Hands-On Tutorial Workshop, July 19th 2011

Thermostats and Thermal Transport in Solids

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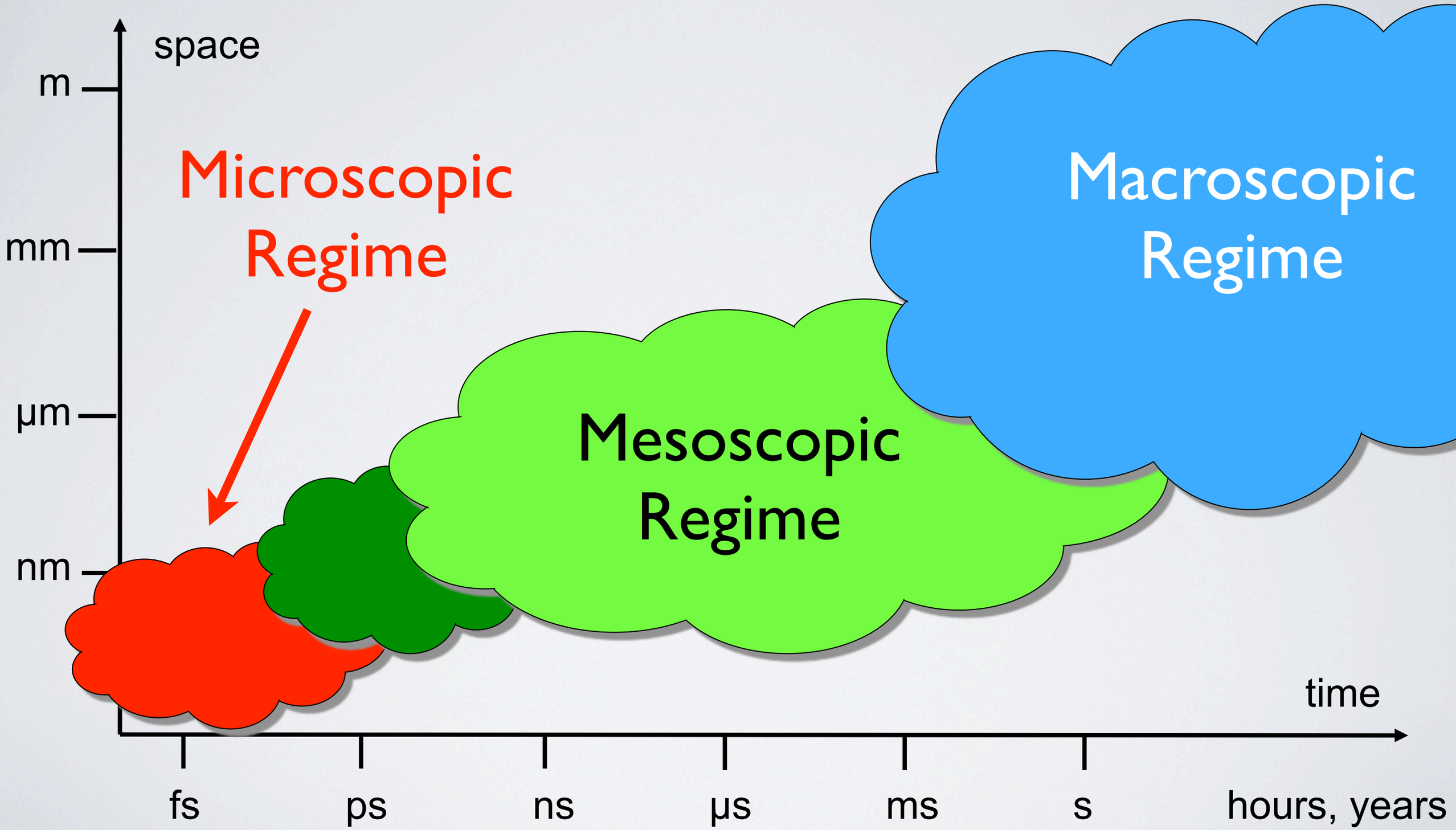
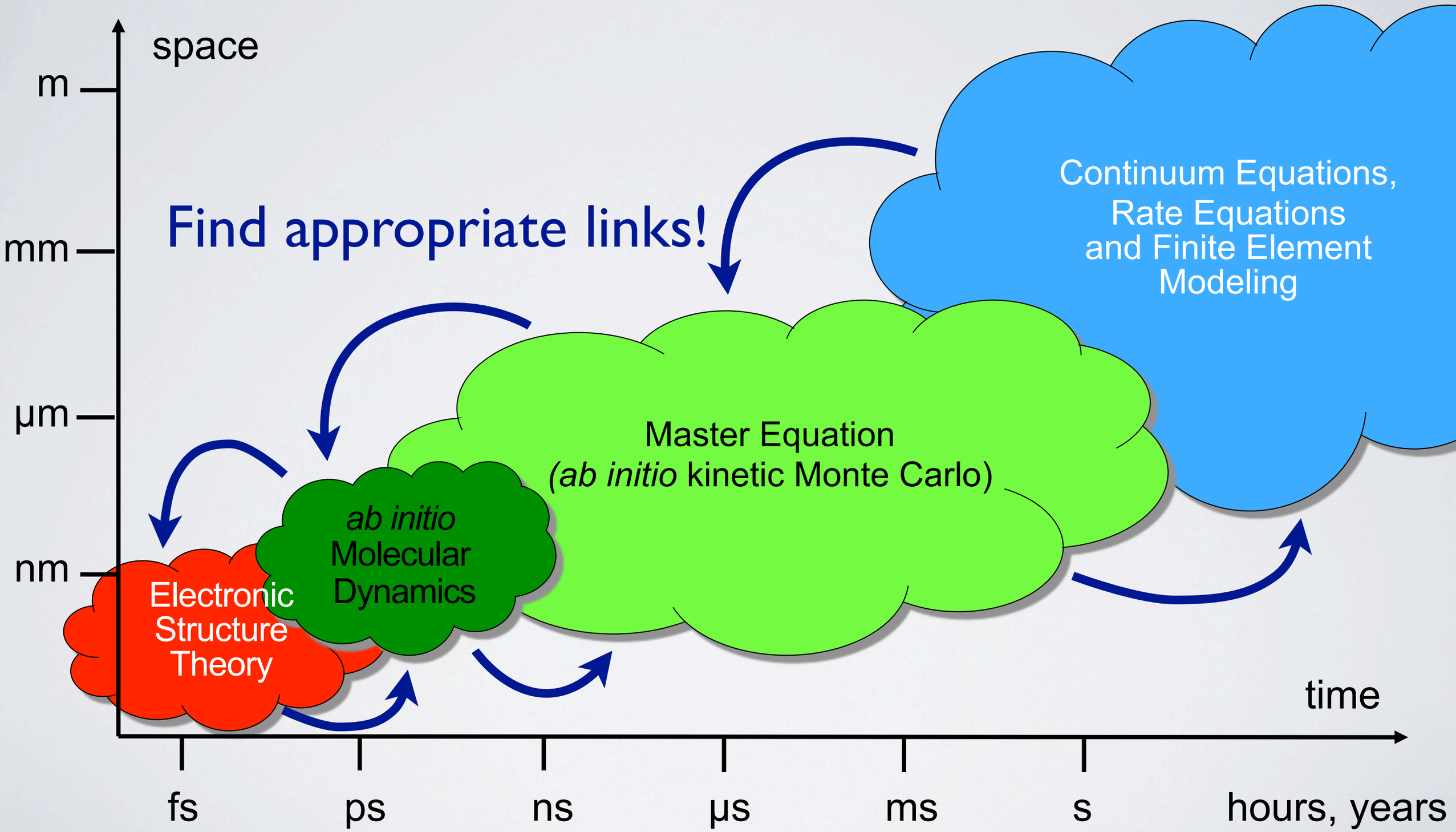
Christian Carbogno

Materials Department,
University of California
Santa Barbara

MULTI-SCALE MODELING



MULTI-SCALE MODELING



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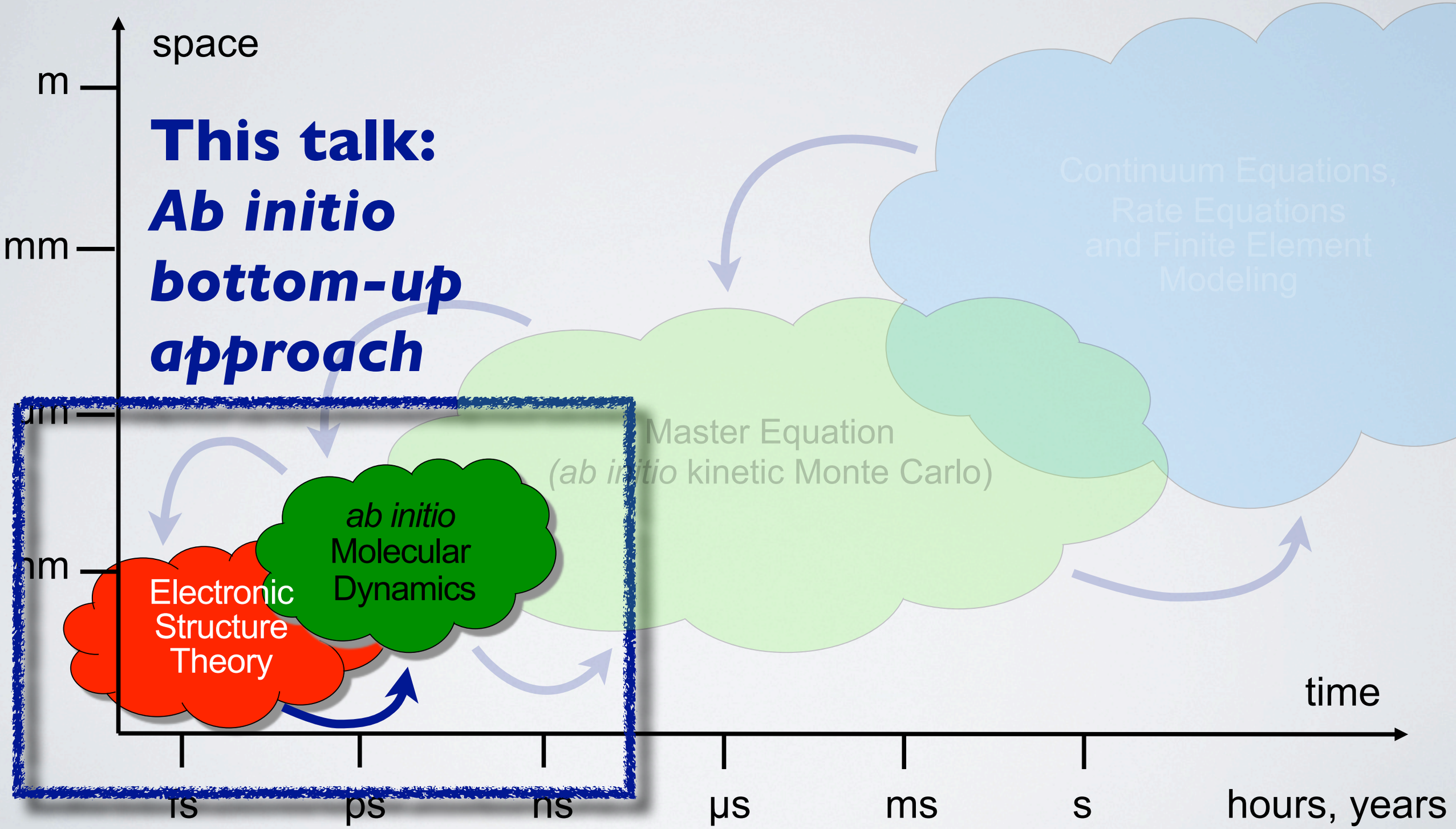


THERMODYNAMIC EQUILIBRIUM IN A NUTSHELL

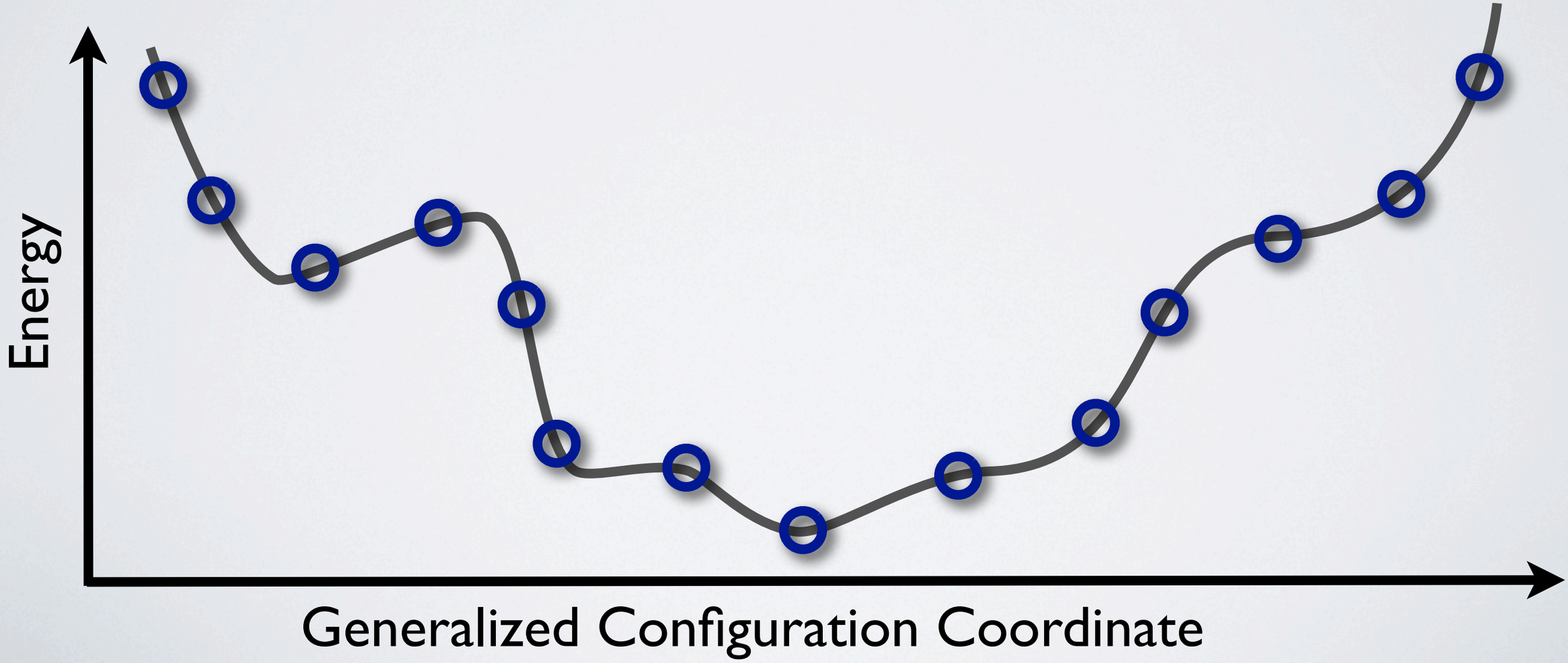
A classical system with **N atoms**, a **Volume V** and a **Temperature T** is described by its **canonical partition function Z(T,V,N)** viz. its **Helmholtz Free Energy F(T,V,N)**.

$$
\begin{aligned}
F(T,V,N) &= -k_B \ln\left(Z(T,V,N)\right) \\
&= -k_B \ln\left(\frac{1}{N!\hbar^{3N}} \int \exp\left(-\frac{\mathcal{H}(\{\mathbf{x}_i\},\{\mathbf{p}_i\})}{k_B T}\right) \{d^3\mathbf{x}_i\}\{d^3\mathbf{p}_i\}\right)
\end{aligned}
$$

Calculating the energy of **all possible configurations {x_i}** is **numerically unfeasible** even for very small systems.

THERMODYNAMIC AVERAGE

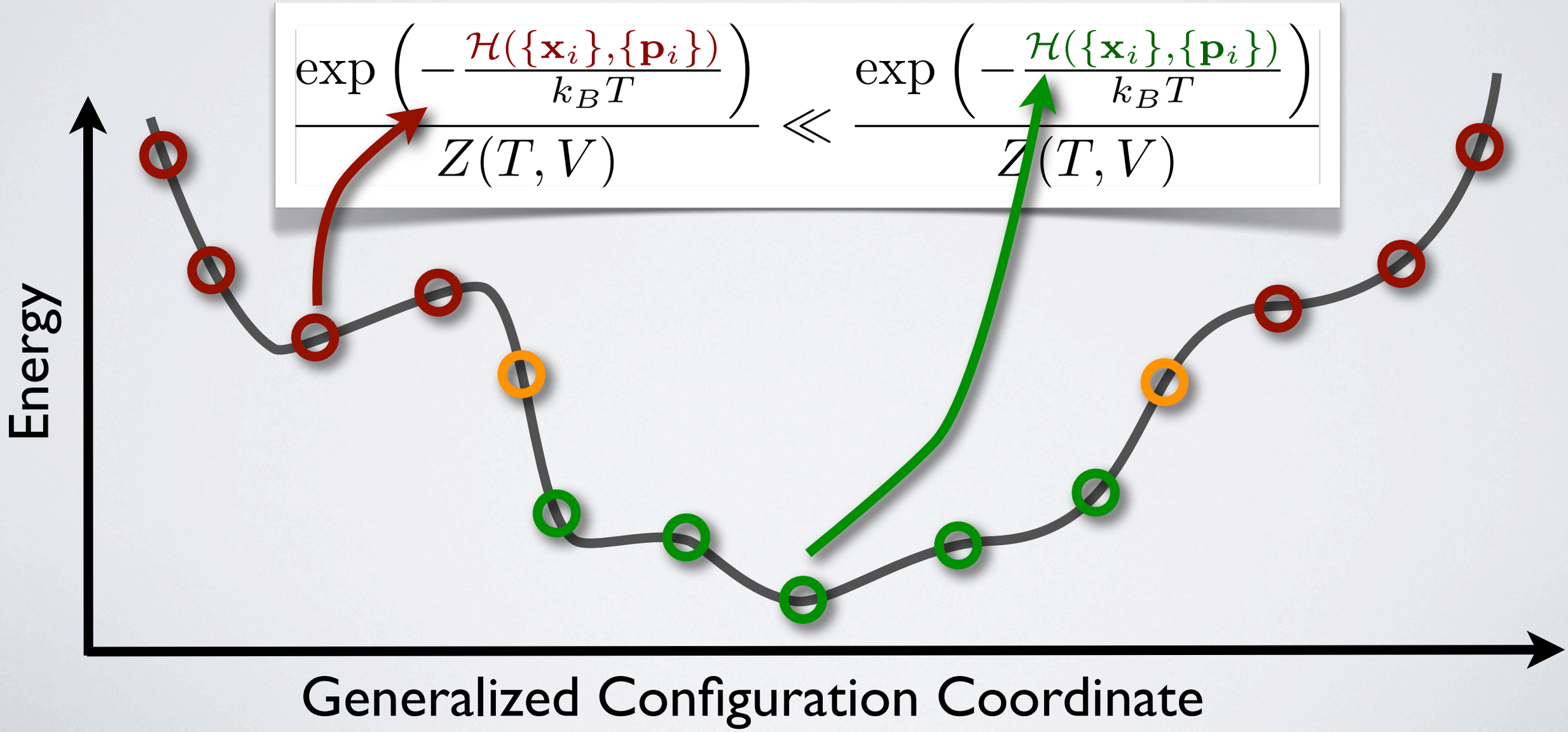
$$\langle X \rangle_{T,V} = \frac{1}{Z(T,V)} \int X \ \exp\left(-\frac{\mathcal{H}(\{\mathbf{x}_i\},\{\mathbf{p}_i\})}{k_B T}\right) \{d^3\mathbf{x}_i\}\{d^3\mathbf{p}_i\}$$



THERMODYNAMIC AVERAGE

$$\langle X \rangle_{T,V} = \frac{1}{Z(T,V)} \int X \ \exp\left(-\frac{\mathcal{H}(\{\mathbf{x}_i\},\{\mathbf{p}_i\})}{k_B T}\right) \{d^3\mathbf{x}_i\}\{d^3\mathbf{p}_i\}$$

$$\frac{\exp\left(-\frac{\mathcal{H}(\{\mathbf{x}_i\},\{\mathbf{p}_i\})}{k_B T}\right)}{Z(T,V)} \ll \frac{\exp\left(-\frac{\mathcal{H}(\{\mathbf{x}_i\},\{\mathbf{p}_i\})}{k_B T}\right)}{Z(T,V)}$$

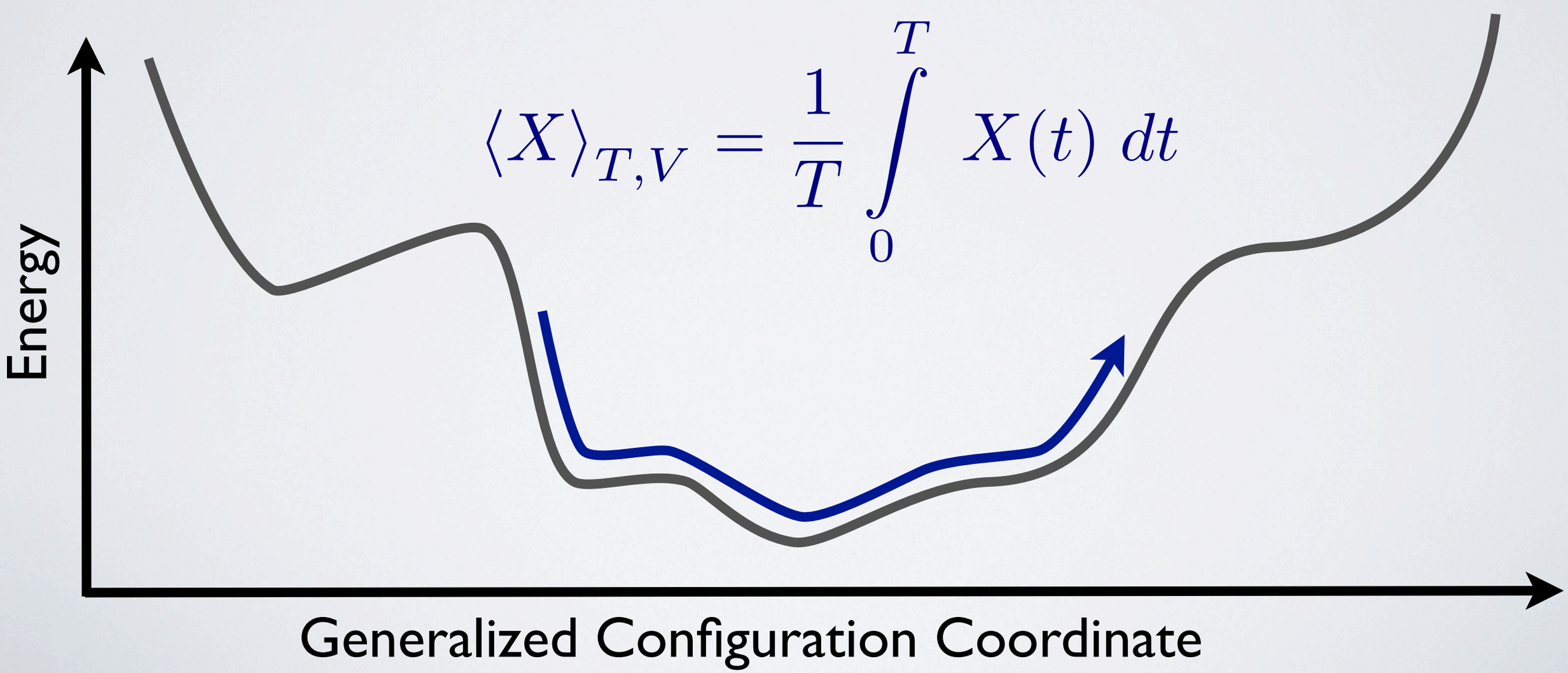


ERGODIC HYPOTHESIS

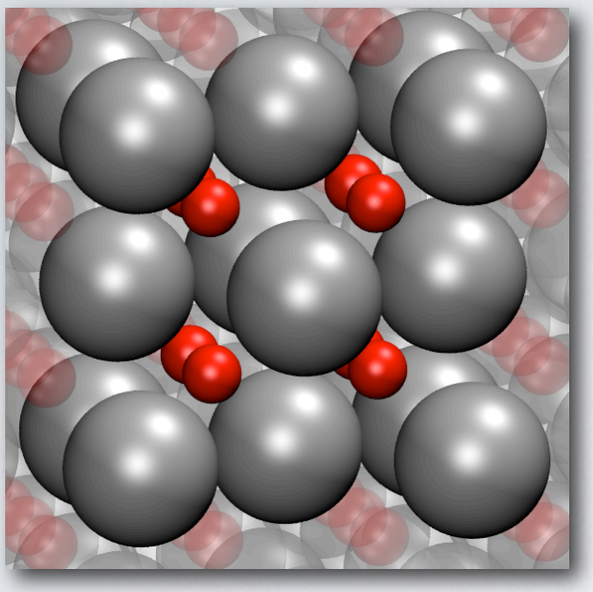
All accessible micro-states are **equiprobable**
over a long period of time:

The Time Average is equal to the Ensemble Average!

