Computational Physics, TFYA90

Modern Techniques in Materials Science
Part I. Molecular dynamics (MD) and Monte Carlo (MC)

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Molecular Dynamics Simulations

* Purely deterministic method in the NVE microcanonical ensemble.#

* Follow time evolution of systems by solving Newton's equation of motion:

$$m\frac{d^2\vec{r}}{dt^2} = \vec{F}(r) \qquad \text{where } \vec{F}(r) = -\nabla V(r)$$

* Properties of statistical ensemble are calculated as time averages.

* Microcanonical ensemble (N, V, E) is a typical choice + other constraints: e.g. momentum M => (N, V, E, M) (isokinetic thermostat to mimic NVT).

* For N particles, problem reduces to solving systems of 6N 1st order ODE:

$$\begin{cases} \dot{\vec{r}}_i = \vec{v}_i \\ m\cdot\dot{\vec{v}}_i = \vec{F} \end{cases} \qquad \vec{F}_i = -\nabla_{r_{ij}} \sum_{i\neq j} V(r_{ij})\,; \quad \nabla_{r_{ij}} = \hat{i}\frac{\partial}{\partial x_{ij}} + \hat{j}\frac{\partial}{\partial y_{ij}} + \hat{k}\frac{\partial}{\partial z_{ij}}$$

\# Not anymore deterministic when thermostat like Nose or Andersen is used:
The thermostat changes stochastically the trajectories.
MD with thermostat becomes deterministic/stochastic

Molecular dynamics solves the classical equations of motion for each atom

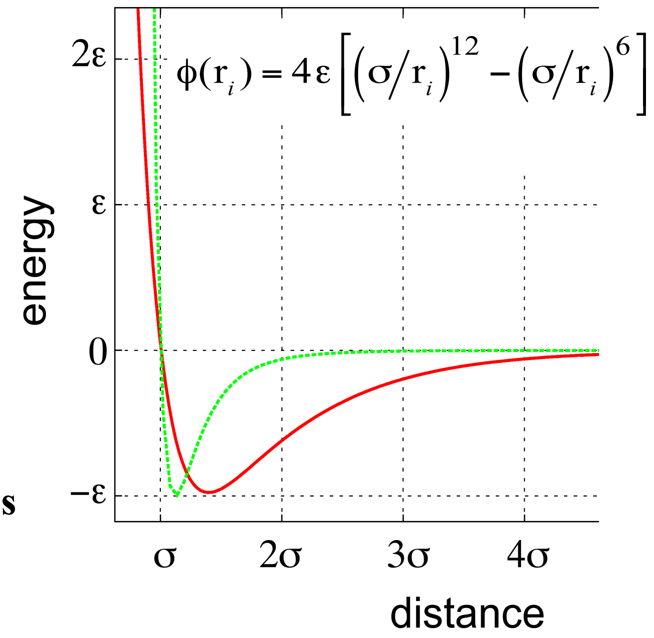
- Set initial nuclei positions $\mathbf{r}_i(t = 0)$
- Initialize nuclei velocities $\mathbf{v}_i(t = 0)$ at temperature T
- Update nuclei positions every timestep Δt ($\approx 10^{-15}$ s)

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\cdot\Delta \mathrm{t} + \tfrac{1}{2}\,\mathbf{a}_i(t)\cdot[\Delta t]^2$$

$$\mathbf{a}_i(t) = \mathbf{F}_i(t)\,/\,\mathrm{m}_i$$

Classical molecular dynamics (CMD)
It is based on semi-empirical model interactions which reduce reduce the intricate problem of electron/electron electron/nuclei and nuclei/nuclei interactions to effective nuclei/nuclei interactions. Examples are:

- Lennard Jones (LJ)
- Embedded atom method
- Stillinger-Weber…



Examples of LJ models: green and red curves have different ε and σ parameters

Molecular dynamics solves the classical equations of motion for each atom

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$$\mathbf{r}_i\,(t+\Delta t) = \mathbf{r}_i\,(t) + \mathbf{v}_i\,(t)\cdot\Delta\mathrm{t} + \tfrac{1}{2}\,\mathbf{a}_i\,(t)\cdot[\Delta t\,]^2$$

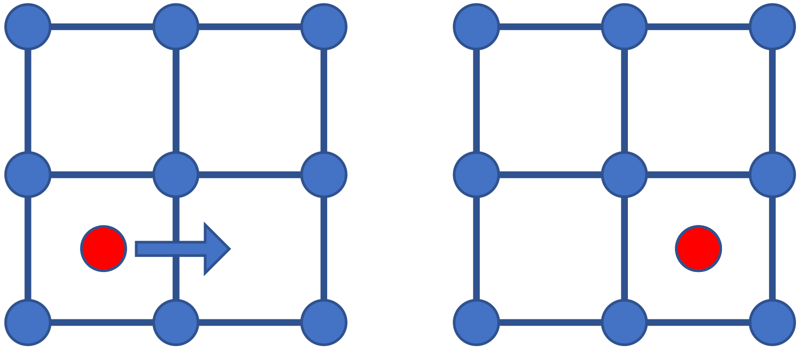
$$\mathbf{a}_i\,(t) = \mathbf{F}_i\,(t)\,/\,\mathrm{m}_i$$

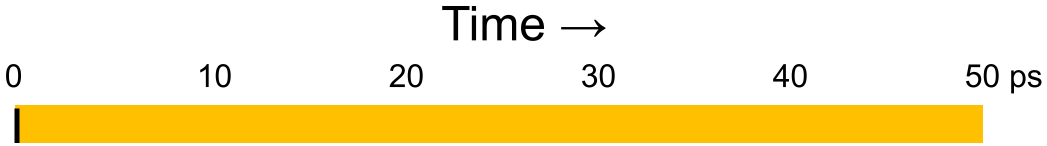
First-principles (or ab initio) molecular dynamics (AIMD) solve the “many-body interaction problem” by starting from the principles of quantum mechanics (yet several approximations are necessary).

Examples are:
- Density-Functional Theory
- Hartree-Fock
- Tight-Binding…

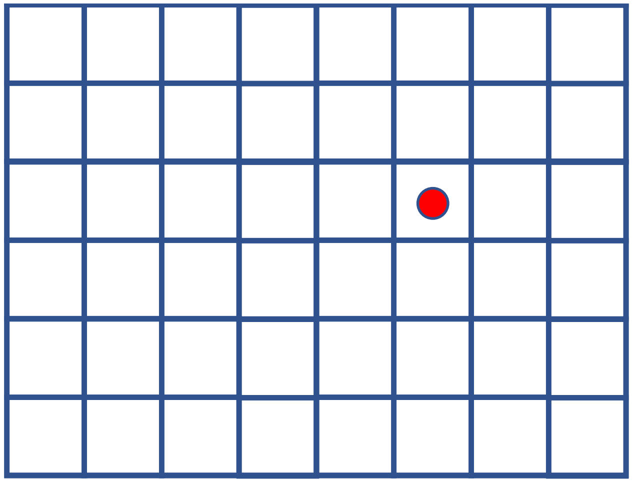
Kinetics of reactions

For example: study migration of adatom on surface





Cartoon of MD simulation
in the NVT ensemble:
adatom migration
on surface at temperature “T”

