Langevin's Dynamics

- Based on Langevin's equations
  - Evolution of degrees of freedom through a differential equation + stochastic term
  - Assumes deg. of freedom are slower than the microscopic events
  - Stochastic term assumes no correlations
  - Lack of correlations indicate that timescale is larger than microscopic timescale
  - Originally devised to describe Brownian Motion:
    - Why are jump frequencies so low compared to molecular collisions?
    - Why are jump lengths so large compared to molecular sizes?

show demo

Langevin's Dynamics

- Forces are no longer calculated explicitly
- Forces are replaced by *stochastic quantities* reflecting local neighborhood
- In essence, solvent effects are treated through extra random terms
  - “Separates” collisions and frictional forces
  - Comes out of convenience: it is applied to eliminate explicit treatment of water molecules
  - Good to simulate very large molecules (DNA)

Langevin's Dynamics

- Langevin's equation:

$$m\frac{d^2}{dt^2}\mathbf{r} = -\nabla V(\mathbf{r}) - m\gamma\frac{d}{dt}\mathbf{r} + \mathbf{R}(t)$$

- Force + damping (prop. to velocity) + white noise
  - The Force is given by a PMF, rather than by a V(r), such as LJ
  - This Force includes the average influence of the “solvent” on the particle
  - The PMF is related to the *g(r)*

$$A(r) = -k_B T \ln g(r) + constant$$

Langevin's Dynamics

- Langevin's equation:

$$m\frac{d^2}{dt^2}\mathbf{r} = -\nabla V(\mathbf{r}) - m\gamma\frac{d}{dt}\mathbf{r} + \mathbf{R}(t)$$

- γ controls frictional force and variance of noise
- For γ small: motion is inertial (low viscosity)
- For γ big: motion is diffusive or Brownian (high viscosity)

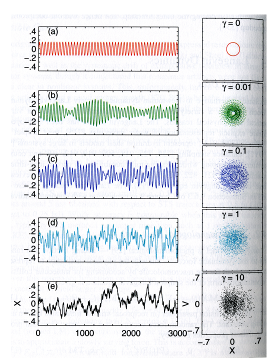
Langevin's Dynamics

- Brownian motion:
  - Motion is very quickly reoriented by frequent collisions with solvent.
  - Velocity Relaxation Time is the time for system to forget previous velocities, γ^{-1}, is small.

Langevin's Dynamics

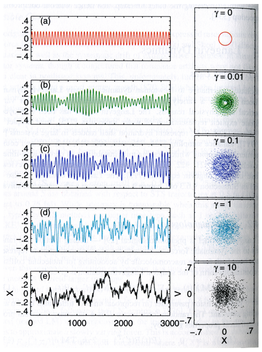
Example: 1D harmonic oscillator

- Simulated with modified Verlet finite diff. method
- γ=0 -> no viscosity
- Erratic motion for large γ mimics motion in dense liquid solvent



Langevin's Dynamics

- Viscosity damps characteristic vibrational frequencies of a molecule in vacuum
- Low freq. Vibrations are over damped



Langevin's Dynamics

$$m\frac{d^2}{dt^2}\mathbf{r} = -\nabla V(\mathbf{r}) - m\gamma\frac{d}{dt}\mathbf{r} + \mathbf{R}(t)$$

- In a simulation, the value of γ can be obtained from other physical parameters:
  - Stoke's law (radius a, particle mass m, viscosity η)

    $$\gamma = 6\pi\eta a/m$$

  - Also, at the diffusive limit, from

    $$D = k_B T/m\gamma$$

Stokes-Einstein law of diffusion for a Brownian spherical particle

Langevin's Dynamics

$$m\frac{d^2}{dt^2}\mathbf{r} = -\nabla V(\mathbf{r}) - m\gamma\frac{d}{dt}\mathbf{r} + \mathbf{R}(t)$$

- Numerical solutions usually are given in terms of values of γ Δt
  - γ Δt << 1, time step much smaller than velocity relaxation time
  - γ Δt >> 1, opposite limit, longer timesteps. Diffusion dominates, velocity is rapidly damped by solvent.
  - Intermediate values (involve explicit integrals)
- Show algorithms (van Gunsteren) for top two cases...