Chapter 9: Molecular-dynamics

- Integrate equations of motion--classical!

- Discrete form of Newton's second law

- Forces from interaction potential

$$\vec{F}_i = -\vec{\nabla}_i U\left(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N\right)$$

- For a simple pair potential, we get

$$U\left(\vec{r}_1, \ldots, \vec{r}_N\right) = \frac{1}{2}\sum_{ij} u(r_{ij})$$

Integrating equations of motion

$$F_{i,x} = m_i \frac{dv_{i,x}}{dt} \qquad F_{i,y} = m_i \frac{dv_{i,y}}{dt} \qquad F_{i,z} = m_i \frac{dv_{i,z}}{dt}$$

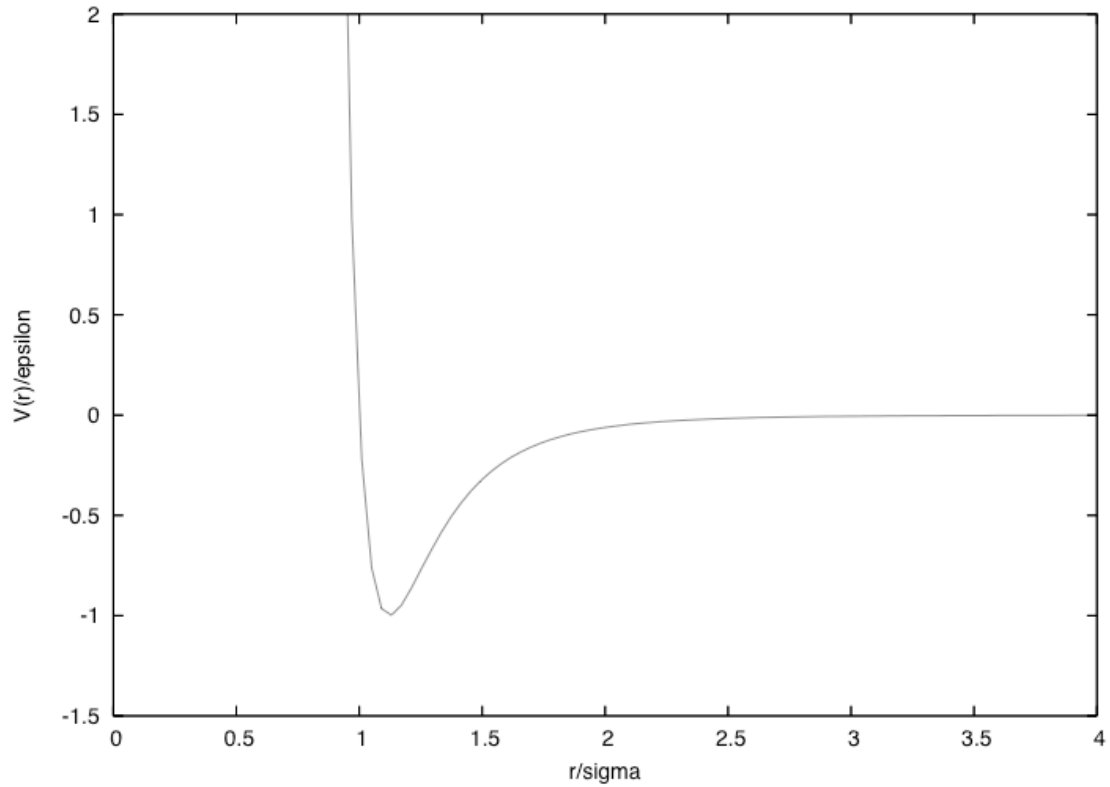
$$\frac{dv_{i,x}}{dt} = \frac{d^2 x_i}{dt^2} \approx \frac{x_i(n+1) - 2x_i(n) + x_i(n-1)}{\Delta t^2}$$

This works out to give the Verlet algorithm,

$$x_i(n+1) = 2x_i(n) - x_i(n-1) + \frac{F_{i,x}}{m_i} \Delta t^2$$

Lennard-Jones potential for noble gas

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



Heat capacity

$$C = \frac{\left\langle H^2 \right\rangle - \left\langle H \right\rangle^2}{k_B T^2}$$

- Angle brackets thermal average
- In MD, thermal averages done by time average
- Heat capacity given by fluctuations in total energy

Radial distribution function

$$g(r) = \frac{1}{\rho N}\left\langle \sum_{i \neq j} \delta\left(r - r_{ij}\right) \right\rangle$$

