Advanced Simulation Techniques

Molecular Dynamics in different statistical ensembles

- Constant Temperature MD
- Constant Pressure MD

Non-Equilibrium Molecular Dynamics

Optimization Techniques in Materials Science

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.

Algorithm 10: Andersen Thermostat with Velocity Verlet

```
program MD_Andersen                          MD at constant T

        call init (temp)                     initialization
        call force (f, en)
        t = 0


do while (t. lt. tmax)                       MD loop
        call integrate (1, f, en, temp)      1st part EOM in VV
        call force (f, en)                   calculate forces
        call integrate (2, f, en, temp)      2nd part EOM in VV
        t = t + dt

        call sample                          calculate averages
enddo


stop
end
```

Obs: Velocity Verlet implies calculation of r(t + dt) and v(t + dt/2). This requires a call of the force subroutine to get f(a + dt), a(t + dt), and v(t + dt) are updated in the 2nd stage.

Algorithm 11: EOM in Andersen Thermostat with Velocity Verlet

```
Subroutine integrate (switch, f, en, temp)

if (switch .eq. 1) then                                    1st stage velocity Verlet
    do i = 1, npart
        x(i) = x(i) + dt*v(i) + dt*dt*f(i)/2              update positions current time
        v(i) = v(i) + dt*f(i)/2                           first update velocity
    enddo


else if (switch .eq. 2) then                              2nd stage velocity Verlet
    tempa = 0
    do i =1, npart
        v(i) = v(i) + dt*f(i)/2                           second update velocity
        tempa = tempa + v(i)**2
    enddo
    tempa = tempa / (s*npart)                             instantaneous T
    sig = sqrt(temp)                                      Andersen heat bath
    do i = 1, npart
        if (ranf () .lt. nu*dt) then                      test for collision with bath.
        v(i) = gauss(sigma)                               give particle Gaussian velocity
        endif                              .
    enddo
endif

return
end                              Obs: Collision frequency nu is set at the beginning of simulation
```

2. Alternative Stochastic Methods

2.1   Andrea et. al. (1983)

Approach is to use "massive stochastic collisions" by resetting the velocities of all particles at once, less frequently, at equally spaced time intervals.

Typical correlation functions are obtained with Newtonian dynamics between collisions, however, they're only averaged over initial canonical distributions.

2.2   Heyes (1983)

Method entails the systematic, and frequent (e.g 10 MD steps) scaling of all velocities up or down, and the acceptance or rejection of the attempt based on a MC technique.

Typical random numbers ξ should be uniformly chosen in a very small range, e.g. $[-0.05, 0.05]$.

New trial velocities are then given by:

$$\dot{r}^n = (1+\xi)\dot{r}^m$$

while the ratio of the probabilities of new and old states in momentum space is:

$$\rho_n/\rho_m = \exp(-A)$$

where:

$$A = \frac{1}{2}m\beta\sum_i |\dot{r}^m|^2[(1+\xi)^2 - 1] - 3N\ln(1+\xi)$$

The trial move is accepted with a probability given by min [1, exp (−A)].

The approach reasonably samples the canonical ensemble, and typical averages can be computed in the typical manner.

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.

In the Lagrangian, $V(r_1, r_2,\ldots, r_N)$ and $T(\dot{r}_1, \dot{r}_{2,\ldots,} \dot{r}_N)$ are replaced by so-called

generalized coordinates: $V(q_1, q_2,\ldots, q_N)$ and $T(\dot{q}_1, \dot{q}_{2,\ldots,} \dot{q}_N)$.

The Lagrangian formalism states that if the Lagrangian function, $L = T - V$, is constructed properly, the Lagrangian equations can be used to derive the EOM governing the dynamics of that particular Lagrangian.

For example, for $T = 1/2mv^2$ and $V = V(x)$, defined as scalar functions, one can

use the Lagrangian equations $\dfrac{d}{dt}\left(\dfrac{\partial L}{\partial \dot{q}_j}\right) - \dfrac{\partial L}{\partial q_j} = 0$ to recover Newton's EOM

(the 1D case here):

$$\frac{d}{dt}\left(\frac{\partial\left(\frac{1}{2}m\dot{x}^2\right)}{\partial\dot{x}}\right) + \frac{\partial V}{\partial x} = 0 \qquad\Longrightarrow\qquad \frac{d}{dt}(m\dot{x}) = -\frac{\partial V}{\partial x} \qquad\Longleftrightarrow\qquad F = ma$$

Note that Lagrangian equations are a set of 2$^{\text{nd}}$ order ODEs with respect to t.

