigid, rotations (water, CO, CH₄)

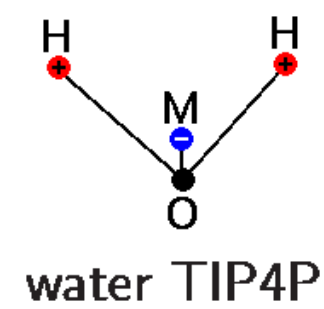
Large molecules: many terms

- bonded forces: vibrating bonds (1–2), angles (1–3) torsions (1–4) and dihedral potentials
- non-bonded forces (partially 1–4, 1–more): Lennard-Jones etc., charge–charge



Models:

- full-atom
 - united-atom (-CH₃, -CH₂-, etc.)
 - auxiliary interaction centers (TIP4P)
 - coarse-grained
- } atomistic



Harmonic approximation:

$$U = K(r - r_0)^2$$

optionally:

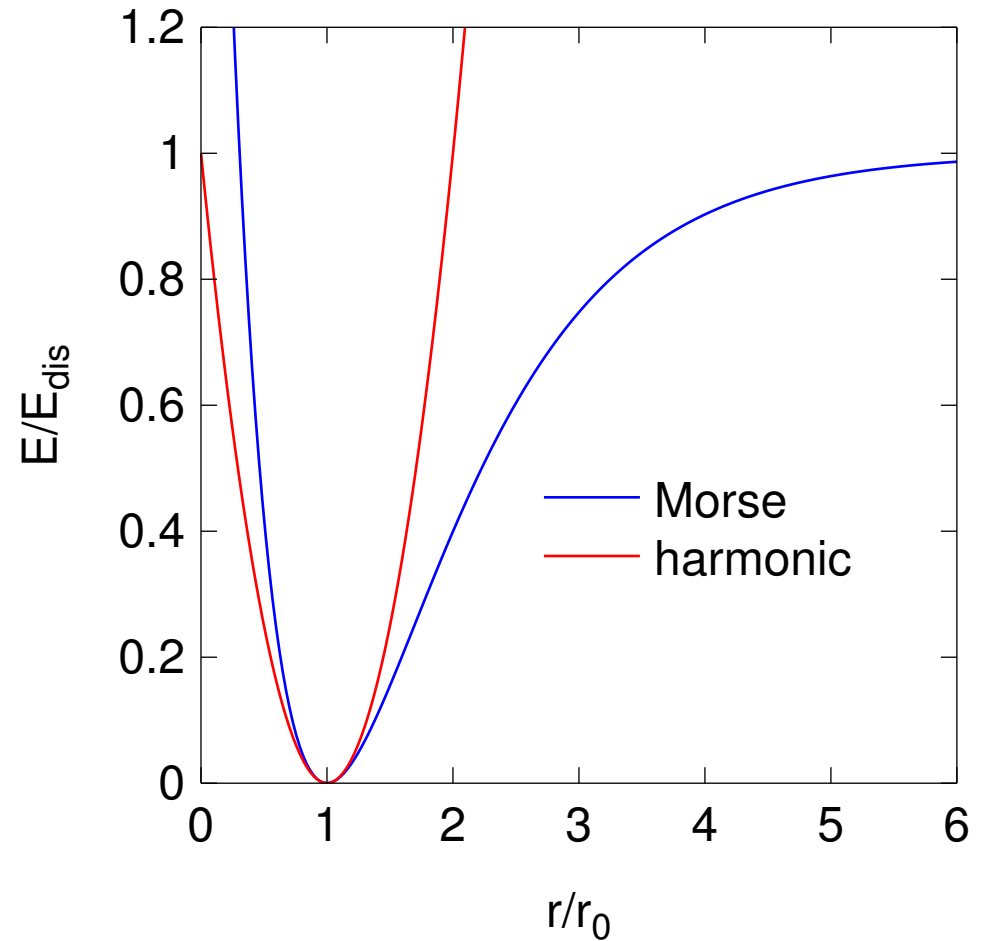
$$U = \frac{K'}{2}(r - r_0)^2$$

Fixed bond length:

$$r = r_0$$

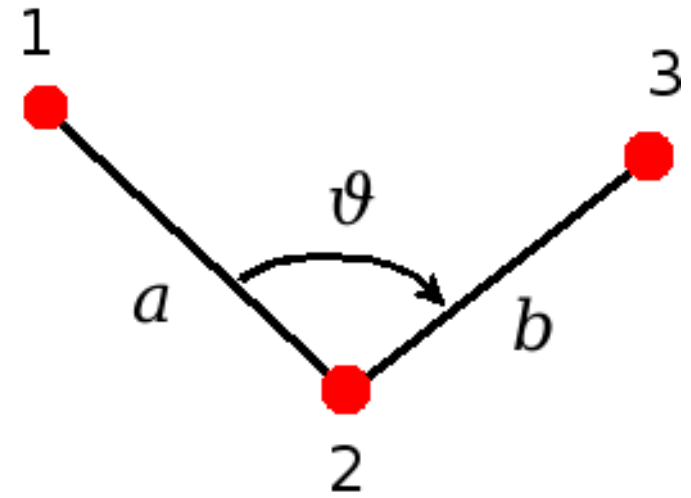
Morse (dissociation):

$$U = E_{\text{dis}} \left[1 - e^{-\alpha(r-r_0)} \right]^2$$



Harmonic approximation:

$$U(\vartheta) = K_{\text{harm}}(\vartheta - \vartheta_0)^2$$



Dihedral potential (proper torsion)

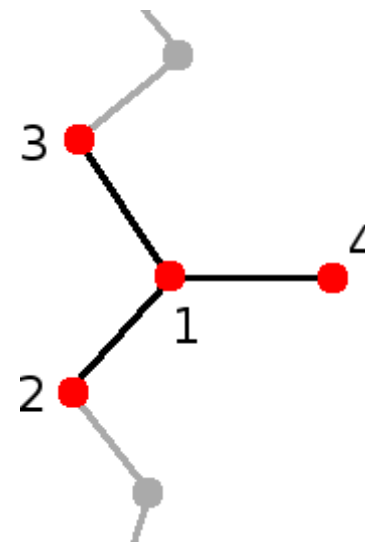
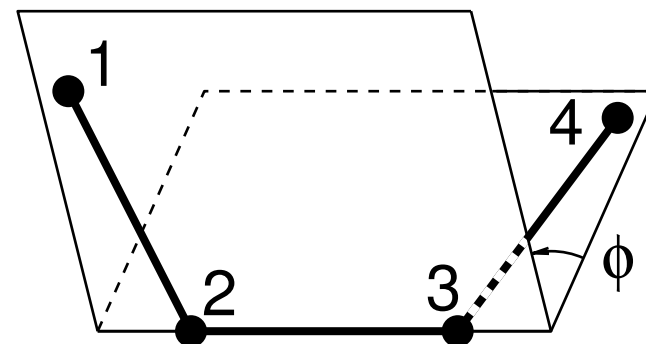
$$U(\phi) = \sum_n K_n \cos(n\phi)$$

Non-bonded 1-4 terms scaled down by certain q (often $q = 0.5$) are usually added. Note that the total dihedral potential is a sum of $U(\phi)$ and 1-4.

To keep the aromatic ring planar:

$$U(\phi) = \sum_n K_0 \phi^2$$

Improper torsion – keep $>C=O$ etc. planar:
the same form, different order of atoms



Lennard-Jones is defined by σ_i, ϵ_i . The energy of two identical atoms is

$$u_{ii}(r) = 4\epsilon_i \left[\left(\frac{\sigma_i}{r} \right)^{12} - \left(\frac{\sigma_i}{r} \right)^6 \right]$$

But what about two different atoms? (There are $\binom{N}{2}$ pairs!).