- ρ is the density N/Ω
- Dirac-delta defined numerically (not infinitely sharp)
- In an ideal gas, g(r) =1
- In a liquid, g(r) =1 at long ranges, short range structure
- In a crystal, g(r) has sharp peaks, long-range order

History and applications of molecular dynamics

- Fermi-Pasta-Ulam (Chapter 9.3)

  Statistical mechanics<-->molecular dynamics

- Ergodic theorem

  System explores all possible states and
  can effectively attain thermal equilbrium

- Equipartition of energy

  In a harmonic system, E=kT per mode.
  Violated in FPU problem

A classic paper… establishing the field

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Correlations in the Motion of Atoms in Liquid Argon*

A. RAHMAN
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(Received 6 May 1964)

A system of 864 particles interacting with a Lennard-Jones potential and obeying classical equations of motion has been studied on a digital computer (CDC 3600) to simulate molecular dynamics in liquid argon at 94.4°K and a density of 1.374 g cm^{-3}. The pair-correlation function and the constant of self-diffusion are found to agree well with experiment; the latter is 15% lower than the experimental value. The spectrum of the velocity autocorrelation function shows a broad maximum in the frequency region $\omega=0.25(k_BT/\hbar)$. The shape of the Van Hove function $G_s(r,t)$ attains a maximum departure from a Gaussian at about $t=3.0\times10^{-12}$ sec and becomes a Gaussian again at about 10^{-11} sec. The Van Hove function $G_d(r,t)$ has been compared with the convolution approximation of Vineyard, showing that this approximation gives a too rapid decay of $G_d(r,t)$ with time. A delayed-convolution approximation has been suggested which gives a better fit with $G_d(r,t)$; this delayed convolution makes $G_d(r,t)$ decay as t^4 at short times and as t at long times.

Only 864 atoms! Today we can approach even billions!

More modern work with MD… highly interdisciplinary

- Physics, materials science, chemistry, chemical engineering and even mechanical engineering groups use MD

- Physics groups at UCF using MD at some level

1. Rahman. Surface science, catalysis, chemical reactions
2. Stolbov. Surface science, catalysis, chemical reactions
3. Kara. Surface science, dynamics, surface vibrations
4. Bhattacharya. DNA, polymer transport
5. Schelling. Thermal and phonon transport, surface science

Florida society for materials simulation

- UF, USF, FSU, UCF participants, engineering, physics and chemistry
- Summer REU program, 12 students per year
- Kickoff meeting with workshops (at UF this year)
- Final FSMS meeting, faculty talks, student posters

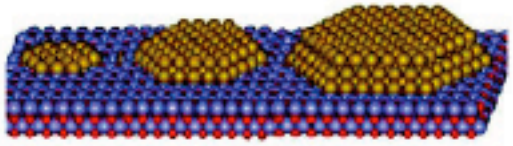
http://www.che.ufl.edu/reu/

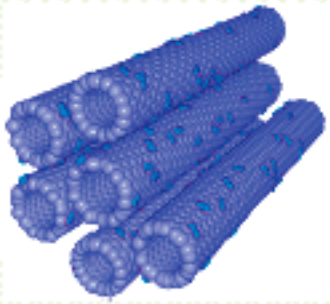
http://physics.ucf.edu/~schellin/workshop/home/fsms.html

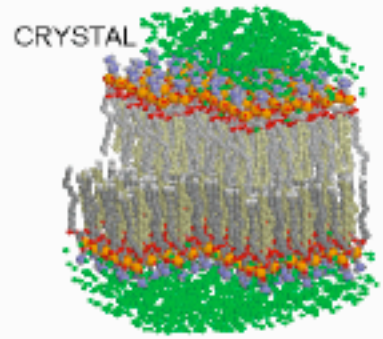
Designing Materials in a Virtual Laboratory

Research Experience for Undergraduates (REU) Program

Exciting research projects at the four major universities of Florida: Univ. of Florida, Univ. of South Florida, Univ. of Central Florida, and Florida State Univ.







Catalysis **Nanoscience** **Biology**

If interested visit: **www.che.ufl.edu/reu** or contact Prof. Asthagiri (aasthagiri@che.ufl.edu)

Challenges of MD simulation

- Potential not always understood well--- many body interactions
- Quantum mechanics can be used, but very costly
- Times scales usually at most nanoseconds
- Length scales usually at most several nanometers

Long length and time scales relevant for many applications and experiments are extremely hard to access

For example, even just a 10nm radius nanoparticle of say gold atoms requires over 200,000 atoms! Much much more (by at least 3 orders of magnitude) than can be handled with quantum mechanics… not to mention time scales….