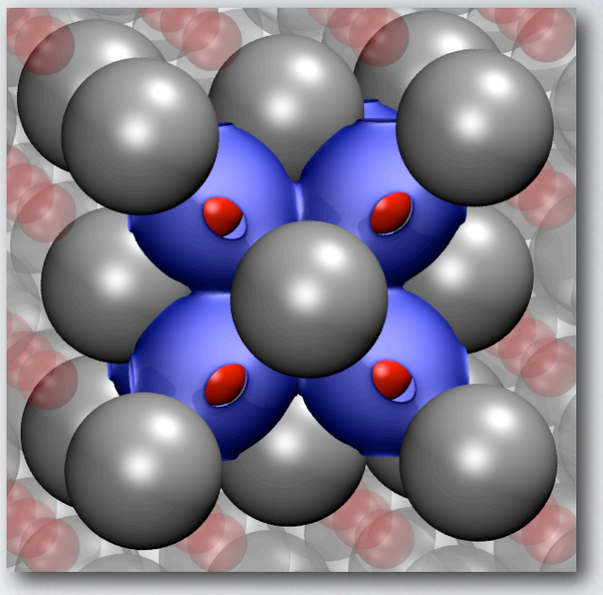
$$\langle X \rangle_{T,V} = \frac{1}{T} \int_0^T X(t)\, dt$$



AB INITIO MOLECULAR DYNAMICS



Electronic Structure Theory Code



Input:
Geometry, Species

Output:
total **energy** & **forces**

Update geometry

Iterative Approach: Explore the Dynamics of the Atoms!

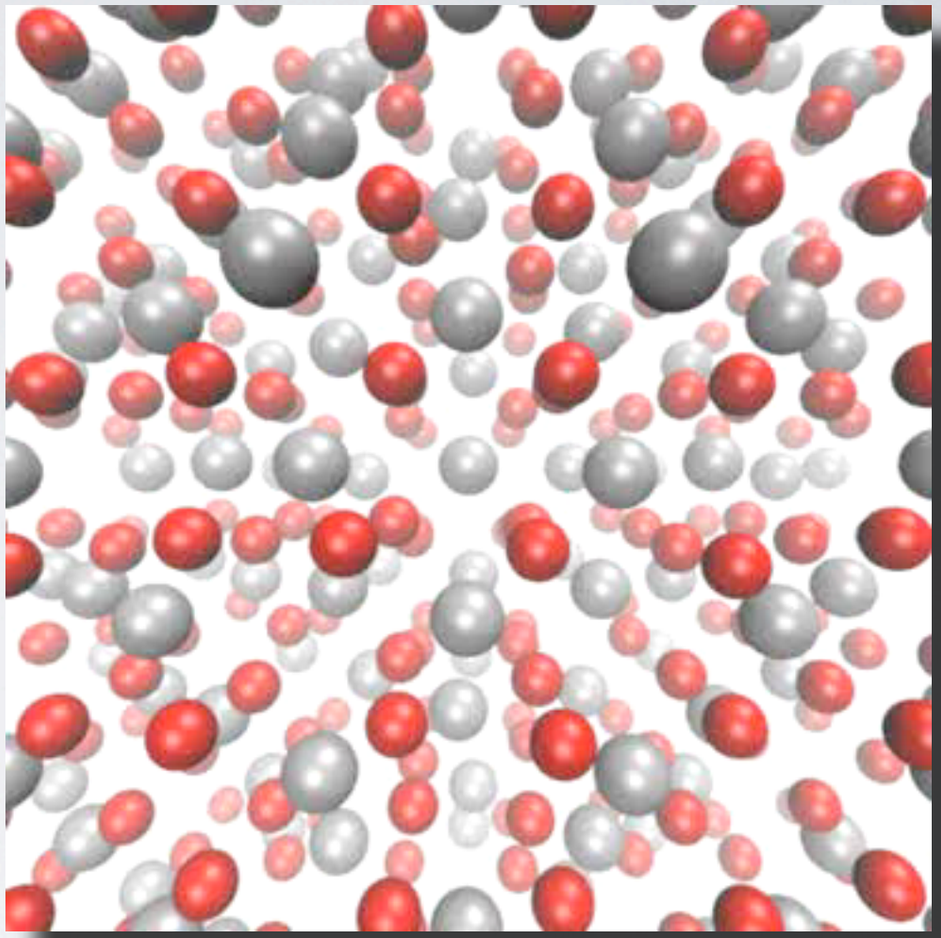
AB INITIO MOLECULAR DYNAMICS

Numerical Integration
of the **equations of motion**

L. Verlet, *Phys. Rev.* **159**, 98 (1967).

$$M_I \ddot{\mathbf{R}}_I(t) = \mathbf{F}_I(\mathbf{R}_1(t), \cdots, \mathbf{R}_N(t))$$

Initial conditions have to be specified!



The **Verlet Algorithm** conserves the number of particles **N**, the volume **V**, and the energy **E**.

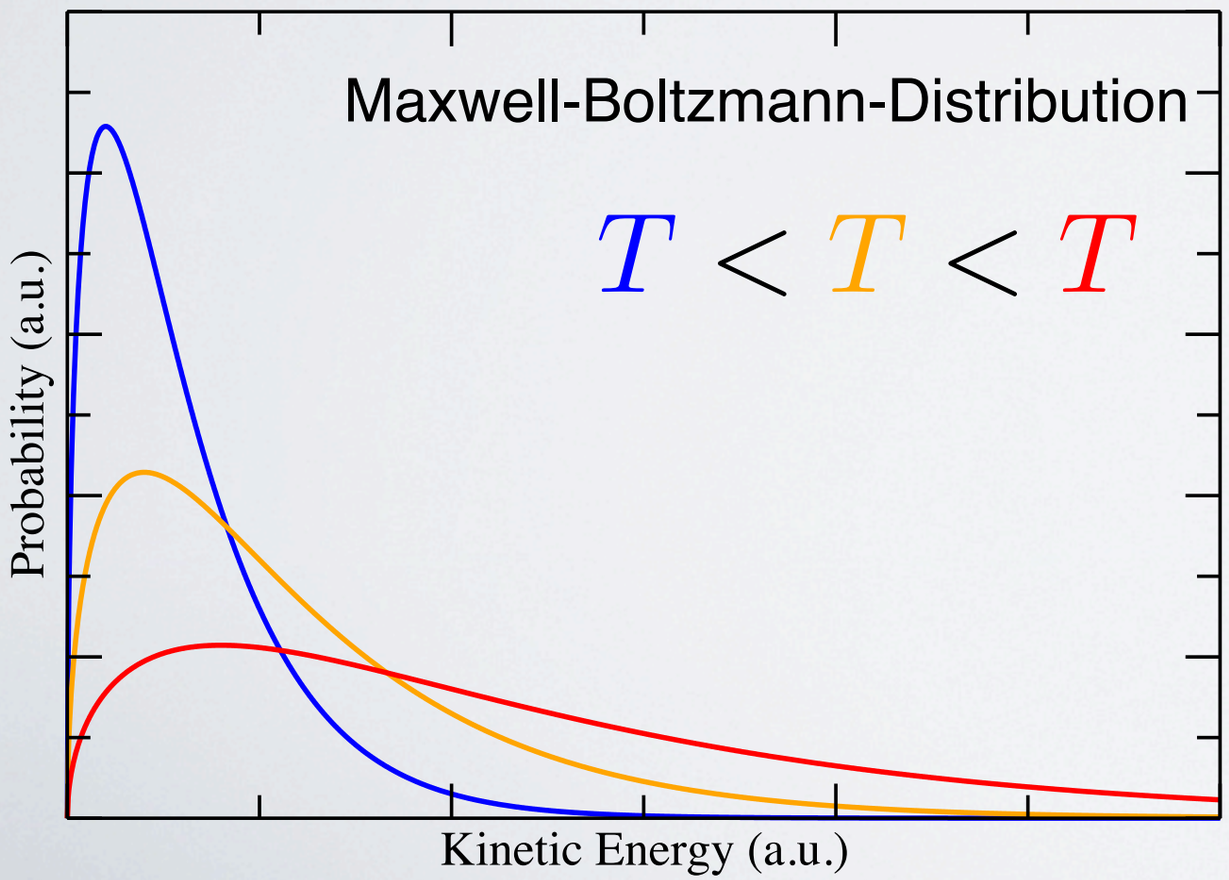
⇒ **Micro-canonical Ensemble**

THE CANONICAL ENSEMBLE

⇒

Conserved quantities:

- Number of particles **N**
- Volume **V**
- Average Temperature **T**



kinetic Energy

$$T = \langle T(t) \rangle = \left\langle \frac{2\ E_{kin}}{3\ k_B\ N_{dof}} \right\rangle$$

$$\sigma_T^2 = \frac{2\ \langle T(t) \rangle^2}{3\ N_{dof}}$$

deg. of freedom

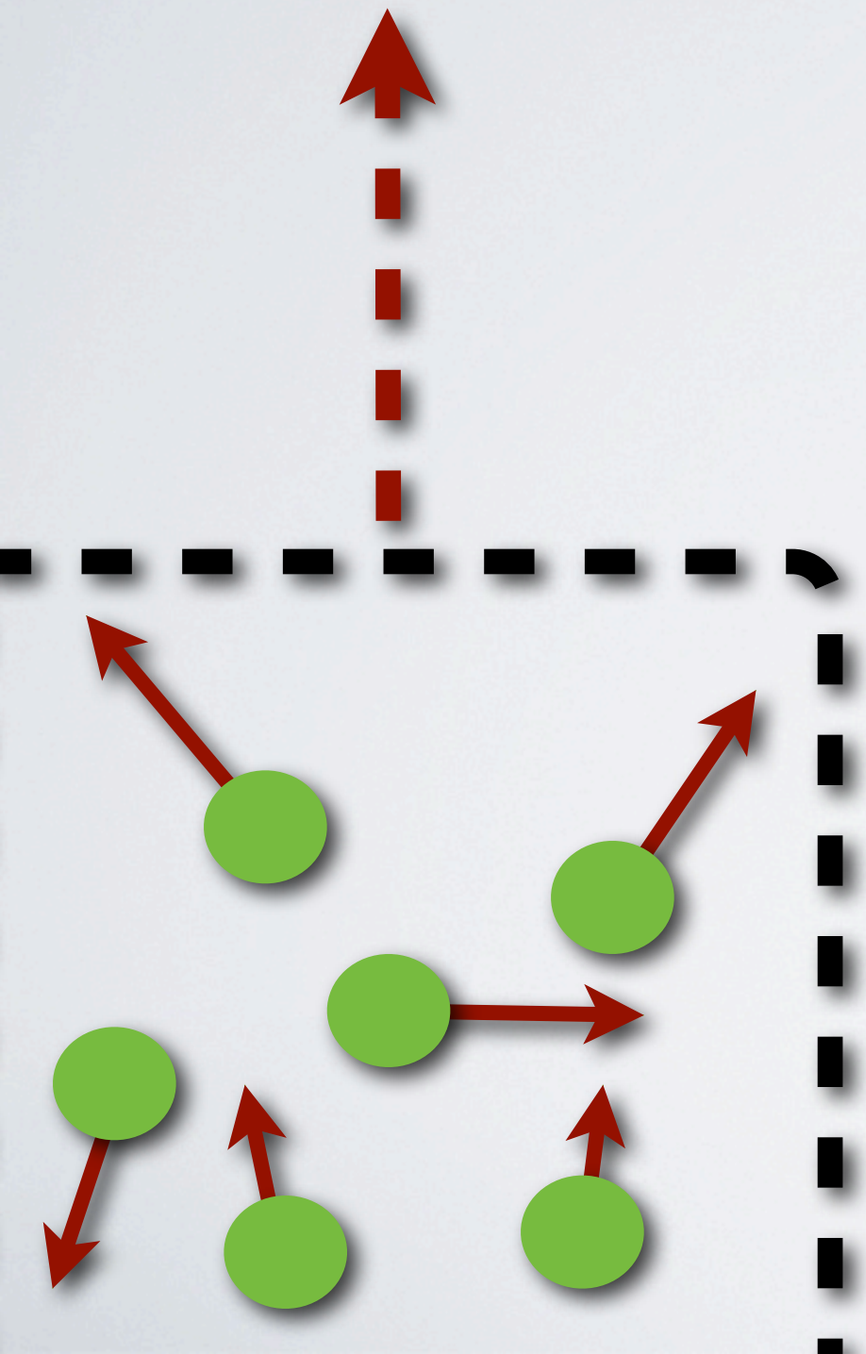
I. Thermostats for the Canonical Ensemble:

A Historical Overview

BERENDSEN THERMOSTAT

H. J. C. Berendsen, *et al. J. Chem. Phys.* **81** 3684 (1984).

1. Calculate **instantaneous temperature $T(t_0)$** of the system



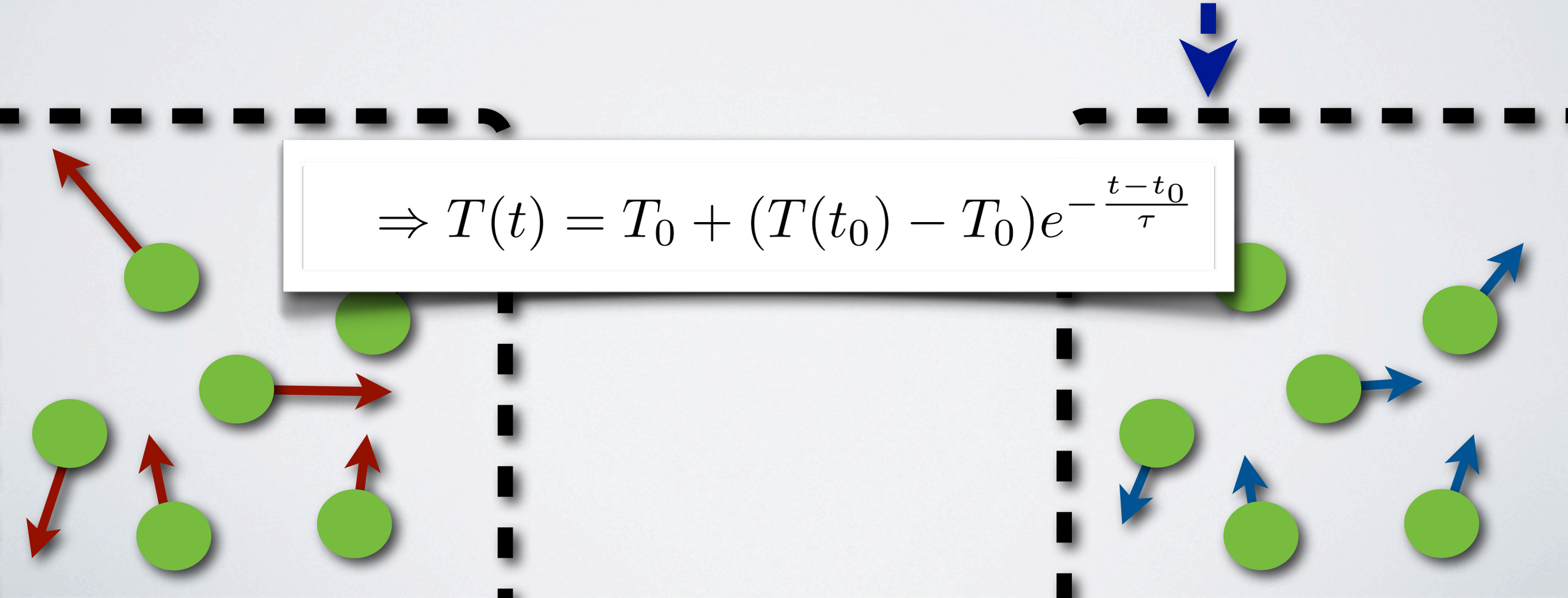
BERENDSEN THERMOSTAT

H. J. C. Berendsen, *et al. J. Chem. Phys.* **81** 3684 (1984).

1. Calculate **instantaneous temperature $T(t_0)$** of the system

2. **Rescale** the velocities by $\lambda = \left[1 + \frac{\Delta t}{\tau}\left(\frac{T_0}{T} - 1\right)\right]^{1/2}$

$$\Rightarrow T(t) = T_0 + (T(t_0) - T_0)e^{-\frac{t-t_0}{\tau}}$$



BERENDSEN THERMOSTAT

H. J. C. Berendsen, *et al. J. Chem. Phys.* **81** 3684 (1984).

Pros & Cons:

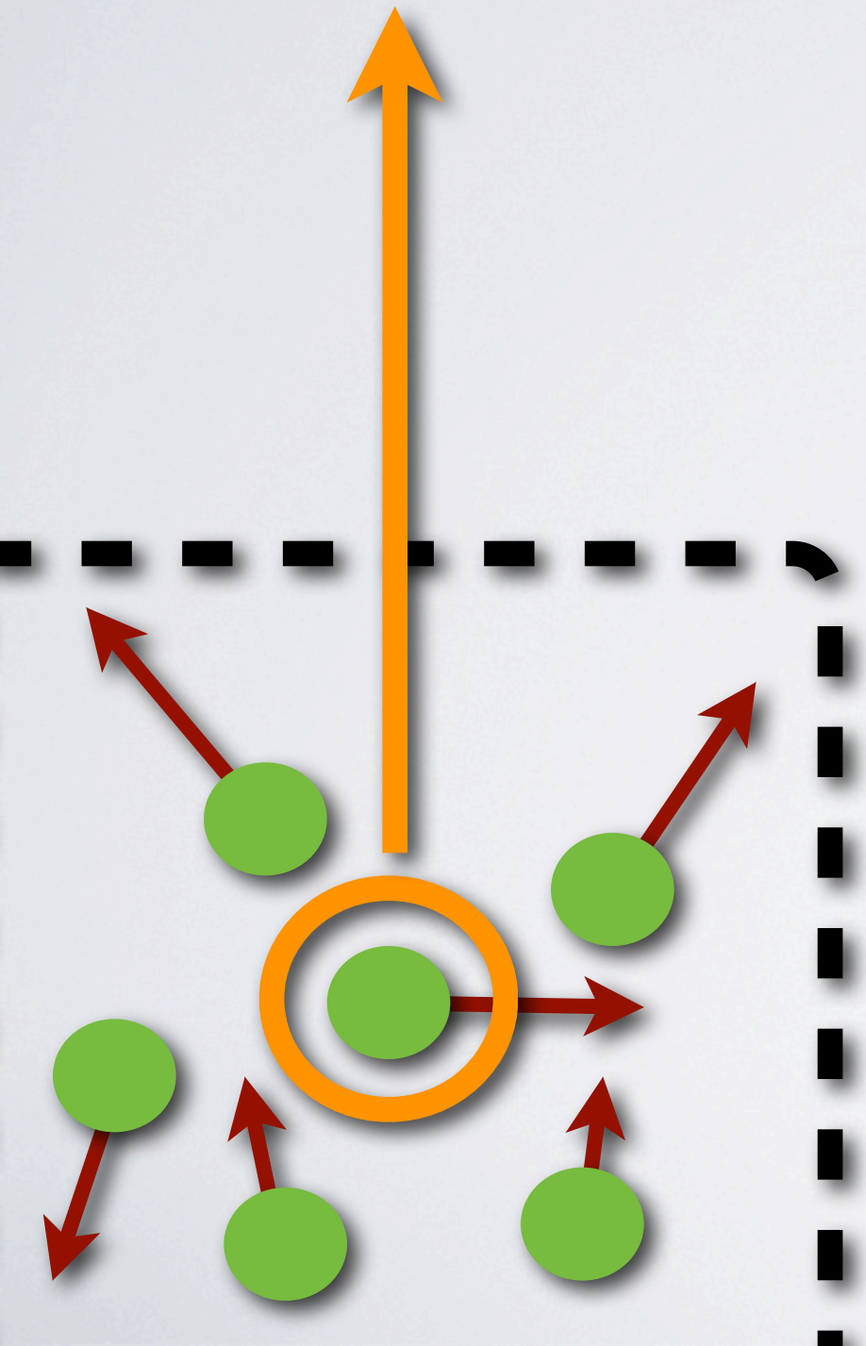
- **Warning:** Suppresses thermal fluctuations
- **Warning:** Does not sample the canonical ensemble
- **Uncertainty:** Sensitive on parameter τ

⇒ Historically important!

ANDERSEN THERMOSTAT

H. C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980).

1. Choose a **random atom each ν^{th} time step**

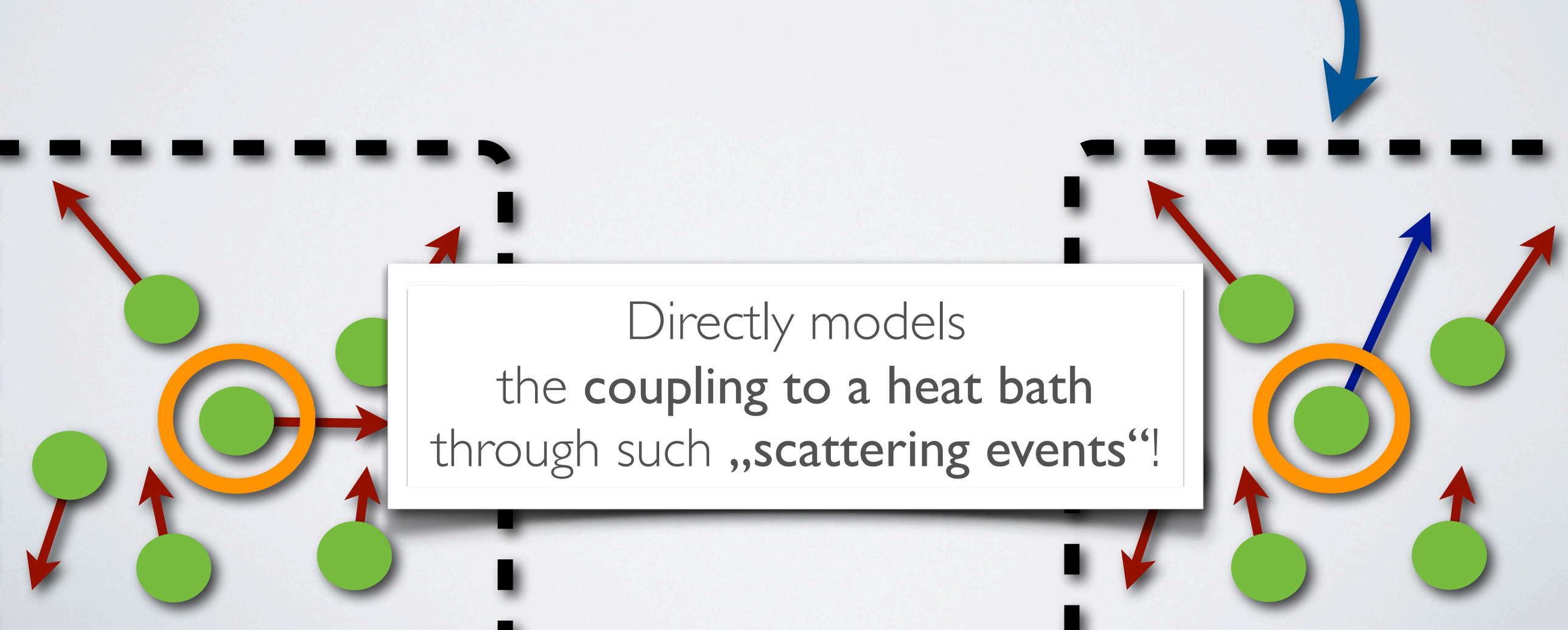


ANDERSEN THERMOSTAT

H. C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980).

1. Choose a **random atom each ν^{th} time step**

2. **Re-assign** a **random velocity** from the **Maxwell-Boltzmann Distribution**



ANDERSEN THERMOSTAT

H. C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980).

Pros & Cons:

☑ **Accurate:** Canonical ensemble in principle sampled

☐ **Uncertainty:** Sensitive on parameter **ν**

☐ **Warning:** Trajectories (Velocities) become discontinuous.

⇒ Historically important!

