Equipartition Theorem Violation

“Flying Ice Cube”

Ladislav Bartoš

March 8, 2021

FB810/C9926 Course

Numerical Integrators

$$\frac{d^2\vec{r}_i}{dt^2} = \frac{\vec{F}_i}{m_i}$$

Newton equations of motion

- solved by **numerical integration** => provides trajectories
- e.g. Verlet algorithm, leap-frog algorithm
- integrators keep the total **energy** constant **(NVE)**

microcanonical ensemble

Temperature Coupling

- to achieve constant **temperature** **(NVT)**, we must employ a **thermostat**

canonical ensemble

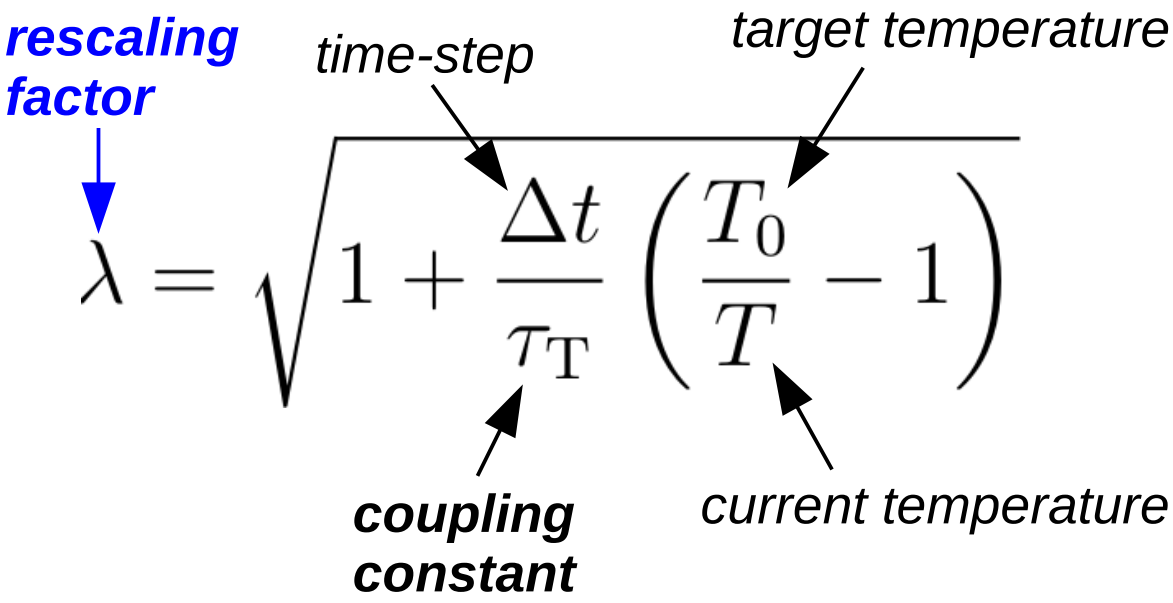
- temperature <= kinetic energy <= particles **velocity**
- **constant** temperature <= **constant** average velocity

$$\langle E_{\mathrm{kin}} \rangle = \frac{3}{2} k_{\mathrm{B}} T \;\; \& \;\; \langle E_{\mathrm{kin}} \rangle = \frac{1}{2} m \langle v^2 \rangle \;\; \Rightarrow \;\; T = \frac{\langle v^2 \rangle m}{3 k_{\mathrm{B}}}$$

- periodically, we must:
  a) generate brand new velocities, or
  b) rescale the current velocities

Berendsen Thermostat

- every time-step, velocity of each particle is multiplied by a **rescaling factor λ**
- current temperature **gradually** changes and converges to the target temperature



