Molecular dynamics

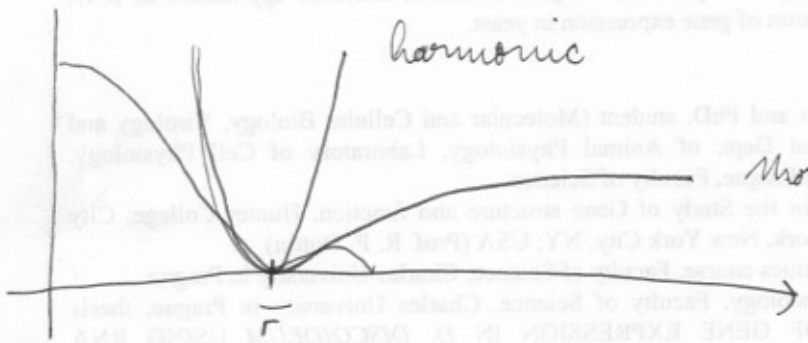
Let's think about how you would find a force field

2 atoms

(i) — (j) Stretching term

$$\rightarrow E^{r}_{harm} = S_n (r - \bar{r})^2$$

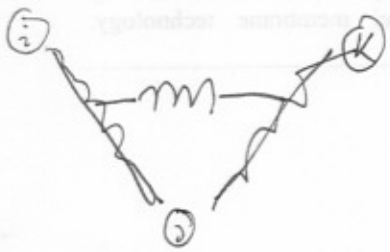
$$E^{r}_{morse} = D \left\{ 1 - e^{-S_m (r - \bar{r})^2} \right\}$$



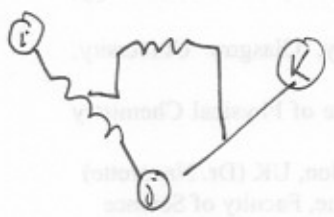
higher-order terms consider even terms

~~Torsional~~ Bond Angle term

$$E^{\theta}_{harm} = K_h \left[\theta - \bar{\theta} \right]^2$$

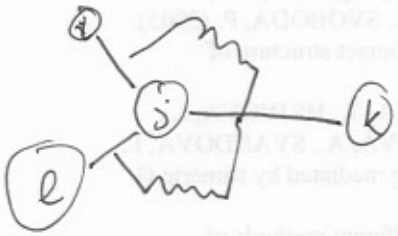


Cross Bond stretch / angle bend terms



stretch / bend:
i-j / j-k stretch terms differ as θ_{ijk} changes

bend / bend



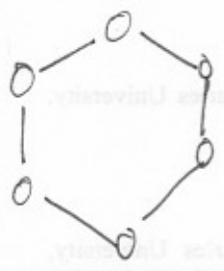
couple bending vibrations →

Torsional potential

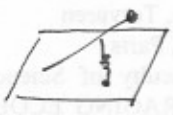
$$E^{\tau}(\tau) = \sum \frac{V_n}{2}\left[1 \pm \cos n\tau\right]$$

τ: torsional angle
V_n: barrier height

Improper terms



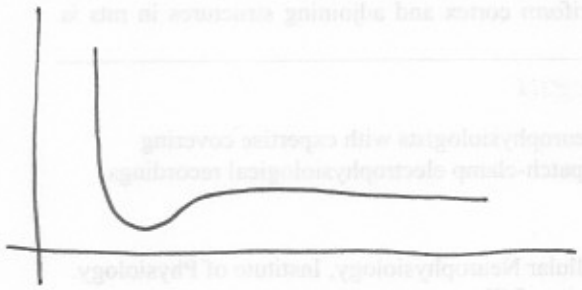
Out of plane - bending



$$E^{\chi}(\chi) = \frac{V'}{2}\chi^2$$

Non-Bonded IA (Van-der Waals pot)

$$E_{Lj} = -\frac{A_{ij}}{r_{ij}^6} + \frac{B_{ij}}{r_{ij}^{12}}$$



Energy minima $A_{ij} = 2\left(r_{ij}^{\circ}\right)^6 V_{ij}$

$$B_{ij} = \left(r_{ij}^{\circ}\right)^{12} V_{ij}$$

$$= \frac{A_{ij}}{2}\left(r_{ij}^{\circ}\right)^6$$

Get $\{\varepsilon_i, r_i\}$ from parametrization

$$V_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$$

$$r_{ij}^{\circ} = \left(r_i + r_j\right)$$

Coulomb potential

$$E_c = K_{coul}\frac{1}{\varepsilon}\frac{q_i q_j}{r_{ij}}$$

Issues:

1) Parameter choice
2) Comp. bottlenecks

Molecular dynamics

Newton's equation

$$m \frac{d^2 \vec{r}_i}{dt^2} = \sum \vec{F}(r_{ij})$$

$$r_i(t+\Delta t) = -r_i(t-\Delta t) + 2r_i(t) \sum \vec{F}(r_{ij}(t)) \Delta t^2$$

Verlet integration step

Problem with MD:

- rapidly varying forces, especially stochastic forces, are modelled explicitely
  → small time steps necessary
  typically $\Delta t \sim 1 fs$
- pairwise potentials
- limits due to cell size of periodic b.c.

Perturbation theory + MD

System response to external perturbing force characterized in terms of time correlations between perturbed and unperturbed systems using linear response theory

Let's look at probabilities

$W_1(y)\,dy$: Prob of finding a particle in range $[y, y+dy]$ at time t

$W_2(y_1, y_2, t)\,dy_1 dy_2$: Prob of finding a particle in range $[y_1, y_1+dy_1]$ at time t_1, and in range $[y_2, y_2+dy_2]$ at time t_2 with $t_2 - t_1 = t$

Markoff process : pos at time t_n depends on pos at time t_{n-1}

$$W_2(y_1, y_2, t) = W_1(y_1)\; P_2(y_1 | y_2 t)$$

→ task : define and sample

$P_2(y_1 | y_2 t)$, i.e. prob for a particle to be in range $(y_2, y_2+dy_2]$ at time t, if it was at y_1 at time 0

Continuum electrostatics : Poisson - Boltzmann

Gauss : $\nabla [\varepsilon(x) \nabla \bar{\Phi}(x)] = -4\tilde{\pi} \rho_{solute}$

typically $\varepsilon(x)$ increases with distance from solute (~~less~~ Change in polarizability)

charge density must consider mobile ions

→ consider charge density resulting from distribution of charges ~~around~~ medium

$$\rho(x) = \sum q_i c_i \; e^{-(\tilde{E}_i(x)/kT)}$$

$$c_i = N_i / V$$

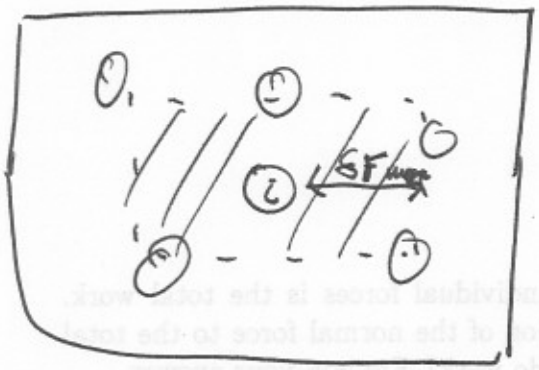
$\tilde{E}$: PMF

$\tilde{E} \sim q_i \bar{\Phi}(x)$

$$\nabla [\varepsilon(x) \nabla \bar{\Phi}(x)] = -4\tilde{\pi} \rho_{solute}(x) - 4\tilde{\pi} \sum_{i=1}^{n_i} q_i c_i \; e^{-q_i \bar{\Phi}(x)/kT}$$

Monte - Carlo Modeling

Most general scheme to sample probability distributions



atom i moved with uniform probability to any point in shaded region

$$r_i^u = r_i^{u-1} + (2a_0 - 1)\,\delta r_{max}$$

a_0 : random number

$$\delta V_{u,u-1} = \left(\sum_j V(r_{ij}^u) - \sum_j V(r_{ij}^{u-1}) \right)$$

Usually involves only IA within cutoff distance r_c

$\delta V_{u,u-1} < 0$ downhill : move accepted

$\delta V_{u,u-1} > 0$ uphill accepted with probability

$$\frac{\rho_u}{\rho_{u-1}} = \frac{e^{-\beta V_u}\, e^{-\beta \delta V_{u,u-1}}}{e^{-\beta V_u}} = e^{-\beta \delta V_{u,u-1}}$$

