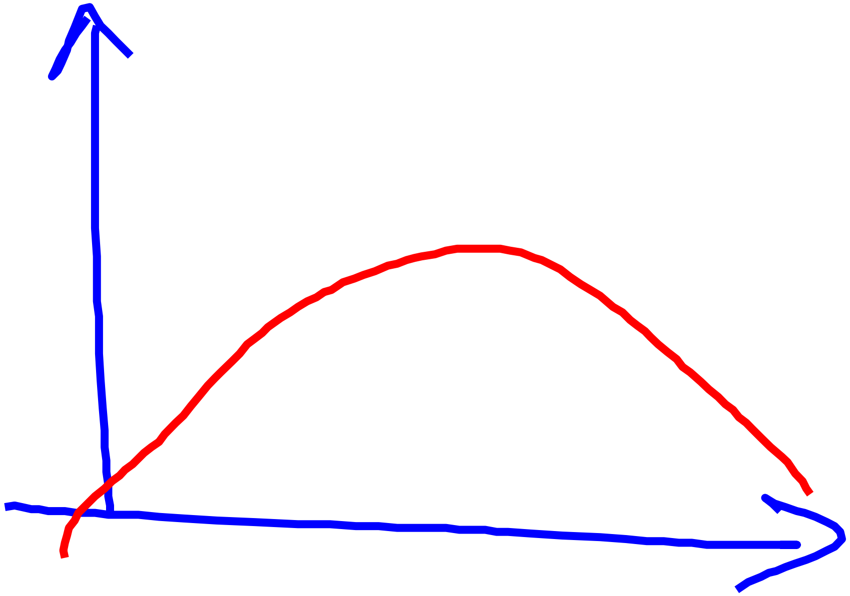
3.320: Lecture 13 (Mar 17 2005)

MOLECULAR DYNAMICS (PLAY IT AGAIN SAM)

A Particle Is a Particle Is a Particle

$$m\frac{d^2\vec{r}}{dt^2} = \overset{\nearrow F}{F(\vec{r})} \longrightarrow \begin{matrix}\vec{r}(t)\\ \vec{v}(t)\end{matrix}$$



N coupled equations

$$m_i \frac{d^2\vec{r}_i}{dt^2} = \vec{F}_i(\vec{r}_1, \cdots, \vec{r}_N)$$

- The force depends on positions only (not velocities)
- The total energy of the system is conserved (microcanonical evolution)

Conservation of the total energy

$$\frac{d}{dt}\left(\frac{1}{2}mv^2 + V(r)\right)$$

$$\Downarrow$$

$$\frac{1}{2}m\,2va + \frac{dV}{dt} \Rightarrow m\cancel{v}a + \overset{-F}{\boxed{\frac{dV}{dr}}}\;\overset{\cancel{v}}{\boxed{\frac{dr}{dt}}}$$

$$ma - F$$

Operational Definition

- We follow the evolution of a system composed of many classical particles
- Each particle interacts simultaneously with every other particle (usually – but can also have ‘hard spheres’ contact interaction), and can experience an additional external potential
- It’s a *many-body* problem – albeit with a simpler informational content than in the case of the electrons (why ?)