Lorentz-Berthelot combining rule (geometric mean for energy, arithmetic mean for diameters, better for vapor-liquid equilibria):

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}, \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$

Geometric rule (better for crystals):

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}, \quad \sigma_{ij} = \sqrt{\sigma_i \sigma_j}$$

... more exist.

- geometry: spectroscopy, diffraction, quantum chemistry calculations (*ab initio*, DFT)
- bonded forces: quantum chemistry calculations, spectroscopy
- Lennard-Jones σ : experimental density, structure
- Lennard-Jones ϵ : vaporization enthalpy

$$\langle U_{\text{pot, intermol.}} \rangle = \Delta_{\text{vap}}U \approx \Delta_{\text{vap}}H - nRT$$

- repulsions more precisely: compressibility, elastic moduli in crystals
- partial charges:
 - dipole moments: spectroscopy, permittivity (dielectric constant)
 - quantum chemistry calculations (Mulliken, CHELPG = CHarges from Electrostatic Potentials using a Grid based method)
- and/or clusters (by quantum chemistry)
- polarizability: experiment, quantum chemistry calculations
- fine-tuning (of partial charges etc.): diffusivity
- structure (radial distribution functions); reverse MC

Electrostatic, gravitational ...

Walls, pores:

● made of atoms

● hard wall

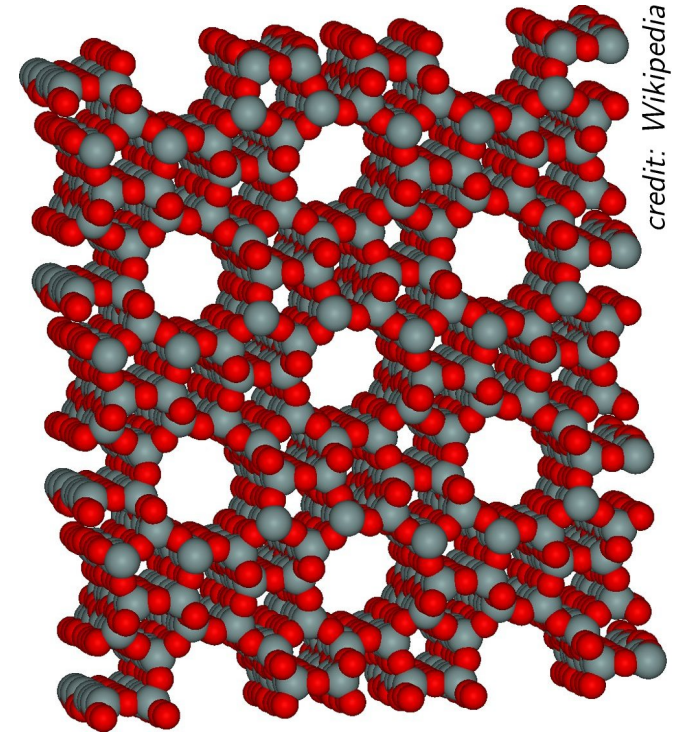
$$U_{\text{hard wall}}(\vec{r}) = \begin{cases} \infty, & \text{for } z < 0, \\ 0 & \text{for } z \geq 0 \end{cases}$$

● integrated (soft) wall of number density* $\mathcal{N} = N/V$

$$U_{\text{soft wall}}(\vec{r}) = \mathcal{N} \int_{z' > 0} u(\vec{r} + \vec{r}') d\vec{r}' = \mathcal{N} \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_0^{\infty} dz' u(\vec{r} + \vec{r}')$$

