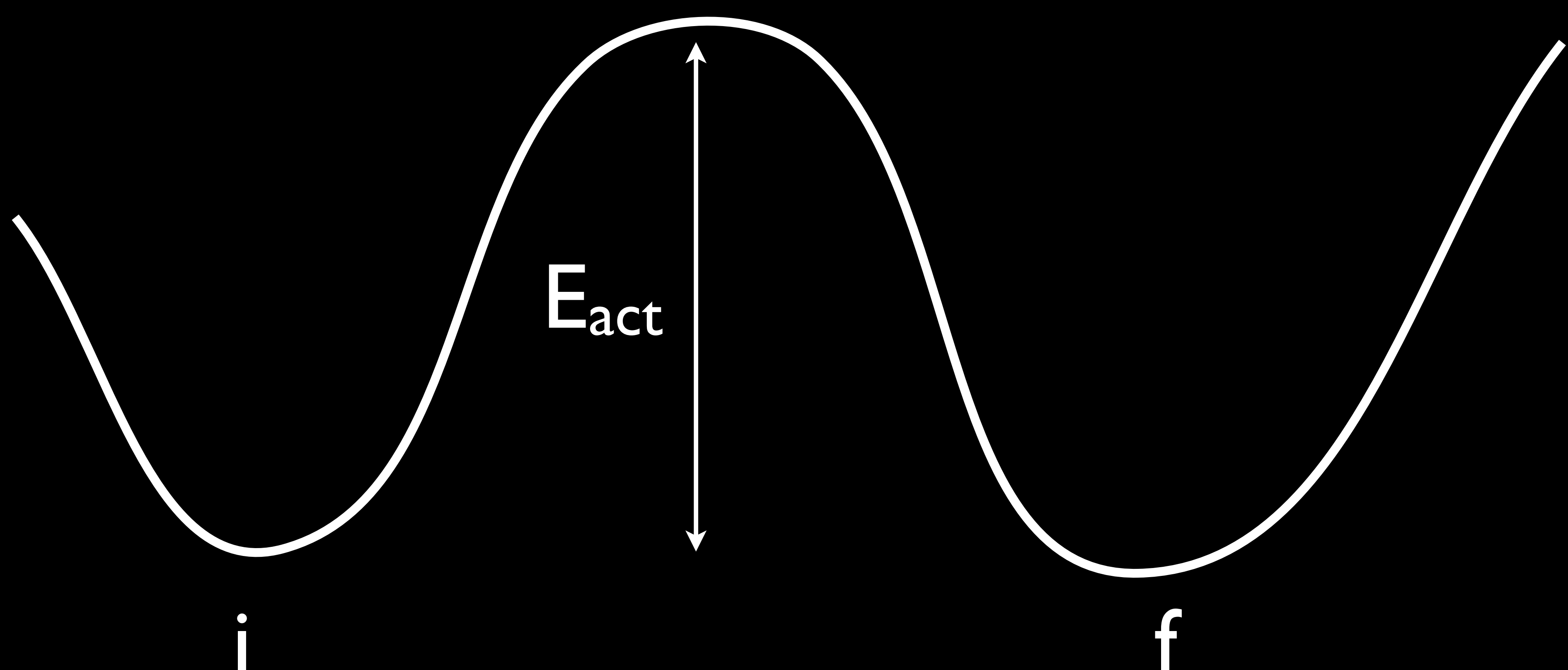
Modelling defect migration

Modelling rare events

Jump probability/reaction constant

$$i \longrightarrow f$$

$$R \propto e^{-\frac{G_{act}}{kT}}$$



Arrhenius law

$$R \propto e^{\frac{-G_{act}}{kT}} = e^{\frac{-(E_{act}-ST)}{kT}}$$

$$Ln(D) = Ln(D0) - \frac{E_{act}}{kT}$$

Reaction rate or diffusion coefficient

?

Rare events?

$$R \propto e^{-\frac{G_{act}}{kT}}$$

$k=8.617\,3324(78)\times10^{-5}\ eVK^{-1}$

G_{act}~1 eV

?