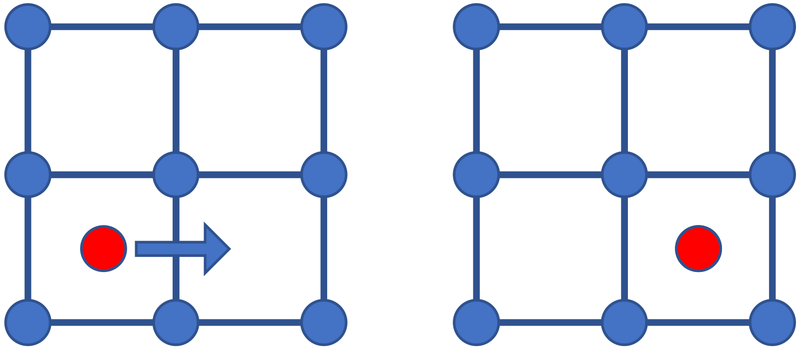


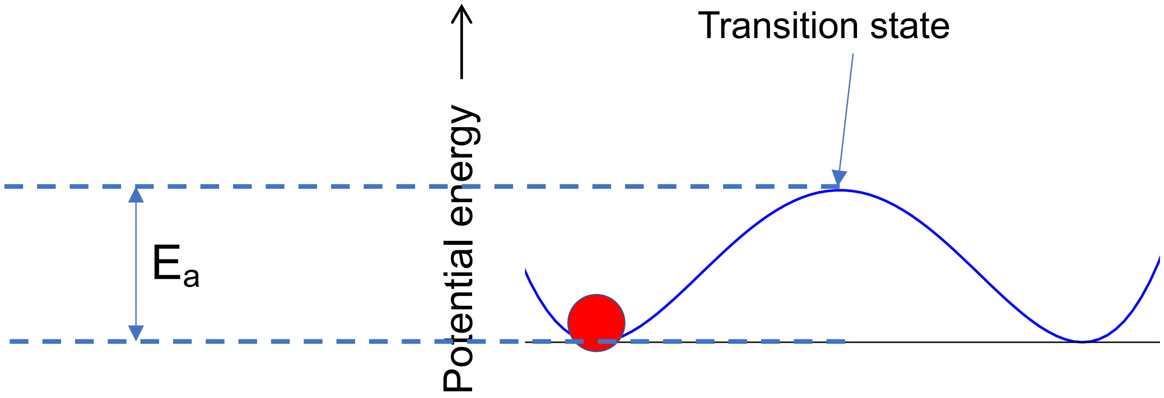
Count
migration events

Average migration
rate (or frequency)
$\Gamma = 15/50\ \text{ps} = 3 \cdot 10^{11}\ \text{s}^{-1}$

Kinetics of reactions

For example: study migration of adatom on surface





To migrate
The atom needs
to overcome
energy barrier E_a

Atomic migration rates as a function of temperature are well described by Arrhenius equation:

$$\Gamma(T)= \nu\cdot\exp[-E_a/(k_BT)]$$

Migration rate (or migration frequency) as a function of temperature

Attempt frequency

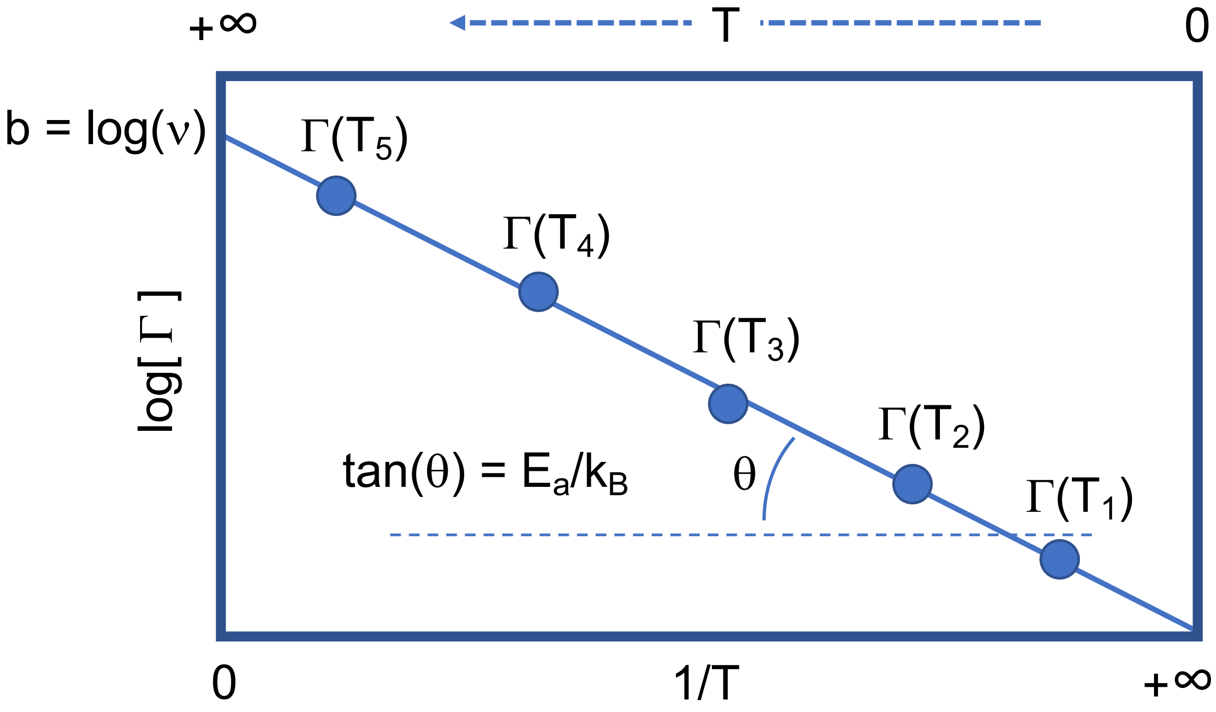
Kinetics of reactions: Arrhenius plot

$$\Gamma(T) = \nu \cdot \exp[-E_a/(k_B T)]$$

$$\log[\Gamma(T)] = \log(\nu) - E_a/(k_B T)$$

Linear equation: $y = b + a \cdot x$

$y = \log[\Gamma]$
$a = -E_a/k_B$
$b = \log(\nu)$
$x = 1/T$



MD integrators

Selection criteria: ***simplicity, efficiency, stability, reliability, parallelization.***

Most integrators are based on Taylor expansion of particle coordinates r(t) around time, for small increments Δt, which is the MD time step.

