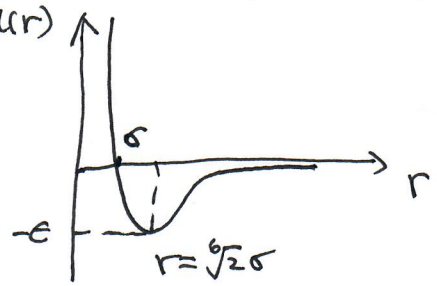
Lecture V Dissipative Particle Dynamics

1. Why?

A special type of Molecular Dynamics simulation technique

Lennard-Jones potential:



Strong repulsion at short inter-particle distance $r<\sigma$ requires a very small time step for integrating Newton's equations of motion.

It's impractical, or computationally unfeasible to simulate systems with large length and time scales. E.g. protein's folding. cell membrane process using MD.

2. Features of DPD

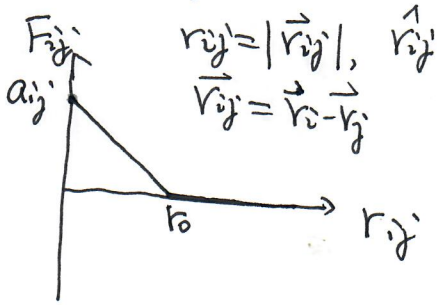
1) groups a few atoms or molecules as a spherical particles. or fluid element (coarse-graining)
2) introduces soft potentials between those particles. which allow a larger time step than MD

pairwise force between particles i and j:

$$\vec{F}_{ij} = F^C_{ij}(\vec{r}_{ij}) + F^D_{ij}(\vec{r}_{ij}, \vec{v}_{ij}) + F^R_{ij}(\vec{r}_{ij})$$

$\vec{F}^C_{ij}$: conservative force, negative gradient of a potential $\vec{F} = -\nabla\phi$

$$\vec{F}^C_{ij} = \begin{cases} a_{ij}\left(1-\frac{r_{ij}}{r_0}\right)\hat{r}_{ij}, & r_{ij} < r_0 \\ 0, & r_{ij} \geq r_0 \end{cases}$$



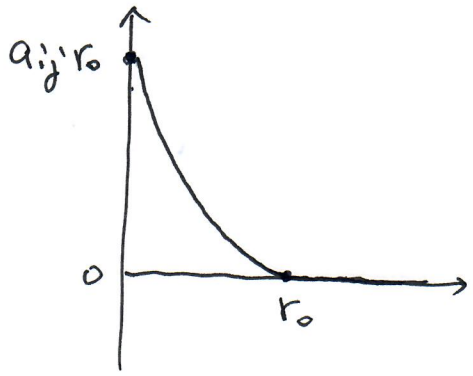
$r_{ij} = |\vec{r}_{ij}|$, $\hat{r}_{ij} = \frac{\vec{r}_{ij}}{r_{ij}}$

$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$

$a_{ij} > 0$, $a_{ij} = a_{ji}$. repulsion force strength

Dimension: $\frac{\text{Energy}}{\text{Length}}$

potential U_{ij}^C:



mathematical form:

$$U_{ij}^C = \frac{a_{ij}}{r_0}\left(r_{ij} - r_0\right)^2 + \text{const}$$

$$= r_0 a_{ij}\left(1 - \frac{r_{ij}}{r_0}\right)^2 + \text{const}$$

truncated quadratic function

Note that:

at $r_{ij}=0$, force F_{ij}^C is finite, not infinite, which means overlap is OK, or tolerated in DPD. Technically, we don't need to calculate the pairwise force F_{ij}^C if $r_{ij}=0$ in program.

$\vec{F}_{ij}^D(\vec{r}_{ij}, \vec{v}_{ij})$: dissipative or frictional force

$$\vec{F}_{ij}^D(\vec{r}_{ij}, \vec{v}_{ij}) = -\gamma_{ij} w^D(r_{ij})\left(\vec{v}_{ij}\cdot\hat{r}_{ij}\right)\hat{r}_{ij}$$

friction coefficient $\gamma_{ij} = \gamma_{ji} > 0$ dependent of particle types

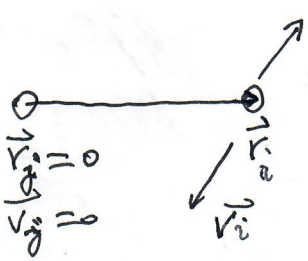
$$w^D(r_{ij}) = \begin{cases} >0, & r_{ij} < r_0 \\ =0, & r_{ij} \geq r_0 \end{cases}$$

$\gamma = \frac{k_B T}{D}$: Dimension $\frac{\text{Energy}\cdot\text{Time}}{\text{Length}^2}$

D: diffusion coefficient: $\text{Length}^2/\text{Time}$

$w^D(r_{ij})$: Dimension 1

$\vec{v}_{ij}\cdot\hat{r}_{ij}$: Length/Time



$\vec{r}_i$: $\vec{v}_{ij}\cdot\vec{r}_{ij} > 0$, $F_{ij}^D < 0$, attraction

$\vec{v}_{ij}\cdot\vec{r}_{ij} < 0$, $F_{ij}^D > 0$, repulsion

F_{ij}^D slows down the particle motion along the joining vector

$\vec{F}^R_{ij}(\vec{r}_{ij})$: random force, representing thermal noise

$$\vec{F}^R_{ij}(\vec{r}_{ij}) = \sigma_{ij} w^R(r_{ij})\, \hat{r}_{ij}\, \theta_{ij}$$

θ_{ij}: Gaussian (~~white~~) noise.

