

Simulations in Statistical Physics

Molecular dynamics

Janos Török

Department of Theoretical Physics

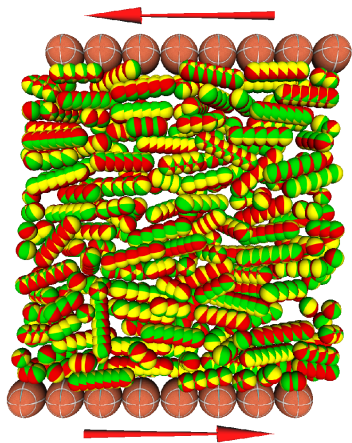
February 27, 2020

Boundary conditions

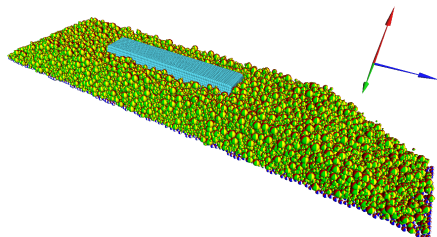
- ▶ Real boundary conditions
 - ▶ Closed (nothing)
 - ▶ Walls (with temperature)
 - ▶ Substrate (often too expensive)
- ▶ Computer based boundary conditions
 - ▶ **Periodic boundary conditions**
 - ▶ Absorbing (whatever leaves is gone)
 - ▶ Reflecting (everything is reflected back)
 - ▶ Walls (some potential)
 - ▶ Substrate (fixed basis)
 - ▶ ~~Wall with temperature~~

Boundary conditions: Examples

- ▶ Periodic boundary conditions
- ▶ Walls (some potential)

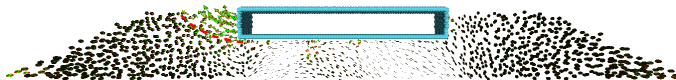
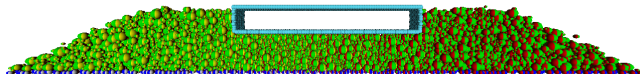


Boundary conditions: Examples

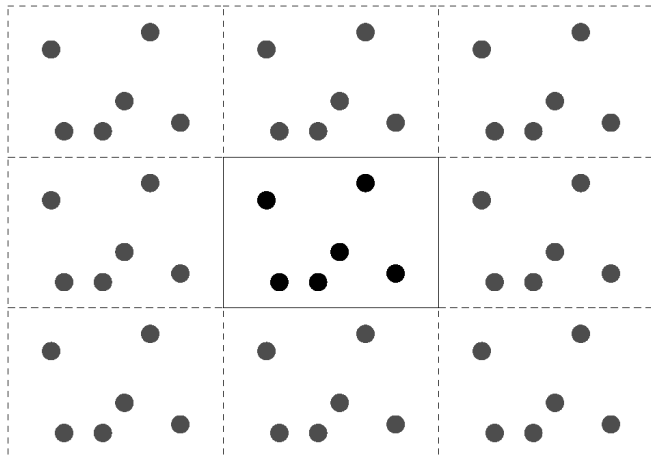


Periodic boundary conditions

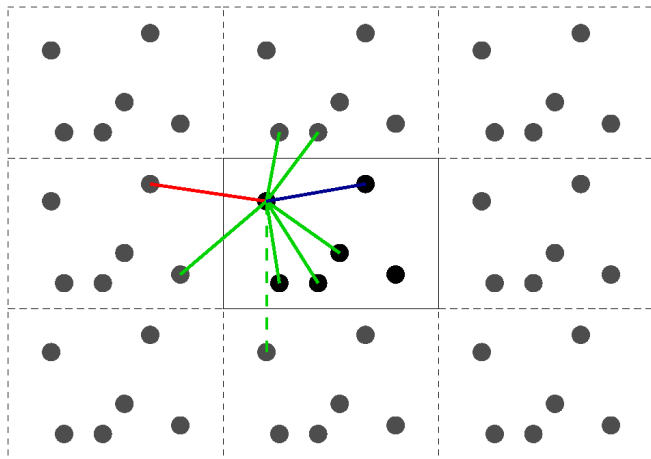
Substrate (fixed basis)