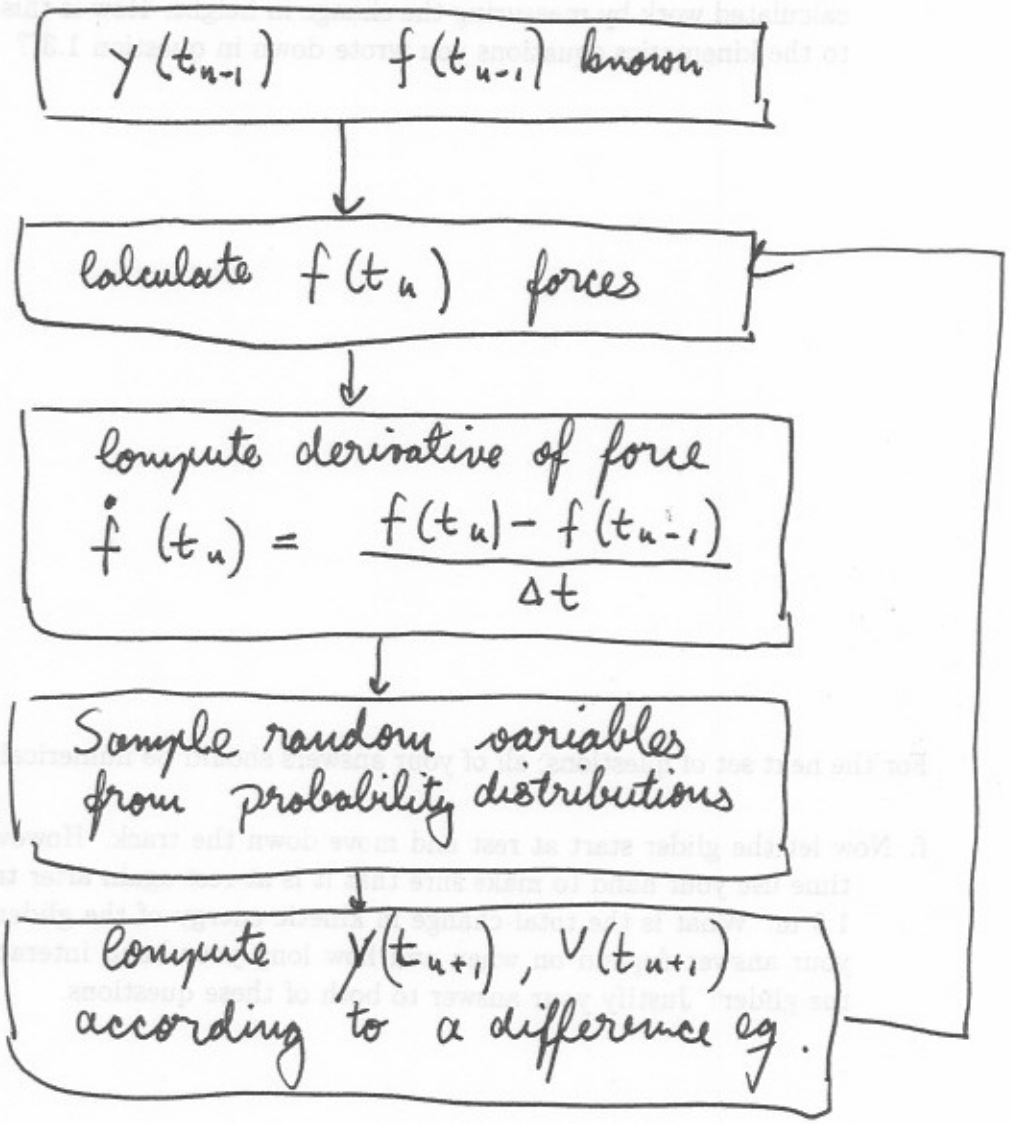
(Boltzmann distribution)

Brownian dynamics

$$m\dot{v}(t) = -\gamma m v(t) + f(t) + R(t)$$

Langevin equation

Algorithm



$\langle R_i(0) R_j(t) \rangle = 2 m_i \gamma_i kT \delta_{ij} \delta_t$

$\Delta t \ll \gamma^{-1}$

Van Gunsteren & Berendsen

- Ignores inertia (sometimes added with mass-dependent correction terms)
- simple hydrodynamics