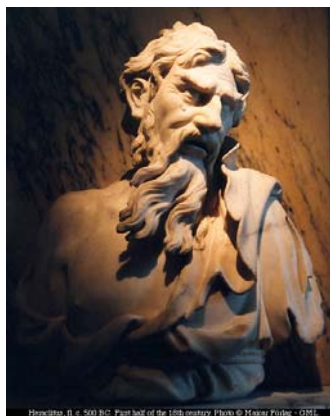




Another pioneer of MD...



**You cannot step twice
in the same river**

Heraclitus (Diels 91)

ποταμῶ γὰρ οὐκ ἔστιν ἐμβῆναι δις τῷ
αὐτῷ καθ' Ἡράκλειτον.

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

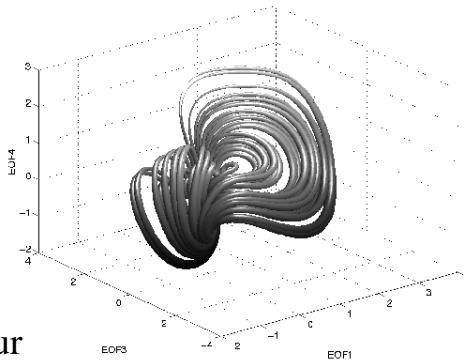
Newton's second law: N coupled equations

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

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

Phase Space Evolution

- 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



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

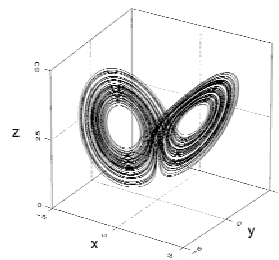
- Time scales
- Length scales (PBC help a lot)
- Accuracy of forces
- Classical nuclei

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

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

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





The Computational Experiment

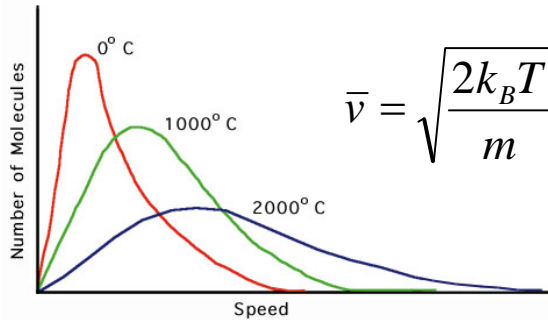
- **Initialize:** select positions and velocities
- **Integrate:** compute all forces, and determine new positions
- **Equilibrate:** let the system reach equilibrium (i.e. lose memory of initial conditions)
- **Average:** accumulate quantities of interest

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 in CP, or small. Then thermalize increasing the temperature

Maxwell-Boltzmann distribution

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



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

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

- Verlet

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

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

Adding the two expressions gives

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

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

Verlet's Algorithms

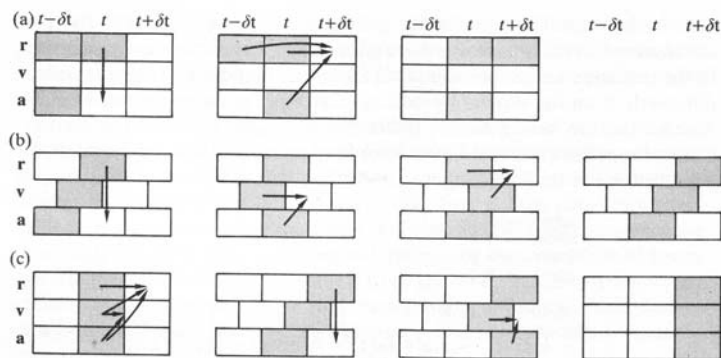


Fig. 3.2 Various forms of the Verlet algorithm. (a) Verlet's original method. (b) The leapfrog form. (c) The velocity form. We show successive steps in the implementation of each algorithm. In each case, the stored variables are in grey boxes.

Lyapunov Instabilities

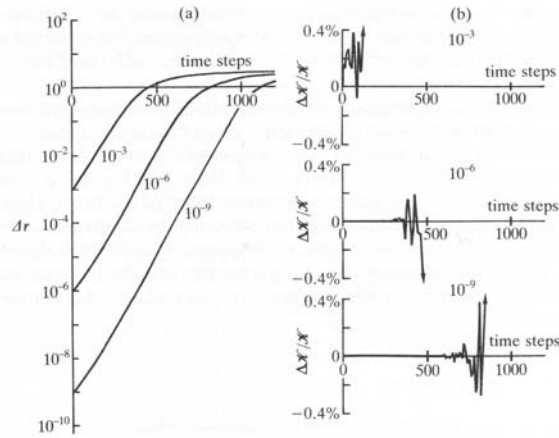
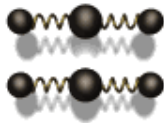
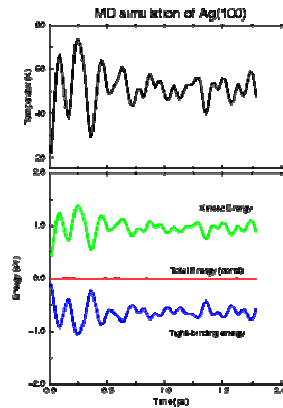
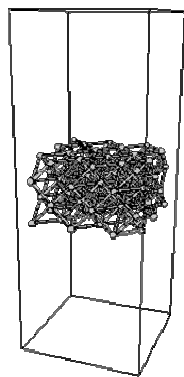


Fig. 3.1 The divergence of trajectories in molecular dynamics. Atoms interacting through the potential $v^{\text{RLJ}}(r)$, eqn (1.10a), were used, and a dense fluid state was simulated ($\rho^* = 0.6$, $T^* = 1.05$, $\delta t^* = 0.005$). The curves are labelled with the initial displacement in units of σ . (a) Δr is the phase space separation between perturbed and reference trajectories. (b) $\Delta K'/K'$ is the percentage difference in kinetic energies.

