

Computational physics

Heiko Rieger and Adam Wysocki

Theoretical Physics
Saarland University

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Introduction into molecular dynamics

- ▶ So far we dealt with **stochastic** simulation methods of many-body systems, namely, with **Monte Carlo** (MC) methods.
- ▶ MC simulation generates states according to Boltzmann (or canonic) distribution.
- ▶ In MC we want to estimate the expectation value

$$\langle \mathcal{O} \rangle_{\text{ens}} = \frac{\int d\mathbf{p}^N d\mathbf{r}^N \mathcal{O}(\mathbf{r}^N, \mathbf{p}^N) e^{-\beta \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)}}{\int d\mathbf{p}^N d\mathbf{r}^N e^{-\beta \mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)}} \quad (1)$$

or rather the configurational version

$$\langle \mathcal{O} \rangle_{\text{ens}} = \frac{\int d\mathbf{r}^N \mathcal{O}(\mathbf{r}^N) e^{-\beta \mathcal{U}(\mathbf{r}^N)}}{\int d\mathbf{r}^N e^{-\beta \mathcal{U}(\mathbf{r}^N)}}, \quad (2)$$

where the Hamiltonian $\mathcal{H} = \mathcal{K} + \mathcal{U}$ is a sum of a kinetic \mathcal{K} and a potential part \mathcal{U} .

Introduction into molecular dynamics

- ▶ The MC simulation generates a stochastic sequence (Markov chain) of states \mathbf{r}^N with distribution

$$\lim_{\tau \rightarrow \infty} P(\mathbf{r}^N(\tau)) = \frac{e^{-\beta U(\mathbf{r}^N(\tau))}}{\int d\mathbf{r}^N e^{-\beta U(\mathbf{r}^N(\tau))}} \quad (3)$$

and the ensemble average becomes

$$\langle \mathcal{O} \rangle_{\text{ens}} = \lim_{\tau_{\text{obs}} \rightarrow \infty} \frac{1}{\tau_{\text{obs}}} \sum_{\tau=1}^{\tau_{\text{obs}}} \mathcal{O}(\mathbf{r}^N(\tau)). \quad (4)$$

- ▶ A **deterministic** type of N-body simulation methods is **molecular dynamics** (MD), it generates trajectories of interacting particles by numerically solving Newton's equations of motion.
- ▶ The Hamiltonian of N classical particles is $\mathcal{H} = \mathcal{K} + \mathcal{U}$ with

$$\mathcal{K} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} \quad \text{and} \quad \mathcal{U} = \sum_{i=1}^N U_1(\mathbf{r}_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N U_2(\mathbf{r}_i, \mathbf{r}_j) + \dots \quad (5)$$

Introduction into molecular dynamics

- ▶ From Hamilton's equations $\dot{\mathbf{p}}_i = -\frac{\partial \mathcal{H}}{\partial \mathbf{r}_i}$ and $\dot{\mathbf{r}}_i = \frac{\partial \mathcal{H}}{\partial \mathbf{p}_i}$ we get Newton's equations of motion

$$m_i \ddot{\mathbf{r}}_i = -\nabla_{\mathbf{r}_i} \mathcal{U} = \mathbf{f}_i = \mathbf{f}_1(\mathbf{r}_i) + \sum_{j \neq i} \mathbf{f}_2(\mathbf{r}_i, \mathbf{r}_j) + \dots \quad (6)$$

- ▶ \mathbf{f}_1 is an external force, like, gravity, electromagnetic forces, container walls, etc.
- ▶ $\mathbf{f}_2(\mathbf{r}_i, \mathbf{r}_j) = \mathbf{f}_2(r_{ij})$, where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, is a force due to a pair potential, like, Lennard-Jones potential, Coulomb potential, etc.
- ▶ The initial conditions $(\mathbf{r}^N(t=0), \mathbf{p}^N(t=0))$ determine the time evolution of the system.
- ▶ The ergodic hypothesis links MC to MD simulations, it states that the time spent by a system in some region of the phase space of microstates with the same energy is proportional to the area of this region.

Introduction into molecular dynamics

- ▶ The ergodic hypothesis: Time averaging (the MD approach) equals ensemble averaging (the MC approach):

$$\begin{aligned}\langle \mathcal{O} \rangle_{\text{time}} &= \lim_{t_{\text{obs}} \rightarrow \infty} \frac{1}{t_{\text{obs}}} \sum_{t=0}^{t_{\text{obs}}} \mathcal{O}(t) \\ \stackrel{!}{=} \langle \mathcal{O} \rangle_{\text{ens}} &= \int d\mathbf{p}^N d\mathbf{r}^N \mathcal{O}(\mathbf{r}^N, \mathbf{p}^N) P(\mathbf{r}^N, \mathbf{p}^N) \quad (7)\end{aligned}$$

Caution: Is not always true. Ergodicity breaking in glasses or spin systems below T_c .

- ▶ Comment on ensembles:
 - ▶ The natural ensemble of MC is the canonical or NVT ensemble, i.e., temperature T is fixed.
 - ▶ The natural ensemble of MD is the microcanonical or NVE ensemble, i.e., total energy E is fixed.
 - ▶ The equivalence of ensembles holds only if we choose E and T consistently: $E = \langle E \rangle_{NVT}$ (or $T = \langle T \rangle_{NVE}$), i.e., if the total energy of MD is chosen to be the average energy of MC.

Caution: Is not always true. Consider, for example, energy fluctuations.

Skeleton of a molecular dynamics simulation

```
initialisation();  
for (t=0;t<t_max;t++)  
{calculate_force();  
  integrate();  
  sample_averages();  
}
```

- ▶ Specify the pair potential, initial temperature, number of particles, box size, time step.
- ▶ Select initial configuration (positions and velocities).
- ▶ Compute force on all particles.
- ▶ Integrate Newton's equation of motion.
- ▶ Calculate averages of observables, like, temperature, pressure, mean-square displacement, etc.

Common pair potentials

- ▶ The Lennard-Jones (or 12-6) potential,

$$U^{LJ}(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right),$$

approximates the interaction between a pair of neutral atoms.

- ▶ The $1/r^{12}$ term describes Pauli repulsion.
- ▶ The $1/r^6$ term describes van der Waals attraction.
- ▶ ϵ is an energy and σ a length scale.
- ▶ Other idealized potentials:
 - ▶ Hard-sphere (no energy scale): $U^{HS}(r) = \begin{cases} \infty & (r < \sigma) \\ 0 & (r \geq \sigma) \end{cases}$
 - ▶ Soft-sphere (ν controls the softness): $U^{SS}(r) = \epsilon(\sigma/r)^\nu$
 - ▶ Square-well potential, see Figure 2.
- ▶ Ions obey Coulomb interaction: $U^{zz}(r_{ij}) = \frac{z_i z_j}{4\pi\epsilon_0 r_{ij}}$, with vacuum permittivity ϵ_0 and charges z_i and z_j on ions i and j .
- ▶ Long-range potential $U(r) \propto r^{-\nu}$ with $\nu \leq d$, where d is the dimension of the system, e.g., Coulomb interaction, needs special treatment.

