Computational Statistical Physics

Pascal Debus *

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Abstract

This is a short summary of the lecture *Computational Statistical Physics* given by Professor Hans J. Herrmann at ETH Zurich in spring 2014. It strongly focuses around the expected exam questions and is hence not complete.

1 General

1.1 Questions of last semester

- Critical behavior of the Ising model
- $M(RT)^2$ canonical Monte Carlo
- Detailed Balance
- Finite size scaling

1.2 Relevant questions

- Fluctuation-dissipation theorem for M
- Dynamic correlations and dynamic scaling
- Glauber and Kawasaki dynamics
- Creutz demons
- Binder cumulants
- First order transitions (Potts model)
- Swendsen-Wang cluster algorithm
- Verlet and leap frog schemes
- Verlet tables and linked cells
- Particle-mesh method
- Constraint method with Lagrange multipliers
- Rigid bodies, quaternions
- Nose-Hoover thermostat
- Event driven simulations
- Inelasticity and finite time singularity

2 Classical Statistical Mechanics

- many body system of N **classical** particles i
- n degrees of freedom $p_i^{(j)}$ (discrete or continuous)
- **Configuration** X

$$\boxed{X = \{p_i^{(j)}, i = 1, \dots, N, j = 1, \dots, n\}}$$

- time evolution described by Hamiltonian H through **Liouville equation**

$$\frac{\partial \rho}{\partial t}(X, t) = -\{H, \rho\}$$

with **distribution of configurations** ρ

- **Thermal equilibirum** defined by steady state Liouville equation

$$\boxed{\frac{\partial \rho}{\partial t} = 0}$$

- **Thermal average over quantity** Q

$$\boxed{\langle Q \rangle = \frac{1}{\Omega} \sum_X Q(X)\rho(X)}$$

with phase space volume Ω

2.1 Ensembles

- **Microcanonical**: fix E, V, N
- **Canonical**: fix T, V, N
- **Grandcanonical**: fix T, V, μ
- **Canonical pressure**: fix T, p, N

*pdebus@student.ethz.ch

2.1.1 Microcanonical Ensemble

$E(X)$ energy of configuration X is *fixed* and probability for system to be in X is equal for all E:

$$\boxed{p_{\text{eq}}(X) = \frac{1}{Z_{\text{mc}}}\delta(H(X) - E)}$$

with partition function Z_{mc}

$$\boxed{Z_{\text{mc}} = \sum_X \delta(H(X) - E) = \text{Tr}[\delta(H(X) - E)]}$$

2.1.2 Canonical Ensemble

Temperature T is fixed and probability to be in X is given by the **Boltzmann factor**

$$\boxed{p_{\text{eq}} = \frac{1}{Z_T}\exp\left(\frac{E(X)}{kT}\right)}$$

with **partition function**

$$\boxed{Z_T = \sum_X e^{-\frac{E(X)}{kT}}}$$

Thermal average of quantity Q

$$\boxed{\langle Q(T)\rangle = \frac{1}{Z_T}\sum_X Q(X)e^{-\frac{E(X)}{kT}}}$$

2.2 Ising Model

Spins on a lattice, interacting via **Hamiltonian**

$$\mathcal{H} = E = -J\sum_{\langle i,j\rangle}^{N}\sigma_i\sigma_j - H\sum_{i=1}^{N}\sigma_i, \quad \sigma_i = \pm 1,\ i = 1,\dots,N$$

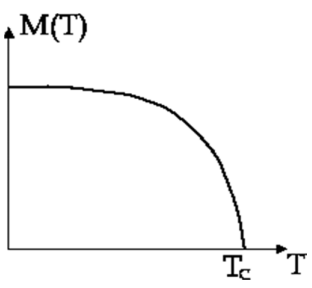
2.2.1 Order parameter

Spontaneous magnetization

$$\boxed{M_S(T) = \lim_{H\to 0}\left\langle \frac{1}{N}\sum_{i=1}^{N}\sigma_i\right\rangle}$$

Critical behavior with exponent $\beta = 1/8$(2D), $\beta \approx 0.326$(3D)

$$\boxed{M_S \propto (T - T_c)^\beta}$$

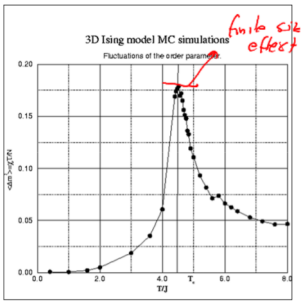


2.2.2 Response functions

measure the sensitivity of a system w.r.t. external field or temperature.

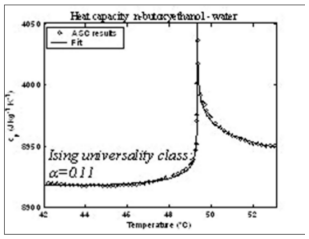
Susceptibility

$$\boxed{\chi(T) = \left.\frac{\partial M}{\partial H}\right|_{T,H=0} \propto |T - T_c|^{-\gamma}}$$



Specific heat

$$\boxed{C_V(T) = \left.\frac{\partial E}{\partial T}\right|_H \propto |T - T_c|^{-\alpha}}$$



$\rightarrow$ both diverge at T_c.

2.2.3 Fluctuation-dissipation theorem

Derivation for the susceptibility. Define

$$\mathcal{H}_0 = \beta J\sum_{\langle i,j\rangle}^{N}\sigma_i\sigma_j, \quad \beta = \frac{1}{kT}$$

We then have

$$\chi(T) = \left.\frac{\partial\langle M(T,H)\rangle}{\partial H}\right|_{H=0} = \frac{\partial}{\partial H}\frac{\sum_X\sum_{i=1}^{N}\sigma_i e^{\mathcal{H}_0+\beta H\sum_{i=1}^{N}\sigma_i}}{\underbrace{\sum_X e^{\mathcal{H}_0+\beta H\sum_{i=1}^{N}\sigma_i}}_{=Z_T(H)}}\Bigg|_{H=0}$$

$$= \left.\frac{\beta\sum_X\left(\sum_{i=1}^{N}\sigma_i\right)^2 e^{\mathcal{H}_0+\beta H\sum_{i=1}^{N}\sigma_i}}{Z_T(H)}\right|_{H=0}$$

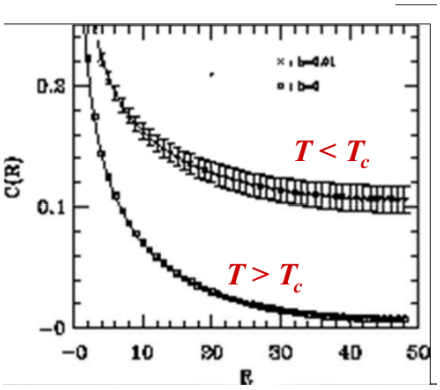
$$- \left.\frac{\beta\left(\sum_X\sum_{i=1}^{N}\sigma_i e^{\mathcal{H}_0+\beta H\sum_{i=1}^{N}\sigma_i}\right)^2}{(Z_T(H))^2}\right|_{H=0}$$

$$= \beta\left[\langle M(T)^2\rangle - \langle M(T)\rangle^2\right] \quad \Rightarrow \quad \chi(T) \geq 0$$

where in the last line we arrive at the expression for the **fluctuation of the magnetizability**
Analogously for the **specific heat**:

$$\boxed{C_V = \beta^2 \left[\langle E^2\rangle - \langle E\rangle^2\right]}$$

2.2.4 Correlation length



Correlation function

$$\boxed{C(R) = \langle \sigma(0)\sigma(R)\rangle}$$

- $T \neq T_c$, large R: $\boxed{C(R) \propto M^2 + ae^{-\frac{R}{\xi}}}$ where ξ is the **correlation length**
- $T = T_c$, large R: $\boxed{C(R) \propto R^{2-d-\eta}}$, $\eta = 1/4(0.05)$
- correlation length *diverges* at T_c

$$\boxed{\xi \propto |T - T_c|^{-\nu}}, \quad \nu = 1(0.63)$$

Exponent relations

$$\alpha + 2\beta + \gamma = 2, \quad 2 - \alpha = d\nu, \quad (2-\eta)\nu = \gamma$$

- First relation: **scaling**
- Other relations: **hyperscaling**
- → only two exponents independent
- used for consistency check in numerical results

3 Monte Carlo Method

Ensemble average over phase space Λ with probability measure $\mathrm{d}\mu$ (normalization with partition function)

$$\langle f\rangle = \int_\Lambda f \,\mathrm{d}\mu = \overline{f}_t = \lim_{T\to\infty} \frac{1}{T}\int_0^T f(x(t))\,\mathrm{d}t \qquad (1)$$

- The normalizing factor of the measure is called **partition function**
- From the ergodic hypothesis follows that all microstates are **equiprobable**
- The energy of configuration X is $E(X)$
- Probability (at thermal equilibrium) given by

$$\boxed{p_{eq} = \frac{1}{Z_T} e^{-\frac{E(X)}{k_B T}}}$$

with the partition function $Z_T = \sum_X e^{-\frac{E(X)}{k_B T}}$.

Discrete ensemble average

$$\langle Q\rangle = \sum_X Q(X) \underbrace{p_{\mathrm{eq}}}_{\text{Boltzmann}} (X) \qquad (2)$$

Problem of Sampling
It is inefficient to calculate ensemble averages in an equally distributed system. Hand-waving argument: Peak of energy increase as $\sqrt{L^{\mathrm{d}}}$, but system size increases as L^d, therefore relative peak width **decreases** with increasing system size.

3.0.5 Markov chains

Start in configuration X and propose new configuration Y with probability $T(X \to Y)$.

Properties for proposing a new state:

- **Ergodicity**: reach any possible configuration after finite number of steps (A state is *ergodic* if it is aperiodic and positively recurrent)
- **Normalization**: $\sum_Y T(X \to Y) = 1$
- **Reversibility**: $T(X \to Y) = T(Y \to X)$

→ not every new configuration is also **accepted**.

Accept a new configuration with some acceptance probability to control dynamics (e.g. temperature dependence), therefore **total Markov chain acceptance probability** (Overall probability of a configuration making it through both steps.)

$$W(X \to Y) = \underbrace{T(X \to Y)}_{\text{Transition Prob}} \cdot \underbrace{A(X \to Y)}_{\text{Acceptance Prob}} \qquad (3)$$

(Can also be interpreted as conditional probability of acceptance for given y)

Master equation

$$\boxed{\frac{\mathrm{d}p(X,t)}{\mathrm{d}t} = \sum_Y p(Y)W(Y \to X) - \sum_X p(X)W(X \to Y)} \qquad (4)$$

where $p(x,t)$ is the probability to find x in time t

Properties of $W(x \to Y)$:

- **Ergodicity**: $\forall X, Y \quad W(X \to Y) > 0$
- **Normalization**: $\sum_Y W(X \to Y) = 1$
- **Homogeneity**: $\sum_Y p_{\mathrm{st}}(Y)W(Y \to X) = p_{\mathrm{st}}(X)$

3.0.6 Detailed Balance

The stationary states of the Markov chains,

$$\frac{\mathrm{d}p(X,t)}{\mathrm{d}t} = 0 \tag{5}$$

should model Boltzmann equilibrium distribution:

$$p_{\mathrm{st}}(X) = p_{\mathrm{eq}}(X) = \frac{1}{Z_T} e^{-\frac{E(X)}{k_B T}} \quad \forall X \tag{6}$$

$$\Rightarrow \sum_Y p_{eq}(Y) W(Y \to X) = \sum_Y P_{eq}(X) W(X \to Y) \tag{7}$$

One finds the **detailed balance condition**

$$\boxed{p_{\mathrm{eq}}(X) W(X \to Y) = p_{\mathrm{eq}}(Y) W(Y \to X) \quad \forall X, Y} \tag{8}$$

such that **the steady state is the thermal equilibrium.**

Since $W(X \to Y) = T(X \to Y) \cdot A(X \to Y)$ and $T(X \to Y) = T(Y \to X)$ one can rewrite the detailed balance condition to

$$p_{\mathrm{eq}}(X) A(X \to Y) = p_{\mathrm{eq}}(Y) A(Y \to X) \quad \forall X, Y \tag{9}$$

3.0.7 MR^{2}T^2

Basic Idea: Carry out importance sampling through a Markov Chain. Acceptance probability is

$$A(X \to Y) = \min\left(1, \frac{p_{\mathrm{eq}}(Y)}{p_{\mathrm{eq}}(X)}\right) \tag{10}$$

$$= \min\left(1, \frac{\frac{1}{Z} e^{-\frac{E(Y)}{kT}}}{\frac{1}{Z} e^{-\frac{E(X)}{kT}}}\right) \tag{11}$$

$$= \min\left(1, e^{-\frac{(E(Y)-E(X))}{kT}}\right) \tag{12}$$

$$\tag{13}$$

$$\boxed{A(X \to Y) = \min\left(1, e^{\frac{\Delta}{k_B T}}\right)}$$

Always accept transitions to lower energy. Thermal equilibrium is enforced by detailed balance.

3.0.8 Glauber dynamics

Acceptance probability is

$$\boxed{A(X \to Y) = \frac{e^{-\frac{\Delta E}{kT}}}{1 - e^{-\frac{\Delta E}{kT}}}} \tag{14}$$

Glauber dynamics are superior at low temperatures due to different acceptance formulation.

3.1 Ising model

Consider a discrete collection of N binary variables(spins) $\sigma_i \in \{-1, +1\}$ Hamiltonian

$$\mathcal{H} = E = -\sum_{i,j} J_{ij} \sigma_i \sigma_j - H_i \sigma_i \tag{15}$$

Coupling $J_{ij} = J$ is typically just for nearest neighbors and H_i usually homogeneous external field.

Example: 1D ferromagnetic Ising: $E = \sum_i \sigma_i \sigma_{i+1}$.

3.1.1 Monte-Carlo-Algorithm

1. Choose randomly site i having spin state σ_i
2. Calculate

$$\Delta E = E(Y) - E(X) = \sum_{<i,j>\text{n.n.}} 2J\sigma_i\sigma_j$$

$$= 2J\sigma_i h_i$$

$$h_i = \sum_{\text{n.n of} i} \sigma_j$$

3. If $\Delta E < 0$ flip spin
4. If $\Delta E \geq 0$ flip spin with probability $e^{-\frac{\Delta E}{kT}}$

Sweep: Group of N steps.

Magnetization Let M be the magenetization, χ magnetic susceptibility and H the magnetic field strength. Then

$$M = \chi H \tag{16}$$

$$M(T) = \frac{1}{N} \lim_{H \to 0} \sum_{i=1}^{N} \sigma_i \tag{17}$$

$$\propto \begin{cases} |T_c - T|^\beta & T < T_c \\ 0 & T > T_c \end{cases} \tag{18}$$

where $\beta = \frac{1}{8}$(2D), 0.326(3D). We have a singularity at the critical temperature(or a maximum if the system is finite).

