10.4. THE MOLECULAR DYNAMICS METHOD.

Objective: Simulate the evolution of a microscopic model of a material in time. Accumulate estimates of structural, thermodynamic, transport and dynamic properties

Advantage wrt. Monte Carlo: Can provide dynamical information.

10.4.1. Formulations of the equations of Motion

(Goldstein, H. *Classical Mechanics*, Addison-Wesley, 1980)

Lagrangian Formulation: $\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{q}_k}\right) - \frac{\partial \mathcal{L}}{\partial q_k} = 0$ (10.33)

q_k : generalized coordinates (independent)

$\mathcal{L} = \mathcal{L}(\underset{\sim}{q}, \underset{\sim}{\dot{q}}, t) = \mathcal{K} - \mathcal{V}$: Lagrangian function

$\mathcal{K} = \mathcal{K}(\underset{\sim}{q}, \underset{\sim}{\dot{q}}, t)$: Kinetic energy function

$\mathcal{V} = \mathcal{V}(\underset{\sim}{q}, t)$: Potential energy function.

Hamilton's (Variational) Principle: For a mechanical system in which all forces, except the forces of constraint, are derivable from a generalized scalar potential $\mathcal{V}$ that may be a function of coordinates, velocities, and time, the motion of the system from time t_1 to time t_2 is such that the line integral $S_{cl} = \int_{t_1}^{t_2} \mathcal{L}(\underset{\sim}{q}, \underset{\sim}{\dot{q}}, t)\, dt$ has a stationary point over the correct path of motion.

Definition of momentum conjugate to the generalized coordinate q_k:

$$p_k = \frac{\partial \mathcal{L}(\underset{\sim}{q}, \dot{\underset{\sim}{q}}, t)}{\partial \dot{q}_k} \tag{3.1}$$

Definition of the Hamiltonian function from the Lagrangian formulation:

$$\mathcal{H}(\underset{\sim}{q}, \underset{\sim}{p}, t) = \sum_k \dot{q}_k \cdot p_k - \mathcal{L}(\underset{\sim}{q}, \dot{\underset{\sim}{q}}, t) \tag{3.2}$$

$$\text{If} \left\{ \begin{array}{l} \text{the generalized coordinate definitions do not depend explicitly on time} \\ \text{Forces are derivable from a conservative potential } \mathcal{V}(\underset{\sim}{q}) \end{array} \right\},$$

the Hamiltonian is a constant of the motion, corresponding to the system total energy:

$$\mathcal{H}(\underset{\sim}{q}, \underset{\sim}{p}, t) = E = \text{const.} \tag{3.6}$$

[One can prove $\frac{d\mathcal{H}}{dt}$ from the Lagrangian equations].

Hamiltonian Formulation (Canonical Equations):

$$\dot{q}_k = \frac{\partial \mathcal{H}}{\partial p_k} \tag{3.5}$$

$$\dot{p}_k = -\frac{\partial \mathcal{H}}{\partial q_k} \tag{3.4}$$

If the Hamiltonian $\mathcal{H}(\underset{\sim}{q}, \underset{\sim}{p}, t)$ does not depend explicitly on time, i.e. it depends on time only through the time dependence of $\underset{\sim}{q}$ and $\underset{\sim}{p}$, then it is a constant of the motion, and the system is conservative.

Newtonian Formulation: For a system of particles i,

$$m_i \ddot{\underset{\sim}{r}}_i = \underset{\sim}{F}_i \tag{10.34}$$

$$\underset{\sim}{F}_i = - \underset{\sim}{\nabla}_{\underset{\sim}{r}_i} \mathcal{V} + \underset{\sim}{g}_i \tag{10.35}$$

m_i = mass of particle i.

$\underset{\sim}{r}_i$ = coordinate vector of particle i.

$\underset{\sim}{F}_i$ = total force acting on particle i.

$\mathcal{V} = \mathcal{V}(\underset{\sim}{r}_1, \dots, \underset{\sim}{r}_i, \dots, \underset{\sim}{r}_N)$ = potential energy due to interparticle interactions and (possibly) an external field.

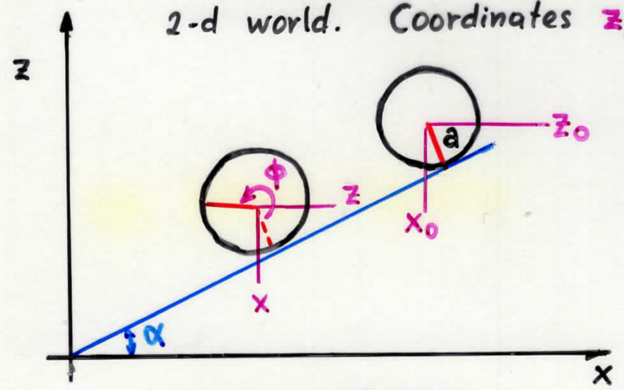
$\underset{\sim}{g}_i$ = constraint force
[in the presence of constraints, $\underset{\sim}{r}_i$ are NOT independent]

Categories of Constraints

HOLONOMIC: Equations involving only coordinates $\underset{\sim}{q}$ and time t.

$$\exists f: \; f(\underset{\sim}{q}_1, \underset{\sim}{q}_2, \dots, t) = 0$$

Example: Circle rolling on an incline in a 2-d world. Coordinates z, x, ϕ



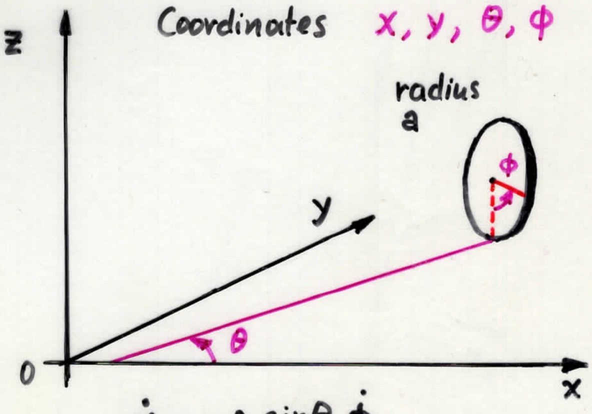
$$z = z_0 - a\phi \sin\alpha$$
$$x = x_0 - a\phi \cos\alpha$$

$$f(x, z, \phi) = (x - x_0)^2 + (z - z_0)^2 - a^2\phi^2 = 0$$

NONHOLONOMIC: Can only be expresse as inequalities, or involve velocitie

Example: Circle rolling on a plane in a 3-d world.

Coordinates x, y, θ, ϕ



$$\dot{x} = -a \sin\theta \, \dot{\phi}$$
$$\dot{y} = -a \cos\theta \, \dot{\phi}$$

$$\nexists f: \; f(x, y, \theta, \phi) = 0$$

- Equations of motion are reversible in time.

- In an isolated system of interacting molecules, in the absence of an external field, the quantities

$$\left.\begin{array}{ll} \mathcal{H} & \text{(total energy)} \\ \underset{\sim}{P} = \sum_i \underset{\sim}{p}_i & \text{(total linear momentum)} \\ \underset{\sim}{L} = \sum_i \underset{\sim}{r}_i \times \underset{\sim}{p}_i & \text{(total angular momentum)} \end{array}\right\} \text{are conserved.}$$

- In a system of molecules confined to a box with periodic boundary conditions, evolving in time subject only to interactions with each other, the conserved quantities are $\mathcal{H}$, $\underset{\sim}{P}$, but <u>not</u> $\underset{\sim}{L}$.

A typical MD simulation is carried out under conditions of constant N, V, E, and $\underset{\sim}{P}$. It samples the microcanonical ensemble, with the additional constraint of constant total momentum.

10.4.2. Difference Methods for the Integration of the Dynamical Equations.

MD constitutes a numerical solution to an initial value problem.

e.g. ATOMIC SYSTEMS

$$\left.\begin{array}{ll} \ddot{\underset{\sim}{r}}_i = \dfrac{1}{m_i} \underset{\sim}{F}_i(\underset{\sim}{r}_1, \ldots, \underset{\sim}{r}_N) & i = 1, 2, \ldots, N \\ \underset{\sim}{r}_i(0)\;,\; \dot{\underset{\sim}{r}}_i(0) \text{ specified} & \end{array}\right\} \text{INITIAL VALUE PROBLEM}$$

Reduction to a system of coupled first-order ODEs possible (but not always necessary for numerical solution).

$$\left.\begin{aligned} \dot{\underset{\sim}{r}}_i &= \underset{\sim}{v}_i \\ \dot{\underset{\sim}{v}}_i &= \frac{1}{m_i}\underset{\sim}{F}_i(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \dots, \underset{\sim}{r}_N) \qquad i=1,2,\dots,N \\ \underset{\sim}{r}_i(0),&\ \underset{\sim}{v}_i(0) \text{ specified} \end{aligned}\right\} \quad \begin{aligned} &\text{Of the general form} \\ &\dot{\underset{\sim}{y}} = \underset{\sim}{f}(t, \underset{\sim}{y}) \\ &\underset{\sim}{y}(0) \text{ specified.} \end{aligned} \tag{10.36}$$

A variety of difference methods are available for the numerical solution of such initial value problems (see Press et al., *Numerical Recipes*, 1986)

Generally, one marches along the independent variable (time) in finite steps δt. The stepsize may either be constant, or changed adaptively during the numerical solution.

ORDER: A numerical scheme for the integration of an initial value problem is called n^{th} order when

$$\text{Error} \quad \epsilon = \| \underset{\sim}{y}^{\text{numerical}}(t) - \underset{\sim}{y}^{\text{exact}}(t) \| = \mathcal{O}[(\delta t)^{n+1}] \tag{10.37}$$

High order does not necessarily imply high accuracy!

Algorithmic Considerations in MD.

- Most time-consuming part of the calculation is the evaluation of forces.

  Good criterion for algorithm efficiency:

  $$\frac{\text{Number of } \underset{\sim}{f}\text{- evaluations}}{\text{Simulated Time}} = \text{minimal}$$

- Speed of integration algorithm immaterial (calculation dominated by $\underset{\sim}{f}$- evaluation).

- Algorithm must not require many $\underline{f}$-evaluations per integration time step.
  (otherwise popular schemes, such as the 4th order Runge-Kutta-Gill, seldom used in MD)

- Algorithm must allow employing a long integration time step δt

(some compromise between $\underline{f}$-calls and δt)

- Algorithm must be accurate. (error ϵ small for reasonably large δt).

- Algorithm must be stable (error ϵ must not blow up with increasing δt
  Stability problem is severe in <u>stiff</u> systems of ODE's, possessing two or more widely disparate time scales. MD problems are typically stiff. Stiffness can be cured by use of <u>implicit</u> algorithms. Such algorithms, however, require many $\underset{\sim}{f}$-evaluations, and are not favored in MD.

- Algorithm should require little memory.

- Algorithm should satisfy conservation laws for energy and momentum, and be time-reversible.