Common pair potentials

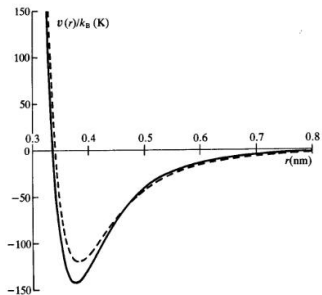


Figure 1: (Solid line) Experimental Argon potential. (Dashed line) Effective 12-6 potential.

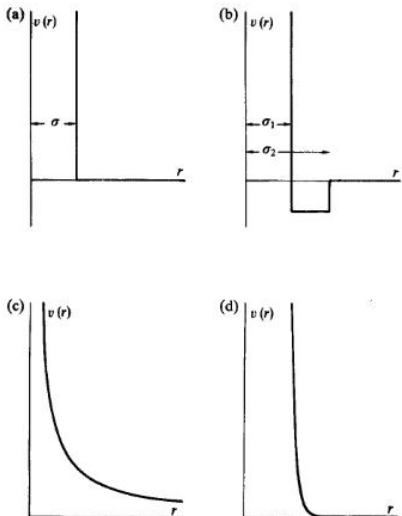


Figure 2: (a) Hard-sphere potential. (b) Square-well potential. (c) Soft-sphere potential with $\nu = 1$ (long-range). (d) Soft-sphere potential with $\nu = 12$ (short-range).

Periodic boundary conditions (PBC)

- ▶ Use PBC in order to mimic an infinite bulk surrounding the N -particle system.
- ▶ The central box with side length L is the primitive cell of an infinite lattice of identical cells.

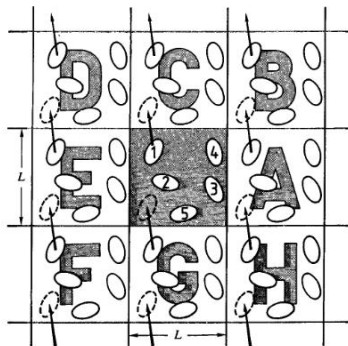


Figure 3: 2D periodic system. Particles can enter or leave each box across each of the 4 edges.

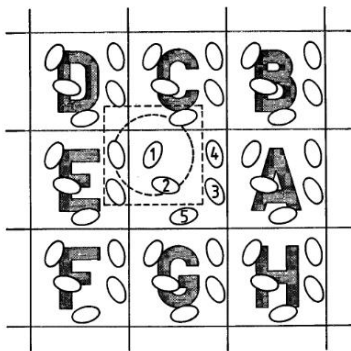


Figure 4: Minimum image convention. Dashed box is centered around particle 1. Dashed circle represents potential cutoff.

Truncation of the interaction

- ▶ Total energy in periodic system is $\mathcal{U} = \frac{1}{2} \sum'_{i,j,\mathbf{n}} U(|\mathbf{r}_{ij} + \mathbf{n}L|)$, where the sum over \mathbf{n} indicates a sum over the whole lattice and the prime indicates that $i = j$ is excluded for $\mathbf{n} = 0$.
- ▶ In practice, we consider only nearest periodic images, i.e.,

$$r_{ij} = \min_{\mathbf{n}} \{|\mathbf{r}_{ij} + \mathbf{n}L|\} \quad (8)$$

and truncate the interaction at some $r_c < L/2$.

- ▶ Total energy is a sum of truncated interactions and a tail contribution:

$$\mathcal{U} \approx \sum_{i < j} U_{trunc}(r_{ij}) + \frac{N\rho}{2} \int_{r_c}^{\infty} dr 4\pi r^2 U(r), \quad (9)$$

assuming homogeneous system for $r \geq r_c$ with an average number density $\rho = N/L^d$.

- ▶ Tail contribution is infinite for $U(r) \propto r^{-\nu}$ with $\nu \leq 3$, which is a criterion for a long-range interaction.

Truncation of the interaction

- ▶ In order to remove discontinuities in the energy (impulsive forces) and problems with energy conservation use a truncated and shifted potential:

$$U_{shift}(r) = \begin{cases} U(r) - U(r_c) & (r \leq r_c) \\ 0 & (r > r_c) \end{cases} \quad (10)$$

- ▶ Even better is a shift-force potential, where force goes smoothly to zero at r_c and which removes problems in energy conservation and numerical instability in the equation of motion,

$$U_{shift-force}(r) = \begin{cases} U(r) - U(r_c) - \left(\frac{dU(r)}{dr} \right)_{r=r_c} (r - r_c) & (r \leq r_c) \\ 0 & (r > r_c) \end{cases} \quad (11)$$

- ▶ **Caution: Shifted potentials change thermodynamic properties of the system** (a correction is possible).

Verlet neighbor list

- ▶ Verlet neighbor list avoids a naive force evaluation with $N(N - 1)/2$ operations.
- ▶ Store initially all neighbors of each particle within $r_l > r_c$ in a list with dimension $\frac{4}{6}\pi r_l^3 \rho N$.
- ▶ Use neighbor list to calculate the forces until

$$\sum_{\text{steps}} \max_i |\mathbf{v}_i| > \frac{r_l - r_c}{2\Delta t},$$

otherwise refresh the list.

- ▶ With increasing $r_l - r_c$ the frequency of updates decreases, on the other hand, the stored number of noninteracting particles increases.

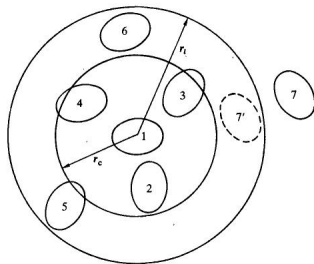


Figure 5: Particle 1 interacts with particles within r_c . Verlet list contains all particles $r_l > r_c$.

Cell-linked list

- ▶ Verlet list becomes inefficient for large N due to huge memory demand and expensive list update.
- ▶ Divide the simulation box into a regular lattice of M^d cells of size r_c^d with approximately $N_c = N/M^d$ particles per cell.
- ▶ A particle interacts with particles within the same cell and with particles from 4 (or 13) neighboring cells in 2D (or 3D).

21	22	23	24	25
16	17	18	19	20
11	12	13	14	15
6	7	8	9	10
1	2	3	4	5

Figure 6: Simulation box is divided into $M \times M$ cells of size $r_c \times r_c$. For example, particles in cell 13 interact with cells 9, 14, 18, 19.

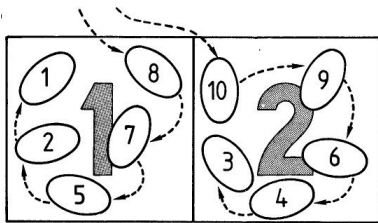


Figure 7: A close-up of cells 1 and 2, showing particles and the link-list structure. Particle 8 (or 10) is the head of chain in cell 1 (or 2).