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\cdot\Delta \mathrm{t} + \tfrac{1}{2}\,\mathbf{a}_i(t)\cdot[\Delta t]^2$$

$$\mathbf{a}_i(t) = \mathbf{F}_i(t) / \mathrm{m}_i$$

Need to integrate the equations of motion numerically

Verlet Algorithm (Verlet, Störmer, 1967)

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2!m}\Delta t^2 + \frac{\Delta t^3}{3!}\dddot{r} + O(\Delta t^4) + ...$$

$$r(t-\Delta t) = r(t) - v(t)\Delta t + \frac{f(t)}{2!m}\Delta t^2 - \frac{\Delta t^3}{3!}\dddot{r} + O(\Delta t^4) + ...$$

Summing the above equations, one obtains:

$$r(t+\Delta t) + r(t-\Delta t) = 2r(t) + \frac{f(t)}{m}\Delta t^2 + O(\Delta t^4)$$

The equation for advancing the positions in Verlet algorithm becomes:

$$r(t+\Delta t) = 2r(t) - r(t-\Delta t) + \frac{f(t)}{m}\Delta t^2 \qquad (1)$$

The errors in the estimations of new positions are of order Δt^4.

$r(t + \Delta t)$ and $r(t - \Delta t)$ play symmetrical roles, the algorithm is time-reversible.

Velocities are not required to compute trajectories.

Yet, velocities are needed to directly calculate kinetic energy and temperature.

Velocities can be computed from:

$$r(t+\Delta t) - r(t-\Delta t) = 2v(t)\Delta t + O(\Delta t^3)$$

and

$$v(t) = \frac{r(t+\Delta t) - r(t-\Delta t)}{2\Delta t} + O(\Delta t^2) \qquad (2)$$

The errors in velocities estimations are of order Δt^2.

Though algorithm is stable, one can improve this accuracy.

Leap-frog Algorithm (Hockney, 1970; Potter, 1972)

Derived from the Verlet algorithm, evaluates velocities at half-step:

$$v(t-\Delta t/2) = \frac{r(t) - r(t-\Delta t)}{\Delta t} \quad \text{and} \quad v(t+\Delta t/2) = \frac{r(t+\Delta t) - r(t)}{\Delta t}$$

New positions can be obtained as:

$$r(t+\Delta t) = r(t) + \Delta t v(t+\Delta t/2) \qquad (3)$$

Velocities can be computed from:

$$v(t + \Delta t/2) = v(t - \Delta t/2) + \Delta t \frac{f(t)}{m} \tag{4}$$

Stored quantities are positions, r(t), and accelerations, a(t) = f(t)/m. Equation (4) is implemented first, and once v(t + Δt/2) are obtained, velocities v(t) at current time step are calculated to permit the computation of quantities which require r(t) and v(t):

$$v(t) = \frac{1}{2}\left[v(t + \Delta t/2) + v(t - \Delta t/2)\right]$$

Upon completion of the half-step above, eq, (3) is used to calculate r(t + Δt). Accelerations a(t) are also evaluated now and stored for next step.

Leap-from algorithm yields identical trajectories to those obtained with Verlet.

pros – significantly smaller numerical errors in velocities evaluation.

cons – positions and velocities are not evaluated at the same time step.

Velocity Verlet Algorithm (Swope, anderson et. al. 1982)

$$r(t+\Delta t) = r(t) + v(t)\Delta t + \frac{f(t)}{2m}\Delta t^2 = r(t) + v(t)\Delta t + \frac{\Delta t^2}{2}a(t) \qquad (5)$$

$$v(t+\Delta t) = v(t) + \frac{f(t)+f(t+\Delta t)}{2m}\Delta t = v(t) + \frac{\Delta t}{2}\left[a(t)+a(t+\Delta t)\right] \qquad (6)$$

Implemented to store r(t), v(t) and a(t) **all** at the same time.

Similar to predictor-corrector algorithms, but equivalent to Verlet:

a: using (5) $r(t+2\Delta t) = r(t+\Delta t) + v(t+\Delta t)\Delta t + \frac{f(t+\Delta t)}{2m}\Delta t^2$

b: from (5) $r(t) = r(t+\Delta t) - v(t)\Delta t - \frac{f(t)}{2m}\Delta t^2$

a+b = c $r(t+2\Delta t) + r(t) = 2r(t+\Delta t) + \left[v(t+\Delta t) - v(t)\right]\Delta t + \frac{f(t+\Delta t) - f(t)}{2m}\Delta t^2$

(6) in c: $r(t+2\Delta t) + r(t) = 2r(t+\Delta t) + \frac{f(t+\Delta t)}{m}\Delta t^2 \equiv$ positions in Verlet alg.

Velocity Verlet Algorithm

Requires storage of r(t), v(t), a(t).

Consists of two stages and a force evaluation in between:

Stage 1: r(t + Δt) are evaluated using (5) and v(t + Δt/2) using:

$$v(t+\Delta t/2) = v(t) + \frac{\Delta t}{2} a(t)$$

Intermediate stage: f(t + Δt) and a(t + Δt) are computed.

Stage 2: velocity move is completed.

$$v(t+\Delta t) = v(t+\Delta t/2) + \frac{\Delta t}{2} a(t+\Delta t)$$

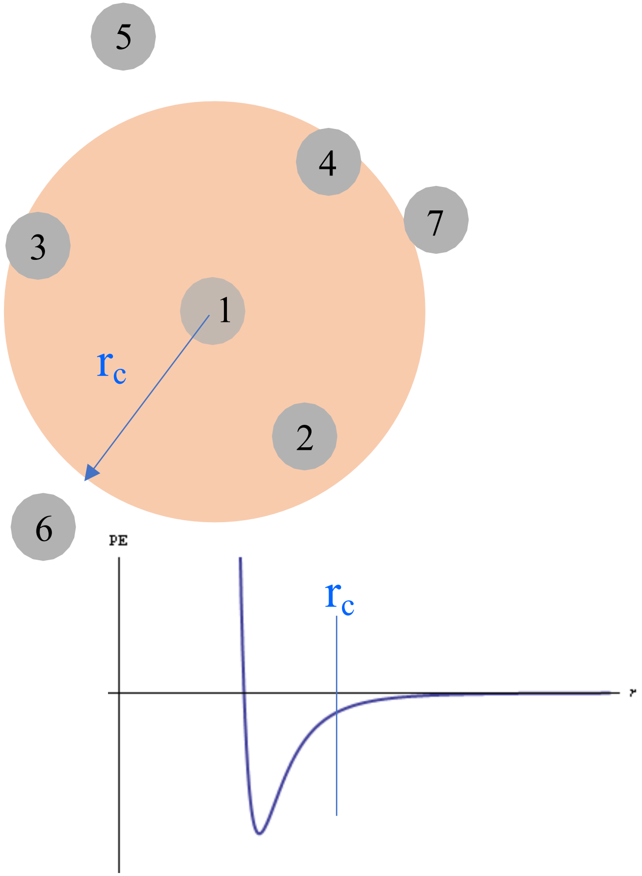
Attractive trade-off between numerical stability, convenience, simplicity.