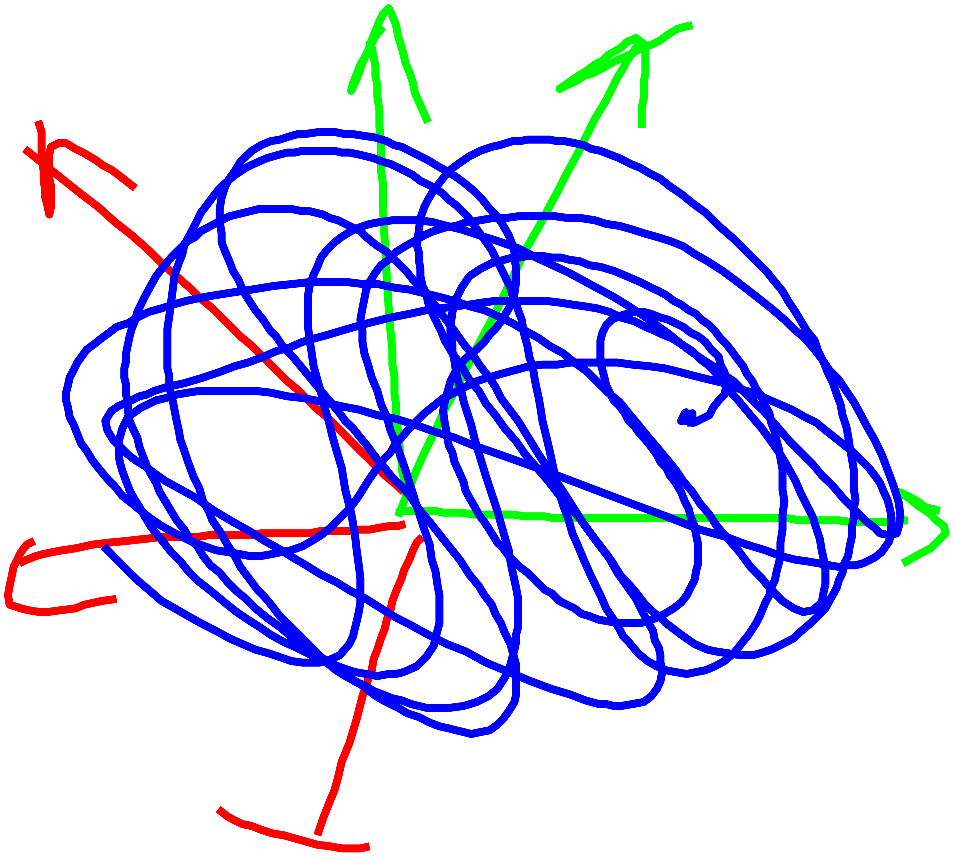
Some history

- MANIAC operational at Los Alamos in 1952
- Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller (1953): Metropolis Monte Carlo method
- Alder and Wainwright (Livermore 1956): dynamics of hard spheres
- Vineyard (Brookhaven 1959-60): radiation damage in copper
- Rahman (Argonne 1964): liquid argon
- Car and Parrinello (Sissa 1985): ab-initio MD

Phase Space

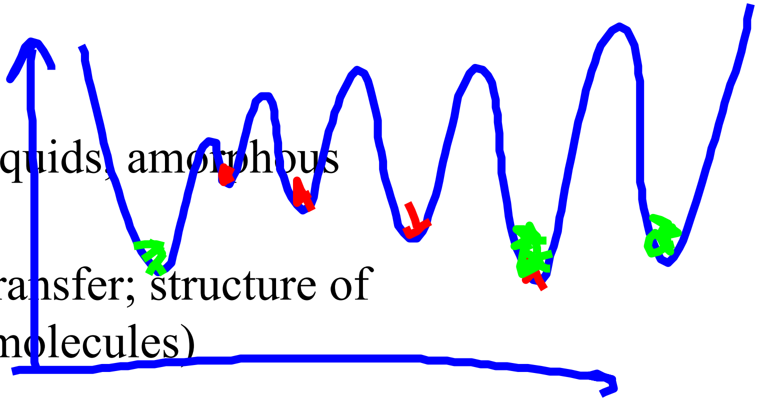
- If we have N particles, we need to specify positions and velocities for all of them (*6N* variables) to uniquely identify the dynamical system
- One point in a *6N* dimensional space (the phase space) represents our dynamical system

Phase Space Evolution



Three Main Goals

- Ensemble averages (thermodynamics)
- Real-time evolution (chemistry)
- Ground-state of complex structures (optimization)
    - Structure of low-symmetry systems: liquids, amorphous solids, defects, surfaces
    - Ab-initio: bond-breaking and charge transfer; structure of complex, non trivial systems (e.g. biomolecules)



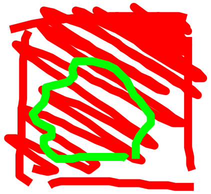
Limitations

- Time scales $\rightarrow 10^{-15} \longmapsto 1\,s$
- Length scales (PBC help a lot)
- Accuracy of forces
- Classical nuclei