Cell-linked list

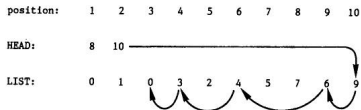


Figure 8: Illustration of the method for the cells 1 and 2, see Figure 7. Consider cell 2: start at HEAD(2)=10 and iterate LIST(10)=9, LIST(9)=6,..., until LIST(3)=0. Last

```

DO 100 ICELL = 1, NCELL
  HEAD(ICELL) = 0
CONTINUE
CELLI = REAL ( M )
DO 200 I = 1, N
  ICELL = 1 + INT ( ( RX(I) + 0.5 ) * CELLI )
  :       + INT ( ( RY(I) + 0.5 ) * CELLI ) * M
  :       + INT ( ( RZ(I) + 0.5 ) * CELLI ) * M * M
  LIST(I) = HEAD(ICELL)
  HEAD(ICELL) = I
200 CONTINUE

```

Figure 9: Construction of the linked-list array LIST and the head-of-chain array HEAD. Here simulation box is a unit cube $[-0.5, 0.5]^3$ and cell size is $1/M$.

- ▶ Only $5NN_c$ (or $14NN_c$) pairs in 2D (or 3D) need to be examined.
- ▶ Construction of Verlet list using the cell-linked list is possible (now size of the cell is r_l).

Force calculation with cell-linked list

```
for (icell=1;icell<=ncell;icell++) // go over all cells
  {i=head[icell]; // head of icell
  while (i!=0) // last particle in cell if list[i]=0
    {j=list[i]; // next particle in icell
    while (j!=0) // go over all particles in icell
      {dx=Rx[i]-Rx[j]; // apply PBC
      if (dx*dx+dy*dy<r_c*r_c)
        {...;} // force calculation
      j=list[j]; // next particle in icell
    }
    jcello=4*(icell-1);
    for (nabor=1;nabor<=4;nabor++) // neighbors of icell
      {jcell=map[jcello+nabor]; // index of neighbor cell
      j=head[jcell]; // head of neighbor cell
      while (j!=0) // go over all particles in jcell
        {...; j=list[j];} // force calculation
      }
    i=list[i]; // next particle in icell
  }
}
```


Integration of the equation of motion

What are properties of a good integrator?

- ▶ Should be accurate at large time steps.
- ▶ Should duplicate the classical trajectory as closely as possible.
- ▶ Like Newton's equation of motion, the integrator must be time-reversal invariant, i.e., under time-reversal $t \rightarrow -t$ ($\mathbf{r} \rightarrow \mathbf{r}$ and $\mathbf{p} \rightarrow -\mathbf{p}$) particles follow the forward trajectory in reverse order.
- ▶ Long-time energy and momentum conservation.
- ▶ The integrator should be symplectic, i.e., should preserve the phase space area as predicted by Liouville's theorem.
- ▶ Single force evaluation per time step.

Verlet algorithm

- ▶ Verlet integration approximates 2nd order derivative with a 2nd order central difference:

$$\ddot{\mathbf{r}}(t) \approx \frac{\frac{\mathbf{r}(t+\delta t) - \mathbf{r}(t)}{\delta t} - \frac{\mathbf{r}(t) - \mathbf{r}(t-\delta t)}{\delta t}}{\delta t} \quad (12)$$

$$= \frac{\mathbf{r}(t + \delta t) - 2\mathbf{r}(t) + \mathbf{r}(t - \delta t)}{\delta t^2} = \frac{\mathbf{f}(t)}{m} \quad (13)$$

- ▶ Basic Verlet algorithm

$$\mathbf{r}(t + \delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \delta t) + \frac{\mathbf{f}(t)}{m} \delta t^2 \quad (14)$$

- ▶ Discretization error via Taylor expansion of the position \mathbf{r} around t

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \mathbf{v}(t)\delta t + \frac{\mathbf{f}(t)}{2m} \delta t^2 + \mathcal{O}(\delta t^3) \quad (15)$$

$$\mathbf{r}(t - \delta t) = \mathbf{r}(t) - \mathbf{v}(t)\delta t + \frac{\mathbf{f}(t)}{2m} \delta t^2 - \mathcal{O}(\delta t^3) \quad (16)$$

Verlet algorithm

- ▶ Summing these two equations gives

$$\mathbf{r}(t + \delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \delta t) + \frac{\mathbf{f}(t)}{m}\delta t^2 + \mathcal{O}(\delta t^4) \quad (17)$$

- ▶ Is time-reversible due to symmetrical roles of $\mathbf{r}(t + \delta t)$ and $\mathbf{r}(t - \delta t)$.
- ▶ Local error is of order δt^4 , because terms of order δt^3 (jerk or $\ddot{\mathbf{r}}$) cancel out.
- ▶ Note that Verlet algorithm does not use \mathbf{v} to compute new positions, however, $\mathbf{v}(t)$ may be obtained via

$$\mathbf{v}(t) = \frac{\mathbf{r}(t + \delta t) - \mathbf{r}(t - \delta t)}{2\delta t} + \mathcal{O}(\delta t^2) \quad (18)$$

Leap Frog algorithm

- ▶ Write Taylor expansion of the position \mathbf{r} in a different form

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \left(\mathbf{v}(t) + \frac{\mathbf{f}(t)}{m} \frac{\delta t}{2} \right) \delta t + \mathcal{O}(\delta t^3) \quad (19)$$

$$\Rightarrow \mathbf{r}(t + \delta t) = \mathbf{r}(t) + \mathbf{v}(t + \delta t/2) \delta t + \mathcal{O}(\delta t^3) \quad (20)$$

- ▶ Taylor expansion of the velocity \mathbf{v} around t

$$\mathbf{v}(t + \delta t/2) = \mathbf{v}(t) + \frac{\mathbf{f}(t)}{m} \frac{\delta t}{2} + \mathcal{O}(\delta t^2) \quad (21)$$

$$\mathbf{v}(t - \delta t/2) = \mathbf{v}(t) - \frac{\mathbf{f}(t)}{m} \frac{\delta t}{2} + \mathcal{O}(\delta t^2) \quad (22)$$

Subtracting these two equations gives

$$\mathbf{v}(t + \delta t/2) = \mathbf{v}(t - \delta t/2) + \frac{\mathbf{f}(t)}{m} \delta t + \mathcal{O}(\delta t^3) \quad (23)$$

- ▶ Note that, velocities are given at mid-step.
- ▶ Leap Frog algorithm is also time-reversible.

The great integrator (Velocity Verlet algorithm)

- ▶ Velocity Verlet algorithm stores positions, velocities and forces at the same time.

$$\mathbf{r}(t + \delta t) = \mathbf{r}(t) + \mathbf{v}(t)\delta t + \frac{\mathbf{f}(t)}{2m}\delta t^2 \quad (24)$$

$$\mathbf{v}(t + \delta t) = \mathbf{v}(t) + \frac{\mathbf{f}(t + \delta t) + \mathbf{f}(t)}{2m}\delta t \quad (25)$$

- ▶ Velocity Verlet algorithm involves two stages:
 - ▶ Calculate $\mathbf{r}(t + \delta t)$ and $\mathbf{v}(t + \delta t/2) = \mathbf{v}(t) + \frac{\mathbf{f}(t)}{2m}\delta t$
 - ▶ Calculate $\mathbf{f}(t + \delta t)$ and $\mathbf{v}(t + \delta t) = \mathbf{v}(t + \delta t/2) + \frac{\mathbf{f}(t + \delta t)}{2m}\delta t$.
- ▶ Velocity Verlet algorithm is equivalent to the original Verlet algorithm.
- ▶ Note that, the Taylor expansion of \mathbf{r} up to δt^2 , see Eq.(24), is the simple Euler integrator. Although it is similar to Verlet method it is not time-reversible and area preserving and exhibits catastrophic energy drift.

