Dissipative particle dynamics

Aim of the authors was to create an algorithm for the treatment of the effects of a solvent onto the particles one wants to consider that

i) has thermal fluctuations that can drive Brownian motion (correct long time diffusion)

ii) is cheap to simulate

iii) satisfies hydrodynamic behaviour

(i) and (ii) are fulfilled by Langevin dynamics but (iii) is not. The Navier-Stokes equation is the field theoretic formulation of momentum conservation in the particle collisions but Langevin dynamics does not conserve momentum !

How to decide the Langevin equation to that momentum conservation is ensured ?

Newtonian mechanics momentum conservation due to actio = reactio and dependence of force only on the distance (translation + rotation) invariance of space ⇒ Galilean invariant !

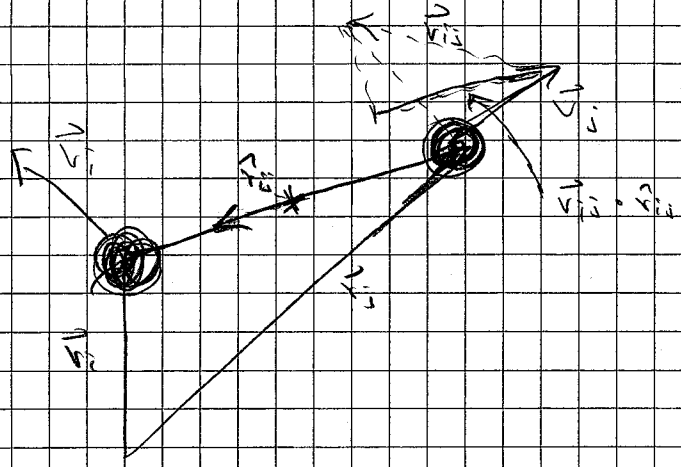
Ansatz:

$$\vec{F}_i = \sum_{j \neq i} \left[\vec{f}^C(\vec{r}_{ij}) + \vec{f}^D(\vec{r}_{ij}, \vec{v}_{ij}) + \vec{f}^R(\vec{r}_{ij}) \right]$$

($\vec{f}^C$: conservative, $\vec{f}^D$: dissipation, $\vec{f}^R$: random force)

$$\vec{f}^D(\vec{r}_{ij}, \vec{v}_{ij}) = -\gamma\, \omega^D(r_{ij})\, (\vec{v}_{ij} \cdot \hat{r}_{ij})\, \hat{r}_{ij}$$

→ so the dissipative force is now pairwise additive, proportional to the projection of the velocity onto the connecting direction and acting along that direction



A similar result is valid for the random force

$$\underline{f}^R(\vec{r}_{ij}) = \nabla\, \omega^R(r_{ij})\, \xi_{ij}\, \hat{r}_{ij}$$

where ξ_{ij} is Gaussian white noise.

Equations of motion (in physics notation)

$$\dot{\vec{r}}_i = \vec{v}_i$$

$$m_i \dot{\vec{v}}_i = \sum_{j \neq i} \vec{f}_{ij}^{\,c}(r_{ij}) - \gamma \sum_{j \neq i} \omega^D(r_{ij})(\vec{v}_{ij} \cdot \hat{r}_{ij})\hat{r}_{ij}$$

$$+ \nabla \sum_{j \neq i} \omega^R(r_{ij})\, \hat{r}_{ij}\, \xi_{ij}(t)$$

Normalization (i.e., the canonical distribution is the equilibrium distribution of the corresponding Fokker-Planck equation requires the fluctuation-dissipation relation in the following form.

$$\omega^D(r_{ij}) = \omega^{R^2}(r_{ij})$$

$$\nabla^2 = 2\gamma m_i k_B T$$

ω^R can be chosen for efficiency: choose it of finite range, so that only a small fraction of the pairs have to be considered

$$\omega^D(r_{ij}) = [\omega^R(r_{ij})]^2 = \begin{cases} (1 - r_{ij}/r_c)^2 & r_{ij} \leq r_c \ (\equiv 1) \\ 0 & r_{ij} > r_c \end{cases}$$

Most applications of DPD included another ingredient:

coarse-graining

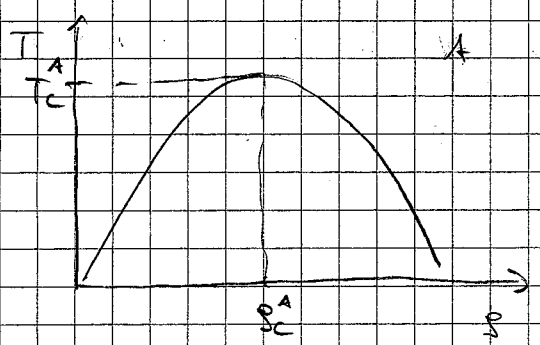
Example: Consider an A/B fluid mixture, for example of Lennard-Jones particles.

