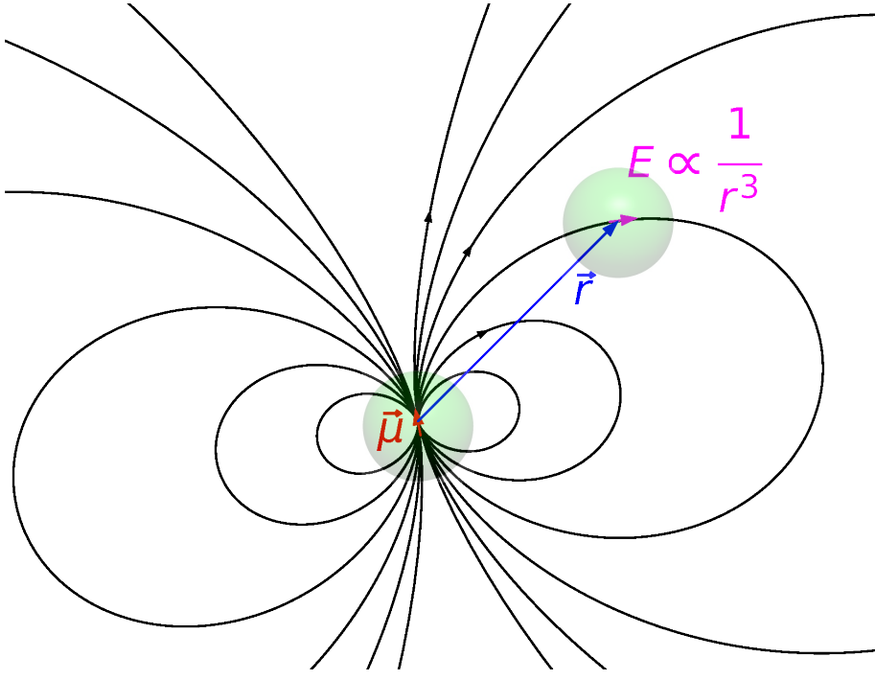
Potential energy atom–atom

London (dispersion) forces: longer separations, always attractive

Fluctuating dipole – fluctuating dipole model:

- electrostatic 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:

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

Total: exp-6

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

$$u(r) = A\mathrm{e}^{-Br} - \frac{C}{r^6}$$

"$\propto$" = "is proportional to"

A, B, C are positive constants

Component of **any** atom–atom interaction

Lennard-Jones potential

Repulsive forces approximated:

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

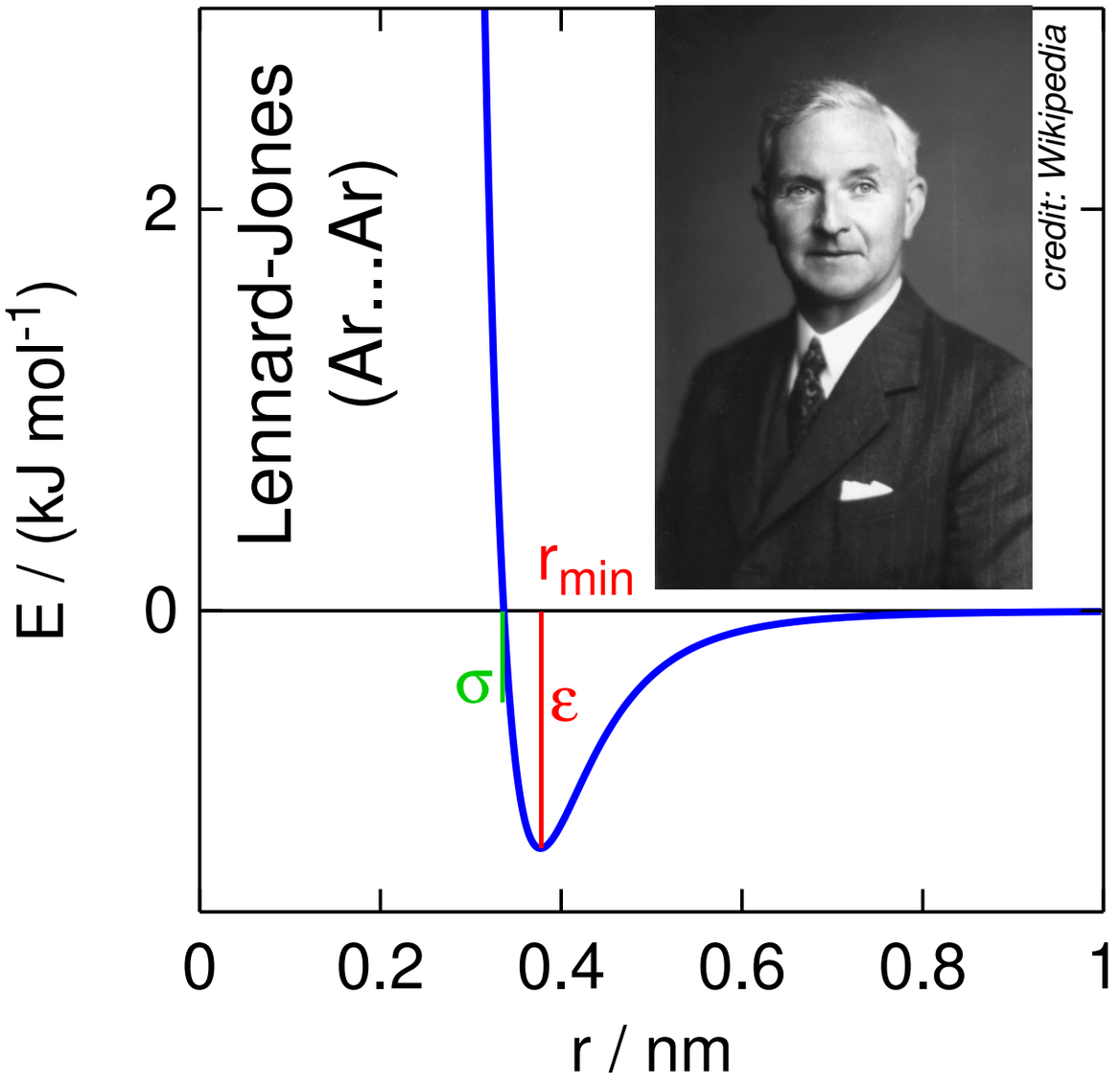
- Common formula:

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

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

- Optional formula:

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



Many molecules

. . . e.g., liquid Ar

Approximation of **pair additivity**, accuracy ≈ 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

