

**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:

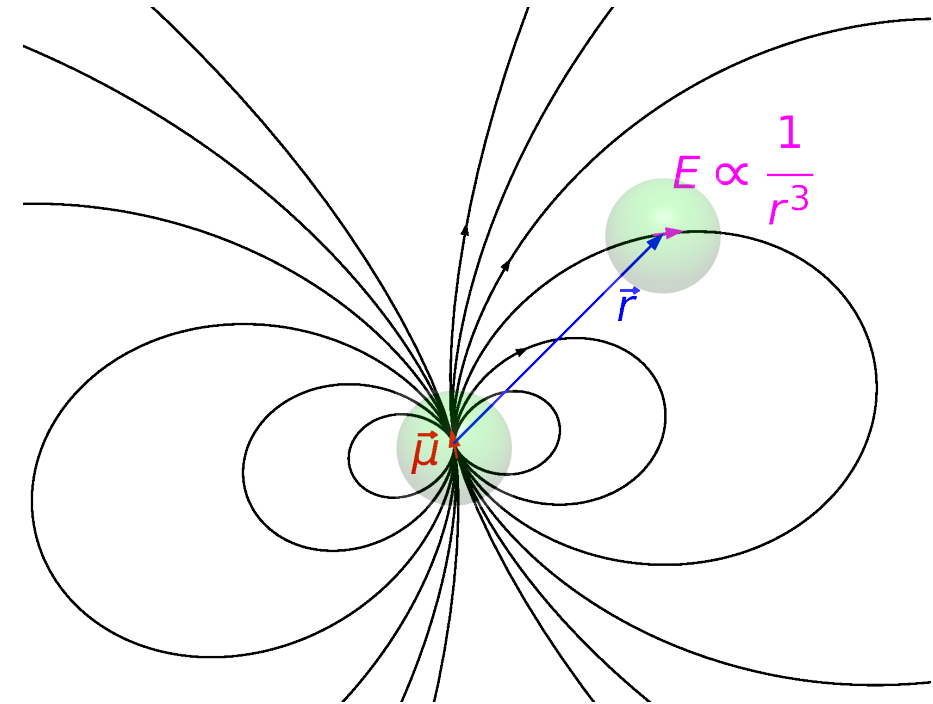
$$u(r) \propto e^{-Br}$$

**Total:** exp-6

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

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

Component of **any** atom–atom interaction



“ $\propto$ ” = “is proportional to”

A, B, C are positive constants

Repulsive forces approximated:

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

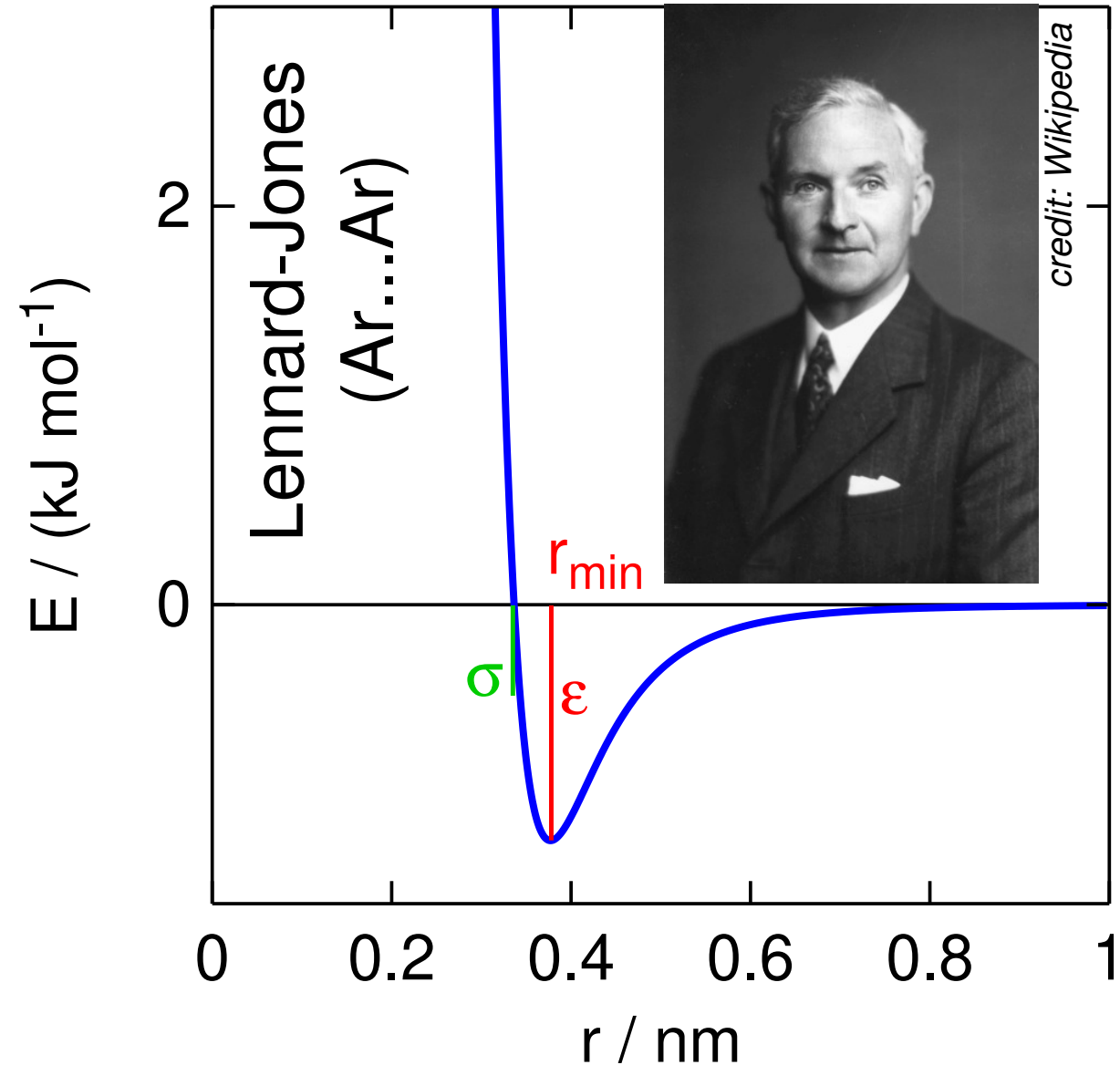
● Common formula:

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

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

● 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., liquid 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

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

- charge–charge (ions)

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

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

- partial charges:

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

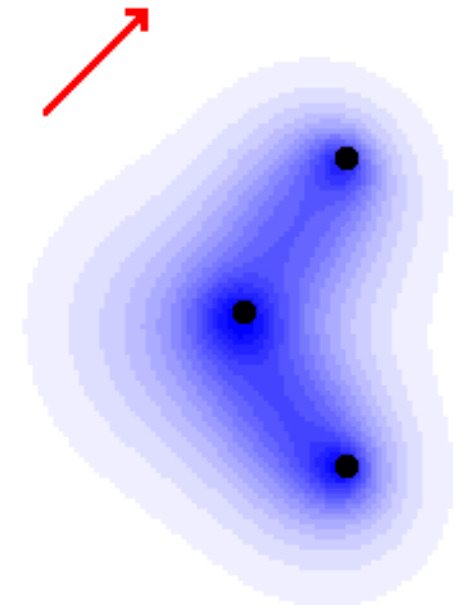
- dipole moment

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

- polarizability (electric field induces a dipole)

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

(is not pair additive)



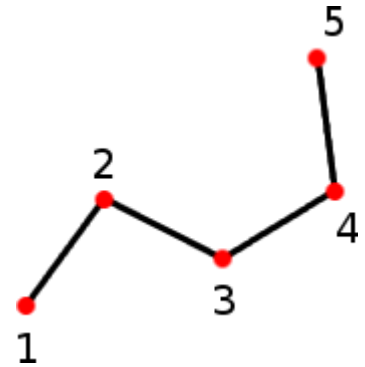
# Force field

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

**Small molecules:** rigid, rotations (water, CO, CH<sub>4</sub>)

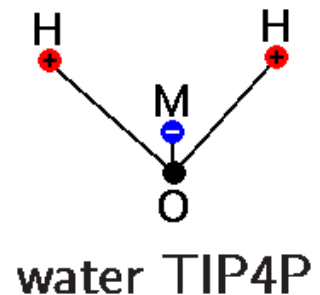
**Large molecules:** many terms

- 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 (-CH<sub>3</sub>, -CH<sub>2</sub>-, etc.)
  - auxiliary interaction centers (TIP4P)
  - coarse-grained
- } atomistic



Harmonic approximation:

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

optionally:

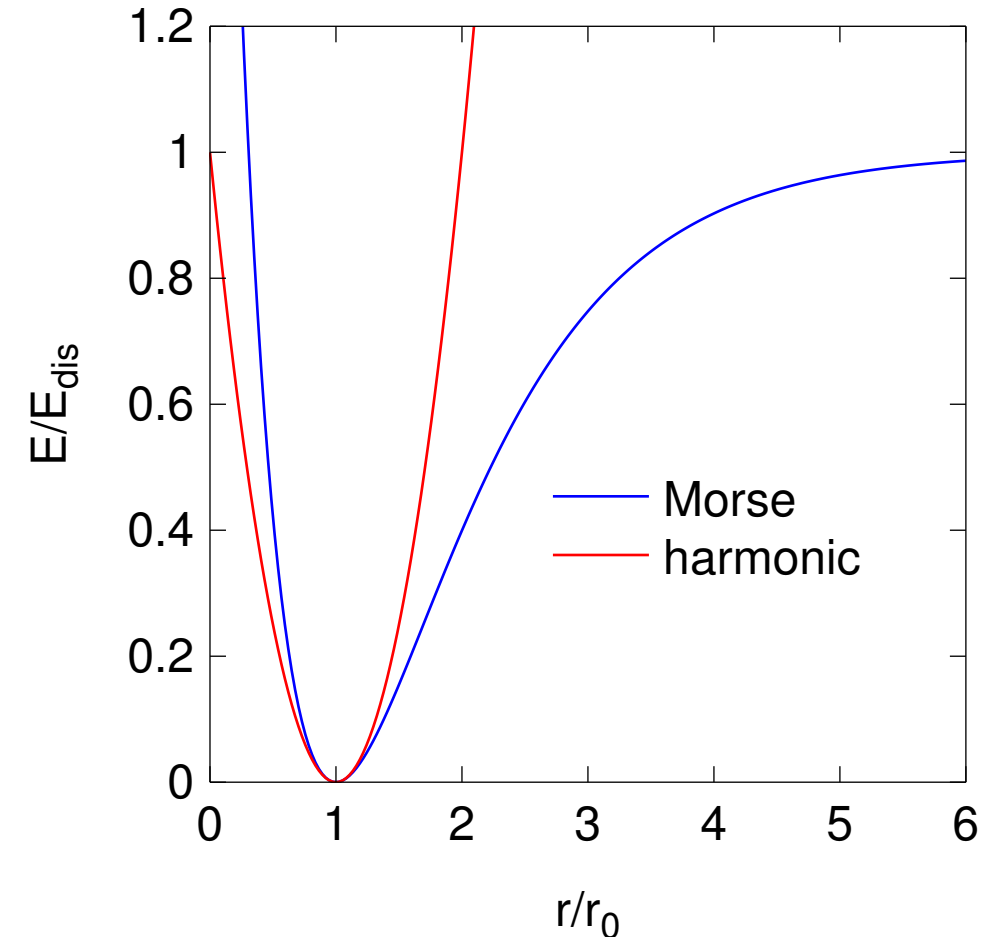
$$U = \frac{K'}{2}(r - r_0)^2$$

Fixed bond length:

$$r = r_0$$

Morse (dissociation):