This formulation in classical mechanics is complemented by the Hamiltonian formulation. The Hamiltonian is a typical Legendre transformation, which can be used to transform the dependency of thermodynamical ensembles on the various functionals.

For example, in the (N, V, E) ensemble, one can transform the functional from energy to free energy, and move to dependency on temperature instead of entropy.

$$F = E - TS \qquad\qquad H = E + PV$$
(for constant T)   (for constant P)

Legendre Transformations

Legendre transformations can thus be used to construct, based on a function for which the Lagrangian was a functional of q and $\dot{q}$, a new function that will not depend on $\dot{q}$, but only on a new variable called the conjugate variable to $\dot{q}$.

Pressure and volume, temperature and entropy, chemical potential and number of particles, are all conjugate variables.

$$H(q, p, t) = \sum_i \dot{q}_i p_i - L(q, \dot{q}, t)$$

$$p_i = \frac{\partial L}{\partial \dot{q}_i}$$

This is the Legendre transform, where p_i is a conjugate variable called conjugate momentum.

For the new function H, which is called Hamiltonian, one can find an alternative set of equations. This is the Hamiltonian formalism, in which one can obtain the EOM for q and p. The Hamiltonian equations are:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

$$-\dot{p}_i = \frac{\partial H}{\partial q_i}$$

Note that this is a set of 1st order ODE, easier to solve on most occasions. These EOM yield identical trajectories to Lagrangian EOM.

If one constructs the Hamiltonian for the case of Newtonian dynamics, it turns out that $H = T + V$. Obviously, the Lagrangian and Hamiltonian formulations are thus equivalent, fact which can be used to develop MD EOM for other ensembles.

To move from the (N,V,E) to the (N,V,T) ensemble in MD, one can add one more generalized coordinate to construct an extended Lagragian or Hamiltonian. One can think of this as adding a pseudoparticle with its own T and V

The T and V of the pseudoparticle can be constructed so that this additional variable interacts with the existing dynamical variables to exchange temperature with them and bring the average temperature (of the real system) to the desired temperature.

For a canonical simulation (constant temperature), the extended Lagrangian is:

$$L_{Nose} = \sum_i \frac{1}{2} m_i s^2 \dot{r}_i^2 - V + \frac{1}{2} Q\dot{s}^2 - (f+1)k_B T \ln s$$

The extra degree of freedom is denoted by s, with conjugate momentum p_s. The corresponding kinetic and potential energy terms are given by:

$$K_s = \frac{1}{2} Q\dot{s}^2 = p_s^2/2Q$$

and

$$V_s = (f+1)k_B T \ln s$$

Q is the **thermal inertia** parameter controlling the rate of temperature fluctuations, **T** is the **desired temperature**, and **f** the number of **degrees of freedom** (3N, or 3N − 3 if the total momentum is fixed.

The real particle velocities are related to the time-derivates of position by:

$$v = s\dot{r} = p/ms$$

The extended Lagrangian, respectively Hamiltonian, of the system become:

$$L = K + K_s - V - V_s \quad \text{and} \quad H = K + K_s + V + V_s$$

where $K = \sum_i \frac{1}{2} m_i v_i^2$ and V are evaluated as a function of r in the usual manner.

One can then derive the EOM as:

$$\ddot{r} = f/ms^2 - 2\dot{s}\dot{r}/s \quad \text{and} \quad Q\ddot{s} = \sum_i m\dot{r}_i^2 s - (f+1)k_B T/s$$

and these can be solved using standard predictor-corrector algorithms.

The choice of Q is naturally important. Too high values for Q would result in slow energy flow between system and reservoir, while too low values result in long-lived, weakly damped oscillations of the energy, hence poor equilibration. For extremely large (infinite) Q values one obtains conventional MD. In practice, trial and error is recommended for satisfactory results.

The Nosé approach is fundamentally sound and one of the methods frequently used to properly do dynamics in the (NPT) 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.