Rare events?

$$R \propto e^{-\frac{G_{act}}{kT}}$$

k=8.617 3324(78)×10^{-5} eVK^{-1}

G_{act}~1 eV

1 eV ~ 10000 K!!!!!!!!!

atomic diffusion

Einstein law

$$D \equiv \frac{1}{2d} lim_{t \to \infty} \frac{\langle [r(t_0 + t) - r(t_0)]^2 \rangle}{t}$$

computationally affordable for T~ T fusion

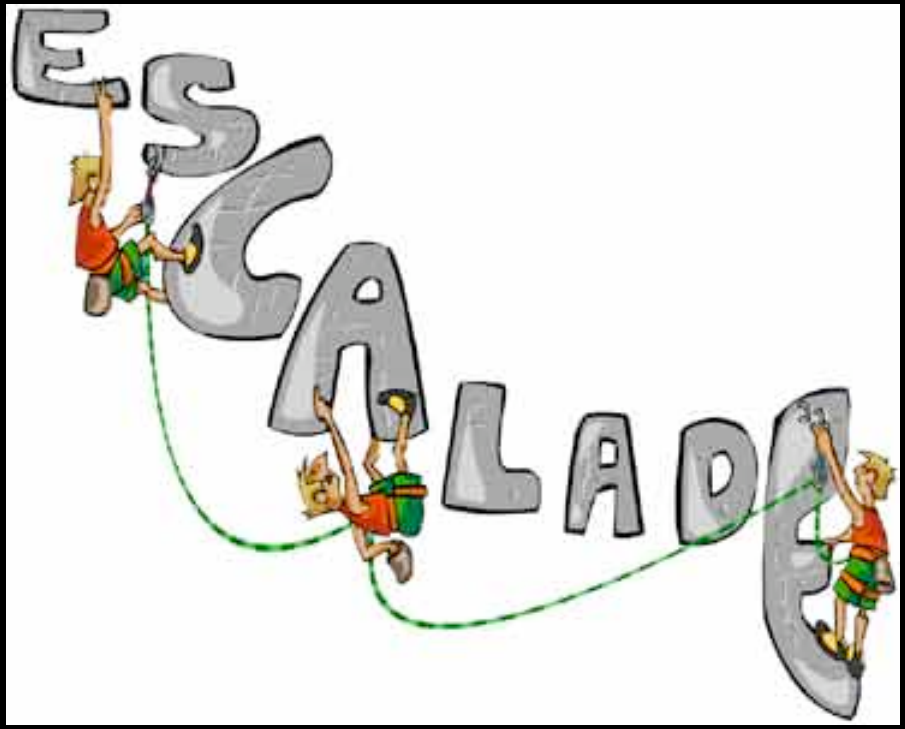
?

- Que pasaria si los atomos estan solo oscilando alrededor de la posicion de equilibrio?
- Y si los atomos se mueven como en un liquido?

Modelling?

