

Potential energy atom-atom

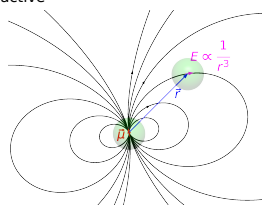
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London (dispersion) forces: longer separations, always attractive
Fluctuating dipole – fluctuating dipole model:

- electrostatic field $E \propto 1/r^3$
- induced dipole $\mu_{ind} \propto E$
- energy $u(r) \propto \mu E \propto 1/r^6$ (negative = attractive)

Repulsion at shorter separations:

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



" \propto " = "is proportional to"

A, B, C are positive constants

Total: exp-6

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

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

Component of **any** atom-atom interaction

Bonded forces – bonds

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Harmonic approximation:

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

optionally:

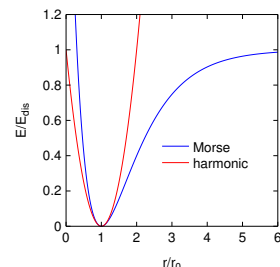
$$U = \frac{K'}{2}(r - r_0)^2$$

Fixed bond length:

$$r = r_0$$

Morse (dissociation):

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



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

$\zeta^{\text{DIP}} \exists$

Lennard-Jones potential

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Repulsive forces approximated:

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

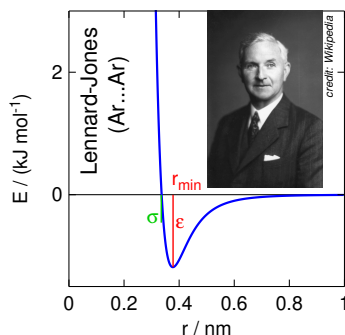
● Common formula:

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

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

● Optional formula:

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



Bonded forces – angles

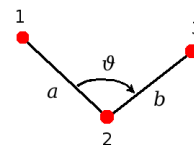
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Harmonic approximation:

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

Urey-Bradley:

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



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

$$K_{ham} = K_{UB} \left[\frac{0.6 \sin \vartheta}{a b} \right]_{\vartheta = \vartheta_0}$$

Many molecules

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... e.g., liquid Ar

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

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

Better:

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

where

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

Bonded forces – torsions

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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.

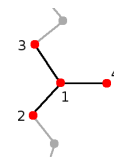
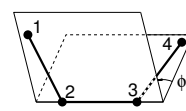
To keep the aromatic ring planar:

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

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:

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



Electrostatic forces

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● charge-charge (ions)

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

$$\vec{F}_{ij} = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}^2} \hat{r}_{ij}$$

● partial charges:

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

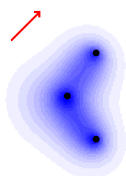
● dipole moment

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

● polarizability (electric field induces a dipole)

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

(is not pair additive)



Non-bonded forces: combining rules

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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.

Force field

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

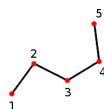
Small molecules: rigid, rotations (water, CO, CH₄)

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



Force field development

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

$$(U_{pot, intern.}) = \Delta_{vap} U \approx \Delta_{vap} H - nRT$$

- 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

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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 $\mathcal{N} = N/V$

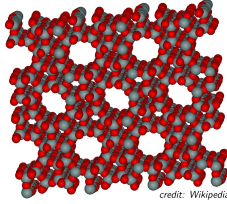
$$U_{\text{soft wall}}(\vec{r}) = \mathcal{N} \int_{z' > 0} u(\vec{r} + \vec{r}') d\vec{r}' = \mathcal{N} \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dy' \int_0^{\infty} dz' u(\vec{r} + \vec{r}')$$

Lennard-Jones 12-6 → 9-3:

each \int reduces the power by 1

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

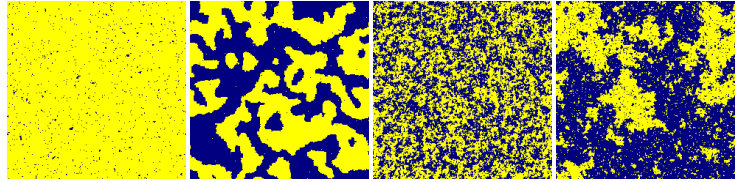
*also denoted ρ or n



credit: Wikipedia

Ising model

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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**

Boundary conditions

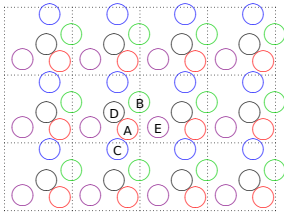
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● vacuum (free, Cartesian): droplet, protein in a vacuum ...