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



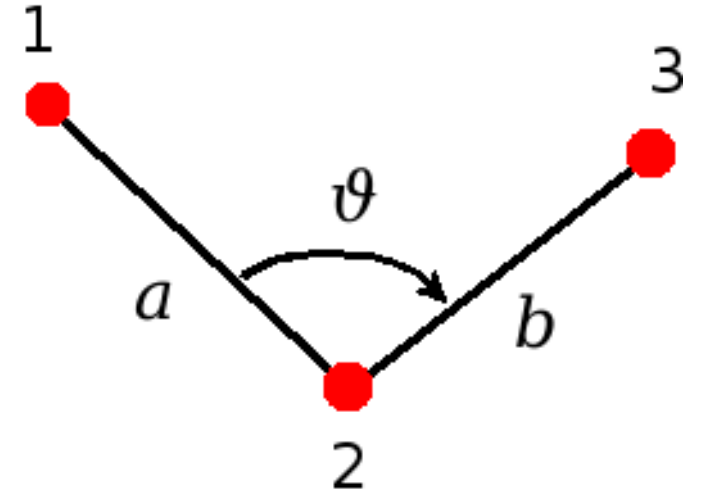
**Example:** Which  $K$  in the harmonic approximation corresponds to the Morse potential at small amplitudes?

Harmonic approximation:

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

Urey–Bradley:

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



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

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

**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.

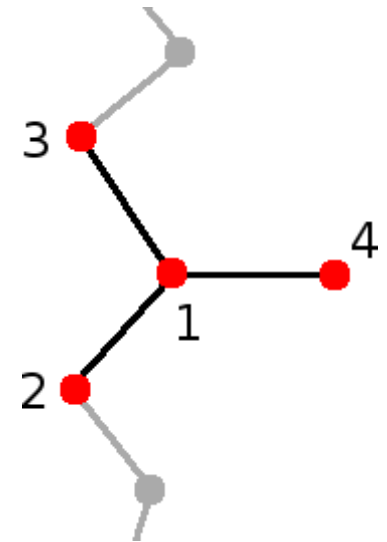
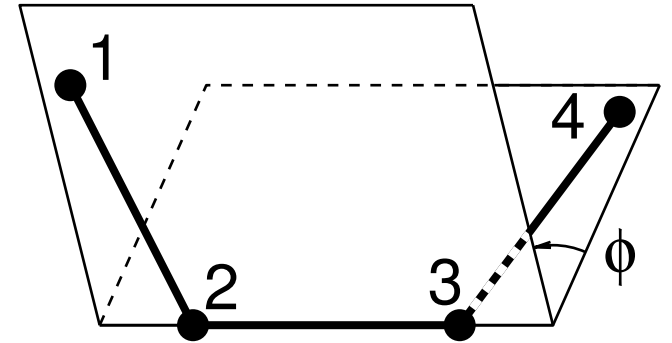
To keep the aromatic ring planar:

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

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

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

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





Lennard-Jones is defined by  $\sigma_i, \epsilon_i$ . 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
- bonded forces: quantum chemistry calculations, spectroscopy
- Lennard-Jones  $\sigma$ : experimental density, structure
- Lennard-Jones  $\epsilon$ : 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 (e.g., zeolite)

● hard wall

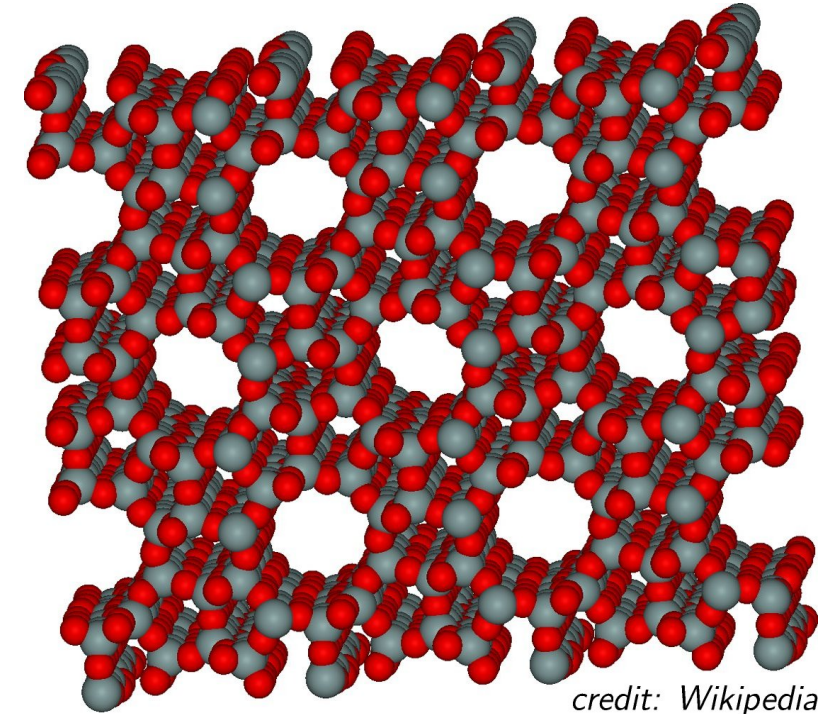
$$U_{\text{hard wall}}(\vec{r}) = \begin{cases} \infty, & \text{for } z < 0, \\ 0 & \text{for } z \geq 0 \end{cases}$$

