L2 * N interacting atoms , $\vec{r}_i$ → Positions

(1) $m_i \frac{\partial^2 \vec{r}_i}{\partial t^2} = \vec{F}_i$, $i = 1, \dots, N$

(2) $\vec{F}_i = -\nabla V(r_1, \dots, r_N)$

} ⇒ $\vec{r}_i(t)$, $v_i(t)$ } Trajectory

* **Approximations**

- Born Oppenheimer

Atom dynamics → Quantum Nature

- State defined by wave function $\Psi(R_e, R_n)$ (electrons, Nuclei)

- Schrödinger eq: $i\hbar \frac{\partial}{\partial t} \Psi(R_e, R_N) = H \Psi(R_e, R_N)$

- BO: separation of { Fast motions of e⁻ / slow motions of nuclei.

$$\Psi = \underbrace{\Psi_n(R_n, t)}_{\text{Nuclei}} \underbrace{\Psi_e(R_e; R_N)}_{\text{Electrons}}$$

Nuclei:
- Time independent
- Move in the energy surface created be e⁻
- P

Electrons
- independent
- Instantaneously adjust to changes in R_N
- Ground state
- R_N → parametrically.

- Classical treatment

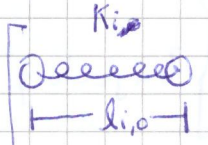
- Separation >> de Broglie wavelength $= \left(\frac{h^2}{2\pi m K_B T}\right)^{1/2}$

- The case for most atoms at room T

- Fails:
  - Chemical reactions
  - Tunneling
  - Electronic excited states.

• Use of empirical interaction function, $V(r)$

"force field"



$$V(\vec{r}) = \sum_{bonds,i} \frac{K_i}{2}\left(l_i - l_{i,0}\right)^2$$

H_2O: $l_{i0} = 0.9572\ \text{Å}$

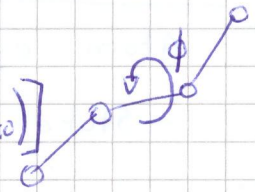
$K_i = 462750.4\ \frac{\text{KJ mol}^{-1}}{\text{nm}^2}$

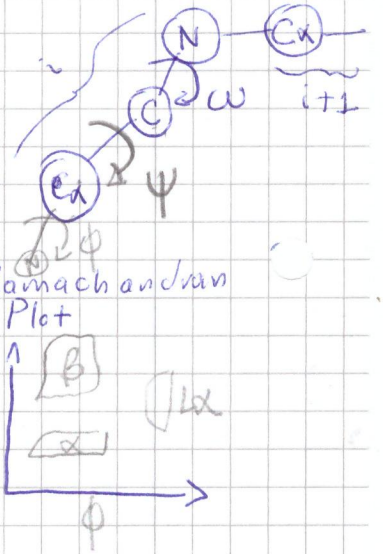
$$+ \sum_{angle,j} \frac{F_i}{2}\left(\theta - \theta_{j,0}\right)^2$$

H_2O: $\theta_0 = 104.520°$

$f = 836.8\ \frac{\text{KJ mol}^{-1}}{\text{nm}^2}$

$$+ \sum_{din,\kappa} \sum_{n} \frac{V_{\kappa,n}}{2}\left[1 + \cos\left(n\phi - \phi_{\kappa 0}\right)\right]$$



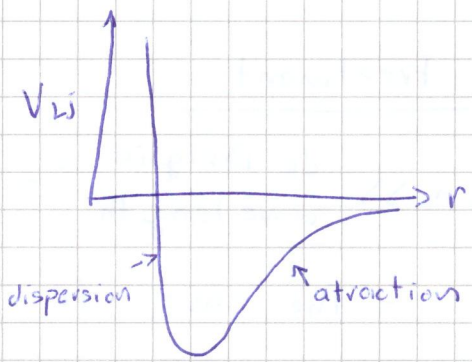


Bonded

$$+ \sum_{ij} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

Van der Waals Int.

Lennard-Jones Potential



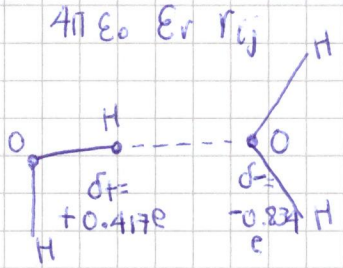
$\sigma = 3.1506\ \text{Å}$

$\varepsilon = 0.636\ \text{KJ/mol}$

non-bonded

$$+ \sum_{ij} \frac{q_i q_j}{4\pi\varepsilon_0\,\varepsilon_r\, r_{ij}}$$

Electrostatic interactions



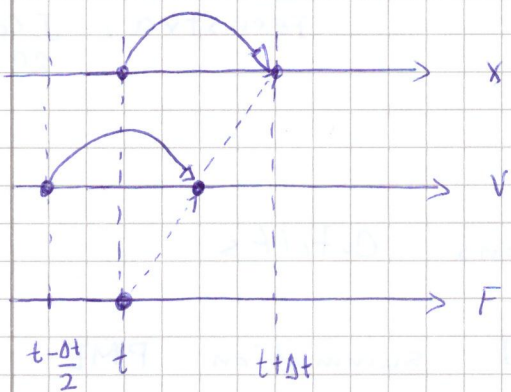
Hydrogen bond distance?

* Solving numerically Newton's eqs of motion

Leap Frog Algorithm

$$V_i\left(t + \frac{\Delta t}{2}\right) = V_i\left(t - \frac{\Delta t}{2}\right) + \frac{F_i(t)}{m_i}\Delta t$$

$$r_i\left(t + \Delta t\right) = r_i(t) + V_i\left(t + \frac{\Delta t}{2}\right)\Delta t$$



$\Delta t = 2$ fs

* Barostats and Thermostats

- We simulate a system coupled to an external bath (NPT, NVT) { → Temperature, → Pressure } constant.
- Temperature:

$$\frac{dT}{d\tau} = \frac{T - T_0}{\tau}$$

τ → Coupling parameter

$$v' = \lambda\, v\left(t - \frac{\Delta t}{2}\right)$$

$$\lambda = \lambda(\Delta t, \tau, T_0, T) \rightarrow \text{Scaling Factor}$$

Berendsen J Chem Phys ~~126 014101~~ 81 3684 (1984)

Bussi J Chem Phys 126 014101 (2007)

- Pressure: similar

$$x' = \chi\, x(t)$$

* Improving efficiency

- Remove fast degrees of freedom:
  - Bonds (H-atoms) vibrations → Constraints
    Lincs, Hess, J Comp Chem 12:1463 1997
    shake
    $\Delta t = 2$ fs
  - Angle vibrations → Vsites
    Feenstra, J Comp Chem 20:786 1999
    $\Delta t = 4$ fs

- Short range interactions: Cutoffs

- Electrostatics: Ewald summation PME
  Darden JCP 98, 10089, 1993
  Essmann JCP 103, 8577, 1995

  N^2 problem → N log N
  Direct calculation
  ~~E~~ Cutoff Direct space
  ~~long~~ rang Reciprocal Space

- Neighborlist
  Verlet Buffer ( )