Simplest Approach (Woodstock, 1971)

Fix to kinetic temperature by correcting the velocities of all particles, each time step. This can be done by rescaling with a factor $[T/T(t)]^{1/2}$. Here T is the desired temperature and T(t) is the instantaneous kinetic temperature at time (t).

Originally used for "isothermal" MD, velocity rescaling is a crude method for solving EOM which differ from the Newtonian ones. Yet, procedure can be used for equilibration processes, heat sink simulations of thin film growth.

More Sophisticated Approaches

Smooth scaling (Berendsen et. al, 1984)
A refinement of the rescale approach above is obtained by rescaling velocities, at each time step, by a factor defined as:

$$\chi = \left[1 + \frac{\delta t}{t_T}\left(\frac{T}{T(t)} - 1\right)\right]^{1/2}$$

Here T and T(t) are defined as above, and t_T is a preset time constant.

The net effect of this method is to "encourage", or "bias" the system in the desired kinetic direction by coupling to a heat bath via the t_T coupling parameter.

System is pushed towards the desired temperature at the rate determined by the coupling parameter while slightly perturbing the forces on each particle. Note that if $t_T = \delta t$, the simplest rescaling is recovered.

The method does not truly sample the canonical ensemble, but is very easy to implement and extremely useful for changing states and equilibrating the system at a new temperature.

Hoover method (1985)

This is an extension of the Nosé thermostat which redefines the time variable as $dt_{old} = s\, dt_{new}$, in order to eliminate s from the Nosé EOM:

$$\dot{r} = p/m; \quad \dot{p} = f - \xi p; \quad \xi = \frac{p_s}{Q}; \quad \dot{\xi} = \frac{fk_B}{Q}\left[T(t) - T\right]$$

where f and Q are defined as for Nosé thermostat, and ξ is a "friction coefficient" which constrains T(t) to a constant value.

Hoover's method does generate states in the true canonical ensemble. The equations for ξ steer the system towards the required temperature in a very gentle manner.

The method complements the original formulation of Nosé, hence the name and heavy use of Nosé-Hoover thermostats and chains.

Berendsen's smooth scaling factor can be reconstructed using Hoover's method to obtain:

$$\xi = \frac{1}{2t_T k_B T(t)} \left(k_B T(t) - k_B T \right)$$

In this formulation, Berendsen's scaling leads to true sampling of the canonical ensemble as well. The system is softly guided towards the desired temperature, though not as gentle as with the Hoover technique.

Given its simplicity, Berendsen's approach is on an almost equal footing with Hoover's method, and extensively used in (N,V,T) MD simulations.

Principle of Least Constraint (Hoover, Ladd, Moran, 1982)

Constraints, which are in fact constraint-forces, introduce perturbations which shift the trajectory of the system from its Newtonian course.

There are two types of constraints:
Holonomic   – which can be integrated out of the EOM.
Nonholonomic   – which are generally non-integrable.

The nonholonomic constraints, often involving particle velocities, are relevant for thermodynamic systems, but they're not limited to constraining temperature in systems. They can be used to constrain any desired quantity, e.g. bond lengths, pressure, stresses, etc.

For constant-temperature MD, an often used approach is to use the Principle of Least Constraint, introduce by Gauss (1829). Shortly, a "Gaussian" constraint acts to constrain system variables in a manner which minimizes the deviations from classical trajectories introduced by the perturbative forces.

For a function which depends on particle accelerations, one can write:

$$f(\ddot{r}_i) = \frac{1}{2} \sum_{i=1}^{N} m_i \left(\ddot{r}_i - \frac{F_i}{m_i} \right)^2$$

If $f = 0$, the equation reduces to Newton's (Hamilton's) EOM for systems with N unconstrained particles.

If $f \neq 0$, however, particles are constrained and evolve under non–Newtonian equations. Gauss's principle states that the physical acceleration of the set of N particles occurs when function f is a minimum.

For a constraint function g, which can be written as a function of acceleration, the constraint equation becomes:

$$\frac{\partial}{\partial \ddot{r}_i} \left[f(\ddot{r}_i) - \xi g(\ddot{r}_i) \right] = 0$$

where ξ is a Lagrangian (Gaussian) multiplier.