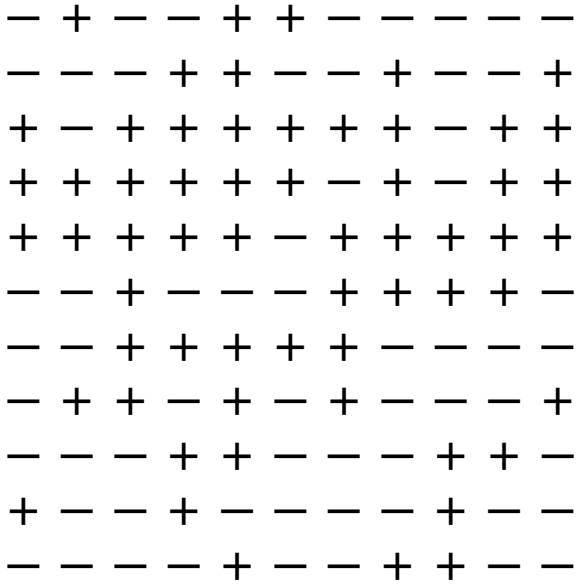
Lennard-Jones \rightarrow 3-9 potential

$$U_{\text{LJ-wall}}(\vec{r}) = -2\pi\epsilon\mathcal{N}\sigma^3 \left[\frac{1}{3} \left(\frac{\sigma}{z} \right)^3 - \frac{2}{45} \left(\frac{\sigma}{z} \right)^9 \right]$$



credit: Wikipedia

*also denoted ρ or n



Ferromagnet:

$$U = -J \sum_{\langle i,j \rangle} s_i s_j + h \sum_i s_i$$

$$s_i \in \{-1, +1\} = \{\downarrow, \uparrow\}$$

J = interaction constant:

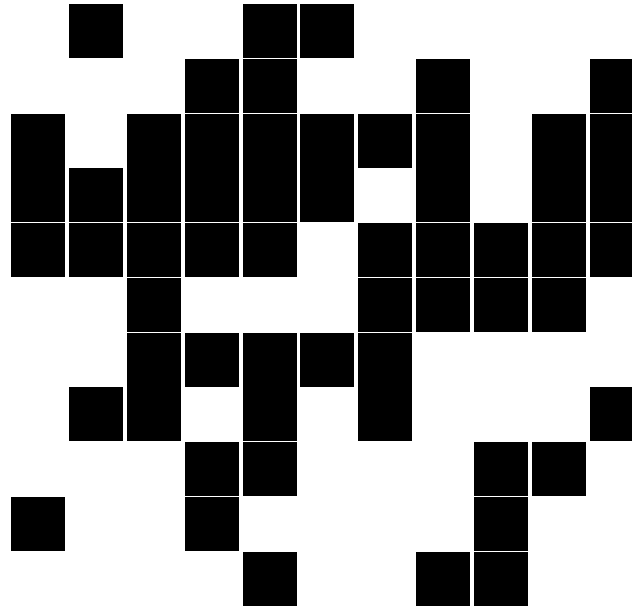
$J > 0$: ferromagnet,

$J < 0$: antiferromagnet

h = magnetic field intensity

Critical (Curie) point: $h_c = 0$;

2D: $T_c/J = 2/\ln(1 + \sqrt{2})$



Lattice gas:

$$U = -\epsilon \sum_{\langle i,j \rangle} n_i n_j + \mu \sum_i n_i$$

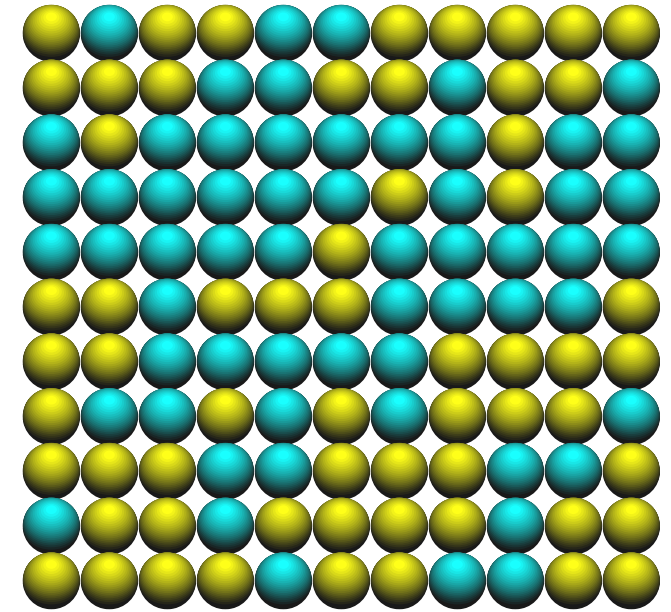
$$n_i \in \{0, 1\} = \{ \text{white square}, \text{black square} \}$$