Magnetic susceptibility

$$M = \chi H \tag{19}$$

$$\chi \propto (T - T_c)^{-\gamma} \tag{20}$$

Energy and heat capacity Energy increases with T (S-like curve), heat capacity has peak at T_c

3.2 MCM Implementation Details

3.2.1 Look-up tables

Consider Ising model on a **square lattice** $\to$ four next neighbors

$$h_i \sum_{j \text{ nn of } i}^{4} \sigma_j \in \{0, \pm 2, \pm 4\}$$

$$\to \frac{\Delta E}{J} = 2\sigma_i h_i \in \{0, \pm 4, \pm 8\}$$

- for $\Delta E \leq$ we accept with probability 1
- $\to$ need to store only two values

$$\boxed{P(k) = e^{-4\beta J k}, \quad k = \frac{1}{2}\sigma_i h_i \in \{1, 2\}}$$

3.2.2 Boundary conditions

- **Open**: no neighbors → needs exception for the boundaries
- **Fixed**: neighbor with fixed spins→ imposes a field
- **Periodic**: define index vectors
- **Helical**: index system as a one dimensional string: For $\boxed{k = i + j(L-1)}$ we have the neighbors $\boxed{k \pm 1,\ k \pm L}$
  → physically corresponds to applying a velocity (sort of)

3.2.3 Multi-spin coding

- technique to increase speed and reduce memory space for Boolean variables
- computer word size is 64 bits
- consider Ising model on **simple cubic lattice**
  - six nearest neighbors
  - energy can have 7 different values $(0, \ldots, 6)$
  - → 3 bits per site

Define ith site in a word $(i = 1, \ldots, 21)$, hence we 21 sites per word:

$$\boxed{N_i = (0, \ldots, 0, 1, 0, \ldots, \underbrace{0, 0, 0}_{\text{site } 1})}$$

Use bitwise `XOR`, since energy changes only if neighboring spins are different.
Store neighboring sites in *different words* N_j and calculate energy of 21 sites simultaneously by

$$\boxed{E = N \texttt{XOR} N_1 + \ldots + N \texttt{XOR} N_6}$$

- **Extract last 3 bits of E** with mask $7 = (0, \ldots, 0, 1, 1, 1)$ through $\boxed{E\&7}$
- **changer word** `cw` 1 if spin is flipped, 0 if spin is not flipped(`XOR`ing with `cw` flips every spin)

Code

```
cw=0;                    //Nothing to be changed
for(i=1;i<=21;i++)       //21 sites in one word
{
    z=ranf();            //select random spin
    if(z<P(E&7))         //lookup energy and test
    cw=(cw|1);           //set first bit of c}w
    cw=ror(cw,3);        //shift by 3 to next site
    E=ror(E,3);          //shift by 3 to next site
}
cw=ror(cw,1);            //shift unused bit to front
N=(N^cw);                //Apply cw: spin flip
```

3.3 Sampling

- each spin flips generates new configuration *very similar* to the previous one
- → samples in our Markov chain are **very correlated**
- for averages statisitically uncorrelated configurations are needed
- also decorrelation from initial configuration is needed

3.3.1 Dynamic interpreation of MC

Time evolution of a quantity A

$$\boxed{\langle A(t)\rangle = \sum_X p(X,t)A(X) = \sum_X p(X,t_0)A(X(t))}$$

with

$$\boxed{\frac{\mathrm{d}p(X,t)}{\mathrm{d}t} = \sum_Y p(Y)W(Y \to X) - \sum_Y p(X)W(X \to Y)}$$

Suppose configuration at t_0 is *not at equilibrium*. Then define the **non-linear correlation function** or **relaxation function**

$$\Phi_A^{\mathrm{nl}} = \frac{\langle A(t)\rangle - \langle A(\infty)\rangle}{\langle A(t_0)\rangle - \langle A(\infty)\rangle}$$

where $A(\infty)$ denotes the equilibrium value. Function is normalized such that it

- starts at value 1 at $t = t_0$
- decays to value 0 at $t = \infty$

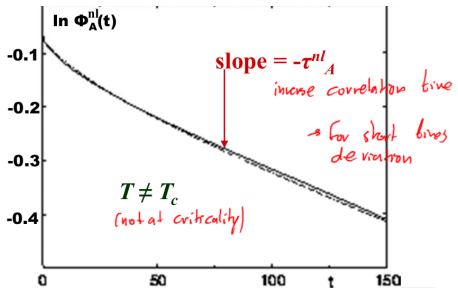
3.3.2 Non-linear correlation time

$$\boxed{\tau_A^{\mathrm{nl}} \equiv \int_0^\infty \Phi_A^{\mathrm{nl}}(t)\,\mathrm{d}t}$$

Connection to non-linear correlation function

$$\boxed{\Phi_A^{\mathrm{nl}}} = e^{-\frac{t}{\tau_A^{\mathrm{nl}}}}$$

Describes relaxation **towards** equilibrium



Critical slowing down

$$\boxed{\tau_A^{\mathrm{nl}} \propto |T - T_c|^{z_A^{\mathrm{nl}}}}$$

- $\rightarrow$ correlation time diverges
- $\rightarrow$ at criticality one never reaches equilibrium
- z_A^{nl} is the **non-linear dynamical exponent**
- depends on the quantity under study, dynamics and dimension

3.3.3 Linear correlation function

$$\boxed{\Phi_{AB}(t) = \frac{\langle A(t_0)B(t)\rangle - \langle A\rangle\langle B\rangle}{\langle AB\rangle - \langle A\rangle\langle B\rangle}}$$

defined for two quantities A and B **in equilibrium** and with

$$\langle A(t_0)B(t)\rangle = \sum_X p(X,t_0)A(X(t_0))B(X(t))$$

For $A = B$ we have **auto correlation**, e.g. **spin-spin correlation**

$$\boxed{\Phi_\sigma(t) = \frac{\left\langle \sigma(t_0)\sigma(t) - \langle\sigma(t_0)\rangle^2 \right\rangle}{\langle\sigma(t_0)^2\rangle - \langle\sigma(t_0)\rangle^2}}$$

3.3.4 Linear correlation time

$$\boxed{\tau_{AB} \equiv \int_0^\infty \Phi_{AB}(t)\,\mathrm{d}t}$$

connection to linear correlation function

$$\Phi_{AB}(t) = e^{-\frac{t}{\tau_{AB}}}$$

Describes relaxation **in** equilibrium.

Critical slowing down

$$\boxed{\tau_{AB} \propto |T - T_c|^{-z_{AB}}}$$

where z_{AB} is the **dynamical critical exponent**. For kinetic Ising model $z_\sigma = 2.16(2.09)$

Conjectured relations to non-linear exponents

$$z_\sigma - z_\sigma^{\text{nl}} = \beta, \quad z_E - z_E^{\text{nl}} = 1 - \alpha$$

3.3.5 Critical dynamics in finite sizes

At T_c we have

$$L = \xi(T) \propto |T - T_c|^{-\nu}$$

and hence

$$\boxed{\tau_{AB} \propto |T - T_c|^{-z_{AB}} \propto L^{\frac{z_{AB}}{\nu}}}$$

- number of discarded samples grows like power law of system size
- finite size $\rightarrow$ finite correlation time
- $\rightarrow$ solution to critical slowing down

3.3.6 Decorrelated configurations

- First to **reach equilibrium** throw away $\boxed{n_0 = c\tau^{\text{nl}}(T)}$ configurations
- Then take only every n_eth configuration with $\boxed{n_e = c\tau(T)}$
- At criticality: τ make no sense any more, $\rightarrow$ replace by system size
- At T_c use:

$$\boxed{n_0 = cL^{\frac{z^{\text{nl}}}{\nu}}, \quad n_e = cL^{\frac{z}{\nu}}, \quad c \approx 3}$$

3.4 Finite size effects

Correlation length ξ cannot be larger than system size L, therefore maximum instead of a singularity:

The correlation length gets cut at the size L of the system Use two points p_1, p_2 bounding the critical region, then

$$L = \xi(p_1) \propto (p_1 - p_c)^{-\nu}$$
$$p_1 - p_2 \approx 2(p_1 - P - c)$$

assuming p_c lies approximately in the center of the region.

It follows for the size of the critical region:

$$(p_1 - p_2) = L^{-\frac{1}{\nu}} \tag{21}$$

Conclusion: If $L \rightarrow \infty$, the critical region vanishes, which is impossible with a finite PC.
Hence we need to extrapolate the behavior

Close to p_c (extrapolation not scaling):

$$\boxed{p_{\text{eff}}(L) = p_c\left(1 - aL^{-\frac{1}{\nu}}\right)} \tag{22}$$

3.5 Finite size scaling

Consider the second moment χ of the cluster size distribution as a function of p and L.
$\rightarrow$ can be reduced to a one variable function.
Self-similarity of percolating clusters near critical point

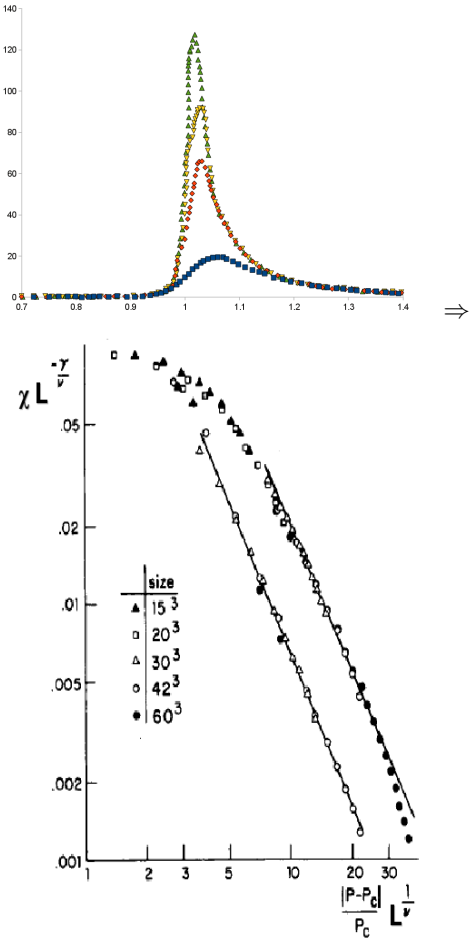
$$\boxed{\chi(p,L) = L^{\frac{\gamma}{\nu}}\mathcal{N}_\chi\left[(p - p_c)L^{\frac{1}{\nu}}\right]} \tag{23}$$

where $\mathcal{N}_\chi$ is the scaling function.

Plotting χ against p for several L-values, leads to differences at the critical value(peak height)

At $p = p_c$ the scaling function approaches a constant and

$$\boxed{\chi_{\max} = L^{\frac{\gamma}{\nu}}} \tag{24}$$



If we find an expression for the size of the peak depending only on L as well as introducing new parameters, based on previous one, a **data collapse** happens:
Only one parameter is necessary to describe the data.

Size dependence of the Order parameter
Fraction of sites in the spanning cluster at p_c:

$$s_\infty \propto L^{d_f}$$
$$\Rightarrow \boxed{PL^d = s_\infty \propto L^{d_f}}$$

3.5.1 Fractal dimension in percolation

Fraction of sites in spanning cluster (order parameter):

$$P(p) = (p - p_c)^\beta \tag{25}$$

consider P as function of p and L, then **finite size scaling**

$$\boxed{P(p, L) = L^{-\frac{\beta}{\nu}} \mathcal{N}_P \left[(p - p_c) L^{\frac{1}{\nu}}\right]} \tag{26}$$

At $p = p_c$ order parameter

$$P = L^{-\frac{\beta}{\nu}} \tag{27}$$

and number of sites of the spanning cluster

$$s_\infty = M \propto L^{d_f} \tag{28}$$

depends on the system size.

We know

$$M = PL^d = L^{-\frac{\beta}{\nu}+d} \overset{!}{=} L^{d_f} \tag{29}$$
$$d_f = d - \frac{\beta}{\nu} \tag{30}$$

3.6 Heat bath method

Start with **Glauber dynamics** spin-flip probability

$$A_i \equiv \frac{e^{-2\beta\sigma_i h_i}}{1 + e^{-2\beta\sigma_i h_i}}, \quad h_i = \sum_{j=\text{nn}} \sigma_j$$

Implementation using random number z:

$$\sigma_i(t+1) = -\sigma_i(t)\,\text{sign}(A_i - z)$$

Probability for (no) spin flip

$$p_{\text{flip}} = A_i(\sigma_i) = \begin{cases} p_i, & \text{for } \sigma_i = -1 \\ 1 - p_i, & \text{for } \sigma_i = +1 \end{cases}, \quad p_i = \frac{e^{2\beta h_i}}{1 + e^{2\beta h_i}}$$

$$p_{\text{no flip}} = 1 - A_i(\sigma_i) = \begin{cases} 1 - p_i, & \text{for } \sigma_i = -1 \\ p_i, & \text{for } \sigma_i = +1 \end{cases}$$

Now we have probability p_i for conserving a spin $\sigma_i = +1$ and probability p_i to flip a spin with $\sigma_i = -1$ such that the following total probability occur for positive and negative spins:

$$\boxed{\sigma_i = +1 \text{ with } p_i, \quad \sigma_i = -1 \text{ with } 1 - p_i}$$

For the heat bath method just choose site i and set spin according to above probabilities.