Schema of the Verlet family

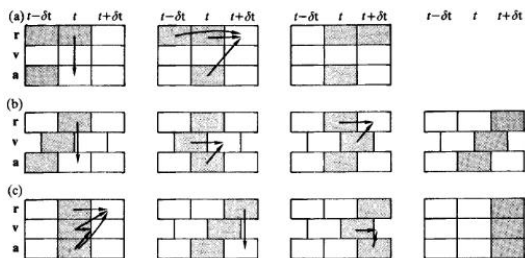


Figure 10: (a) Verlet method. (b) Leap-frog form. (c) Velocity-Verlet algorithm. Acceleration is denoted as $\mathbf{a} = \mathbf{f}/m$.

- ▶ Absence of long-term energy drift, phase area preservation and time reversibility of the Verlet algorithm can be proofed using discretized version of the Liouville equations.
- ▶ Verlet algorithm can be derived from variational principle, as a consequence a Verlet trajectory can still be close to some true trajectory of the system over a time that is longer than the time it takes the Lyapunov instability to develop.

Reduced units

- ▶ It is convenient to express quantities in reduced units due to:
 - ▶ Law of corresponding states, i.e., many combinations of ρ , T , ϵ and σ correspond to the same state in reduced units.
 - ▶ Avoidance of numerical over- or underflow, i.e., all quantities are of order $\mathcal{O}(1)$.
- ▶ For a pair potential of the form $U(r) = \epsilon f(r/\sigma)$ the natural choice of basic units is
 - ▶ σ as length scale
 - ▶ ϵ as energy scale
 - ▶ mass m
- ▶ Some quantities in reduced units
 - ▶ Number density $\rho^* = \rho\sigma^3$
 - ▶ Temperature $T^* = k_B T/\epsilon$
 - ▶ Time $t^* = \sqrt{\epsilon/m\sigma^2}t$
 - ▶ Energy $E^* = E/\epsilon$
 - ▶ Pressure $P^* = P\sigma^3/\epsilon$
- ▶ Alternatively, use $k_B T$ as energy scale.

Starting up the simulation

- ▶ Initial positions
 - ▶ Face-centered cubic lattice will melt rapidly.
 - ▶ Start with an ideal gas and slowly increase the interaction (via σ or ϵ) to the desired value.
- ▶ Initial velocities
 - ▶ Chose randomly velocities form $P(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{mv_x^2}{k_B T}\right)$ and analogously for v_y and v_z .
 - ▶ Alternatively, chose uniformly distributed velocities from $[-v_{max}, v_{max}]$ (system rapidly relaxes to Maxwell-Boltzmann distribution)
 - ▶ Ensure that the overall momentum vanishes: $\sum_{i=1}^N m_i \mathbf{v}_i = 0$
 - ▶ Adjust velocities to the desired mean kinetic energy.
 - ▶ In thermal equilibrium: $\langle \frac{1}{2} m \mathbf{v}^2 \rangle = \frac{3}{2} k_B T$ in 3D.
 - ▶ The instantaneous kinetic temperature is $k_B T_K = \sum_{i=1}^N \frac{m v_i^2}{N_f}$ with N_f ($= 3N - 3$ for a system with fixed total momentum) degrees of freedom.
 - ▶ Rescale velocities $\mathbf{v}_{new} = \mathbf{v}_{old} \sqrt{T/T_K}$ in order to enforce the target temperature T .

Typical observables

- ▶ Kinetic energy: $\langle \mathcal{K} \rangle = \left\langle \sum_{i=1}^N \frac{1}{2} m \mathbf{v}_i^2 \right\rangle$
- ▶ Potential energy: $\langle \mathcal{U} \rangle = \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^N U(r_{ij}) \right\rangle$
- ▶ Specific heat $C_V = \left(\frac{\partial E}{\partial T} \right)_V$ via

$$\begin{aligned} \langle \mathcal{U}^2 \rangle_{NVE} - \langle \mathcal{U} \rangle_{NVE}^2 &= \langle \mathcal{K}^2 \rangle_{NVE} - \langle \mathcal{K} \rangle_{NVE}^2 \\ &= \frac{3}{2} N k_B^2 T^2 \left(1 - \frac{3 N k_B}{2 C_V} \right) \end{aligned}$$

- ▶ Virial pressure: $P = \rho k_B T + \frac{1}{3V} \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^N \mathbf{r}_{ij} \mathbf{f}_{ij} \right\rangle$

Equation of state $P(\rho)$ of the Lennard-Jones fluid

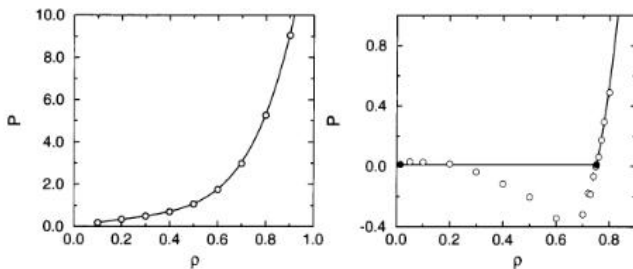


Figure 11: Equation of state $P(\rho)$ of the Lennard-Jones fluid $P(\rho)$. Left: Isotherm at $T^* = 2$. Right: Isotherm below the critical temperature $T^* = 0.9 < T_c^* \approx 1.32$. Filled circles indicate the coexisting vapor and liquid phases. Circles are simulation results ($N = 500$).

Structural observable

Pair correlation function for isotropic and translation symmetric systems

$$g(r) = \frac{V}{N^2} \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^N \delta(r - r_{ij}) \right\rangle,$$

is the probability to find a pair of particles at distance r , relative to the probability of an corresponding ideal gas.

$$\rho g(r) 4\pi r^2 dr \equiv \text{average number of particles with interparticle distance in } [r, r + dr]$$

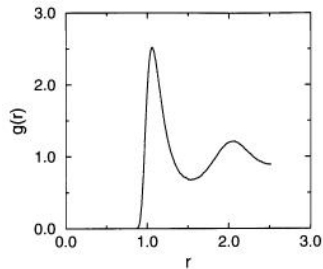


Figure 12: $g(r)$ of a Lenard-Jones fluid close to triple point: $T^* \approx 1.504$ and $\rho^* \approx 0.844$

Time correlation functions and transport coefficients

- ▶ Time correlation functions $\langle \delta A(t) \delta B(0) \rangle$ provide information about the dynamics of the system.
- ▶ Their integrals are often related to macroscopic transport coefficients.
- ▶ Transport coefficients relate a response of a system to a external perturbation.
 - ▶ For example: a particle drifts with a constant velocity $v_{drift} = \mu f_{ext}$ when dragged through a viscous environment by an external force f_{ext} , where μ is called mobility.
- ▶ In equilibrium the system is thermally perturbed and the transport coefficients can be obtained:
 - ▶ via velocity autocorrelation function (VACF):

$$D = \mu k_B T = \frac{1}{d} \int_0^\infty dt \langle \mathbf{v}_i(t) \mathbf{v}_i(0) \rangle, \quad (26)$$

which is called Green-Kubo relation and where D is the diffusion constant.