ϵ = attraction constant

μ = chemical potential

Equivalence:

$$n_i = (1 + s_i)/2$$



Binary alloy:

$$U = - \sum_{\langle i,j \rangle} \epsilon_{k_i k_j} + \sum_i \mu_{k_i}$$

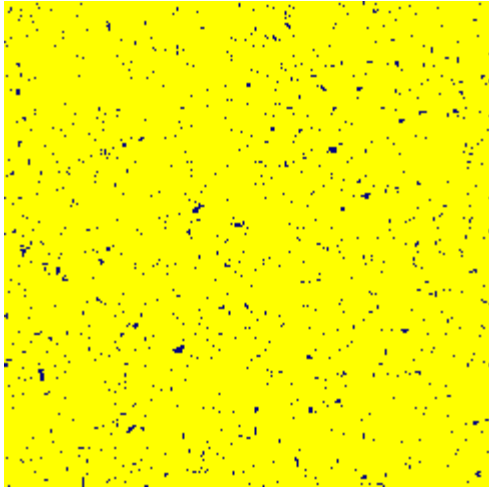
$$k_i \in \{\text{blue sphere}, \text{yellow sphere}\}$$

$\epsilon_{\text{blue,blue}}, \epsilon_{\text{blue,yellow}}, \epsilon_{\text{yellow,yellow}}$ = nearest-neighbor interactions

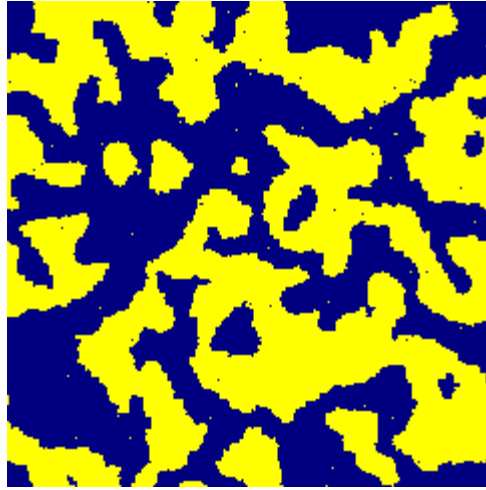
$\mu_{\text{blue}}, \mu_{\text{yellow}}$ = chem. potentials

Equiv.: $n_i = 0 \sim k_i = \text{blue sphere}$

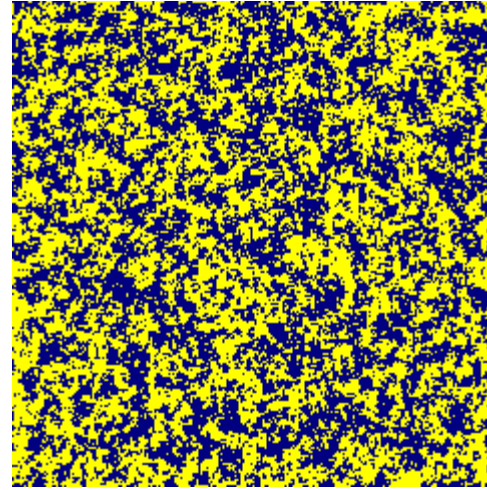
$n_i = 1 \sim k_i = \text{yellow sphere}$.