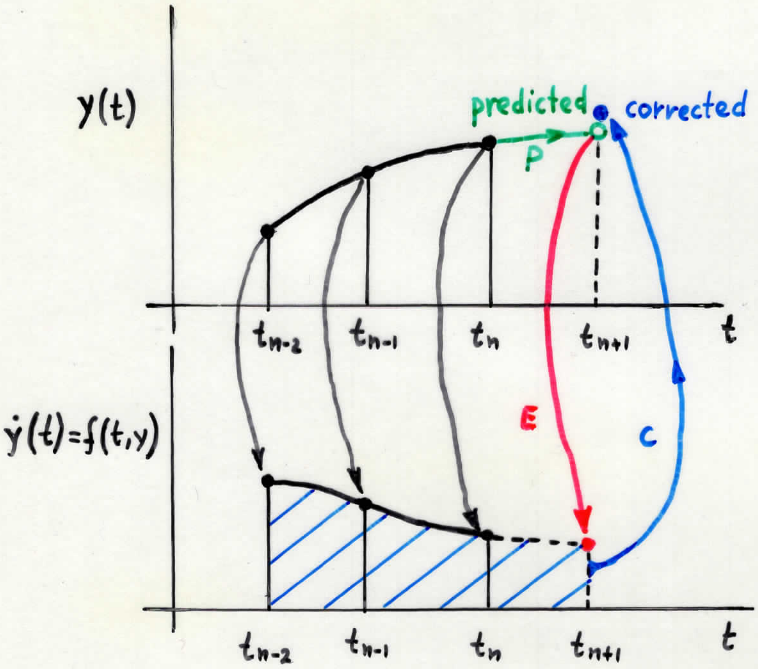
- Algorithm should be simple and easy to program.

- Algorithm should duplicate the "exact" classical trajectory as closely as possible.

MD problems, being highly nonlinear, are characterized by tremendous sensitivity to initial conditions: Any two classical trajectories that are initially very close will eventually diverge from each other exponentially with time. Clearly, there is no hope of tracing the "real" trajectory at long times. This is NO PROBLEM, provided that

- the trajectory stays reasonably close to the "real" trajectory over the correlation times of interest.
- Energy is conserved, so that the trajectory provides correct sampling of the NVE ensemble.

Gear Predictor-Corrector Methods



Problem: $\dot{\underset{\sim}{y}} = f(t, \underset{\sim}{y})$

$\underset{\sim}{y}(0)$ specified

Basic idea:

P: extrapolate information about y and its derivatives, accumulated over steps $n-l+1$ to n, to obtain estimate $\underset{\sim}{y}_{n+1}^{P}$.

E: Evaluate $\dot{\underset{\sim}{y}}_{n+1}^{P} = f(t_{n+1}, \underset{\sim}{y}_{n+1}^{P})$

C: Through polynomial interpolation of $\dot{\underset{\sim}{y}}(t)$ curve, evaluate the area under that curve. Use area to obtain corrected estimate $\underset{\sim}{y}_{n+1}^{C}$.

- P and C steps must be of <u>same order</u>.
- E, C steps can be repeated: $P(EC)^m E$ Usually, $m = 1$ (or 2). It <u>doesn't pay</u> to iterate until convergence. (can't beat finite order of corrector)

k- value method: uses k previously calculated values of $\underset{\sim}{y}$ or its derivatives.

ℓ - step method: uses values calculated at ℓ previous mesh points along the t-axis.

Representations (k-value method) Vector stored and updated:

Adams - Bashforth - Moulton $[\ell = k-1]$ $(\underset{\sim}{y}_n, \ \delta t\, \dot{\underset{\sim}{y}}_n, \ \delta t\, \dot{\underset{\sim}{y}}_{n-1}, \ \ldots, \ \delta t\, \dot{\underset{\sim}{y}}_{n-k+2})$

Nordsieck representation $[\ell = 1]$ $(\underset{\sim}{y}_n, \ \delta t\, \dot{\underset{\sim}{y}}_n, \ \frac{\delta t^2}{2}\ddot{\underset{\sim}{y}}_n, \ \ldots, \ \delta t^{k+1} \frac{y_n^{(k-1)}}{(k-1)!})$

Equivalence between representations can be shown by transformation from one to the other (van Gunsteren and Berendsen, <u>Molec. Phys.</u> 1977, <u>34</u>, 1311-1327)

An Example: Four-value Predictor-Corrector Algorithm in the Nordsieck representatio

(Gear, C.W. <u>Numerical Initial Value Problems in Ordinary Differential Equations</u>, Prentice Hall, Englewood Cliffs, 1971)

Equation of motion: $\ddot{\underset{\sim}{r}} = \underset{\sim}{f}(\underset{\sim}{r})$

Predictor:

$$\begin{bmatrix} \underset{\sim}{r}^p(t+\delta t) \\ \delta t\, \dot{\underset{\sim}{r}}^p(t+\delta t) \\ \frac{\delta t^2}{2}\ddot{\underset{\sim}{r}}^p(t+\delta t) \\ \frac{\delta t^3}{6}\dddot{\underset{\sim}{r}}^p(t+\delta t) \end{bmatrix} \equiv \begin{bmatrix} \underset{\sim}{r}_0^p(t+\delta t) \\ \underset{\sim}{r}_1^p(t+\delta t) \\ \underset{\sim}{r}_2^p(t+\delta t) \\ \underset{\sim}{r}_3^p(t+\delta t) \end{bmatrix} = \underset{\substack{\uparrow \\ \text{Pascal triangle matrix.}}}{\begin{bmatrix} 1 & 1 & 1 & 1 \\ 0 & 1 & 2 & 3 \\ 0 & 0 & 1 & 3 \\ 0 & 0 & 0 & 1 \end{bmatrix}} \begin{bmatrix} \underset{\sim}{r}_0(t) \\ \underset{\sim}{r}_1(t) \\ \underset{\sim}{r}_2(t) \\ \underset{\sim}{r}_3(t) \end{bmatrix} \qquad (10.38$$

(a set of four Taylor series expansions)

Corrector:

$$\begin{bmatrix} \underset{\sim}{r}_0^c(t+\delta t) \\ \underset{\sim}{r}_1^c(t+\delta t) \\ \underset{\sim}{r}_2^c(t+\delta t) \\ \underset{\sim}{r}_3^c(t+\delta t) \end{bmatrix} = \begin{bmatrix} \underset{\sim}{r}_0^p(t+\delta t) \\ \underset{\sim}{r}_1^p(t+\delta t) \\ \underset{\sim}{r}_2^p(t+\delta t) \\ \underset{\sim}{r}_3^p(t+\delta t) \end{bmatrix} + \begin{bmatrix} 1/6 \\ 5/6 \\ 1 \\ 1/3 \end{bmatrix} \left(\frac{\delta t^2}{2} \underset{\sim}{f}(\underset{\sim}{r}_0^p) - \underset{\sim}{r}_2^p \right) \qquad (10.39)$$

What is the order of this scheme? (4th ?

Analogous schemes available for the forms $\dot{\underset{\sim}{r}} = \underset{\sim}{f}(\underset{\sim}{r})$, $\ddot{\underset{\sim}{r}} = \underset{\sim}{f}(\underset{\sim}{r}, \dot{\underset{\sim}{r}})$

Corrector coefficients calculated for optimal stability and accuracy (see Allen + Tildesley, App. E

- For a system with a total of N coordinates (N/3 atoms), four-value Gear algorithm requires <u>5N words of storage</u> ($\underset{\sim}{r}_0$, $\underset{\sim}{r}_1$, $\underset{\sim}{r}_2$, $\underset{\sim}{r}_3$, new accelerations)

The Verlet Algorithms

- Simple, accurate, easy to program, economical in storage, popular.
- Can be thought of as a 3-value, 2-step predictor-corrector, where predictor and corrector recipes coincide (no corrector evaluation).

Verlet's Original Method (1967) for the problem $\ddot{\underset{\sim}{r}} = \underset{\sim}{f}(\underset{\sim}{r}) \equiv \underset{\sim}{a}(\underset{\sim}{r})$

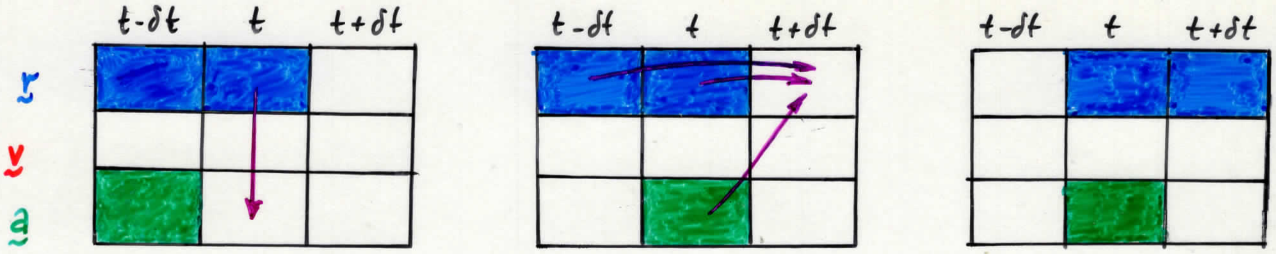
Method based on positions $\underset{\sim}{r}(t)$, accelerations $\underset{\sim}{a}(t)$, positions $\underset{\sim}{r}(t-\delta t)$ from the previous time step.

Positions advanced by: $\underset{\sim}{r}(t+\delta t) = 2\underset{\sim}{r}(t) - \underset{\sim}{r}(t-\delta t) + \delta t^2 \underset{\sim}{a}(t) + \mathcal{O}(\delta t^{\overset{!}{4}})$ (10.40)

$$\left\{ \text{A consequence of} \quad \begin{aligned} \underset{\sim}{r}(t+\delta t) &= \underset{\sim}{r}(t) + \delta t\, \underset{\sim}{v}(t) + \tfrac{1}{2}\delta t^2 \underset{\sim}{a}(t) + \tfrac{1}{6}\delta t^3 \underset{\sim}{b}(t) + \cdots \\ \underset{\sim}{r}(t-\delta t) &= \underset{\sim}{r}(t) - \delta t\, \underset{\sim}{v}(t) + \tfrac{1}{2}\delta t^2 \underset{\sim}{a}(t) - \tfrac{1}{6}\delta t^3 \underset{\sim}{b}(t) + \cdots \end{aligned} \right\}$$

Velocity estimation: $\underset{\sim}{v}(t) = \dfrac{\underset{\sim}{r}(t+\delta t) - \underset{\sim}{r}(t-\delta t)}{2\delta t} + \mathcal{O}(\delta t^{\overset{\text{inferior}}{2}})$ (10.41)

- Requires only 3N words of storage.
- Time reversible, guaranteed to conserve linear momentum.
- Excellent energy conservation (for liq. Ar, energy fluctuations $10^{-4}\epsilon$ for $\delta t = 10^{-14}$ s, $2\times10^{-3}\epsilon$ for $\delta t = 4\times10^{-14}$ s)
- Velocities are of inferior accuracy.
- Trajectory generated by adding a small $\mathcal{O}(\delta t^2)$ term to the difference of two large $\mathcal{O}(\delta t^0)$ terms. This may introduce numerical imprecision.



(One step of trajectory generation according to original Verlet algorithm).

The Verlet "leap-frog" scheme (Hockney 1970)

Use of mid-step velocities.