Thermodynamical averages

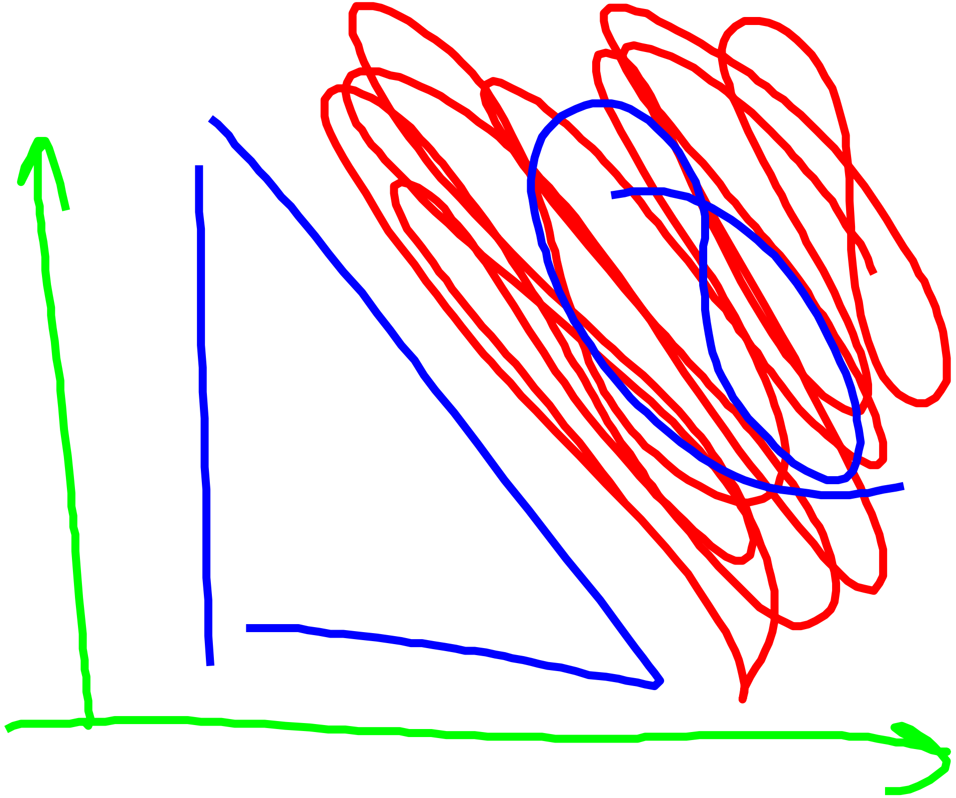
- Under hypothesis of ergodicity, we can assume that the temporal average along a trajectory is equal to the ensemble-average over the phase space

$$\langle A \rangle = \frac{\int A \exp(-\beta E)\, d\vec{r}\, d\vec{p}}{\int \exp(-\beta E)\, d\vec{r}\, d\vec{p}}$$



$$\overline{A} = \frac{1}{T}\int_0^T A(t)\, dt$$

Are you ergodic ?



Thermodynamical averages

- Let's start with the simple case: straightforward integration of the equations of motion (i.e. microcanonical: N, V and E are constant)
- The trajectory in the phase space spans states belonging to the microcanonical ensemble
- A long trajectory generates an excellent sample of microstates

The Computational Experiment

- Initialize: select positions and velocities
- Integrate: compute all forces, and determine new positions
- Equilibrate: let the system reach equilibrium (i.e. lose memory of initial conditions)
- Average: accumulate quantities of interest

Initialization

- Second order differential equations: boundary conditions require initial positions and initial velocities
- Initial positions: reasonably compatible with the structure to be studied. Avoid overlap, short distances.
- Velocities: zero, or small. Then thermalize increasing the temperature