Periodic boundary conditions

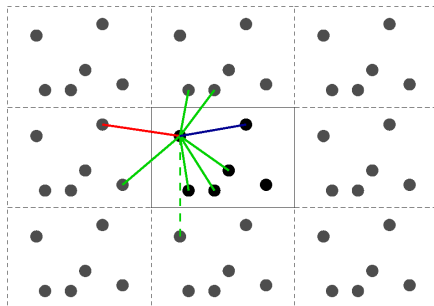


Periodic boundary conditions → contacts



Periodic boundary conditions

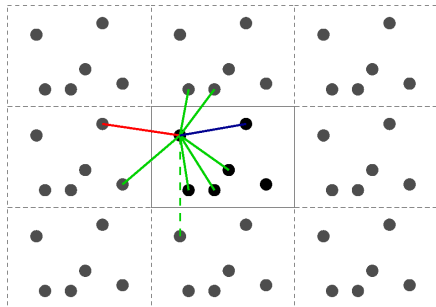
- ▶ Infinitely many neighboring cells if long range interactions
- ▶ Possibility of self interaction (must be charge neutral)
 - ▶ General solution: long range interactions are handled in k -space
- ▶ Linear momentum is conserved
- ▶ Angular momentum is **not** conserved



Periodic boundary conditions

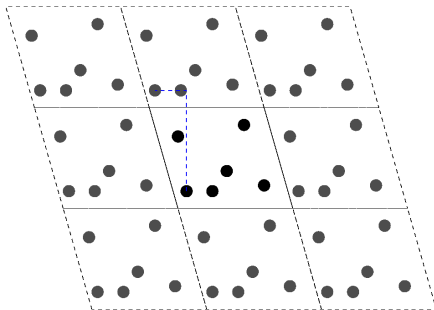
Distance

```
dx = x[i] - x[j]  
if (dx < -Lx/2) dx+=Lx;  
if (dx >  Lx/2) dx-=Lx;
```



Periodic boundary conditions deformed box

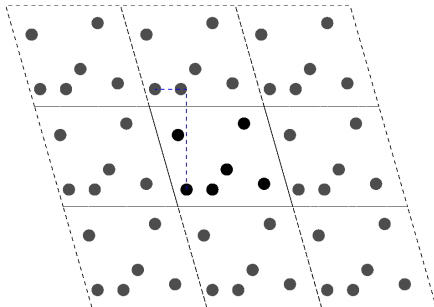
- ▶ Box is tilted, positions of particles artificially moved
- ▶ Homogeneous shear



Periodic boundary conditions deformed box

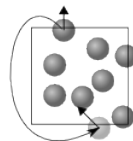
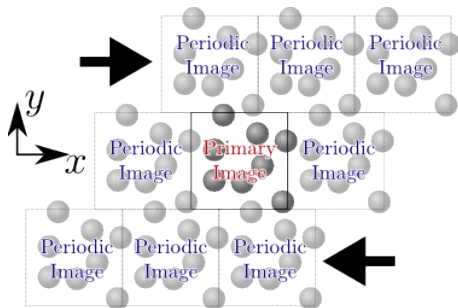
Distance

```
dx = x[i] - x[j]
dy = y[i] - y[j]
dz = z[i] - z[j]
if (dz < -Lz/2) { dz+=Lz; dx+=Dxz; dy+=Dyz; }
if (dz > Lz/2) { dz-=Lz; dx-=Dxz; dy-=Dyz; }
if (dy < -Ly/2) { dy+=Ly; dx+=Dxy; }
if (dy > Ly/2) { dy-=Ly; dx-=Dxy; }
if (dx < -Lx/2) dx+=Lx;
if (dx > Lx/2) dx-=Lx;
```



Periodic boundary conditions Lees-Edwards boundary conditions → shear

- ▶ Images are shifted
- ▶ Particles gain velocity
- ▶ Different from box tilt

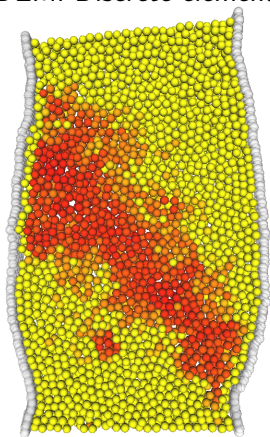


When a particle leaves the primary image, a periodic image enters on the opposite side with an additional velocity and displacement due to the sliding boundaries.