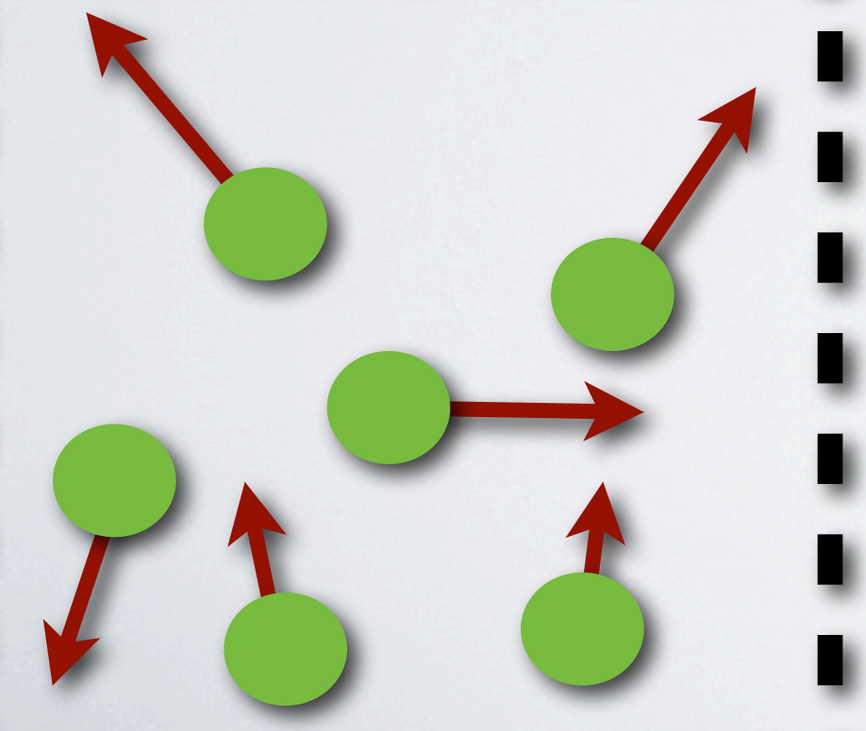
LANGEVIN'S STOCHASTIC DYNAMICS

S. A. Adelman and J. D. Doll, *J. Chem. Phys.* **64**, 2375 (1976).

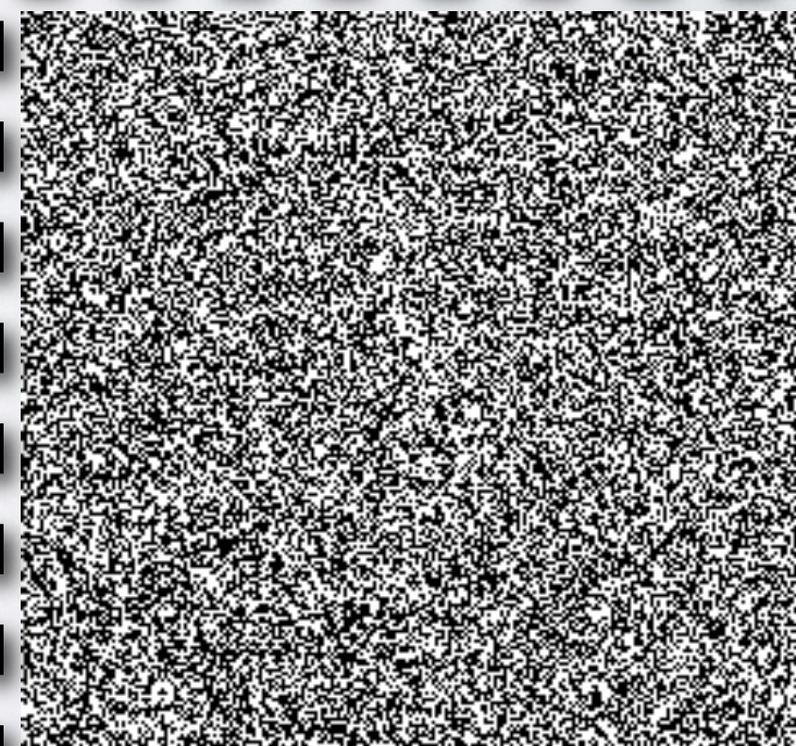
Augmented Equations of Motion:

$$m_i \ddot{\mathbf{R}}_i = \mathbf{F}_i - \gamma_i \dot{\mathbf{R}}_i + \Phi_i(t)$$

Original system



Friction & White Noise



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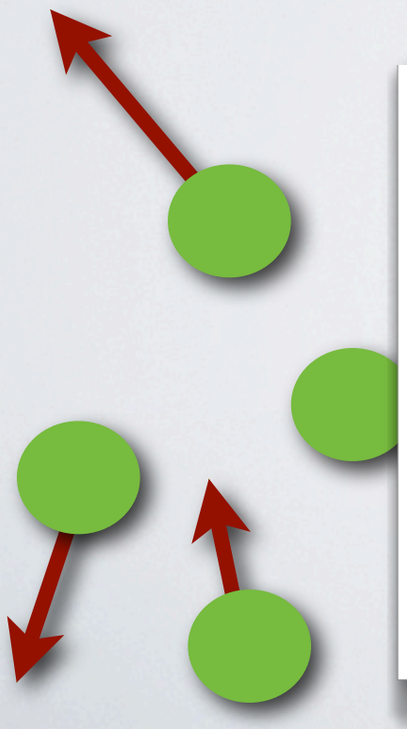


Friction **cools**, Noise **heats** the system:

$$\langle \mathbf{\Phi}_i(t) \cdot \mathbf{\Phi}_i(t') \rangle = 6 k_B T \gamma_i \, \delta(t - t')$$

LANGEVIN'S STOCHASTIC DYNAMICS

S. A. Adelman and J. D. Doll, *J. Chem. Phys.* **64**, 2375 (1976).

Pros & Cons:

☑ **Accurate:** Canonical ensemble in principle sampled

☑ **Accurate:** Dynamic properties assessed accurately

☐ **Uncertainty:** Sensitive on parameter(s) γ_I

⇒ Accurate,

but there is no continuity of momentum!

NOSÉ-HOOVER THERMOSTAT

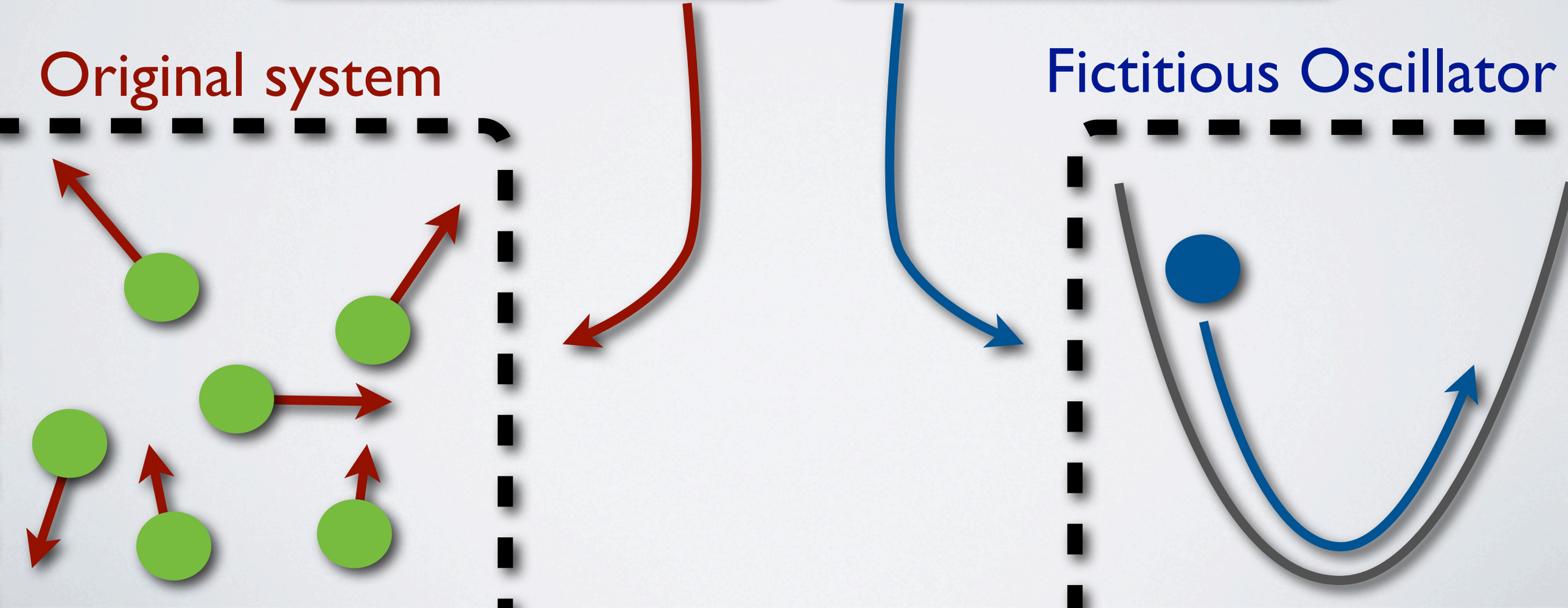
S. Nosé, *J. Chem. Phys.* **81**, 511 (1984) & W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).

Augmented Hamiltonian:

$$\varepsilon = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + U\left(\mathbf{r}^N\right) + \frac{1}{2}Q\,\dot{\eta} + 3Nk_BT\,\eta$$

Original system

Fictitious Oscillator



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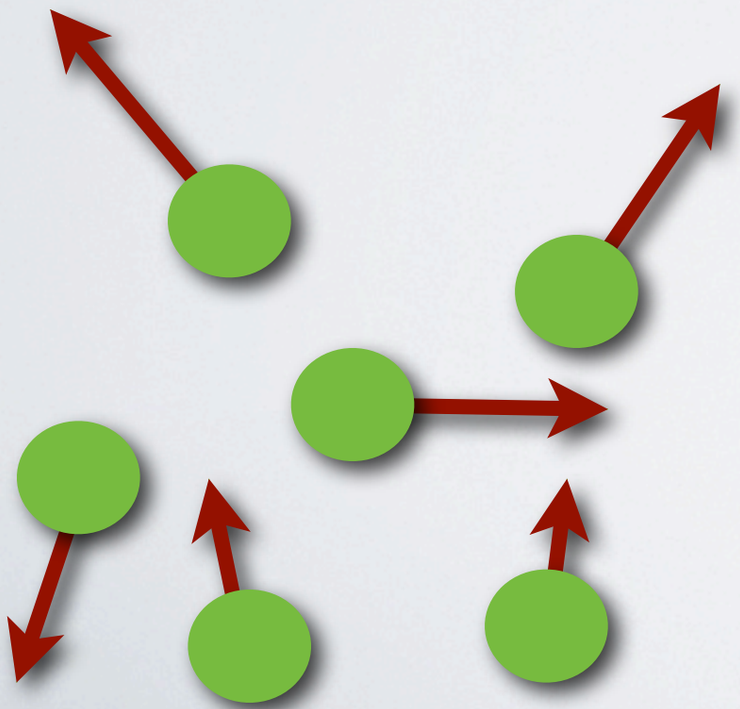


Explicit **coupling** to a heat bath!

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \dot{\eta}\mathbf{p}_i$$

NOSÉ-HOOVER THERMOSTAT

S. Nosé, *J. Chem. Phys.* **81**, 511 (1984) & W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).

Pros & Cons:

☑ **Accurate:** Canonical ensemble sampled

☑ **Convenient:** Augmented Total Energy is conserved

☐ **Warning:** Trajectories still „feel“ the harmonic oscillation.

☐ **Sensitivity:** **Q** has to be chosen with care

⇒ Accurate,

but **Q** has to be chosen with care!

BUSSI-DONADIO-PARRINELLO THERMOSTAT

G. Bussi, D. Donadio, and M. Parrinello, *J. Chem. Phys.* **126**, 014101 (2007).

Combine concepts from **velocity rescaling (fast!)** with concepts from **stochastic thermostats (accurate!)**.

Target Temperature follows a Stochastic Diff. Eq.:

$$dT = \left(\overline{T} - T(t)\right)\frac{dt}{\tau} + 2\sqrt{\frac{T(t)\overline{T}}{N_f}}\frac{dW(t)}{\sqrt{\tau}}$$

Berendsen' thermostat

White Noise

BUSSI-DONADIO-PARRINELLO THERMOSTAT

G. Bussi, D. Donadio, and M. Parrinello, *J. Chem. Phys.* **126**, 014101 (2007).

Pros & Cons:

☑ **Accurate:** Canonical ensemble sampled

☑ **Accurate:** Dynamic properties assessed accurately

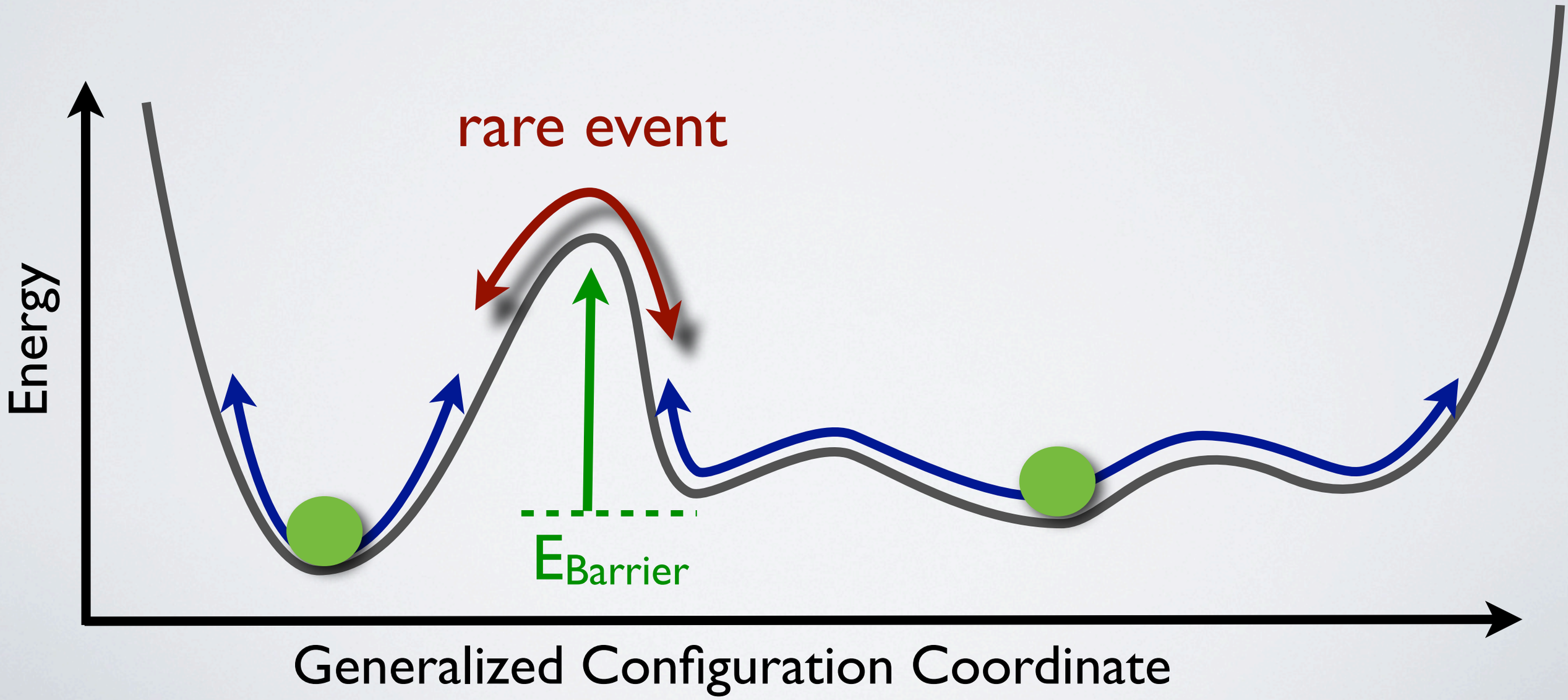
☑ **Sensitivity:** Almost independent from parameter **τ**

☑ **Convenient:** Pseudo-Hamiltonian is conserved

⇒ Accurate & very promising,
but also still topic of research!

CAVEAT: RARE EVENTS

Simulating **processes** hindered by **high energetic barriers** can be **extremely expensive** with conventional MD.



CAVEAT: RARE EVENTS

Possible routes:

- **Simulated Annealing**
  e.g., S. Kirkpatrick, C. D. Gelatt, and M. P. Vecchi, *Science* **220**, 671 (1983).

- **Accelerated Molecular Dynamics**
  e.g., A. F. Voter, *Phys. Rev. Lett.* **78,** 3908 (1997).

- **Bond Boost**
  e.g., R. A. Miron, K. A. Fichthorn, *Phys. Rev. Lett.* **93**, 128301 (2004).

- **Transition Path Sampling**
  e.g., P. G. Bolhuis *et al. Annu. Rev. Phys. Chem.* **53**, 291 (2002).

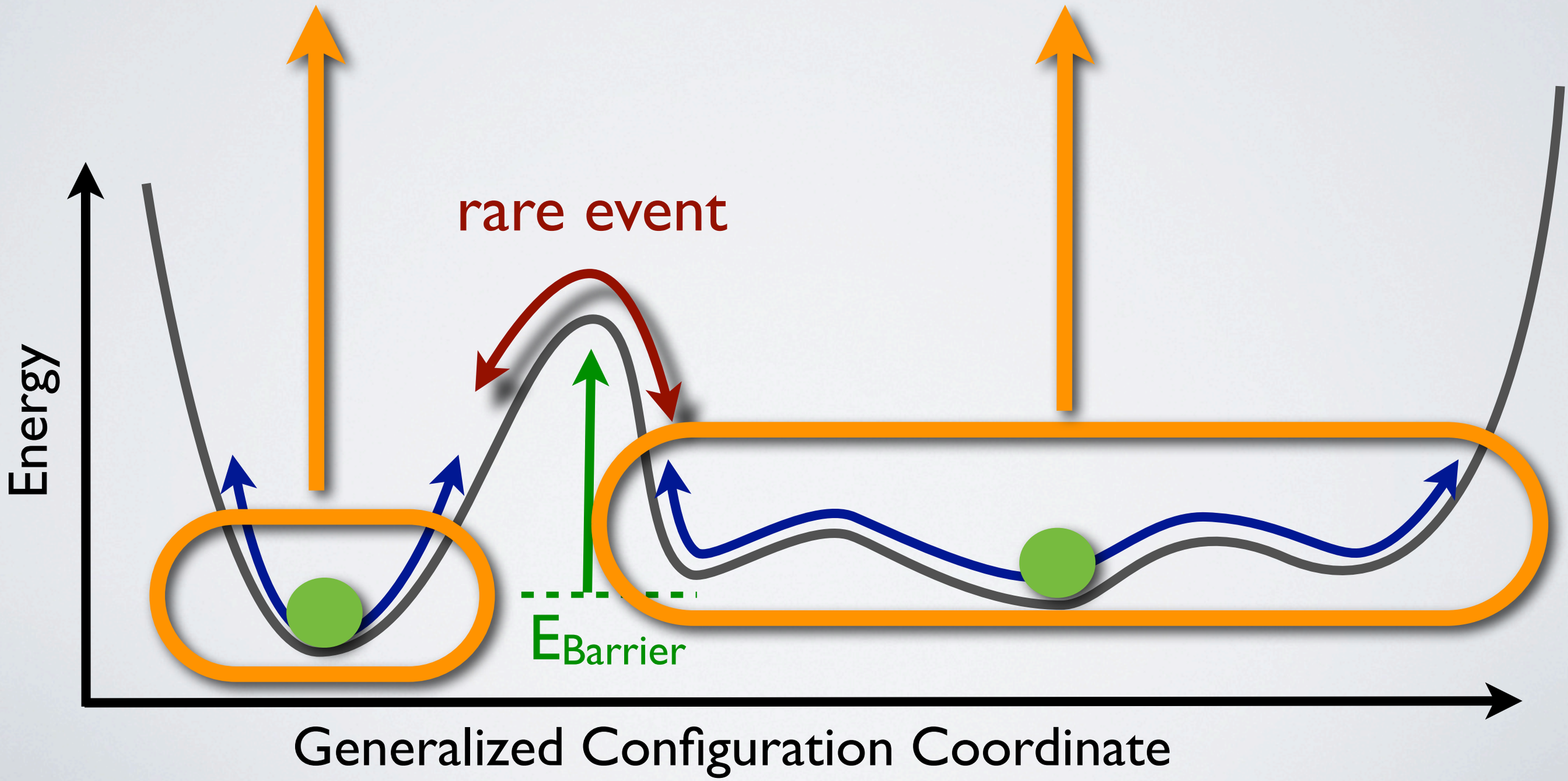
- **Kinetic Monte Carlo**
  e.g., J. Rogal, K. Reuter, and M. Scheffler, *Phys. Rev. B* **77**, 155410 (2008).
  ⇒ **Talk on Thursday 21nd**

Energy

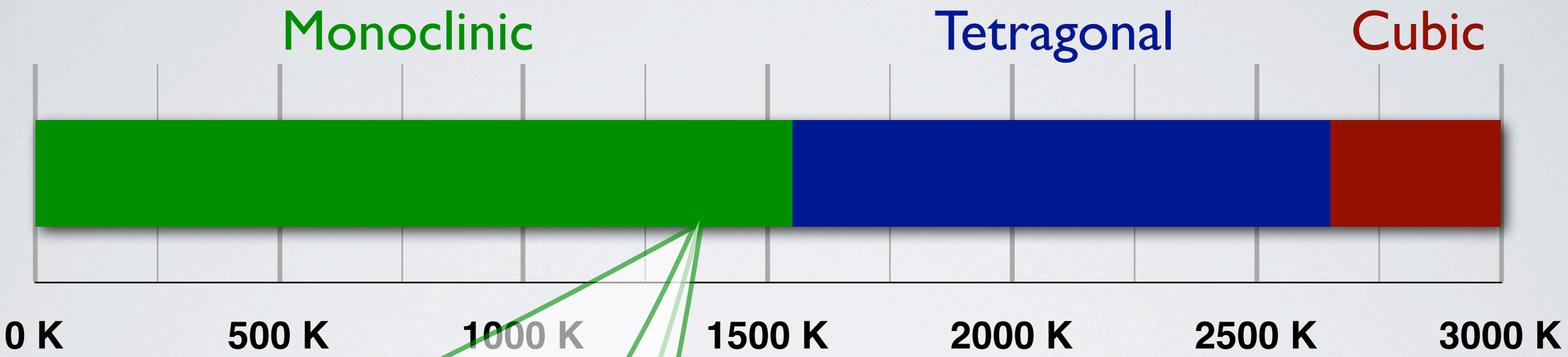
Generalized Configuration Coordinate

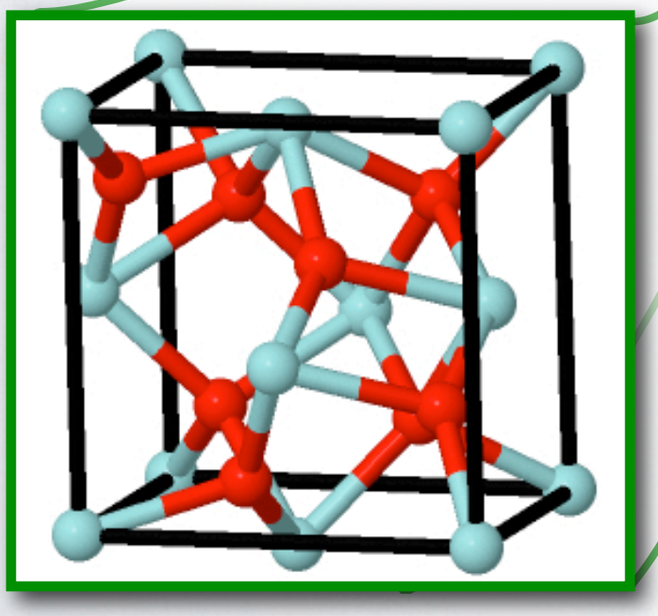
CAVEAT: RARE EVENTS

Assess **relative stability**
without simulating the **rare event** itself.