In MD simulations this principle is applied to constrain the kinetic energy of the system. Consequently, total energy is not conserved, and fluctuates around some average values.

The constraint function, G, which keeps the kinetic energy constant in MD can be written as:

$$G(\dot{r}_i, t) = \sum_{i=1}^{N} \frac{m_i \dot{r}^2}{2} - \frac{3Nk_BT}{2} = 0$$
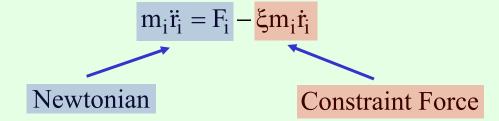
To express the equation in terms of acceleration, one can differentiate with respect to time:

$$g(\ddot{r}_i, \dot{r}_i, t) = \frac{dG(\dot{r}_i, t)}{dt} = \sum_{i=1}^{N} m_i \dot{r}_i \cdot \ddot{r}_i = 0$$

And by using the minimum condition relation:

$$\frac{\partial}{\partial \ddot{r}_i} \left[\frac{1}{2} \sum_{j=1}^{N} m_j \left(\ddot{r}_j - \frac{F_j}{m_j} \right)^2 + \xi \sum_{j=1}^{N} m_j \dot{r}_j \cdot \ddot{r}_j \right] = 0$$

which reduces to:
$$m_i \ddot{r}_i = F_i - \xi m_i \dot{r}_i$$

Newtonian

Constraint Force

The 2nd order DE above is equivalent to two 1st order DE, the EOM for system with constant kinetic energy (T):

$$\dot{r}_i = p_i / m_i ; \quad \dot{p}_i = F_i - \xi m_i \dot{r}_i$$

Here $\xi = \xi(r, p)$ acts as a "friction coefficient" which varies to constraint T(t) at a constant value, and has the following form:

$$\xi = \frac{\sum_{i=1}^{N} \dot{r}_i \cdot F_i}{\sum_{i=1}^{N} m_i \dot{r}_i^2}$$

At each time step, ξ is calculated and used to integrate the EOM.

In general ξ is chosen to satisfy: $\dot{T}(t) \propto \dfrac{d}{dt}\left(\sum_i p_i^2 \right) = 0$

Obs: The method keeps only E_{kin} constant, significantly different to Hoover and Berendsen scaling, where true (NVT) MD trajectories are generated.

The EOM for the constrained system are typically integrated using the Gear, predictor-corrector algorithm.

Alternatively, one can use a leap-frog variant (Brown and Clarke, 1984), which contains a modified velocity equation:

$$\dot{r}(t + \frac{1}{2}\Delta t) = \dot{r}(t - \frac{1}{2}\Delta t) + \left[f(t)/m - \xi \dot{r}(t) \right] \Delta t$$

which can be implemented in the following manner:

1. Make an unconstrained half step

$$\dot{r}'(t) = \dot{r}(t - \frac{1}{2}\Delta t) + \frac{1}{2} f(t) \Delta t/m$$

2. Calculate $\chi = \left[(T/T(t) \right]^{1/2}$ with T(t) calculated using unconstrained velocities.

3. Complete the full step using:

$$\dot{r}(t + \frac{1}{2}\Delta t) = (2\chi - 1)\dot{r}(t - \frac{1}{2}\Delta t) + \chi f(t) \Delta t/m$$

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.

Extended system methods (Andersen, 1980)

   The approach is to couple the system to an external variable V, the volume of the simulation box.

   The coupling mimics the action of a piston on the system. The piston is given a "mass" Q [with units of (mass)*(length)$^{-4}$] and an associated kinetic energy:

$$K_V = \frac{1}{2}Q\dot{V}^2$$

   The potential energy associated with V can be expressed using the desired pressure P as:

$$U_V = PV$$

   This leads to the following scaled variables:

$$r = V^{1/3}s; \quad \dot{r} = v = V^{1/3}\dot{s}$$

leading to potential, respectively kinetic, energies expressed as:

$$U = U(V^{1/3}s); \qquad K = \frac{1}{2}m\sum_i v_i^2 = \frac{1}{2}mV^{2/3}\sum_i \dot{s}_i^2$$

The extended Lagrangian then takes the usual form:

$$L_V = K + K_V - U - U_V$$

and the EOM for this system are:

$$\ddot{s} = f/(mV^{1/3}) - (2/3)\dot{s}\,\dot{V}/V; \quad \ddot{V} = [P(t) - P]/Q$$

Here f and P(t) are calculated using the normal, unscaled coordinates and momenta. The extended Hamiltonian can also be expressed as:

$$H_V = K + K_V + U + U_V$$

The Hamiltonian is conserved, however, as it turns out, is equal to the enthalpy of the system, plus an additional $1/2k_BT$ factor, which is associated with kinetic energy of the volume fluctuation.