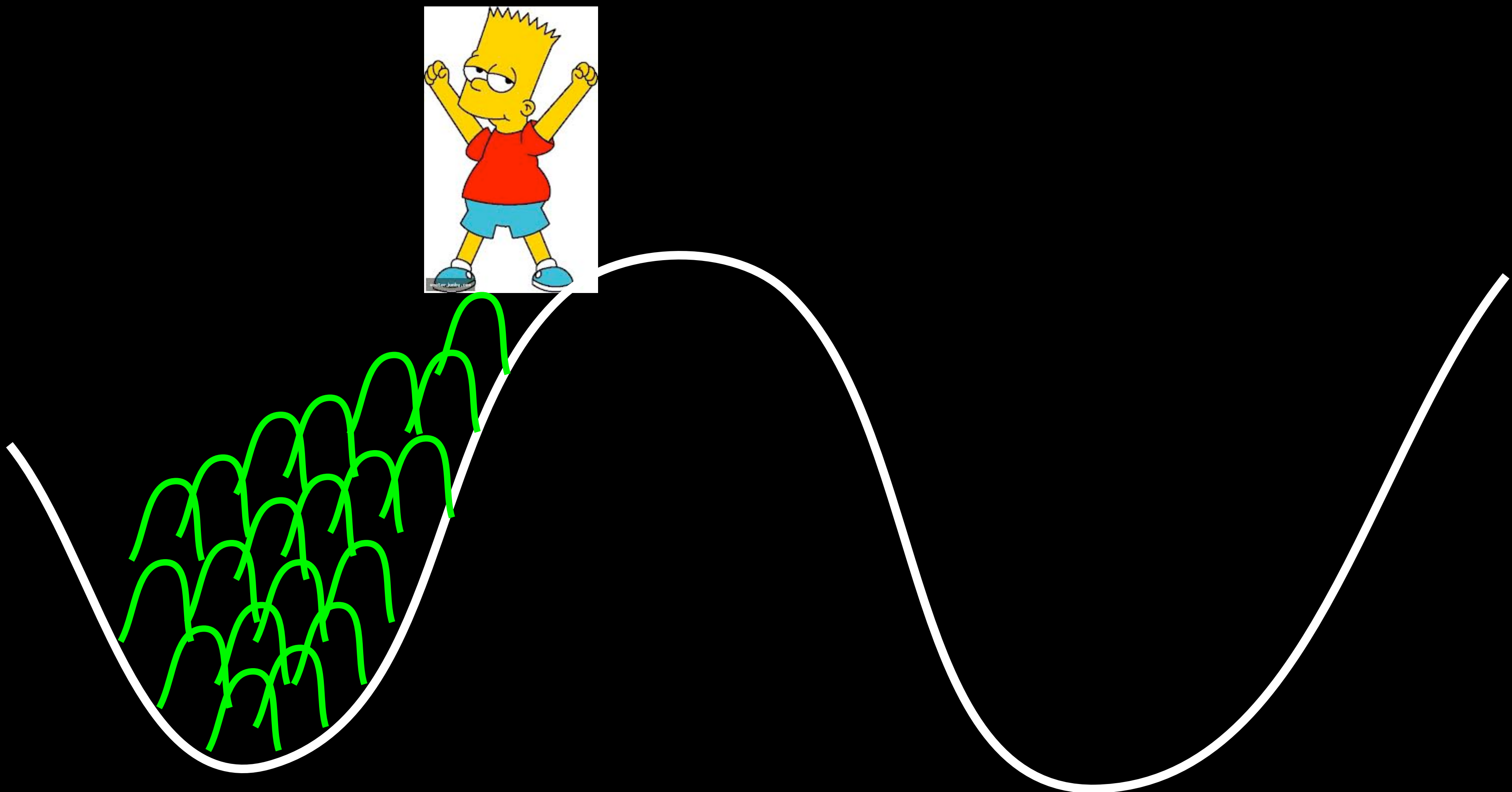
"Force the atoms to climb"

Drag like approaches



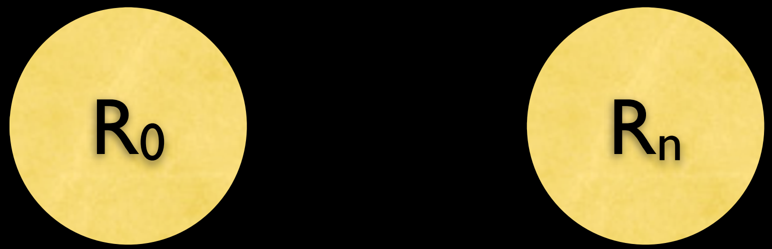
Nudged Elastic Band

"Fill the wells"



METADYNAMICS

Drag method



1) identification of drag coordinate
2) the forces parallel to the drag direction are inverted
-> forcing the system to climb
3) minimisation algorithm on parallel velocities