Molecular dynamics

MD: Molecular dynamics

DEM: Discrete element method



Particle based simulation

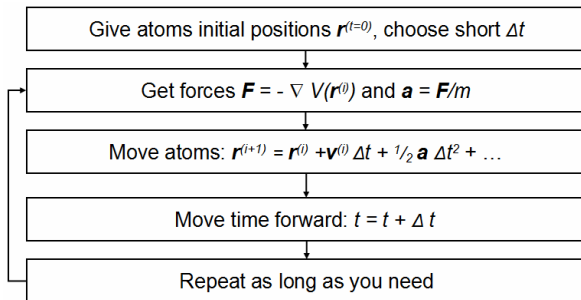
- ▶ Molecular dynamics
- ▶ Event Driven Dynamics
- ▶ Contact Dynamics
- ▶ Kinetic Monte Carlo

Molecular dynamics

Simulate nature

- Solve Newton's equation of motion

$$m_i \ddot{\mathbf{r}}_i = \mathbf{f}_i = \mathbf{f}_i^{\text{ext}} + \sum_j \mathbf{f}_{ij}^{\text{int}}, \quad i, j = 1, 2 \dots N$$



Application of molecular dynamics

- ▶ Molecular systems (classic potentials, temperature)
 - ▶ Biophysics
 - ▶ Structural biology
 - ▶ Glasses
 - ▶ Amorphous materials
 - ▶ Liquids
- ▶ Granular materials (hard core, dissipative)
 - ▶ Stones, seeds, pills
 - ▶ Railbed
- ▶ Pedestrians
- ▶ Astrological systems (conservative, large scale)

Program

- ▶ Have an algorithm to calculate forces
- ▶ Get list of interacting particles
- ▶ Determine accelerations and velocities; step particles
- ▶ Set temperature

Forces

Internal forces

- ▶ Pair potential:

$$\mathbf{f}_{ij}^{\text{int}} = -\mathbf{f}_{ji}^{\text{int}} = -\nabla V(r_{ij})$$

- ▶ Many body potentials (molecular bonds)

$$\mathbf{f}_{ijk}^{\text{int}} = \mathbf{F}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$$

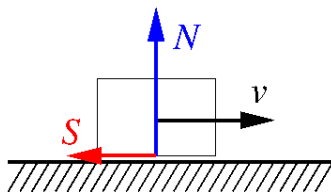
- ▶ e.g. 3-body Stillinger-Weber potential:

$$\begin{aligned} E &= \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j \neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk}) \\ \phi_2(r_{ij}) &= A_{ij} \epsilon_{ij} \left[B_{ij} \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{q_{ij}} \right] \exp \left(\frac{\sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right) \\ \phi_3(r_{ij}, r_{ik}, \theta_{ijk}) &= \lambda_{ijk} \epsilon_{ijk} [\cos \theta_{ijk} - \cos \theta_{0ijk}]^2 \exp \left(\frac{\gamma_{ij} \sigma_{ij}}{r_{ij} - a_{ij} \sigma_{ij}} \right) \exp \left(\frac{\gamma_{ik} \sigma_{ik}}{r_{ik} - a_{ik} \sigma_{ik}} \right) \end{aligned}$$

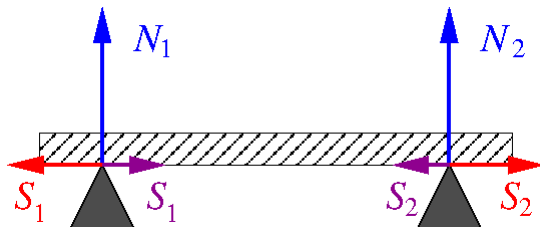
- ▶ Friction forces (next slide...)

Friction forces

- Moving:



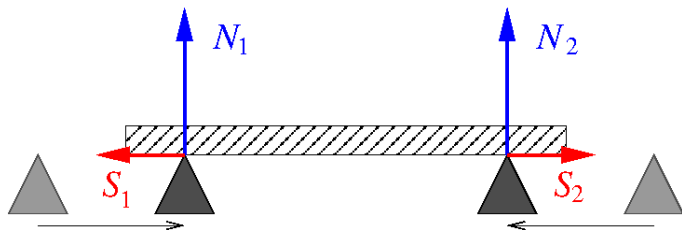
- Stationary:



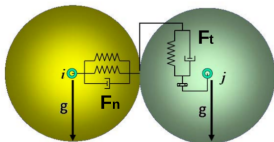
Friction forces

- ▶ Position is not enough to set friction forces
- ▶ No movement \rightarrow no friction forces
- ▶ Solution:

We need history:



Contact history



- ▶ Position is not enough to set friction forces
- ▶ Normal force:

$$\mathbf{F}_n = k_n \delta \mathbf{n}_{ij} - m_{\text{eff}} \gamma_n \Delta \mathbf{v}_n$$

- ▶ Tangential force:

$$\mathbf{F}_t = k_t \Delta \mathbf{s}_t + m_{\text{eff}} \gamma_t \Delta \mathbf{v}_t$$

$$\Delta \mathbf{s}_t = \mathbf{n}_t \int_{t_c}^t \{ \Delta \mathbf{v}_t(t') + [\omega_i(t') r_i - \omega_j(t') r_j] \} dt'$$

- ▶ Limit $\Delta \mathbf{s}_t$ to satisfy $|\mathbf{F}_t| \leq \mu \mathbf{F}_n$
- ▶ k stiffness, γ damping (critical)

Program

- ▶ Have an algorithm to calculate forces
- ▶ **Get list of interacting particles**
- ▶ Determine accelerations and velocities; step particles
- ▶ Set temperature

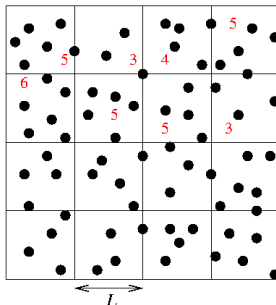
Find pairs

Now we know how to calculate forces. How to get pairs?

- ▶ All pairs: $\sim N^2$ calculations. *Only* if there is no other way!
- ▶ Short range interactions: box method
- ▶ Long range interactions: k-space

Bucketing algorithm

Finite interaction length L



$b[0,0]=\{1,7,9,14,8\};$

$b[0,1]=\{12,8,99\};$

- ▶ Grid with size L
- ▶ Grid of array with particle indexes in box
- ▶ Maximum number of neighbors or dynamic array
- ▶ If there is v_{\max} then $L' = L + v_{\max} \Delta t$, then reset array every Δt timesteps

k-space solution

- ▶ Long range interactions (e.g. Coulomb) cannot be cut off
- ▶ Often more periodic images are needed
- ▶ k-space (Fourier-transformation in 3d!)
 - ▶ Solution of linear problems by Green's-function
 - ▶ Coulomb problem: in Fourier space \rightarrow multiplication with $1/k^2$!
 - ▶ Generally it is done by Ewalds summation

Ewald summation

- ▶ The total electrostatic potential energy

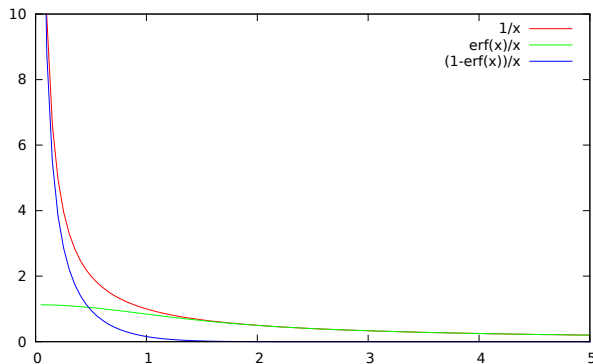
$$W = \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- ▶ Factor 2 is for double counting all contacts
- ▶ For infinite system the expression does not converge
- ▶ Ewald's idea:

$$\frac{1}{r} = \frac{\text{erf}(\sqrt{\eta}r/2)}{r} + \frac{1 - \text{erf}(\sqrt{\eta}r/2)}{r}$$

- ▶ The first term goes to a constant for small r but has long range interactions
- ▶ The second term has a singular behavior at $r \rightarrow 0$ but vanishes exponentially
- ▶ $\text{erfc}(x) = 1 - \text{erf}(x)$

Ewald summation



► Thus the calculation of the electrostatic energy is

$$W = \frac{1}{8\pi\epsilon_0} \left(\sum_{i \neq j} \frac{q_i q_j \text{erf}(\sqrt{\eta} |\mathbf{r}_i - \mathbf{r}_j|/2)}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i \neq j} \frac{q_i q_j \text{erfc}(\sqrt{\eta} |\mathbf{r}_i - \mathbf{r}_j|/2)}{|\mathbf{r}_i - \mathbf{r}_j|} \right)$$