PHASE DIAGRAM OF ZrO_2



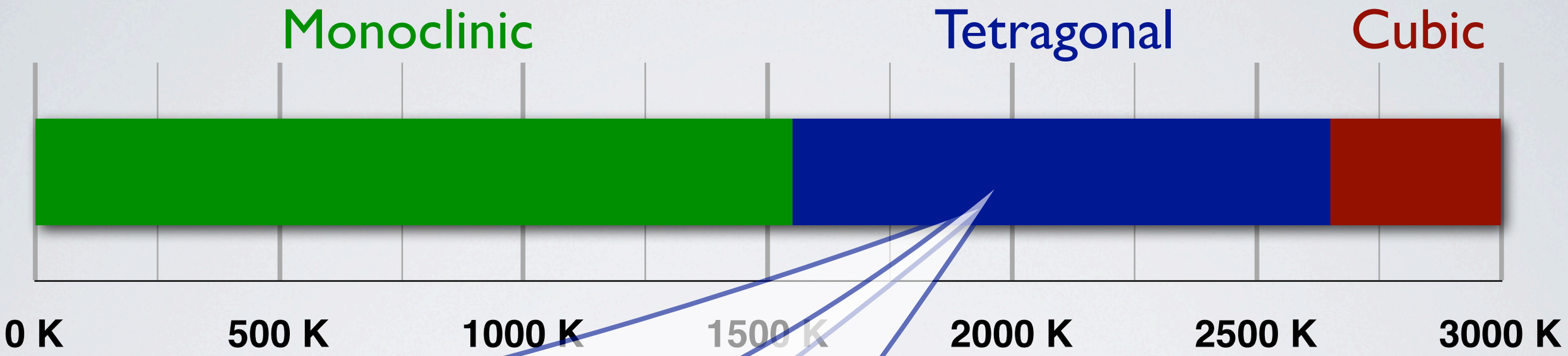


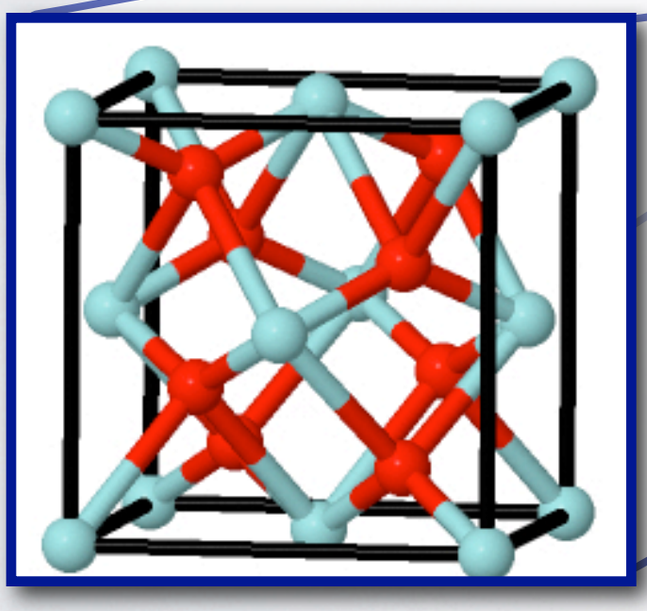
T < 1200°C

„Monoclinic“

Baddeleyite Structure

PHASE DIAGRAM OF ZrO_2





1200°C < T < 2400°C

„Tetragonal“

$P4_2/nmc$ Structure

PHASE DIAGRAM OF ZrO_2

Monoclinic

Tetragonal

Cubic

0 K

500 K

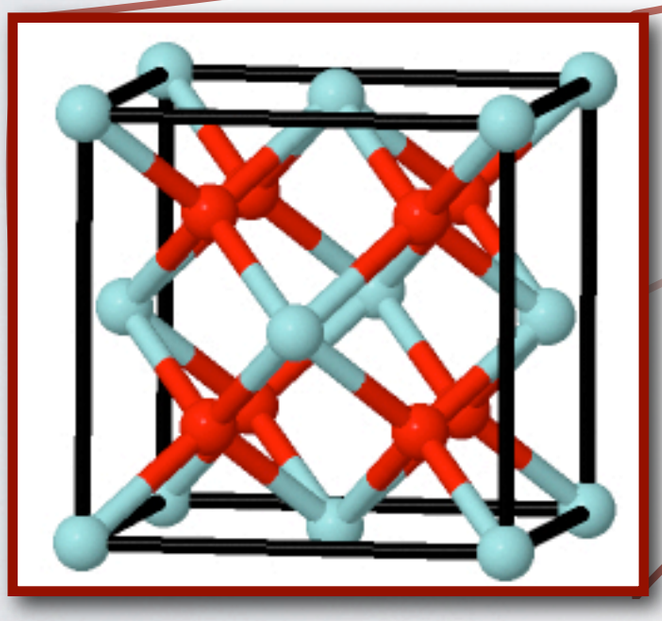
1000 K

1500 K

2000 K

2500 K

3000 K



T > 2400°C

„Cubic“

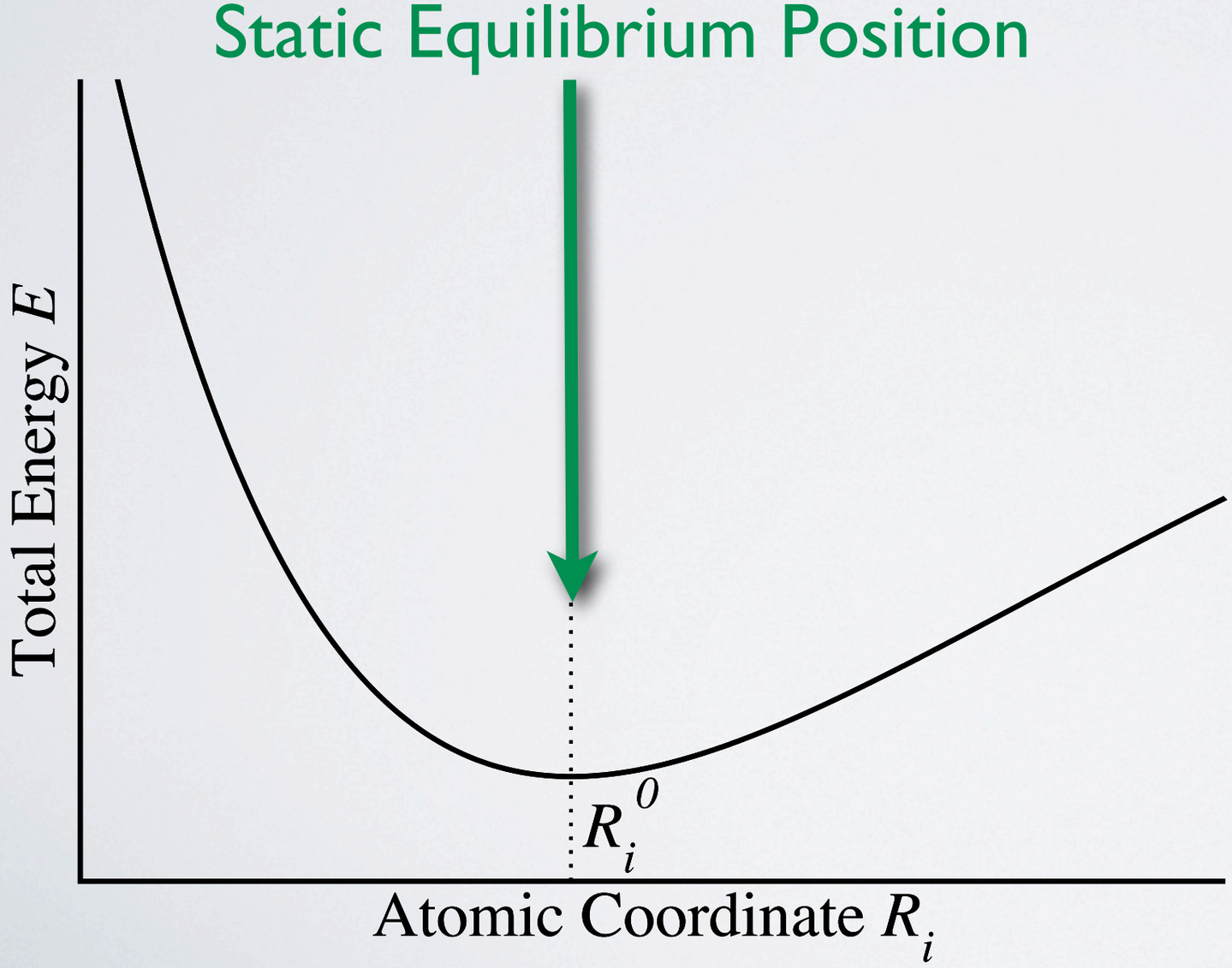
Fluorite Structure

II. The Harmonic Crystal

THE INTERATOMIC INTERACTION

The total energy ***E*** is a ***3N-dimensional surface***

$$E = V\left(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_N\right)$$



THE INTERATOMIC INTERACTION

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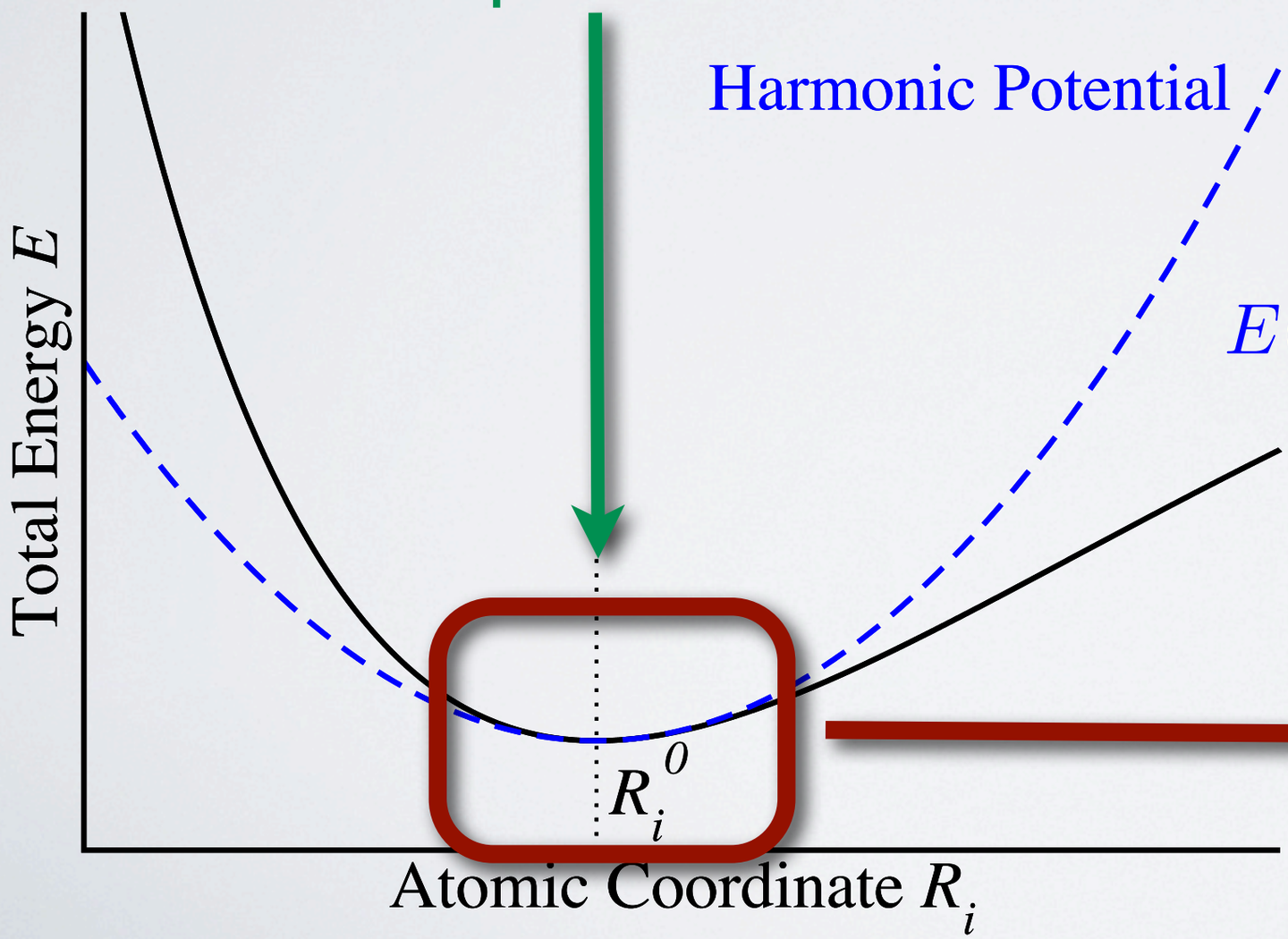


Taylor expansion:

$$E \approx$$

$$E(\mathbf{R}_0) + \frac{1}{2}\sum_{i,j}\Phi^{i,j}\left(\Delta\mathbf{R}_i\right)\left(\Delta\mathbf{R}_j\right)$$

Only valid for small elongations!

THE HARMONIC APPROXIMATION

$$E\left(\{\mathbf{R}_0+\Delta\mathbf{R}\}\right) \approx E\left(\{\mathbf{R}_0\}\right) + \sum_i \left.\frac{\partial E}{\partial \mathbf{R}_i}\right|_{\mathbf{R}_0} \Delta\mathbf{R}_i + \frac{1}{2}\sum_{i,j} \left.\frac{\partial^2 E}{\partial \mathbf{R}_i \partial \mathbf{R}_j}\right|_{\mathbf{R}_0} \Delta\mathbf{R}_i \Delta\mathbf{R}_j$$

Static Equilibrium Energy

Forces vanish at $\mathbf{R_0}$

Hessian Φ_{ij}

Determine ***harmonic force constants*** Φ_{ij}:

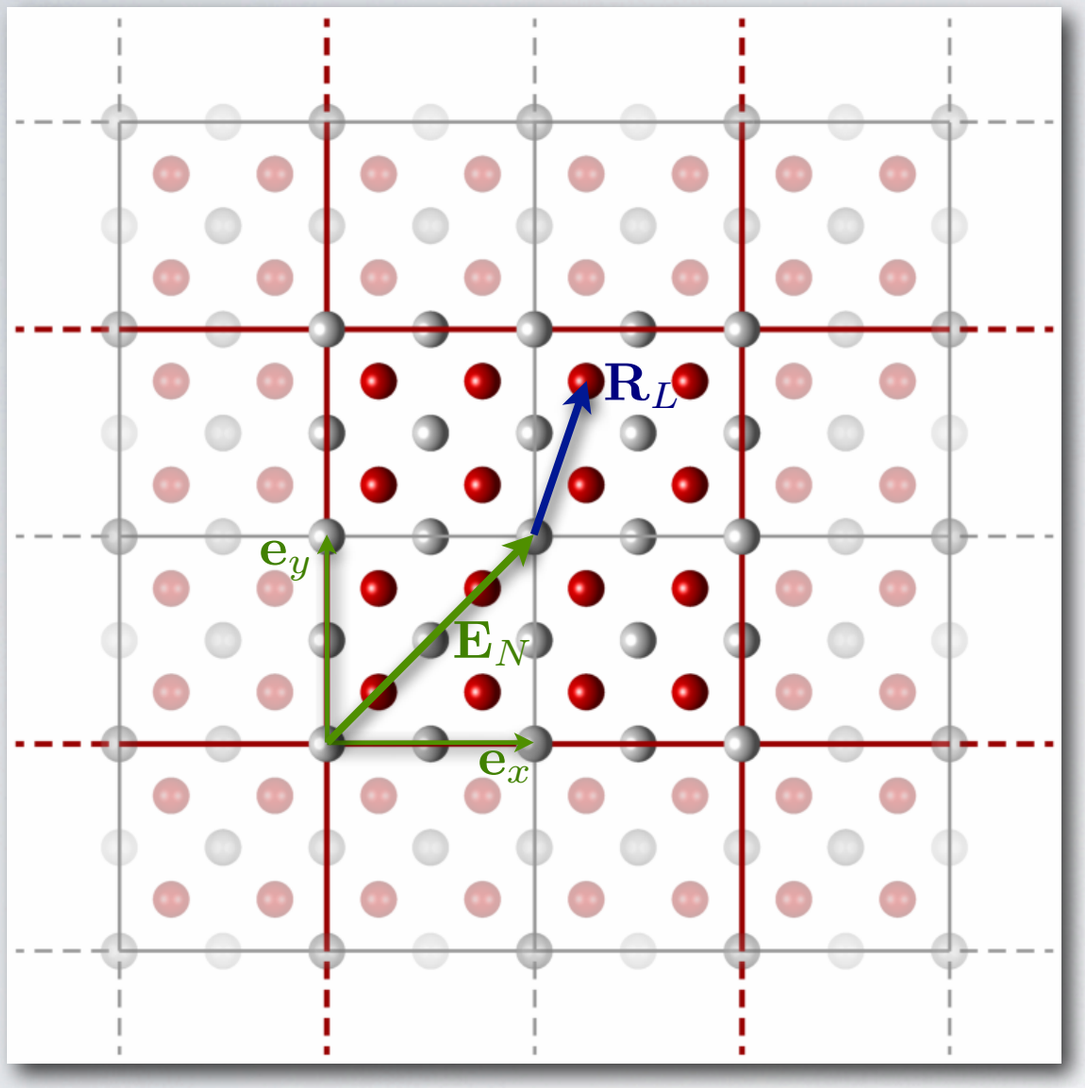
- from **DFT-Perturbation Theory**

  S. Baroni, P. Giannozzi, and A. Testa, *Phys. Rev. Lett.* **58**, 1861 (1987) &
  S. Baroni, *et al., Rev. Mod. Phys.* **73**, 515 (2001).

- from **Finite Differences**

  K. Kunc, and R. M. Martin, *Phys. Rev. Lett.* **48**, 406 (1982) &
  K. Parlinski, Z. Q. Li, and Y. Kawazoe, Phys. Rev. Lett. 78, 4063 (1997).

THE HARMONIC SOLID



Periodic Boundary Conditions
⇒ Reciprocal Space **q**

$$D_{ij}(\mathbf{q}) = \sum_{\mathbf{E}_N} \frac{e^{i(\mathbf{q}\cdot\mathbf{E}_N)}}{\sqrt{M_i M_j}} \Phi_{ij}$$

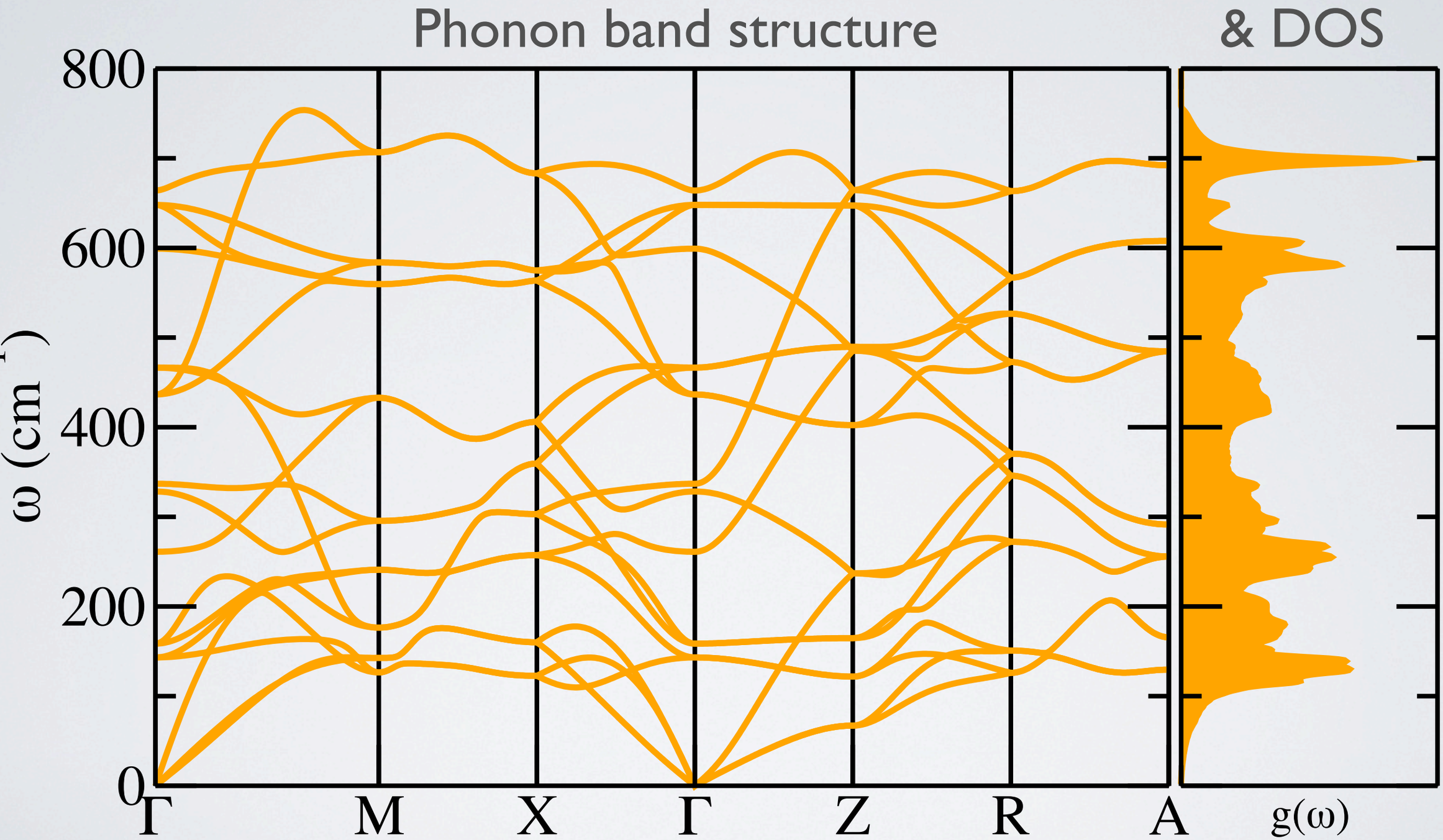
Eigenvalue problem:

$$\mathbf{D}(\mathbf{q})\ [\nu(\mathbf{q})] = \omega^2(\mathbf{q})\ [\nu(\mathbf{q})]$$

Real space: Superposition of *harmonic oscillations*

$$\mathbf{R} \quad = \quad R_0 + \sum_s A_s \ \frac{\cos\left(\phi_s + \omega_s t\right)}{\sqrt{M_i}} \cdot \nu_s$$

THE HARMONIC APPROXIMATION



Tetragonal ZrO_2, DFT

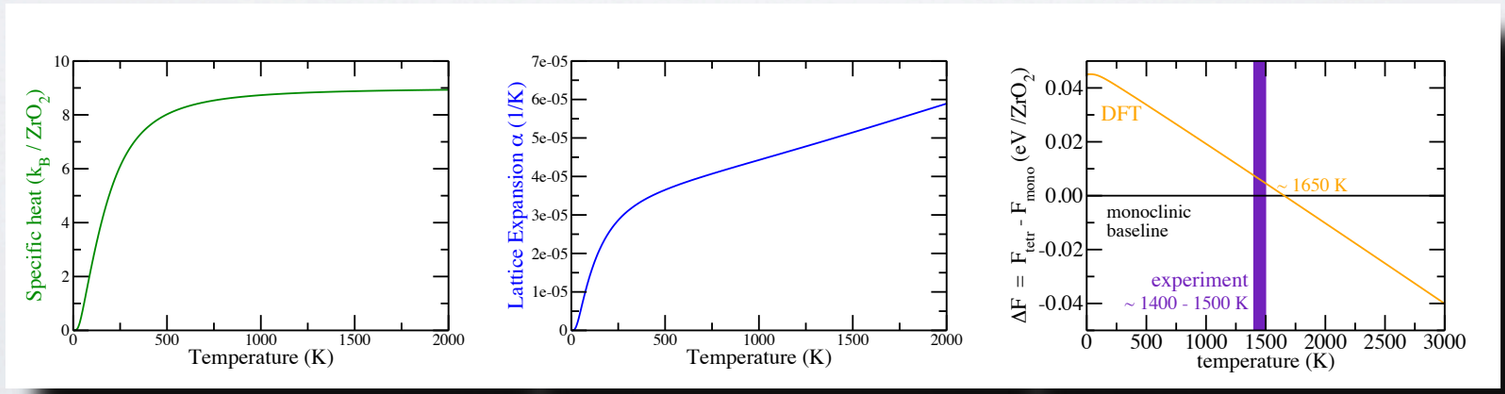
THE HARMONIC FREE ENERGY

$$F^{ha}(T) = E(\{\mathbf{R}_0\}) + \int d\omega\, g(\omega) \frac{\hbar\omega}{2} + \int d\omega\, g(\omega)\, k_B T \ln\left(1 - e^{\left(-\frac{\hbar\omega}{k_B T}\right)}\right)$$