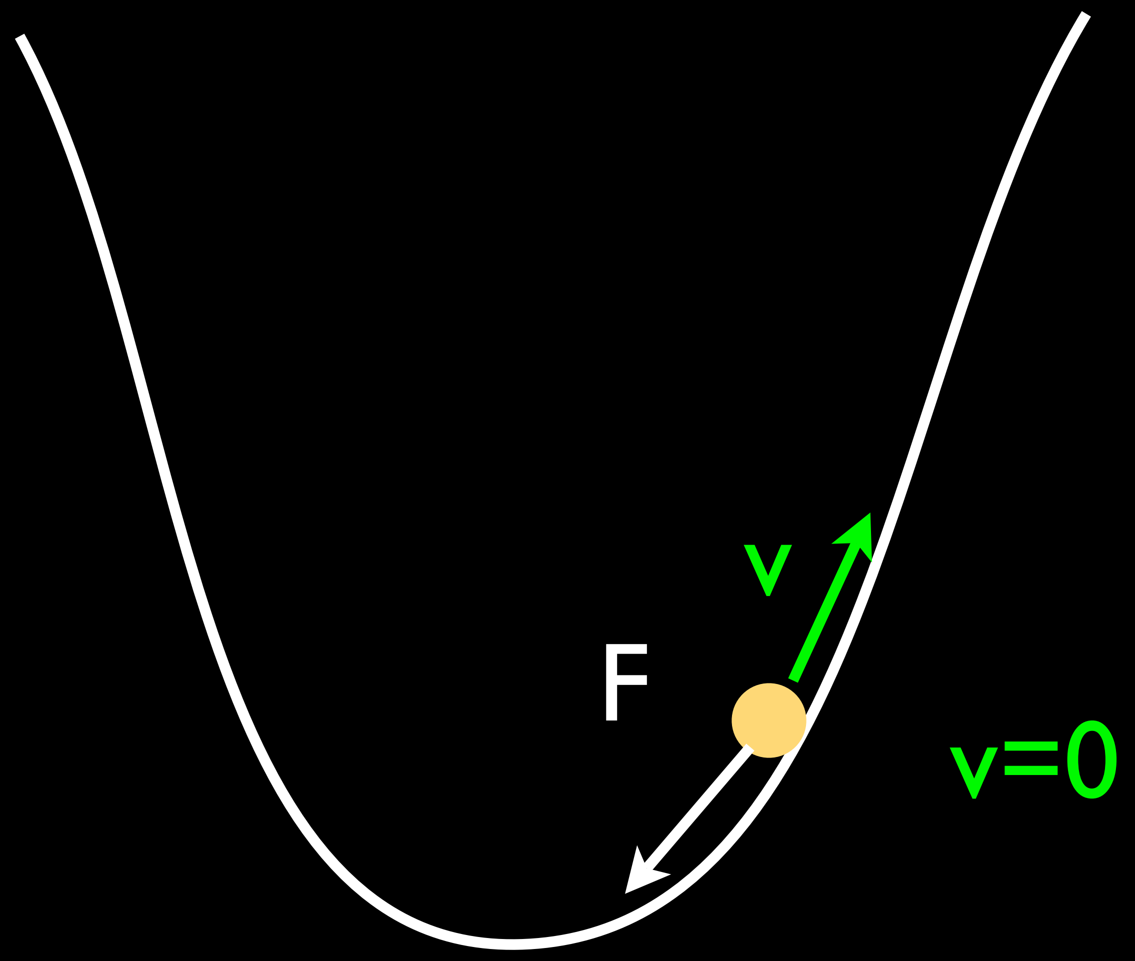
minization: dumped verlet

$$\frac{d^2 x_i(t)}{dt^2} = \frac{Fi}{mi}$$

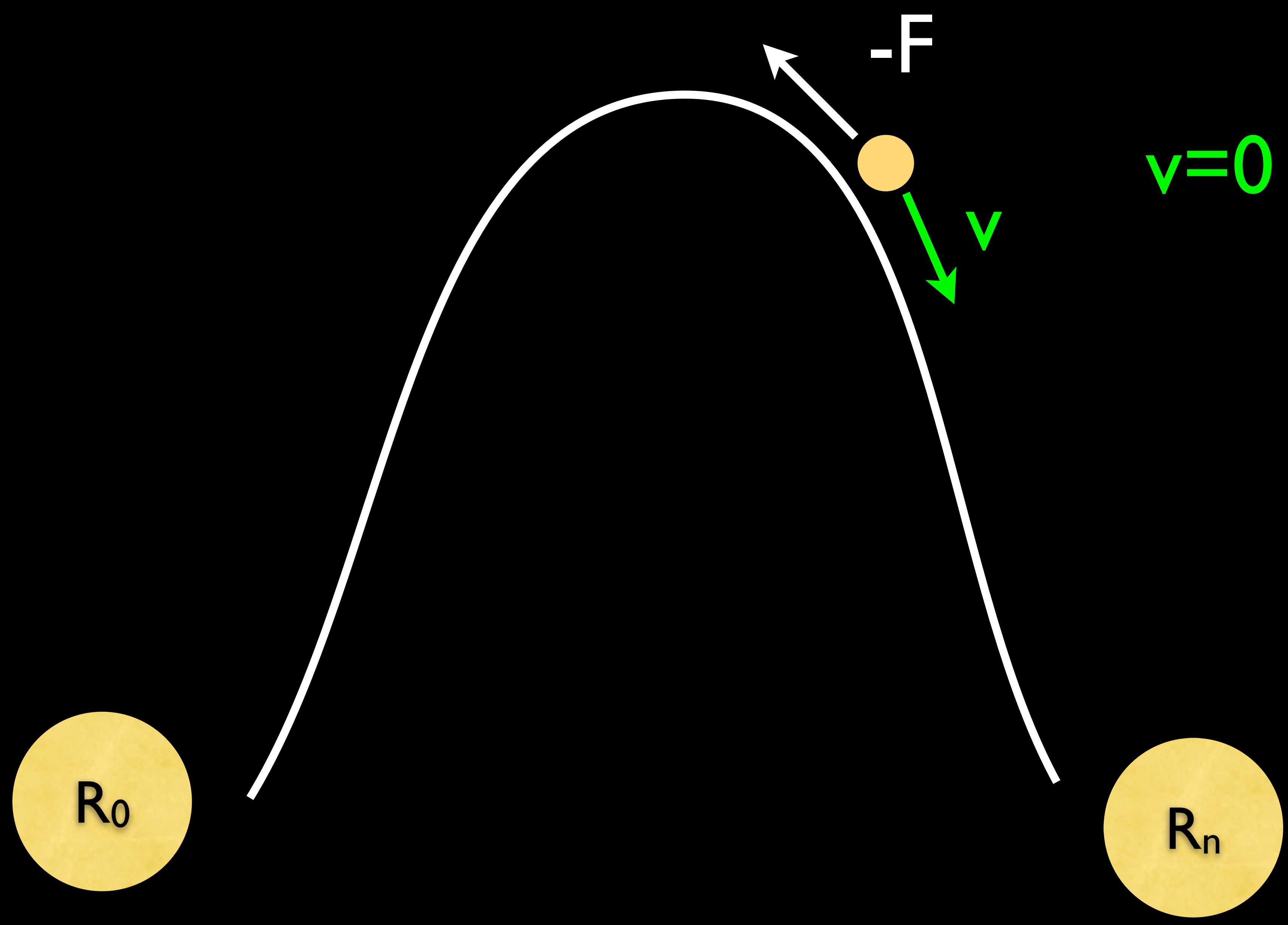
$$\frac{d^2 x_i(t)}{dt^2} =\sim \frac{x_i(t+\Delta t) - x_i(t)}{\Delta t^2} - \frac{x_i(t) - x_i(t-\Delta t)}{\Delta t^2}$$

$$x_i(t+\Delta t) - x_i(t) - x_i(t) - x_i(t-\Delta t) = \frac{F_i}{m_i}\Delta t^2$$