3.7 Binary mixtures

- Two species A and B with given concentrations on the lattice sites
- E_{AA} energy of A-A-bond
- E_{BB} energy of B-B-bond
- E_{AB} energy of A-B-bond
- Set $E_{AA} = E_{BB}$ and $E_{AB} = 1$
- $\rightarrow$ Ising model with $J = 1$ and constant M

Kawasaki dynamics

1. Choose random A-B-bomd
2. Calculate ΔE for A-A $\rightarrow$ B-A
3. Flip according to Metropolis or Glauber

4 Microcanonical Monte Carlo

4.1 Creutz algorithm

Deterministic algorithm. Softens energy conservation restriction:
Introduce *small* energy reservoir E_d called **demon** which can store a maximum energy $E_{\max}$

1. choose randomly a site
2. calculate ΔE for spin flip
3. Accept flip if

$$E_{\max} \geq E_d - \Delta E \geq 0 \quad \Leftrightarrow \quad E_d - \Delta E \in [0, E_{\max}]$$

- algorithm is **deterministic**
- **reversible**, there exist no transients
- good for multi-spin coding and parallelisation
- obtain temperature T trough **histogram** $P(E_d)$ of the energies E_d of the demon

$$\boxed{P(E_d) \propto e^{-\frac{E_d}{kT}}}$$

- should follow Boltzmann distribution
- demon corresponds to heat bath

4.2 Q2R

Case $\boxed{E_{\max} = 0}$ of Creutz algorithm on square lattice.
Totalistic cellular automaton

$$\sigma_{ij}(t+1) = \underbrace{f(x_{ij})}_{\text{changer word}} \oplus \sigma_{ij}(T), \quad \sigma_{ij} \in \{1, 0\}$$

$$f(x) = \begin{cases} 1, & \text{if } x = 2 \\ 0, & \text{if } x \neq 2 \end{cases}$$

Sum over next neighbors

$$x_{ij} = \sigma_{i-1,j} + \sigma_{i+1,j} + \sigma_{i,j-1} + \sigma_{i,j+1}$$

Expression with logical functions

$$\sigma(t+1) = \sigma(t) \oplus ((\sigma_1 \oplus \sigma_2) \wedge (\sigma_3 \oplus \sigma_4) \vee ((\sigma_1 \oplus \sigma_3) \wedge (\sigma_2 \oplus \sigma_4)))$$

- deterministic and reversible, but **not ergodic**
- Energy

$$\boxed{E = \sum_{\langle i,j \rangle} \sigma_i \oplus \sigma_j}$$

is a conserved quantity

4.2.1 Implementation

Divide lattice in two sub-lattices σ and $\widehat{\sigma}$ and use **multi-spin coding** to implement reversbile bitwise logical automaton

$$\boxed{R = \begin{cases} \sigma_i(t+1) = f(\widehat{\sigma}_j(t))_{j=\mathrm{nn}(i)} \oplus \sigma_i(t) \\ \sigma_i(t+1) = f\left(f(\widehat{\sigma}_k(t))_{j=\mathrm{nn}(j)} \oplus \sigma_j(t)\right) \widehat{\sigma}_i(t) \end{cases}}$$

5 Binder cumulants

→ Method to obtain the **critical Temperature**, more accurate than determining the maximum of χ at T_c

5.1 General definition: Cumulants

Cumulants of a random variable X are defined via the **cumulant-generating function** $g(t)$ which is the logarithm of the **moment-generating function**. The cumulants are given as coefficients κ_n in the seris expansion:

$$g(t) = \log \left\langle e^{tX} \right\rangle = \sum_{n=1} \kappa_n \frac{t^n}{n!}$$

- **First cumulant**: expected value
- **Second and third cumulant**: second(variance) and third **central moment**
- **Higher cumulants**: polynomial expression of the moments, e.g. $\boxed{\kappa_4 = \mu_4 - 3\mu_2^2}$
- In statistical physics: normalized with respect to Gaussian fluctations

$$\tilde{\kappa} = 1 - \frac{\mu_4}{3\mu_2^2}$$

which for finite size L systems directly leads to the definition of

5.2 Binder cumulants

$$\boxed{U_L \equiv 1 - \frac{\langle M^4 \rangle_L}{3 \langle M^2 \rangle_L^2}}$$

$$\frac{\langle M^4 \rangle_L}{\langle M^2 \rangle_L^2} = \frac{L^{\frac{4\beta}{\nu}} \mathfrak{J}\left((T - T_c) L^{\frac{1}{\nu}}\right)}{\left(L^{\frac{2\beta}{\nu}} \mathfrak{J}\left((T - T_c) L^{\frac{1}{\nu}}\right)\right)^2} = \mathfrak{Je}\left((T_c - T) L^{\frac{1}{\nu}}\right)$$

which becomes **independent** of L at T_c

5.2.1 Above critical Temperature $T > T_c$

magnetization follows Gaussian distribution

$$P_L = \sqrt{\frac{L^d}{\pi\sigma_L}} e^{-\frac{M^2 L^d}{\sigma_L}}, \quad \sigma_L = kT2\chi_L$$

such that

$$\boxed{\langle M^4 \rangle_L = 3 \langle M^2 \rangle_L^2 \quad \Rightarrow \quad U_L = 0}$$

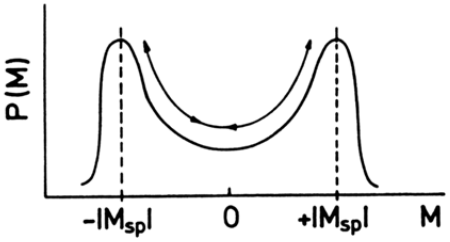
5.2.2 Below critical Temperatur $T < T_c$

magnetization follows superposition of two Gaussians

$$P_L(M) = \frac{1}{2}\sqrt{\frac{L^d}{\pi\sigma_L}} \left[e^{\frac{(M-M_s)^2 L^d}{\sigma_l}} + e^{\frac{(M-M_s)^2 L^d}{\sigma_l}} \right]$$

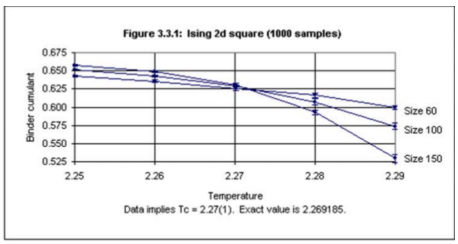
such that

$$\boxed{\langle M^4 \rangle_L = \langle M^2 \rangle_L^2 \quad \Rightarrow \quad U_L = \frac{2}{3}}$$



5.3 Critical temperature

$$\boxed{U_L = 1 - \frac{\langle M^4 \rangle_L}{3 \langle M^2 \rangle_L^2} \xrightarrow{L\to\infty} \begin{cases} 0, & \text{for } T > T_c \\ \frac{2}{3}, & \text{for } T < T_c \end{cases}}$$



6 Corrections to Scaling

$\rightarrow$ Scaling laws onyl hold at T_c

$$M(T) = A(T_c - T)^{\beta} + A_1(T_c - T)^{\beta_1} + \cdots$$
$$\xi(T) = C(T_c - T)^{-\nu} + C_1(T_c - T)^{-\nu_1} + \cdots$$

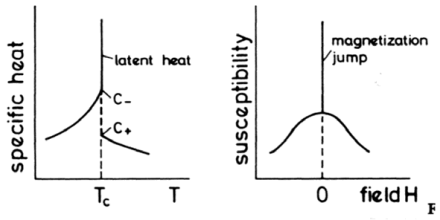
with non-integer subdominant exponents $\beta_1 > \beta$ and $\nu_1 < \nu$, as **universal correction to scaling exponents**, obtained numerically as fit parameters

$$\boxed{M(T,L) = L^{\frac{\beta}{\nu}} \mathfrak{I}_M \left((T_c - T) L^{\frac{1}{\nu}} \right) + L^x \mathfrak{I}_M^1 \left((T_c - T) L^{\frac{1}{\nu}} \right) + \cdots}$$

where $\boxed{x = \max \left[\frac{\beta_1}{\nu}, \frac{\beta}{\nu_1}, \frac{\beta}{\nu} - 1 \right]}$

7 First order transition

- For $T < T_c$ Ising model has at $H = 0$ **phase transition of first order**
- $\rightarrow$ jump in **magnetization** of ΔM, **entropy** ΔS and
- $\rightarrow$ susceptibility and specific heat exhibit **delta function** behavior at transition **latent heat** ΔE
- we have hysteresis and for small systems, magnetization jumps after **ergodic time** T_e



7.1 Finite Size Scaling of first order transitions

Consider times much larger than T_e. From the distribution of the magnetization of two Gaussians one can derive

$$M(H) = \chi_L^D H + M_L \tanh(\beta H M_L L^d)$$
$$\chi_L(H) = \frac{\partial M}{\partial H} = \chi_L^D + \frac{\beta M_L^2 L^d}{\cosh^2(\beta H M_L L^d)}$$

Maximum of susceptibility and width of the peak

$$\chi_L(H = 0) \sim L^d, \quad \Delta\chi_L \sim L^{-d}$$

- finite size behavior: no critical points, no critical epxonents
- BUT signals of the delta function in numerics
- above behavior of maximum and width similar to delta function

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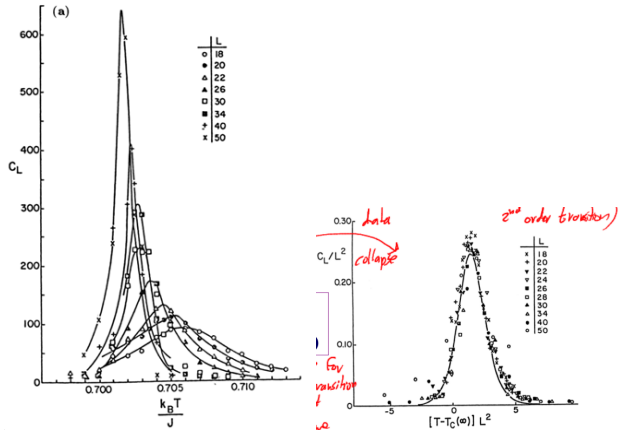
7.2 Potts model

Generalization of the Ising model to more than two states

$$\boxed{\mathcal{H} = E = -J \sum_{\langle i,j \rangle} \delta_{\sigma_i,\sigma_j} - H_1 \sum_i \delta_{\sigma_1,1} \quad \sigma_i = 1, \ldots, q}$$

- $q = 2$ corresponds to Ising model
- $q \to 1$ bond percolation due to Theorem of **Kasteleyn and Fortuin**
- application in surface science, opinion model, QCD

- prototype model for **first order transition** (in T)
- 2D: for $q > 4$ and in $D > 2$ for $q > 2$

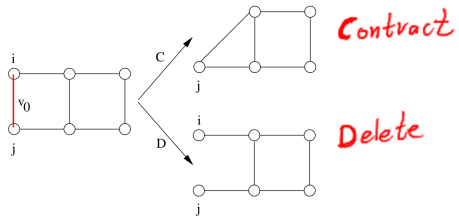


7.3 Kasteleyn and Fortuin

Consider Potts model on arbitrary graph with bonds ν

$$E = J\sum_\nu \epsilon_\nu, \quad \epsilon_\nu = \begin{cases} 0, & \text{if endpoints are in same state} \\ 1, & \text{if endpoints are in different state} \end{cases}$$

Define on bond ν_0 operators of **Contract** C and **Deletion** D.



Transformation of the partition function

$$Z = \sum_X e^{-\beta E(X)} = \sum_X e^{-\beta J\sum_\nu \epsilon_\nu} = \sum_X \prod e^{-\beta J\epsilon_\nu}$$

Consider bond ν_0 with endpoints i and j

$$\begin{aligned} Z &= \sum_X e^{-\beta J\epsilon_{\nu_0}} \prod_{\nu\neq\nu_0} e^{-\beta J\epsilon_\nu} \\ &= \underbrace{\sum_{X:\sigma_i=\sigma_j} \prod_{\nu\neq\nu_0} e^{-\beta J\epsilon_\nu}}_{i,j \text{ equal states} \Rightarrow \epsilon_\nu = 0} + e^{-\beta J} \underbrace{\sum_{X:\sigma_i\neq\sigma_j} \prod_{\nu\neq\nu_0} e^{-\beta J\epsilon_\nu}}_{i,j \text{ different states} \Rightarrow \epsilon_\nu = 1} \end{aligned}$$

- first term: contains all configurations where states at endpoint i and j are **equal**.
- $\rightarrow$ partition function Z_C after application of the **contraction** operator C
- second term: contains all configurations where states at endpont i and j are **different**, factor out $e^{-\beta J\epsilon_{\nu_0}} = e^{-\beta J}$
- partition function Z_D after application of **deletion** operator D on bond ν_0 such that bond ν_0 contribution is missing.
- Z_D still contains contributions for arbitrary i and j, especially the case $\sigma_i = \sigma_j$ which is already included in Z_C.
- $\rightarrow$ subtract those cases for the second term $\boxed{Z_D - Z_C}$

$$\begin{aligned} Z &= Z_C + e^{-\beta J}(Z_D - Z_C) = (1 - e^{-\beta J})Z_C + e^{-\beta J} Z_D \\ &\equiv pZ_C + (1-p)Z_D, \quad p \equiv 1 - e^{-\beta J} \end{aligned}$$

Partition function splitting for bond ν_0

$$\boxed{Z = pZ_{C_{\nu_0}} + (1-p)Z_{D_{\nu_0}}}$$

Partition function subsequent splitting for bond ν_1

$$\boxed{Z = p^2 Z_{C_{\nu_0}C_{\nu_1}} + p(1-p)Z_{C_{\nu_0}D_{\nu_1}} + (1-p)pZ_{D_{\nu_0}C_{\nu_1}} + (1-p)^2 Z}$$

- Repeat for all edges until only disconnected sites remain
- $\rightarrow$ graph is reduced to **set of separated points**
- $\rightarrow$ correspond to **connected, contracted, (occupied) bonds (clusters)**
- each can be in q different states, hence $q^{\#\text{of clusters}}$ possibile states.

$$\boxed{Z = \sum_{\mathcal{C}} q^{\#\text{of clusters}} p^c (1-p)^d = \left\langle q^{\#\text{of clusters}} \right\rangle}$$

with configuration of bond percolation $\mathcal{C}$, c and d number of contracted or deleted bond, respectively.
Within the percolation representation c can be also interpreted as the number of **occupied bonds** and d as the number of **empty bonds**

7.4 Coniglio-Klein Clusters

- consider unit of all **connected sites** that are in **same** state
- remove **bonde** between them with probability $\boxed{p \equiv 1 - e^{-\beta J}}$

8 Cluster algorithms

- Single flip algorithms are slow for $T < T_c$
- probability to flip group of n spins simultaneously even smaller: $(e^{-2\beta J})^n \xrightarrow{s\gg 1} 0$

Probability that cluster C is in state σ_0

$$\boxed{p(C,\sigma_0) = p^{c_C}(1-p)^{d_C} \sum_{\mathcal{C}\setminus C} q^{\#} p^c (1-p)^d}$$

is **independent of** σ_0
Detailed Balance for change $\sigma_0 \rightarrow \sigma_1$

$$\boxed{p(C,\sigma_0)W((C,\sigma_0)\rightarrow(C,\sigma_1)) = p(C,\sigma_1)W((C,\sigma_1)\rightarrow(C,\sigma_1))}$$

is fullfilled since by above independence of σ_i $p(C,\sigma_0) = p(C,\sigma_1)$

Glauber

$$\boxed{W((C,\sigma_0)\to(C,\sigma_1)) = \frac{p(C,\sigma_1)}{p(C,\sigma_0)+p(C,\sigma_1)} = \frac{1}{2}}$$

$\to$ choose new state always with probability $\frac{1}{2}$.