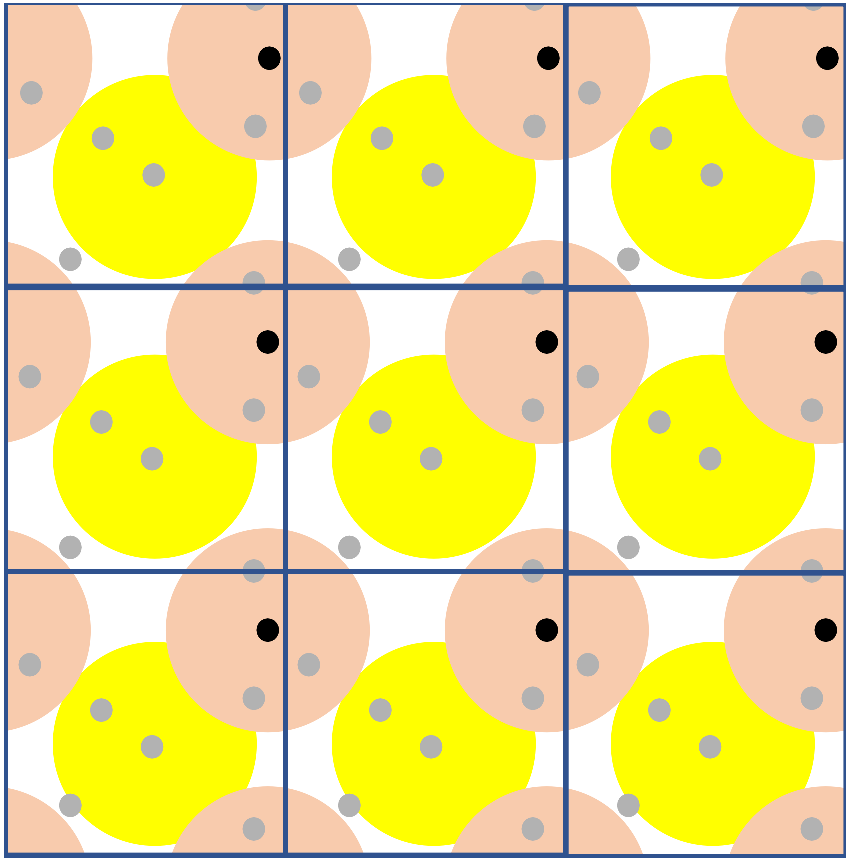
Ensures excellent energy conservation, solid trajectories evolution.

Nearly universal choice in available MD codes.

Neighbors Lists and potential truncation

The atomic interactions in CMD are generally limited to a radial distance r_c. This significantly reduces the number of computations at each time step





After cutoff, the V and dV/dr curves need to remain continuous

Phys.Chem.Chem.Phys., 2020, 22, 10624

Molecular dynamics (MD)

examples of code implementation

Molecular dynamics solves the classical equations of motion for each atom

- Assign initial positions to each particle $\mathbf{r}_i\,(t = 0)$
- Initialize the velocities $\mathbf{v}_i\,(t = 0)$ according to temperature (Boltzmann-Maxwell distribution of velocities)
- Update position of each particle every step Δt ($\approx 10^{-15}$ s)

Classical equations of motion:

$$\mathbf{r}_i\,(t+\Delta t) = \mathbf{r}_i\,(t) + \mathbf{v}_i\,(t)\cdot\Delta \mathrm{t} + \tfrac{1}{2}\,\mathbf{a}_i\,(t)\cdot(\Delta t)^2$$

$$\mathbf{a}_i\,(t) = \mathbf{F}_i\,(t)\,/\,\mathrm{m}_i$$

Calculate forces on each atom
(need interatomic potential parameterized to material of interest)

Boltzmann-Maxwell distribution of velocities in ideal gas

$$n = \frac{N\, g_i \exp[-E_i/(k_B T)]}{\sum_i \{g_i \exp[-E_i/(k_B T)]\}}$$

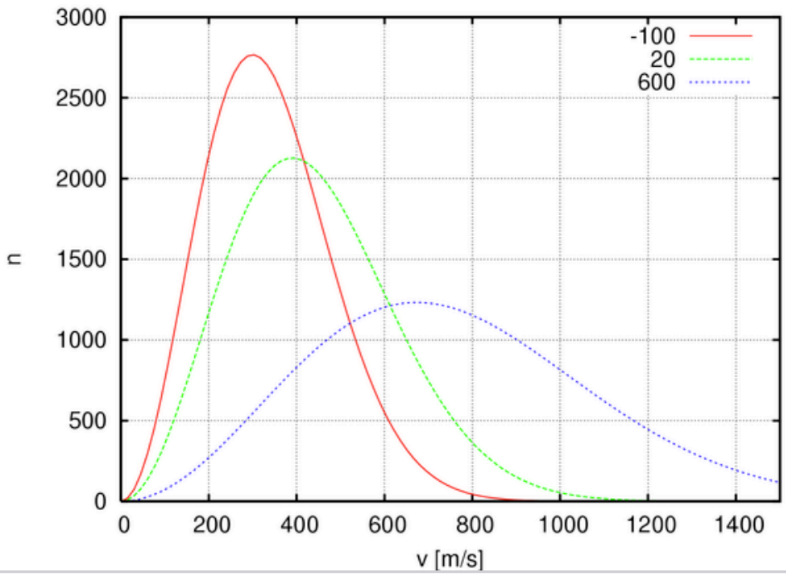
Partition function Z

n: average number of particles with energy E_i at a temperature T

N: total number of particles in the system

g_i: degeneracy of energy level "i"

k_B: Boltzmann's constant



Maxwell–Boltzmann statistics can be used to derive the Maxwell–Boltzmann distribution of particle speeds in an ideal gas. Shown: distribution of particle speed for 10^6 oxygen particles at -100, 20 and 600 °C.

At each MD step, the temperature of a system of N particles is calculated from the average nuclear translational kinetic energy (equipartition theorem)

$$\langle E_k \rangle = (1/N) \sum(\tfrac{1}{2} m_i v_i^2) = (3/2)\, k_B T \;\Rightarrow\; T = [1/(3N k_B)] \sum m_i v_i^2$$

https://en.wikipedia.org/wiki/Maxwell%E2%80%93Boltzmann_statistics

Simple MD-code implementation: leapfrog algorithm

For each particle "*i* " at a given instant "*t* "

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\cdot\Delta \mathrm{t} + \tfrac{1}{2}\,\mathbf{a}_i(t)\cdot(\Delta t)^2$$

$$\mathbf{a}_i(t) = \mathbf{F}_i(t) / \mathrm{m}_i$$

$$\mathbf{v}_i(t + \tfrac{1}{2}\Delta t) = \mathbf{v}_i(t - \tfrac{1}{2}\Delta t) + \mathbf{a}_i(t)\cdot\Delta t$$

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t + \tfrac{1}{2}\Delta t)\cdot\Delta \mathrm{t}$$

Simple MD-code implementation: leapfrog algorithm in 1 dimension “x” (easily generalized to 3D)

Set positions $x_i(t = 0)$ and assign velocities $vx_i(t = -1/2)$

Then, for each time “t”, compute:

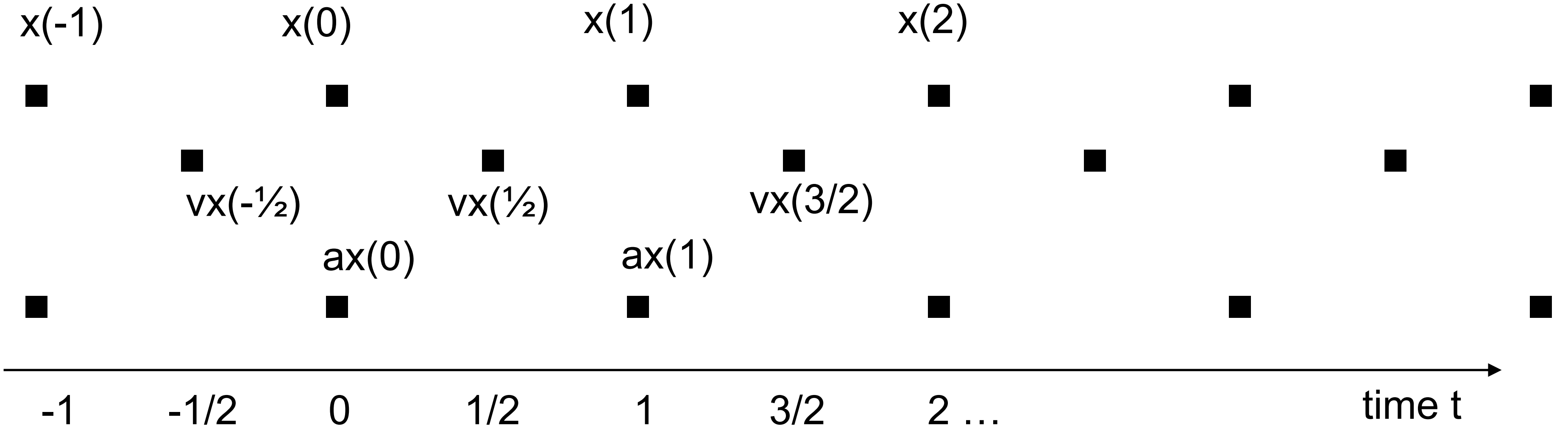
(1) $ax_i(t) = Fx_i(t) / m_i$

(2) $vx_i(t + \frac{1}{2}\Delta t) = vx_i(t - \frac{1}{2}\Delta t) + ax_i(t)\cdot\Delta t$

(3) $x_i(t+\Delta t) = x_i(t) + vx_i(t + \frac{1}{2}\Delta t)\cdot\Delta t$

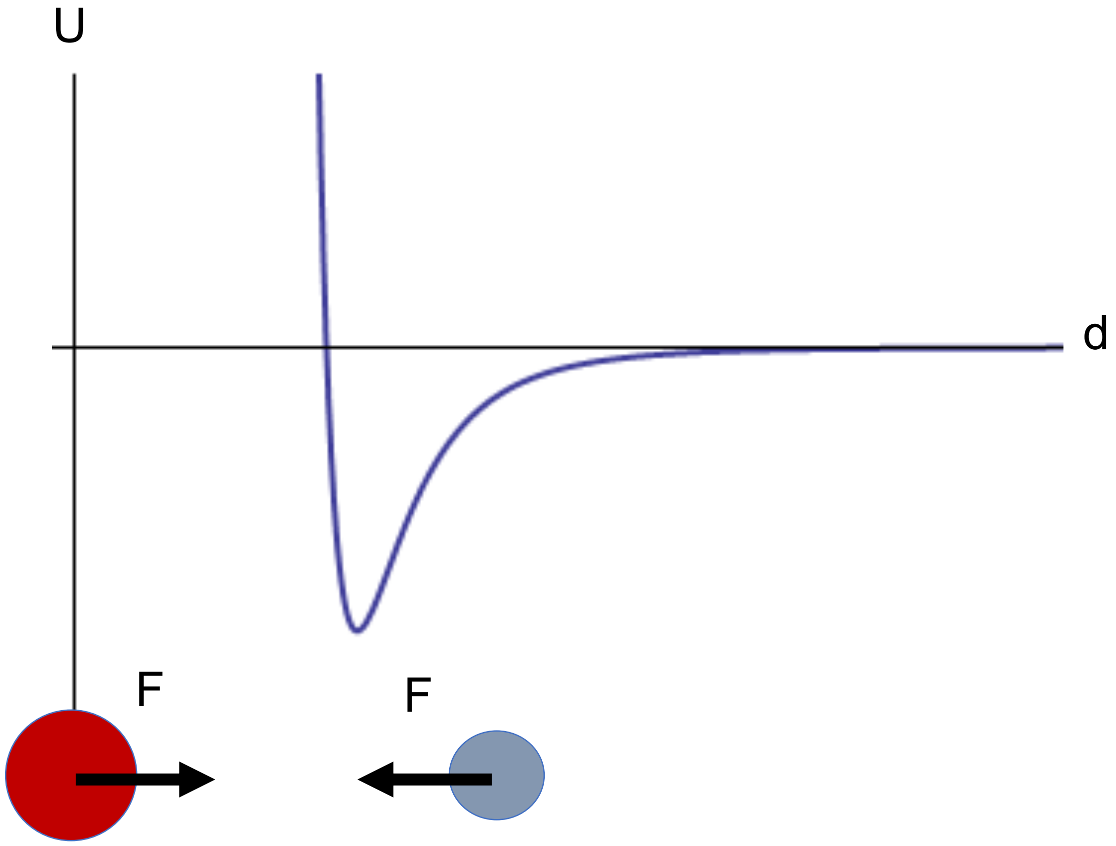
Time progression: Loop over steps (1),(2),(3)

$\Delta t = 1$



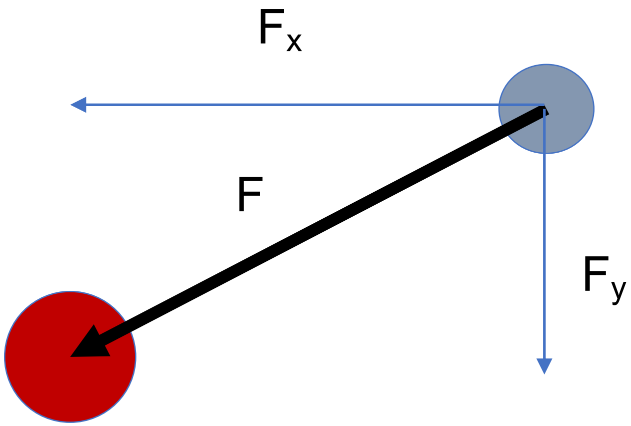
Example Lennard-Jones type of Interaction in diatomic molecule