● 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 12-6  $\rightarrow$  9-3:

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



each  $\int$  reduces the power by 1

\*also denoted  $\rho$  or  $n$

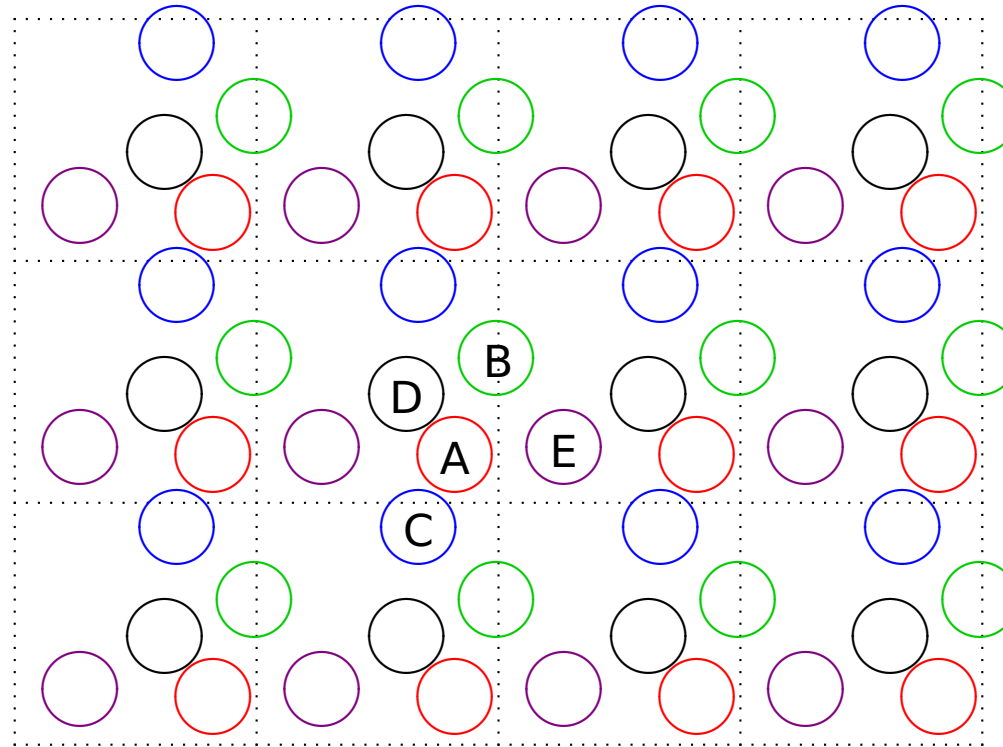
# Boundary conditions

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

free surface or hard walls  $\Rightarrow$  large surface effects

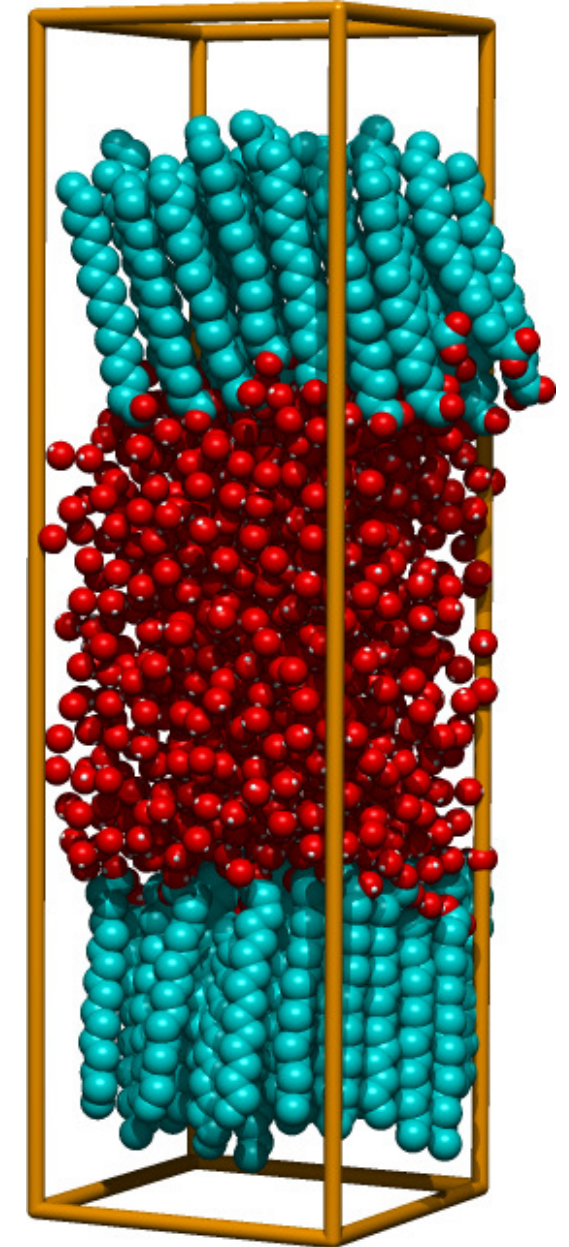
1000 molecules in a cube  $10^3 \rightarrow 8^3 = 512$  are "inside"