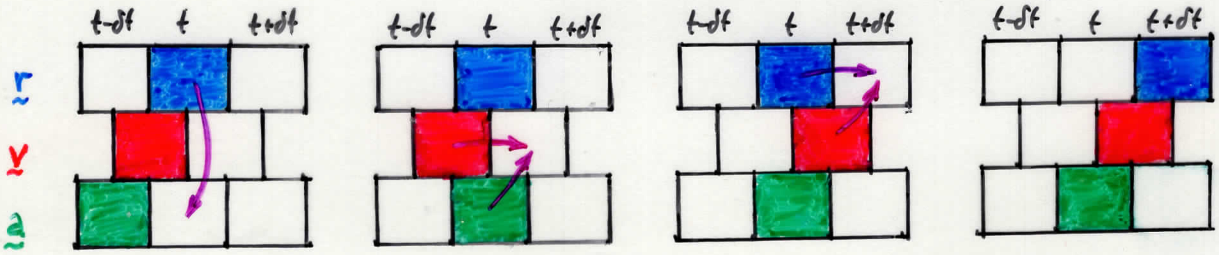
$$\underset{\sim}{r}(t+\delta t) = \underset{\sim}{r}(t) + \delta t \; \underset{\sim}{v}(t+\tfrac{1}{2}\delta t) \qquad (10.42)$$

$$\underset{\sim}{v}(t+\tfrac{1}{2}\delta t) = \underset{\sim}{v}(t-\tfrac{1}{2}\delta t) + \delta t \; \underset{\sim}{a}(t) \qquad (10.43)$$

Calculation of current velocities:

$$\underset{\sim}{v}(t) = \frac{1}{2}\left[\underset{\sim}{v}(t+\tfrac{1}{2}\delta t) + \underset{\sim}{v}(t-\tfrac{1}{2}\delta t)\right] \qquad (10.44)$$

- Method is algebraically equivalent to original Verlet algorithm.
- Method does not involve taking difference between large numbers to estimate a small quantity.
- Storage 3N words, can be compressed to 2N by sacrificing (10.44).



(one step of trajectory generation according to the Verlet leap-frog scheme).

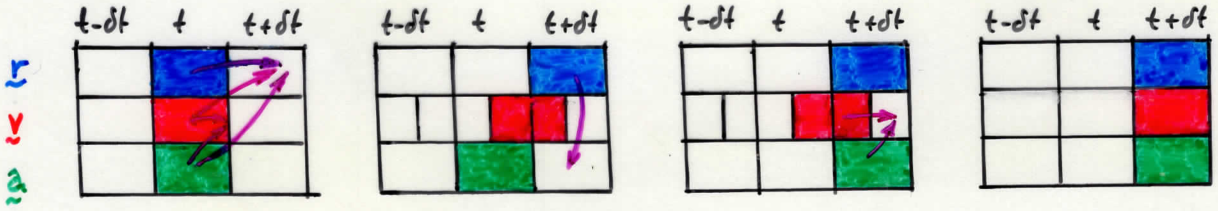
The "velocity Verlet" algorithm (Swope, Andersen, Berens, Wilson, 1982).

$$\underset{\sim}{r}(t+\delta t) = \underset{\sim}{r}(t) + \delta t\, \underset{\sim}{v}(t) + \frac{1}{2}\delta t^2 \underset{\sim}{a}(t) \qquad (10.45)$$

$$\underset{\sim}{v}(t+\tfrac{1}{2}\delta t) = \underset{\sim}{v}(t) + \frac{1}{2}\delta t\, \underset{\sim}{a}(t) \qquad (10.46)$$

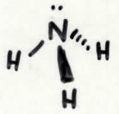
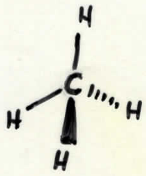
$$\underset{\sim}{v}(t+\delta t) = \underset{\sim}{v}(t+\tfrac{1}{2}\delta t) + \frac{1}{2}\delta t\, \underset{\sim}{a}(t+\delta t) \qquad (10.47)$$

- 3N words of storage
- Perhaps the most attractive Verlet method proposed to date.



(one step of trajectory generation according to the velocity Verlet algorithm)

10.4.3. MD of Rigid, Nonlinear Polyatomic Molecules in Generalized Coordinates.

e.g.  ,  ,  , 

- If potential expressions are used for all bonded forces, the system can be treated as an atomic system.

Problems
- Stiffness : extremely small time step needed to track fast bond vibrations.
- Classical approach questionable for bond vibrations.

- Computational economy through fixing "hard" degrees of freedom:
  - bond lengths
  - bond angles (less reasonable for molecules with torsional degrees of freedom

Fixing bond lengths / bond angles amounts to introducing constraints among Cartesian coordinates of atoms, which are no longer independent.

e.g. fixing bond 12 amounts to the constraint $|\underset{\sim}{r}_1 - \underset{\sim}{r}_2|^2 = d_{12}^2$

Here, concerned with rigid polyatomic nonlinear molecules.

Configuration of such a molecule fully specified by 6 generalized coords

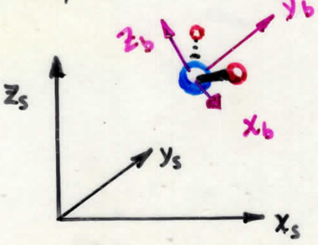
$$\underset{\sim}{r}_{CM} \quad , \quad \underbrace{\Phi, \Theta, \Psi}$$

center of mass position vector

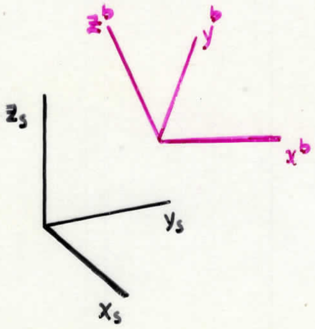
Eulerian angles, specifying the overall orientation of the molecule with respect to laboratory frame of reference.

Let b = body-fixed frame of reference (e.g. frame of reference defined by principal axes).

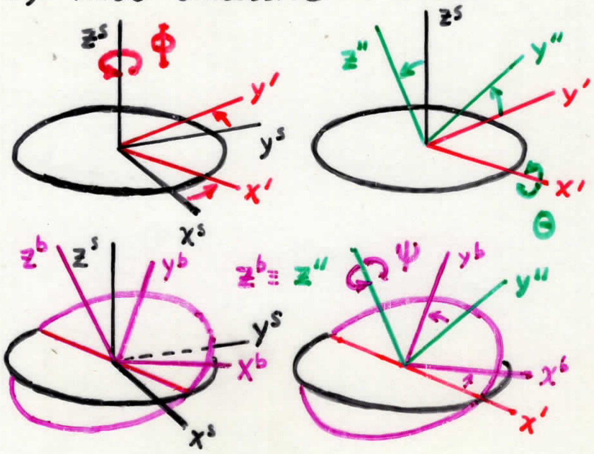
s = space-fixed frame of reference (lab frame)



One way of defining the Euler angles: (Goldstein)



Bring (x_s, y_s, z_s) system onto (x^b, y^b, z^b) system by three successive rotations:



orthogonal coordinate transformation matrix betw. the two systems.

$$\underset{\sim}{v}^b = \underline{\underline{A}}\, \underset{\sim}{v}^s$$

representation of a vector in space-fixed system

representation of same vector in body-fixed system.

$$\underline{\underline{A}} = \begin{bmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\text{or} \quad \underline{\underline{A}} = \begin{bmatrix} \cos\phi\cos\psi - \sin\phi\cos\theta\sin\psi & \sin\phi\cos\psi + \cos\phi\cos\theta\sin\psi & \sin\theta\sin\psi \\ -\cos\phi\sin\psi - \sin\phi\cos\theta\cos\psi & -\sin\phi\sin\psi + \cos\phi\cos\theta\cos\psi & \sin\theta\cos\psi \\ \sin\phi\sin\theta & -\cos\phi\sin\theta & \cos\theta \end{bmatrix} \tag{10.48}$$

Orthogonality (metric-preserving property of $\underline{\underline{A}}$): $\underline{\underline{A}}^{-1} = \underline{\underline{A}}^{T}$

Dynamical Equations in generalized coordinates

C.M. translation, under the influence of total force

$$\underset{\sim}{f} = \sum_\alpha \underset{\sim}{f}_\alpha \quad (\alpha = \text{interaction sites})$$

Linear velocity $\dot{\underset{\sim}{r}}_{CM}$

Rotation around center of mass, under the influence of total torque,

$$\underset{\sim}{\tau} = \sum_\alpha \underbrace{(\underset{\sim}{r}_\alpha - \underset{\sim}{r}_{CM})}_{\underset{\sim}{r}'_\alpha} \times \underset{\sim}{f}_\alpha \tag{10.49}$$

Angular velocity $\underset{\sim}{\omega}$

Some definitions

Angular momentum $\underset{\sim}{L} = \sum_\alpha m_\alpha \underset{\sim}{r}'_\alpha \times \dot{\underset{\sim}{r}}'_\alpha$

One can show $$\underset{\sim}{L} = \underset{\approx}{I} \cdot \underset{\sim}{\omega} \qquad (10.50)$$

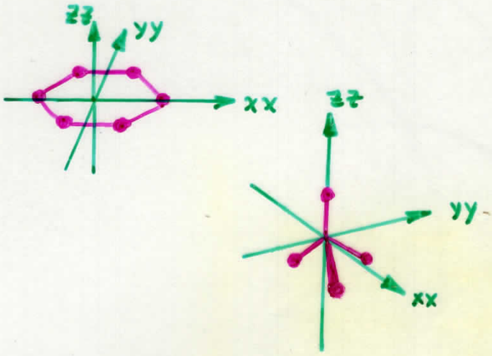
where <u>Moment of Inertia tensor</u>

$$\underset{\approx}{I} \equiv \sum_\alpha m_\alpha \left(r'^2_\alpha \underline{\underline{1}} - \underset{\sim}{r}'_\alpha \underset{\sim}{r}'_\alpha \right) = \sum_\alpha m_\alpha \begin{pmatrix} y'^2_\alpha + z'^2_\alpha & r'^2_\alpha - x'_\alpha y'_\alpha & r'^2_\alpha - x'_\alpha z'_\alpha \\ r'^2_\alpha - y'_\alpha x'_\alpha & z'^2_\alpha + x'^2_\alpha & r'^2_\alpha - y'_\alpha z'_\alpha \\ r'^2_\alpha - z'_\alpha x'_\alpha & r'^2_\alpha - z'_\alpha y'_\alpha & x'^2_\alpha + y'^2_\alpha \end{pmatrix} \qquad (10.51)$$

Diagonalitation of $\underline{\underline{I}}$ $\begin{cases} \text{principal axes (eigenvectors)} \\ \text{principal moments of inertia (eigenvalues) } I_{xx}, I_{yy}, I_{zz}. \end{cases}$

Cylindrical Symmetry: $I_{xx} = I_{yy}$

Spherical Symmetry: $I_{xx} = I_{yy} = I_{zz}$



Equations of rotational motion: $$\underset{\sim}{\tau} = \dot{\underset{\sim}{L}} \qquad (10.52)$$

(analogous to $\underset{\sim}{F} = \dot{\underset{\sim}{p}}$)

Convenient to choose body-fixed coordinate system b as the <u>principal axis system</u>. In that system, equations of motion become:

$$\underset{\begin{pmatrix} I_{xx} & 0 & 0 \\ 0 & I_{yy} & 0 \\ 0 & 0 & I_{zz} \end{pmatrix}}{\underset{\nearrow}{\underset{\approx}{I}^b}} \cdot \dot{\underset{\sim}{\omega}}^b + \underset{\sim}{\omega}^b \times \left(\underline{\underline{I}}^b \cdot \underset{\sim}{\omega}^b \right) = \underset{\sim}{\tau}^b \qquad (10.53)$$

(Euler equations)