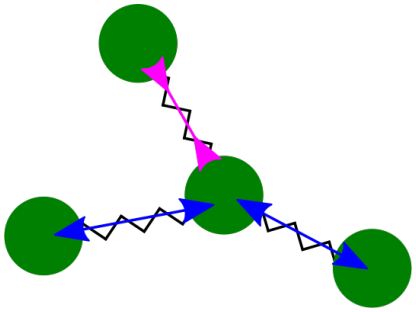
$$\tau_T = \Delta t$$

target temperature will be reached in **1 step**

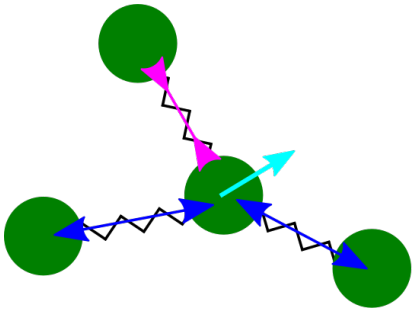
$$\tau_T = \infty$$

target temperature will **never** be reached

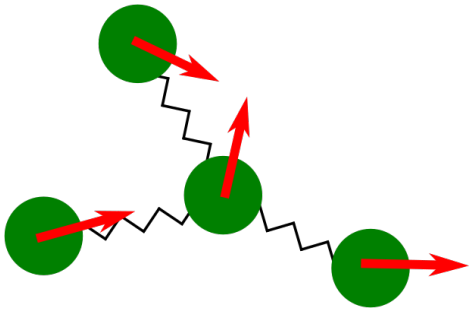
Flying Ice Cube



vib



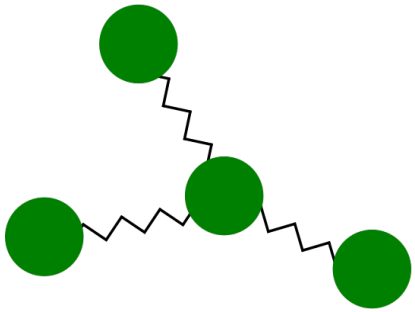
vib+trans



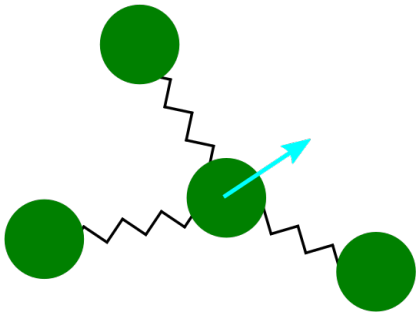
TOTAL

the system effectively **freezes**

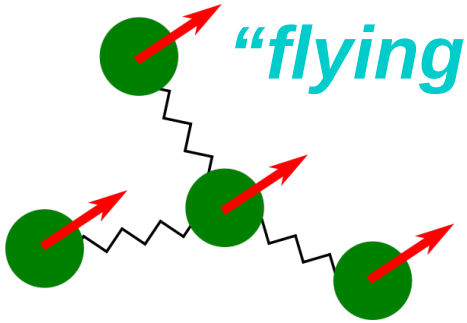
"flying ice cube"



vib



vib+trans



TOTAL

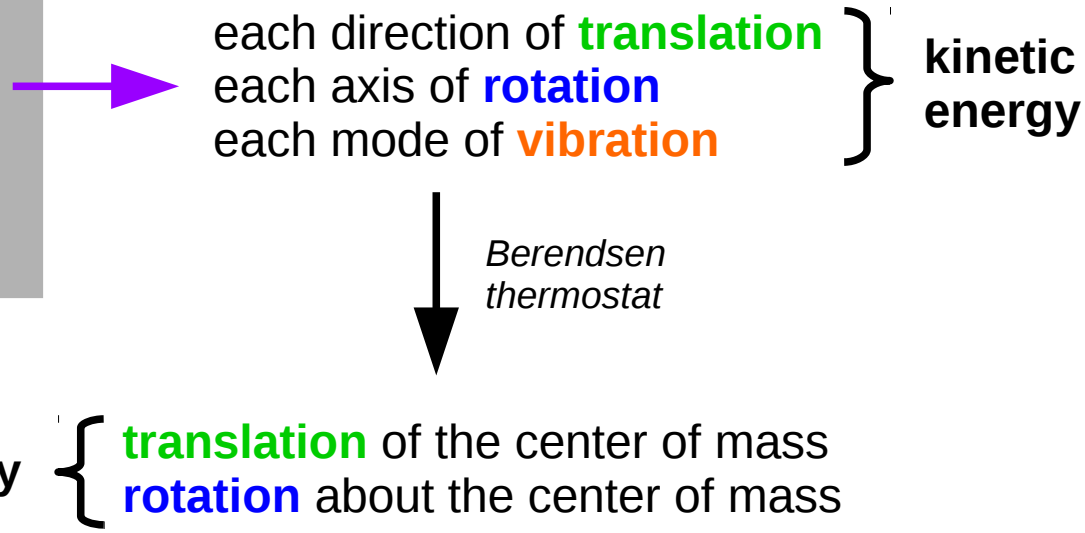
- **kinetic energy** is the same in both cases
- the ***distribution*** of kinetic energy differs

Equipartition Theorem

- “real systems *usually* do not behave as flying ice cubes”
- equipartition theorem is **violated**

Equipartition theorem

*Each **degree of freedom** has the same average kinetic energy.*



Cause of the Problem

- why does Berendsen thermostat **remove** some motions?
- it tries to achieve constant *instantaneous* kinetic energy => fluctuations of E_{kin} are **suppressed**
- NVT ensemble **does** allow the kinetic energy to fluctuate!
- BT samples some vaguely defined ensemble, not NVT

> *"Suppressed E_{kin} fluctuations force the thermostat to convert E_{kin} associated with high frequency motions to E_{kin} associated with low frequency motions."*
>
> – Math, unknown date

Solutions

- use Monte Carlo instead of Molecular Dynamics

- **remove** the center of mass motions
  `comm-mode = Linear / Angular`
- use **very long** coupling time
- periodically **reassign** velocities