Static Equilibrium Energy

Zero-point vibration

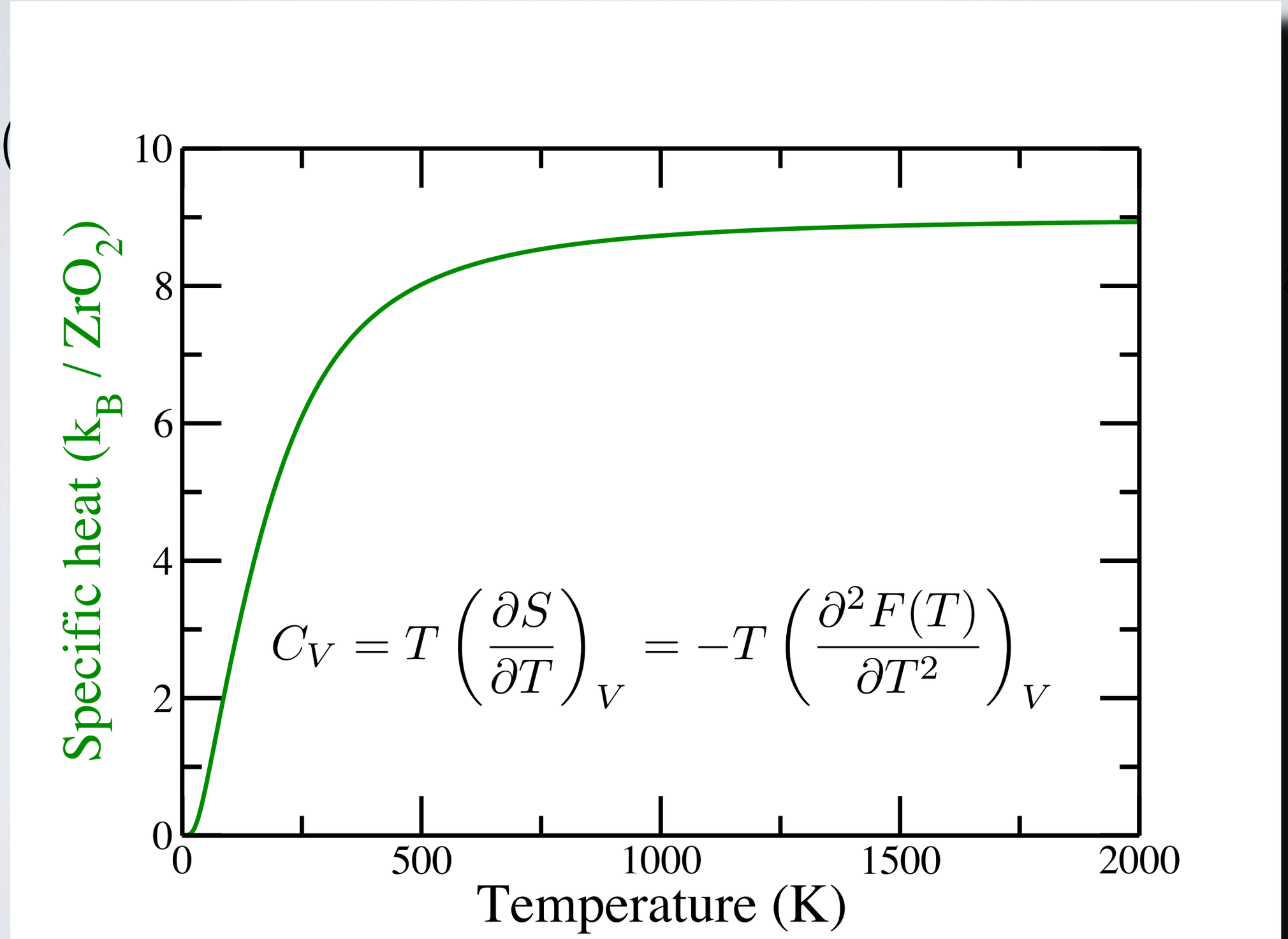
Thermally induced vibrations



THE HARMONIC FREE ENERGY

$F^{ha}($ Energy

ation

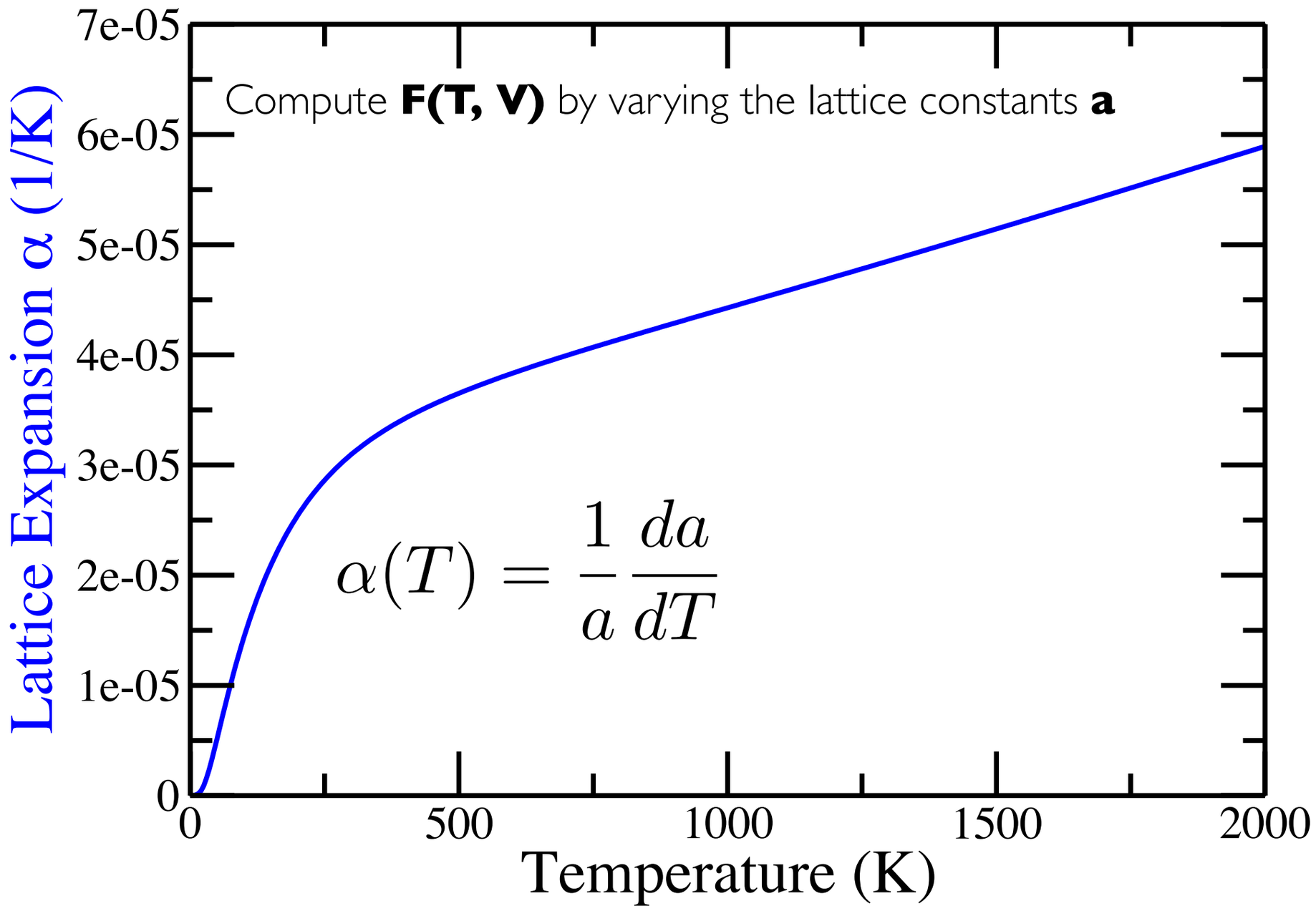


THE HARMONIC FREE ENERGY

$F^{ha}($ Energy

ation

Quasi-harmonic approximation:

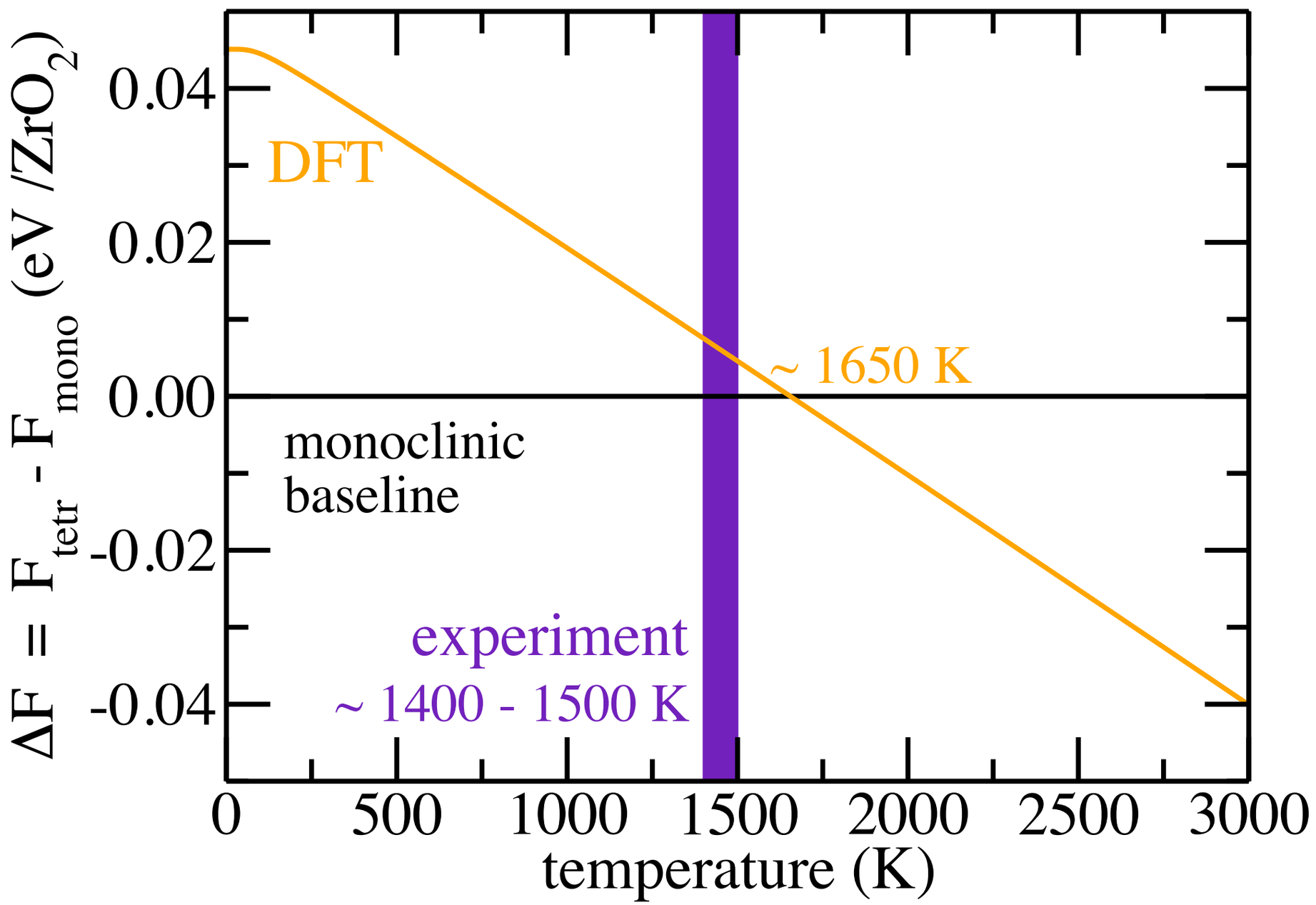


THE HARMONIC FREE ENERGY

$F^{ha}($ Energy

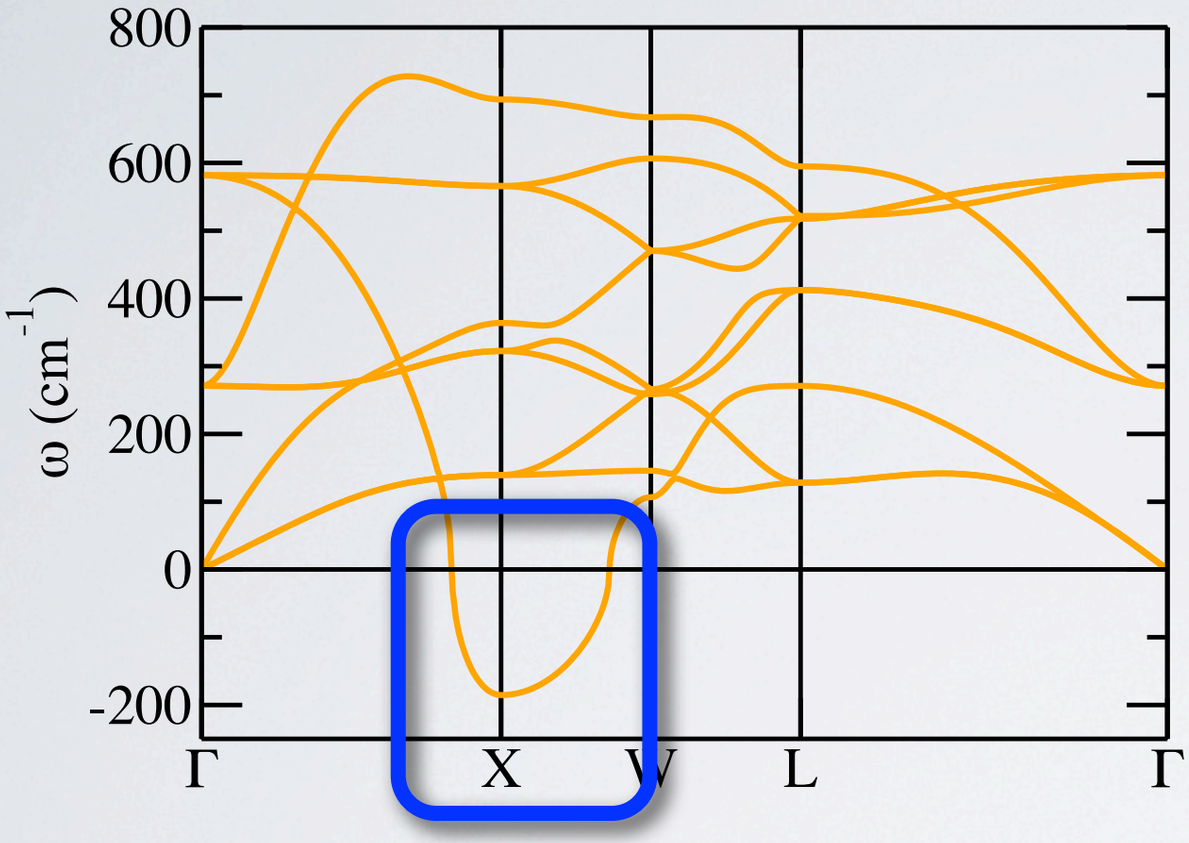
ation

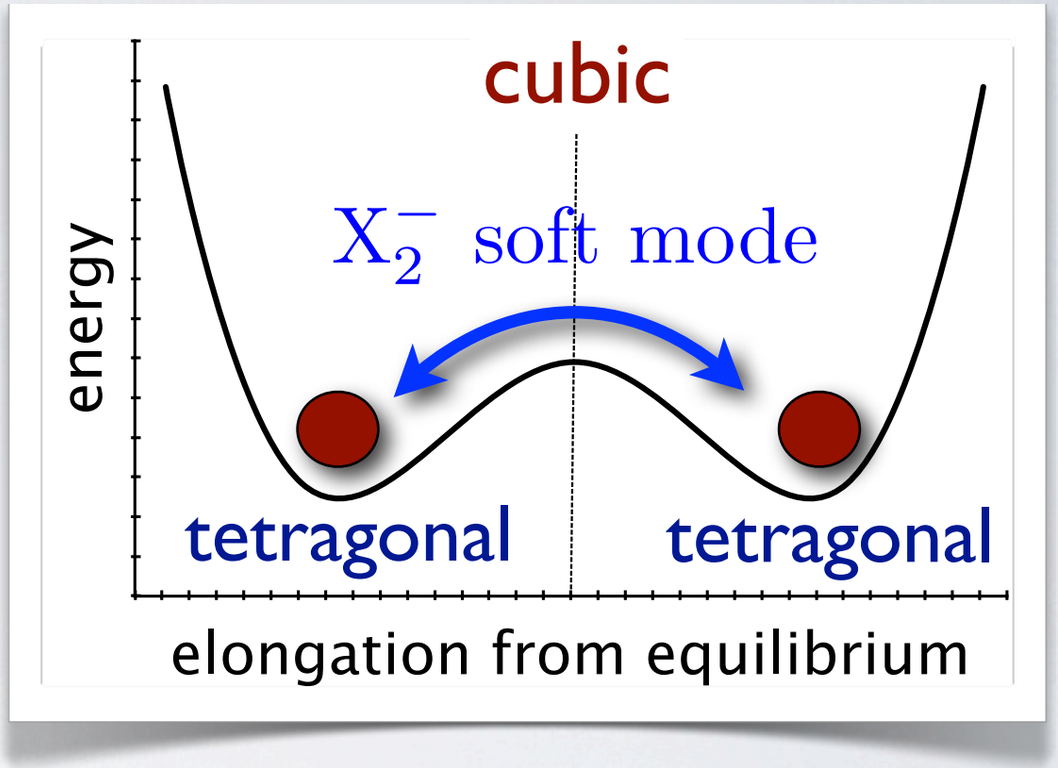
Harmonic free energy difference:

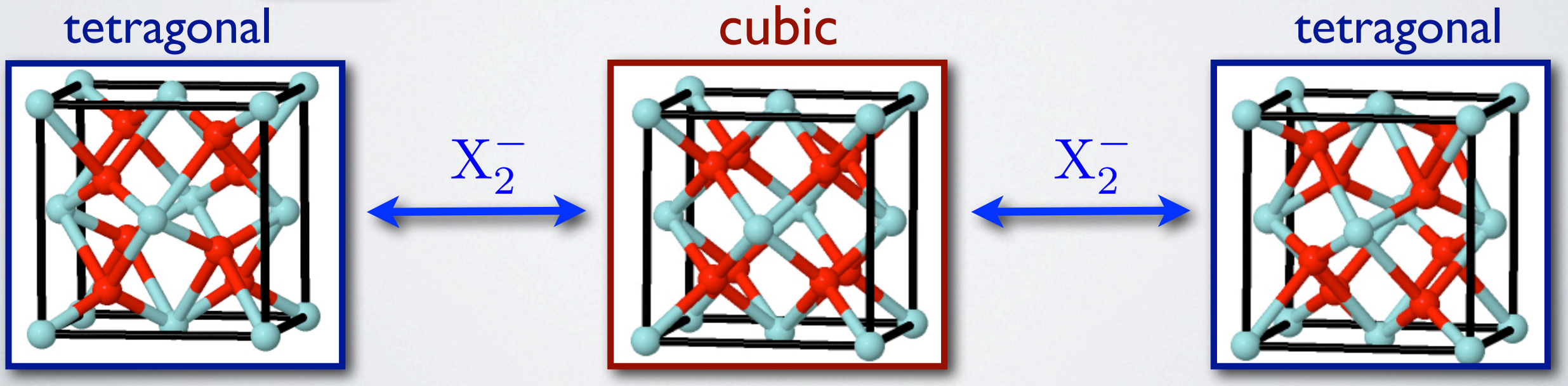


THE CUBIC ZrO_2 STRUCTURE

K. Parlinski, Z. Q. Li, and Y. Kawazoe, *Phys. Rev. Lett.* **78**, 4063 (1997).







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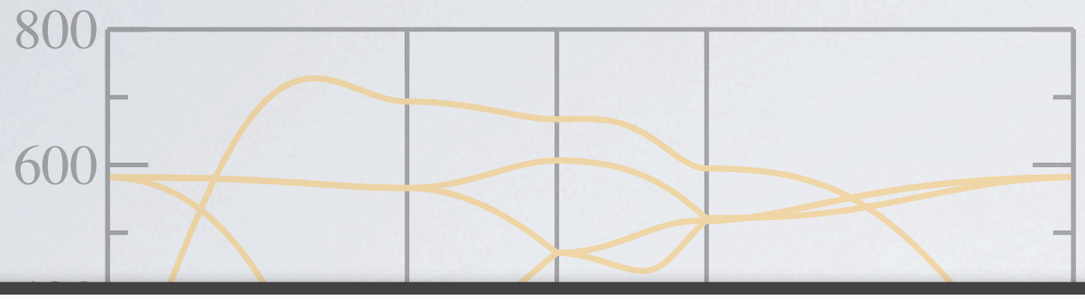
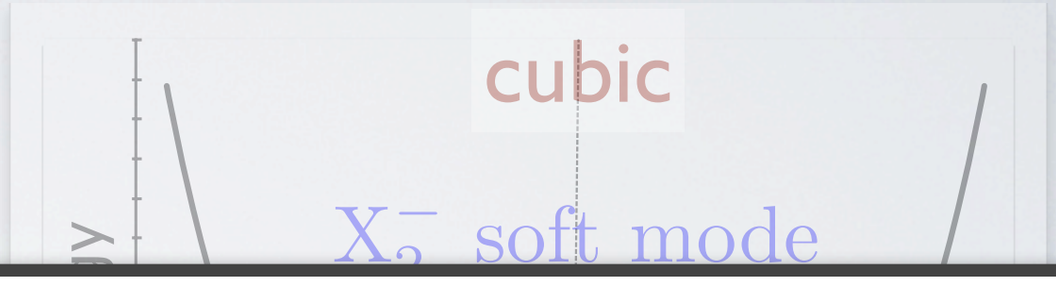
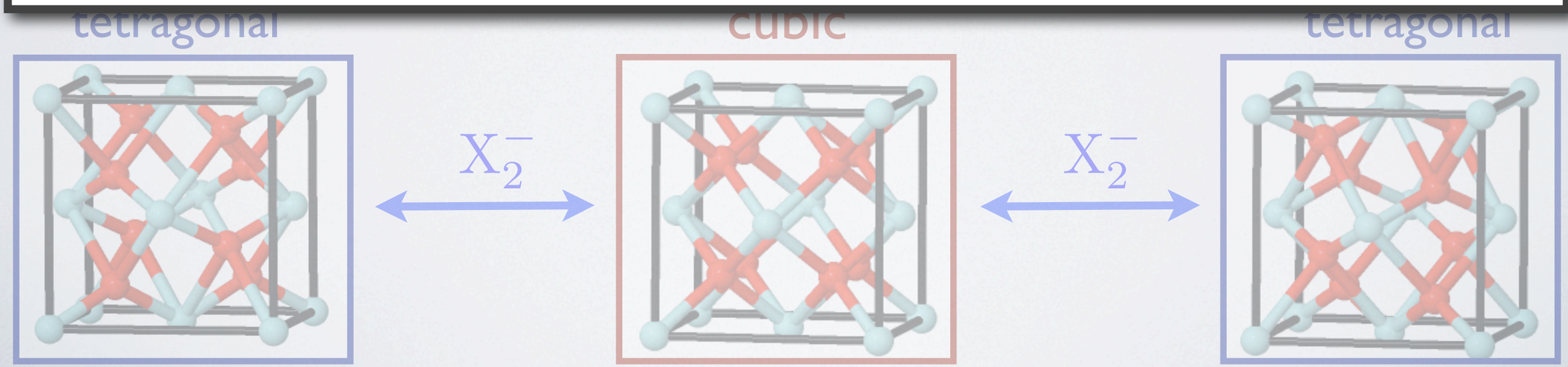




The Harmonic Approximation does not hold in the case of Soft Modes!