$$\mathbf{F} = -\nabla U(|r_1 - r_2|)$$

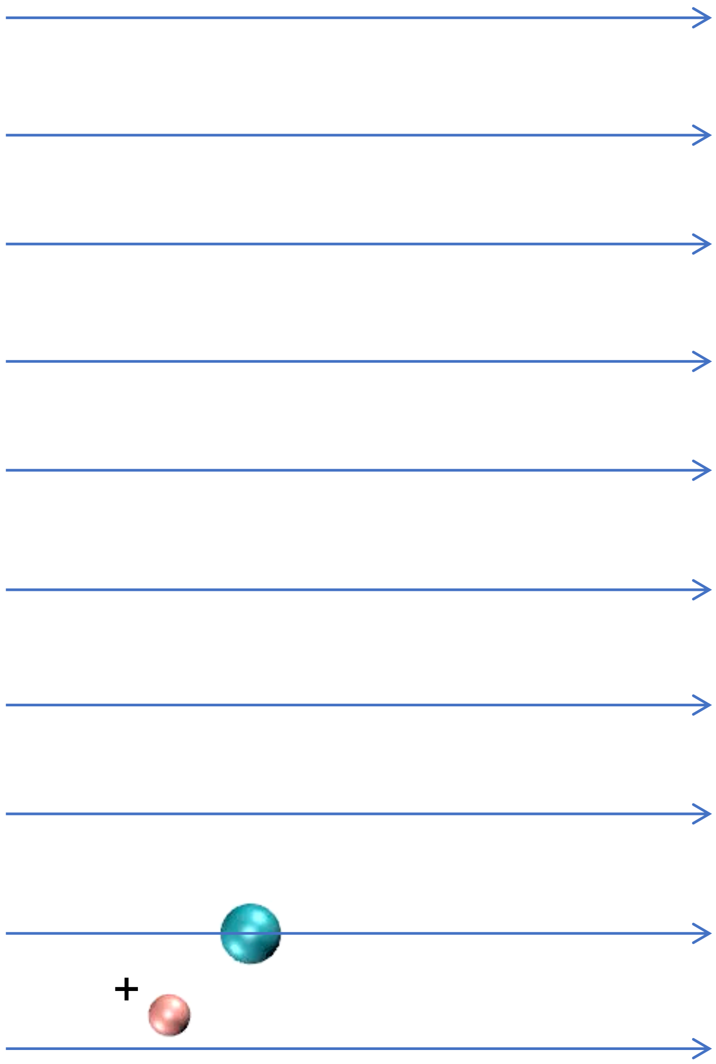


The total force on particle "i" at each given time "t" is obtained by summation over all forces "F_i" that act on that particle

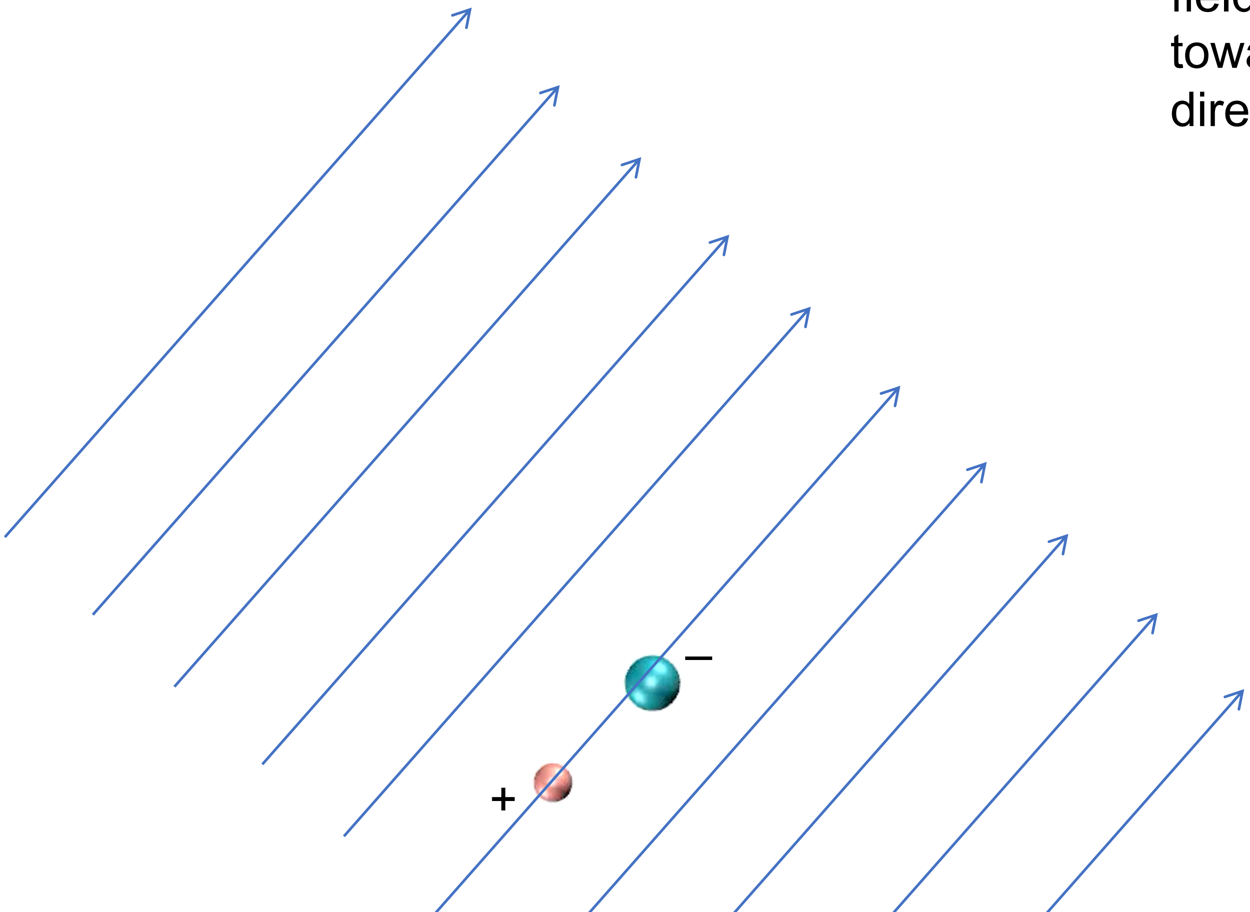
It is convenient to express the total force as sum of Cartesian components. This facilitates the computation of the components of the acceleration a_x, a_y, a_z



example:
translational, rotational and vibrational motion of a diatomic molecule using a Lennard-Jones-type of interaction



Same initial positions, but the molecule is immersed in a homogeneous constant electrostatic field which accelerates the positively-charged pink ion toward the right



In this case, the initial distance between the atoms is larger and the particles are charged differently: the electric field accelerates them toward opposite directions.

Molecular Dynamics in different statistical ensembles

- Constant Temperature MD
- Constant Pressure MD

Non-Equilibrium Molecular Dynamics

Constant temperature MD

As already stated, MD in the NVE ensemble will conserve besides N, and V, the total energy of the system.

The EOM used so far are Hamiltonian, hence conservative. Consequently, MD simulations using these EOM will conserve both total energy and momenta.