● "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
```

In MC, usually the vector  $\vec{r}_{12} = r_2 - r_1$  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)*

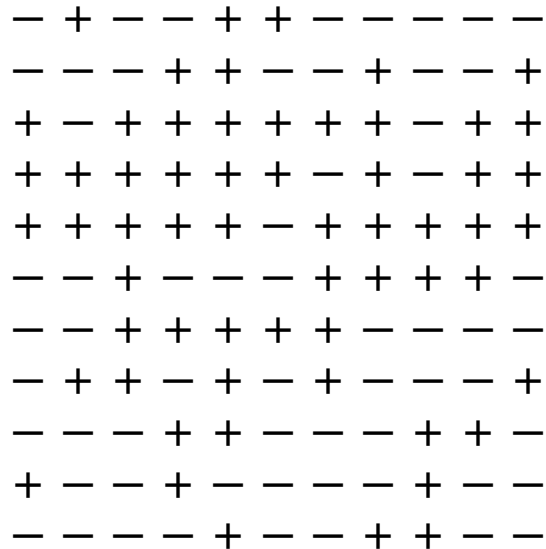
*both vectors must lie in the basic box*

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
```

## 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,

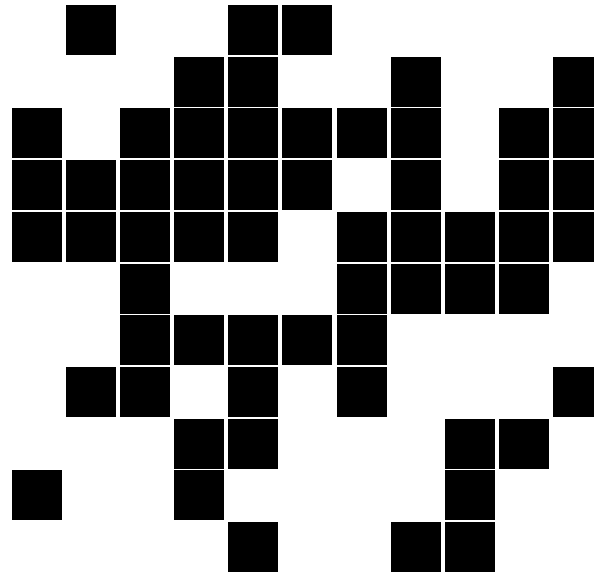
$J < 0$ : antiferromagnet

$h$  = magnetic field intensity

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

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

## lattice gas



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

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

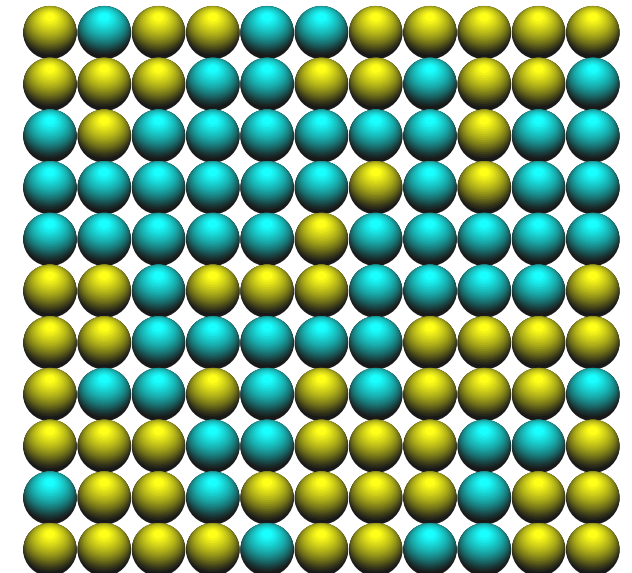
$\epsilon$  = attraction constant

$\mu$  = chemical potential

Equivalence:

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

## binary alloy



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

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

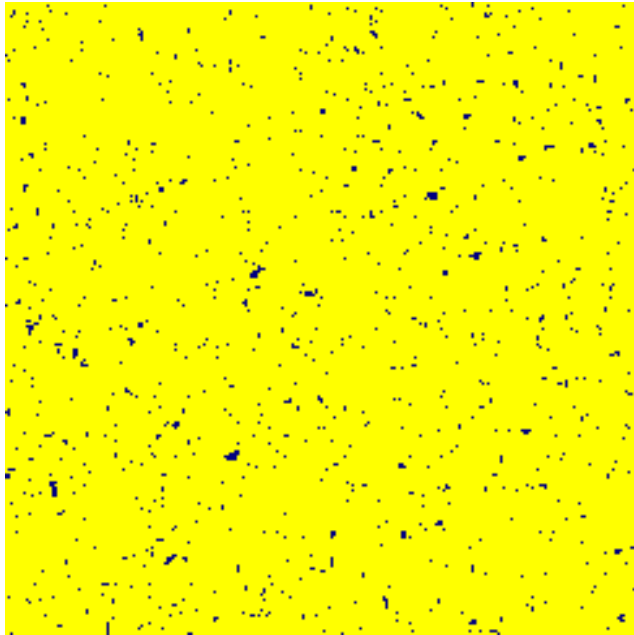
$\epsilon_{\text{blue,blue}}, \epsilon_{\text{blue,yellow}}, \epsilon_{\text{yellow,yellow}}$  = interactions of nearest neighbors