Ewald summation

- ▶ Thus the calculation of the electrostatic energy is

$$W = \frac{1}{8\pi\epsilon_0} \left(\sum_{i \neq j} \frac{q_i q_j \operatorname{erf}(\sqrt{\eta} |\mathbf{r}_i - \mathbf{r}_j|/2)}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i \neq j} \frac{q_i q_j \operatorname{erfc}(\sqrt{\eta} |\mathbf{r}_i - \mathbf{r}_j|/2)}{|\mathbf{r}_i - \mathbf{r}_j|} \right)$$

- ▶ For an appropriate choice of η , the second term converges fast
- ▶ The first term is evaluated in the Fourier space

$$W_1 = \frac{4\pi}{L^3} \sum_{i \neq j} q_i q_j \left(\sum_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{r}_{ij}} \frac{1}{k^2} e^{-k^2/4\eta^2} \right)$$

Program

- ▶ Have an algorithm to calculate forces
- ▶ Get list of interacting particles
- ▶ Determine accelerations and velocities; step particles
- ▶ Set temperature

Symplectic integrator

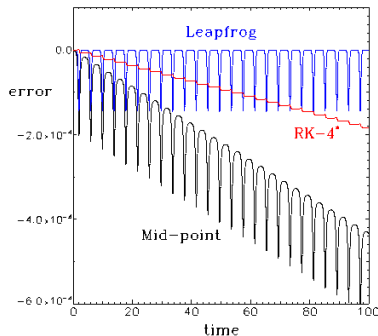
- ▶ Energy (slightly modified) is conserved
- ▶ Time reversibility
 - ▶ Verlet
 - ▶ Leapfrog
- ▶ Most molecular dynamics methods use Verlet!
 - ▶ Forces are calculated once per turn
 - ▶ Microcanonical (NVE) modelling can be only done with these

Multiple time scale integration

- ▶ Different force range
 - ▶ Short range change fast
 - ▶ Long range change slowly
- ▶ Recalculate long range forces only in every n th times-step
 - ▶ Forces are calculated once per turn
- ▶ Typical examples:
 - ▶ Intramolecular forces: strong, high frequency
 - ▶ Intermolecular forces (e.g. Lennard-Jones, Coulomb) slow

Error

Method	Error	Cumulative error
Euler:	Δt^3	Δt
Runge-Kutta:	Δt^5	Δt^4
Verlet:	Δt^4	Δt^2
Leapfrog:	Δt^4	Δt^2



Molecular dynamics

Program:

- ▶ Have an algorithm to calculate forces
- ▶ Get list of interacting particles
- ▶ Determine accelerations and velocities; step particles
- ▶ Set temperature

Temperature

Definition:

- ▶ Encyclopedia Britannica, Wikipedia:
"A temperature is a numerical measure of hot or cold."
- ▶ Manifestation of thermal energy
- ▶ Thermodynamics:
Second law of thermodynamics & Carnot engine

$$\delta Q = TdS$$

$$\eta_{\max} = \eta_{\text{Carnot}} = 1 - T_C/T_H$$

- ▶ Statistical physics:

$$\beta \equiv \frac{1}{k_B} \left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{k_B T}$$

Definition of temperature

Temperature is a measure of the random submicroscopic motions and vibrations of the particle constituents of matter.

The average **kinetic** energy per particle degrees of freedom is

$$\bar{E} = \frac{1}{2} k_B T$$

Molecular dynamics conserves only the *total* energy!

Task: Control kinetic energy!

Setting temperature

- ▶ Experiment
 - ▶ Environment
 - ▶ Mixing → uniform temperature
- ▶ Simulation
 - ▶ Control the kinetic energy (velocities)
 - ▶ Mixing → Maxwell-Boltzmann distribution

Nosé-Hoover thermostat

- ▶ Original Hamiltonian

$$H_0 = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{q})$$

- ▶ Heatbath in the Hamiltonian:

$$H_n = \sum_i \frac{\mathbf{p}'_i{}^2}{2m_i} + U(\mathbf{q}') + \frac{p_s^2}{2Q} + gk_B T \log(s)$$

- ▶ Extra degree of freedom s .
- ▶ Q "mass" related to $s \rightarrow$ controls the speed of convergence
- ▶ $g = 3N$ the number degrees of freedom
- ▶ \mathbf{p}' and \mathbf{q}' are virtual coordinates