   Consequently, the EOM generate trajectories in the isobaric-isoenthalpic (NPH) ensemble, hence this method leads to constant (NPH) MD simulations.

   Long range corrections are extremely important in constant-pressure MD, since the instantaneous pressure P(t) needs to be compared with the desired pressure P. These corrections must be added each time step during the simulation, since the density is continually changing.

$$(PV)_{Full} \approx (PV)_C + (PV)_{LRC} = (PV)_C - (2/3)\pi N\rho \int_{r_c}^{\infty} r^2 w(r)dr$$

where $(PV)_{Full}$ and $(PV)_C$ are the desired, respectively calculated pressure in the simulation using potential cutoff, and $w(r)$ is the pair virial function.

$$w(r) = r\frac{dU(r)}{dr}$$

For the LJ potential, the pressure long range correction, in reduced units, is:

$$P^*_{LRC} = (32/9)\pi\rho^{*2}\, r_c^{*-9} - (16/3)\pi\rho^{*2}\, r_c^{*-3}$$

The pair distribution function, namely for g(r) ≈ 1, is typically used to estimate these corrections.

In constant (NPH) MD simulations, the EOM are typically integrated using a predictor-corrector integrator such as Gear. However, the modified leap-frog algorithm of Brown and Clarke is better since $\dot{s}$ is needed at each time step to evaluate the unscaled velocities:

$$\dot{r} = V^{1/3}\dot{s} + \frac{1}{3}V^{-2/3}\dot{V}s$$

The "piston mass" Q is adjustable. A low Q value results in raid box size oscillations difficult to damp. High Q values, on the other hand yield a slow exploration of the volume-space.
Conventional MD is regained for infinite Q values.

Constraints Methods

   As for the constant temperature case, one can redefine the EOM the make P(t) a constant of motion and use Gauss's principle to minimize the dynamics change.

   By using the appropriate Lagrange multiplier one can thus obtain:

$$\dot{r} = p/m + \chi(r,p)r; \quad \dot{p} = f - \chi(r,p)p; \quad \dot{V} = 3V\chi(r,p)$$

where $\chi(r,p)$ is the Lagrange multiplier, equivalent with the rate of dilation of the system. To obtain χ, one must differentiate the expression defining P(t):

$$3\dot{P}(t)V + 3P(t)\dot{V} = \sum_i (2/m)p_i \cdot \dot{p}_i + \dot{r}_i \cdot f_i + \dot{f}_i \cdot r_i$$

and use the fact that P(t) = P (constant of motion) and $\dot{P}(t) = 0$.

$$\chi = \frac{(2/3)\sum_i p_i \cdot f_i - (1/m)\sum_i \sum_{j>i}\left(r_{ij} \cdot p_{ij}\right)\chi(r_{ij})/r_{ij}^2}{(2/m)\sum_i p_i^2 + \sum_i \sum_{j>i} x(r_{ij}) + 9PV}$$

In addition to the long range corrections for the PV term, each step corrections for the x(rij) term must be included:

$$9\chi_{LRC} = \left(\sum_i \sum_{j>i} x(r_{ij}) \right)_{LRC} = 2\pi\rho N \int\limits_{r_c}^{\infty} x(r_{ij}) r_{ij}^2 dr_{ij}$$

Standard predictor-corrector techniques can be used to integrate the EOM. Care should be taken since calculations of velocities require the derivatives of χ.

$$\ddot{r} = \dot{p} + \chi r + \dot{\chi} r; \qquad \dot{\chi} = \left(\ddot{V}V - \dot{V}^2 \right) / 3V^2$$

As in the case of extended system method, the EOM sample the constant (NPH) ensemble.