THERMODYNAMIC INTEGRATION

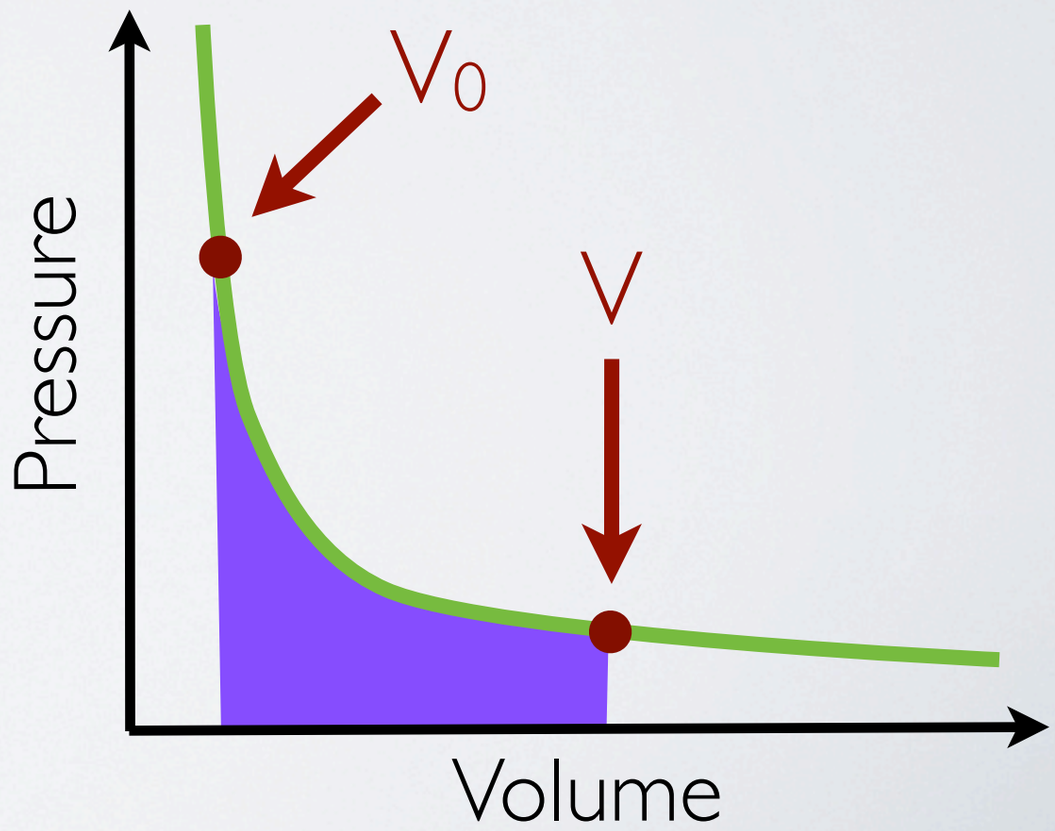
J. G.Kirkwood, *J. Chem. Phys,* **3**, 300 (1935).

The absolute value of the **Thermodynamic Potentials** is **not measurable**, but their **derivatives** are, e.g., **the pressure**

$$p = -\left(\frac{\partial F(T,V)}{\partial V}\right)_T$$

$$F(V) - F(V_0) = -\int_{V_0}^{V} p\, dV$$

Free energy differences can be computed by **integration** along a **thermodynamic path**!



THERMODYNAMIC INTEGRATION

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Free energy **differences** can be computed by integration along a **λ**-parametrized path that connects two **distinct** systems.

e.g., M. Watanabe and W. P. Reinhardt , *Phys. Rev. Lett.* **65**, 3301(1990) &
O. Sugino and R. Car, *Phys. Rev. Lett.* **74**, 1823 (1995).

$$F_{\mathrm{anh}}(T,V) = F_{\mathrm{DFT}}(T,V) - F_{\mathrm{har}}(T,V) = \int_0^1 d\lambda \left\langle \frac{\partial U_{\mathrm{hyb}}(\lambda)}{\partial \lambda} \right\rangle_{\mathrm{hyb}}$$

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Harmonic reference

„Complete“ free energy — free energy

$$F_{\mathrm{anh}}(T,V) = F_{\mathrm{DFT}}(T,V) - F_{\mathrm{har}}(T,V) = \int_0^1 d\lambda \left\langle \frac{\partial U_{\mathrm{hyb}}(\lambda)}{\partial \lambda} \right\rangle_{\mathrm{hyb}}$$

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Thermodynamic expectation value for the „hybrid“ system

$$U_{\mathrm{hyb}}(\lambda) = \lambda \cdot U_{\mathrm{DFT}} + (1-\lambda) \cdot U_{\mathrm{har}}$$

ab initio potential

harmonic potential

THERMODYNAMIC INTEGRATION

J. G.Kirkwood, *J. Chem. Phys,* **3**, 300 (1935).

Molecular Dynamics for the hybrid system:

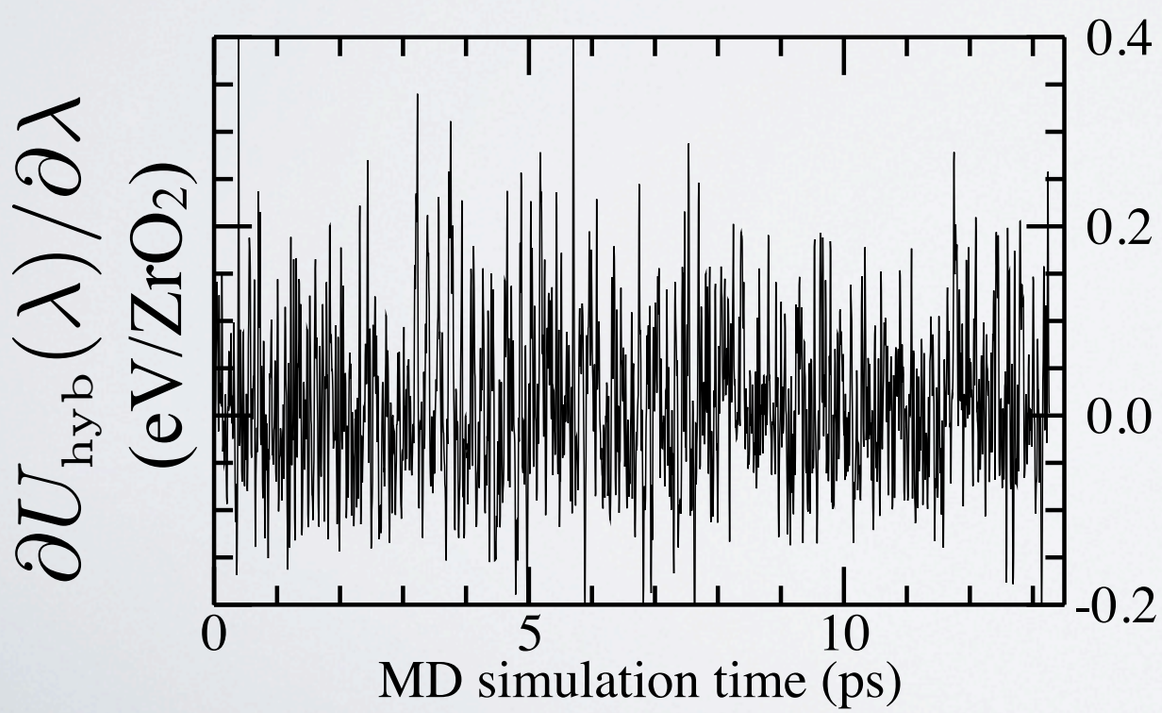
B. Grabowski *et al., Phys. Rev. B* **79**,134106 (2009).

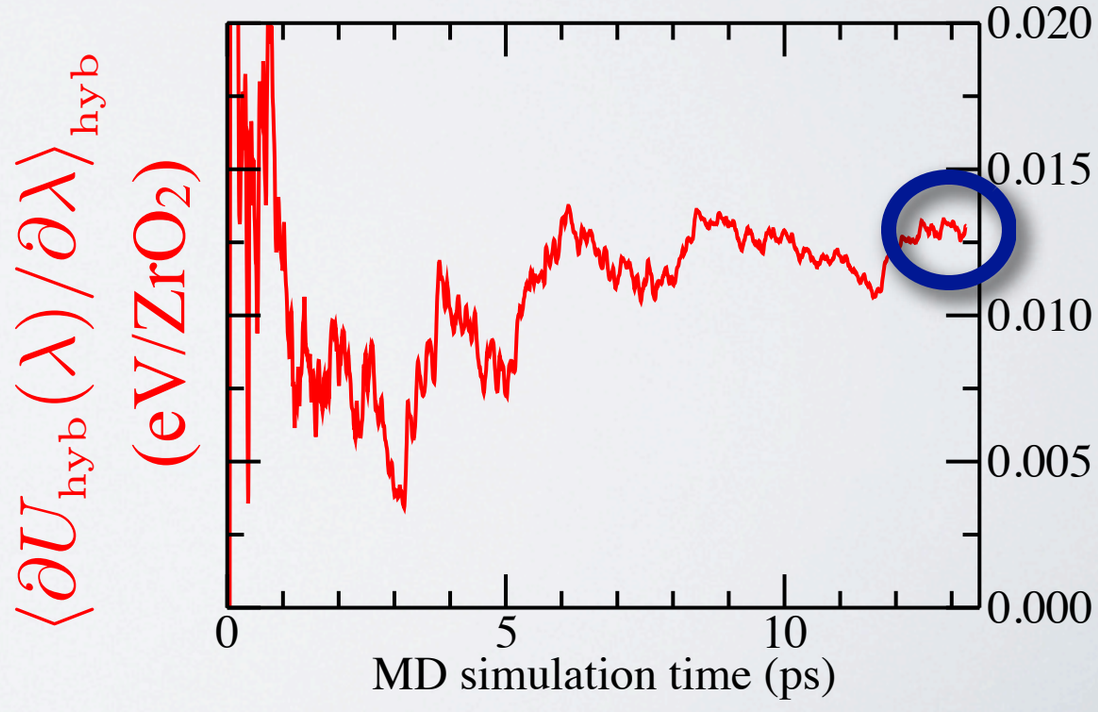
$$U_{\mathrm{hyb}}(\lambda) = \lambda \cdot U_{\mathrm{DFT}} + (1-\lambda) \cdot U_{\mathrm{har}}$$

ab initio potential

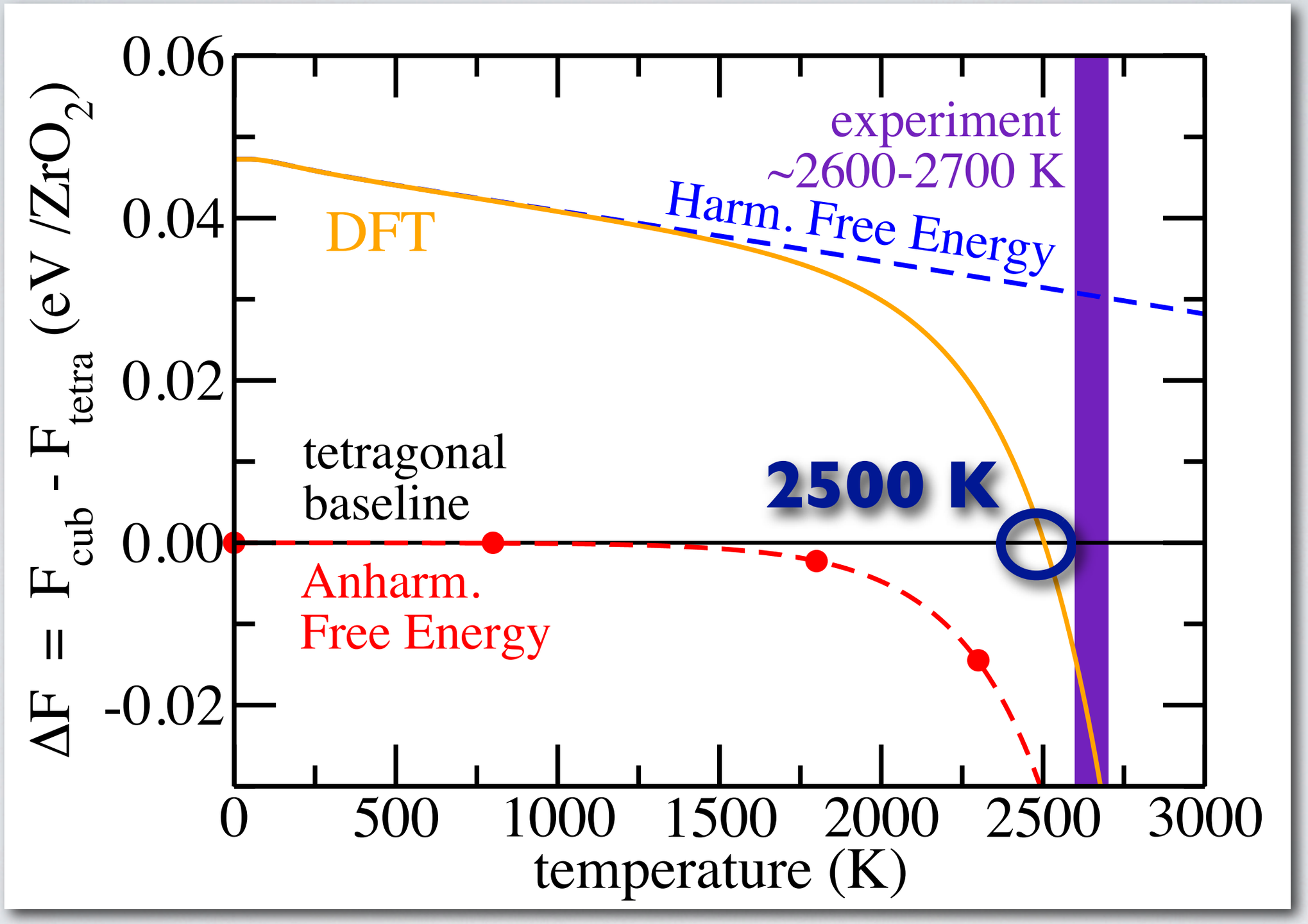
harmonic potential

LDA, $\lambda = 0.5$, $T = 2800$ K





CUBIC PHASE STABILITY

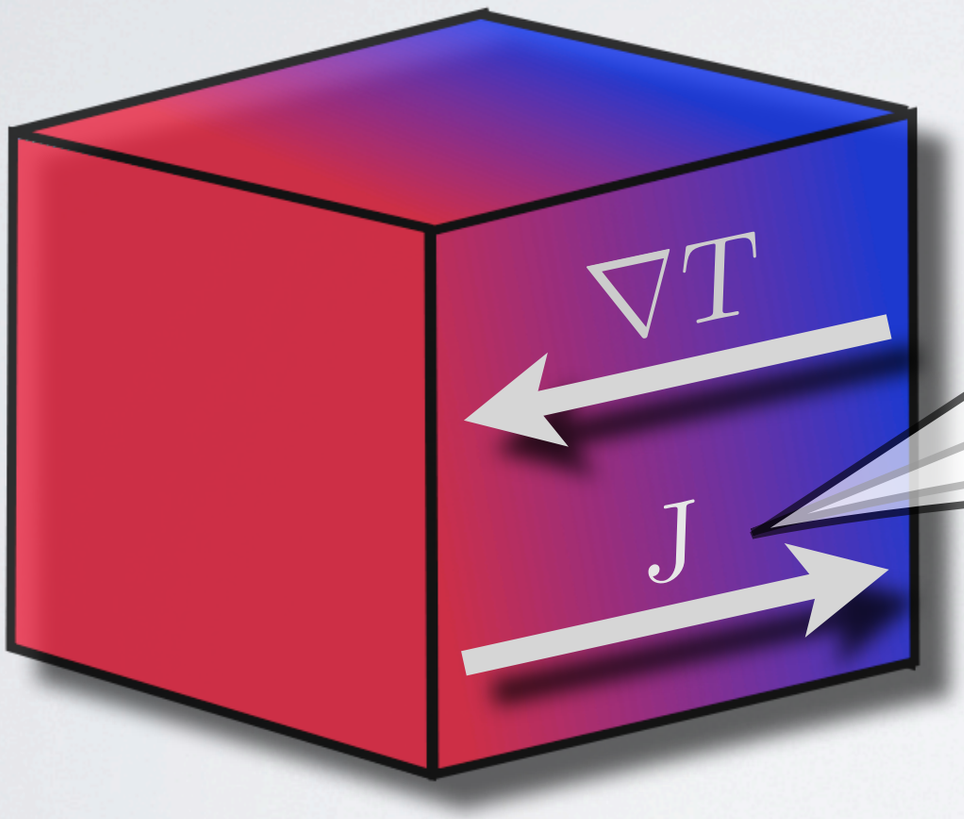


Noticeable Anharmonic Effects for T > 1500 K !

III. Non-Equilibrium Thermodynamics

THERMAL CONDUCTIVITY

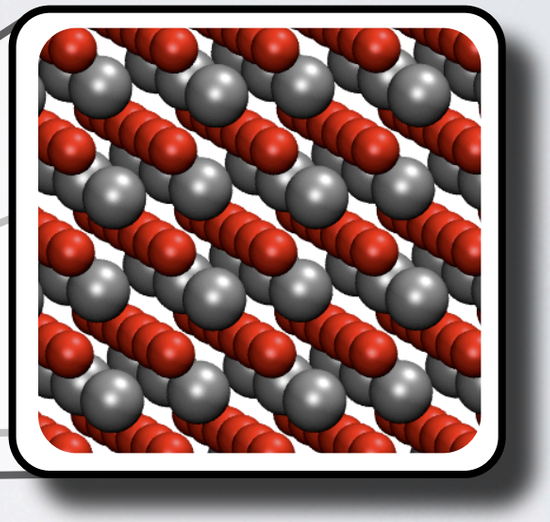
Macroscopic Effect:



Fourier's Law:

$$\mathbf{J} = -\kappa \, \nabla T$$

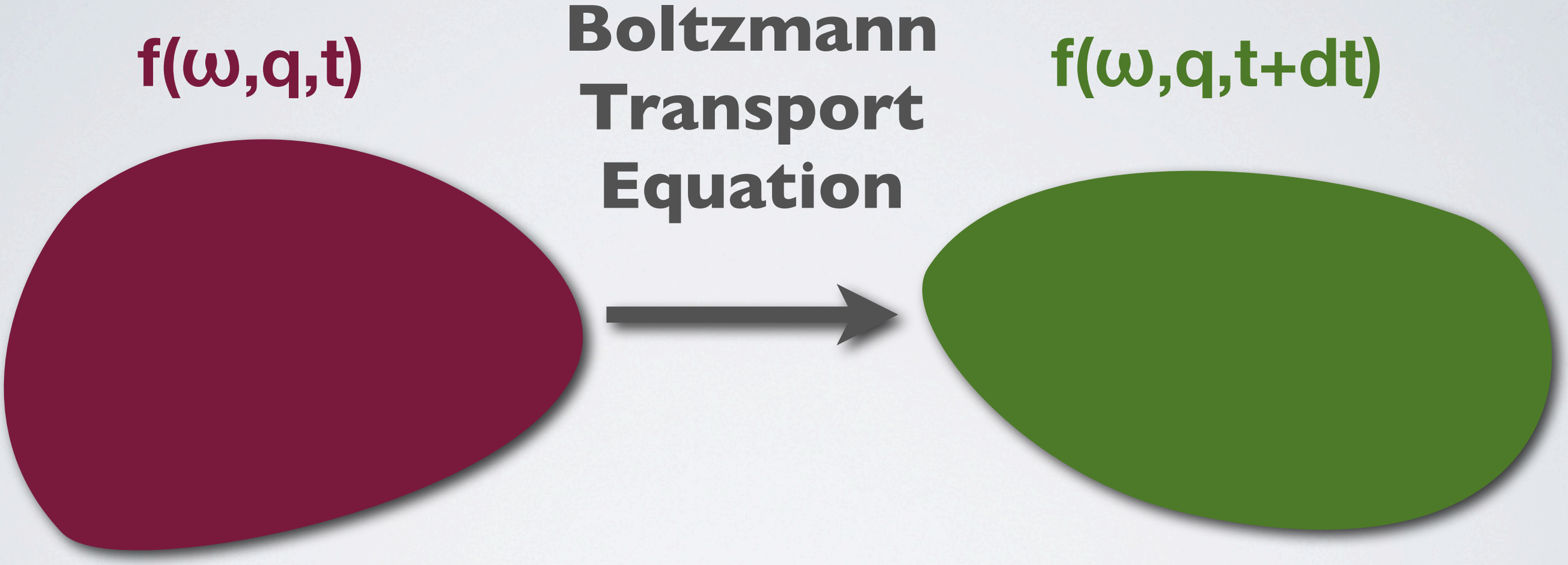
Microscopic Nature:



Can we calculate and understand the **thermal conductivity** from **first principles**?

(A) BOLTZMANN TRANSPORT EQUATION

R. Peierls, *Ann. Phys.* **395**,1055 (1929).
D. A. Broido *et al., Appl. Phys. Lett.* **91**, 231922 (2007).



Boltzmann-Peierls-Transport-Equation describes the evolution of the **phonon** phase space distribution **f(ω,q,t)**.

(A) BOLTZMANN TRANSPORT EQUATION

R. Peierls, *Ann. Phys.* **395**,1055 (1929).
D. A. Broido *et al.*, *Appl. Phys. Lett.* **91**, 231922 (2007).

Single-mode relaxation time approximation

$$\kappa \sim \sum_s c_s^2 \; \omega_s^2 \; n_s(n_s+1) \; \tau_s$$

Group velocity | **Frequency** | **Equilibrium population** | **phonon lifetime**

Harmonic phonon theory

?

Phonon Lifetimes from First Principles

- from **Density Functional Perturbation Theory**
  J. Garg *et al., Phys. Rev. Lett.* **106**, 045901 (2011).

- from **fitting** the **forces** in ***ab initio MD***
  K. Esfarjani, and H.T. Stokes, *Phys. Rev. B* **77**, 1441112 (2008).

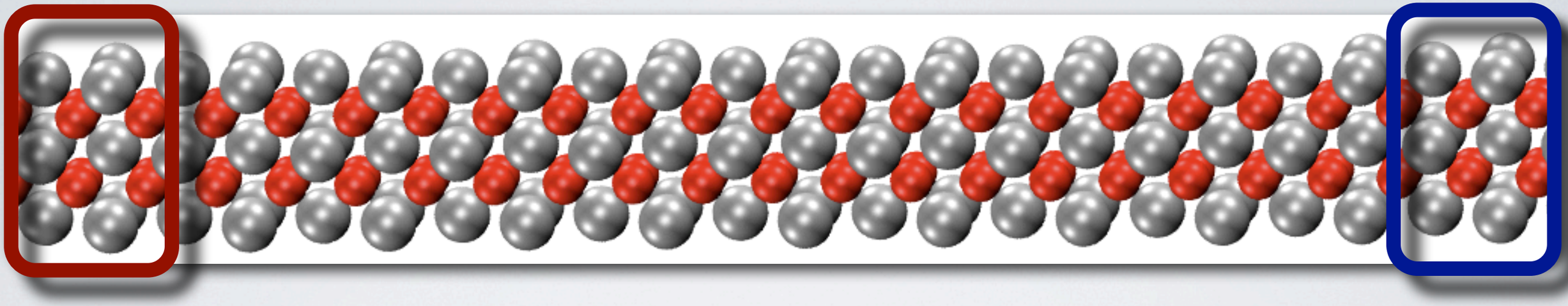
- from **fitting** the **phonon line width** determined via ***ab initio MD***
  N. De Koker, *Phys. Rev. Lett.* **103**,125902 (2009).

All these approaches give very **accurate** results for **good thermal conductors** at **low** temperatures.

Results are **questionable** at high levels of **anharmonicity**!

(B) NON-EQUILIBRIUM MD

S. Stackhouse, L. Stixrude, and B. B. Karki, *Phys. Rev. Lett.* **104**, 208501(2010).



heat source → • Temperature gradient ∇T • Stationary heat flux **J** → **heat sink**

⇓

Thermal conductivity can be calculated by applying Fourier‘ s Law.

$$\mathbf{J} = -\kappa \nabla T$$

PROS & CONS

- [x] **Relatively easy implementation:**
  Use *standard thermostats* for *heat source & sink*

- [ ] **Modeling of the steady state**
  Long simulation time needed for *good statistics*

- [ ] **Heat source & sink create artifacts**
  Large simulation cells needed

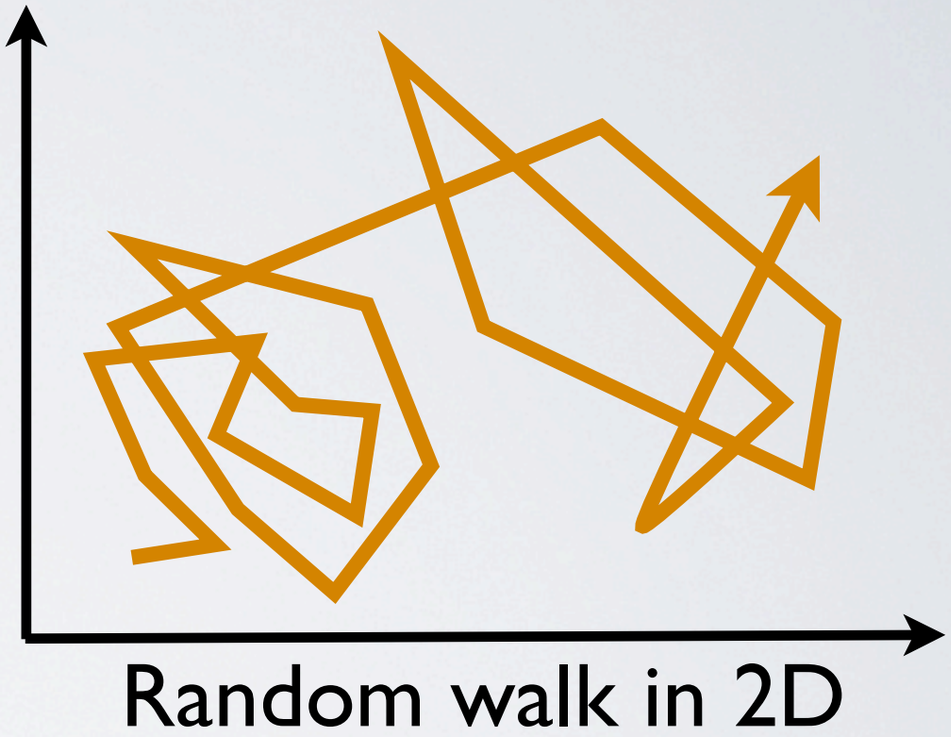
- [ ] **Huge temperature gradient**
  Possible undesired *non-linear* effects

FLUCTUATION-DISSIPATION THEOREM

Brownian Motion:

A. Einstein, *Ann. Phys.* **322**, 549 (1905).

The erratic motion of the particles
is closely related to
frictional force under perturbation.