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

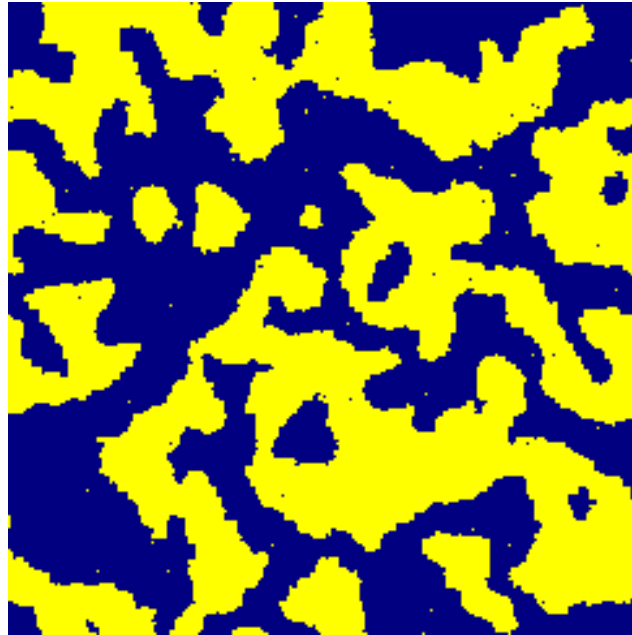
Equivalence:  $n_i = 0 \sim k_i = \text{blue sphere}$

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

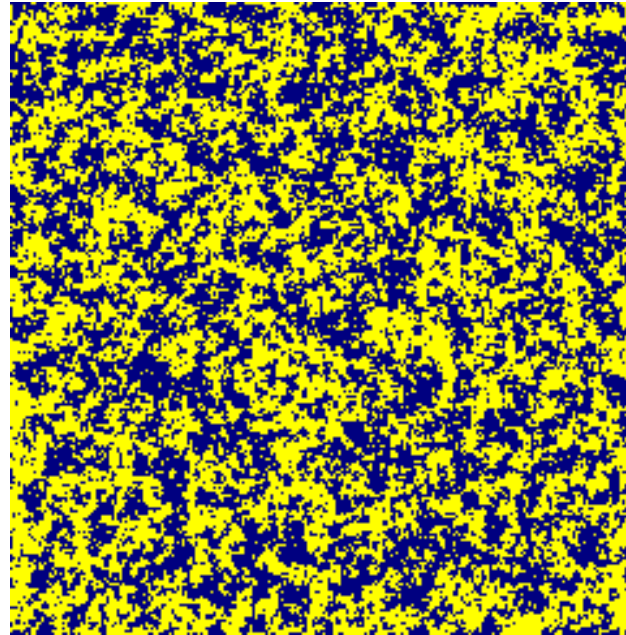




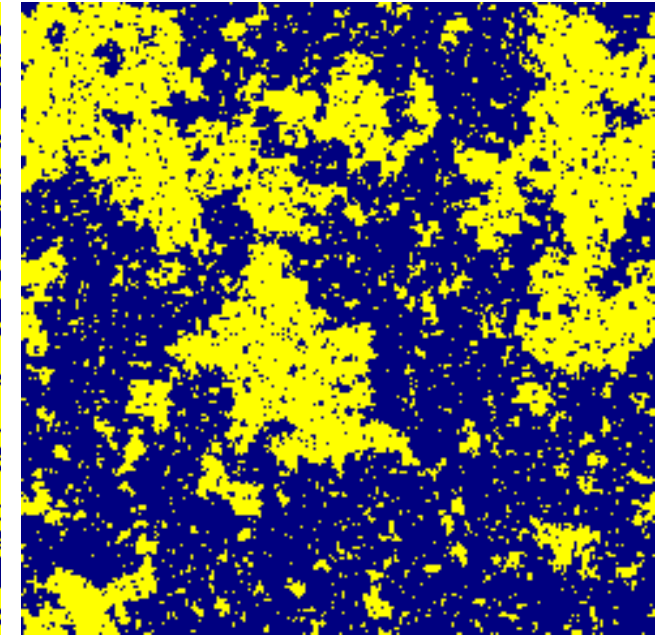
low temperature  
 $T = 0.8T_{\text{crit}}$   
one phase (of 2)



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



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



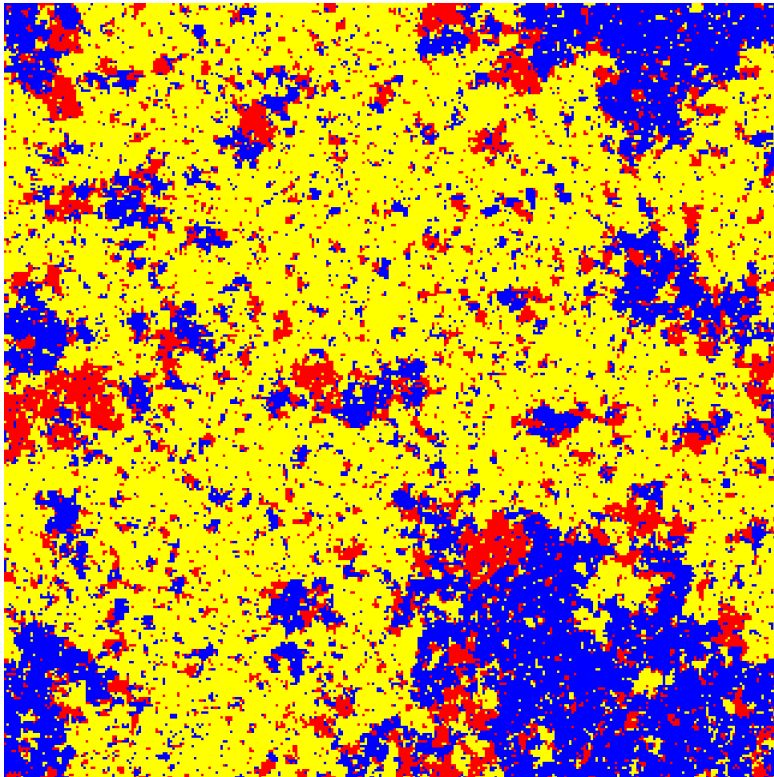
Site  $i \mapsto$  "spin"  $s_i \in \{1, 2, \dots, n\}$