Maxwell-Boltzmann distribution

$$n(v) \propto \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 \exp\left(\frac{-mv^2}{2k_B T}\right)$$

$$\bar{v} = \sqrt{\frac{2k_B T}{m}}, \quad v_{rms} = \sqrt{\frac{3k_B T}{m}}$$

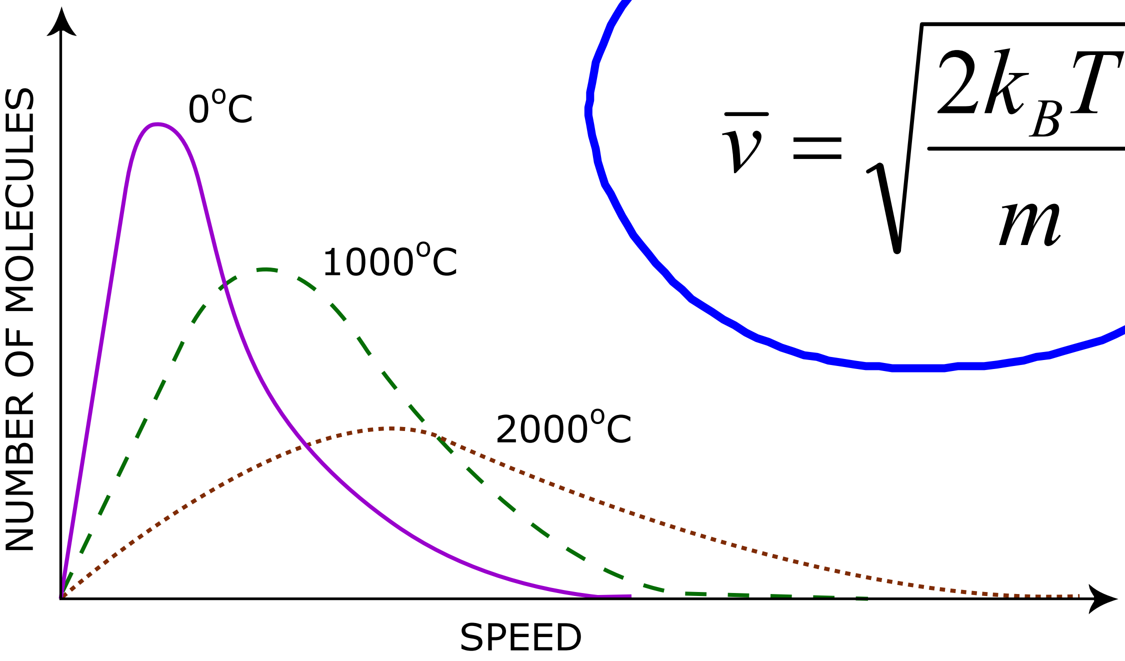


Figure by MIT OCW.

Oxygen at room T:

10^5 cm/s

Integrate

- Use an integrator… (Verlet, leapfrog Verlet, velocity Verlet, Gear predictor-corrector)
- Robust, long-term conservation of the constant of motion, time-reversible, constant volume in phase space
- Choose thermodynamic ensemble (microcanonical NVE, or canonical NVT using a thermostat, isobaric-isothermic NPT with a barostat…)
- Stochastic (Langevin), constrained (velocity rescaling), extended system (Nose-Hoover)

Integrators

- (Simple) Verlet

$$\boxed{\mathbf{r}(t+\Delta t)} = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + (1/2)\mathbf{a}(t)\Delta t^2 + (1/6)\mathbf{b}(t)\Delta t^3 + O(\Delta t^4)$$

$$\mathbf{r}(t-\Delta t) = \mathbf{r}(t) - \mathbf{v}(t)\Delta t + (1/2)\mathbf{a}(t)\Delta t^2 - (1/6)\mathbf{b}(t)\Delta t^3 + O(\Delta t^4)$$

Adding the two expressions gives

$$\boxed{\mathbf{r}(t+\Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t-\Delta t) + \mathbf{a}(t)\Delta t^2 + O(\Delta t^4)}$$

$$\mathbf{a}(t) = -(1/m)\nabla V\left(\mathbf{r}(t)\right) \qquad \mathbf{v}(t) = \frac{\mathbf{r}(t+\Delta t) - \mathbf{r}(t-\Delta t)}{2\Delta t}.$$

Bibliography

- Allen and Tildesley, *Computer Simulations of Liquids* (Oxford)
- Frenkel and Smit, *Understanding Molecular Simulations* (Academic)
- Ercolessi, *A Molecular Dynamics Primer* (http://www.fisica.uniud.it/~ercolessi/md)