Nosé-Hoover thermostat

- ▶ Virtual coordinates, vs. original ones:

$$\mathbf{p} = \mathbf{p}'/s$$

$$\mathbf{q} = \mathbf{q}'$$

$$t = \int \frac{1}{s} dt'$$

- ▶ Solution of the new Hamiltonian:

$$\xi = \dot{s}/s = p_s/Q$$

$$\dot{\mathbf{q}}' = \frac{\mathbf{p}'}{m}$$

$$\dot{\mathbf{p}}'_i = -\frac{\partial U}{\partial \mathbf{q}'_i} - \xi \mathbf{p}'_i$$

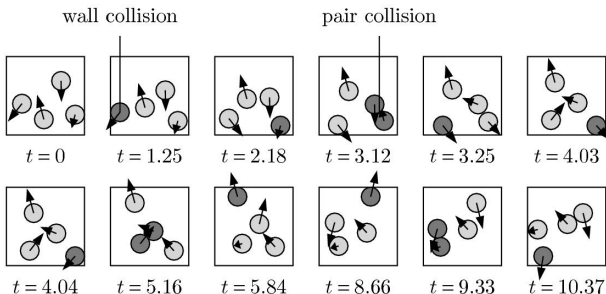
$$\dot{\xi} = \frac{1}{Q} \left(\sum_i \frac{\dot{\mathbf{p}}'^2_i}{m_i} - g k_B T \right)$$

Molecular dynamics

- ▶ Create sample
 - ▶ Crystal
 - ▶ Random deposition
 - ▶ Distorted crystal
 - ▶ Simulation
- ▶ Temperate sample
- ▶ Make test
- ▶ Collect data
 - ▶ Data size: e.g. $N = 10^4$, $t = 10^6$ small simulation:
 - ▶ 1 hour on 1 core PC
 - ▶ 3 doubles/atom \rightarrow 24 bytes/atom/timesteps
 - ▶ Result $2.4 \cdot 10^{11}$ bytes = 240 Gigabytes

Event driven dynamics

- ▶ Hard core interactions
- ▶ Interactions short in time compared to flight
- ▶ (MD needs $\sim 20 - 50$ timesteps per collision, overlap of $10^{-3}d$)
- ▶ Integrable path \rightarrow do it



Event driven algorithm

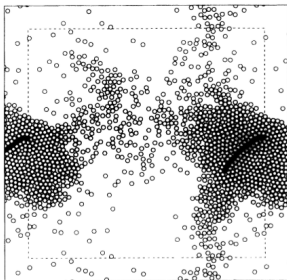
- ▶ No gravity
- ▶ Particles: $\mathbf{r}_i(t)$, $\mathbf{v}_i(t)$, $\omega_i(t)$, R_i
- ▶ Calculate collision time: Let $\mathbf{d}_{ij} = |\mathbf{r}_i - \mathbf{r}_j| - R_i - R_j$, Then

$$\tau_{ij} = \frac{|\mathbf{d}_{ij}|^2}{(\mathbf{v}_i - \mathbf{v}_j) \cdot \mathbf{d}_{ij}}$$

- ▶ Order collision times, get the smallest $\tau_c = \min_{ij}(\tau_{ij})$
- ▶ Go to time $t + \tau_c$ $\mathbf{r}_i(t + \tau_c)$
- ▶ Calculate velocities after collision $\mathbf{v}_i(t + \tau_c)$ (may be hard...)
- ▶ Restart loop
- ▶ Next time Calculate collision time only with i, j
- ▶ Dynamic list, change only newly calculate collision times

Inelastic collapse

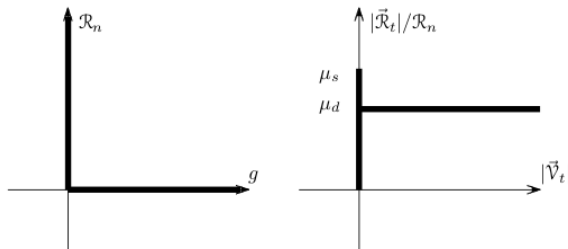
- ▶ Coefficient of restitution $r = v_n(t_c+)/v_n(t_c-)$
- ▶ Energy is lost in an exponential way (Ping Pong)
- ▶ Infinite collisions in finite time
- ▶ Solution $\rightarrow r = 1$ if collisions occur more frequently than a parameter t_{cont} , the contact duration
- ▶ Contact \rightarrow small vibration :-(well...)