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

Electrostatic forces

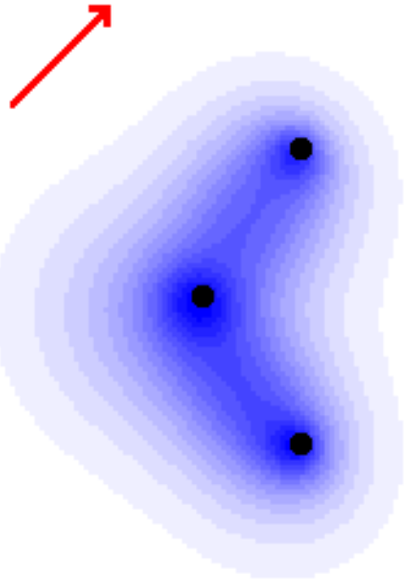
- charge–charge (ions)

$$F_{ij} = \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}^2}$$

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

- 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 (electric field induces a dipole)

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

(is not pair additive)

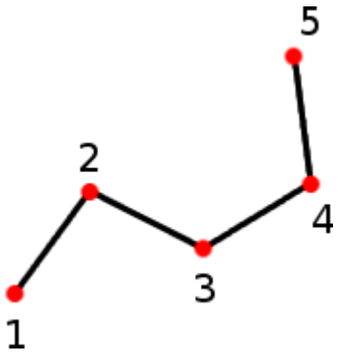
Force field

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

Small molecules: rigid, rotations (water, CO, CH_4)

Large molecules: many terms

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

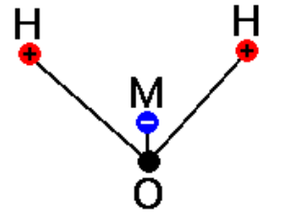


Models:

- full-atom
- united-atom (-CH_3, -CH_2-, etc.)
- auxiliary interaction centers (TIP4P)

} atomistic

- coarse-grained



water TIP4P

Bonded forces – bonds

Harmonic approximation:

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

optionally:

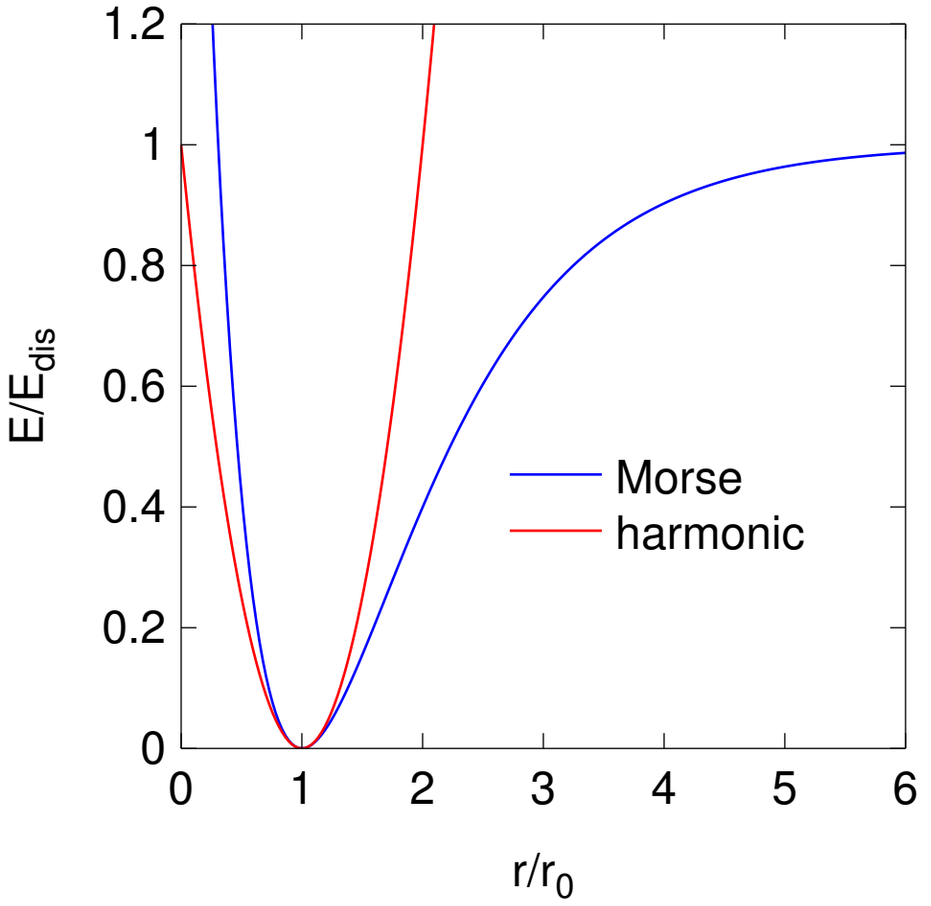
$$U = \frac{K'}{2}(r - r_0)^2$$

Fixed bond length:

$$r = r_0$$

Morse (dissociation):

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



Example: Which K in the harmonic approximation corresponds to the Morse potencial at small amplitudes?

$E_{\mathrm{dis}}a^2$

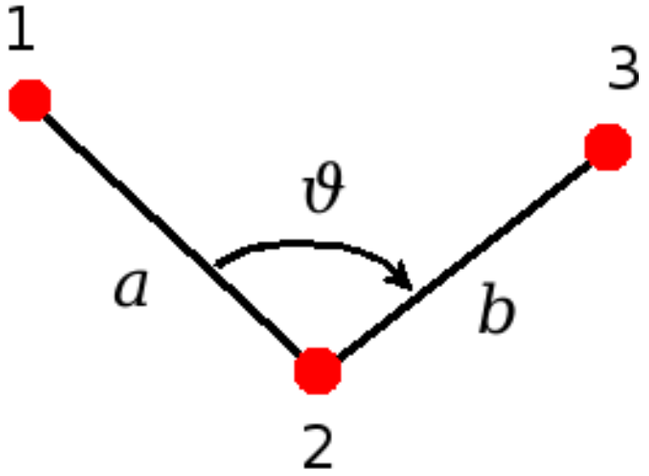
Bonded forces – angles

Harmonic approximation:

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

Urey–Bradley:

$$U(\vartheta) = K_{\mathrm{UB}}(|\vec{r}_1 - \vec{r}_3| - s)^2$$



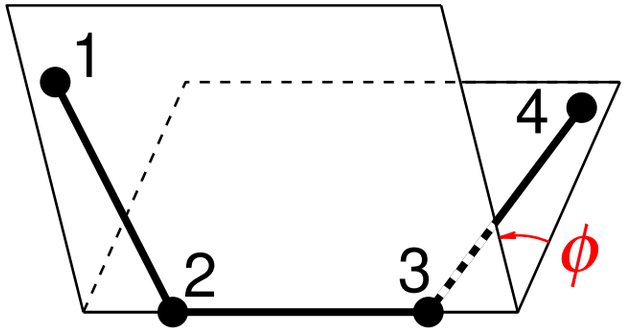
+ **Example:** Both formulas are equivalent if the amplitudes are small. How are both constants related? Hint: remember the l'Hôpital's rule.

$$K_{\mathrm{harm}} = K_{\mathrm{UB}}\left[\frac{ab}{s}\sin\vartheta_0\right]^2$$

Bonded forces – torsions

Dihedral potential (proper torsion)

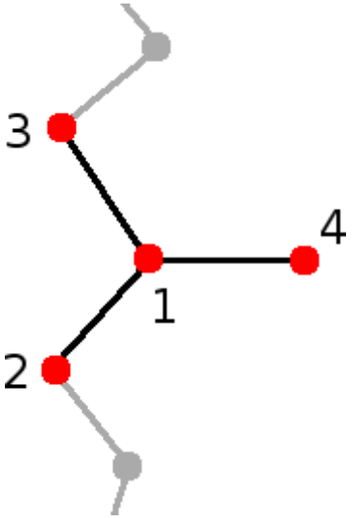
$$U(\phi) = \sum_n K_n \cos(n\phi)$$



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

United-atom group CH: we need to keep tetrahedrality around C:

$$U(\phi) = \sum_n K_0 [\phi - \arcsin(1/\sqrt{3})]^2$$

Non-bonded forces: Combining rules

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):

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

- Of course, more rules exist.
- Sometimes a **non-bonded fix** has to be used instead of a combining rule.

Force field development

- geometry: spectroscopy, diffraction, quantum chemistry calculations
- bonded forces: quantum chemistry calculations, spectroscopy
- Lennard-Jones σ: experimental density, structure
- Lennard-Jones ϵ: vaporization enthalpy

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

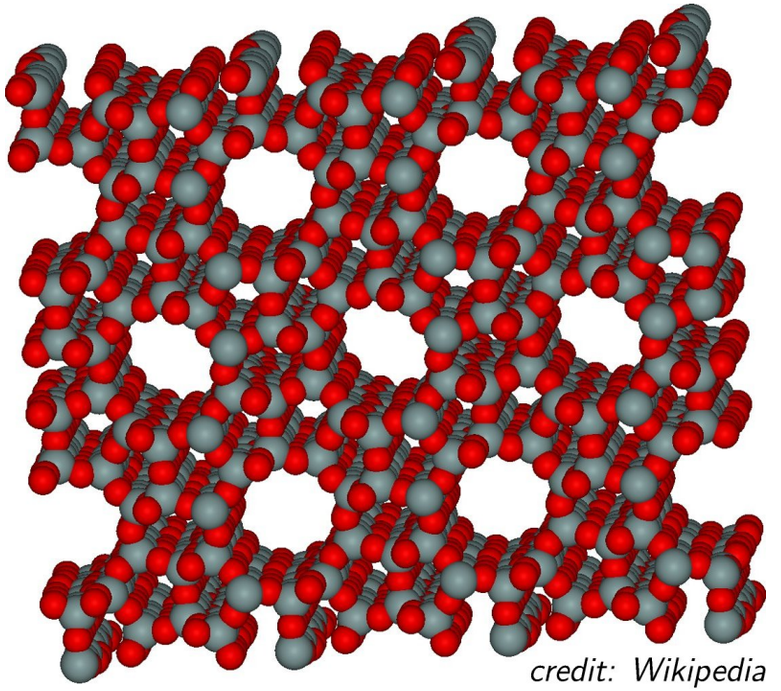
- repulsions more precisely: compressibility, elastic moduli in crystals
- partial charges:
  - dipole moments: spectroscopy, permittivity (dielectric constant)
  - quantum chemistry calculations (Mulliken, CHELPG = CHarges from Electrostatic Potentials using a Grid based method)
- and/or clusters (by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

External forces

Electrostatic, gravitational . . .

Walls, pores:

- made of atoms (e.g., zeolite)



credit: Wikipedia

- 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* $\mathcal{N} = N/V$

$$U_{\text{soft wall}}(\vec{r}) = \mathcal{N} \int_{z'>0} u(\vec{r}+\vec{r}')\mathrm{d}\vec{r}' = \mathcal{N} \int_{-\infty}^{\infty} \mathrm{d}x' \int_{-\infty}^{\infty} \mathrm{d}y' \int_{0}^{\infty} \mathrm{d}z' u(\vec{r}+\vec{r}')$$

Lennard-Jones 12-6 → 9-3:

each $\int$ reduces the power by 1

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

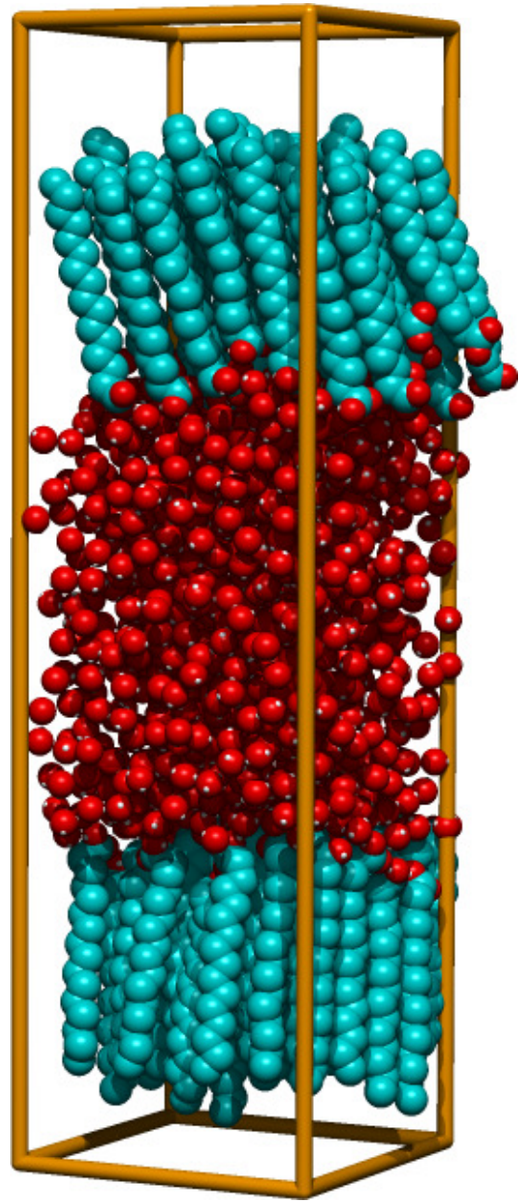
*also denoted ρ or n

Boundary conditions

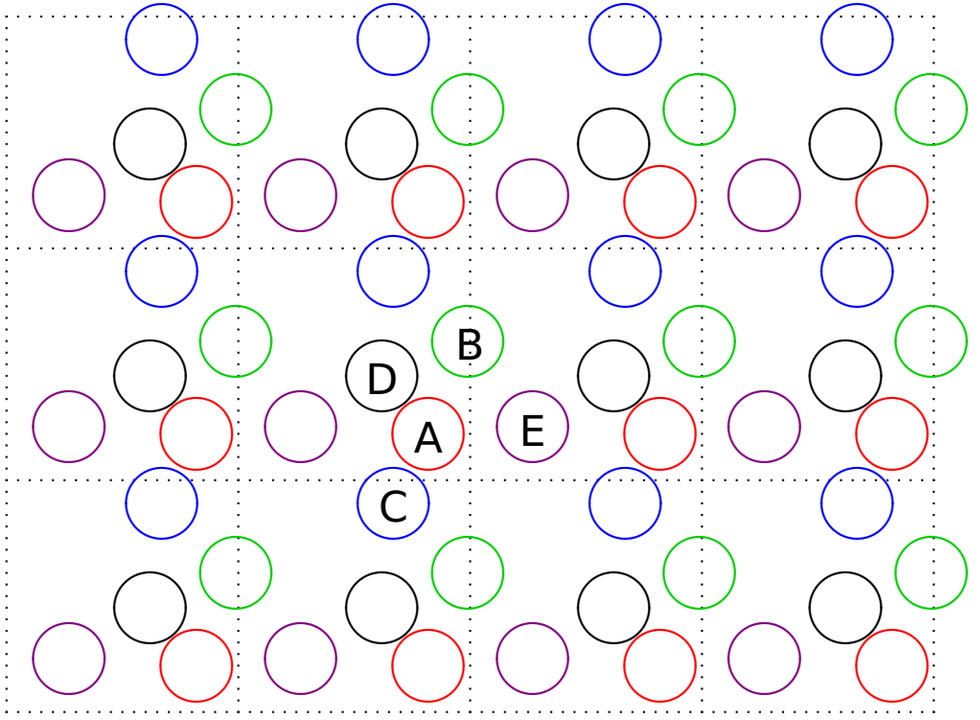
- vacuum (free, Cartesian): droplet, protein in a vacuum . . .

free surface or hard walls ⇒ large surface effects

1000 molecules in a cube 10^3 ⟶ $8^3 = 512$ are “inside”



- “strange flask”: periodic boundary conditions (also cyclic, torroidal)



- periodic in some coordinates only: pores, slabs, . . .

Ted Chiang: *Tower of Babylon*

Periodic boundary conditions: MD


```
REAL L edge size of the cubic simulation box (cell)
VECTOR r1, r2 where vector r = (r.x,r.y,r.z)
              both vectors must lie in the basic box
VECTOR dr := r2 - r1 difference of vectors
                    (ignoring the boundary conditions)

IF      dr.x < -L/2 THEN dr.x := dr.x + L
ELSE IF dr.x >  L/2 THEN dr.x := dr.x - L

IF      dr.y < -L/2 THEN dr.y := dr.y + L
ELSE IF dr.y >  L/2 THEN dr.y := dr.y - L

IF      dr.z < -L/2 THEN dr.z := dr.z + L
ELSE IF dr.z > -L/2 THEN dr.z := dr.z - L
Vector dr now goes from r1 to the nearest image of r2

Squared distance to the nearest image:
REAL rr := dr.x**2 + dr.y**2 + dr.z**2
```

Periodic boundary conditions: MC

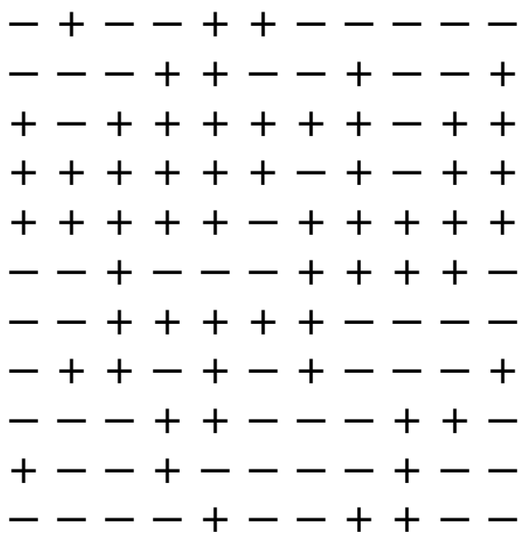
In MC, usually the vector $\vec{r}_{12} = \mathrm{r2} - \mathrm{r1}$ is not needed, the distance is enough

```
REAL L edge size of the cubic simulation box (cell)
VECTOR r1, r2 where vector r = (r.x,r.y,r.z)
              both vectors must lie in the basic box
VECTOR dr := r2 - r1 difference of vectors
                     (ignoring the boundary conditions)

REAL rr := (L/2 - abs(L/2-abs(dr.x)))**2
         + (L/2 - abs(L/2-abs(dr.y)))**2
         + (L/2 - abs(L/2-abs(dr.z)))**2
```

Lattice models: Ising

ferromagnet



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

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

J = interaction constant:

$J > 0$: ferromagnet,

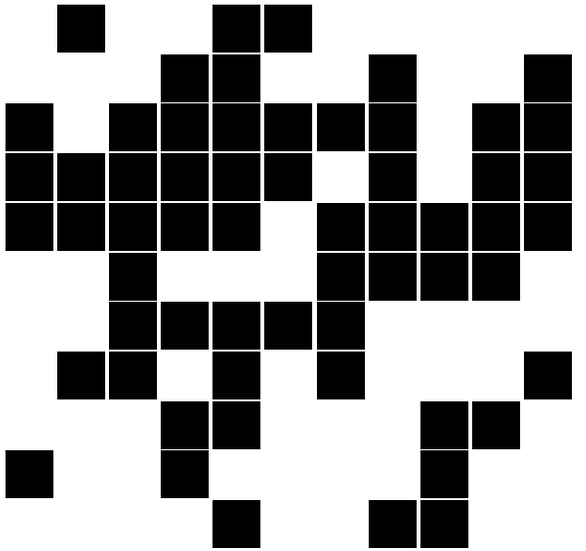
$J < 0$: antiferromagnet

h = magnetic field intensity

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

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

lattice gas



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

$$n_i \in \{0, 1\} = \{\ \ , \blacksquare\}$$

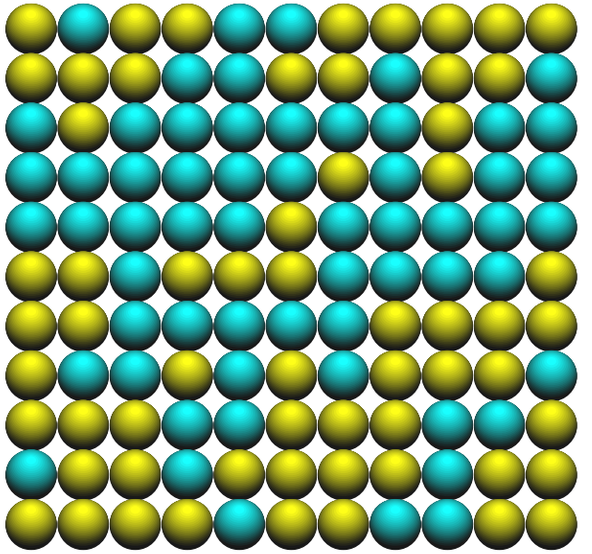
ϵ = attraction constant

μ = chemical potential

Equivalence:

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

binary alloy



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

$$k_i \in \{\bullet, \bullet\}$$

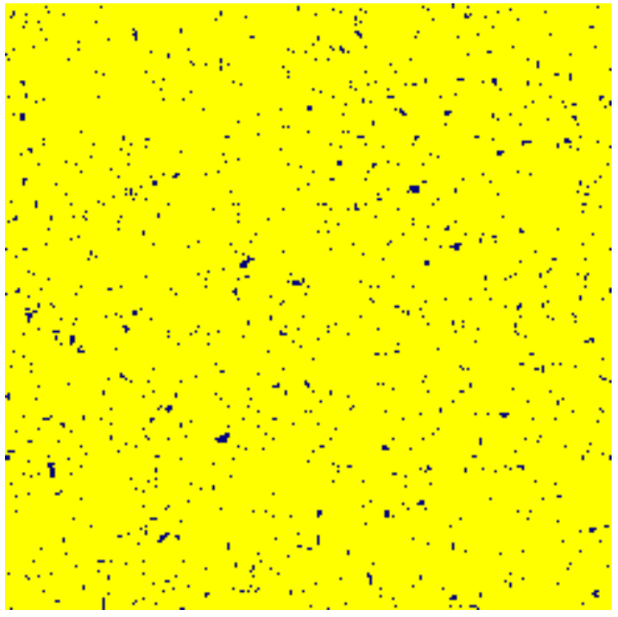
$\epsilon_{\bullet,\bullet}$, $\epsilon_{\bullet,\bullet}$, $\epsilon_{\bullet,\bullet}$ = interactions of nearest neighbors

$\mu_{\bullet}$, $\mu_{\bullet}$ = chem. potentials

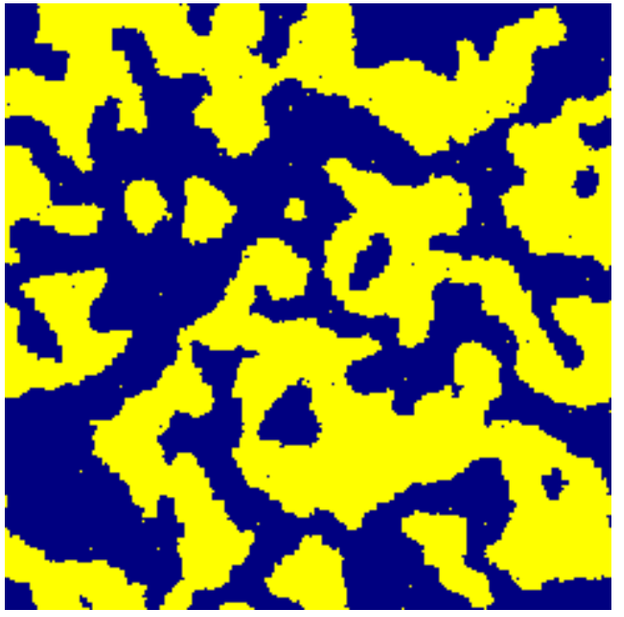
Equivalence: $n_i = 0 \sim k_i = \bullet$

$n_i = 1 \sim k_i = \bullet$

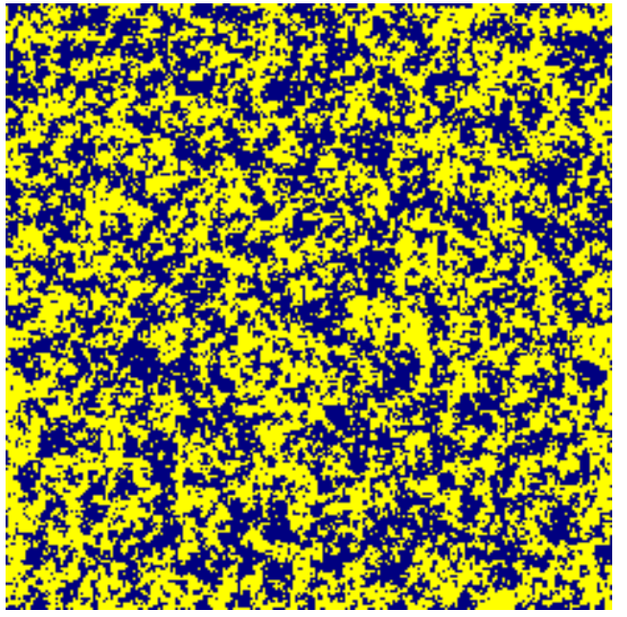
Ising model



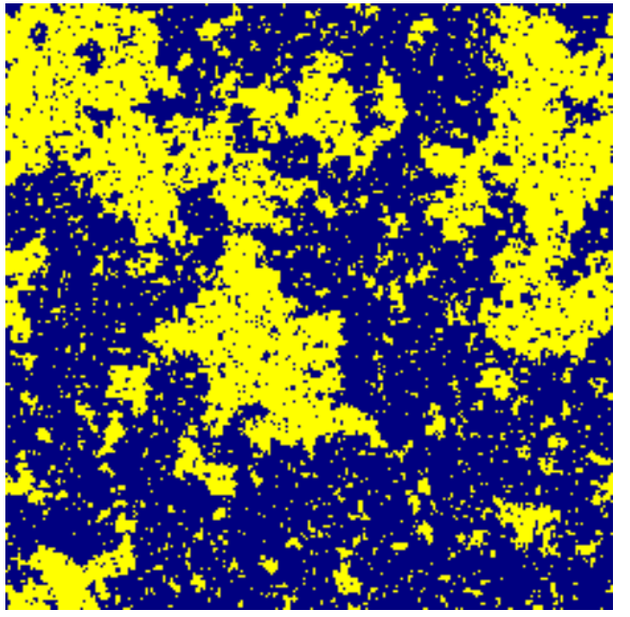
low temperature
$T = 0.8 T_{\text{crit}}$
one phase (of 2)