$\langle \theta_{ij}(t) \rangle = 0$

Kronecker delta ↑ → Dirac delta

$$\langle \theta_{ij}(t)\, \theta_{kl}(t') \rangle = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\, \delta(t-t').$$

$$\delta_{ik} = \begin{cases} 1 & i=k \\ 0 & i\neq k \end{cases}$$

$$\int_{-\infty}^{\infty} \delta(t)\, dt = 1$$

noise terms for different pairs are uncorrelated

$$\langle \theta_{ij}^2(t) \rangle = \Delta t^{-1}.$$

To recover NVT ensemble.

$$w^D(r_{ij}) = [w^R(r_{ij})]^2, \quad \sigma_{ij}^2 = 2\gamma_{ij} k_B T$$

$$= \begin{cases} \left(1 - \frac{r_{ij}}{r_0}\right)^2, & r_{ij} < r_0 \\ 0, & r_{ij} \geq r_0 \end{cases}$$

Quantity	Dimension
σ_{ij}	$\frac{\text{Energy} \cdot \text{Time}^{1/2}}{\text{Length}}$
θ_{ij}	$\text{Time}^{-1/2}$
$\delta(t-t')$	Time^{-1}

The three forces act along the line of particle centers. So the linear and angular momentum are both conserved. DPD preserves hydrodynamics.

Put together:

$$\vec{F}^C_{ij} + \vec{F}^D_{ij} + \vec{F}^R_{ij}$$

$$= \left[a_{ij}\left(1 - \frac{r_{ij}}{r_0}\right) - \frac{\sigma_{ij}^2}{2k_BT}\left(1 - \frac{r_{ij}}{r_0}\right)^2 (\vec{v}_{ij} \cdot \hat{r}_{ij}) + \sigma_{ij}\left(1 - \frac{r_{ij}}{r_0}\right) \zeta_{ij} \Delta t^{-1/2} \right] \vec{r}_{ij}$$

$\zeta_{ij} = \zeta_{ji}$: gaussian random number with variance 1

$$= \left[a_{ij}\left(\frac{1}{r_{ij}} - \frac{1}{r_0}\right) - \frac{\sigma_{ij}^2}{2k_BT}\left(\frac{1}{r_{ij}} - \frac{1}{r_0}\right)^2 (\vec{v}_{ij} \cdot \vec{r}_{ij}) + \sigma_{ij}\left(\frac{1}{r_{ij}} - \frac{1}{r_0}\right) \Delta t^{-\frac{1}{2}} \zeta_{ij} \right] \vec{r}_{ij}$$

Important aspects of DPD:

① preserves hydrodynamics
② includes thermal fluctuations
③ allows for large time steps.

3. Numerical implementation of DPD

3.1 Integration scheme

Review velocity-Verlet algorithm in MD

$$\vec{r}_i(t+\delta t) = \vec{r}_i(t) + \vec{v}_i(t)\,\delta t + \frac{1}{2}\frac{\vec{f}_i(t)}{m_i}\delta t^2$$

$$\vec{v}_i(t+\tfrac{1}{2}\delta t) = \vec{v}_i(t) + \frac{1}{2}\frac{\vec{f}_i(t)}{m_i}\delta t$$

$$\vec{f}_i(t+\delta t) = \vec{f}_i[\vec{r}_i(t+\delta t)] \quad (*)$$

$$\vec{v}_i(t+\delta t) = \vec{v}_i(t+\tfrac{1}{2}\delta t) + \frac{1}{2}\frac{\vec{f}_i(t+\delta t)}{m_i}\delta t = \vec{v}_i(t) + \frac{1}{2}\frac{\vec{f}_i(t)+\vec{f}_i(t+\delta t)}{m_i}\delta t$$

In DPD, (*) should be replaced by

$$\vec{f}_i(t+\delta t) = \vec{f}_i[\vec{r}_i(t+\delta t), \vec{v}_i(t+\delta t)] \quad \text{because of } F_{ij}^D(\vec{r}_{ij}, \vec{v}_{ij})$$

one could solve $\vec{v}_i(t+\delta t)$ iteratively. but this would be rather expensive.

Modified velocity-verlet algorithm for DPD:

$$\vec{v}_i(t+\lambda\delta t) = \vec{v}_i(t) + \lambda\frac{\vec{f}_i(t)}{m_i}\delta t, \qquad 0<\lambda<1$$

$$\vec{f}_i(t+\delta t) \approx \vec{f}_i[\vec{r}_i(t+\delta t), \vec{v}_i(t+\lambda\delta t)]$$

$$\vec{v}_i(t+\delta t) = \vec{v}_i(t) + \frac{1}{2}\frac{\vec{f}_i(t)+\vec{f}_i(t+\delta t)}{m_i}\delta t$$

Note that $\lambda=\frac{1}{2}$ recovers velocity-verlet algorithm.

3.2 choice of parameters Ref: JCP. 107(11): 4423-4435, 1997

To recover the physical properties of water at temperature T=300K,

$a_{ij} = a_{ww} = 25\,k_BT/r_0$, $\rho = 3/r_0^3$ (number density, number of particles per volume

$r_0 \sim 1$ nm

time step for integration: $\Delta t \sim 0.03-0.06 \approx 10\,\Delta t_{MD}$

4. Applications of DPD in soft matter systems

Polymer system

Lipid membrane