The **fluctuations of the forces** in thermodynamic **equilibrium** is related to the **generalized resistance** in **non-equilibrium** for linear dissipative systems.

H. B. Callen, and T. A. Welton, *Phys. Rev.* **83**, 34 (1951).

(C) GREEN-KUBO METHOD

R. Kubo, M. Yokota, and S. Nakajima, *J. Phys. Soc. Japan* **12**, 1203 (1957).

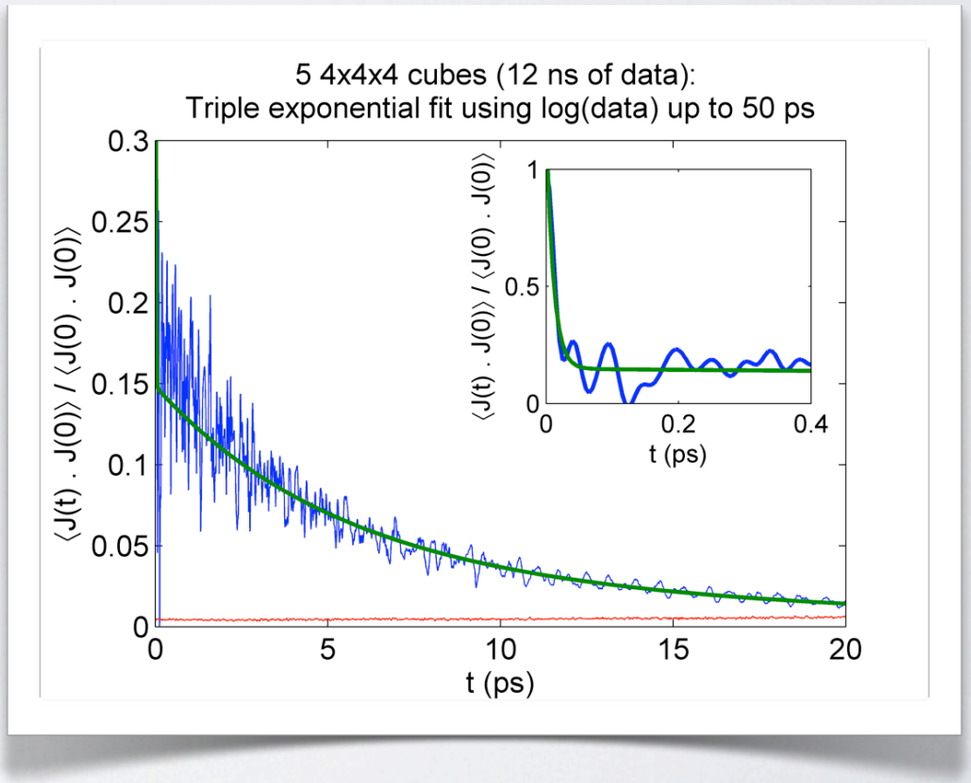
Simulations of the **thermodynamic equilibrium**

⇓ ⇓ ⇓

Information about **non-equilibrium processes**

$$\kappa \sim \int_0^\infty d\tau \, \langle \, \mathbf{J}(0) \, \mathbf{J}(\tau) \rangle_{eq}$$

The **thermal conductivity** is related to the **autocorrelation function** of the **heat flux**



Si at 1000 K, Courtesy of P. Howell, Siemens AG

PROS & CONS

- [x] Standard MD method
- [x] No heat source & sink needed
- [x] No temperature gradient needed
- [ ] Long simulation time

Looks promising, but...

THE HEAT FLUX

R. J. Hardy, *Phys. Rev.* **132**,168 (1963).

$$\mathbf{J}(t) = \frac{d}{dt}\left(\sum_i \mathbf{r}_i(t)\,\varepsilon_i(t)\right)$$

$\mathbf{r}_i$ ⋯ Position of atom i

ε_i ⋯ Energy of atom i

Energic contributions $\boldsymbol{\varepsilon_i}$ of the **single atoms** required!

A **partitioning** of the **total energy** is
ill-defined, cumbersome and error-prone!

⇒ Green-Kubo Method hitherto only used with classical potentials!

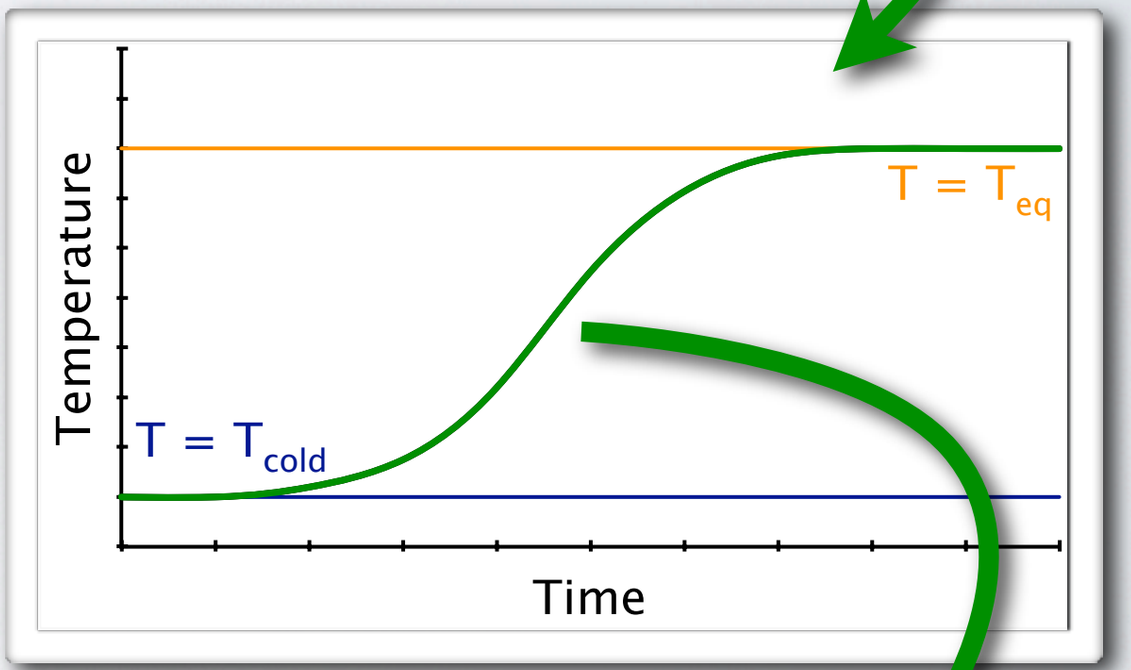
„LASER FLASH“ MEASUREMENTS

W. J. Parker *et al., J. Appl. Phys.* **32**,1679 (1961).

heat diffusion

$T = T_{hot}$

$T = T_{cold}$



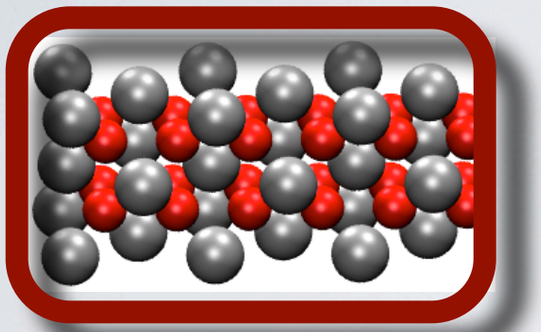
Heat Diffusion Equation:

$$\frac{\partial T(x,t)}{\partial t} + \frac{\kappa}{\rho \cdot c_V} \frac{\partial^2 T(x,t)}{\partial x^2} = 0$$

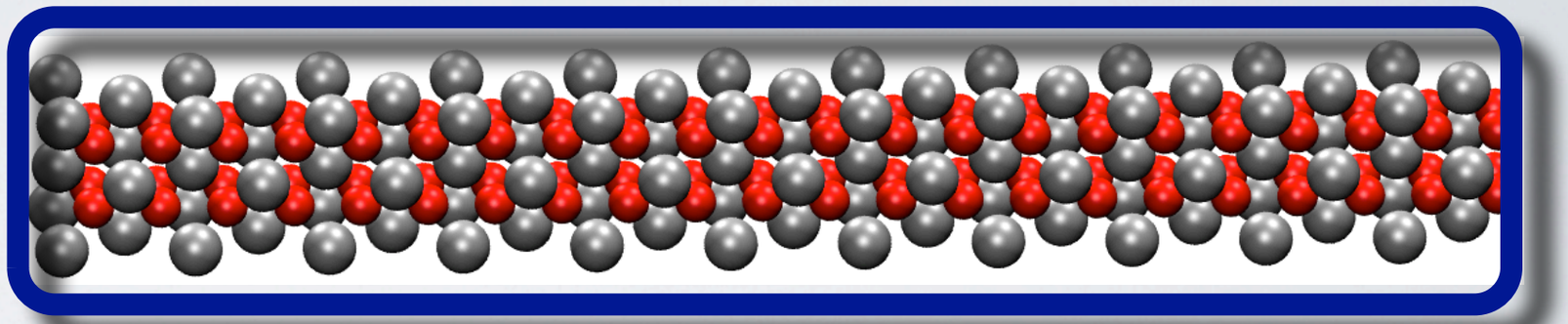
Extract the ***thermal conductivity*** by fitting **T(x,t)**

(D) LASER FLASH METHOD

T. M. Gibbons and S. K. Estreicher, *Phys. Rev. Lett.* **102**, 255502 (2009).



hot SC

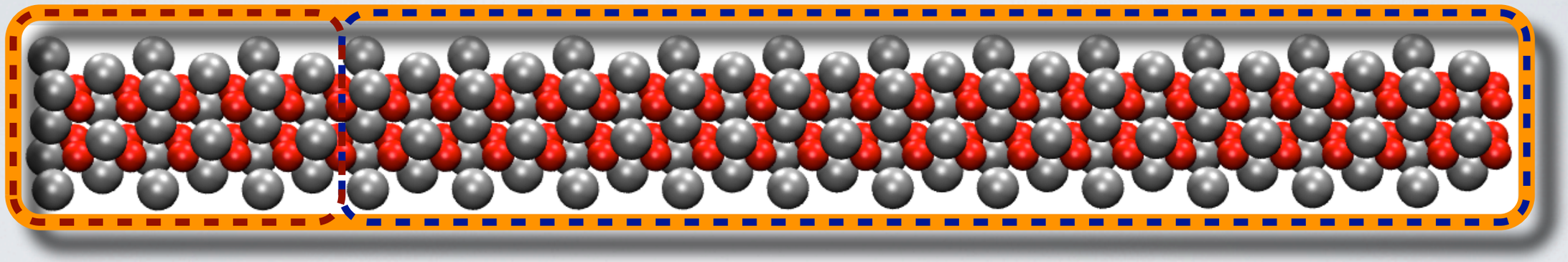


cold supercell

(1) Prepare two supercells:
a **small hot** one and a **large cold** one.

(D) LASER FLASH METHOD

T. M. Gibbons and S. K. Estreicher, *Phys. Rev. Lett.* **102**, 255502 (2009).



Thermal Diffusion

(1) **Prepare two supercells:**
a **small hot** one and a **large cold** one.

(2) **Connect** the **two** supercells and
let the **heat diffuse**.

(I) SUPERCELL PREPARATION

S. K. Estreicher, and T. M. Gibbons, *Physica B* **404**, 4509 (2009).

In the **quasi-harmonic approximation**, the **positions $\mathbf{r}_i$** and the **velocities $\mathbf{v}_i$** are related to the **vibrational eigenfrequencies ω_s** and -vectors **ν_s**.

$$R_{0i} + \Delta\mathbf{R}_i = + \sum_s A_s(T) \frac{\cos(\phi_s + \omega_s t)}{\sqrt{M_i}} \cdot \nu_s$$

$$\mathbf{V}_i = - \sum_s A_s(T) \frac{\sin(\phi_s + \omega_s t)}{\sqrt{M_i}} \cdot \omega_s \cdot \nu_s$$

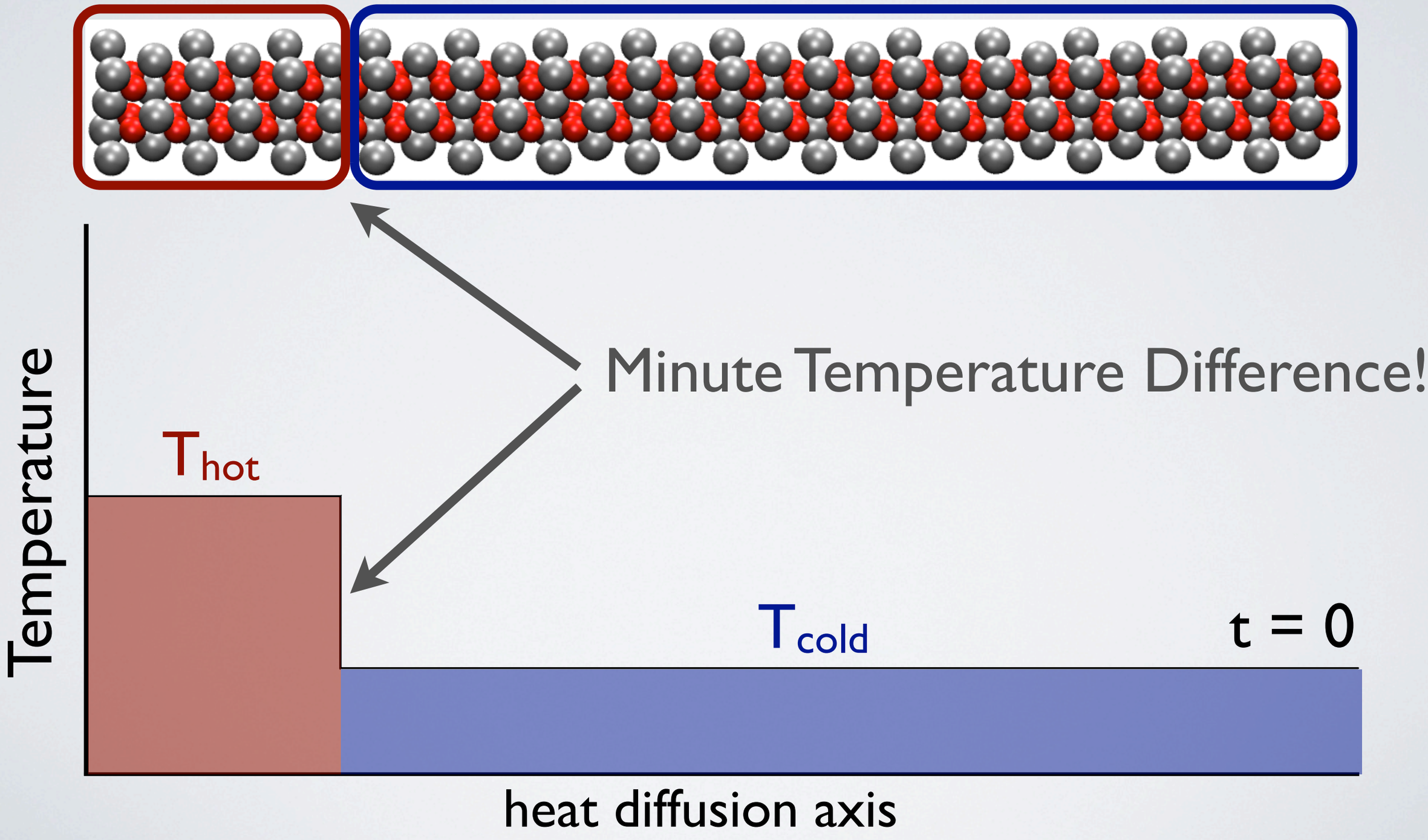
Maxwell-Boltzmann distributed amplitudes

random phase

harmonic approximation

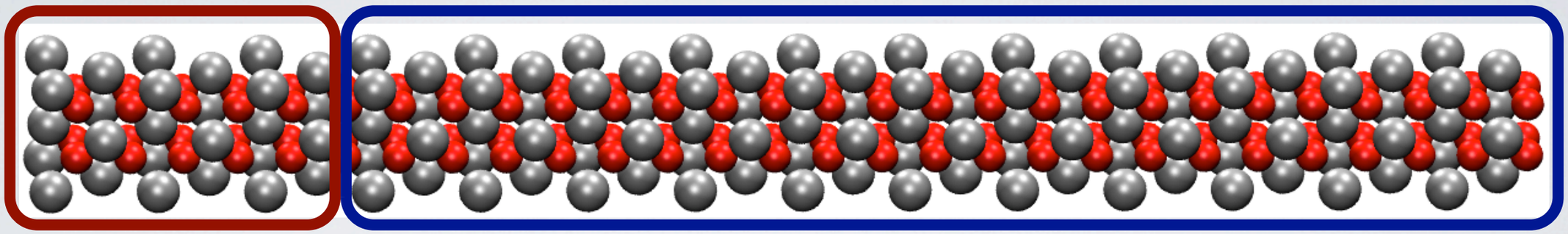
(1) SUPERCELL PREPARATION

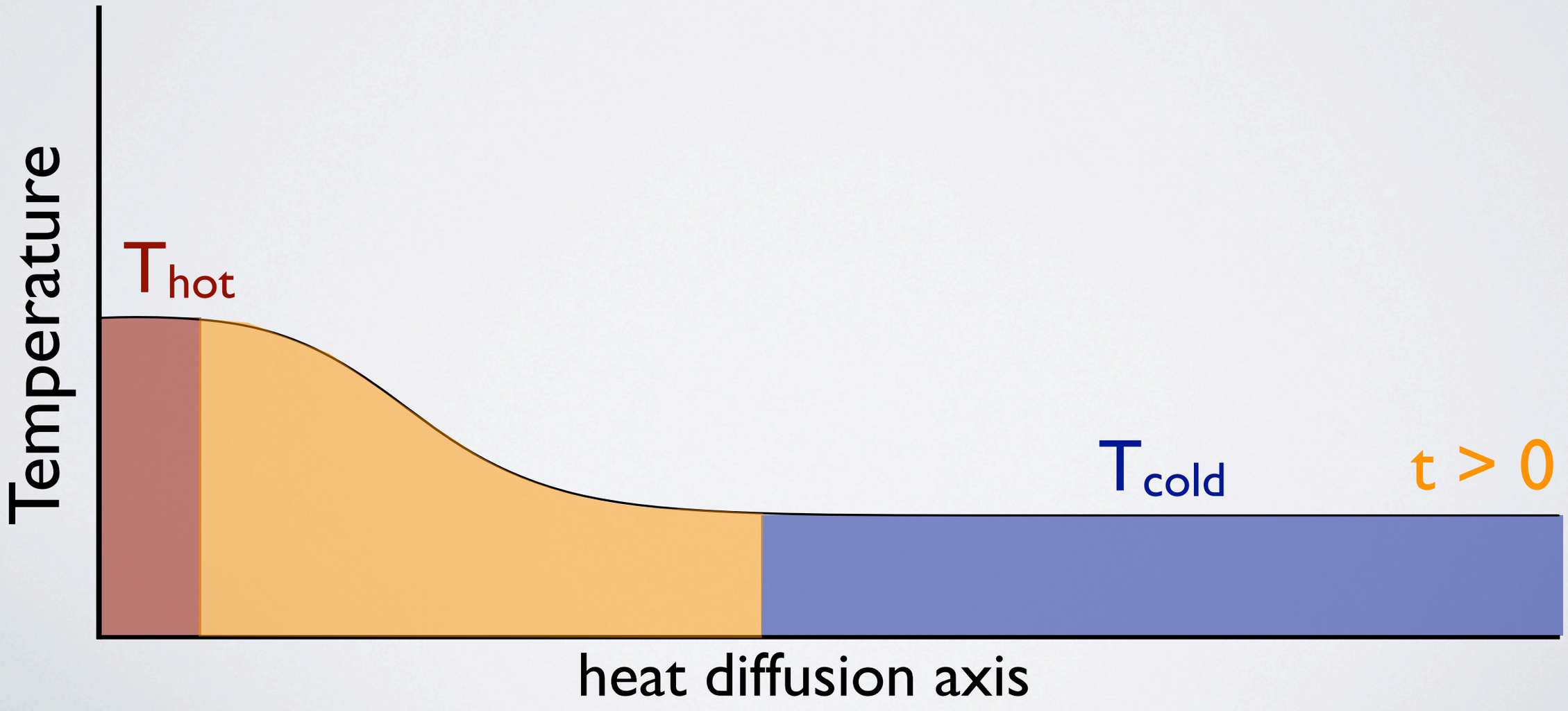
S. K. Estreicher, and T. M. Gibbons, *Physica B* **404**, 4509 (2009).