quenched system
$T = 5 T_{\text{crit}} \rightarrow 0.5 T_{\text{crit}}$
spinodal decomposition



high temperature
$T = 1.25 T_{\text{crit}}$
one phase



critical point
$T = T_{\text{crit}}$
one (critical) phase

- critical exponents – it is believed that all critical points (in the same dimension) have the same **universal behavior**

Lattice models: Potts

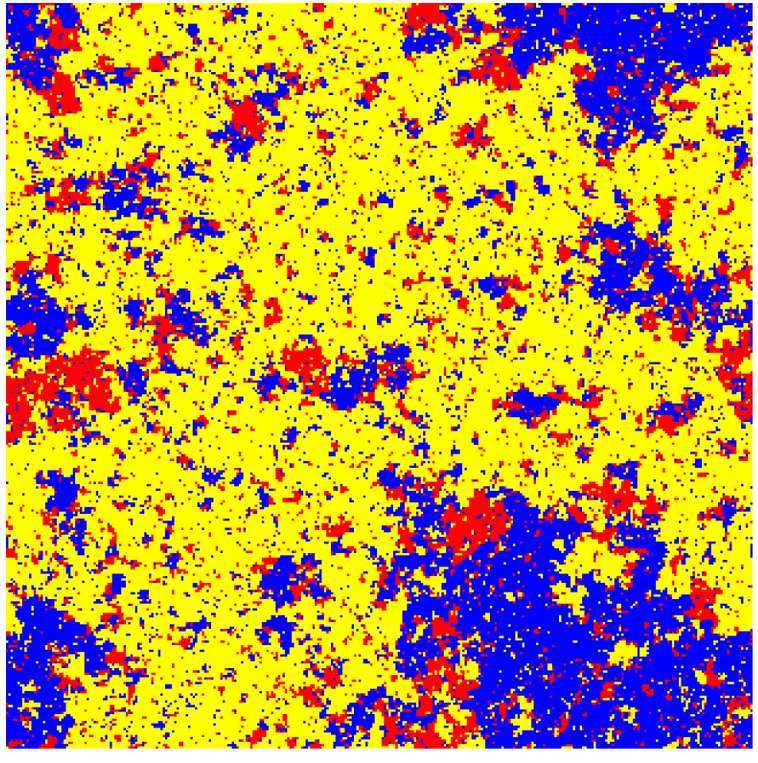
Site $i \mapsto$ "spin" $s_i \in \{1, 2, \ldots, n\}$

$$\mathcal{H} = -J \sum_{<i,j>} \delta_{s_i, s_j}, \quad \text{where } \delta = \text{Kronecker's delta}$$

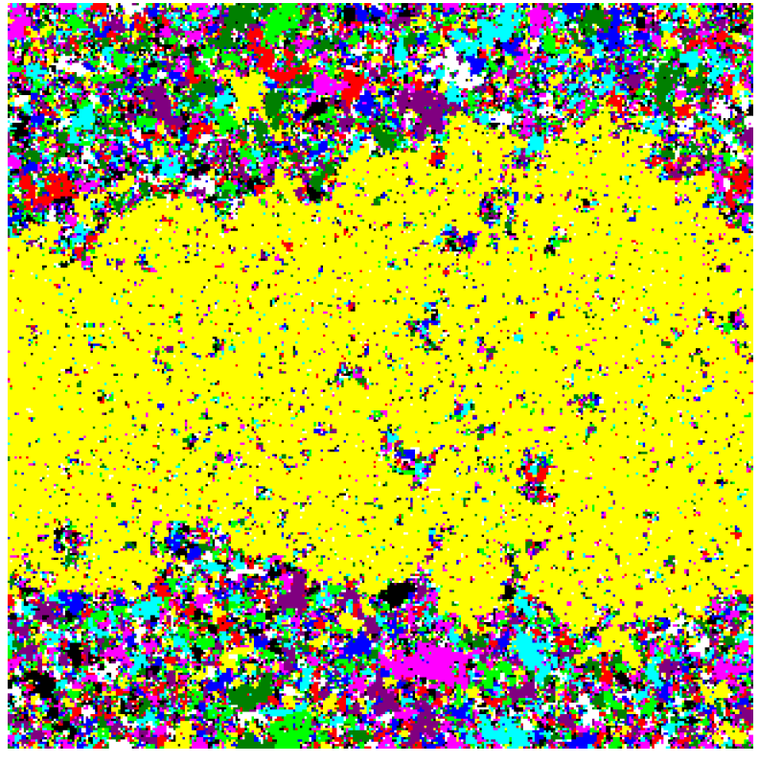
In 2D it holds for the phase transition:

$$k_B T_{tr} = \frac{J}{\ln(1+\sqrt{n})} \quad \begin{cases} n = 2, 3, 4 & \text{continuous transition} \\ n > 4 & \text{1st order phase transition} \end{cases}$$

$n = 3, T_{tr}$:



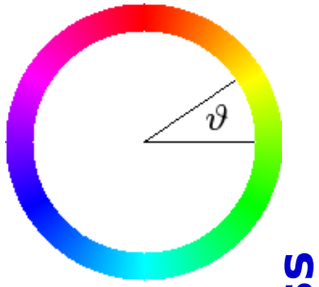
$n = 10, T_{tr}$:

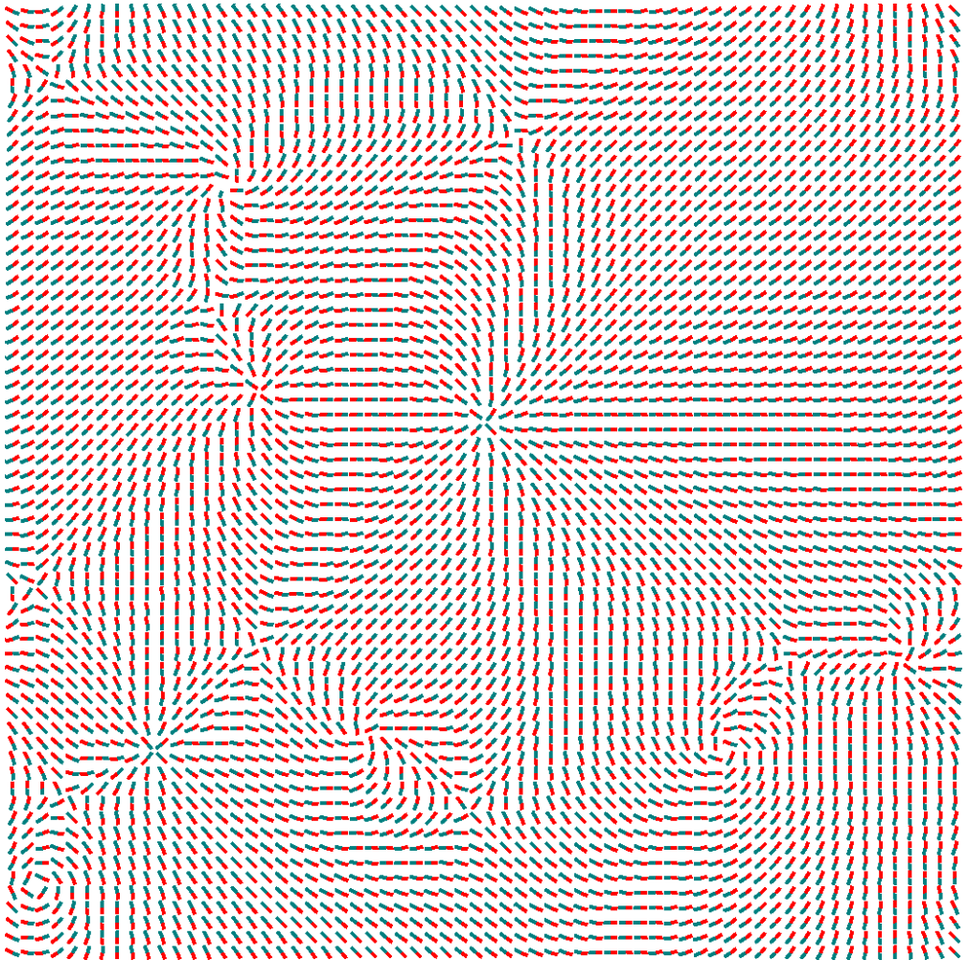


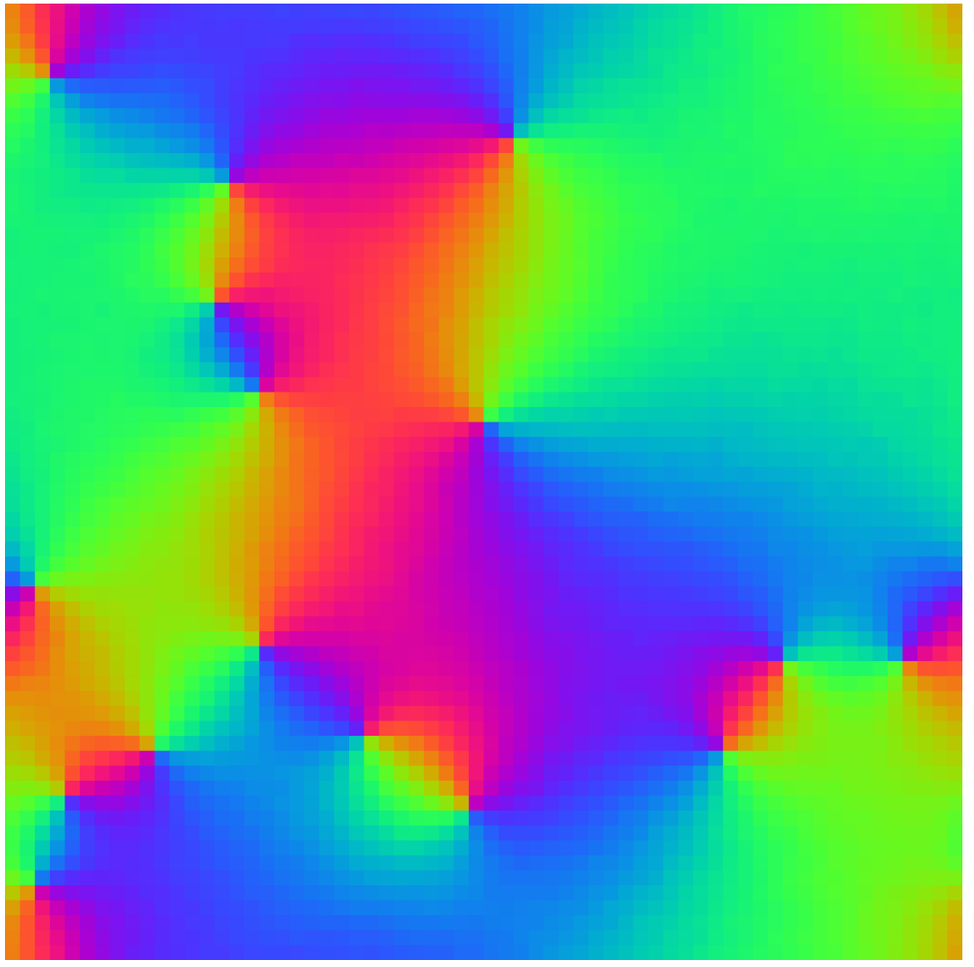
Lattice models: XY in 2D

Site $i \mapsto$ continuous "spin" $\vartheta_i \in [0, 2\pi)$ = 0°, = 120°, = 240°