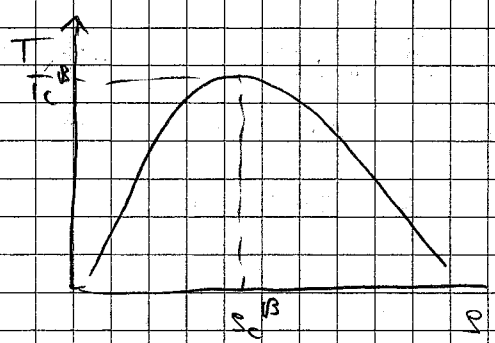
$$U_{\alpha\beta}(r_{ij}) = 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{6}\right] \quad ; \quad \alpha,\beta = A,B$$

Let us assume that for the single component system a Lennard-Jones description using

$(\varepsilon_{AA}, \sigma_{AA})$ and $(\varepsilon_{BB}, \sigma_{BB})$

works OK, for instance in reproducing the vapour-liquid coexistence of the liquids.



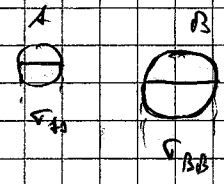


Knowledge of (T_c, ρ_c) fixes (ε, σ)

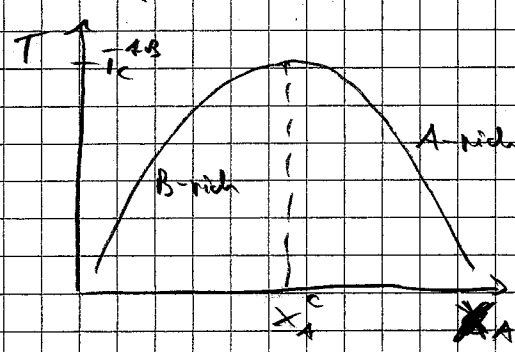
What happens in the mixture? Typically one assumes the Lorentz-Berthelot mixing rule

$$\sigma_{AB} = \frac{1}{2}(\sigma_{AA} + \sigma_{BB})$$

$$\varepsilon_{AB} = \sqrt{\varepsilon_{BB}\,\varepsilon_{AA}}$$



⇒ Phase diagram of the mixture



Critical unmixing point

(x_A^c, T_c^{AB})

$x_B = 1 - x_A$

When I use the LJ model I have a time unit

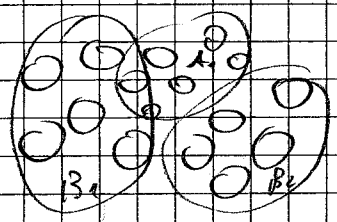
$$\tau = \sqrt{\frac{m\sigma^2}{\varepsilon}}$$

To be save choose: i) smallest $m\sigma^2/\varepsilon$

ii) $\Delta t = (0.001 - 0.002)\,\tau$

→ typically small time steps and long simulation times

Idea: coarse grain configurations and work with effective units



grouping $n = 5 - 10$ LJ particles of the same sort.

New unit sits at center of mass

$$\vec{R}_i = \frac{1}{n}\sum_{k=1}^{n} \vec{r}_k$$

How do the units interact? Not known exactly but it is possible that $\vec{R}_i = \vec{R}_m$?

→ soft interactions

Again one often chooses:

$$\omega^c(R_{ij}) = \begin{cases} \alpha\left(1 - \frac{R_{ij}}{R_c}\right) & R_{ij} \le R_c \\ 0 & R_{ij} > R_c \end{cases}$$

or something similar.

→ i) Only qualitative results on phase diagram

ii) no guarantee that the phase diagram topology is correct

Advantage: Soft potentials → large time steps Δt

Back to the equations of motion

$$d\vec{r}_i = \vec{v}_i\, dt$$

$$m_i\, d\vec{v}_i = \sum_{r_{ij}<r_c} \frac{\alpha}{r_c}\hat{r}_{ij} - \gamma \sum_{r_{ij}<r_c} \left(1-\frac{r_{ij}}{r_c}\right)^2 \left(\vec{v}_{ij}\cdot\hat{r}_{ij}\right)\hat{r}_{ij}$$

$$\sqrt{2m_i\gamma k_B T}\sum_{r_{ij}<r_c} \left|1-\frac{r_{ij}}{r_c}\right| \hat{r}_{ij}\, d\vec{W}_{ij}(t)$$

Think back to the remark on discretizations of SDEs.

What do I get from a combination of an Euler algorithm with a big time step?

→ large errors &

example: T measured was very different from T imposed (in T)

→ several papers and years of discussion &