(2) HEAT DIFFUSION

T. M. Gibbons and S. K. Estreicher, *Phys. Rev. Lett.* **102**, 255502 (2009).



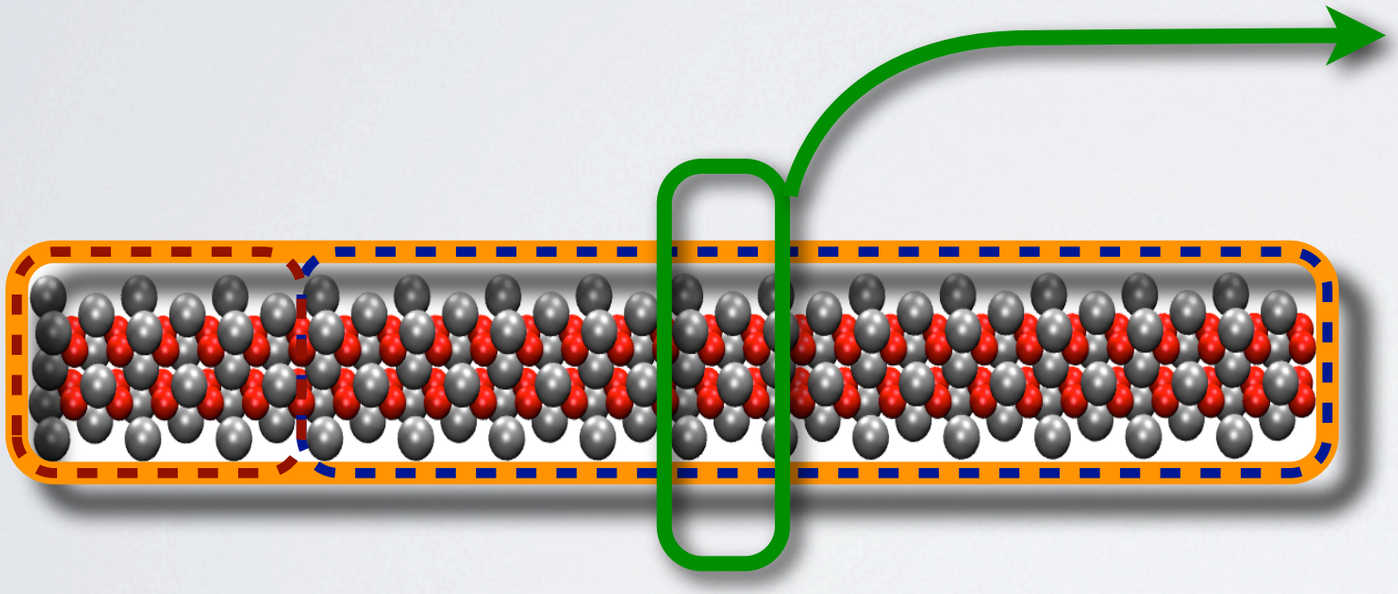


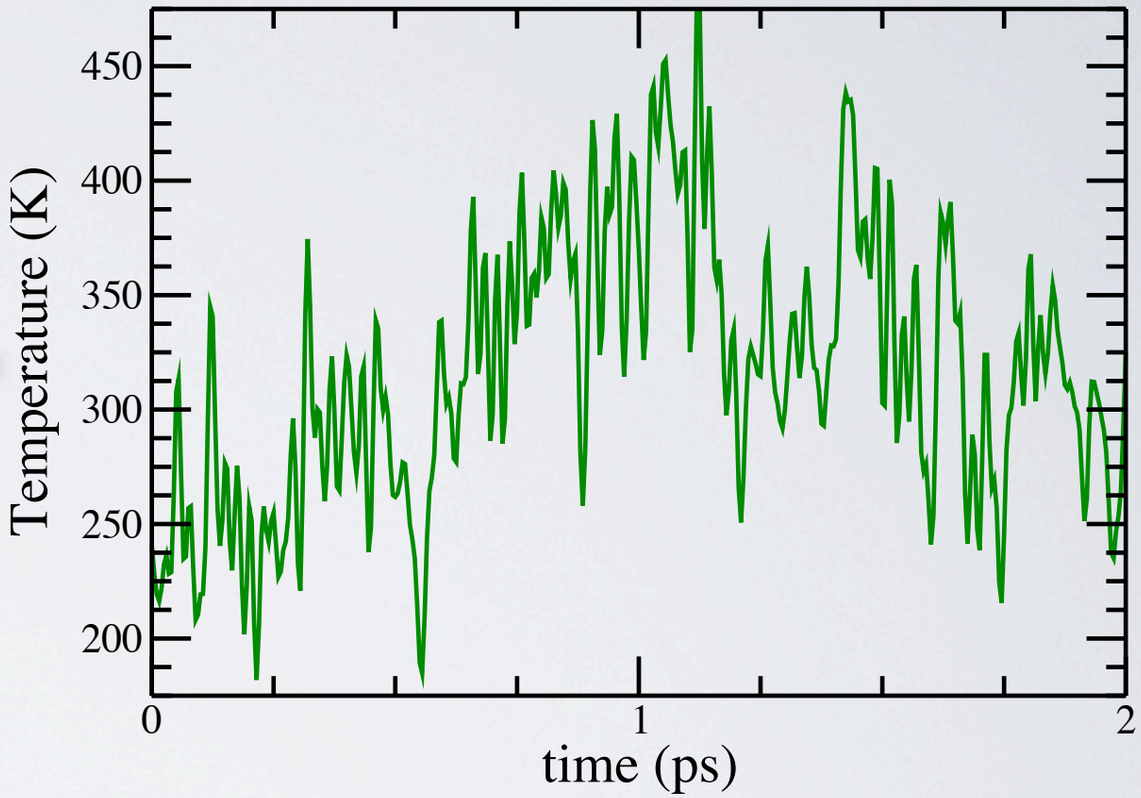
(2) HEAT DIFFUSION

T. M. Gibbons and S. K. Estreicher, *Phys. Rev. Lett.* **102**, 255502 (2009).

Monitor $T(x,t)$

during thermal equilibration





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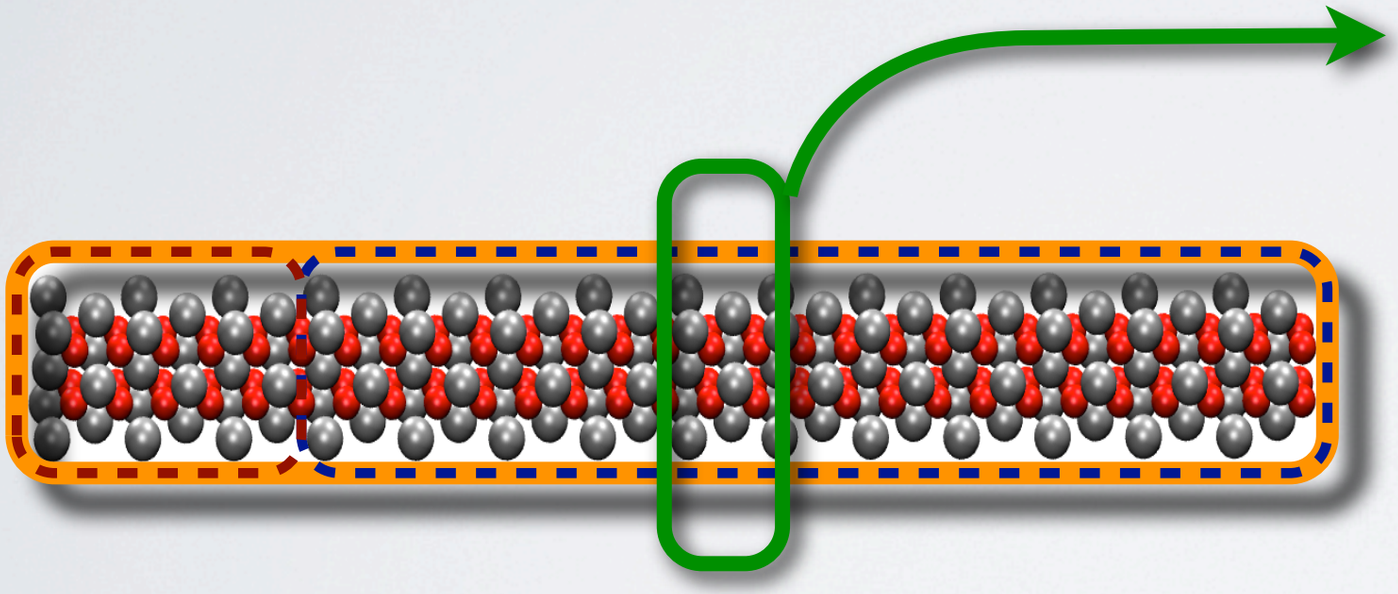
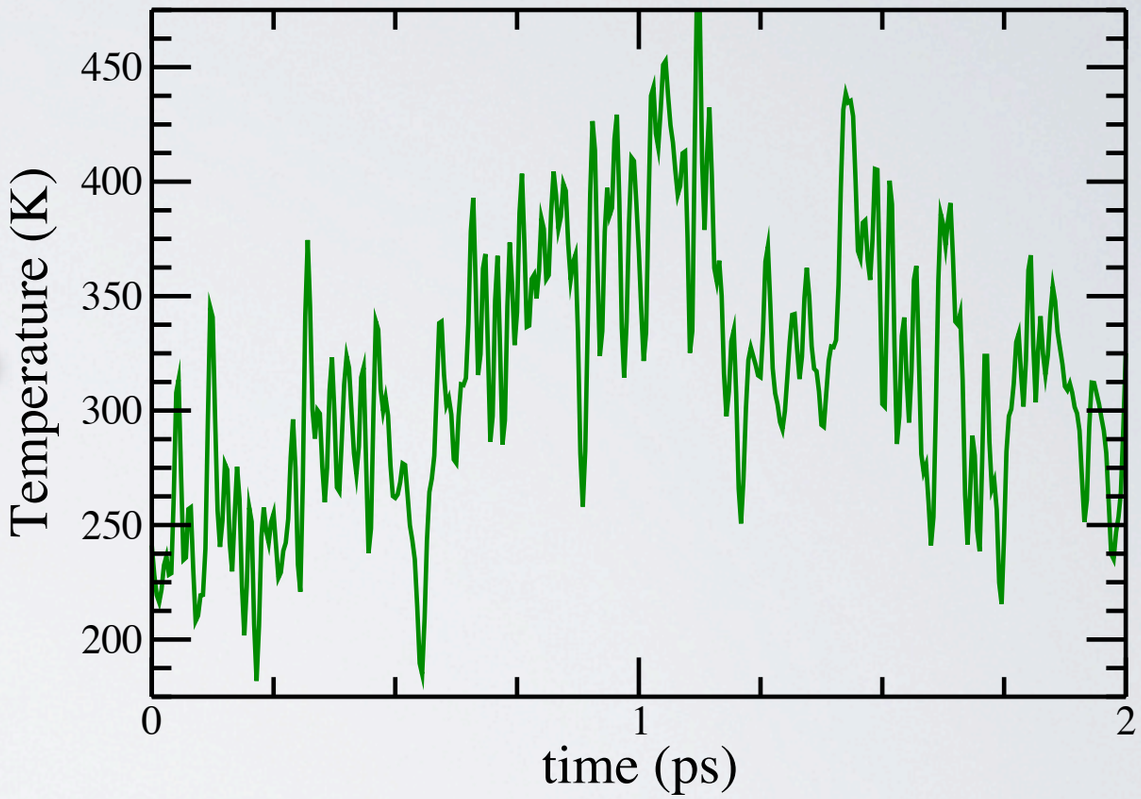
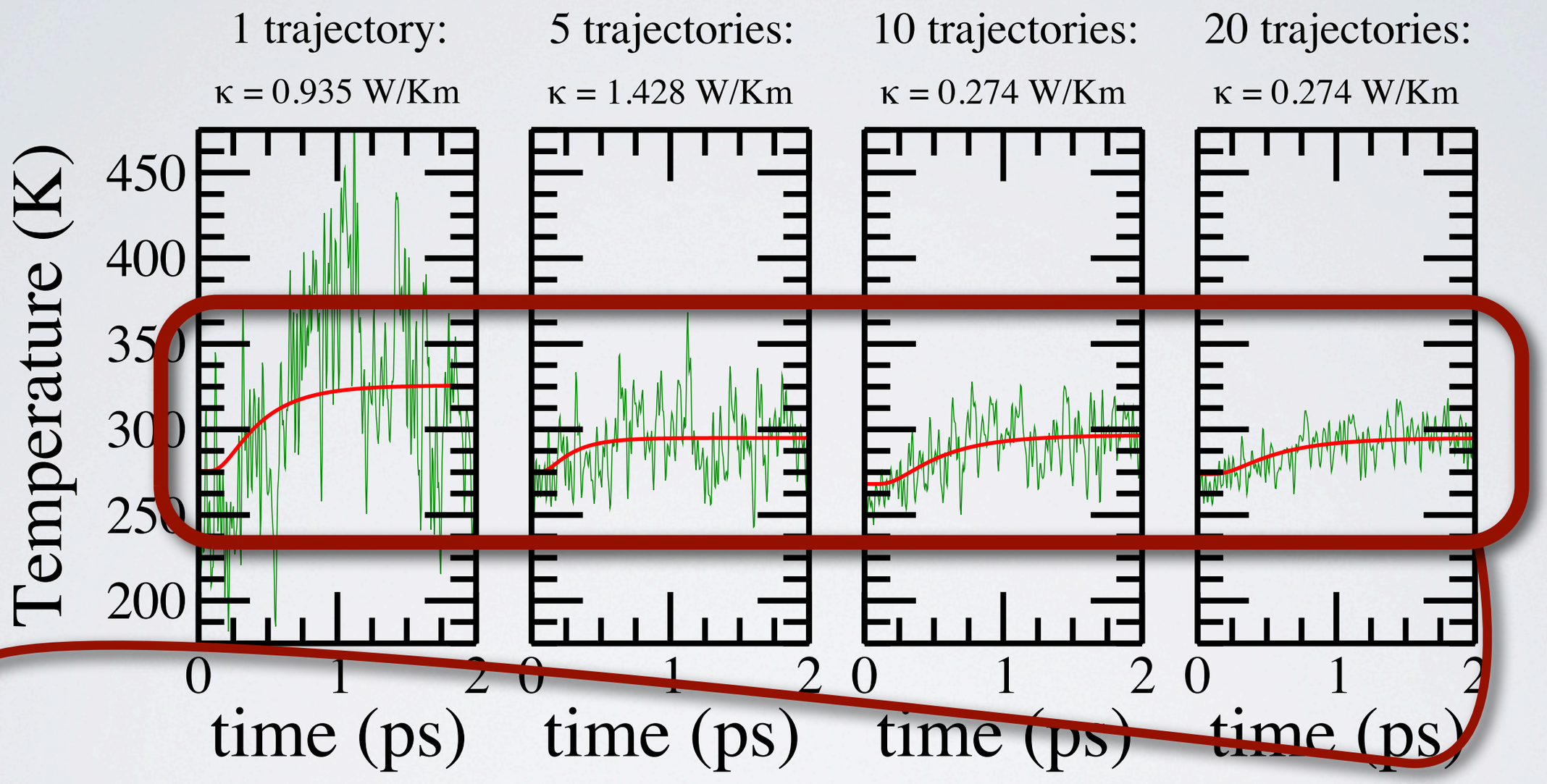




Finite supercell size leads to large **temperature fluctuations**.

(2) HEAT DIFFUSION

T. M. Gibbons and S. K. Estreicher, *Phys. Rev. Lett.* **102**, 255502 (2009).



Fit to $T(x,t) = T_{cold} + (T_{final} - T_{cold}) \sum_n (-1)^n \exp\left(-\frac{n^2\pi^2\kappa\, t}{\rho\, C_V}\right)$

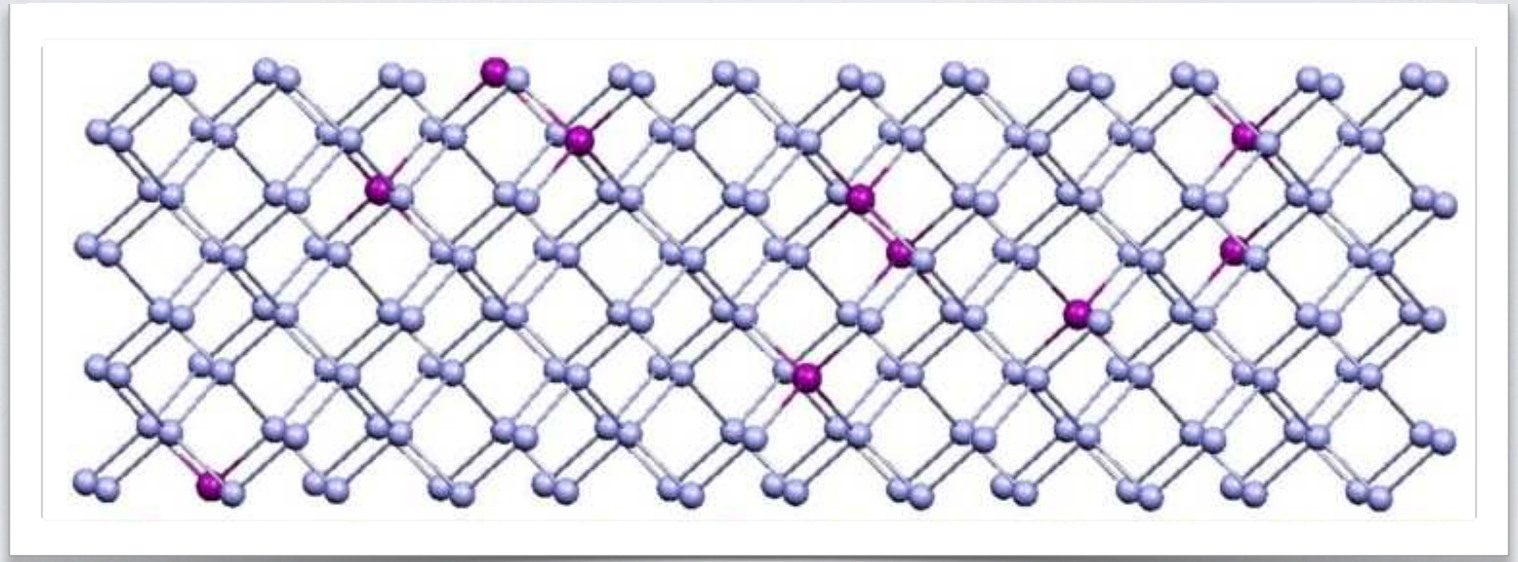
W. J. Parker *et al., J. Appl. Phys.* **32**,1679 (1961).

PROS & CONS

- [x] Standard MD method
- [x] No heat source & sink needed
- [x] Minute temperature gradients
- [ ] Only applicable at **low** temperatures

(3) APPLICATION TO IMPURITIES IN SI

T. M. Gibbons, By. Kang, S. K. Estreicher, and C. Carbogno, *Phys. Rev, B (accepted).*

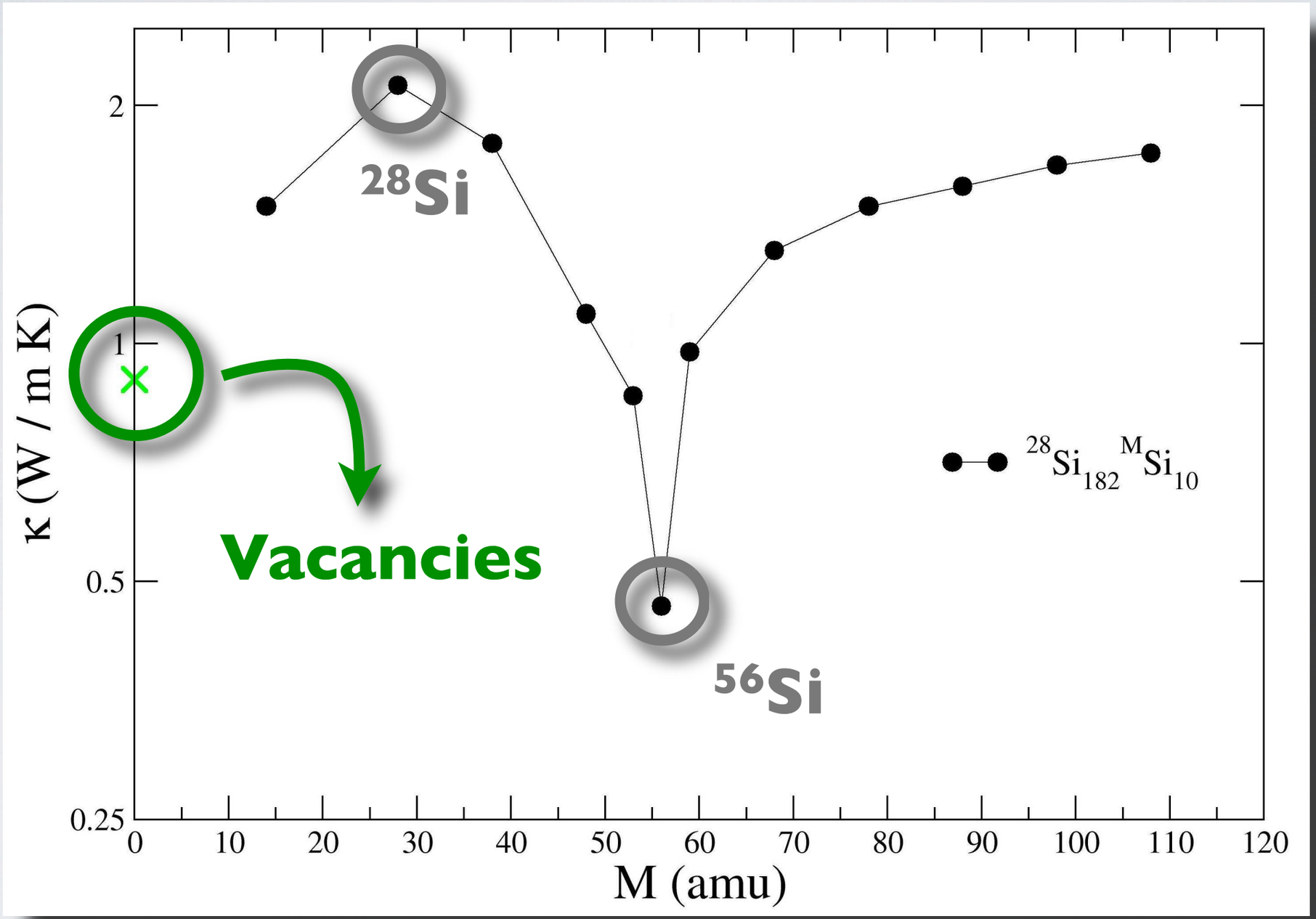


Si_{192} supercell containing **~5.2% impurities**

How do the
properties of the impurities
affect the
thermal conductivity of the system?

(C) APPLICATION TO IMPURITIES IN SI

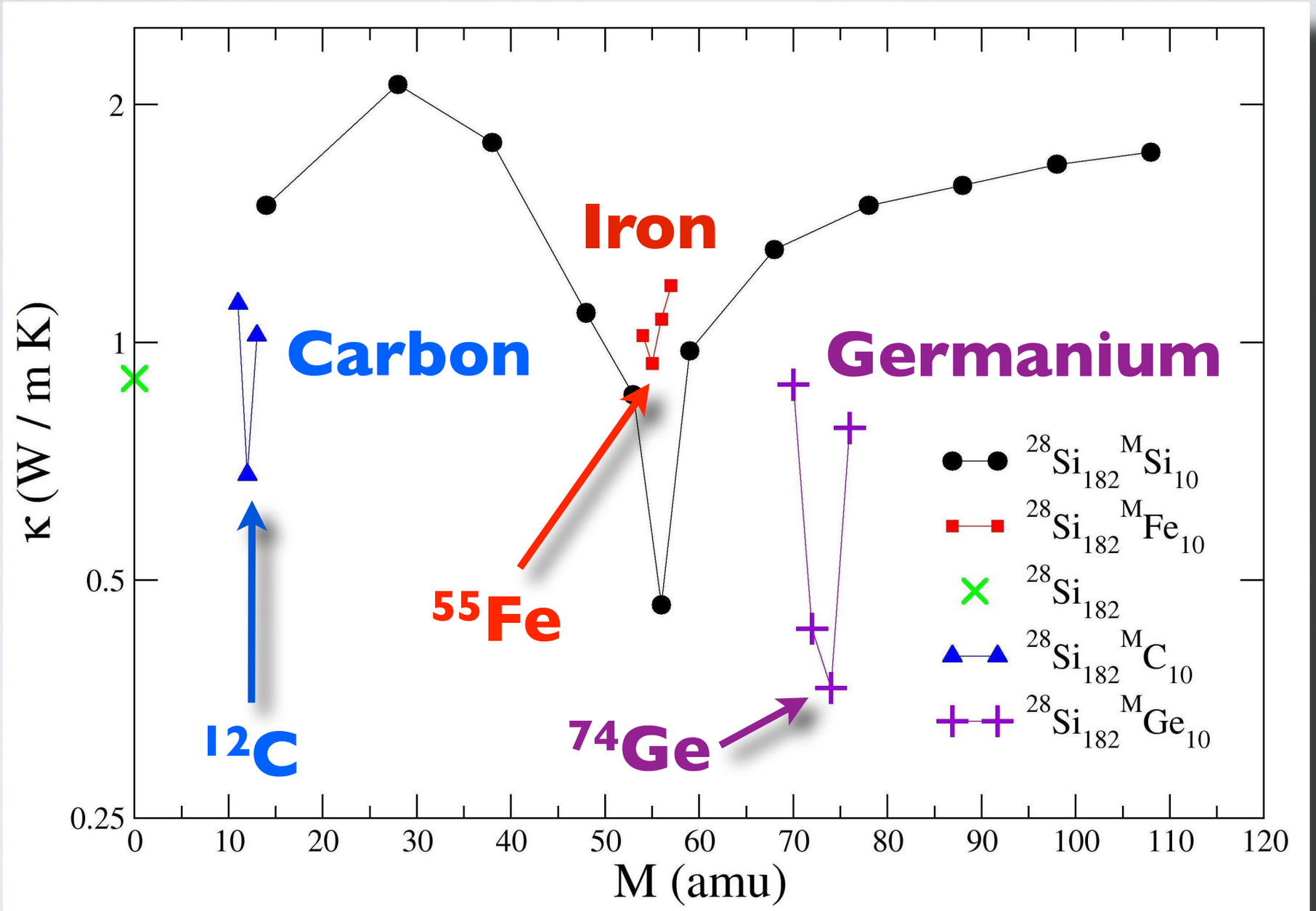
T. M. Gibbons, By. Kang, S. K. Estreicher, and C. Carbogno, *Phys. Rev, B (accepted).*



Thermal conductivity can be controlled via the impurities‘ mass!

(C) APPLICATION TO IMPURITIES IN SI

T. M. Gibbons, By. Kang, S. K. Estreicher, and C. Carbogno, *Phys. Rev, B (accepted).*



Not all impurities are created equal!

CONCLUSION AND SUMMARY

Molecular Dynamics:
Application in Thermodynamics, Thermostats, and Caveats

Harmonic Approximation:
Basic concepts, Application: Heat Capacities & Lattice Expansion

Thermodynamic Integration:
Complete(!) Anharmonic Free Energy from First Principles

Non-equilibrium dynamics:
Thermal Conductivity from First Principles