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

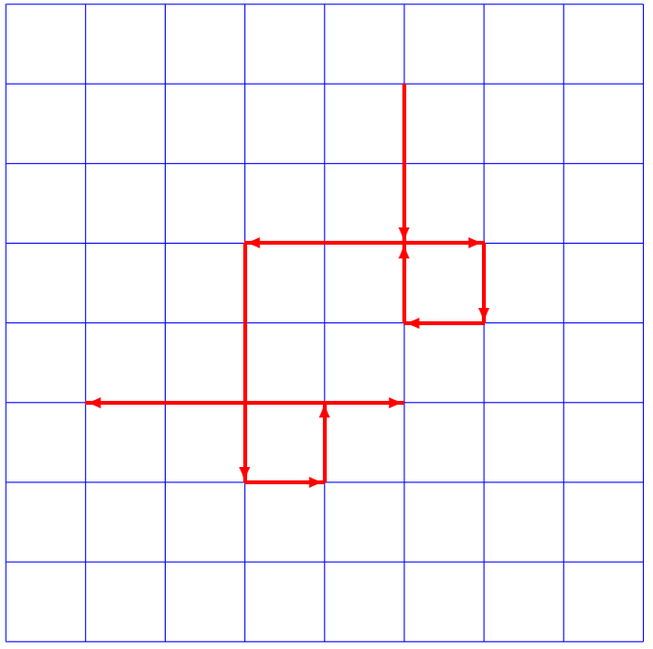




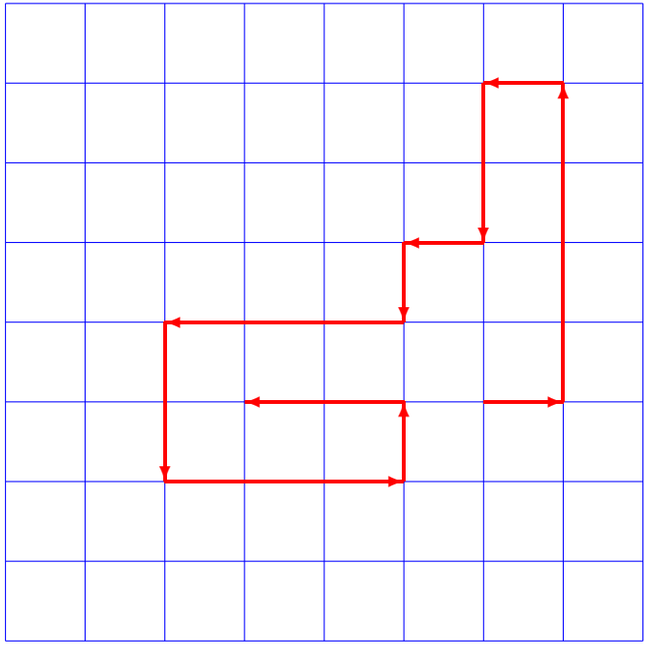


Kosterlitz–Thouless **universality class**

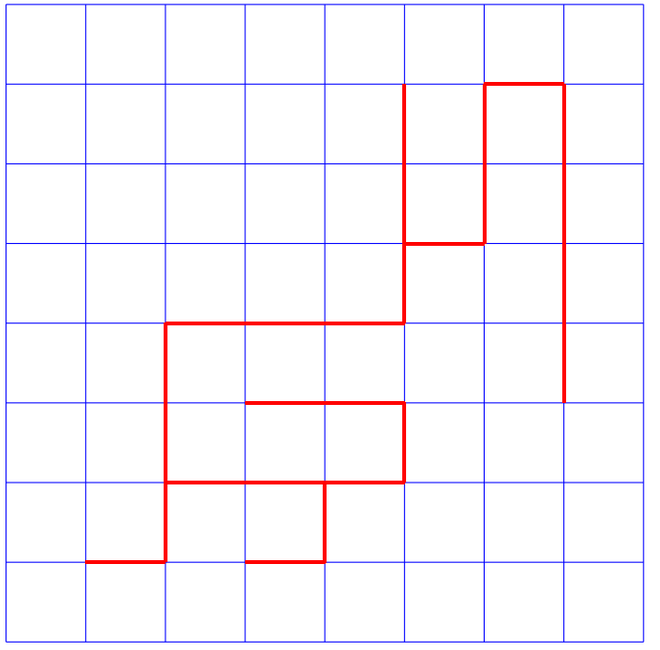
Lattice models: Polymers



random walk



self-avoiding walk



branched polymer

universal behavior of a linear polymer in 3D:

- random walk = Brownian motion = polymer in θ solvent, dim = 2
- self-avoiding random walk = polymer in athermal (very good) solvent, dim = 1.7
- with attraction (crossing more probable) = polymer in a bad solvent, dim = 3

Note on energy units

A classical parameterization of the Lennard-Jones potential of argon can be written as:

ϵ	σ
$1.654 \cdot 10^{-21}$ J	1.405 Å
996.1 $\mathrm{J\,mol^{-1}}$	0.1405 nm
238.1 $\mathrm{cal\,mol^{-1}}$	$1.405 \cdot 10^{-10}$ m
119.8 K	
0.01032 eV	

$$
\begin{aligned}
N_\mathrm{A} &= 6.02214076 \cdot 10^{23}\,\mathrm{mol^{-1}} \ \text{(exact)} \\
k_\mathrm{B} &= 1.380649 \cdot 10^{-23}\,\mathrm{J\,K^{-1}} \ \text{(exact)} \\
\mathrm{eV} &= 1.602176634 \cdot 10^{-19}\,\mathrm{J} \ (\mathrm{C \cdot V = J}) \\
1\,\mathrm{cal} &= 4.184\,\mathrm{J} \ \text{(thermochemical calorie)}
\end{aligned}
$$

All values are equivalent! Conversions:

$$
\begin{aligned}
996.1\,\mathrm{J\,mol^{-1}} &\mathrel{\hat{=}} \frac{996.1\,\mathrm{J\,mol^{-1}}}{N_\mathrm{A}} = \frac{996.1\,\mathrm{J\,mol^{-1}}}{6.022 \cdot 10^{23}\,\mathrm{mol^{-1}}} = 1.654 \cdot 10^{-21}\,\mathrm{J} \\
238.1\,\mathrm{cal\,mol^{-1}} &= 4.184\,\mathrm{J\,cal^{-1}} \cdot 238.1\,\mathrm{cal\,mol^{-1}} = 996.2\,\mathrm{J\,mol^{-1}} \\
119.8\,\mathrm{K} &\mathrel{\hat{=}} 119.8\,\mathrm{K} \cdot k_\mathrm{B} = 119.8\,\mathrm{K} \cdot 1.381 \cdot 10^{-23}\,\mathrm{J\,K^{-1}} = 1.654 \cdot 10^{-21}\,\mathrm{J} \\
119.8\,\mathrm{K} &\mathrel{\hat{=}} 119.8\,\mathrm{K} \cdot R = 119.8\,\mathrm{K} \cdot 8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}} = 996.1\,\mathrm{J\,mol^{-1}} \\
0.01032\,\mathrm{eV} &= 0.01032 \cdot 1.6022 \cdot 10^{-19}\,\mathrm{C} \cdot 1\,\mathrm{V} = 1.654 \cdot 10^{-21}\,\mathrm{J}
\end{aligned}
$$