Metropolis

$$\boxed{W((C,\sigma_0)\to(C,\sigma_1)) = \min\left[\frac{p(C,\sigma_1)}{p(C,\sigma_0)},1\right] = 1}$$

8.1 Swendsen-Wang algorithm

- occupy bond with probability $p = 1 - e^{-\beta J}$ if states are eqial, otherwise leave empty
- identify clusters with **Hoshen-Kopelman** algorithm
- Flip each cluster with probability 1/2 for Ising or choose always a new state for $q > 2$
- critical slowing down significantly reduced $z \approx 0.3(0.55)$

8.2 Wolff algorithm

- choose a site randomly
- if neighboring site is in the same state add to cluster with $p = 1 - {}^{-\beta J}$
- Repeat until every site on the boundary of the cluster has been checked exactly once
- choose new state for the cluster (with probabiltiy one)

8.3 General formalism

after D. Kandel, E. Domany and A. Brandt (1989)
partition function

$$\boxed{Z = \sum_X \sum_G (X,G) = \sum_X p(X), \quad \text{e.g. } p(X) = e^{-\beta E(X)}}$$

Detailed Balance

$$\boxed{p(X,G)W((X,G)\to(X',G)) = p(X',G)W((X',G)\to(X,G))}$$

Glauber

$$\boxed{W((X,G)\to(X'G)) = \frac{p(X',G)}{p(X,G)+p(X',G)}}$$

Metropolis

$$\boxed{W((X,G)\to(X'G)) = \min\left[\frac{p(X',G)}{p(X,G)},1\right]}$$

Algorithm simplification

$$p(X,G) = \Delta(X,G)V(g), \quad \Delta(X,G) = \begin{cases}1\\0\end{cases}$$

8.4 Improved estimators

From one configuration one can already get an average over many states because one can flip any subset of clusters.
magnetization

$$\boxed{\langle M_i\rangle = \left\langle \frac{1}{2}(\sigma_i - \sigma_i)\right\rangle = 0}$$

correlation function

$$\langle \sigma_i\sigma_j\rangle = \begin{cases}1, & \text{if } i,j \text{ in the same cluster}\\ 0, & \text{otherwise}\end{cases}$$

Susceptibility

$$\boxed{\chi = \beta\left(\langle M^2\rangle - \langle M\rangle^2\right),\ \langle M^2\rangle = \frac{1}{N^2}\sum_{i,j}\langle\sigma_i\sigma_j\rangle = \frac{1}{N^2}\left\langle \sum_{\text{Cluster}} \sigma_i^2}$$

9 Histogram methods

Obtain results for a new temperature T^* using simulation results one already has for temperature T

Time average of quantity Q at temperature T

$$Q(T) = \frac{1}{Z_T}\sum_E Q(E)p_T(E)$$
$$Z_T = \sum_E p_T(E), \quad p_T(E) = g(E)e^{-\frac{E}{kT}}$$

with **density of states** $g(E)$.
Quantity at new temperature T^*

$$Q(T^*) = \frac{1}{Z_{T^*}}\sum_E Q(E)p_{T^*}(E)$$

Express new probabilities

$$\boxed{p_{T^*}(E) = g(E)e^{-\frac{E}{kT^*}} = p_T(E)\underbrace{e^{-\frac{E}{kT^*}\frac{E}{kT}}}_{\equiv f_{T,T^*}(E)}}$$

to obtain

$$\boxed{Q(T^*) = \frac{\sum_E Q(E)p_T(E)f_{T,T^*}(E)}{\sum_E p_T(E)f_{T,T^*}(E)}}$$

9.1 Broad histogram method

- problem of above method: values for $Q(E)$ were sampled close to the maximum of $p_T(E)$, very peaked for large systems
- $\rightarrow$ Overlap of $p_T(E)$ and $p_{T^*}(E)$ very small
- $\rightarrow$ very few samples at the maximum of p_{T^*}
- statistics become very bad for large $|T - T^*|$

Markov process in energy space

- N_{up} number of all processes that **increase** the energy $\boxed{E \rightarrow E + \Delta E}$
- N_{down} number of processes that **decrease** the energy $\boxed{E \rightarrow E - \Delta E}$
- ***Detailed balance***

$$\boxed{g(E + \Delta E) N_{\text{down}}(E + \Delta E) = g(E) N_{\text{up}}(E)}$$

number of energy decreasing processes with $E + \Delta E \rightarrow E$ equals number of energy increasing processes with $E \rightarrow E + \Delta E$.

- **Metropolis**: Chosse new configuration for instance by flipping randomly a spin $E \rightarrow E - \Delta E$ accept if $E \rightarrow E + \Delta E$ accept with probability

$$\boxed{\frac{N_{\text{down}}(E + \Delta E)}{N_{\text{up}}(E)}}$$

Take logarithm of detailed balance and divide by ΔE. For small ΔE

$$\log g(E + \Delta E) - \log g(E) = \log N_{\text{up}}(E) - \log N_{\text{down}}(E + \Delta E)$$
$$\Rightarrow \quad \frac{\partial \log g(E)}{\partial E} = \frac{1}{\Delta E} \log \frac{N_{\text{up}}(E)}{N_{\text{down}}(E + \Delta E)}$$

1. Check for each site of a configuration if change of state would increase or decrease energe and change N_{up} and N_{down} accordingly
2. Choose a site randomly and change state if energy is decreased. If energy is increased change state with probability $\boxed{N_{\text{down}}/N_{\text{up}}}$
3. At each accumulate values for N_{up}, N_{down} and $Q(E)$ and calculate

$$\boxed{Q(T) = \frac{\sum_E Q(E) g(E) e^{-\frac{E}{kT}}}{\sum_E g(E) e^{-\frac{E}{kT}}}}$$

10 Real space renormalization

- power laws at criticality are a result of **scale invariance** of the system
- $\rightarrow$ different properties of the system remain unchanged in different length scale: e.g. distribution of areas with aligned spins versus boiling water
- $\rightarrow$ scale invariance is basic idead of **renormalization group**
- map from small scale system to large scale system demanding invariance of the basic form of physical description (for a likewise rescaled temperature/magnetic field)
- **critical point** becomes a **fixed point** in the description

Example: spin model an quadratic lattice

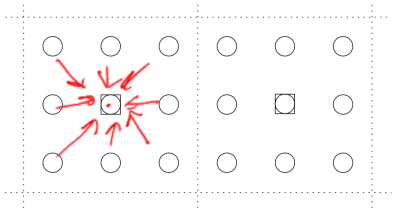


Abb. 7.4 *Renormierung eines Spinsystems. Die quadratischen Gitterplätze sind die Gitterplätze des renormierten Systems. Das Gitter des renormierten Systems ist gepunktet eingetragen.*

- we choose **dimension** $d = 2$ and **scale factor** $l = 3$
- $\rightarrow$ new spin state $\tilde{s}_j$ replace nine old states s_j

Free energy

- free energy is **extensive**, thus proportional to the degrees of freedom of the system
- $\rightarrow$ free energy density must invariant under transformation:

$$\boxed{\tilde{F}(\tilde{\varepsilon}, \tilde{H}) = l^{-d} F(\varepsilon, H), \quad \epsilon \equiv T - T_c}$$

- **near criticality** for all thermodynamic quantities hold **homogeneous scaling laws**:

$$\boxed{F(\varepsilon, H) = l^d F(l^{Y_T}, l^{y_H} H)}$$

where y_T and y_H are critical exponents related to the classical ones

- By comparison with the first formula

$$\boxed{\Rightarrow \widehat{\varepsilon} = l^{y_T} \varepsilon, \quad \widehat{H} = l^{y_H} H}$$

Correlation length

Described by critical exponent $\boxed{\xi \sim |\varepsilon|^{-\nu}}$

Rescaling with l yields $\boxed{\widehat{\varepsilon}^{-\nu} \sim \widehat{\xi} = \frac{\xi}{l}}$ and we get for the **temperature exponent**

$$\widehat{\varepsilon} = \frac{\varepsilon}{l^{-\frac{1}{\nu}}} = l^{\frac{1}{\nu}} \varepsilon \stackrel{!}{=} l^{y_t} \varepsilon, \quad y_T = \frac{1}{\nu}$$

and similiarly for the magnetic field exponent.

Renormalization by decimation Remove every second spin $\rightarrow l = \sqrt{2}$

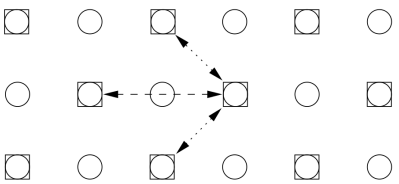


Abb. 7.5 *Die quadratischen Gitterplätze gehören zum renormierten System. Wechselwirkungen mit übernächsten Nachbarn (L) sind gestrichelt eingetragen. Wechselwirkungen mit nächsten Nachbarn (K) sind gepunktet dargestellt*

10.1 Renormalized Hamiltonian

11 Molecular Dynamics

generalized coordinates with α degrees of freedom of particle i

$$\boxed{\mathbf{q}_i = (q_i^1, \ldots, q_i^\alpha), \quad \mathbf{p}_i = (p_i^1, \ldots, p_i^\alpha)}$$

N particles

$$Q = (\mathbf{q}_1, \ldots, \mathbf{q}_N), \quad P = (\mathbf{p}_1, \ldots, \mathbf{p}_N)$$

Hamiltonian and kinetic energy

$$\mathcal{H}(P,Q) = K(P) + V(Q), \quad K(P) = \sum_i \sum_{k=1}^{\alpha} \frac{(p_i^k)^2}{2m_i}$$

Expansion of potential

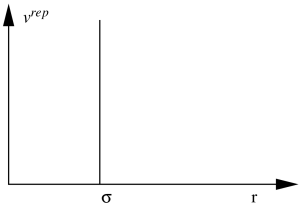
$$\boxed{V(Q) = \sum_i v_1(q_i) + \sum_i \sum_{j>i} v_2(q_i, q_j) + \sum_i \sum_{j>i} \sum_{k>j} v_3(q_i, q_j, q_k) + \cdots}$$

Three or more body interactions neglected and their effect considered in **effective two body interaction**

$$\boxed{v_2^{\text{eff}}(q_i, q_j) = v^{\text{attr}}(r) + v^{\text{rep}}(r), \quad r = |\mathbf{q}_i - \mathbf{q}_j|}$$

11.1 Potentials

11.1.1 Hard core interaction



$$v^{\text{rep}}(r) = \begin{cases} \infty, & r < \sigma \approx 0.35nm \\ 0, & r \geq \sigma \end{cases}$$

Problem: forces $\mathbf{F} = -\nabla V$ are delta function like

11.1.2 Elastic repulsion

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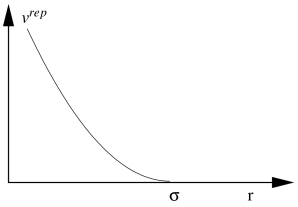
$$v^{\text{rep}}(r) = \begin{cases} \frac{k}{2}(R-r)^2, & r < R \\ 0, & r \geq R \end{cases}, \quad R = R_1 + R_2$$

Repulsive part of elastic spring potential with spring constant k, force grows linearly with increasing overlap. Finite range unrealistic.

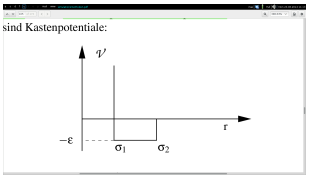
11.1.3 Soft core repulsion



$$v^{\text{rep}}(r) = \varepsilon \left(\frac{\sigma}{r}\right)^{\nu}$$

- $\nu = 1$ electrostatics and gravity, $\nu = 12$ soft repulsion
- slowly decaying potentials problematic in numerics

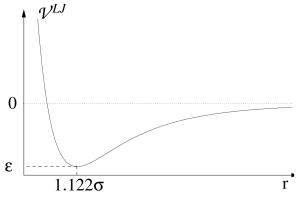
11.1.4 square potentials



$$v(r) = \begin{cases} \infty, & r < \sigma_1 \\ \infty, & \sigma_1 \leq r < \sigma_2 \\ \infty, & r \geq \sigma_2 \end{cases}$$

again infinite forces

11.1.5 Lenard Jones potential



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

11.2 Equations of motion

Hamiltonian equations of motion

$$\dot{q}_i^k = \frac{\partial \mathcal{H}}{\partial p_i^k}, \quad \dot{p}_i^k = -\frac{\partial \mathcal{H}}{\partial q_i^k}, \quad k = 1, \ldots, \alpha, \quad i = 1, \ldots, N$$

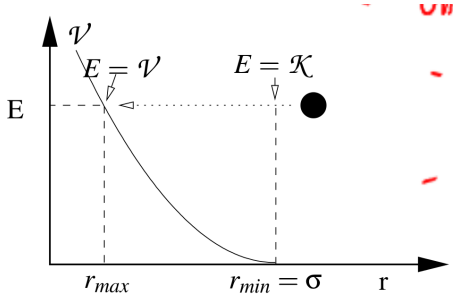
Coupled Newtonian equations of motion

$$\begin{aligned} \mathbf{q_i} &= \mathbf{x}_i, & \dot{\mathbf{q}}_\mathbf{i} &= \mathbf{v}_i \\ \dot{\mathbf{x}}_\mathbf{i} &= \mathbf{v}_i = \frac{\mathbf{p}_i}{m_i} & \dot{\mathbf{p}}_\mathbf{i} &= -\nabla_i V(Q) = \mathbf{f}_i \\ m_i \ddot{\mathbf{x}}_\mathbf{i} &= \mathbf{f}_i = \sum_j \mathbf{f}_{ij} \end{aligned}$$

11.3 Conservation laws

- **Energy conservation** as long as $K(P)$ and $V(Q)$ do not explicitely depend on time
- **Momentum conservation** (if the system has no walls) $\boxed{\mathbf{P} = \sum_i \mathbf{p}_i}$
- **Angular momentum** for spherical systems $\mathbf{L} = \sum_i \mathbf{x}_i \times \mathbf{p}_i$
- **Time reversal invariance**

11.4 Contact time



- $r_{\max}$ turning point of a colliding particle
- $\rightarrow \boxed{E = V}$ maximal potential energy, no kinetic energy
- $r_{\min}$ maximum range of the potential
- $\rightarrow \boxed{E = K}$ maximal kinetic energy, for elastic potential: starting point σ, for potentials with attractive part: minimum
- contact time for hard core potentials would be instantly

Energy and velocity

$$\boxed{E = \frac{1}{2}m\dot{r}^2 + V(r) = \text{const} \;\Rightarrow\; \frac{\mathrm{d}r}{\mathrm{d}t} = \left[\frac{2}{m}(E - V(r))\right]^{\frac{1}{2}}}$$

Contact time

$$t_c = 2\int_0^{\frac{t_c}{2}} = 2\int_{r_{\min}}^{r_{\max}} \frac{\mathrm{d}t}{\mathrm{d}r}\,\mathrm{d}r = 2\int_{r_{\min}}^{r_{\max}} \left[\frac{2}{m}(E - V(r))\right]^{-\frac{1}{2}} \mathrm{d}r$$

