Diffusion in Liquids

" If the reader has by now concluded that little is known about the prediction of dense gas and liquid diffusivities, he is correct. There is an urgent need for experimental measurements, both for their own value and for development of future theories.

Bird, Stewart and Lightfoot, *Transport Phenomena* (Wiley, N.Y. 1960) p. 515

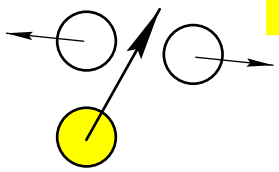
- Diffusion: relative motion of (unlike) molecules
- In contrast to solids and standard gases, liquids possess a complex, T-dependent structure

  → Dynamics of molecules in liquids not well understood
- Different structural and kinetic features perceived by different authors as governing parameters

  jump length and time
  vibration frequencies
  activation energies
  critical volume
  density fluctuations
  correlations to other transport mechanisms

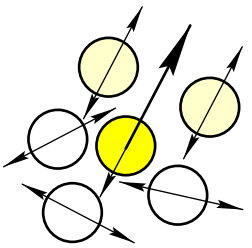
  → Numerous theoretical models of (self-) diffusion in liquids

$$D(T) \sim e^{-\Delta E/kT}\, T^n$$



jumps through activated state

$\Delta E > 0$, $n = 0$



cooperative motion of groups including subatomic steps

$\Delta E = 0$, $n = 1/2, 1, 3/2, 2$

Molecular dynamics modeling $1.7 \leq n \leq 2.2$