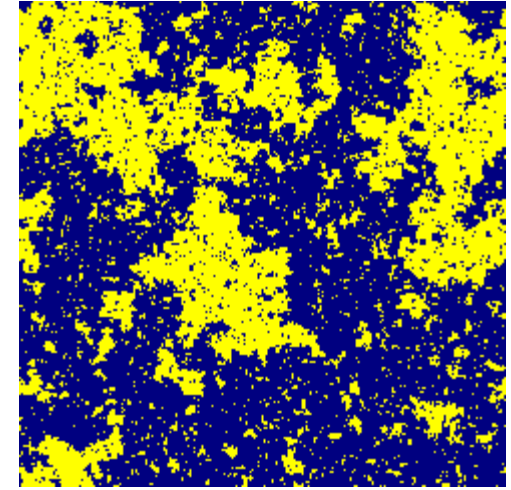
low temperature
 $0.8T_{\text{crit}}$



quenched system
 $5T_{\text{crit}} \rightarrow 0.5T_{\text{crit}}$



high temperature
 $1.25T_{\text{krit}}$

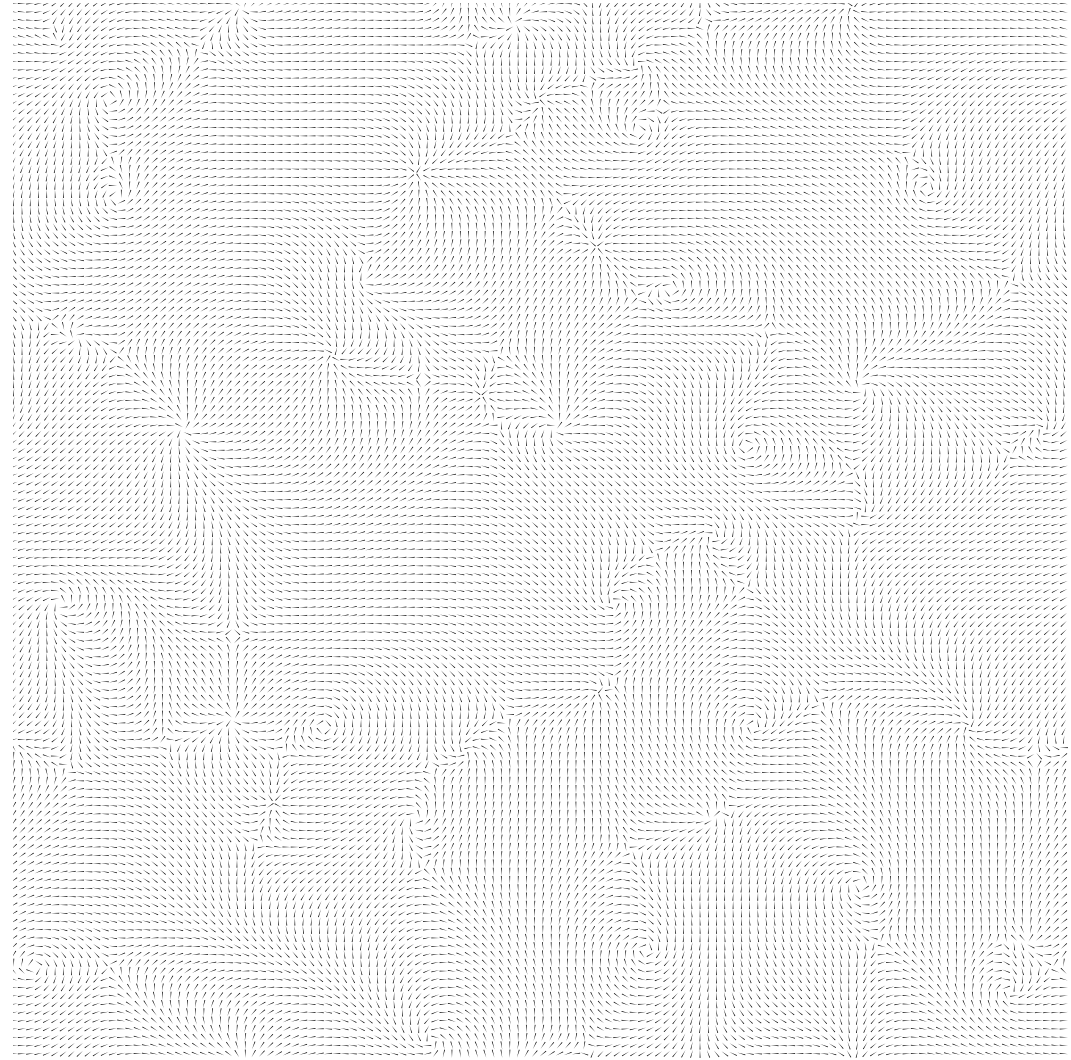
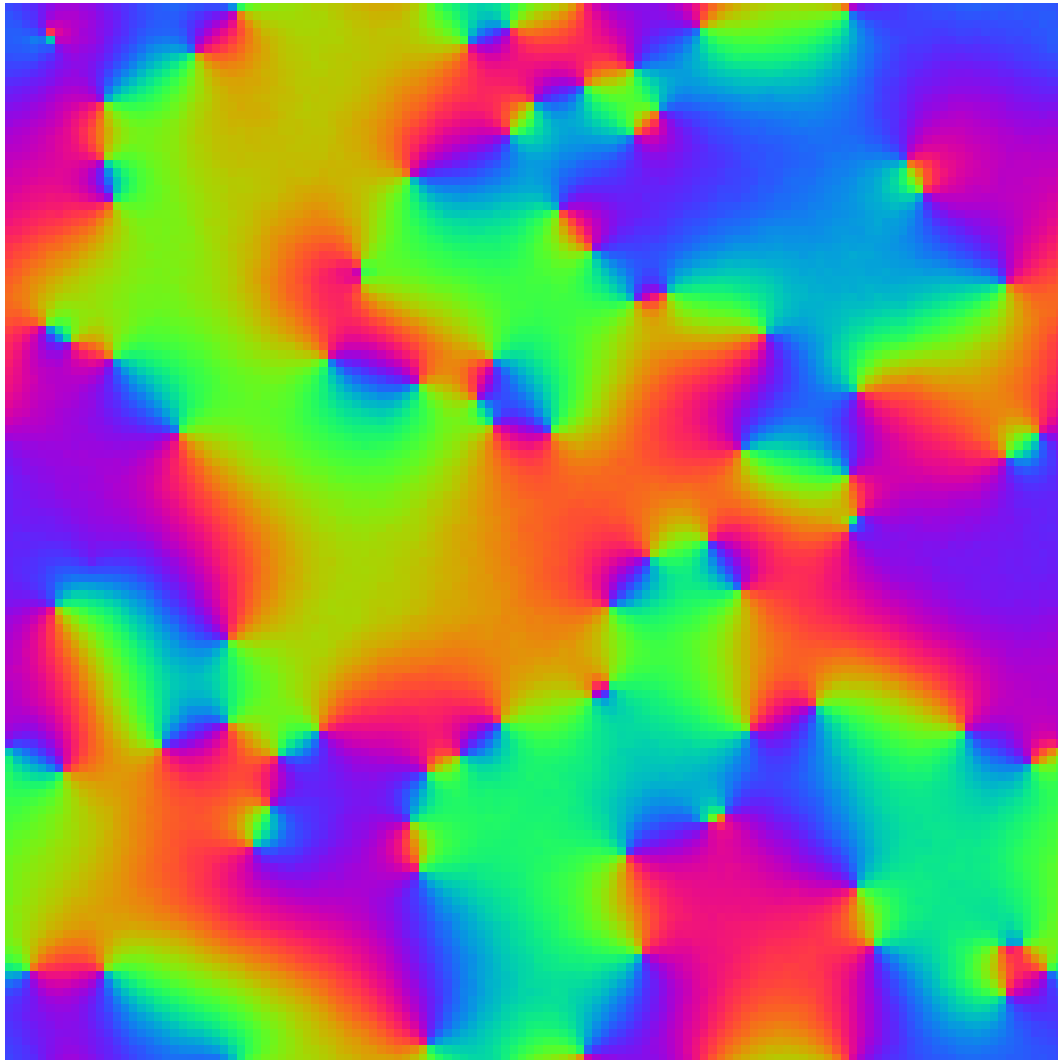
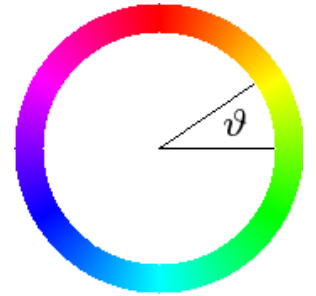