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

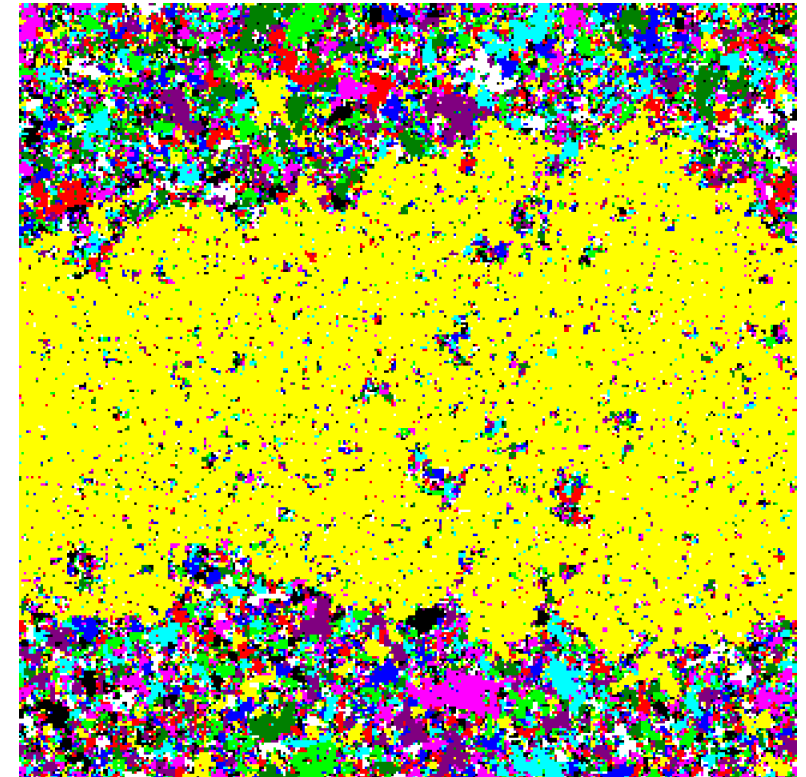
In 2D it holds for the phase transition:

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

$n = 3, T_{\text{tr}} :$

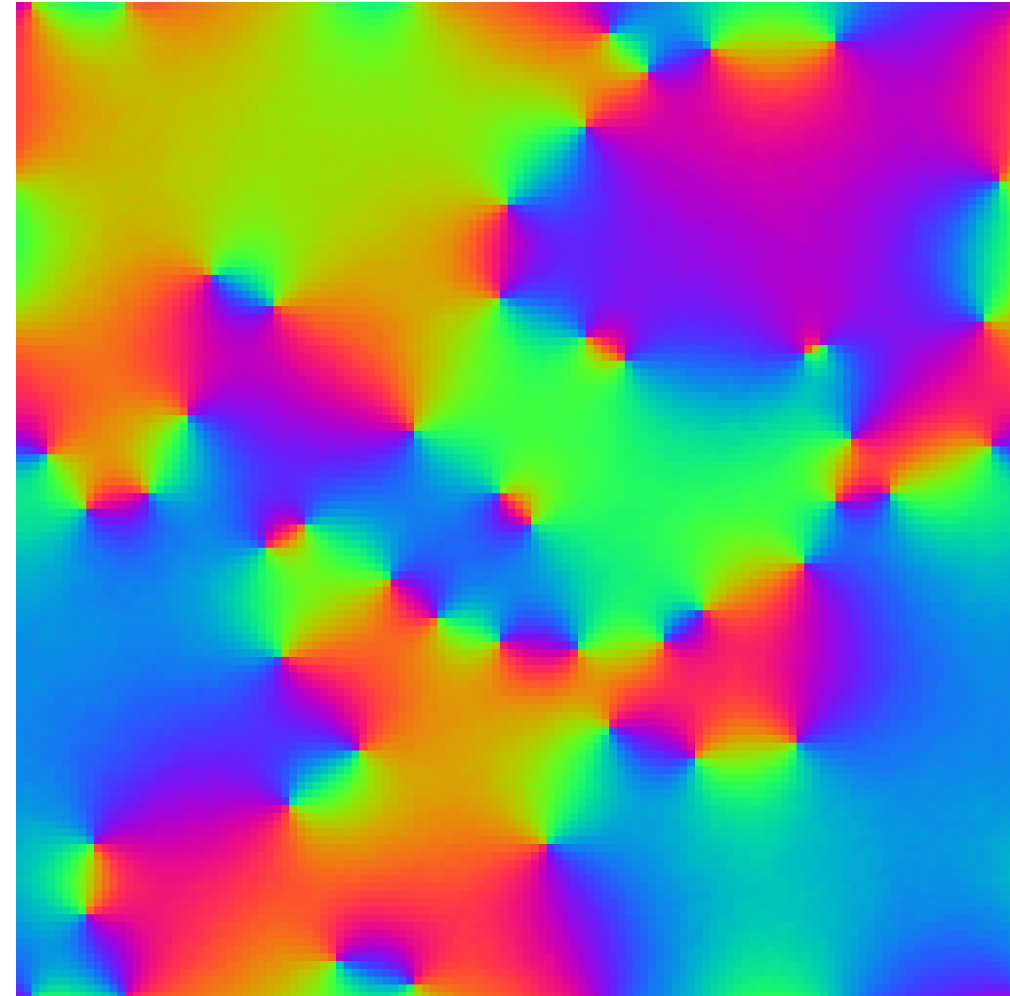
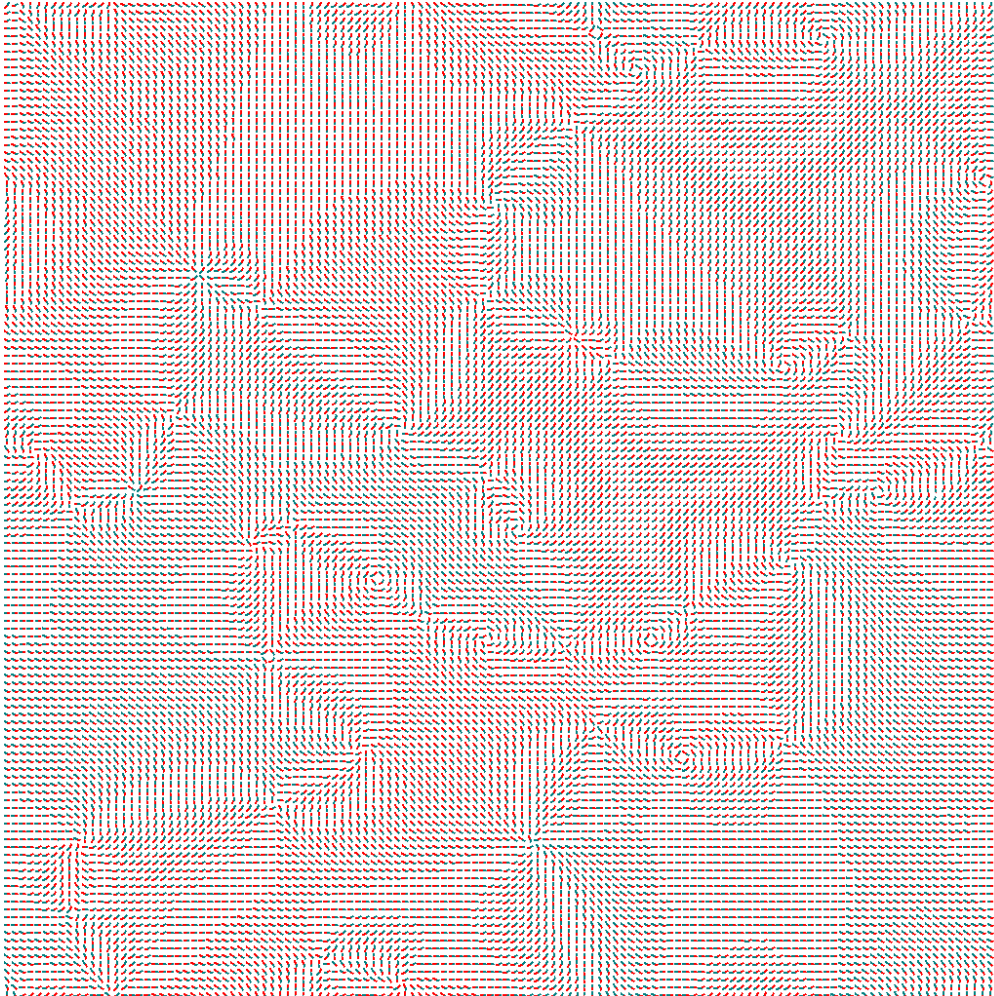
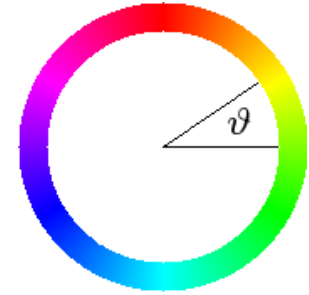


$n = 10, T_{\text{tr}} :$



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

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



Kosterlitz–Thouless **universality class**



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

$\epsilon$	$\sigma$
$1.654 \times 10^{-21} \text{ J}$	$1.405 \text{ \AA}$
$996.1 \text{ J mol}^{-1}$	$0.1405 \text{ nm}$
$238.1 \text{ cal mol}^{-1}$	$1.405 \times 10^{-10} \text{ m}$
$119.8 \text{ K}$	
$0.01032 \text{ eV}$	

$$N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1} \text{ (exact)}$$

$$k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1} \text{ (exact)}$$

$$\text{eV} = 1.602176634 \times 10^{-19} \text{ J} \text{ (C} \cdot \text{V} = \text{J)}$$

$$1 \text{ cal} = 4.184 \text{ J} \text{ (thermochemical calorie)}$$

All values are equivalent! Conversions:

$$996.1 \text{ J mol}^{-1} \hat{=} \frac{996.1 \text{ J mol}^{-1}}{N_A} = \frac{996.1 \text{ J mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}} = 1.654 \times 10^{-21} \text{ J}$$

$$238.1 \text{ cal mol}^{-1} = 4.184 \text{ J cal}^{-1} \cdot 238.1 \text{ cal mol}^{-1} = 996.2 \text{ J mol}^{-1}$$

$$119.8 \text{ K} \hat{=} 119.8 \text{ K} \cdot k_B = 119.8 \text{ K} \cdot 1.381 \times 10^{-23} \text{ J K}^{-1} = 1.654 \times 10^{-21} \text{ J}$$

$$119.8 \text{ K} \hat{=} 119.8 \text{ K} \cdot R = 119.8 \text{ K} \cdot 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 996.1 \text{ J mol}^{-1}$$

$$0.01032 \text{ eV} = 0.01032 \cdot 1.6022 \times 10^{-19} \text{ C} \cdot 1 \text{ V} = 1.654 \times 10^{-21} \text{ J}$$