MOVIE

Contact dynamics

- ▶ Perfectly rigid particles
- ▶ Non-smooth dynamics
- ▶ Constraints



- ▶ Molecular dynamics
 - ▶ Normal force: overlap (smooth)
 - ▶ Shear force: history

Contact dynamics

- Implicit forces

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{1}{m_i} \mathbf{F}_i(t + \Delta t) \Delta t$$

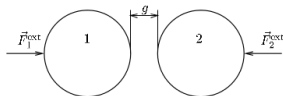
$$\mathbf{x}_i(t + \Delta t) = \mathbf{x}_i(t) + \mathbf{v}_i(t + \Delta t) \Delta t$$

such as constraints are fulfilled

- if gap would be negative increase force
- if there would be a shear displacement increase shear force
- if shear force is larger than allowed restrict it to that value

Contact dynamics, force calculation

- Two particles with gap g



$$\text{if } \mathcal{V}_n^{\text{free}} \Delta t + g^{\text{pos}} > 0$$

$$\text{then } \begin{cases} \vec{\mathcal{R}}^{\text{new}} = 0 \end{cases} \quad (\text{no contact})$$

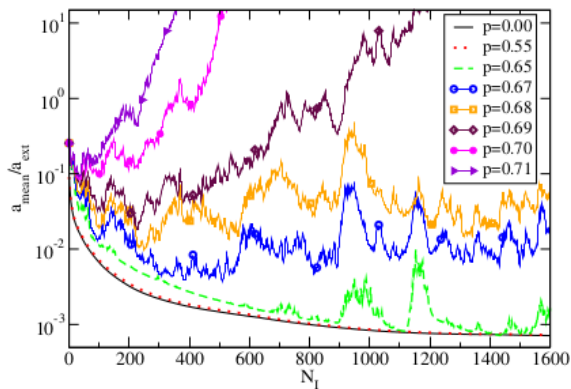
$$\text{else } \begin{cases} \mathcal{R}_n^{\text{new}} = -\frac{1}{\Delta t} m_n \left(\frac{g^{\text{pos}}}{\Delta t} + \mathcal{V}_n^{\text{free}} \right) \\ \vec{\mathcal{R}}_t^{\text{new}} = -\frac{1}{\Delta t} m_t \vec{\mathcal{V}}_t^{\text{free}} \end{cases} \quad (\text{sticking contact})$$

$$\text{if } \left| \vec{\mathcal{R}}_t^{\text{new}} \right| > \mu \mathcal{R}_n^{\text{new}}$$

$$\text{then } \begin{cases} \vec{\mathcal{R}}_t^{\text{new}} = \mu \mathcal{R}_n^{\text{new}} \frac{\vec{\mathcal{R}}_t^{\text{new}}}{\left| \vec{\mathcal{R}}_t^{\text{new}} \right|} \end{cases} \quad (\text{sliding contact})$$

Iterative solver

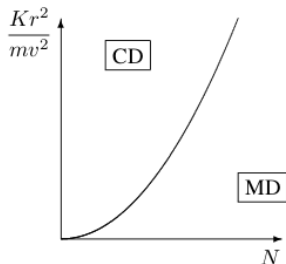
- Updates:
 - Parallel: calculate all contacts with old values then change to new at once → serious instabilities
 - Serial: update contacts one-by-one in random order



Molecular versus Contact dynamics

Limit

$$\frac{Kr^2}{mv^2} = N^{4/d}$$

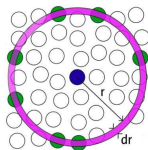


DEM plus differential equations

- ▶ Standard interfaces
- ▶ Solve the differential equations using the particles as boundaries
- ▶ Transfer back forces to DEM
- ▶ Integrate DEM

MOVIE

Practice: Pair correlation function



1. Data: x y type
2. Calculate the pair correlation function, the average density of the particles at distance r from any particle. Only the center of the particles count

$$g(r) = \frac{1}{4\pi r^2} \frac{1}{N_\rho} \sum_{i=1}^N \sum_{j \neq i}^N \delta(r - |\mathbf{r}_j - \mathbf{r}_i|)$$

- ▶ Instead: do histogram of pair distance
 - ▶ System is periodic in x direction $L_x = 69$
3. Calculate the angular distribution of the neighbours (Make histogram using the angle of the distance vector with the horizontal)
 - ▶ Do the same only for identical particles.
 - ▶ Neighbors are the ones with distance less than 1.1