The following is a complete formulation of the dynamical equations of rotational motion in the generalized coordinates Ψ, Θ, Φ

$$\underset{\sim}{\tau}^{s} = \sum_{\alpha} \left(\underset{\sim}{r}_{\alpha}^{s} - \underset{\sim}{r}_{CM}^{s} \right) \times \underset{\sim}{f}_{\alpha}^{s}$$

$$\underset{\sim}{\tau}^{b} = \underline{\underline{A}} \cdot \underset{\sim}{\tau}^{s}$$

$$\left.\begin{aligned}
\dot{\omega}_x^{\,b} &= \frac{\tau_x^{\,b}}{I_{xx}} + \frac{I_{yy} - I_{zz}}{I_{xx}}\, \omega_y^{\,b}\, \omega_z^{\,b} \\
\dot{\omega}_y^{\,b} &= \frac{\tau_y^{\,b}}{I_{yy}} + \frac{I_{zz} - I_{xx}}{I_{yy}}\, \omega_z^{\,b}\, \omega_x^{\,b} \\
\dot{\omega}_z^{\,b} &= \frac{\tau_z^{\,b}}{I_{zz}} + \frac{I_{xx} - I_{yy}}{I_{zz}}\, \omega_x^{\,b}\, \omega_y^{\,b}
\end{aligned}\right\} \text{(Euler equations)}$$

$$\underset{\sim}{\omega}^{s} = \underline{\underline{A}}^{T} \cdot \underset{\sim}{\omega}^{b}$$

$$\left.\begin{aligned}
\dot{\phi} &= -\omega_x^{s} \frac{\sin\phi \cos\theta}{\sin\theta} + \omega_y^{s} \frac{\cos\phi \cos\theta}{\sin\theta} + \omega_z^{s} \\
\dot{\theta} &= \omega_x^{s} \cos\phi + \omega_y^{s} \sin\phi \\
\dot{\psi} &= \omega_x^{s} \frac{\sin\phi}{\sin\theta} - \omega_y^{s} \frac{\cos\phi}{\sin\theta}
\end{aligned}\right\} \begin{array}{l}\text{Relationships between}\\ \text{rate of change in}\\ \text{Eulerian angles and}\\ \text{angular velocities}\\ \text{in lab frame.}\end{array}$$

where

$$\underline{\underline{A}} = \underline{\underline{A}} \left(\Phi, \theta, \psi \right) \qquad (10.48)$$

$$\underset{\sim}{r}_{\alpha}^{s} - \underset{\sim}{r}_{\beta}^{s} = \underline{\underline{A}}^{T} \left(\underset{\sim}{r}_{\alpha}^{b} - \underset{\sim}{r}_{\beta}^{b} \right) \;\; \forall \;\; \alpha, \beta \qquad (10.54)$$

This system of equations can be solved as an initial value problem.

DRAWBACK: Equations for $\dot{\phi}, \dot{\theta}, \dot{\psi}$ diverge as $\theta \to 0$, due to $(\sin\theta)^{-1}$ factor.
[Physical reason: For $\theta = 0$, axes z^s and z^b coincide, and Φ, Ψ become degenerate].

REMEDY: Switch axes x^s, y^s, z^s whenever $\theta \to 0$, or use QUATERNIONS (Evans, 1977)

10.4.4. Constraint Dynamics

For molecules with torsional degrees of freedom, formulating the dynamical equations in generalized coordinates is quite laborious. (e.g. n-butane : Ryckaert and Bellemans , 1975).
Preferable approach: Formulate and carry out the MD simulation in Cartesian coordinates, while at the same time accounting for bond constraints.

Objective of Constraint Dynamics: Integrate (Cartesian) equations of motion for a system of particles subject to holonomic constraints.

- No laborious transformations needed between laboratory and internal coordinates.
- Algorithm must ensure that constraints are satisfied (molecular shape preserved).

Applicability: GENERAL
→ Rigid, nonlinear polyatomics.
→ Rigid, linear molecules.
→ Flexible, hinged polyatomics.

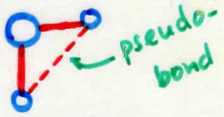
Can selectively impose rigid constraints on some parts of the molecule, without much effort.

Imposition of Constraints.

Bond-angle constraints best represented as pseudo-bond-length constraints.

e.g.

rigid H_2O:

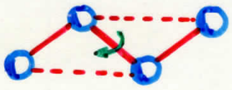


3 length constraints
(9 - 3 = 6 degrees of freedom)

rigid CH_4:

9 length constraints
(15 - 9 = 6 degrees of freedom)

rotatable C_4H_{10}
(united atom representation)
5 length constraints
($12 - 5 = 7$ degrees of freedom)

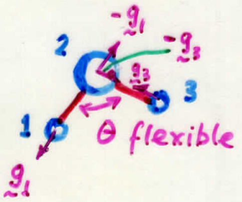


"TRIANGULATION" possible for every molecule.

- Each length constraint gives rise to a force acting along the bond or pseudobond.

- Constraint forces appear in the Newtonian equations of motion for the molecule.

e.g. Water with fixed bond lengths, flexible bond angle.



$\underset{\sim}{g}_1$ = constraint force on atom 1 due to bond 12
[$-\underset{\sim}{g}_1$ = constraint force on atom 2 due to bond 12]
$\underset{\sim}{g}_3$ = constraint force on atom 3 due to bond 23
[$-\underset{\sim}{g}_3$ = constraint force on atom 2 due to bond 23]

Dynamical equations:

$$m_1 \ddot{\underset{\sim}{r}}_1 = \underset{\sim}{f}_1 + \underset{\sim}{g}_1$$

systematic force, due to intermolecular interactions and those intramolecular interactions that are included explicitly in the potential.

$$m_3 \ddot{\underset{\sim}{r}}_3 = \underset{\sim}{f}_3 + \underset{\sim}{g}_3$$

$$m_2 \ddot{\underset{\sim}{r}}_2 = \underset{\sim}{f}_2 - \underset{\sim}{g}_1 - \underset{\sim}{g}_3$$

undetermined multipliers

$$\underset{\sim}{g}_1 = \lambda_{12} (\underset{\sim}{r}_1 - \underset{\sim}{r}_2)$$

$$\underset{\sim}{g}_3 = \lambda_{23} (\underset{\sim}{r}_3 - \underset{\sim}{r}_2)$$

(9 differential equations and 8 algebraic equations in 17 unknown functions $\underset{\sim}{r}_1(t)$, $\underset{\sim}{r}_2(t)$, $\underset{\sim}{r}_3(t)$, $\underset{\sim}{g}_1(t)$, $\underset{\sim}{g}_2(t)$, $\lambda_{12}(t)$, $\lambda_{13}(t)$)

Constraints:

$$\chi_{12} = (\underset{\sim}{r}_1 - \underset{\sim}{r}_2)^2 - d_{12}^2 = 0$$

$$\chi_{23} = (\underset{\sim}{r}_3 - \underset{\sim}{r}_2)^2 - d_{23}^2 = 0 \qquad (10.55)$$

constraint forces
directed along constrained
bond vectors.

$$\alpha=1: \quad m_1 \ddot{\underset{\sim}{r}}_1 = \underset{\sim}{f}_1 + \tfrac{1}{2}\lambda_{12} 2(\underset{\sim}{r}_1-\underset{\sim}{r}_2) + \tfrac{1}{2}\lambda_{12}(0) \Rightarrow m_1 \ddot{\underset{\sim}{r}}_1 = \underset{\sim}{f}_1 + \lambda_{12}(\underset{\sim}{r}_1-\underset{\sim}{r}_2)$$

$$\alpha=2: \quad m_2 \ddot{\underset{\sim}{r}}_2 = \underset{\sim}{f}_2 + \tfrac{1}{2}\lambda_{12}[-2(\underset{\sim}{r}_1-\underset{\sim}{r}_2)] + \tfrac{1}{2}\lambda_{23}[-2(\underset{\sim}{r}_3-\underset{\sim}{r}_2)] \Rightarrow m_2 \ddot{\underset{\sim}{r}}_2 = \underset{\sim}{f}_2 - \lambda_{12}(\underset{\sim}{r}_1-\underset{\sim}{r}_2) - \lambda_{23}(\underset{\sim}{r}_3-\underset{\sim}{r}_2$$

$$\alpha=3: \quad m_3 \ddot{\underset{\sim}{r}}_3 = \underset{\sim}{f}_3 + \tfrac{1}{2}\lambda_{12}(0) + \tfrac{1}{2}\lambda_{23}[2(\underset{\sim}{r}_3-\underset{\sim}{r}_2)] \Rightarrow m_3 \ddot{\underset{\sim}{r}}_3 = \underset{\sim}{f}_3 + \lambda_{23}(\underset{\sim}{r}_3-\underset{\sim}{r}_2)$$

with the constraints:
$$\chi_{12}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = (\underset{\sim}{r}_1-\underset{\sim}{r}_2)^2 - d_{12}^2 = 0$$
$$\chi_{23}(\underset{\sim}{r}_2,\underset{\sim}{r}_3) = (\underset{\sim}{r}_3-\underset{\sim}{r}_2)^2 - d_{23}^2 = 0$$

OMCT

This system of equations is equivalent to equations (2.4.28) above!

A numerical algorithm for constraint dynamics must calculate the constraint forces in parallel with integrating the equations of motion governing the system trajectory.

A Generic Constraint Dynamics Algorithm.

(Ryckaert, Ciccotti, Berendsen
J. Comput. Phys. 1977, 23, 327)

interaction potential,
not including constr. forces

Equations:
$$-\nabla_{\underset{\sim}{r}_i} V$$
total force on i
due to constraints.

$$m_i \ddot{\underset{\sim}{r}}_i = \underset{\sim}{f}_i + \underset{\sim}{g}_i \qquad (10.56)$$

Constraints: $\chi_{ij} \equiv \underset{\sim}{r}_{ji}^2 - d_{ij}^2 = 0$ (total of n_c constraints) (10.57)

def. $\underset{\sim}{r}_{ji} = \underset{\sim}{r}_i - \underset{\sim}{r}_j$

whence
$$\underset{\sim}{g}_i = \frac{1}{2}\sum_j \lambda_{ij} \nabla_{\underset{\sim}{r}_i} \chi_{ij} = \sum_j \lambda_{ij} \underset{\sim}{r}_{ji} \qquad (10.58)$$

Lagrange multiplier
Magnitude of constraint force along ij.

Must solve (10.56), (10.57), (10.58) simultaneously.

Algorithm:

- Use Verlet to advance (10.56) by one step, ignoring constraint forces (molecule distorted).

$$\underset{\nwarrow\text{distorted.}}{\mathbf{r}_i'}(t+\delta t) = 2\,\mathbf{r}(t) - \mathbf{r}(t-\delta t) + \frac{\delta t^2}{m_i}\,\mathbf{f}_i(t)$$

- Actual positions of atoms, taking into account constraint forces, will be (Verlet):

$$\underset{\nwarrow\text{actual}}{\mathbf{r}_i}(t+\delta t;\{\lambda_{ij}\}) \overset{(10.56)}{\overset{\downarrow}{=}} \underset{\nwarrow\text{distorted}}{\mathbf{r}_i'}(t+\delta t) + \frac{\delta t^2}{m_i}\,\underset{\nwarrow\text{restores molecular geometry.}}{\mathbf{g}_i}(t;\{\lambda_{ij}\}) \overset{(10.58)}{\overset{\downarrow}{=}} \mathbf{r}_i'(t+\delta t) - \frac{\delta t^2}{m_i}\sum_j \lambda_{ij}\,\mathbf{r}_{ij}\,(\qquad (10.59)$$

where λ_{ij} are yet undetermined.