$$x_i(t+\Delta t) = 2x_i(t) - x_i(t-\Delta t) + \frac{F_i}{m_i}\Delta t^2$$

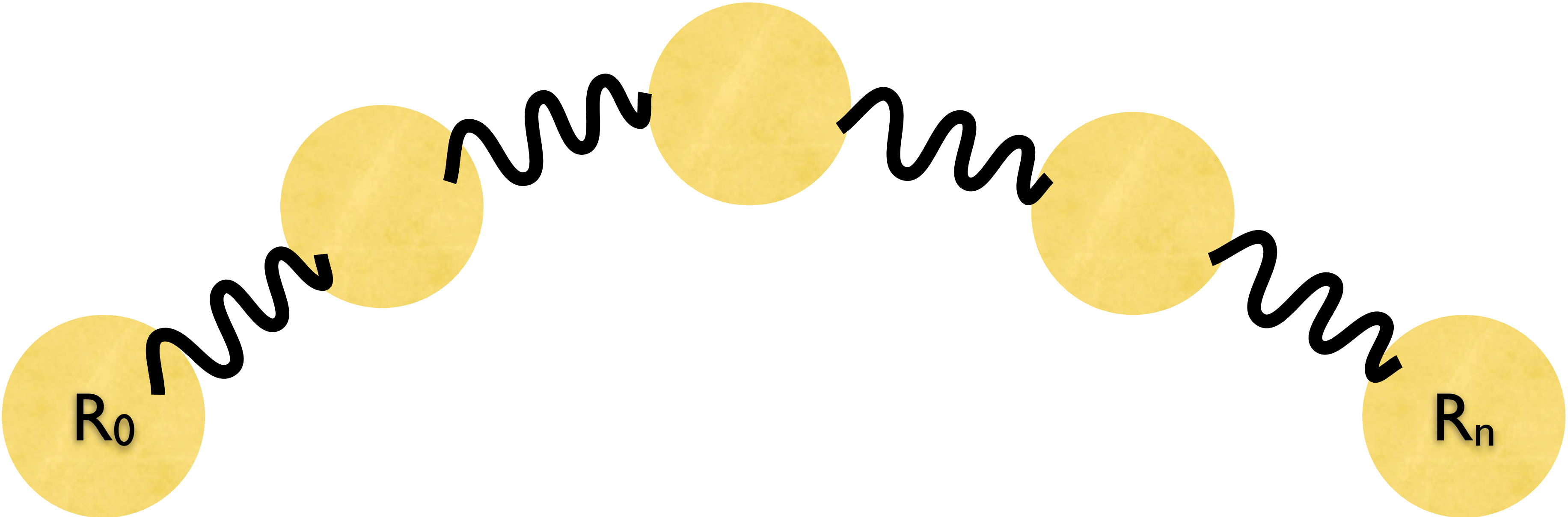

v
F
v=0

Drag method



NEB

$$R_i = R_0 + \frac{i}{n}(R_n - R_0)$$



$$S(R_1, R_2, R_3, ...R_n) = \sum_{i=1}^{n-1} E(Ri) + \sum_{i=1}^{n} \frac{k}{2}(R_i - R_{i-1})^2$$

NEB

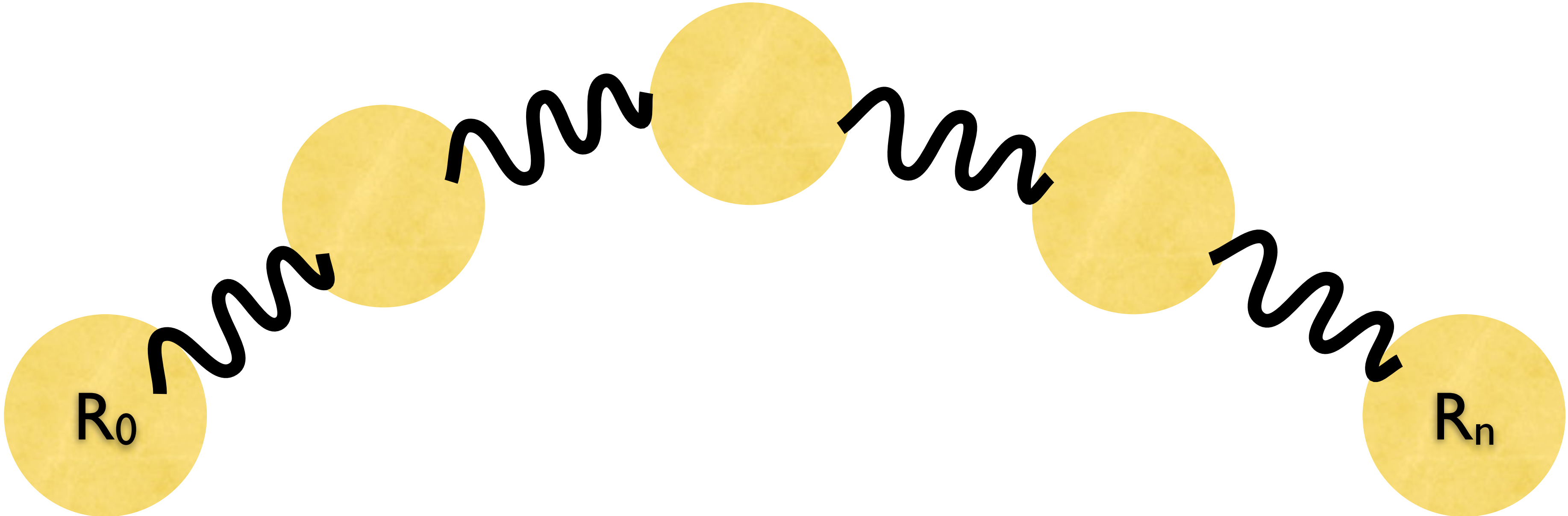
$$F_i = -\nabla E(R_i) + k((R_{i+1} - R_i) - (R_i - R_{i-1}))$$