Other Methods

Berendsen (1984) devised a relatively simple method to couple the system to a "pressure bath".

An extra term is included in the EOM and the system obeys the equation:

$$dP(t)/dt = [P - P(t)]/t_P$$

where P is the desired pressure and t_P is a time constant.

At each step, the volume of the simulation box is scaled by a factor χ and the coordinates of the particles by a factor $\chi^{1/3}$:

$$r' = \chi^{1/3} r \quad \text{where} \quad \chi = 1 - \beta_T \frac{\Delta t}{t_P} [P - P(t)] \quad \text{and } \beta_T \text{ isothermal compressibility.}$$

This technique does not alter drastically dynamic trajectories, is easy to program, however, no ensemble has been associated with it.

Constant Temperature and Pressure MD

The constant isobaric-isothermal (NPT) ensemble is quite often of interest.

To properly sample the constant (NPT) ensemble, the constant-pressure method can be combined with any of the constant-temperature techniques described.

Any of the following approaches are valid for MD simulations:

1. Couple the system with a piston and maintain temperature with the stochastic method, including collisions with the piston.

2. Redefine EOM to constrain T and P, with χ and ξ defined as before:

$$\dot{p} = f - \chi(r,p)p - \xi(r,p)p = f - (\chi + \xi)p$$

Here $(\chi + \xi)$ takes the role of ξ in the equation for constraining temperature. The EOM of solved as before.

Constant Temperature and Pressure MD

3. Take Hoover's formulation, who used the Andersen and Nosé approaches to obtain the following EOM for MD in the constant (NPT) ensemble:

$$\dot{s} = p/mV^{1/3}; \qquad \dot{p} = f - (\chi + \xi)p; \qquad \chi = \dot{V}/3V;$$

$$\dot{\xi} = \left(\sum_i |p_i|^2 / m - fk_BT \right) / Q; \qquad \dot{\chi} = [P(t) - P]V/t_P^2 k_BT$$

Changing the Box Shape

To change size/shape of primary simulation cell one can use a transformation matrix to scale the coordinates. This requires the use of an extended Lagrangian to include the extra "potential" and "kinetic" energy associated with the box.

More details can be found in the book.

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.

For the CDIO project, Andersen thermostat, simple and/or Berendsen scaling (T/P) are easy to implement, therefore recommended.

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)   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.

Generally used to study fluid systems, but 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.

For a single component system containing N particles:

$$\dot{r}_i = p_i / m_i ; \qquad \dot{p}_i = F_i + F_E - \xi\left(\frac{p_i}{m_i} - \boldsymbol{u}(r,t)\right)$$

Here r_i, p_i are the usual position and momenta, F_i the sum of all interatomic forces acting upon atom i, F_E is the external field (e.g. a gravitational field), ξ a thermostat multiplier (might be used to keep temperature constant) and $\boldsymbol{u}(r,t)$ is the streaming velocity of the fluid.

The EOM are integrated at each time step to obtain trajectories, from which principles of nonequilibrium statistical mechanics to calculate properties of interest (elements of the pressure tensor, heat flux vector, transport coefficients).

NEMD is an excellent complement for computational fluid dynamics (CFD), as it allows the ab-initio calculation of transport coefficients, which can be used as input for CFD studies (e.g. test Navier-Stokes equations for heat transfer, etc)

Special PBC required. More details in the book, other references available.

Optimization techniques – Simulated Annealing (SA)

General method to find the global minimum of a given function in a large space. Name analogue to the metallurgy technique of heating and controlled cooling, to Increase crystal size, reduce defects.

SA is extensively used in conjunction with MD as well as MC and requires:
1. A description of possible system configurations.
2. A generator of random changes in the configurations.
3. An objective function (typically energy).
4. A control parameter (typically T) and an annealing schedule:
    - Slow cooling (annealing), one can find global ground state (real world).
    - Fast cooling (quenching), one can find local minimum (glass).

In MD, following steps are needed to implement SA:
    - choose annealing schedule (cooling rate).
    - solve Newton's EOM for each atom.
    - control T via coupling to heat bath (Andersen, Nosé-Hoover thermostats).

Downhill energy moves with Steepest Descent, Conjugate Gradient methods.