- Substituting the above expressions for $\mathbf{r}_i(t+\delta t,\{\lambda_{ij}\})$ into the constraint eqs.(10.57), one obtains:

$$\left[\mathbf{r}_i(t+\delta t;\{\lambda_{ij}\}) - \mathbf{r}_j(t+\delta t;\{\lambda_{ij}\})\right]^2 - d_{ij}^2 = 0 \quad , \text{ i.e.} \qquad (10.60)$$

a set of algebraic equations in $\{\lambda_{ij}\}$.
Equations are quadratic in $\{\lambda_{ij}\}$. Solution must be obtained iteratively (usually, by successive substitutions). Solution of an $n_c \times n_c$ system of linear equations required at each iteration.

- Substitute determined $\{\lambda_{ij}\}$ into expressions for $\mathbf{r}_i(t+\delta t,\{\lambda_{ij}\})$ and thus determine actual atomic positions at $t+\delta t$. (integration step completed). Ready to take next step.

The SHAKE algorithm (Ryckaert et al., J. Comput. Phys. 1977, 23, 327)

- Avoids numerical solution of the quadratic $n_c \times n_c$ system in $\{\lambda_{ij}\}$.
- Goes through the constraint equations one by one, cyclically, adjusting the coordinates so as to satisfy each equation in turn.
- Procedure iterated, until all constraints are satisfied within prescribed tolerance.
  - Very popular in biological macromolecule simulation packages.
  - Can be inefficient, especially in the presence of bond angle constraints.

The RATTLE algorithm (Andersen, J. Comput. Phys. 1983, 52, 24-34)

A modification of the SHAKE algorithm, employing the velocity version of the Verlet algorithm.

The algorithm of Edberg, Evans, and Morriss (J. Chem. Phys. 1986, 84, 6933)

In place of quadratic equations for the constraint forces $\{\lambda_{ij}\}$, use a linear system of equations in $\{\lambda_{ij}\}$.

Instead of the constraint equations (10.57), use their second time derivatives:

$$(10.57): \ \underset{\sim}{r}_{ji}^{2} - d_{ij}^{2} = 0 \ \Rightarrow \ \cancel{2}\, \underset{\sim}{r}_{ji} \cdot \dot{\underset{\sim}{r}}_{ji} = 0 \ \Rightarrow \ \underline{\underset{\sim}{r}_{ji} \cdot \ddot{\underset{\sim}{r}}_{ji} + (\dot{\underset{\sim}{r}}_{ji})^{2} = 0} \qquad (10.61)$$

One then solves the following system of differential and algebraic equations simultaneously:

$$m_i \ddot{\underset{\sim}{r}}_i = \underset{\sim}{f}_i + \sum_j \lambda_{ij} \underset{\sim}{r}_{ji} \qquad [(10.56),\ (10.58)] \qquad (10.62)$$

$$\underset{\sim}{r}_{ji} \cdot \ddot{\underset{\sim}{r}}_{ji} + (\dot{\underset{\sim}{r}}_{ji})^2 = 0 \qquad (10.61)$$

- Velocities enter the formulation explicitly.
- Determination of the $\{\lambda_{ij}\}$ requires the solution of a linear matrix equation.
- Standard predictor-corrector or velocity Verlet algorithm usable.

Molecular shape is distorted gradually as numerical error accumulates. (Note that bond lengths d_{ij} are not involved in the dynamical equations!)
Periodic restoration of correct molecular geometry by minimizing the functions:

$$\Phi = \sum_{ij} \left(\underset{\sim}{r}_{ij}^2 - d_{ij}^2\right)^2 \qquad \text{(bond penalty function)} \qquad (10.63)$$

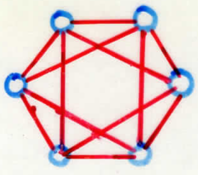
$$\Psi = \sum_{ij} \left(\underset{\sim}{r}_{ij} \cdot \dot{\underset{\sim}{r}}_{ij}\right)^2 \qquad \text{(velocity penalty function)} \qquad (10.64)$$

Constraint dynamics of linear and planar polyatomic molecules

Problem:

(CO_2)

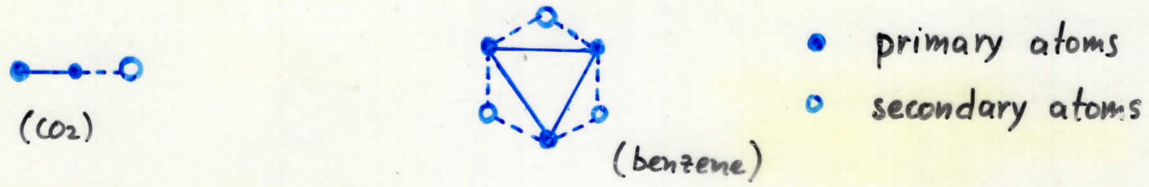
Constraint MD should employ $9-5=4$ constraints. It is impossible to write four bond constraints for a linear triatomic!



(benzene)

Constraint MD should employ $18-6=12$ constraints
Constraint matrix is singular, because all bond constraints that can be written lie on a plane.

Solution: Monitor the dynamics of a basic subset of "primary" atoms. Forces on secondary atoms transferred to primary atoms via bonds.



(Ciccotti, Ferrario, Ryckaert Molec. Phys. 1982, 47, 1253)

10.4.5. General Guidelines: Which Algorithm should One Choose?

- Simple fluid (monatomic) systems

  Verlet velocity algorithm recommended.

- Rigid polyatomic systems

  competitive { MD in generalized coordinates (quaternions with modified Verlet leap-frog)
  Constraint methods, dealing with a rigid core of "primary" atoms.

- Flexible polyatomic systems
  - Use constraint methods, and not generalized coordinates (Edberg-Evans-Morriss, RATTLE).
  - Best constrain bonds, but not bond angles (dynamics of conformational isomerization affected).

10.4.6. MOLECULAR DYNAMICS IN ENSEMBLES OTHER THAN NVE

Conventional MD carried out in NVE ensemble.

Calculation of temperature: $T = \langle \mathcal{T} \rangle \leftarrow$ ensemble average, estimated as time average at equilibrium.

"Instantaneous temperature"

$$\mathcal{T} = \frac{2\mathcal{K}}{(3N-N_c)k_B} = \frac{1}{(3N-N_c)k_B}\sum_{i=1}^{N}\frac{|\underset{\sim}{p}_i|^2}{m_i} \qquad (10.65)$$

N: number of atoms in system, each with mass m_i and momentum $\underset{\sim}{p}_i$

N_c: total number of constraints; includes

- internal constraints in molecular model (e.g., fixed bond lengths, bond angles)
- global constraints on system (e.g., fixed total momentum)

In a conventional $NVE\underset{\sim}{P}$ - MD simulation with $\underset{\sim}{P}=0$, one must use $N_c = 3$ to calculate the instantaneous temperature from the total kinetic energy.

Calculation of pressure: $P = \langle \mathcal{P} \rangle$ (virial theorem)

"Instantaneous pressure"

$$\mathcal{P} = \rho k_B \mathcal{T} + \frac{1}{V}\mathcal{W}^{int} =$$

$$= \rho k_B \mathcal{T} + \frac{1}{3V}\sum_i \sum_{j>i} (\underset{\sim}{r}_i - \underset{\sim}{r}_j)\cdot \underset{\sim}{F}_{ij} \leftarrow \text{on } i \text{ due to } j \qquad (10.66)$$

Fluctuation relations: e.g. $\langle \delta \mathcal{V}^2 \rangle = \langle \delta \mathcal{K}^2 \rangle = \frac{3}{2} N k_B^2 T^2 \left(1 - \frac{3Nk_B}{2C_v}\right)$ (10.67)

Since the seminal paper of H.C. Andersen (1980), there has been much interest in designing MD methods that sample ensembles other than NVE.

Techniques for non-NVE MD:

- Heuristic methods (e.g., "stochastic collisions" rescaling atomic velocities for const. T).
- Constraint methods (e.g., imposition of nonholonomic constraint $\sum_i m_i \dot{\underset{\sim}{r}}_i^2 = \frac{3}{2} N k_B T$ for const. T ; Evans et al.)
- Extended System, or Extended Ensemble Methods.

Extended System MD Methods.

OBJECTIVE : Simulate the dynamics of a system under a set of macroscopic constraints other than constant N, V, E.

BASIC IDEA

- Introduce one or more additional degrees of freedom (along with microscopic degrees of freedom), corresponding to one or more macroscopic quantities. Physically, each additional degree of freedom represents a "reservoir", with which the original system can interact.

- Associated with each new degree of freedom are a "coordinate", a "velocity" (rate of change), and a "mass" (inertia).

- Assign a potential energy and a kinetic energy to each additional degree of freedom.

- Write a Lagrangian for the extended system, incorporating original system and reservoir contributions.

- Derive the equations of motion for all degrees of freedom from the Lagrangian. These, in general, will be different from the Newtonian equations of motion describing the time evolution of the system in NVE dynamics.

- Numerically integrate the extended system equations of motion.

- If the potential energy and kinetic energy expressions for the new degrees of freedom have been chosen appropriately, the steady-state probability density distribution in the phase space of the original system, as generated by the extended system dynamics, follows the desired ensemble.

- There is an extended system Hamiltonian (derivable from the Lagrangian), which no longer corresponds to the total energy of the original system, but is conserved by the dynamics.

An extended System method for MD in the NVT ensemble

Nose', S. Molec. Phys. 1984, 52, 255-268

- Extra degree of freedom: s
  Allows for energy to flow dynamically between system and reservoir, and change the kinetic energy of the system.
  Set reservoir temperature: T_{eq}.
  "Thermal inertia" (mass) term associated with extra degree of freedom: Q

- Definition of s: It appears as a scaling factor for particle velocities:

$$\underset{\sim}{v} = s\,\dot{\underset{\sim}{r}} \qquad (10.68)$$

derivatives of position vectors with respect to simulation time

actual velocities of particles, defined wrt real time.

In essence, s is a scaling factor for time:

$$(\text{Real time step}) = (\text{simulation time step}) \cdot \frac{1}{s} \qquad (10.69)$$

- Extra potential energy term: $\mathcal{V}_s = (f+1)\, k_B\, T_{eq} \ln s$ (10.70)

set temperature.

number of degrees of freedom of original system.
$f = 3N-3$, if total $\underset{\sim}{P}$ fixed.

Extra kinetic energy term: $\mathcal{K}_s = \frac{1}{2} Q \dot{s}^2$ (10.71)

"inertia"

- Extended system Lagrangian:

$$\mathcal{L}' = \mathcal{K}' - \mathcal{V}' = \mathcal{K} + \mathcal{K}_s - \mathcal{V} - \mathcal{V}_s =$$

original system

new degree of freedom

$$= \frac{1}{2}\sum_{i=1}^{N} m_i s^2 \dot{\underset{\sim}{r}}_i^2 + \frac{1}{2} Q \dot{s}^2 - \mathcal{V}(\underset{\sim}{r}) - (f+1)\, k_B\, T_{eq} \ln s \qquad (10.72)$$

- Equations of motion derived from

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}'}{\partial \dot{q}_k}\right) - \frac{\partial \mathcal{L}'}{\partial q_k} = 0 \qquad \underset{\sim}{q} = \begin{bmatrix} \underset{\sim}{r}_1 \\ \vdots \\ \underset{\sim}{r}_N \\ s \end{bmatrix}$$

Dynamical equations:

$$\left.\begin{aligned} \ddot{\underset{\sim}{r}}_i &= \frac{\underset{\sim}{f}_i}{m_i s^2} - 2\,\frac{\dot{s}\,\dot{\underset{\sim}{r}}_i}{s} \\ Q\,\ddot{s} &= \sum_{i=1}^{N} m_i\, s\, \dot{\underset{\sim}{r}}_i^{\,2} - (f+1)\,\frac{k_B}{s}\,T_{eq} \end{aligned}\right\} \text{integrable, e.g. by Gear predictor-corrector scheme} \qquad (10.73)$$

- The generalized momenta of the extended system will be $p_k = \dfrac{\partial \mathcal{L}'}{\partial \dot{q}_k}$

$$\underset{\sim}{p}_i = \frac{\partial \mathcal{L}'}{\partial \dot{\underset{\sim}{r}}_i} = m_i\, s^2\, \dot{\underset{\sim}{r}}_i$$

$$p_s = \frac{\partial \mathcal{L}'}{\partial \dot{s}} = Q\,\dot{s}$$

A conserved quantity of the dynamics will be the extended system Hamiltonian:

$$\mathcal{H}'(\underset{\sim}{p}, \underset{\sim}{q}) = \sum_k \dot{q}_k\, p_k - \mathcal{L}(\underset{\sim}{q}, \dot{\underset{\sim}{q}})$$

$$(10.74)$$

$$\mathcal{H}' = \frac{1}{2}\sum_i m_i s^2 \dot{\underset{\sim}{r}}_i^{\,2} + \underbrace{\frac{1}{2}\,Q\,\dot{s}^2}_{\text{reservoir kinetic energy}} + \mathcal{V}(\underset{\sim}{r}) + \underbrace{(f+1)\,k_B\,T_{eq}\,\ln s}_{\text{reservoir potential energy}}$$

$\mathcal{H}'$ is maintained at a constant value E'.