real force Elastic force (F_s)

$$F_i^{'} = -\nabla E(R_i)|_{perp} + F_s|_{paral} \rightarrow 0$$

INPUT PARAMETERS

$$R_i = R_0 + \frac{i}{n}(R_n - R_0)$$



$$S(R_1, R_2, R_3, ...R_n) = \sum_{i=1}^{n-1} E(Ri) + \sum_{i=1}^{n} \frac{k}{2}(R_i - R_{i-1})^2$$

?

- Como se escribe el vector tangente a la cadena en i?

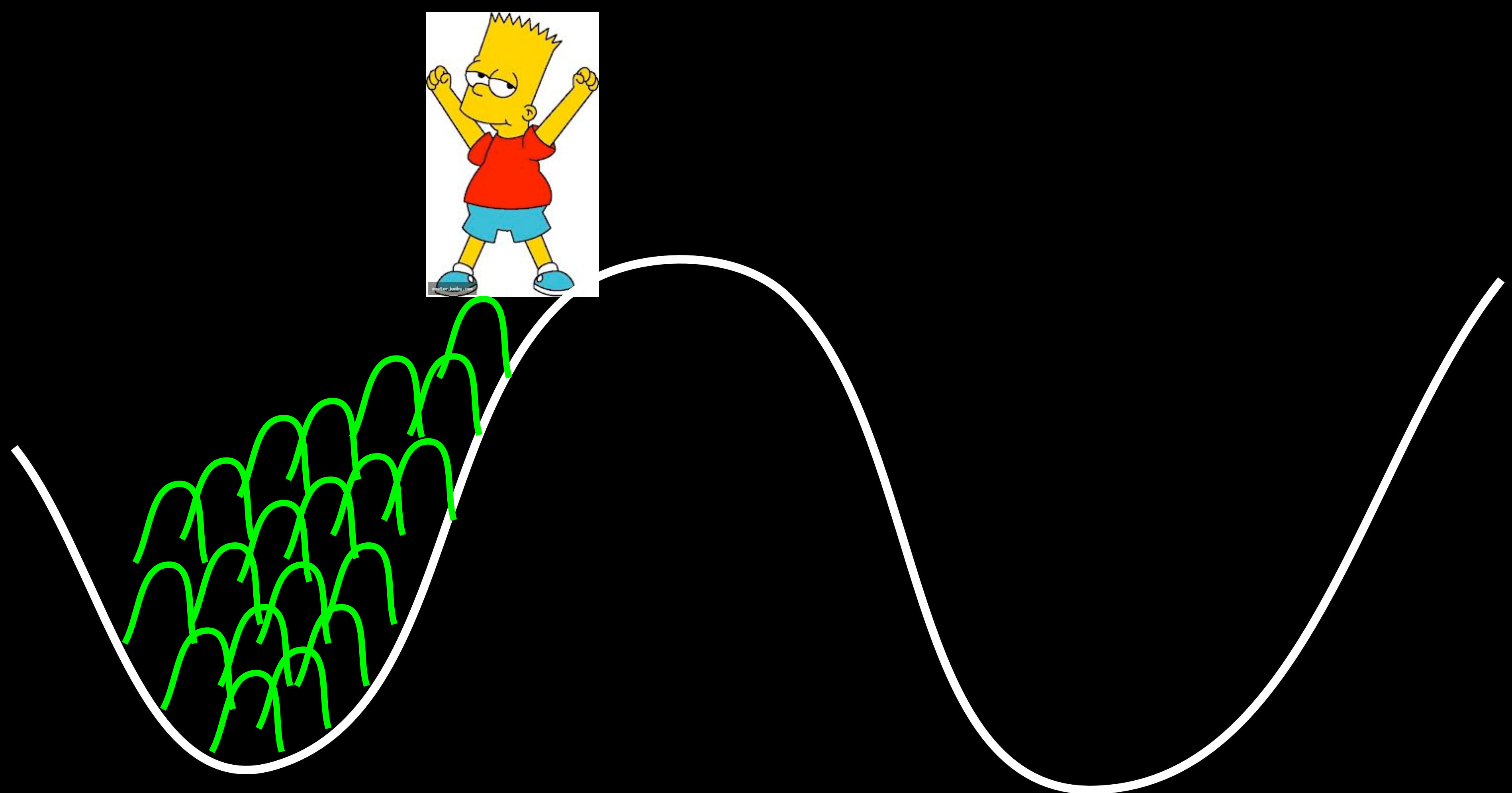
Climbing NEB

- "Highest" E configuration, spring force set to 0, real parallel force sign inverted.

Metadynamics

- “Constraint” dynamics.
- Explore the free energy as a function of a set of Collective Variables (CV).
- History-dependent random-walk (MD).
- A repulsive Gaussian is added each g*MD steps.

“Fill the wells”



Collective variables s : distance between atoms, dihedral angle, ...

bias potential: "external potential"

$$V(\vec{s},t) = \sum_{k\tau<t} W(k\tau) \exp\left(-\sum_{i=1}^{d} \frac{(s_i - s_i^{(0)}(k\tau))^2}{2\sigma_i^2}\right)$$

Collective variables s : distance between atoms, dihedral angle, ...

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Height

Collective variables s : distance between atoms, dihedral angle, ...

bias potential: "external potential"

$$V(\vec{s},t) = \sum_{k\tau<t} W(k\tau) \exp\left(-\sum_{i=1}^{d} \frac{(s_i - s_i^{(0)}(k\tau))^2}{2\sigma_i^2}\right)$$