- ▶ or via mean-square displacement (MSD):

$$2dDt = \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle \quad (27)$$

Velocity autocorrelation function

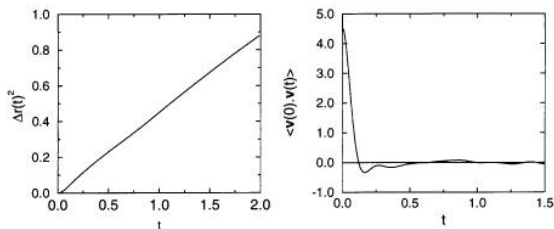


Figure 13: Left: MSD $\langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle$ as a function of t . Note that for long times $\langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle = 2dDt$. Right: VACF $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$ as a function of t .

- ▶ Short-time behaviour of VACF:

$$\langle \mathbf{v}_i(t) \cdot \mathbf{v}_i(0) \rangle \approx \langle \mathbf{v}_i^2 \rangle - \frac{1}{2} \langle \dot{\mathbf{v}}_i^2 \rangle t^2 = \langle \mathbf{v}_i^2 \rangle \left(1 - \frac{1}{2} \omega_E t^2 \right) \quad (28)$$

with Einstein frequency $\omega_E = \frac{\langle \nabla_{\mathbf{r}_i}^2 \mathcal{U} \rangle}{3m}$ of a vibrating particle in the mean force of its neighbors.

Long-time tail of VACF

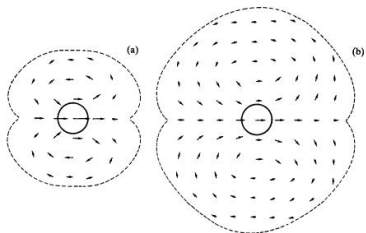


Figure 14: Velocity field of a 2D fluid surrounding a central particle (a) at short and (b) at long times.

- ▶ VACF does not decay exponentially at long times, but rather, algebraically

$$\langle \mathbf{v}_i(t) \mathbf{v}_i(0) \rangle \propto t^{-d/2}, \quad (29)$$

where d is the dimension of the system.

- ▶ Simple explanation: a moving particle compresses the liquid in front of it and causes a vortex flow to circulate around it, due to momentum conservation.

Further transport coefficient: shear viscosity

- ▶ The viscosity of a fluid η expresses its resistance to shearing flows.
- ▶ Newtonian fluid: shear stress $-P_{yx}$ is linearly proportional to the velocity gradient $\frac{\partial v_x}{\partial y}$:

$$\langle P_{yx}(t \rightarrow \infty) \rangle_{ne} = -\eta \frac{\partial v_x}{\partial y} \quad (30)$$

- ▶ Shear viscosity from Green-Kubo relation:

$$\eta = \frac{V}{k_B T} \int_0^\infty dt \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle, \quad (31)$$

where

$$P_{\alpha\beta} = \frac{1}{V} \left(\sum_{i=1}^N m v_{i\alpha} v_{i\beta} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N r_{ij\alpha} f_{ij\beta} \right) \quad (32)$$

are the off-diagonal elements of the pressure tensor.

Calculation of ACF

For $\tau = 0, \dots, \tau_{cor}$: $\langle A(\tau)A(0) \rangle = \frac{1}{\tau_{max}} \sum_{\tau_0=1}^{\tau_{max}} A(\tau_0)A(\tau_0 + \tau)$

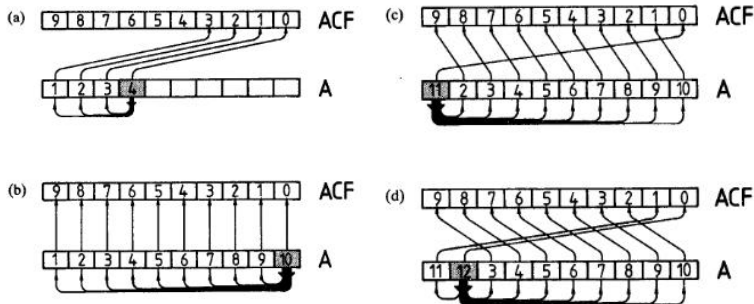


Figure 15: Calculation of ACF in single sweep. Here $\tau_{cor} = 10$. The data A is correlated with itself to give the ACF. The latest imported data is shaded.

Canonical MD

- ▶ In the canonical (or NVT) ensemble the system is in thermal contact with a large heat bath.
- ▶ In NVT ensemble states are distributed according to $P(\mathbf{r}^N, \mathbf{p}^N) \propto e^{-\beta\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)}$ resulting in Maxwell-Boltzmann distribution of momenta $P(\mathbf{p}) = \left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\frac{\beta p^2}{2m}}$
- ▶ The relative variance of the kinetic energy per particle is

$$\frac{\langle (\frac{\mathcal{K}}{N})^2 \rangle_{NVT} - \langle \frac{\mathcal{K}}{N} \rangle_{NVT}^2}{\langle \frac{\mathcal{K}}{N} \rangle_{NVT}^2} = \frac{2}{3N} \quad (33)$$

- ▶ Thus, the kinetic energy per particle fluctuates in the canonical ensemble of a finite system.
- ▶ Note, the definition of the instantaneous kinetic temperature:

$$k_B T_{\mathcal{K}} = \frac{\langle 2\mathcal{K} \rangle}{N_f}, \quad (34)$$

where N_f is the number of degrees of freedom.

Problematic method: Berendsen thermostat

- ▶ At each time step rescale velocities by a factor

$$\mathbf{v}_{\text{new}} = \mathbf{v}_{\text{old}} \sqrt{1 + \frac{\delta t}{\tau} \left(\frac{T}{T_{\mathcal{K}}} - 1 \right)}, \quad (35)$$

where τ is the relaxation time of the thermostat.

- ▶ For $\tau = \delta t$ the thermostat keeps $\langle \mathcal{K} \rangle$ constant and $\langle \mathcal{K}^2 \rangle = 0$, which is not the property of the canonical ensemble.
- ▶ Berendsen thermostat is an isokinetic scheme, which does not generate a canonical distribution.
- ▶ The equation of motion are not the Newtonian ones:

$$m\ddot{\mathbf{r}} = \mathbf{f} - \xi m\mathbf{v}, \quad (36)$$

with friction coefficient $\xi = \frac{k_B T_{\mathcal{K}} - k_B T}{2\tau k_B T_{\mathcal{K}}}$.

- ▶ Berendsen thermostat dissipate energy uniformly in the system, it is a global thermostat.

Problematic method: Andersen thermostat

- ▶ Coupling to the heat bath via stochastic collisions.
- ▶ Each particle has a probability $\nu\delta t$ per time step δt of undergoing a bath collision, where ν is the collision frequency.
- ▶ A bath collision involves assigning the particle a new velocity taken from the Maxwellian distribution with the desired temperature T .

$$\mathbf{v}_{\text{new}} = \begin{cases} \mathbf{v}_{\text{old}} & \text{if } \nu\delta t < \zeta' \\ \boldsymbol{\eta} & \text{if } \nu\delta t \geq \zeta' \end{cases} \quad (37)$$

with uniform random number $\zeta' \in [0, 1]$ and

$\boldsymbol{\eta} = \sqrt{\frac{k_b T}{m}} (\zeta_1, \zeta_2, \zeta_3)$ where ζ_i are sampled from normal distribution with zero mean and unit variance.