Nosé presents a proof that the partition function corresponding to this Hamiltonian is

$$Q_{NVE'} = \frac{1}{(f+1)\,h}\left(\frac{2\pi Q}{k_B T_{eq}}\right)^{1/2} \exp\left(\frac{E'}{k_B T_{eq}}\right)\cdot \frac{1}{N!\,h^f}\int d\underset{\sim}{p}'\int d\underset{\sim}{r}\, \underbrace{\exp\Big[-\overset{\text{Hamiltonian of original system}}{\overset{\downarrow}{\mathcal{H}}}(\underset{\sim}{p}',\underset{\sim}{r})\cdot\frac{1}{k_B T_{eq}}\Big]}_{P_{NVT}(\underset{\sim}{p}',\,\underset{\sim}{r})} \qquad (10.75)$$

where $\underset{\sim}{p}_i' = \dfrac{\underset{\sim}{p}_i}{s} = m_i\, s\, \dot{\underset{\sim}{r}}_i = m_i\, \underset{\sim}{v}_i$, actual momentum vector.

This gives a canonical ensemble distribution in the variables $\underset{\sim}{p}', \underset{\sim}{r}$.

For any function of atomic coordinates and momenta,

$$\underbrace{\left\langle \mathcal{A}\left(\frac{\underset{\sim}{p}}{s}, \underset{\sim}{r}\right)\right\rangle'}_{\text{extended system averaging}} = \underbrace{\left\langle \mathcal{A}\left(\underset{\sim}{p}_i', \underset{\sim}{r}\right)\right\rangle_{NVT}}_{\text{original system, sampled according to canonical ensemble.}} \qquad (10.76)$$

Instantaneous temperature $\mathcal{T} = \frac{2}{f k_B} \sum_{i=1}^{N} \frac{\underset{\sim}{p}_i^2}{2 m_i s^2} = \frac{2}{f k_B} \sum_{i=1}^{N} \frac{m_i}{2} \underset{\sim}{v}_i^2$

Average $\langle \mathcal{T} \rangle = \underset{\nwarrow \text{ preset}}{T_{eq}}$

Variance $\langle (\delta \mathcal{T})^2 \rangle = \langle (T - T_{eq})^2 \rangle = T_{eq}^2 \cdot \frac{2}{f}$

Note that simulation time in the Nosé MD algorithm is not the same as real time! Equal simulation time steps may be unequal in real time. Averaged real time duration of the simulation obtained by multiplying simulation time by $\langle s^{-1} \rangle$.

Role of the inertial factor Q.

Q affects the dynamics!

- $Q \to \infty$: Infinitely slow energy transfer between system and reservoir. NVE MD recovered.

- Q very small: Perturbation of the dynamics relative to microcanonical ensemble, especially as concerns collective dynamic behavior.

- For "reasonable" choice of Q, it is empirically confirmed (but not rigorously proven) that estimates of dynamic characteristics, such as the self-diffusivity, coincide with corresponding estimates from NVE simulation.

- "Reasonable" Q chosen by looking at s-oscillations. Period of s-oscillation, $t_0 = 2\pi \left(\frac{Q \langle s^2 \rangle}{2 f k_B T_{eq}}\right)^{1/2}$. Nosé recommends $t_0 = 1\,\text{ps}$.

Hoover, W.G. Phys. Rev. A 1985, 31, 1695-1697 modified Nosé's constant temperature technique to arrive at an equivalent set of dynamical equations that are free of time scaling. (Nosé-Hoover thermostat).

An Extended System Method for MD in the NPH ensemble

(constant pressure MD: Andersen, H.C. J. Chem. Phys. 1980, 72, 2384).

- Extra degree of freedom: Box volume, V. (pulsating box; walls substituted by "piston", allowing interactions with a pressure reservoir. Inertial property resisting volume changes (piston "mass") W.

  Use scaled molecular positions and velocities:

$$\underset{\sim}{r} = V^{1/3}\, \underset{\sim}{s} \quad , \quad \underset{\sim}{v} = V^{1/3}\, \dot{\underset{\sim}{s}} \qquad (10.77)$$

- Extra potential energy term: $\mathcal{V}_V = P_{eq}\, V$
  Extra kinetic energy term: $\mathcal{K}_V = \frac{1}{2} W \dot{V}^2$ (10.78)

- Lagrangian formulation for the extended system leads to the equations of motion:

$$\ddot{\underset{\sim}{s}}_i = \frac{1}{m_i V^{1/3}}\, \underset{\sim}{f_i} - \frac{2}{3}\, \dot{\underset{\sim}{s}}_i\, \frac{\dot{V}}{V}$$

$$\ddot{V} = (\mathcal{P} - P_{eq}) \cdot \frac{1}{Q} \quad ; \quad \mathcal{P} = \frac{1}{3V} \left(\sum_i m_i \underset{\sim}{v}^2 + \sum_{i<} \sum_j (\underset{\sim}{r_i} - \underset{\sim}{r_j}) \cdot \underset{\sim}{f_{ij}} \right) \qquad (10.79)$$

- Conserved quantity: Hamiltonian of the extended system,

$$\mathcal{H}' = V^{2/3} \sum_{i=1}^{N} \frac{m_i \dot{\underset{\sim}{s}}_i^2}{2} + \mathcal{V}(V^{1/3} \underset{\sim}{s}_1, \dots, V^{1/3} \underset{\sim}{s}_N) + \frac{1}{2} W \dot{V}^2 + P_{eq} V \qquad (10.80)$$

- Andersen gives a rigorous proof that the equilibrium distribution of microstates generated by the extended system dynamics corresponds to an NPH ensemble (H = enthalpy) of the original system.

Enthalpy of original system:

$$H = \mathcal{H}' - \frac{1}{2} W \langle \dot{V}^2 \rangle' = \mathcal{H}' - \frac{1}{2} k_B \langle T \rangle'$$

— kinetic energy associated with volume fluctuations.

Role of the inertial factor ("piston mass") W

- Large W → slow volume fluctuations (W→∞: NVE dynamics)
- Small W → fast volume fluctuations, distortion of system dynamics.
- Andersen recommends choosing W so that the period of volume fluctuations is roughly equal to the time for a sound wave to cross the simulation box.

Mention Winkler NPT

Other developments

- Parrinello, M.; Rahman, A. Phys. Rev. Lett. 1980, 45, 1196; J. Appl. Phys. 1981, 52, 7182; J. Chem. Phys. 1982, 76, 2662.
  Extension of Andersen method to allow for fluctuations in the box shape. ($N\,\underline{\underline{t}}\,H$ - Molecular Dynamics). Application: Phase transformations in solids.

- Nosé, S. J. Chem. Phys. 1984, 81, 511: NPT (or $N\,\underline{\underline{t}}\,T$) Molecular Dynamics, by combination of Andersen (Parrinello-Rahman) and Nosé methods.

- Nosé, S.; Klein, M.L. Phys. Rev. Lett. 1983, 50, 1207; J. Chem. Phys. 1983, 78, 6928; Molec. Phys. 1983, 50, 1055: Extension of extended system methods to molecular syste

- Car, R.; Parrinello, M. Phys. Rev. Lett. 1985, 55, 2471: Unified approach for MD and Quantum Mechanical Density Functional Theory, by inclusion of electronic degrees of freedom in extended system. Application: Si and GaAs melts, H_2O liquid

10.5. STRUCTURE FROM MOLECULAR SIMULATIONS

Information stored in tape file

MC: system configuration: $\underset{\sim}{r}_i$, $\underset{\sim}{\psi}_i$ ← (Euler angles)

potential energy $\mathcal{V}$, virial $\mathcal{W}$, monitored orientational and conformational characteristics of molecules.

Store every 5th or 10th cycle (1 cycle = N attempted moves).

MD: time t

system configuration $\underset{\sim}{r}_i$ (with/without periodic boundary conditions), $\underset{\sim}{\psi}_i$

Velocities $\underset{\sim}{v}_i$, $\underset{\sim}{\omega}_i$

Forces $\underset{\sim}{f}_i$, torques $\underset{\sim}{\tau}_i$

Energy E, instantaneous $\mathcal{V}$, $\mathcal{T}$, $\mathcal{W}$

Store every 5th or 10th integration time step.

Block average analysis can be used to determine the degree of correlation between stored configurations and estimate the error in obtained ensemble averages. (See Allen and Tildesley, p 192).

Accumulation of Pair Distribution Functions.

In an isotropic material system,

$$g(r) = \frac{\rho(r)}{\rho} \qquad (10.81)$$

← local density of particles within a spherical shell of radius r to r+dr, centered at a given particle in the fluid, and averaged over all configurations

↖ mean (macroscopic) density

In a simulation, analyze stored configurations to determine distances between all minimum image pairs.

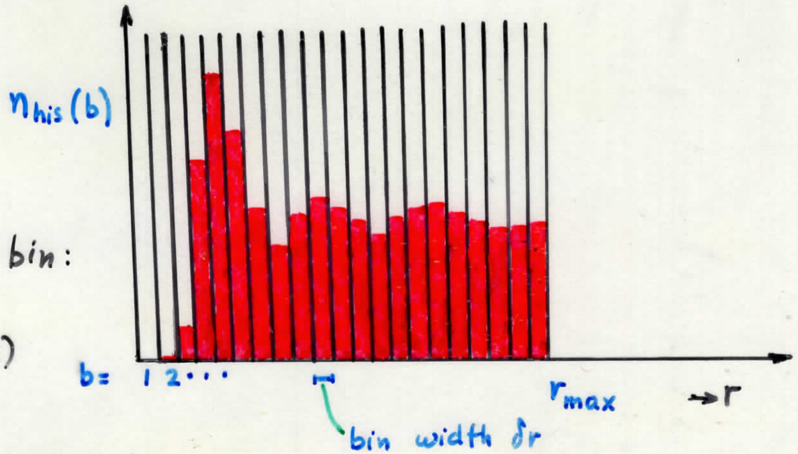
$$g(r) = \frac{\text{Number of particles at distance } r \text{ to } r+\delta r \text{ from a central particle}}{\text{Number of particles at distance } r \text{ to } r+\delta r \text{ from a central particle in an ideal gas system of the same density.}} \qquad (10.82)$$

Procedure for computing numerator of (10.82):

- Discretize r-axis between 0 and r_{max} into bins, of width δr.
  Let b = index of bin between r and $r+\delta r$.