width (standard deviation)

Collective variables s : distance between atoms, dihedral angle, ...

bias potential: "external potential"

position of the centroid

$$V(\vec{s},t) = \sum_{k\tau<t} W(k\tau) \exp\left(-\sum_{i=1}^{d} \frac{(s_i - s_i^{(0)}(k\tau))^2}{2\sigma_i^2} \right)$$

Collective variables s : distance between atoms, dihedral angle, ...

bias potential: "external potential"

$$V(\vec{s},t) = \sum_{k\tau<t} W(k\tau)\exp\left(-\sum_{i=1}^{d}\frac{(s_i - s_i^{(0)}(k\tau))^2}{2\sigma_i^2}\right)$$

"history" dependence

Basic assumption:

$$lim_{t\to\infty} V(s,t) \sim -F(s)$$

$$F(s) \sim < V(s,t) >_t$$

time average

In a practical implementation the forces are modified

$$F = -\nabla V$$

?

Drag coordinate/CV examples

Moral de la historia

- Hay que saber muy bien que fenomeno se quiere estudiar y con que se quiere comparar.
- Las reacciones quimicas/ la migration hay que elegir "inteligentemente" un camino inicial.
- El problema de N electrones que interaccionan es muy complejo. Hay que conocer muy bien el rango de validez de las approximaciones.
- Sistema desordenado ... hay que cojerselo con filosofia y tanta tanta tila!!

email address and useful links

- lmartinsamos@gmail.com
- www.quantum-espresso.org
- www.yambo-code.org
- www.sissa.it