11.5 Solving equations of motion

- Euler method
- Runge-Kutta method
- Predictor-Corrector method
- Verlet method
- Leap-frog method

11.6 Programming Tricks

$\rightarrow$ most time consuming loop is calculattion of forces since all pairs ($\sim N^2$) of particles need to be considered

- **For potentials with *even* powers**: Instead of calculating the square root, work with the square if possible:

$$r_{ij} = \sqrt{\sum_{\alpha=1}^{d}(x_i^\alpha - x_j^\alpha)^2} \;\rightarrow\; V(r) \sim r^{2n} \;\Rightarrow\; \mathbf{f}_i = f(r^{2(n-1)})\mathbf{r}_i$$

- *cut-off* radius r_c possible for some (short range) potentials: exactly zero for larger distances. e.g $r_c = 2.5\sigma$ for LJ-Potenial
- for *simple* potentials **Look-up tables** are possible: Divide intervall $(0, r_c^2)$ in K pieces with points l_k create look-up table $F(k)$:

$$\boxed{l_k = \frac{k}{K}r_c^2, \quad F(k) = f(\sqrt{l_k})}$$

where the index must be calculated through

$$k = \left\lfloor S\sum_\alpha (x_i^\alpha - x_j^\alpha)(x_i^\alpha - x_j^\alpha) \right\rfloor + 1, \quad S = \frac{K}{r_c^2}$$

- **Newton-Gregory Interpolation** to decrease error from discretization of the potential:

$$\boxed{f(x) = F(k) + (k - zS)(F(k-1) - F(k)), \quad z = \sum_\alpha (x_i^\alpha -}$$

12 Verlet method

Taylor expansion in time step $\Delta t \approx t_c/20$

$$(x + \Delta t) = \mathbf{x}(t) + \Delta t\mathbf{v}(t) + \frac{1}{2}\Delta t^2\dot{\mathbf{v}}(t) + \cdots$$
$$(x - \Delta t) = \mathbf{x}(t) - \Delta t\mathbf{v}(t) + \frac{1}{2}\Delta t^2\dot{\mathbf{v}}(t) + \cdots$$

and add equations

$$\mathbf{x}(t + \Delta t) = 2\mathbf{x}(t) - \mathbf{x}(t - \Delta t) + \Delta t^2\ddot{\mathbf{x}}_\mathbf{i}(t)$$

with forces $\ddot{\mathbf{x}}$ from Newtonian equations of motion

$$\ddot{\mathbf{x}}_\mathbf{i} = \frac{1}{m_i}\sum_j \mathbf{f}_{ij}, \quad \mathbf{f}_{ij} = -\nabla V(r_{ij}(t)), \quad \Delta t \approx \frac{1}{10}$$
$$\int_{t_{\min}}^{r_{\max}} \left[\frac{2}{m}(E - V(r))\right]^{-\frac{1}{2}} \mathrm{d}r$$

and insert all in

$$\boxed{\mathbf{x}_i(t + \Delta t) = 2\mathbf{x}_i(t) - \mathbf{x}_i(t - \Delta t) + \Delta t^2\ddot{\mathbf{x}}_\mathbf{i}(t)}$$

- needs to store two time steps t and $t - \Delta t$
- (Local) error is $\mathcal{O}(\Delta t^4)$: third order algorithm
- exact time reversal

- **velocities** can be obtained through

$$\boxed{\mathbf{v}(t) = \frac{\mathbf{x}(t+\Delta t) - \mathbf{x}(t-\Delta t)}{2\Delta t}}$$

- **Problem**: last term $\mathcal{O}(\Delta^0)$ is very small compared to previous ones $\mathcal{O}(\Delta t^2) \rightarrow$ roundoff errors
- Improve systematically adding more orders

12.1 Leap-Frog method

Consider velocities at intermediate times

$$\mathbf{v}(t + \frac{1}{2}\Delta t) = \mathbf{v}(t - \frac{1}{2}\Delta t) + \Delta \ddot{\mathbf{x}}(t)$$
$$\mathbf{x}(t + \Delta t) = \mathbf{x}(t) + \Delta t \mathbf{v}(t + \frac{1}{2}\Delta t)$$

Comparison Verlet Leap frog

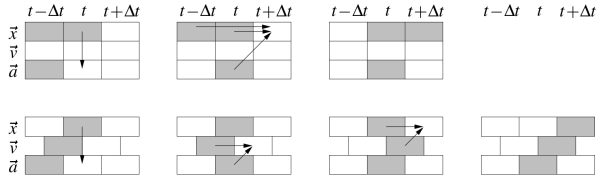


Abb. 8.1 *Veranschaulichung der Vorgehensweise der Verlet-Methode (obere Reihe) und der leap-frog Methode (untere Reihe) (nach [15])*

Comparison Euler Leap frog
Leap frog:

$$\dot{\mathbf{v}}(t + \Delta t) = \frac{\mathbf{f}(\mathbf{x}(t))}{m}$$
$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \Delta t \dot{(}\mathbf{t} + \mathbf{\Delta t})$$
$$\mathbf{x}(t + \Delta t) = \mathbf{x}(t) + \Delta t \mathbf{v}(t + \Delta t)$$

Euler

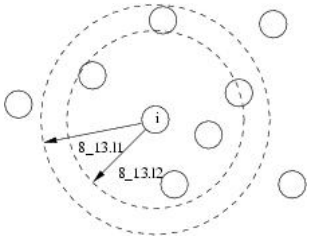
$$\dot{\mathbf{v}}(t + \Delta t) = \frac{\mathbf{f}(\mathbf{x}(t))}{m}$$
$$\mathbf{x}(t + \Delta t) = \mathbf{x}(t) + \Delta t \mathbf{v}(t)$$
$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \Delta \dot{\mathbf{v}}(t + \Delta t)$$

- No addition of $\mathcal{O}(\Delta t^0)$ and $\mathcal{O}(\Delta t^2)$ terms any more
- for larger Δt we have larger energy fluctuations but *on average* energy should be constant
- **Precision given by**

$$\boxed{\sqrt{\langle E^2 \rangle - \langle E \rangle^2}}$$

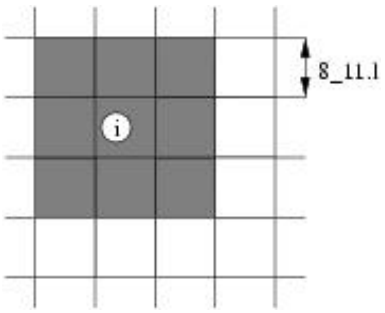
12.2 Verlet tables

Avoids to query every $\mathcal{O}(N^2)$ particle pairs in every step.

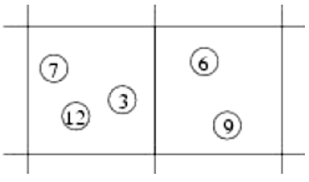


- Define a neighborhood with radius $\boxed{r_l > r_c}$ around each particle i
- store all the coordinates if the particles in this neighborhood in a vector `LIST` with length $N \cdot N_u$, where N_u is the average number of particles in the neighbothood
- `LIST` is a one-dimensional vector which stores all point neighborhoods sequentially
- a vector `POINT[i]` contains the index of the first neighbor particle of particle i
- $\rightarrow$ particles in the neighborhood of i are: `LIST[POINT[i]],...,LIST[POINT[i+1]-1]`
- Every $\boxed{n = \frac{r_l - 2r_c}{\Delta t v_{\max}}}$ time steps, Verlet table must be **renewed** $(n \approx 10 - 20)$ since otherwise particles beyond distance r_l could reach r_c
- Renewal requires still N^2 operations

12.3 Linked cell method



- Place grid of size M^d above system, s.t. each cell is larger than $2r_c$
- all particles that can interact with particle i lie in the shaded region
- $\rightarrow$ on average only necessary to test $N \cdot 3^d N/M^d$ paritcles reducing the loop by $(M/3)^3$
- Store in vector `FIRST` with length M^d **for each cell** the index of the first particle
- No particle in cell j set `FIRST[j]=0`
- In vector `LIST[i]` with length N store **for each particle** i the index of the next particle in the same cell
- for *last* particle in a cell `LIST[i]=0`
- when particle flies from one cell to another, renew `FIRST` and `LIST` locally
  $\Rightarrow$ algorithm is $\mathcal{O}(N)$



Program to find all particles in cell $i = 2$

```
                M[1]=FIRST[i];
i=2;
while(M[i-1]!=0)
    M[j]=LIST[M[j-1]];
```

13 Molecules

- atoms are bind together through the attractive part of their potential
- → needs *deep* potentials and is hence computationally expensive
- forces *inside* molecules at least one order of magnitude larger than *between* them
- assume covalent bonds do not break and keep bond and angles fixed.
- → two possibilities

13.1 Lagrange multipliers

Consider the example of a water molecule with fixed bond length. Atom i $(i = 1, 2, 3)$ follows the equation:

$$\boxed{m_i \ddot{\mathbf{x}}_\mathbf{i} = \mathbf{f}_i + \mathbf{g}_i}$$

where f_i are forces from other molecules and $\mathbf{g}_i$ forces to impose the contraints.

Contraint equation
bond length should be gevin by d_{12} and d_{23}

$$\chi_{12} = r_{12}^2 - d_{12}^2 = 0, \quad r_{ij} = \|\mathbf{r}_{ij}\|$$
$$\chi_{23} = r_{23}^2 - d_{23}^2 = 0, \quad \mathbf{r}_{ij} = \mathbf{x}_i - \mathbf{x}_j$$

yields contraint forces

$$\boxed{\mathbf{g}_k = \frac{1}{2}\lambda_{12}\nabla_{\mathbf{x}_k}\chi_{12} + \frac{1}{2}\lambda_{23}\nabla_{\mathbf{x}_k}\chi_{23}}$$

with yet to be determined **Lagrange multipliers** λ_{12} and λ_{23}

$$\Rightarrow \mathbf{g}_1 = \lambda_{12}\mathbf{r}_{12}, \quad \mathbf{g}_2 = \lambda_{23}\mathbf{r}_{23} - \lambda_{12}\mathbf{r}_{12}, \quad \mathbf{g}_3 = -\lambda_{23}\mathbf{r}_{23}$$

Time stepping
Execute **Verlet** in two steps: **Without constraint forces**:

$$\boxed{\mathbf{x}_i^!(t + \Delta t) = 2\mathbf{x}_i - \mathbf{x}_i(t - \Delta t) + \Delta t^2 \frac{\mathbf{f}_i}{m_i}}$$

Correction with yet unknown constraint forces

$$\boxed{\mathbf{x}_i(t + \Delta t) = \mathbf{x}_i^!(t + \Delta t) + \Delta t^2 \frac{\mathbf{g}_i}{m_i}}$$

Finally, insert $\mathbf{g}_i$

$$\mathbf{x}_1(t + \Delta t) = \mathbf{x}_1^!(t + \Delta t) + \Delta t^2 \frac{\lambda_{12}}{m_1}\mathbf{r}_{12}(t)$$
$$\mathbf{x}_2(t + \Delta t) = \mathbf{x}_2^!(t + \Delta t) + \Delta t^2 \frac{\lambda_{23}}{m_2}\mathbf{r}_{23}(t) - \Delta t^2 \frac{\lambda_{12}}{m_2}\mathbf{r}_{12}(t)$$
$$\mathbf{x}_3(t + \Delta t) = \mathbf{x}_3^!(t + \Delta t) + \Delta t^2 \frac{\lambda_{23}}{m_3}\mathbf{r}_{23}(t)$$

Insert these expression into the **constraint condition** to obtain λ_{12} and λ_{23}

$$\|\mathbf{x}_1(t + \Delta t) - \mathbf{x}_2(t + \Delta t)\|^2 = d_{12}^2$$
$$\|\mathbf{x}_2(t + \Delta t) - \mathbf{x}_3(t + \Delta t)\|^2 = d_{23}^2$$

leading to a coupled system of quadratic equations

$$\left[\mathbf{x}_1^!(t + \Delta t) - \mathbf{x}_2^! + \Delta t^2 \mu_{12}\mathbf{r}_{12}(t) - \Delta t^2 \frac{\lambda_{23}}{m_2}\mathbf{r}_{23}(t)\right]^2 = d_{12}^2$$
$$\left[\mathbf{x}_2^!(t + \Delta t) - \mathbf{x}_3^! + \Delta t^2 \mu_{23}\mathbf{r}_{23}(t) - \Delta t^2 \frac{\lambda_{12}}{m_2}\mathbf{r}_{23}(t)\right]^2 = d_{23}^2$$

where $\mu_{ij} = \left(\frac{1}{m_i} + \frac{1}{m_j}\right)$ is the reduced mass.
Solve for λ_{12} and λ_{23} and use to calculate $\mathbf{x}_i(t + \Delta t)$.

13.2 Rigid bodies

Consider rigid body of n points i of mass m_i
Coordinates of the center of mass

$$M\mathbf{x}_\text{cm} \equiv \sum_{i=1}^{n} \mathbf{x}_i m_i, \quad M \equiv \sum_{i=1}^{n} m_i$$

which follows the equation

$$\boxed{M\ddot{\mathbf{x}}_\text{cm} = \sum_{i=1}^{n} \mathbf{f}_i \equiv f_\text{cm}}$$

Torque

$$\boxed{\mathbf{T} \equiv \sum_{i=1}^{n} \mathbf{d}_i \times \mathbf{f}_i, \quad \mathbf{d}_i \equiv \mathbf{x}_i - \mathbf{x}_\text{cm}}$$

13.2.1 Degrees of freedom

- **2D**: ω always direct orthogonal to plane.
- → rotations can be described by **scalar** angle
- → **three** degrees of freedom (2 translational and 1 rotational)
- **3D**: ω: three generalized coordinates (angles) necessary
- → **six** degrees of freedom (3 translational and 1 rotational)

13.2.2 Two dimension

moment of inertia and torque

$$\boxed{I = \int\int_A r^2 \rho(r)\,\mathrm{d}A, \quad T = \int\int_A f_t(r) r\,\mathrm{d}A}$$

equation of motion for rotation

$$\boxed{I\omega = T}$$

Time evolution of the angle ϕ using Verlet

$$\phi(t+\Delta t) = 2\phi(t) - \phi(t-\Delta t) + \Delta t^2 \underbrace{T(t)}\, I_{\dot{\omega}}$$

$$T(t) = \sum_{j\in A} \left(f_j^y(t)\cdot d_j^x(t) - f_j^x(t)\cdot d_j^y(t)\right)$$

where $d_j^x(t)$ denotes the x-component of the vector connecting the center of mass to mass element j **Full time evolution**

$$\mathbf{x}(t+\Delta t) = 2\mathbf{x}(t) - \mathbf{x}(t-\Delta t) + \Delta t^2 M^{-1} \sum_{j\in A} \mathbf{f}_j(t)$$

$$\phi(t+\Delta t) = 2\phi(t) - \phi(t-\Delta t) + \Delta t^2 I^{-1} T(t)$$

13.2.3 Three dimensions

Angular momentum

$$\mathbf{L} \equiv m_i \mathbf{d}_i \times \mathbf{v}_i = \sum_{i=1}^{n} m_i \mathbf{d}_i \times (\mathbf{d}_i \times \omega)$$

$$= \sum_{i=1}^{n} m_i \left(\mathbf{d}_i (\mathbf{d}_i \cdot \omega) - \mathbf{d}_i^2 \omega \right) = \mathbf{I}\omega$$

Equation of motion

$$\boxed{\dot{\mathbf{L}} = \mathbf{I}\dot{\omega} = \mathbf{T}}$$

such that $\mathbf{I}$ is not a scalar any more.