This type of MD simulations will however not conserve T. Total energy is the sum of potential and kinetic contributions, whereas T is associated only with kinetic degrees of freedom.

During equilibration in NVE MD runs, systems relax to conserve energy, but temperature will fall from its initial value to some equilibrium value, as some of the initial kinetic energy is lost to configurational degrees of freedom. E_{pot} increases at the expense of E_{kin}, and both stabilize such that E_{tot} is always constant.

Nevertheless, there are many thermodynamically relevant systems, as well as many material science processes, which operate/occur at constant temperature.

Naturally, this in turn resulted in significant work devoted to the design of efficient MD sampling of the constant-temperature, (N,V,T) ensemble.

The techniques used to implement constant-temperature MD can be classified according to the approach taken to achieve this goal.

Currently, three approaches are used for MD in the canonical ensemble:

- Stochastic methods

- Extended System Methods

- Constraints Methods

Stochastic methods

1. The Andersen Thermostat (Andersen, 1980)

The fundamental approach is to couple the MD system to a heat bath which ultimately imposes the desired temperature.

The coupling translates into “weak interactions” with a heat bath at specified T.

The “weak interactions” are implemented by occasionally selecting a random particle and give it new velocity from the M-B distribution, according to the desired T.

The process is equivalent to stochastic collisions with an imaginary heat bath, and corresponds to Monte Carlo moves which take the system from one constant-energy phase point to another. Between collisions, the system evolves in the phase space on a constant energy surface following Newtonian laws (MD in NVE ensemble).

The mixing of Newtonian dynamics with stochastic collisions turns the MD run into a Markov process (MC moves), generating an irreducible Markov chain. The entire procedure yields the correct canonical (NVT) ensemble averages.

Times between collision are typically chosen from a Poisson distribution with given mean collision time, but the initial choice does not affect final phase-space distribution:

$$P(t;\nu) = \nu \exp\left[-\nu t\right]$$

The following rules of thumb apply:

Low collision rates = E_{kin}, or T, fluctuations similar to conventional MD, slow fluctuations in E_{tot}, slow sampling of canonical distribution of energies.
High collision rates = E_{kin} fluctuations dominated by collisions, not dynamics, slow down the speed at which particle in system explore configuration space.

Original suggestion for collision rate: $\propto \dfrac{\lambda_T}{\rho^{1/3} N^{2/3}}$ with λ_T the thermal conductivity.

General scheme for constant-temperature MD becomes:

1. Start with initial $[r^N(0), p^N(0)]$ and integrate EOM:

2. Probability for a particle to undergo a stochastic collision in a time step Δt is $\nu\Delta t$.

3. Give particle *i* selected to undergo collision new velocity from M-B distribution corresponding to desired T. All other particles are unaffected by this collision.

Extended system methods (Nosé, 1984)

Fundamental approach of the method is to include a degree of freedom which represents the heat reservoir. The MD simulation is carried out on this extended system.

The procedure require the use of an extended Lagrangian and Hamiltonian, and the derivation of new EOM from an appropriate functional which includes the extra degrees of freedom.

It is a well known technique to replace Newtonian laws with the more general formalism of Lagragian dynamics, from which more complex EOM are derived:

$$\frac{d}{dt}\left[\frac{\partial L}{\partial \dot{q}_j}\right] - \frac{\partial L}{\partial q_j} = 0$$

The Lagrangian has to be constructed first. Here we use L = T – V, i.e. as the difference between kinetic and potential energy.

The Nosé approach is fundamentally sound and one of the methods frequently used to properly do dynamics in the (NVT) ensemble and thermostat MD runs.

Yet, the procedure is not the most robust, as it fails to perform poorly in very harmonic systems, i.e. where the potential energy of every particle is a quadratic function of the displacement from its equilibrium position (eg. solids at very low temperatures).

The solution in this situation is to use the Nosé-Hoover chains. This involves the inclusion, besides the dynamical system and original thermostat, of an additional thermostat which controls the 1st thermostat, a 3rd thermostat which thermostats the 2nd thermostat, etc.

Obviously, this a complex procedure, and unless the Nosé thermostat is the mandatory approach to the system studied, one can construct equivalent methods to correctly thermostat Newtonian dynamics during MD simulations.

Among the frequently used techniques used in this sense are the constraint methods discussed in the next section.

Constraint methods

Basic approach in most of these methods is to constrain the kinetic energy to be constant during the MD simulation, as it is directly connected to temperature:

$$K = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{r}_i^2 = \frac{3}{2} N k_B T$$

In principle, the approach does not generate true exploration of the constant (N,V,T) ensemble, but rather what is known as “isothermal” or “isokinetic” MD. Clearly, there is a difference between the true canonical trajectory of the system and the isothermal/isokinetic one.

However, as long as this difference is sufficiently small, one can use this type of MD simulations to constrain the system to the desired temperature. Fortunately this is indeed the case in most situations, so one can confidently use the methods described herein to carry out constant T MD simulations.

Constant Pressure MD

General observations

Constant-pressure MD simulations call upon similar, analogue techniques, to those used for constant-temperature MD:

- constraints methods

- extended system methods

Note that there are no equivalent “stochastic” approaches to constant pressure MD simulations.

Additional requirements

Regardless of the approach used, this type of MD simulations must include a new feature: provide for and ensure that the primary cell size/shape can vary during simulations in order allow for changes in its volume.

Long range corrections are important and necessary in most approaches.

What Method to Use?

Scaling is simple, easy to implement, and in most cases requires no parameters. It is a valid approach for equilibration purposes. However, does not truly sample canonical/isobaric/isothermal-isobaric ensembles.

Constraints methods are somewhat more complicated, but no parameters are required. Remember however, techniques only keep T/P constant, so trajectories deviate from those in desired ensembles.

Stochastic approaches are more stable compared to simple scaling, however, procedure is no longer (fully) deterministic.

Extended system methods are the only methods which sample the constant (NVT), (NPH) and/or (NPT) ensembles. They are however quite complicated and require parameters as well.

Summary

It is possible to constrain/choose temperature and/or pressure in a molecular dynamics simulation.

The temperature can be fixed by:

a) scaling the velocities (partially or completely) or simply redefining the equations of motion so that *T* does not change.

b) changing some or all of the velocities of the particles to a randomly selected member of the Maxwell- Boltzmann distribution of the desired *T*.

c) coupling the system to a heat bath.

Analogous methods exist to chose/maintain constant pressure.

Combinations of methods can be used to simulate a system at constant temperature and pressure.

Nonequilibrium Molecular Dynamics (NEMD)

So far, equilibrium MD have been exclusively considered.

Nonequilibrium MD are an important development in computational physics.

Typically, NEMD refers to the MD study of systems upon which an external field acts to drive the system away from equilibrium, towards a nonequilibrium steady-state.

Nonequilibrium MD can be used to study, for example, “rare” events[1] (as atomic migration in hard materials) and fluid systems. No real restriction for gases/solids exists, in principle any system away from thermodynamic equilibrium can be studied.

