A bit more formal approach:
constrain the equations of motions to fix T

Force added to restrict a particle motion to a constraint hypersurface should be normal to the surface of realistic dynamics.

$\rightsquigarrow$ add $-\alpha p_i$ to force term of Hamiltonian Eqs.

$$\frac{\partial q_i}{\partial t} = \frac{p_i}{m_i} \quad ; \quad \frac{\partial p_i}{\partial t} = -\frac{\partial V(q)}{\partial q_i} - \alpha p_i$$

$\uparrow$ ~ friction

Determine α so that $\frac{dT}{dt} = 0$

$$\frac{g k_B T}{2} = \sum_i \frac{p_i^2}{2 m_i} \quad \Big| \ \frac{\partial}{\partial t}$$

$$\frac{g k_B}{2} \frac{\partial T}{\partial t} = \sum_i \frac{p_i}{m_i} \frac{\partial p_i}{\partial t} \overset{!}{=} 0$$

insert from above

$$\sum_i \frac{p_i}{m_i} \left(-\frac{\partial V(q)}{\partial q_i} - \alpha p_i \right) = 0$$

$$-\sum_i \frac{\partial V(q)}{\partial q_i} \frac{p_i}{m_i} = \alpha \sum_i \frac{p_i^2}{m_i}$$

$$\Rightarrow \quad \alpha = -\frac{\sum \frac{\partial V(q)}{\partial q_i} \frac{p_i}{m_i}}{\sum_i \frac{p_i^2}{m_i}}$$

Conserves canonical distribution in coordinate space.

§ 8.4 Proportional Timescaling: Berendsen thermostat

Velocity rescaling works too well. Temperature is really fixed, while in the canonical ensemble, the avrage energy is fixed and allowed fluctuations also translate into fluctuations of the instantaneous temperature.

Idea: Use a weaker coupling and try to drive the system dynamics towards the desired T_0

How? Velocities are scaled at each time-step in such a way that the rate of change of temperature is proportional to the difference in temperature:

$$\frac{dT}{dt} = \frac{1}{\tau}(T_0 - T) \qquad (*)$$

τ: coupling parameter

$$\Rightarrow T = T_0 - C_1 e^{-t/\tau}$$

exponential decay of T to T_0.

$(*)$ in discrete version:

$$\Delta T = \frac{\Delta t}{\tau}(T_0 - T)$$

and modification of momenta

$$p_i \to \lambda p_i$$

with $$\lambda^2 = 1 + \frac{\Delta t}{\tau}\left(\frac{T_0}{T} - 1\right)$$

§9. Barostats

As with temperature control, there are different ways of how to ensure constant pressure in Molecular Dynamics simulations.

The obvious question to start from is how to measure pressure?

§9.1 The Virial

Starting from the equations of motion

$$m_i \ddot{q}_i = \underline{F}_i^{tot}$$

we multiply this with q_i

$$\Rightarrow \quad m_i q_i \ddot{q}_i = q_i \underline{F}_i^{tot} \qquad (*)$$

Now consider : $q \ddot{q}_i = \frac{d}{dt}(q \dot{q}) - \dot{q}^2$

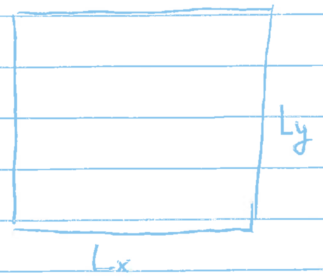
$$\Rightarrow \quad \frac{\partial}{\partial t}(m_i q_i \dot{q}_i) - m_i \dot{q}_i^2 = \underline{F}_i^{tot} q_i$$

Summing $(*)$ over all particles and integrating over the trajectory, leads to

$$\langle W \rangle = \langle \sum_i q_i \underline{F}_i^{tot} \rangle = - \underbrace{\langle m_i \dot{q}_i^2 \rangle}$$

$$= -2 \cdot E_{kin}$$

Why did we write F^{tot}?



macroscopically we have particles in a box with fixed walls

In addition to the internal forces prescribed by the force-field, the walls cause an extra force F^{ext}

Assume the box is ~~cubic~~ a parallelepipedic container with L_x, L_y, L_z.
Then the average virial caused by the external force is

$$\langle W^{ext} \rangle = L_x(-pL_yL_z) + L_y(-pL_xL_z) + L_z(-pL_xL_y)$$

$$= -3pV$$

$\Rightarrow$

$$\langle W \rangle = \underbrace{\left\langle \sum_i q_i F_i^{int} \right\rangle}_{:= \Theta} - 3pV = -2E_{kin}$$

Or if rearranged:

$$p = \frac{2}{3V}\left(\frac{\Theta}{2} - E_{kin}\right)$$

$\Rightarrow$ Indicates two possible dials the adjust pressure.

- changing E_{kin}
- changing Θ

/2

Adjusting the kinetic energy means modifying particle velocities

$\Rightarrow$ changing temperature of the simulated system

↯

§ 9.2 Berendsen barostat

Situation:
- system is weakly coupled to an external bath, allowing for a pressure change

$$\frac{dP}{dt} = \frac{P_0 - P}{\tau_P}$$

τ_P: some time constant for the coupling

- make modifications so that the local pertubations are small

Berendsen achieved this by modifying the equation

$$\dot{\underline{q}} = \underline{v}$$

into

$$\dot{\underline{q}} = \underline{v} + \alpha \underline{x}$$

This corresponds to a simple rescaling of coordinates – and concomitantly – the volume

$$\dot{V} = 3\alpha V$$

What is α?

Let's consider the pressure change again:

$$\frac{dP}{dt} = -\frac{1}{\beta V}\frac{dV}{dt} \qquad \beta\text{: isothermal compressibility}$$

$$= -\frac{3\alpha}{\beta} = \frac{p_0 - p}{\tau_p}$$

$$\Rightarrow \quad \alpha = -\frac{\beta(p_0 - p)}{3\tau_p}$$

$\Rightarrow$ in Eq. for $\dot{q}$

$$\dot{q} = v - \frac{\beta(p_0 - p)}{3\tau_p} q$$

via $q(\cancel{t+\Delta t}) = \cancel{\Delta} v \Delta t - \frac{\beta(p_0 - p)}{3\tau_p} \Delta t \, q$

$\Rightarrow$ scaling of all coordinates

with factor $\boxed{\mu = 1 - \frac{\beta \Delta t}{\tau_p}(p_0 - p)}$

$$q \rightarrow \mu q$$

But one should know some good value for β.

$\Rightarrow$ generalizations to anisotropic systems possible