Tensor of intertia

$$\boxed{\mathbf{I} = \sum_{i=1}^{n} m_i \left(\mathbf{d}_i^T \otimes \mathbf{d}_i - d_i^2 \mathbf{I} \right)}$$

where $\otimes$ denotes the **dyadic product**.

- eigenvectors span a body-fixed coordinate system with origin in the center of mass
- transform from **lab-fixed** to **body-fixed** system with $\boxed{\mathbf{e}^b = \mathbf{A}\mathbf{e}^l}$ where the transformation matrix is unfortunatetly unknown and changes with time

Equations in body-frame

$$\dot{\mathbf{L}} = \mathbf{T}^l \quad \Rightarrow \quad \dot{\mathbf{L}}^{\mathbf{b}} + \omega^b \times \mathbf{L}^b = \mathbf{I}\dot{\omega}^{\mathbf{b}} + \omega^b \times \mathbf{L}^b = \mathbf{T}^b$$

leading to the following system of equation with *separated* $\dot{\omega}_{\mathbf{i}}^{\mathbf{b}}$

$$\boxed{\mathbf{I}\dot{\omega}^{\mathbf{b}} = \mathbf{T}^b - \omega^b \times \mathbf{L}^b \;\Leftrightarrow\; \begin{cases} \dot{\omega}_x^b &= \frac{T_x^b}{I_{xx}} + \left(\frac{I_{yy}-I_{zz}}{I_{xx}}\right)\omega_y^b\omega_z^b \\ \dot{\omega}_y^b &= \frac{T_y^b}{I_{xx}} + \left(\frac{I_{zz}-I_{xx}}{I_{yy}}\right)\omega_z^b\omega_x^b \\ \dot{\omega}_z^b &= \frac{T_z^b}{I_{xx}} + \left(\frac{I_{xx}-I_{yy}}{I_{zz}}\right)\omega_x^b\omega_y^b \end{cases}}$$

Strategy

1. Calculate torque in lab system and transform to body system

$$\mathbf{T}^l = \sum_{i=1}^{n} \mathbf{d}_i \times \mathbf{f}_i \quad \rightarrow \quad \mathbf{T}^b = \mathbf{A}\mathbf{T}^l$$

2. evolve angular velocities in body frame

$$\omega_x^b(t+\Delta t) = \omega_x^b(t) + \Delta t \frac{T_x^b(t)}{I_{xx}} + \Delta t \left(\frac{I_{yy}-I_{zz}}{I_{xx}}\right)\omega_y^b(t)\omega_z^b(t)$$

$$\omega_y^b(t+\Delta t) = \omega_y^b(t) + \Delta t \frac{T_y^b(t)}{I_{yy}} + \Delta t \left(\frac{I_{zz}-I_{xx}}{I_{yy}}\right)\omega_z^b(t)\omega_x^b(t)$$

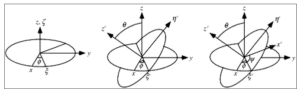
$$\omega_z^b(t+\Delta t) = \omega_z^b(t) + \underbrace{\Delta t \frac{T_z^b(t)}{I_{zz}}}_{\text{torque forces}} + \underbrace{\Delta t \left(\frac{I_{xx}-I_{yy}}{I_{zz}}\right)\omega_x^b(t)\omega_y^b(}_{\text{inertial forces}\propto\omega^2}$$

3. transform back to lab frame

$$\omega^l(t+\Delta t) = \mathbf{A}^T \omega^b(t+\Delta t)$$

13.2.4 Euler angles

Rotation in three dimensions described by three **Euler angles** ϕ, θ and ψ.



1. rotate around z**-axis** by ϕ
2. rotate around x**-axis** by θ
3. rotate around ***new*** z**-axis** by ψ

$$\mathbf{A} = \begin{pmatrix} \cos\psi & -\sin\psi & 0 \\ \sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} \cos\phi & -\sin\delta \\ \sin\phi & \cos\phi \\ 0 & 0 \end{pmatrix}$$

Relation to angular velocties

$$\dot{\phi} = -\omega_x^l \frac{\sin\phi\cos\theta}{\sin\theta} + \omega_y^l \frac{\cos\phi\cos\theta}{\sin\theta} + \omega_z^l$$

$$\dot{\theta} = \omega_x^l \cos\theta + \omega_y^l \sin\phi$$

$$\dot{\psi} = \omega_x^l \frac{\sin\phi}{\sin\theta} - \omega_y^l \frac{\cos\phi}{\sin\theta}$$

$\rightarrow$ equations become *singular* for $\theta = 0$ and $\theta = \pi$!

13.3 Quaternions

$$\boxed{\mathbb{Q} = (q_0, q_1, q_2, q_3), \text{ with } q_0^2 + q_1^2 + q_2^2 + q_3^2 = 1}$$

Definition from Euler angles

$$\begin{aligned} q_0 &\equiv \cos\frac{1}{2}\theta\cos\frac{1}{2}(\phi+\psi) \\ q_1 &\equiv \sin\frac{1}{2}\theta\cos\frac{1}{2}(\phi-\psi) \\ q_2 &\equiv \sin\frac{1}{2}\theta\sin\frac{1}{2}(\phi-\psi) \\ q_3 &\equiv \cos\frac{1}{2}\theta\sin\frac{1}{2}(\phi+\psi) \end{aligned}$$

Transformation matrix

$$\boxed{\mathbf{A} = \begin{pmatrix} q_0^2+q_1^2-q_2^2-q_3^2 & 2(q_1q_2+q_0q_3) & 2(q_1q_3-q_0q_2) \\ 2(q_1q_2-q_0q_3) & q_0^2-q_1^2+q_2^2-q_3^2 & 2(q_2q_3+q_0q_1) \\ 2(q_1q_3+q_0q_2) & 2(q_2q_3-q_0q_1) & q_0^2-q_1^2-q_2^2+q_3^2 \end{pmatrix}}$$

First order linear equations

$$\begin{pmatrix} \dot{q}_0 \\ \dot{q}_1 \\ \dot{q}_2 \\ \dot{q}_3 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} q_0 & -q_1 & -q_2 & -q_3 \\ q_1 & q_0 & -q_3 & q_2 \\ q_2 & q_3 & q_0 & -q_1 \\ q_3 & -q_2 & q_1 & q_0 \end{pmatrix}\begin{pmatrix} 0 \\ \omega_x^b \\ \omega_y^b \\ \omega_z^b \end{pmatrix}$$

Back transformation to Euler angles

$$\begin{aligned} \phi &= \arctan\left(\frac{2(q_0q_1-q_2q_3)}{1-2(q_1^2+q_2^2)}\right) \\ \theta &= \arctan\left(2(q_0q_2-q_1q_3)\right. \\ \psi &= \arctan\left(\frac{2(q_0q_3+q_1q_2)}{1-2(q_2^2+q_3^2)}\right) \end{aligned}$$

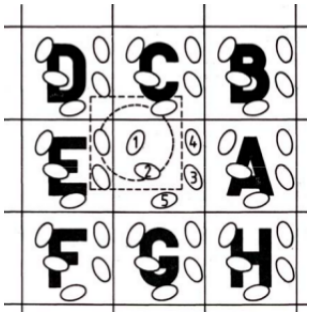
Strategy

- Calculate torque $T(t)$ in body-frame
- Use to obtain $\omega_b(t+\Delta t)$ and map to quaternions $q_i(t+\Delta t)$
- also possible: insert torque directly into e.o.m. of the quaternions an obtain second order differential equation
- $\rightarrow$ avoid to calculate ω

13.4 Long-range potentials

- potentials that decay *slower* than r^{-d}
- e.g. electrostatics, gravity, dipoles
- no cut-off r_c possible
- $\rightarrow$ would be equivalent in the electrostatic case to introduction of a charged sphere of radius r_c around considered particle
- **methods**
  - Ewald method
  - particle-mesh methods
  - reaction field method

13.5 Ewald summation



- consider periodic boundaries and periodic images
- length of original system L, number of original particles N
- sum over all images

$$\boxed{V = \frac{1}{2}\sum_{\mathbf{n}}{}' \sum_{i,j}^{N} z_i z_j |\mathbf{r}_{ij}+\mathbf{n}|^{-1}, \ \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j,}$$

  where $\sum'$ denotes the exclusion of $\mathbf{n}=0$ for $i=j$ to avoid self-interaction and $\mathbf{n} = (n_xL, n_yL, n_zL)$ with $n_i \in \mathbb{Z}$ connects the center of the system to the center of the images.

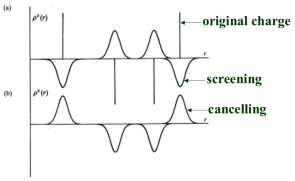
- $\rightarrow$ conditionally convergent(order-dependent) and converges very slowly

13.6 Ewald method

- each charge be screened by **Gaussian charge distribution** of opposite sign and equal magnitude

$$\boxed{\rho_i(r) = \frac{z_i\kappa^3}{\pi^{\frac{3}{2}}}e^{-\kappa^2 r^2}}$$

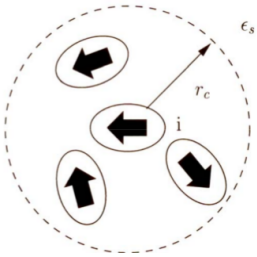
- κ describes smearing out of the charge
- extra screening charge must again be cancelled by charge density of opposite sign



$$V = \frac{1}{2}\sum_{ij}\left(\sum_{\mathbf{n}}{}' z_i z_j \frac{\operatorname{erfc}(\kappa|\mathbf{r}_{ij}+\mathbf{n}|)}{|\mathbf{r}_{ij}+\mathbf{n}|}\right.$$

$$\left. + \frac{1}{\pi L^3}\sum_{\mathbf{k}\neq 0} z_i z_j \frac{4\pi^2}{k^2} e^{-\frac{k^2}{4\kappa^2}} \cos(\mathbf{k}\cdot\mathbf{r}_{ij})\right) - \frac{\kappa}{\sqrt{\pi}}\sum_i z_i^2$$

13.7 Reaction field method



- usually weakly charged, weak interaction, more or less neutral, no clustering
- mostly for dipole-dipole interaction
- define sphere(cavity) N_i of radius r_c
- calculate forces inside exactly
- treat rest as a **dieletric continuum** of dielectric constant ε_S (model parameter)

(Reaction) Field of cavity N_i generated by the dipole moments $\mu_j$of the particles inside the cavity:

$$\boxed{\mathbf{E}_i = \frac{2(\varepsilon_S - 1)}{2\varepsilon_S + 1} \frac{1}{r_c^3} g \sum_{j \in N_i} \mu_j}$$

Total force on particle

$$\mathbf{F}_i = \sum_{j \in N_i} \mathbf{F}_{ij} + \mathbf{E}_i \times \mu_i$$

where $\mathbf{F}_{ij}$ are local forces from neighbors.
Weight function to avoid jump in the forces each time a particle enter or leaves cavity

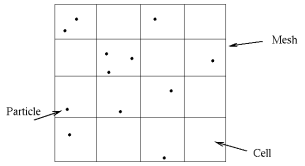
$$g(\mathbf{r}_j) = \begin{cases} 1, & \text{for } r_j < r_i \\ \frac{r_c - r_j}{r_c - r_t} & \text{for } r_t \le r_j \le r_c \\ 0, & \text{for } r_c < r_j \end{cases}$$

with $r_t \approx 0.95 r_c$
Modified Coulomb potential due to reaction field method

$$U_c = \frac{1}{4\pi\epsilon_0} \sum_{i>j} q_i q_j \left(\frac{1}{r_{ij} - \frac{B_0 r_{ij}^2}{2R_c^3}} \right)$$

infinite sum is replaced by final one plus reaction field

14 Particle-Mesh algorithm



- Put fine mesh on top of system ($M \approx N$)
- Distribute charges onto mesh points
- Calculate the electrostatic potential by solving Poisson equation on the mesh using FFT
- Calculate force on each particle by numerically differentiating the potential and interpolating back from the mesh to the particle position
- **Nearest Grid Point (NGP)**: put particle on nearest grid point and also evaluate it force ate nearest point
- **Cloud In Cell (CIC)**: Assign the charge to the 2^d nearest grid points and also interpolate from these 2^d grid points.
- method goes like $\mathcal{O}(N \log N)$ due to FFT

Criteria for a good PM scheme

- Erros should vanish at large particle distances
- momentum conservation: $\boxed{\mathbf{F}_{ij} = -\mathbf{F}_{ij}}$
- charges on mesh and interpolated forces should

Weaknesses of PM algorithm

- very inhomogeneous distribution of masses
- strong correlations, like bound states
- complex geometries
- $\rightarrow$ use P^3M, AP^3M, treed codes or multipole expansion

Distribution for a charge q at position (x, y) to the four corners of cell (i, j) for CIC

$$\begin{aligned} \rho_{ij} &= q(x_{i+1} - x)(y_{i+1} - y) \\ \rho_{i+1j} &= q(x - x_i)(y_{i+1} - y) \\ \rho_{ij+1} &= q(x_{i+1} - x)(y - y_{i+1}) \\ \rho_{i+1j+1} &= q(x - x_i)(y - y_{i+1}) \end{aligned}$$

Solve Poisson in Fourier space

$$\phi(\mathbf{r}) = \int \rho(\mathbf{r}') g(\mathbf{r} - \mathbf{r}') \, \mathrm{d}^d \mathbf{r}'$$

with **Green's function** for 3D gravity $\boxed{g(\mathbf{r}) = \frac{G}{\|\mathbf{r}\|}}$
Fourier transform

$$\widehat{\phi}(\mathbf{k}) = \widehat{\rho}(\mathbf{k}) \widehat{g}(\mathbf{k})$$

with $\boxed{\widehat{g}(\mathbf{k}) = \frac{G}{\mathbf{k}^2}}$ or on finite lattice of size L^3

$$\widehat{g}(\mathbf{k}) \propto \frac{1}{\sin^2(k_x \frac{L}{2}) + \sin^2(k_y \frac{L}{2}) + \sin^2(k_z \frac{L}{2})}$$