- Loop over all stored configurations

```
Loop over all stored configurations
    Loop over all pairs of particles, (i,j), in a given configuration.
        Calculate minimum image distance $(r_{ij})_{min}$
        Sort distance $(r_{ij})_{min}$, i.e., determine the bin b it falls into.
        Add 2 to the contents of the bin into which $(r_{ij})_{min}$ falls
            (1 for each atom involved)    $n_{his}(b) = n_{his}(b) + 2$
```



- Numerator of (10.82) for each bin:

$$n(b) = \frac{n_{his}(b)}{N \cdot T_{run}} \qquad (2.5.2)$$

N: total number of particles

T_{run}: total number of configurations analyzed

- Denominator of (2.5.1) for each bin:

$$n^{id}(b) = \frac{4\pi\rho}{3}\left[(r+\delta r)^3 - r^3\right]$$

← volume of spherical shell betw. r and r+dr

(This expression is valid for $r_{max} \leq L/2$, where L = box edgelength. Structural information can be accumulated up to $r_{max} = L\sqrt{3}/2$. For calculating $n^{id}(b)$ in the case $r_{max} > L/2$, see J. Chem. Phys. 1985, 25, 180)

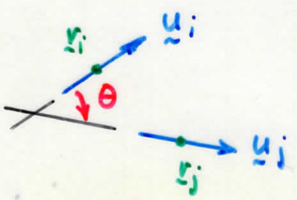
- Calculate g from histogram information:

$$g\left(r+\tfrac{1}{2}\delta r\right) = \frac{n(b)}{n^{id}(b)} \qquad (10.83)$$

NOTES

- In molecular fluids, site-site pair distribution functions $g^{\alpha\beta}(r)$ can be accumulated in this way for all pairs of sites (α,β).
- X-ray and neutron diffraction patterns can be computed from pair distribution functions and compared against experiment.

Quantifying Molecular Orientation



$\underset{\sim}{u}_i$: unit vector fixed rigidly on a molecule (e.g., a principal axis, or a bond vector, or an end-to-end vector)

$$P_2(\cos\theta) = \frac{1}{2}\left[3(\underset{\sim}{u}_i\cdot\underset{\sim}{u}_j)^2 - 1\right] \qquad (10.84)$$

provides info. on relative orientation of i, j.

"order parameter"

Useful to accumulate $\langle P_2(\cos\theta)\rangle_{|\underset{\sim}{r}_i-\underset{\sim}{r}_j|=r} = \frac{1}{2}\left[3\langle \underset{\sim}{u}_i\cdot\underset{\sim}{u}_j\rangle^2_{|\underset{\sim}{r}_i-\underset{\sim}{r}_j|=r} - 1\right]$ as a function of r

Order parameter = 1 → parallel orientation; −1/2 → perpendicular; 0 → random orientation

10.6. DYNAMICAL INFORMATION FROM EQUILIBRIUM M.D.

Time Correlation Functions

Consider a system at equilibrium under given external constraints. The probability distribution of the system in phase space will conform to an equilibrium ensemble, with density $\rho^{eq}(\underset{\sim}{X}^N) = \rho^{eq}(\underline{p}^N, \underline{q}^N)$

Let
$$\mathcal{A}(\underset{\sim}{X}^N) = \mathcal{A}(\underset{\sim}{p}^N, \underset{\sim}{q}^N) \qquad (10.85)$$
$$\mathcal{B}(\underset{\sim}{X}^N) = \mathcal{A}(\underline{p}^N, \underline{q}^N)$$

two functions of the phase-space representative point (microscopic state) of the system. As the microscopic state changes with time, so does the value of $\mathcal{A}$ and $\mathcal{B}$. We will use the notation
$$\mathcal{A}(t) \equiv \mathcal{A}(\underline{p}^N(t), \underline{q}^N(t)) \qquad (10.86)$$
$$\mathcal{B}(t) \equiv \mathcal{B}(\underset{\sim}{p}^N(t), \underline{q}^N(t))$$

Furthermore, we will use the symbolism $\delta\mathcal{A}(t)$, $\delta\mathcal{B}(t)$ to denote the deviations between the instantaneous values of $\mathcal{A}$ and $\mathcal{B}$ along a dynamical trajectory and the corresponding ensemble averaged values.

equil. ensemble average, indep. of time
$$\delta\mathcal{A}(t) \equiv \mathcal{A}(t) - \langle\mathcal{A}(t)\rangle = \mathcal{A}(t) - \langle\mathcal{A}\rangle \qquad (10.87)$$
$$\delta\mathcal{B}(t) \equiv \mathcal{B}(t) - \langle\mathcal{B}(t)\rangle = \mathcal{B}(t) - \langle\mathcal{B}\rangle$$

We define the non-normalized time correlation function between $\mathcal{A}$ and $\mathcal{B}$ by

$$C_{\mathcal{A}\mathcal{B}}(t) \equiv \langle \delta\mathcal{A}(t_1)\,\delta\mathcal{B}(t_1+t)\rangle = \langle [\mathcal{A}(t_1) - \langle\mathcal{A}\rangle][\mathcal{B}(t_1+t) - \langle\mathcal{B}\rangle]\rangle \qquad (10.88)$$

For a system at equilibrium, the ensemble average on the right-hand side of (10.89) will not depend on the time origin t_1, but only on the time separation t. Also, by the ergodic hypothesis, the ensemble averages in (10.89) can be substituted by time averages over all time origins t_1.

$$C_{\mathcal{A}\mathcal{B}}(t) = C_{\mathcal{A}\mathcal{B}}(-t) = \langle \delta\mathcal{A}(0)\, \delta\mathcal{B}(t) \rangle = \langle \delta\mathcal{A}(t)\, \delta\mathcal{B}(0) \rangle \qquad (10.90)$$

Here, we will restrict our attention to the case where $\mathcal{A}$ and $\mathcal{B}$ are the same quantity. We will call

$$C_{\mathcal{A}\mathcal{A}}(t) = \langle \delta\mathcal{A}(t_1)\, \delta\mathcal{A}(t_1+t) \rangle = \langle \delta\mathcal{A}(0)\, \delta\mathcal{A}(t) \rangle \qquad (10.91)$$

the non-normalized (time) autocorrelation function of $\mathcal{A}$.

We define the normalized autocorrelation function of $\mathcal{A}$ as

$$c_{\mathcal{A}\mathcal{A}}(t) = \frac{C_{\mathcal{A}\mathcal{A}}(t)}{C_{\mathcal{A}\mathcal{A}}(0)} = \frac{\langle \delta\mathcal{A}(t)\, \delta\mathcal{A}(0) \rangle}{\langle (\delta\mathcal{A})^2 \rangle \leftarrow \text{a measure of the fluctuation of } \mathcal{A}.} \qquad (10.92)$$

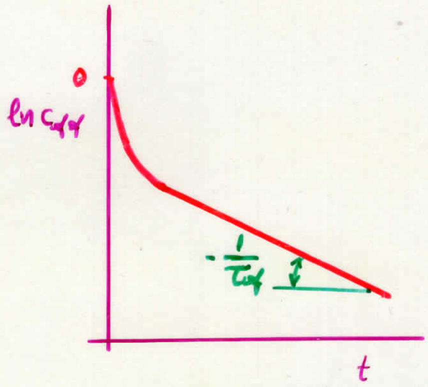
$c_{\mathcal{A}\mathcal{A}}$ assumes a value of 1 for $t=0$ (perfect correlation at the time origin). It decays as $t>0$, ultimately approaching zero as $t \to \infty$. Physically, $c_{\mathcal{A}\mathcal{A}}$ measures how the property $\mathcal{A}$ loses memory of its initial value as a result of molecular motion in the system. The characteristic time, over which this memory persists, can be defined by

$$\tau_{\mathcal{A}} = \int_0^\infty c_{\mathcal{A}\mathcal{A}}(t)\, dt \qquad \text{(correlation time)} \qquad (10.93)$$

For many (but not all!) systems and properties, $c_{\alpha\alpha}(t)$ is found to decay exponentially with time at long times.

Autocorrelation functions are of great interest, because

- they give a picture of molecular motion in a system
- the time integrals $\tau_{\alpha\alpha}$ are often directly related to macroscopic transport coefficients.
- their Fourier transforms $\hat{c}_{\alpha\alpha}(\omega)$ are often related to experimental spectra.



$\tau_{\alpha\alpha}$: correlation time
"relaxation" time

An example: Velocity autocorrelation function in a fluid.

$\delta v_{i\alpha} \equiv v_{i\alpha}$, as $\langle v_{i\alpha}\rangle = 0$

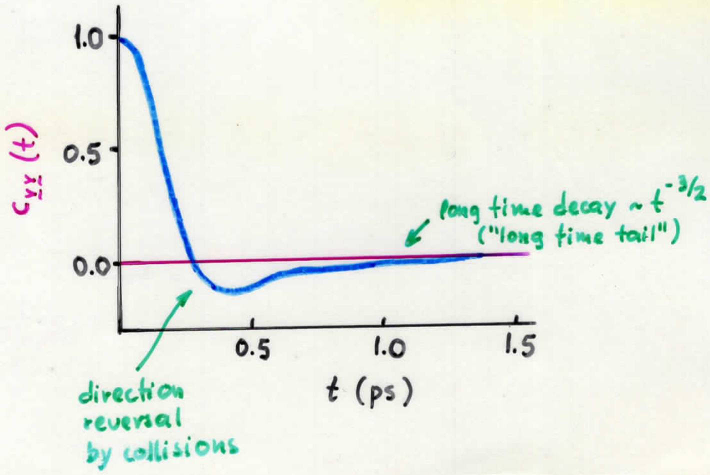
useful in simulations (increases samplesize

$$C_{v_\alpha v_\alpha}(t) = \langle v_{i\alpha}(t)\, v_{i\alpha}(0)\rangle = \frac{1}{N}\left\langle \sum_i v_{i\alpha}(t)\, v_{i\alpha}(0)\right\rangle \qquad (10.94)$$

$$C_{\underset{\sim}{v}\underset{\sim}{v}}(t) = \langle \underset{\sim}{v}_i(t)\, \underset{\sim}{v}_i(0)\rangle = C_{v_x v_x}(t) + C_{v_y v_y}(t) + C_{v_z v_z}(t) \qquad (10.95)$$

$$c_{\underset{\sim}{v}\underset{\sim}{v}}(t) = \frac{C_{\underset{\sim}{v}\underset{\sim}{v}}(t)}{C_{\underset{\sim}{v}\underset{\sim}{v}}(0)} = \frac{C_{\underset{\sim}{v}\underset{\sim}{v}}(t)}{\langle \underset{\sim}{v}^2\rangle} = \frac{C_{\underset{\sim}{v}\underset{\sim}{v}}(t)}{\frac{3k_BT}{m}} = \frac{m}{3k_BT}\langle \underset{\sim}{v}_i(t)\cdot \underset{\sim}{v}_i(0)\rangle \qquad (10.96)$$

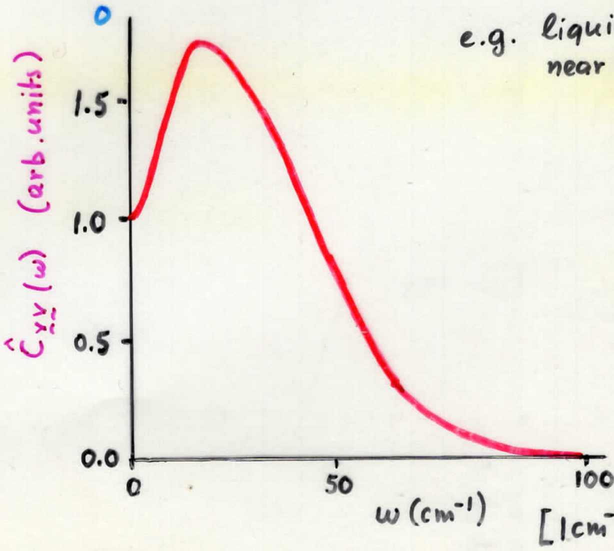
$$\hat{C}_{\underset{\sim}{v}\underset{\sim}{v}}(\omega) = \int_{-\infty}^{+\infty} C_{\underset{\sim}{v}\underset{\sim}{v}}(t)\, e^{-i\omega t}\, dt = 2\int_0^{\infty} C_{\underset{\sim}{v}\underset{\sim}{v}}(t) \cos\omega t \, dt \qquad (10.97)$$



long time decay $\sim t^{-3/2}$
("long time tail")

direction reversal by collisions

e.g. liquid argon near triple pt.