free surface or hard walls → large surface effects

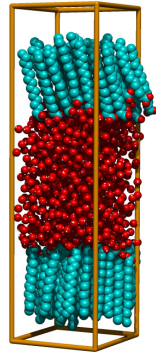
1000 molecules in a cube $10^3 \rightarrow 8^3 = 512$ are "inside"

● "strange flask": periodic boundary conditions (also cyclic, toroidal)



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

Ted Chiang: Tower of Babylon



Lattice models: Potts

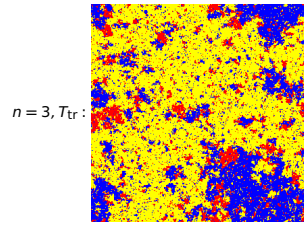
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Site $i \rightarrow$ "spin" $s_i \in \{1, 2, \dots, n\}$

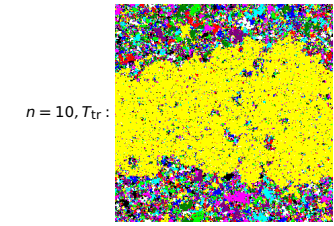
$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \delta_{s_i, s_j}, \quad \text{where } \delta = \text{Kronecker's delta}$$

In 2D it holds for the phase transition:

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



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



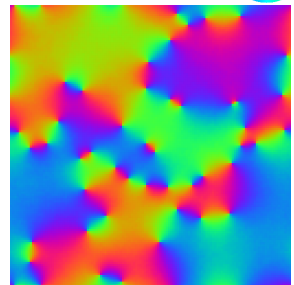
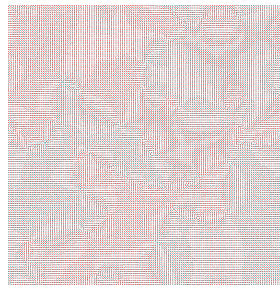
$n = 10, T_{\text{tr}}$:

Lattice models: XY in 2D

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

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



Kosterlitz-Thouless universality class

Periodic boundary conditions: MD

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REAL L edge size of the cubic simulation box (cell)

VECTOR r1, r2 where vector $\vec{r} = (r.x, r.y, r.z)$

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

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In MC, usually the vector $\vec{r}_{12} = \vec{r}_2 - \vec{r}_1$ is not needed, the distance is enough

REAL L edge size of the cubic simulation box (cell)

VECTOR r1, r2 where vector $\vec{r} = (r.x, r.y, r.z)$

both vectors must lie in the basic box

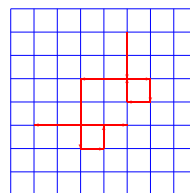
VECTOR dr := r2 - r1 difference of vectors

(ignoring the boundary conditions)

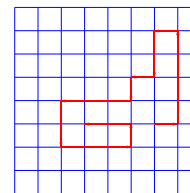
REAL rr := (L/2 - abs(L/2 - abs(dr.x)))**2
+ (L/2 - abs(L/2 - abs(dr.y)))**2
+ (L/2 - abs(L/2 - abs(dr.z)))**2

Lattice model of polymer

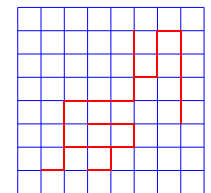
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random walk



self-avoiding walk



branched polymer

universal behavior of a linear polymer in 3D:

● random walk = Brownian motion = polymer in θ solvent, dim = 2

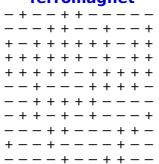
● self-avoiding random walk = polymer in athermal (very good) solvent, dim = 1.7

● with attraction (crossing more probable) = polymer in a bad solvent, dim = 3

Lattice models: Ising

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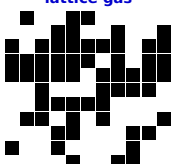
ferromagnet



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

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

lattice gas



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

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

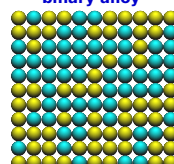
ϵ = attraction constant

μ = chemical potential

Equivalence:

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

binary alloy



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

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

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

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

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

$$n_i = 1 \sim k_i = \circ$$

Note on energy units

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

ϵ	σ
1.654×10^{-21} J	1.405 Å
996.1 J mol ⁻¹	0.1405 nm
238.1 cal mol ⁻¹	1.405×10^{-10} m
119.8 K	
0.01032 eV	

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

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

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

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

All values are equivalent! Conversions:

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

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

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

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

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