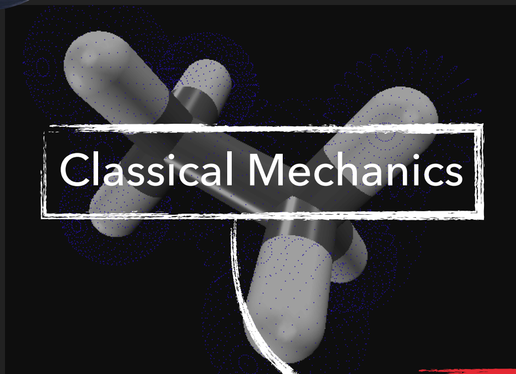
MOLECULAR DYNAMICS

THEORY

TRISTAN JOHNSTON-WOOD

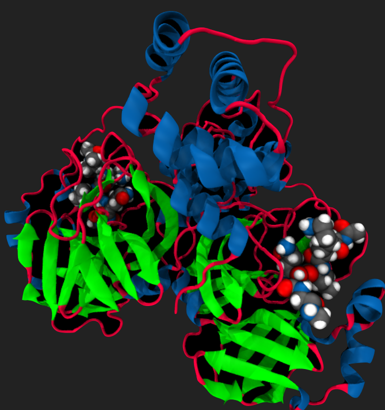
THE AIM



Classical Mechanics

Statistical Mechanics

Molecular dynamics



Constant temperature

Constant pressure

Model of physical system

CLASSICAL MECHANICS

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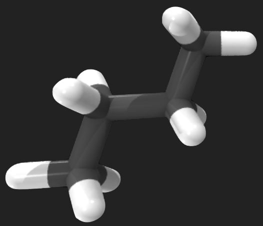
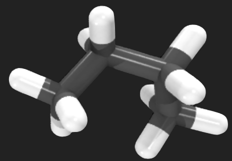
First, describe positions:

$$r(t) = (x(t), y(t), z(t))$$



$r(t)$



$r(t)'$

Second, find equations of motion:

$$\bar{F} = m\bar{a} = m\frac{dv}{dt} = \frac{d^2r}{dt^2}$$
$$\equiv \ddot{r}$$

Third, define phase space:

$$\mathbf{x}_t = (r_1(t), \ldots, r_N(t), p_1(t), \ldots, p_N(t))$$

$$\Downarrow$$

Complete description

STATISTICAL MECHANICS

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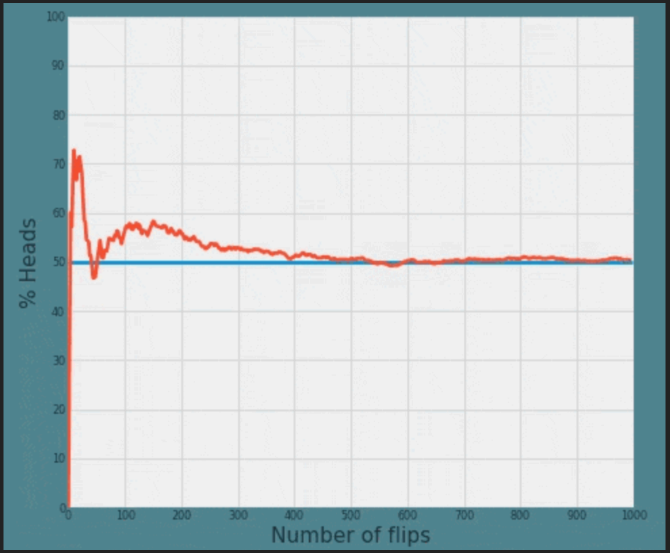
Application of statistics to physics to obtain thermodynamic properties



$\boxed{\text{Expectation value}}$

$$A = \sum_i P_i \, a_i$$

$$A = \text{“}\int p(\tau)\, a(\tau)\, d\tau\text{”} \text{ — TOM Young 2020}$$

$$= \int a \; e^{-\epsilon_i / k_B T} / Z$$

$$P_i = \frac{e^{-\epsilon_i / k_B T}}{Z}$$

E.g. pressure: $P = \int p \; e^{-\epsilon_i / k_B T} / Z$

Partition function

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Can we derive equations for position and velocity at a later time?*

Toolkit

$$\bar{F} = m\ddot{r}_i(t)$$

$$v_i(t) = \dot{r}_i(t)$$

$$r(t+\Delta t) \approx r(t) + \dot{r}(t)\Delta t + \frac{\ddot{r}(t)\Delta t^2}{2}$$

$$\underbrace{r(t+\Delta t)} = r(t) + v(t)\Delta t + \frac{F(t)\Delta t^2}{2m}$$

$$r(t) = \overbrace{r(t+\Delta t)} - v(t+\Delta t)\Delta t + \frac{F(t+\Delta t)\Delta t^2}{2m}$$

$$\cancel{r(t)} = \cancel{r(t)} + v(t)\cancel{\Delta} t + \frac{F(t)\Delta t^{\cancel{2}}}{2m} - v(t+\Delta t)\cancel{\Delta} t + \underline{F(t+\Delta t)\Delta t^{\cancel{2}}}$$