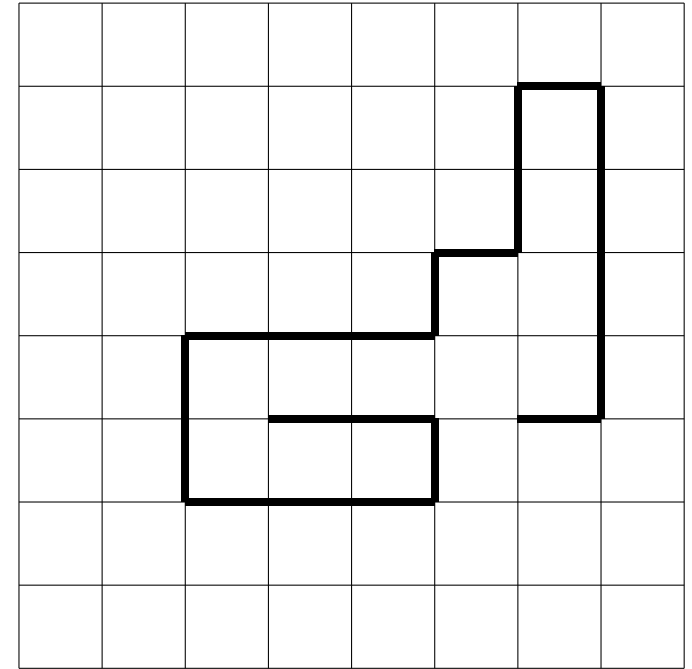
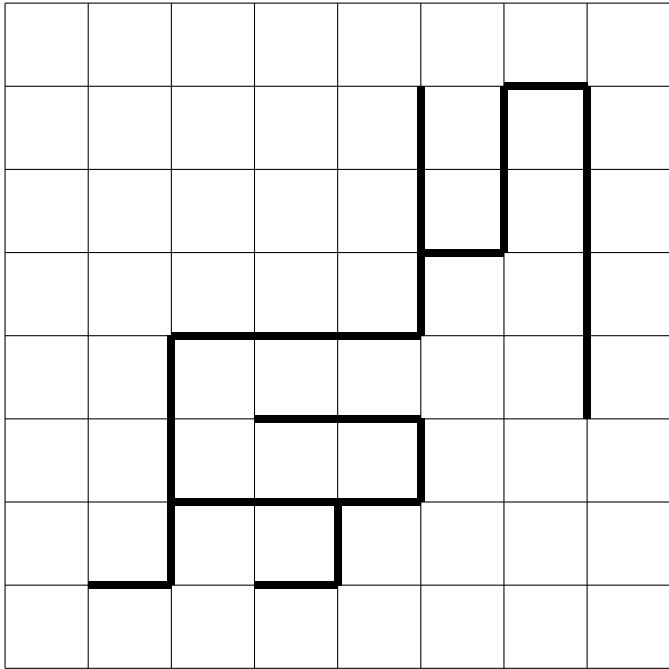
critical point
 T_{crit}

Lattice models: XY

Site $i \mapsto$ continuous 2D “spin” $\vartheta_i \in [0, 2\pi)$ ■ = 0° , ■ = 120° , ■ = 240°

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \cos(\vartheta_i - \vartheta_j) + h \sum_i \cos(\vartheta_i)$$





no branching = self-avoiding random walk