$[1\text{cm}^{-1} = 0.03\ \text{ps}$

Transport Coefficients describe the response (flux) elicited in a system by the imposition of a perturbation (driving force) that causes the system to depart from equilibrium.

Autocorrelation Functions describe the rate at which spontaneous fluctuations created within a system at equilibrium die out with time.

Linear response theory establishes relations between autocorrelation functions and transport coefficients in a system not too far from equilibrium. A prominent role in these relations is played by autocorrelation functions of the type $\langle \dot{\mathcal{A}}(t)\, \dot{\mathcal{A}}(0) \rangle$. These appear in relationships of the form:

$\delta\dot{\mathcal{A}}(t) = \dot{\mathcal{A}}(t)$ for $\langle \dot{\mathcal{A}} \rangle = 0$

$$\gamma = \int_0^\infty dt \, \langle \dot{\mathcal{A}}(t)\, \dot{\mathcal{A}}(0) \rangle = \int_0^\infty dt \, C_{\dot{\mathcal{A}}\dot{\mathcal{A}}}(t) \qquad (10.98)$$

(GREEN- KUBO RELATION)

where γ is a transport coefficient, within a multiplicative constant.

Example

$$D_{s,xx} = \int_0^\infty dt \, \langle \dot{x}_i(t)\, \dot{x}_i(0) \rangle = \int_0^\infty dt \, \langle v_{ix}(t)\, v_{ix}(0) \rangle \qquad (10.99)$$

(self- diffusivity along x- direction)

$$D_s = \frac{1}{3}\int_0^\infty dt \, \langle \underset{\sim}{v}_i(t) \cdot \underset{\sim}{v}_i(0) \rangle = \frac{1}{3}\left(D_{s,xx} + D_{s,yy} + D_{s,zz}\right) = \frac{1}{3}\mathrm{Tr}(\underset{=}{D_s}) \qquad (10.100)$$

(Green- Kubo relation for orientationally averaged self- diffusivity)

Equivalent to the expression (2.6.13) is the relation:

$$2\gamma t = \langle [\mathcal{A}(t) - \mathcal{A}(0)]^2 \rangle \qquad (10.101)$$

(EINSTEIN RELATION)

holds for $t >> t_{\dot{\mathcal{A}}}$, long times.

Example

$$2 D_{s,xx} t = \langle [x_i(t) - x_i(0)]^2 \rangle, \text{ or } D_{s,xx} = \lim_{t\to\infty} \left\{ \langle [x_i(t) - x_i(0)]^2 \rangle / 2t \right\} \qquad (10.10$$

$$2 D_s t = \frac{1}{3}\langle [\underset{\sim}{r}_i(t) - \underset{\sim}{r}_i(0)]^2 \rangle, \text{ or } D_s = \lim_{t\to\infty} \frac{\langle [\underset{\sim}{r}_i(t) - \underset{\sim}{r}_i(0)]^2 \rangle}{6t} \qquad (10.103)$$

(Einstein equation for self- diffusivity)

Interdiffusion Coefficient, D in a binary system.

Green - Kubo: $$D = \frac{1}{3N}\left(\frac{\partial^2(\beta G/N)}{\partial x_1^2}\right)_{P,T}\int_0^\infty \langle \underset{\sim}{j}^c(t)\cdot\underset{\sim}{j}^c(0)\rangle\, dt \qquad (10.104)$$

G = total Gibbs energy

N = total number of molecules

x_ν = mole fraction of species ν $(\nu=1,2)$; $x_\nu = \frac{N_\nu}{N}$

$\underset{\sim}{j}^c(t)$ = microscopic interdiffusion current

$$\underset{\sim}{j}^c(t) = x_2\,\underset{\sim}{j}^1(t) - x_1\,\underset{\sim}{j}^2(t) \qquad (10.105)$$

$$\underset{\sim}{j}^\nu(t) = \sum_{i=1}^{N_\nu}\underset{\sim}{u}_i(t) = \text{Number of molecules of species } \nu \times \text{velocity of center of mass of molecules of species } \nu \qquad (10.106)$$

Sheer Viscosity η

Green - kubo: $$\eta = \frac{V}{k_B T}\int_0^\infty dt\,\langle \mathcal{P}_{\alpha\beta}(t)\,\mathcal{P}_{\alpha\beta}(0)\rangle \;,\; \alpha\neq\beta \qquad (10.107)$$

$\mathcal{P}_{\alpha\beta}$: a nondiagonal component of the instantaneous pressure tensor

$$\mathcal{P}_{\alpha\beta} = \frac{1}{V}\left(\sum_i \frac{p_{i\alpha}\,p_{i\beta}}{m_i} + \sum_i r_{i\alpha} f_{i\beta}\right) \quad \text{(compare virial theorem)} \qquad (10.108)$$

Einstein: $$2t\eta = \frac{V}{k_B T}\langle(\mathcal{Q}_{\alpha\beta}(t) - \mathcal{Q}_{\alpha\beta}(0))^2\rangle \qquad (10.109)$$

$$\mathcal{Q}_{\alpha\beta} = \frac{1}{V}\sum_i r_{i\alpha}\,p_{i\beta} \qquad (10.110)$$

Thermal Conductivity λ_T

Green- Kubo
$$\lambda_T = \frac{V}{k_B T^2} \int_0^\infty dt \, \langle j_\alpha^\varepsilon(t) \, j_\alpha^\varepsilon(0) \rangle \qquad (10.111)$$

$$j_\alpha^\varepsilon = \frac{d}{dt} \left\{ \frac{1}{V} \sum_i r_{i\alpha} \left(\varepsilon_i - \langle \varepsilon_i \rangle \right) \right\} \qquad (10.112)$$

a component of the energy current.

$$\varepsilon_i = \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{j \neq i} v(r_{ij}) \qquad (10.113)$$

, energy per molecule.

Einstein
$$2t\,\lambda_T = \frac{V}{k_B T^2} \left\langle \left(\delta\varepsilon_\alpha(t) - \delta\varepsilon_\alpha(0) \right)^2 \right\rangle \qquad (10.114)$$

$$\delta\varepsilon_\alpha = \frac{1}{V} \sum_i r_{i\alpha} \left(\varepsilon_i - \langle \varepsilon_i \rangle \right) \qquad (10.115)$$

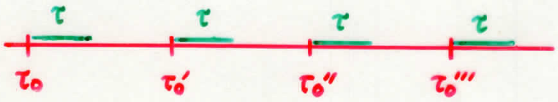
As opposed to D_s, the properties D, η, and λ_T are collective properties of the system, and not properties of individual particles. Their accurate estimation requires much more computer time (lengthier MD simulation).

Direct calculation of autocorrelation function $C_{\mathcal{A}\mathcal{A}}(t)$ from MD

- Let $t = \tau\,\delta t$, δt = time interval between configurations stored on tape.

- Substitute ensemble average by a time average:

$$C_{\mathcal{A}\mathcal{A}}(\tau) = \langle \mathcal{A}(\tau)\mathcal{A}(0)\rangle = \frac{1}{\tau_{max}} \sum_{\tau_0=1}^{\tau_{max}} \mathcal{A}(\tau_0)\,\mathcal{A}(\tau_0+\tau)$$



averaging of $\mathcal{A}(\tau_0)\mathcal{A}(\tau_0+\tau)$ over τ_{max} time origins.

NOTES:

- $\tau_{max} \leq \tau_{run} - \tau$. Short-time correlations obtainable with greater precision (Sample size limited at large τ)

  duration of run.

- To safely estimate the entire $C_{\mathcal{A}\mathcal{A}}(t)$, length of simulation must be such that $C_{\mathcal{A}\mathcal{A}}(t)$ decays over time $\tau_{cor} \ll \tau_{run}$.

- $C_{\mathcal{A}\mathcal{A}}(t)$ values usually accumulated in parallel for all $0 \leq \tau \leq \tau_{cor}$, through a double loop over stored data.

```
τ0 = 1, τrun                           Loop over origins
    τ = 0, min(τcor, τrun - τ0)        loop over time intervals
        Sum $\mathcal{A}(\tau_0)\,\mathcal{A}(\tau_0+\tau)$
```

- Special memory-saving techniques available. (see Allen & Tildesley)

Autocorrelation functions by the Fast Fourier Transform (FFT) Method

When autocorrelation functions are required up to $\tau_{cor} \simeq \tau_{run}$, computation associated with the double loop of the direct method becomes excessive

Alternative method:

- Use FFT to obtain Fourier transform of $\mathcal{A}(t) = \hat{\mathcal{A}}(\omega)$ ($\tau_{run} \log_2 \tau_{run}$ calculation
- Use correlation theorem of Fourier transforms to obtain F.T. of $C_{\mathcal{A}\mathcal{A}}(t)$ from $\hat{\mathcal{A}}($

$$\hat{C}_{\mathcal{A}\mathcal{A}}(\omega) = \frac{1}{\tau_{max}} \hat{\mathcal{A}}^*(\omega)\, \hat{\mathcal{A}}(\omega)$$

- Back transform $\hat{C}_{\mathcal{A}\mathcal{A}}(\omega)$ by FFT, to obtain $C_{\mathcal{A}\mathcal{A}}(t)$.

10.7. GENERAL ORGANIZATION OF A SIMULATION CODE

Design so that minimal information is lost in the event of a crash, and so that restart can be accomplished with minimal difficulty.

I/O

- Keep file manipulations to a minimum.
- Output file: instantaneous $\mathcal{V}$, E, P, T, … at frequent intervals. Accumulated simulation averages at end.
- Configuration file: Store configuration and accumulators of average properties periodically. (for restart)
- Tape file: Positions, velocities, accelerations every ~10 steps (for future analysis). Very large. Need only be machine-readable (condense!)

Program Structure

- Read/print simulation parameters and information about run.

- Set up auxiliary parameters. Initialize potential tables, neighbor lists.
- Read in configuration file.
- Initialize property accumulators for calculation of averages.
- Position tape file at right point for output.
- Calculate/print forces/energy in initial configuration
- Body of simulation (loop over simulation steps)
  - Move particles
  - Update running averages
  - Print out instantaneous properties and current averages in output file (once every IPRINT steps)
  - Print out detailed information on tape file (once every ITAPE steps)
    Save current configuration (once every ISAVE steps)
- Accumulate final averages, fluctuations, statistics on run.
- Close files and exit.