Force at grid points

$$\boxed{\mathbf{F}(\mathbf{r}_{ij}) = -\nabla \phi(\mathbf{r}_{ij})}$$

Force at particle position is obtained through interpolation over a neighborhood of grid points for each component:

$$\boxed{F^{(k)}(\mathbf{r}) = \sum_j W(\mathbf{r} - \mathbf{r}_j) F^{(k)}(\mathbf{r}_j)}$$

14.1 P^3M algorithm

P^3M =**Particle-Particle-Particle-Mesh**
→ split force into **short** and **long range** part: $\boxed{\mathbf{F} = \mathbf{F}_s + \mathbf{F}_l}$

- $\mathbf{F}_l$: small and smooth at short distances, calculated using PM algorithm
- $\mathbf{F}_s$: is calculated exactly by solving Newton's equation
- → field is no longer independent of particle any more

14.2 AP^3M algorithm

- **Adaptive** P^3M
- for homogeneous mass distribution $F_s \sim \mathcal{O}(N)$ and $F_l \sim \mathcal{O}(N \log N)$
- masses cluster under gravity and then $F_s \sim \mathcal{O}(N^2)$
- → refine mesh in regions where density of masses is higher

14.3 Tree codes

- treat far-away clusters as quasi-particles
- they form hierarchical structures (clusters of clusters)
- bookeping of structures by trees (e.g. wuad trees)
- also usable in linked cell algorithm when one has particles i.e. cells of very different size

14.4 Multipole expansion

- **FMM** Fast Multipole Method
- calculate force from high order multipole expansion
- implies high computational effort to reach sufficient accuracy $\sim (N \log N)$
- used in combination with tree codes

15 Canonical Ensemble Molecular Dynamics

Temperature measurement
Equipartition theorem

$$\left\langle p_i^{(\alpha)} \frac{\partial \mathcal{H}}{\partial p_i^{(\alpha)}} \right\rangle = \left\langle q_i^{(\alpha)} \frac{\partial \mathcal{H}}{\partial q_i^{(\alpha)}} \right\rangle = kT$$

such that for one particle

$$3kT = \left\langle \mathbf{p}_i \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} \right\rangle = \left\langle \sum_\alpha p_i^\alpha \frac{2p_i^{(\alpha)}}{2m_i} \right\rangle = 2\frac{1}{2m_i} \left\langle \mathbf{p}_i^2 \right\rangle = 2E_{\text{kin},i}$$

Instantaneous temperature $\mathcal{T}$

$$\boxed{\mathcal{T} \equiv \frac{2}{k(3N-3)} \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i}}$$

where 3 degrees of freedom are subtracted to exclude the overall translation of the whole system.

15.1 Velocity rescaling

Simulate a given fixed temperature T

- Each time step **rescale** all velocities by a factor α: $\mathbf{v}_i \to \alpha \mathbf{v}_i$
- → measured temperature scales as $\mathcal{T} \to \alpha^2 \mathcal{T}$
- in order to stay at temperatur T we must use

$$\boxed{\alpha = \sqrt{\frac{T}{\mathcal{T}}}}$$

- **main problem**: one changes physics and in particular time
- soften problem using relaxation time t_T

$$\alpha = \sqrt{q + \frac{\Delta t}{t_T}\left(\frac{T}{\mathcal{T}} - 1\right)}$$

- still does not obay Maxwell-Boltzmann → only good to initialize a configuration at given temperature

15.2 Constraint method

Add a friction term to the equation of motion

$$\boxed{\dot{\mathbf{p}} = \mathbf{f}_i - \xi \mathbf{p}_i, \quad \mathbf{p}_i = m_i \dot{\mathbf{x}}_\mathbf{i}}$$

- friction with *both* signs possible
- system becomes dissipative
- can be interpreted as Langrange multiplier

Berendsen et al define

$$\xi = \gamma \left(q - \frac{T}{\mathcal{T}}\right)$$

15.3 Stochastic method

- combine molecular MD with Monte Carlo
- very n time steps select randomly one particle and give **new momentum** according to **Maxwell-Boltzmann distribution**:

$$P(\mathbf{p}) = \frac{1}{(\pi kT)^{3/2}} e^{-\frac{-(\mathbf{p}-\mathbf{p}_0)^2}{kT}}$$

- adjustable model n where κ is the thermal conductivity

$$n^{-1} \propto \frac{\kappa}{\kappa \rho^{1/3} N^{2/3}}$$

- for n to small we have pure Monte Carlo and lose the real time scale,e.g. long time tail of the velocity correlation
- for n too large coupling to the heat bath is too weak, equilibration is slow and we work rather microcanonically

15.4 Nose-Hoover thermostat

New degree of freedom s
which describes the heat bath (can transfer heat from an to the system)

$$\boxed{\mathcal{V}(s) = (3N+1)kT \log s, \quad K(s) = \frac{1}{2} Q \dot{s}^2}$$

where Q can be interpreted as **thermal inertia**, controlling the energy flow between system and heat bath.

Coupling to particle motion by changing the time scale $\boxed{\mathrm{d}t' = s\,\mathrm{d}t}$:

$$\begin{aligned}
\mathbf{v}_i' = \mathrm{d}\mathbf{x}_i t' = \frac{\mathrm{d}\mathbf{x}_i}{\mathrm{d}t}\frac{\mathrm{d}t}{\mathrm{d}t'} = \frac{\mathbf{v}_i}{s} \\
\mathbf{p}_i' = \frac{\mathrm{d}K}{\mathrm{d}\mathbf{v}_i'} = \frac{\mathrm{d}K}{\mathrm{d}\mathbf{v}_i}\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}\mathbf{v}'} = s\mathbf{p}_i \\
\Rightarrow \mathbf{p}_i' = m_i s^2 \mathbf{v}_i'
\end{aligned}$$

New Hamiltonian

$$\boxed{\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i'^2}{2m_i s^2} + \frac{1}{2} Q \dot{s}^2 + \mathcal{V}(\mathbf{x}_1, \ldots, \mathbf{x}_N) + \mathcal{V}(s)}$$

Define $\boxed{p_s \equiv Q\dot{s}}$, then **Hamilton equations** in virtual time give:

$$\begin{aligned}
\frac{\mathrm{d}\mathbf{x}_i}{\mathrm{d}t'} &= \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i'} = \frac{\mathbf{p}_i'}{m_i s^2} \\
\frac{\mathrm{d}s}{\mathrm{d}t'} &= \frac{\partial \mathcal{H}}{\partial p_s} = \frac{p_s}{Q} \\
\frac{\mathrm{d}\mathbf{p}_i'}{\mathrm{d}t'} &= -\frac{\partial \mathcal{H}}{\partial \mathbf{x}_i} = -\nabla_{\mathbf{x}_i} \mathcal{V}(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \mathbf{f}_i \\
\frac{\mathrm{d}p_s}{\mathrm{d}t'} &= -\frac{\partial \mathcal{H}}{\partial s} = \frac{1}{s}\left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i s^2} - (3N+1)kT \right) \\
\rightarrow \mathbf{p}_i' &= m_i s^2 \dot{\mathbf{x}}_\mathbf{i} \\
\frac{\mathrm{d}\mathbf{p}_i'}{\mathrm{d}t'} &= 2m_i s \dot{s} \dot{\mathbf{x}}_\mathbf{i} + m_i s^2 \ddot{\mathbf{x}}_\mathbf{i}
\end{aligned}$$

Equations of motion in virtual time t'

$$\boxed{m_i s^2 \ddot{\mathbf{x}}_\mathbf{i} = \mathbf{f}_i - 2m_i \dot{s} s \dot{\mathbf{x}}_\mathbf{i}, \quad Q\ddot{s} = \sum_{i=1}^{N} m_i s \dot{\mathbf{x}}_\mathbf{i}^2 - \frac{1}{s}(3N+1)kT}$$

$\rightarrow$ entire system is conservative and its ensemble microcanonical.

Transformation to real time using $\boxed{\Delta t = \frac{\Delta t'}{s}, \quad \mathbf{p}_i' = s\mathbf{p}_i}$ we have the **Hamilton equations**

$$\begin{aligned}
\frac{\mathrm{d}\mathbf{x}_i}{\mathrm{d}t} &= s\frac{\mathrm{d}\mathbf{x}_i}{\mathrm{d}t'} = \frac{\mathbf{p}_i'}{m_i s} = \frac{\mathbf{p}_i}{m_i} \\
\frac{\mathrm{d}s}{\mathrm{d}t} &= s\frac{\mathrm{d}s}{\mathrm{d}t'} = s\frac{p_s}{Q} \\
\frac{\mathrm{d}\mathbf{p}_i}{\mathrm{d}t} &= s\frac{\mathrm{d}}{\mathrm{d}t'}\frac{\mathbf{p}_i'}{s} = \frac{\mathrm{d}\mathbf{p}_i'}{\mathrm{d}t'} - \frac{1}{s}\frac{\mathrm{d}s}{\mathrm{d}t'}\mathbf{p}_i' = \mathbf{f}_i - \frac{1}{s}\frac{\mathrm{d}s}{\mathrm{d}t}\mathbf{p}_i \\
\frac{\mathrm{d}p_s}{\mathrm{d}t} &= s\frac{\mathrm{d}p_s}{\mathrm{d}t'} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{m_i} - (3N+1)kT
\end{aligned}$$

Equations of motion in real space

$$\boxed{\ddot{\mathbf{x}}_\mathbf{i} = \frac{\mathbf{f}_i}{m_i} - \xi \dot{\mathbf{x}}_\mathbf{i}, \quad \frac{1}{2}Q\dot{\xi} = \frac{1}{2}\sum_{i=1}^{N} m_i \dot{\mathbf{x}}_\mathbf{i}^2 - \frac{1}{2}(3N+1)kT}$$

with $\boxed{\xi \equiv \frac{\dot{s}}{s}}$. The $\log s$ is needed such that the total energy, obtained from integration is $\boxed{\frac{\mathrm{d}\log s}{\mathrm{d}t} = \xi}$

Choice of Q

- must be chosen empirically
- too large Q leads to slow equilibration,
- for $Q \rightarrow \infty$ **microcanonical MD** is recovered
- Q too small leads to spurious temperature fluctuations SLIDE 111
- $\rightarrow$ check that the wisth of temperature distribution follows

$$\overline{\Delta T} = \sqrt{\frac{2}{Nd}}\overline{T}$$

PARTIONFUNCTION $\rightarrow$ ADD NEW SLIDES 133 through 135

- only method with a single friction parameter that gives the correct canonical distribution
- Hoover thermostate satisfies Liouville equation, i.e. density of states is conserved in phase space

16 Constant pressure ensemble

Generalized equipartition theorem

$$\left\langle \mathbf{p}_i \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i} \right\rangle = \left\langle \mathbf{q}_i \frac{\partial \mathcal{H}}{\partial \mathbf{q}_i} \right\rangle = 3kT, \quad \mathcal{H} = K(\mathbf{p}) + \mathcal{V}(\mathbf{x})$$

Split potential forces into **forces from walls** and **forces from particles**

$$\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{x}_i \cdot \nabla_{\mathbf{x}_i} \mathcal{V}(\mathbf{x}_i) \right\rangle = NkT$$

$$\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{x}_i \cdot \left(\mathbf{f}_i^{\text{ext}} + \mathbf{f}_i^{\text{part}}\right) \right\rangle = -NkT$$

$$\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{x}_i \cdot \mathbf{f}_i^{\text{ext}} \right\rangle + \underbrace{\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{x}_i \mathbf{f}_i^{\text{part}} \right\rangle}_{\equiv w \text{ virial}} = -NkT$$

Then

$$\frac{1}{3}\left\langle \sum_{i=1}^{N} \mathbf{x}_i \cdot \mathbf{f}_i^{\text{ext}} \right\rangle = -\frac{1}{3}\int_{\Gamma} p\mathbf{x}\,\mathrm{d}\mathbf{A} = -\frac{1}{3}p\int_{V} \nabla \cdot \mathbf{c}\,\mathrm{d}V = -pV$$

Instantaneous pressure

$$\boxed{\mathcal{P}V \equiv= NkT + \langle w \rangle}$$

→ keep pressure p fixed by changing the V using a piston of mass W. ADD SLIDE 121

16.1 Coordinate rescaling (Anderson)

Volume change

$$V = 1 - \alpha_t \frac{\Delta t}{t_p}(p - \mathcal{P})$$

- α_T isothermal compressibility
- t_p relaxation time for the pressure
- → corresponds to **rescaling of length** $\mathbf{x} \to V^{1/3}\mathbf{x}$

16.2 Berendsen thermostat

New Hamiltonian

$$\boxed{\mathcal{H} = \sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{x}_i^2 + \underbrace{\frac{1}{2} W \dot{V}^2}_{E_k in \text{ of Volume change}} + V(\mathbf{x}_1, \ldots, \mathbf{x}_N) + pV}$$

where the new variable V is a **volume change** controlled by a piston of mass W which defines a **canonical momentum**

$$\boxed{p_V = W\dot{V}}$$

Equations of motion

$$\ddot{\mathbf{x}}_\mathbf{i} = \frac{\mathbf{f}_i}{m_i} - \frac{\dot{V}}{3V}\dot{\mathbf{x}}_\mathbf{i}, \quad W\dot{V} = \frac{1}{3v}\sum_{i=1}^{N} m_i \dot{\mathbf{x}}_\mathbf{i}^\mathbf{2} + \frac{1}{3V}\sum_{i=1}^{n} \mathbf{f}_i \mathbf{x}_i - p$$

16.3 Parinello-Rahman barostat

→ also change the shape of the box described three vectors $\mathbf{a}, \mathbf{b}$ and $\mathbf{c}$ and thus having a volume

$$\boxed{V = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = \det(\mathbf{H}), \quad \mathbf{H} = \{\mathbf{a}, \mathbf{b}, \mathbf{c}\}}$$

Position of particle i in this box

$$\boxed{\mathbf{r}_i) = \mathbf{H}\mathbf{s}_i = x_i\mathbf{a} + y_i\mathbf{b} + z_i\mathbf{c}, \quad x_i, y_i, z_i \in (0, 1)}$$

Distance between particles i and j

$$\boxed{\mathbf{r}_{ij}^2 = \mathbf{s}_{ij}^T \mathbf{G} \mathbf{s}_{ij}, \quad \mathbf{G} = \mathbf{H}^T\mathbf{H}}$$