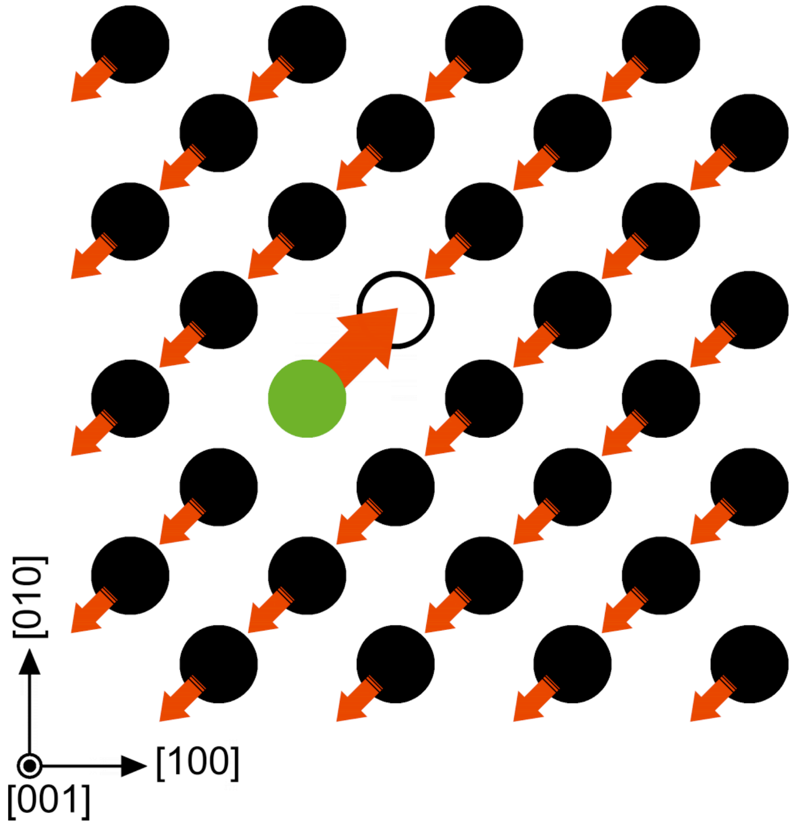
Principles are the same, to solve the EOM, which now however include the effect of the external field.

[1] D.G. Sangiovanni, O. Hellman, B. Alling, I.A. Abrikosov,
Efficient and accurate determination of lattice-vacancy diffusion coefficients via non-equilibrium ab initio molecular dynamics
Physical Review B 93, 094305 (2016)

Color-diffusion non-equilibrium molecular dynamics

One atom (green) is pushed by an external bias force F (large red arrow) toward a neighbor vacancy

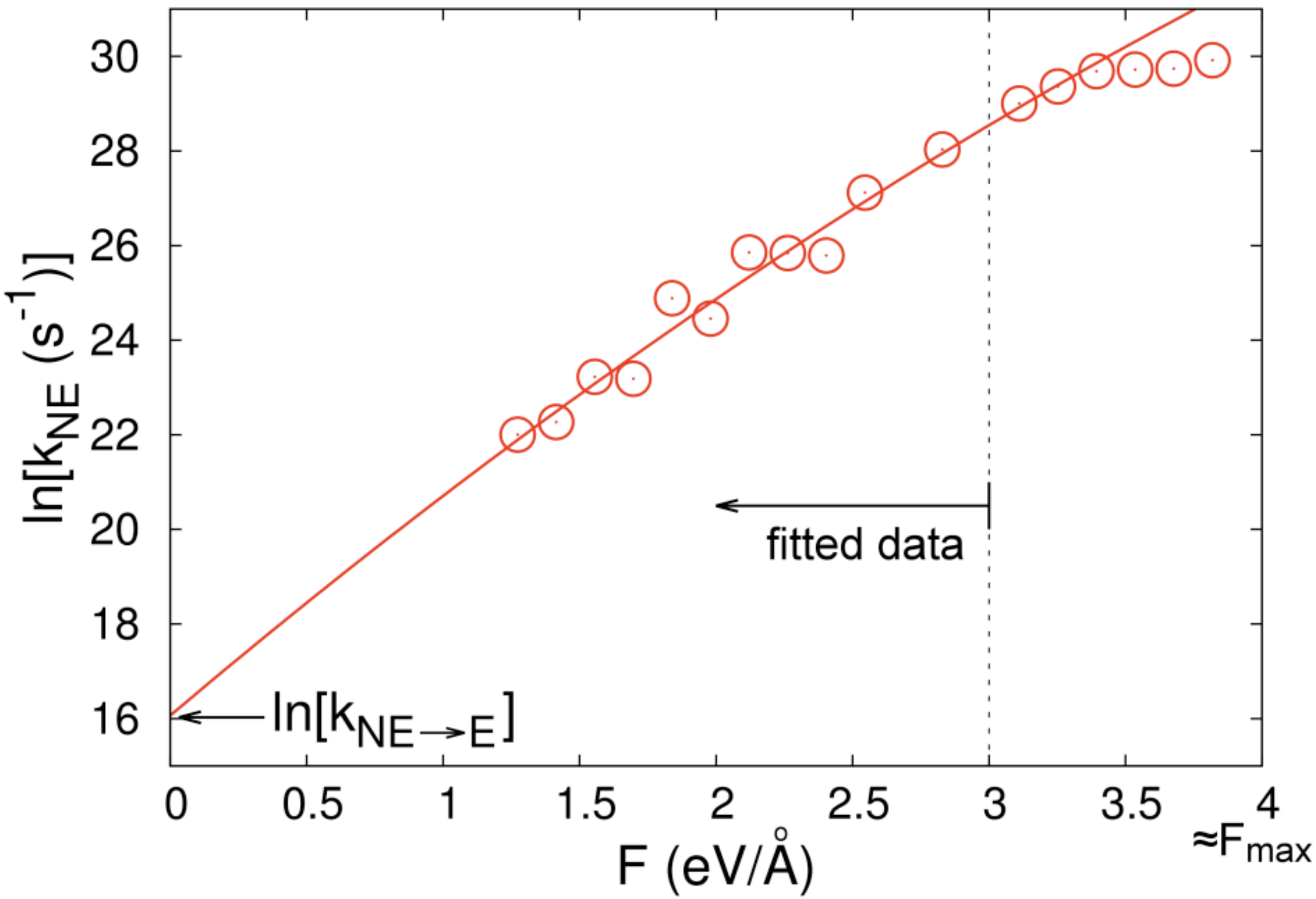
Opposite small balancing forces (small red arrows) maintain mechanical equilibrium: 0 drift of the center of mass and 0 torque



D. Gambino et al. PHYSICAL REVIEW B 96, 104306 (2017)

Color-diffusion non-equilibrium molecular dynamics

Non-equilibrium migration rates (red circles) are rapidly calculated for large force intensities.
The quantity of interest (equilibrium migration rate) is extrapolated to 0-force intensity



D.G. Sangiovanni Thin Solid Films 688 (2019) 137297