*yes

$$2m$$

$$0 = v(t) - v(t+\Delta t) + \frac{F(t)\Delta t + F(t+\Delta t)\Delta t}{2m}$$

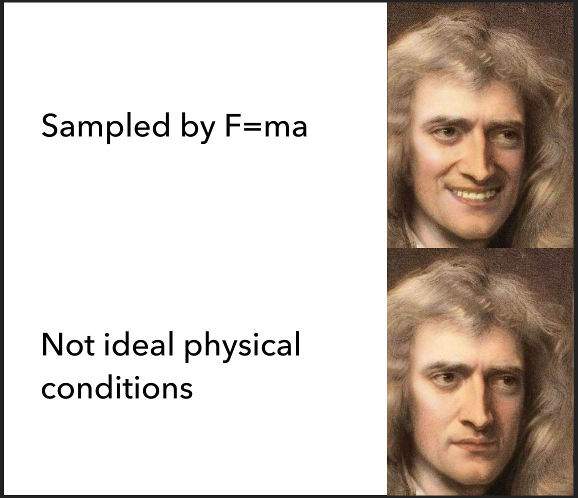
$$\boxed{\begin{aligned} v(t+\Delta t) &= v(t) + \frac{\Delta t}{2m}\left[F(t) + F(t+\Delta t)\right] \\ r(t+\Delta t) &= r(t) + v(t)\Delta t + \frac{F(t)\Delta t^2}{2m} \end{aligned}}$$

Velocity Verlet Algorithm

NVT ENSEMBLE

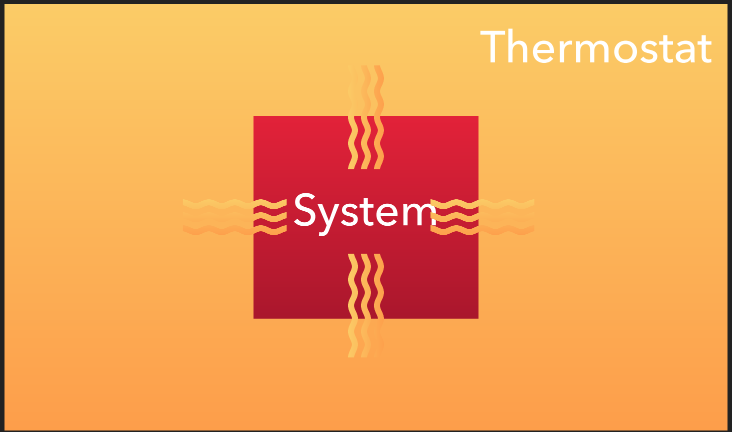
NVE – constant moles, volume, energy

– "Microcanonical ensemble"



NVT – constant moles, volume, temperature

– "Canonical ensemble"



NVT ENSEMBLE

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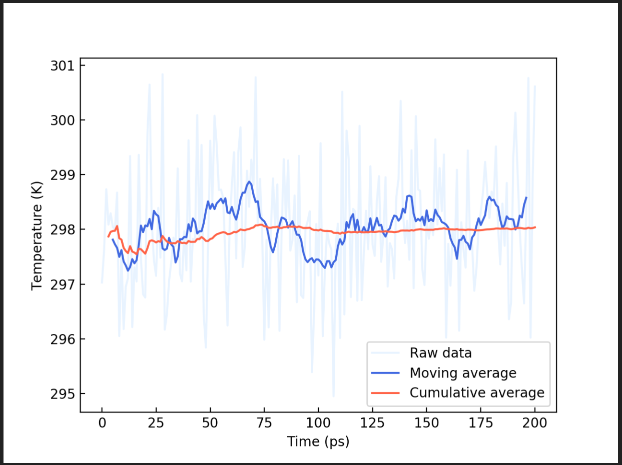
Berendsen thermostat

–rescales velocities by λ

$$T - T_0 = Ae^{-t/\tau}$$

Velocity–rescaling thermostat

–rescales velocities by λ
and correct ensemble



Nosé–Hoover thermostat

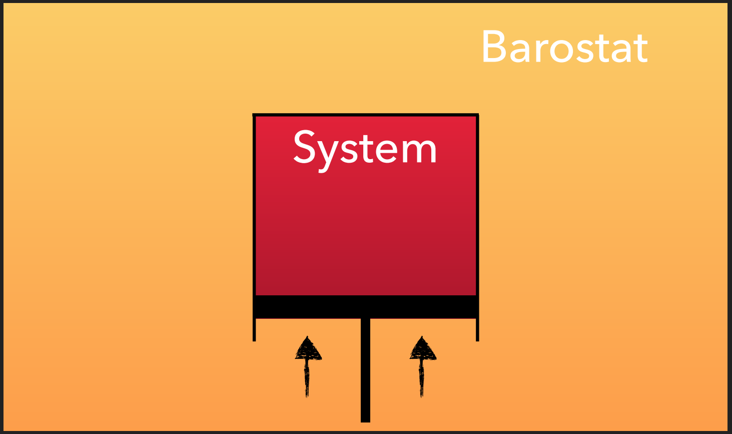
–friction terms *generate* correct ensemble

$$H_N = \sum_{i=1}^{N} \frac{\bar{p}_i^2}{2m_i s^2} + U(\bar{r}_1, \ldots, \bar{r}_N) + \frac{p_s^2}{2Q} + gkT \ln s$$

NPT ENSEMBLE

NPT – constant moles, pressure, temperature

– "Isobaric-isothermic ensemble"



Berendsen barostat

$$P - P_0 = Ae^{-t/\tau}$$

Parrinello–Rahman barostat

$$\frac{d^2\bar{r}_i}{dt^2} = \frac{\bar{F}_i}{m_i} - \bar{M}\frac{d\bar{r}_i}{dt}$$

ACKNOWLEDGEMENTS