- ▶ High ν leads to a totally stochastic dynamics, at low ν the dynamics is rather deterministic.
- ▶ This method satisfies detailed balance and generates canonical distribution.

Problematic method: Andersen thermostat

- ▶ Andersen thermostat dissipate energy on a spatially localized scale, it is a local thermostat.
- ▶ Momentum is not conserved (dynamics is unphysical).
 - ▶ Method disturbs the dynamics substantially for high ν .
 - ▶ Enhanced exponential decay of the VACF with increasing ν .
 - ▶ Decreasing diffusion with increasing ν .

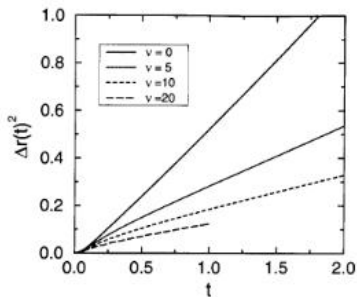


Figure 16: MSD versus time for various values of the collision frequency ν of the Andersen thermostat.

Less problematic method: Langevin thermostat

- ▶ The original Langevin equation describes Brownian motion, i.e., every particle is coupled to viscous background and a stochastic heat bath.
- ▶ Langevin equation reads as

$$m\ddot{\mathbf{r}}_i = \mathbf{f}_i - \xi m\mathbf{v}_i + \sqrt{2m\xi k_B T}\boldsymbol{\eta}_i, \quad (38)$$

where ξ is the friction constant. The stochastic variable $\boldsymbol{\eta}$ is assumed to be Gaussian white noise with zero mean and

$$\langle \eta_{i\alpha}(t)\eta_{j\beta}(t') \rangle = \delta_{ij}\delta_{\alpha\beta}\delta(t-t'), \quad (39)$$

where $\alpha, \beta \in \{x, y, z\}$, such that equipartition is fulfilled.

- ▶ We assume that the random force is memoryless (or delta-correlated) and independent for different particles.
- ▶ The dynamics becomes diffusive in the long-time limit with diffusion constant $D = \frac{k_B T}{m\xi}$.

Numerical solution of overdamped Langevin equation

- ▶ For negligible inertia the 1D version of Eq.(38) becomes

$$\dot{x} = \frac{f}{\xi m} + \sqrt{\frac{2k_B T}{\xi m}} \eta = \frac{f}{\xi m} + \sqrt{2D} \eta \quad (40)$$

- ▶ Introducing a Wiener process $\eta(t) = \frac{dW}{dt}$ and using first order discretisation of the derivatives:

$$x(t + \delta t) = x(t) + \frac{f}{\xi m} \delta t + \sqrt{2D} [W(t + \delta t) - W(t)] \quad (41)$$

- ▶ Increments of the Wiener process $W(t + \delta t) - W(t)$ are normally distributed with mean 0 and variance δt .
- ▶ Hence $W(t + \delta t) - W(t) = \sqrt{\delta t} \zeta$, where ζ are a Gaussian random numbers with $\langle \zeta \rangle = 0$ and $\langle \zeta^2 \rangle = 1$.
- ▶ First order integrator of the overdamped Langevin equation

$$x(t + \delta t) = x(t) + \frac{f}{\xi m} \delta t + \sqrt{2D \delta t} \zeta, \quad (42)$$

Numerical solution of Langevin equation

- ▶ Define $\sigma = \sqrt{\frac{2\xi k_B T}{m}}$ and $a = \frac{f}{m}$, and integrate Eq.(38) over a time step δt :

$$v(t + \delta t) = v(t) + \int_t^{t+\delta t} [a(x(s)) - \xi v(s)] ds + \sigma [W(t + \delta t) - W(t)] \quad (43)$$

- ▶ Approximate $v(s)$ in $s \in [t, t + \delta t]$ with

$$v(s) = v(t) + (s - t) [a(x(t)) - \xi v(t)] + \sigma [W(s) - W(t)]$$

and hence

$$\int_t^{t+\delta t} v(s) ds = v(t)\delta t + \frac{\delta t^2}{2} [a(x(t)) - \xi v(t)] + \sigma \int_t^{t+\delta t} [W(s) - W(t)] ds \quad (44)$$

Numerical solution of Langevin equation

- ▶ Proceed in the same way with $a(x(s))$ using $\frac{da(x(t))}{dt} = \dot{x} \frac{\partial a}{\partial x}$, which yields

$$\int_t^{t+\delta t} a(x(s)) ds = \frac{\delta t}{2} [a(x(t + \delta t)) + a(x(t))] \quad (45)$$

- ▶ The integral of the Wiener increment in Eq.(44), $\int_t^{t+\delta t} [W(s) - W(t)] ds$, is a Gaussian variable with

$$\begin{aligned} \left\langle \left(\int_t^{t+\delta t} [W(s) - W(t)] ds \right)^2 \right\rangle &= \frac{\delta t^3}{3} \\ \left\langle [W(t + \delta t) - W(t)] \left(\int_t^{t+\delta t} [W(s) - W(t)] ds \right) \right\rangle &= \frac{\delta t^2}{2}, \end{aligned}$$

using $\langle W(s)W(s') \rangle = \min(s, s')$.

- ▶ The last relation means that the stochastic variables $W(t + \delta t) - W(t)$ and $\int_t^{t+\delta t} [W(s) - W(t)] ds$ are correlated.

Numerical solution of Langevin equation

- ▶ As above, see Eq.(42), $W(t + \delta t) - W(t)$ is Gaussian with mean 0 and variance δt , thus

$$W(t + \delta t) - W(t) = \sqrt{\delta t} \zeta \quad (46)$$

$$\int_t^{t+\delta t} [W(s) - W(t)] ds = \delta t^{3/2} \left(\frac{\zeta}{2} + \frac{\zeta'}{2\sqrt{3}} \right), \quad (47)$$

where ζ and ζ' are independent Gaussian variables with mean zero and variance $\langle \zeta^2 \rangle = \langle \zeta'^2 \rangle = 1$ and $\langle \zeta \zeta' \rangle = 0$.

- ▶ Second order integrator of Langevin equation

$$x(t + \delta t) = x(t) + v(t)\delta t + A(t)$$

$$v(t + \delta t) = v(t) + [a(x(t + \delta t)) + a(x(t))] \frac{\delta t}{2}$$

$$- \xi v(t)\delta t + \sigma\sqrt{\delta t}\zeta - \xi A(t)$$

$$A(t) = [a(x(t)) - \xi v(t)] \frac{\delta t^2}{2} + \sigma\delta t^{3/2} \left(\frac{\zeta}{2} + \frac{\zeta'}{2\sqrt{3}} \right)$$

Comments on the Langevin thermostat

- ▶ Langevin thermostat generates Maxwellian velocity distribution.
- ▶ VACF decays exponentially as

$$\langle \mathbf{v}(t)\mathbf{v}(0) \rangle = \langle \mathbf{v}^2 \rangle e^{-\xi t} = \frac{3k_B T}{m} e^{-\xi t} \quad (48)$$

- ▶ The equation of motion does not conserve momentum, i.e., center of mass of the overall system diffuses.
- ▶ Hydrodynamic correlations are damped on length scales larger than $\sqrt{\frac{\eta}{m\xi\rho}}$, where ρ is the number density and η the shear viscosity of the molecular fluid.
- ▶ Langevin thermostat is local.