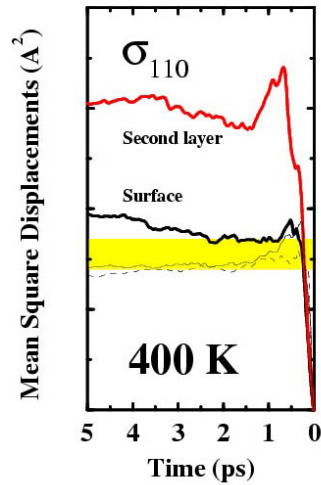


Time Step



How to test for equilibration ?

- Drop longer and longer initial segments of your dynamical trajectory, when accumulating averages



Accumulate averages

- Potential, kinetic, total energy (conserved)
- Temperature ($K=3/2 N k_B T$)
- Pressure
- Caloric curve $E(T)$: latent heat of fusion
- Mean square displacements (diffusion)
- Radial (pair) distribution function

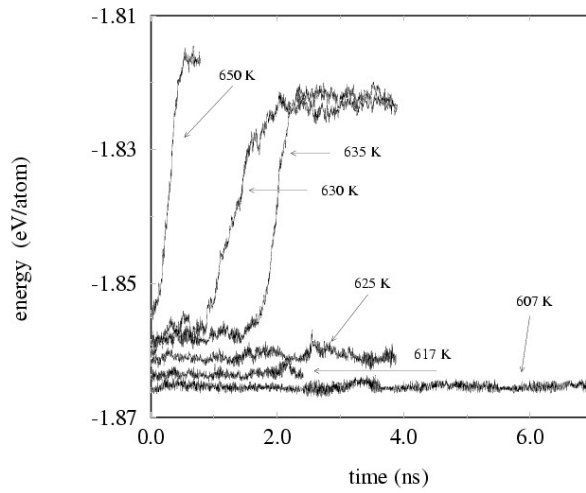
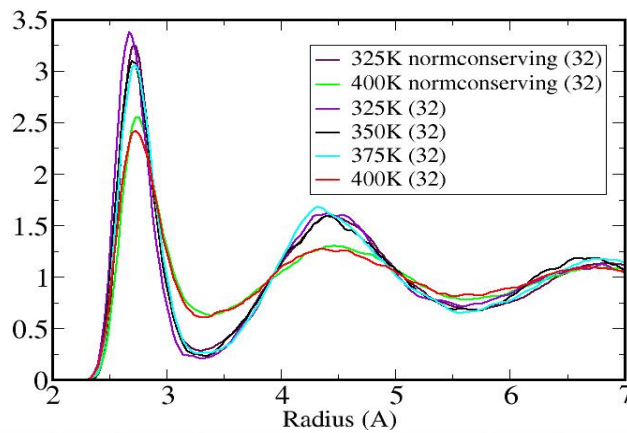


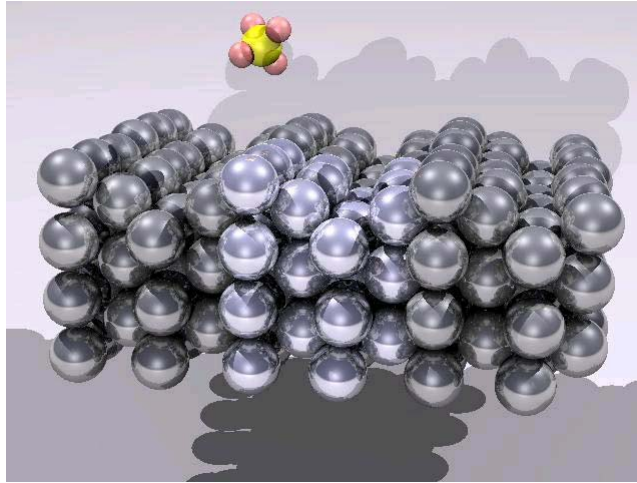
Figure 5.13: Time evolution of the total energy of Pb(100) (sample of 32 layers, 200 particles per layer). At 607 K ($\sim T_m$ in this simulation) the surface is incompletely melted, and survives in this metastable state until $T \leq 625$ K. The energy increase between 607 K and 625 K mostly reflects the increase of the quasi-liquid layer thickness, from ~ 1.3 to ~ 3 ML. For $T \geq 630$ K the slab melts and irreversibly releases the latent heat corresponding to ~ 26 layers.

Correlation Functions

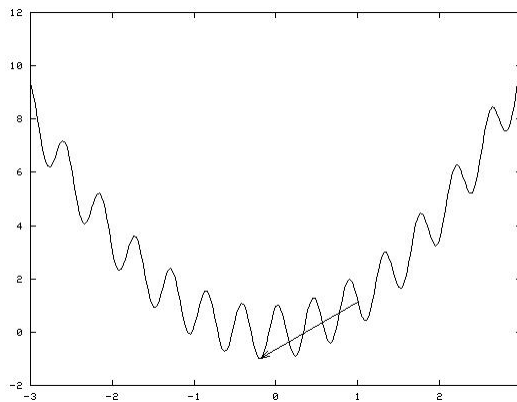


$$g(r) = \rho^{-2} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r}_i) \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle = \frac{V}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle$$

Real Time Evolution



Simulated Annealing



Classical MD 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>)