Hamiltonian

$$\boxed{\mathcal{H} = \frac{1}{2}\sum_i m_i \dot{\mathbf{s}}_\mathbf{i}^\mathbf{T} \mathbf{G} \dot{\mathbf{s}}_\mathbf{i} + \sum_{ij} \mathcal{V}(\mathbf{r}_{ij}) + \mathrm{Tr}\,\dot{\mathbf{H}}^\mathbf{T}\dot{\mathbf{H}} + pV}$$

equations of motion

$$m_i \ddot{\mathbf{s}}_\mathbf{i} = \mathbf{H}^{-1} - m_i \mathbf{G}^{-1}(\dot{\mathbf{G}}\dot{\mathbf{s}}_\mathbf{i}), \quad W\ddot{\mathbf{H}} = \mathbf{p}V(\mathbf{H}^{-1})^T$$

16.4 NPT ensemble

ADD (eventually) SLIDE 127f SLIDE 127f

17 Event driven Molecular Dynamics

- flow of the program is not determined by **loops** but by events
- for riged bodies of finite volume one would normally want to describes by a **hard core potential** in classicla MF
- event driven simulations: collisions are considere as instantaneous events and particles do not interact in between
- → no forces calculated
- → only binary collisions considered
- → ballistic tracectories between collision
- calculate time t_c between two collision
- obtain velocities of the two particles **after** the collisions from the velocities of ther particles from a **look-up table**

17.1 Collision event (2d)

ADD SLIDE 5 Consider collision of to rigid disks i and j, where the **collision angle** θ is between $\boxed{\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j}$ and **relative velocity** $\boxed{vbv_{ij} = \mathbf{v}_i - \mathbf{v}_j}$

17.2 Collision time t_c

1. Let t_0 be the time at which the **last collision** occured and set $\mathbf{r}_{ij}^0 = \mathbf{r}_{ij}(t_0)$.
2. Calculate for each pair of particles (i,j) the time t_{ij} when the **next collision** will occur.

$$|\mathbf{r}_{ij}(t_{ij})| = R_i + R_j \quad \Rightarrow \quad |\mathbf{r}_{ij}(t_0) + \mathbf{v}_{ij}t_{ij}| = R_i + R_j$$
$$\Rightarrow v_{ij}^2 t_{ij}^2 + 2(\mathbf{r}_{ij}^0 \mathbf{v}_{ij}) + (\mathbf{r}_{ij}^0)^2 - (R_i + R_j)^2 = 0$$

3. the time t_c when the **next collision in the system** occurs is the **minimum over all pairs** (i,j)

$$\boxed{t_c = \min_{ij}(t_{ij})}$$

17.3 Propagation step

- due to global minimization not easlily parallelizable or vectorizable
- once t_c is determined, particles are moved by

$$\boxed{\mathbf{r}_i^! = \mathbf{r}_i + \mathbf{v}_i t_c, \quad \phi_i^! = \phi_i + \omega_i t_c \; \forall i}$$

- then collision between the pair (i^*, j^*) occurs
- one can also add simple accelerations like gravity
- knowon position and angle of particle i at a time t^* since which it had no collision, one can determine position and angle at later time as

$$\boxed{\mathbf{r}_i(t) = \mathbf{r}_i(t^*) + \mathbf{v}_i(t^* - t) + \frac{1}{2} g \mathbf{e}_z (t^* - t)^2, \quad \phi_i(t) = \phi_i(t^*) + \omega_i(t^* - t)}$$

17.4 Lubachevsky tricks

- simple loop over all pairs to determine t_c is $\mathcal{O}(N^2)$
- using lists of events and binary stacks: $\mathcal{O}(N \log N)$
- Create **list of events** (length N) storing for each particle **last event** and **next event**
- $\rightarrow$ keep track of time of event and partner particle involved
- from list one get for each particle i time $t^(i)$ for the next collision involving thus particle
- $\rightarrow$ we can find in $\mathcal{O}(N)$ $\boxed{t_c = \min_i(t^{(i)})}$

Implementation Organize $t^{(i)}$ in increasing order implicitely in a **stack**

- vector `part[m]` points to particle i which is at position m in the stack
- vecotr `pos[i]` gives position m of particle i in the stack
- this constitutes implicit ordering og the collision times $t^{(i)}$, where $m = 1$ points to the smallest time
- `part[1]` is particle with minimal collisio time: $t_c = t^{(\texttt{part[1]})}$
- after event the time $t^{(\texttt{part[1]})}$ must be updated and the list reordered
- store additionally to position and velocity for each particle the **last event** and **next event** in 6 arrays of dimension N
- **Last event** is needed as particles are only updated after being involved in an event
- After event for both particles all six entries (event times, new partners, positions and velocities) have to be updated
- additionally `part[m]` has to be reordered

Complexity

- Straightforward calculation of the new collision times would be of order $\mathcal{O}(N)$ when checking for both particles with all other particles
- Collision lists for each particle or division into sectors (cells) reduce the order to $\mathcal{O}(1)$ per event
- sector boundaries have to be treated similar as obstacles, i.e. when particles cross sector boundaries a collision event happens
- Re-ordering the heap after each event is of order $\mathcal{O}(\log N)$ when using, e.g. binary trees for sorting
- typically: number of events proportional to $N \rightarrow$ order of method $\mathcal{O}(N \log N)$.

Tournament sorting INSERT SLIDE 17
Depth of the tree ($\mathcal{O}(\log_2 N)$) determines maximum number of comparisons for re-ordering.

17.5 Collision with perfect slip

- in tangential direction
- no momentum transferred
- $\rightarrow$ angular velocity irrelevant

Momentum conservation

$$\boxed{\mathbf{v}_i^{\text{after}} = \mathbf{v}_i^{\text{before}} + \frac{\Delta \mathbf{p}_n}{m_i}, \quad \mathbf{v}_j^{\text{after}} = \mathbf{v}_j^{\text{before}} + \frac{\Delta \mathbf{p}_n}{m_j}}$$

where $\Delta \mathbf{p}_n = \Delta \mathbf{p} \cdot \mathbf{n}$ denotes the normal component of the momentum difference.

Energy conservation

$$\boxed{\frac{1}{2} m_i (\mathbf{v}_i^{\text{before}})^2 \frac{1}{2} m_j (\mathbf{v}_j^{\text{before}})^2 = \frac{1}{2} m_i (\mathbf{v}_i^{\text{after}})^2 \frac{1}{2} m_j (\mathbf{v}_j^{\text{after}})^2}$$

The momentum change must be **parallel to normal direction n** and therefore

$$\boxed{\Delta \mathbf{p}_n = -2 m_{\text{eff}} \left[(\mathbf{v}_i^{\text{before}} - \mathbf{v}_j^{\text{before}}) \mathbf{n} \right] \mathbf{n}, \quad m_{\text{eff}} \equiv \frac{m_i m_j}{m_i + m_j}}$$

for collision between particles i and j

$$\mathbf{v}_i^{\text{after}} = \mathbf{v}_i^{\text{before}} - \left[(\mathbf{v}_i^{\text{before}} - \mathbf{v}_j^{\text{before}})\mathbf{n}\right]\mathbf{n}$$
$$\mathbf{v}_j^{\text{after}} = \mathbf{v}_i^{\text{before}} + \left[(\mathbf{v}_i^{\text{before}} - \mathbf{v}_j^{\text{before}})\mathbf{n}\right]\mathbf{n}$$

for $m_i = m_j$ we have

$$\mathbf{v}_i^{\text{after}} = \mathbf{v}_i^{\text{before}} - \mathbf{u}_{ij}^n\mathbf{n}$$
$$\mathbf{v}_j^{\text{after}} = \mathbf{v}_j^{\text{before}} - \mathbf{u}_{ij}^n\mathbf{n}$$

→ make look-up table

17.6 Collision with rotation

Equation of motion for rotation

$$\boxed{I\frac{\mathrm{d}\omega_i}{\mathrm{d}t} = \mathbf{r}\times\mathbf{f}_{ij} = m\mathbf{r}\times\frac{\mathrm{d}\mathbf{v}_i}{\mathrm{d}t}}$$

Consider collision between spheres i and j having the same radius R, moment of inertia I and mass m

$$I(\omega_i' - \omega_i) = -Rm(\mathbf{v}_i' - \mathbf{v}_i)\times\mathbf{n}$$
$$I(\omega_j' - \omega_j) = Rm(\mathbf{v}_j' - \mathbf{v}_j)\times\mathbf{n}$$
$$\mathbf{v}_i' + \mathbf{v}_j' = \mathbf{v}_i + \mathbf{v}_j$$
$$\Rightarrow \omega_i' - \omega_i = \omega_j' - \omega_j = \frac{Rm}{I}(\mathbf{v}_i' - \mathbf{v}_i)\times\mathbf{n}$$

17.7 Collision with general slip

Condition for the relative velocity $\mathbf{u}$ between the particles at their contact point

$$\mathbf{u}_{ij}^n = (\mathbf{u}_{ij}\mathbf{n})\mathbf{n}$$
$$\mathbf{u}_{ij}^t = \mathbf{u}_{ij}\times\mathbf{n} = [(\mathbf{v}_i - \mathbf{v}_j) - R(\omega_i + \omega_j)]\times\mathbf{n}$$

General slip condition

$$\mathbf{u}_{ij}^{t'} = e_t\mathbf{u}_{ij}^t, \quad |e_t| = 1, \quad e_t = \begin{cases}1, & \text{perfect slip}\\ 0, & \text{no slip}\end{cases}$$

$$\mathbf{v}_i' = \mathbf{v}_i - \mathbf{u}_{ij}^n - \frac{(1-e_t)\mathbf{u}_{ij}^t}{2(1+q)} \qquad \mathbf{v}_j' = \mathbf{v}_j - \mathbf{u}_{ij}^n - \frac{(1-e_t)\mathbf{u}_{ij}^t}{2(1+q)}$$
$$\omega_i' = \omega_i - \frac{(1-e_t)\mathbf{u}_{ij}^t\times\mathbf{n}}{2R(1+q^{-1})} \qquad \omega_j' = \omega_j - \frac{(1-e_t)\mathbf{u}_{ij}^t\times\mathbf{n}}{2R(1+q^{-1})}$$

where $\boxed{\frac{m_{\text{eff}}R^2}{I_{\text{eff}}}}$, make a look-up table

17.8 Collision without slip

Use conservation of momentum, energy

$$E = \frac{1}{2}\sum_{i=1}^{2} m_i v_i^2 + \frac{1}{2}\sum_{i=1}^{2} I_i\omega_i^2 = \text{const}, \quad J = \sum_{i=1}^{2} m_i(\mathbf{r}_i\times\mathbf{v}_i) = \sum_{i=1}^{2} I_i\omega_i$$

momentum transfer

$$\boxed{\Delta\mathbf{p} = -2m_{\text{eff}}\left[(\mathbf{v}_{ij}\mathbf{n})\mathbf{n} + \frac{I}{I + m_{\text{eff}}R^2}(\mathbf{v}_{ij}\mathbf{s})\mathbf{s}\right]}$$

17.9 Inelastic collision

- most real collisions are inelastic
- energy dissipated through vibrations, plastic deformation, heat production
- dissipation quantified through material dependent **restitution coefficient** r which is fraction of *not* dissipated energy after a collision
- $r = 1$ for elastic collision, $r = 0$ perfect plasticity

Measurement of restitution coefficient
Let particle fall from height h^{initial} on a plate of same material and measuring rebounce height h^{final}

$$\boxed{r = r_n = \frac{E^{\text{after}}}{E^{\text{before}}} = \frac{h^{\text{final}}}{h^{\text{initial}}} = \left(\frac{v_n^{\text{after}}}{v_n^{\text{before}}}\right)^2}$$

Normal and tangential coefficients

$$\boxed{e_n = \sqrt{r_n} = \frac{v_n^{\text{after}}}{v_n^{\text{before}}}, \quad e_t = \sqrt{r_t} = \frac{v_t^{\text{after}}}{v_t^{\text{before}}}}$$

Energy conservation condition replaced by

$$(\mathbf{v}_j^{\text{after}} - \mathbf{v}_i^{\text{after}})\cdot\mathbf{n} = -e_n(\mathbf{v}_j^{\text{before}} - \mathbf{v}_i^{\text{before}})\cdot\mathbf{n}$$

examples for e_n (steel:0.92, aluminium:0.8, plastic: 0.6)

Inelastic normal collision
normal component of relative velocity $\mathbf{u}$ between particles at their contact point

$$\mathbf{u}_{ij}^n = (\mathbf{u}_{ij}\mathbf{n})\mathbf{n} = [(\mathbf{v}_i - \mathbf{v}_j)\mathbf{n}]\cdot\mathbf{n}$$

dissipation through normal coefficient of restitution e_n

$$\mathbf{u}_{ij}^{n'} = e_n\mathbf{u}_{ij}^n$$

ADD DETAILS SLIDE 37 **Perfect slip**

$$\boxed{\Delta\mathbf{p}_n = -m_{\text{eff}}(1+e_n)\left[(\mathbf{v}_i^{\text{before}} - \mathbf{v}_j^{\text{before}})\cdot\mathbf{n}\right]\mathbf{n}}$$

General slip

$$\mathbf{v}_i' = \mathbf{v}_i - \frac{1+e_n}{2}\mathbf{u}_{ij}^n - \frac{(1-e_t)\mathbf{u}_{ij}^t}{2(1+q)} \qquad \mathbf{v}_j' = \mathbf{v}_j + \frac{1+e_n}{2}\mathbf{u}_{ij}^n + \frac{(1-e}{2(1}$$
$$\omega_i' = \omega_i - \frac{(1-e_t)\mathbf{u}_{ij}^t\times\mathbf{n}}{2R(1+q^{-1})} \qquad \omega_j' = \omega_j - \frac{(1-e_t)\mathbf{u}_{ij}^t\times\mathbf{n}}{2R(1+q^{-1})}$$

where $\boxed{\frac{m_{\text{eff}}R^2}{I_{\text{eff}}}}$, make a look-up table

17.10 Finite time singularity

If an inelastic sphere jumps on a plate it will perform in a finite time t_{tot} an infinity of collisions.

$$\boxed{t_{\text{tot}} = \sum_{j=1}^{\infty} t_j = 2\sqrt{\frac{2h^{\text{initial}}}{g}}\sum_{j=1}^{\infty}\sqrt{r^j} = 2\sqrt{\frac{2h^{\text{initial}}}{g}}\left(\frac{1}{1-\sqrt{r}} - 1\right)}$$

Effect occurs for three particles if $r < 7 - 4\sqrt{3}$

Minimum number of particles for which if $r \approx 1$

$$n_{\min} \sim -\frac{\log(1-r)}{1-r}$$