} a combination of these three

- use **Andersen thermostat**

historical solutions

- **use a proper NVT velocity-rescaling thermostat**

Velocity-Rescaling Thermostat

- works similarly to the Berendsen thermostat
- but adds a **random** (stochastic) **factor** to the rescaling factor λ
- this allows for the **fluctuations** of kinetic energy

  => canonical ensemble is generated (sampled)

  => equipartition theorem is **not** violated

  => **no flying ice cube effect**

Take-Home Message

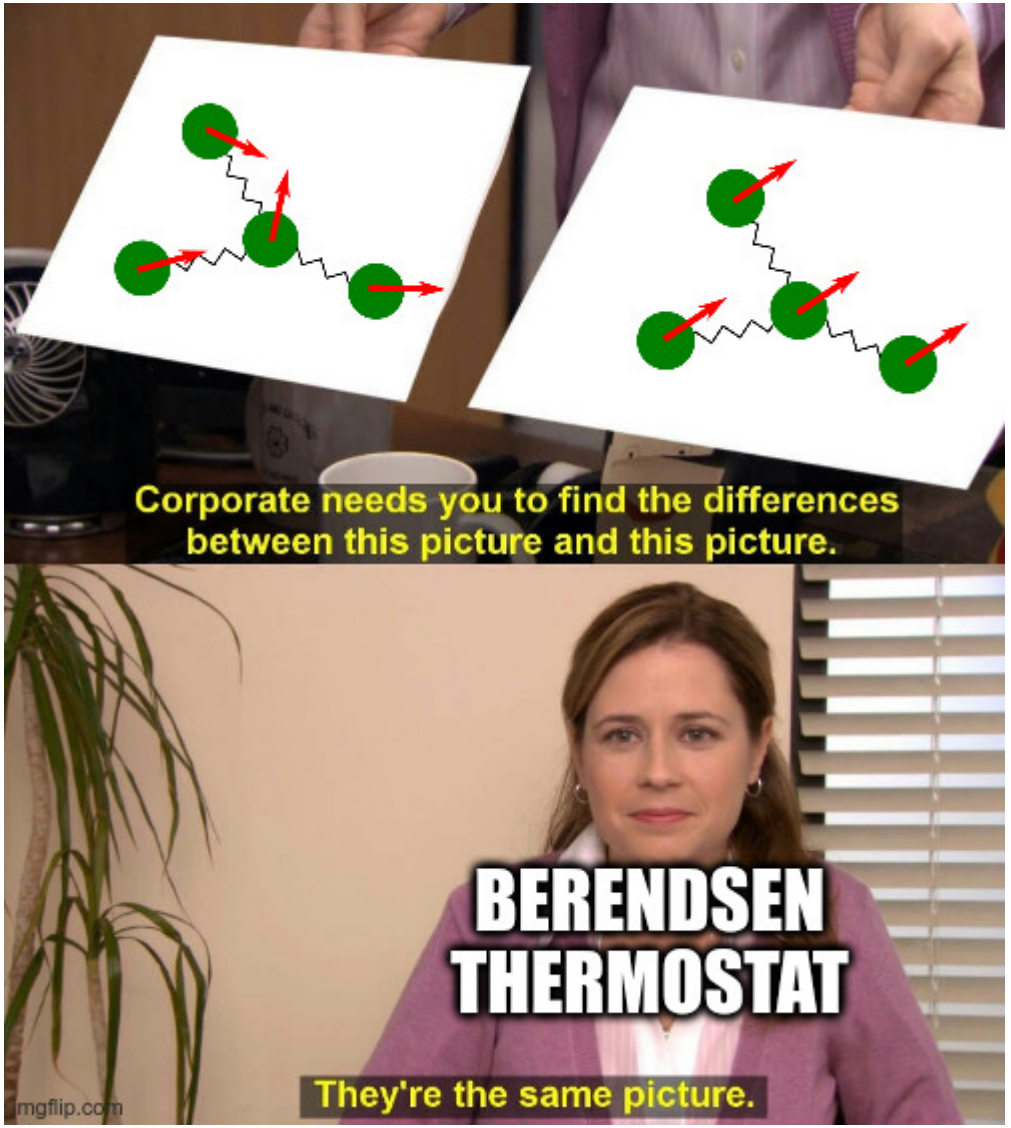
Do not use Berendsen thermostat!

Gromacs

- `tcoupl = berendsen` ✗
- `tcoupl = v-rescale` ✓
- `tcoupl = nose-hoover` ✓
- `tcoupl = andersen` ✓

Disclaimer

- system may **freeze** also for other reasons
- e.g. Martini CG water tends to freeze when generated on a lattice (grid)
- using the right thermostat does **not** solve everything!


Corporate needs you to find the differences between this picture and this picture.
BERENDSEN THERMOSTAT
They're the same picture.
imgflip.com