Up-to-date method: dissipative particle dynamics (DPD)

- ▶ DPD is similar to Langevin dynamics, there is also local friction and noise.
- ▶ However, in DPD the dissipative and the random force are pairwise and velocity differences of nearby particles are damped.
- ▶ DPD thermostat is local, Galilean invariant and conserves linear and angular momentum, which are the basic requirements for recovering the hydrodynamics on large length and time scales.
- ▶ The equation of motion is $m\ddot{\mathbf{r}}_i = \mathbf{f}_i$ with total forces

$$\mathbf{f}_i = \sum_{j(\neq i)} \left[\mathbf{f}^C(\mathbf{r}_{ij}) + \mathbf{f}^D(\mathbf{r}_{ij}, \mathbf{v}_{ij}) + \mathbf{f}^R(\mathbf{r}_{ij}) \right], \quad (49)$$

where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$.

- ▶ $\mathbf{f}^C(\mathbf{r}_{ij})$ denotes a conservative force, for example, due to Lennard-Jones interaction.

Dissipative particle dynamics

- ▶ The dissipative force reads as

$$\mathbf{f}^D(\mathbf{r}_{ij}, \mathbf{v}_{ij}) = -\xi\omega^D(r_{ij})(\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij})\hat{\mathbf{r}}_{ij}, \quad (50)$$

with friction constant ξ , weight function $\omega^D(r_{ij})$ and $\hat{\mathbf{r}}_{ij} = \frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|}$.

- ▶ The random force reads as

$$\mathbf{f}^R(\mathbf{r}_{ij}) = \sigma\omega^R(r_{ij})\zeta_{ij}\hat{\mathbf{r}}_{ij}, \quad (51)$$

with noise strength σ , weight function $\omega^R(r_{ij})$ and Gaussian white noise $\zeta_{ij} = \zeta_{ij}$ with,

$$\langle \zeta_{ij} \rangle = 0 \quad \text{and} \quad \langle \zeta_{ij}(t)\zeta_{kl}(t') \rangle = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t-t') \quad (52)$$

- ▶ DPD generates states according to canonical distribution if

$$\sigma^2 = 2k_B T \xi \quad (53)$$

and

$$[\omega^R(r_{ij})]^2 = \omega^D(r_{ij}), \quad (54)$$

which is the fluctuation-dissipation theorem for the DPD method.

Dissipative particle dynamics

- ▶ One can rewrite DPD into a Langevin-type equations and thus into a Fokker-Planck equation, which describes the time evolution of the probability density function of \mathbf{r}^N and \mathbf{v}^N .
- ▶ The canonical distribution is the solution of the Fokker-Planck equation in the steady-state if both conditions Eq.(53) and Eq.(54) are satisfied.
- ▶ A simple choice of the weight functions

$$\omega^D(r) = \omega^R(r) = \begin{cases} 1 & \text{if } r < r_c \\ 0 & \text{else} \end{cases} \quad (55)$$

with cut-off distance r_c , i.e., the thermostat operates only if the interparticle distance is smaller than r_c .

Low-Andersen thermostat: DPD plus Andersen

- ▶ Bath collision between a pair of particles takes place with probability $\nu\delta t$ provided that their distance is smaller than r_c .
- ▶ A bath collision then takes the form

$$m_i\mathbf{v}'_i = \begin{cases} m_i\mathbf{v}_i & \text{if } \nu\delta t < \zeta \\ m_i\mathbf{v}_i + \Delta\mathbf{p}_{ij} & \text{if } \nu\delta t \geq \zeta \end{cases} \quad (56)$$

$$m_j\mathbf{v}'_j = \begin{cases} m_j\mathbf{v}_j & \text{if } \nu\delta t < \zeta \\ m_j\mathbf{v}_j - \Delta\mathbf{p}_{ij} & \text{if } \nu\delta t \geq \zeta \end{cases} \quad (57)$$

where $\zeta \in [0, 1]$ is a uniform random number and

$$\Delta\mathbf{p}_{ij} = \mu_{ij} \left(\zeta_{ij} - \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|} \cdot (\mathbf{v}_i - \mathbf{v}_j) \right) \frac{\mathbf{r}_i - \mathbf{r}_j}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (58)$$

is the momentum change.

Low-Andersen thermostat

- ▶ The stochastic variable with a dimension of a velocity is given by

$$\zeta_{ij} = \sqrt{\frac{k_B T}{\mu_{ij}}} \zeta', \quad (59)$$

where ζ' is sampled from normal distribution with zero mean and unit variance, and $\mu_{ij} = \frac{m_i m_j}{m_i + m_j}$ is the reduced mass.

- ▶ The procedure is carried out sequentially for each pair.
- ▶ Low-Andersen thermostat is local, Galilean invariant, and conserves linear and angular momentum.
- ▶ Further, it is straightforward to implement, e.g., mix velocity-Verlet integrator with bath collision scheme.

Non-equilibrium MD: shear flow

- ▶ Green-Kubo relation allows the estimation of the shear viscosity η in the limit of vanishing velocity gradients $\dot{\gamma} = \frac{\partial v_x}{\partial y}$.
- ▶ Non-equilibrium simulation method allows to investigate nonlinear regimes of fluids, for example:

- ▶ Non-Newtonian character of the fluids at high shear rates, where

$$\langle P_{yx}(t \rightarrow \infty) \rangle_{ne} = -\eta(\dot{\gamma}) \dot{\gamma} \quad (60)$$

- ▶ Shear banding, where the translational symmetry in y -direction is spontaneously broken as a result of a hydrodynamic instability.
- ▶ In order to simulate shear flows without introduction of walls the periodic boundary conditions must be modified.
- ▶ Such a modification was proposed by Lees and Edwards.

Non-Newtonian viscosity of suspensions

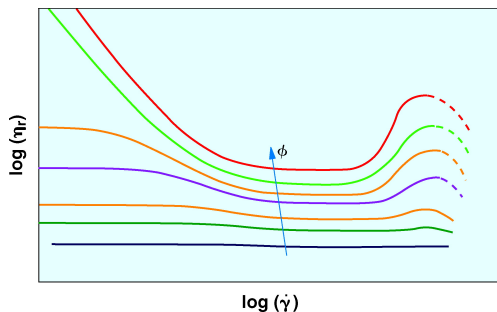


Figure 17: Representation of relative viscosity η_r versus shear rate $\dot{\gamma}$ for a fluid suspension. ϕ denotes the packing fraction.

- ▶ For $\dot{\gamma} \rightarrow 0$, the suspension is Newtonian except for the yield stress behavior of very dense suspensions.
- ▶ All suspensions generally shear-thin at low to intermediate $\dot{\gamma}$.
- ▶ With increasing shear rate, there is a Newtonian plateau and finally a steep shear-thickening region.

Lees-Edwards boundary condition

- ▶ Boxes in the top layer (B,C,D) move with velocity $L\dot{\gamma}$ to the right, boxes in the bottom layer (F,G,H) move with velocity $L\dot{\gamma}$ to the left.
- ▶ A particle that leaves the box in y direction at the top and reenters at the bottom is displaced appropriately both in position and velocity space.

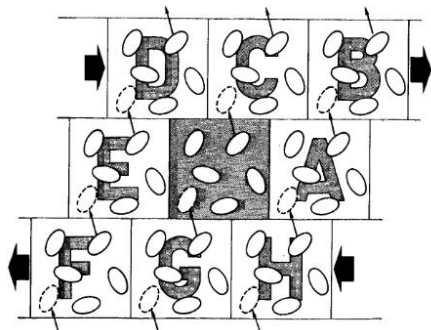


Figure 18: Homogeneous shear boundary conditions.

Lees-Edwards boundary condition

- ▶ Displacement of the upper box relative to the central box:

```
STRAIN+=shear_rate*ly*dt;  
STRAIN-=lx*floor(STRAIN/lx);
```

shear_rate refers to $\dot{\gamma}$.

- ▶ Periodic minimum image convention (force calculation):

```
dx=Rx[i]-Rx[j];  
dy=Ry[i]-Ry[j];  
dx-=STRAIN*floor(0.5+dy/ly);  
dx-=lx*floor(0.5+dx/ly);  
dy-=ly*floor(0.5+dy/ly);
```

- ▶ Periodic boundary crossing:

```
Rx[i]-=STRAIN*floor(Ry[i]/ly);  
Vx[i]-=shear_rate*ly*floor(Ry[i]/ly);  
Rx[i]-=lx*floor(Rx[i]/lx);  
Ry[i]-=ly*floor(Ry[i]/ly);
```

- ▶ Note that a sheared system heats (viscous heating) up and a thermostat is needed.
- ▶ Viscous heating is the transfer of coherent motion into non-coherent molecular fluctuations. Neighboring fluid layers move at different velocities relative to each other. This leads to collisions between the particles and to redistribution of kinetic energy.
- ▶ We favor profile-unbiased thermostat, which does not perturb the velocity profile.
- ▶ A DPD or Lowe-Andersen thermostat is by construction unbiased, because it act on relative velocities.

Hard sphere event-driven MD

- ▶ Calculate the time of the next collision $t + t_{ij}$ between a pair of particles with positions \mathbf{r}_i and \mathbf{r}_j and velocities \mathbf{v}_i and \mathbf{v}_j at time t .
- ▶ The overlap condition is

$$|\mathbf{r}_{ij}(t + t_{ij})| = |\mathbf{r}_{ij} + \mathbf{v}_{ij}t_{ij}| = \sigma, \quad (61)$$

where σ is the diameter, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ and $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$.

- ▶ If $\mathbf{r}_{ij} \cdot \mathbf{v}_{ij} = b_{ij} > 0$ particles are going away from each other.
- ▶ For $b_{ij}^2 - v_{ij}^2(r_{ij}^2 - \sigma^2) > 0$ there are two real solutions and the smaller corresponds to impact:

$$t_{ij} = \frac{-b_{ij} - \sqrt{b_{ij}^2 - v_{ij}^2(r_{ij}^2 - \sigma^2)}}{v_{ij}^2} \quad (62)$$

Hard sphere event-driven MD

- ▶ Using linear momentum and kinetic energy conservation we obtain the collision dynamics:

$$m_i \mathbf{v}'_i = m_i \mathbf{v}_i + \Delta \mathbf{p}_{ij} \quad (63)$$

$$m_j \mathbf{v}'_j = m_j \mathbf{v}_j - \Delta \mathbf{p}_{ij} \quad (64)$$

with momentum change

$$\Delta \mathbf{p}_{ij} = -\mu_{ij} (\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij}) \hat{\mathbf{r}}_{ij} = -\frac{\mu_{ij}}{\sigma^2} (\mathbf{r}_{ij} \cdot \mathbf{v}_{ij}) \mathbf{r}_{ij} \quad (65)$$

where $\mu_{ij} = \frac{m_i m_j}{m_i + m_j}$ is the reduced mass and $\hat{\mathbf{r}}_{ij} = \frac{\mathbf{r}_{ij}}{|\mathbf{r}_{ij}|}$ is the unit vector along the line connecting the centers of i and j . At impact $|\mathbf{r}_{ij}| = \sigma$.

Rough hard sphere

- ▶ Rough hard spheres are characterized by a diameter σ , mass m and a moment of inertia I (or $\kappa = 4I/m\sigma^2$).
- ▶ They have a translational \mathbf{v} and a angular velocity $\boldsymbol{\omega}$.
- ▶ Conservation laws are total kinetic energy (rotational plus translational), linear momentum and total angular momentum

$$\sum_i m \mathbf{r}_i \times \mathbf{v}_i + \sum_i I \boldsymbol{\omega}_i \quad (66)$$

- ▶ The relative velocity at impact point (just before collision) is

$$\mathbf{V}_{ij} = (\mathbf{v}_i - \mathbf{v}_j) - \frac{1}{2}(\boldsymbol{\omega}_i + \boldsymbol{\omega}_j) \times \mathbf{r}_{ij} \quad (67)$$

- ▶ During impact the relative velocity is reversed and the change in relative velocity is

$$\Delta \mathbf{V}_{ij} = \mathbf{V}'_{ij} - \mathbf{V}_{ij} = -2\mathbf{V}_{ij} \quad (68)$$

Rough hard sphere

- ▶ Using conservation laws the change in momentum is

$$\Delta \mathbf{p}_{ij} = \frac{1}{2} m \left(\Delta \mathbf{V}_{ij}^{\parallel} + \frac{\kappa}{1 + \kappa} \Delta \mathbf{V}_{ij}^{\perp} \right) \quad (69)$$

where $\Delta \mathbf{V}_{ij}^{\parallel} = (\hat{\mathbf{r}}_{ij} \cdot \Delta \mathbf{V}_{ij}) \hat{\mathbf{r}}_{ij}$ is the parallel component of the relative velocity change and $\Delta \mathbf{V}_{ij}^{\perp} = \Delta \mathbf{V}_{ij} - \Delta \mathbf{V}_{ij}^{\parallel}$ is the corresponding perpendicular component.

- ▶ Collision dynamics:

$$m \mathbf{v}'_i = m \mathbf{v}_i + \Delta \mathbf{p}_{ij} \quad (70)$$

$$m \mathbf{v}'_j = m \mathbf{v}_j - \Delta \mathbf{p}_{ij} \quad (71)$$

$$I \boldsymbol{\omega}'_i = I \boldsymbol{\omega}_i - \frac{1}{2} \mathbf{r}_{ij} \times \Delta \mathbf{p}_{ij} \quad (72)$$

$$I \boldsymbol{\omega}'_j = I \boldsymbol{\omega}_j - \frac{1}{2} \mathbf{r}_{ij} \times \Delta \mathbf{p}_{ij} \quad (73)$$

Note that, the spin angular momentum is not conserved.

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