The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

2145-8

Spring College on Computational Nanoscience

17 - 28 May 2010

Coloring the Noise or Cheating One's Way to Quantum Effects

Michele PARRINELLO

Dept. of Chemistry and Applied Biosciences, ETH
Lugano
Switzerland

Strada Costiera 11, 34151 Trieste, Italy - Tel.+39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it

Coloring the noise

Michele Parrinello

Department of Chemistry and Applied Biosciences ETH
USI Campus, Lugano, Switzerland

Newtonian dynamics and statistical mechanics

From Newtons equations

$$\dot{R} = \frac{P}{M} \qquad \dot{P} = F$$

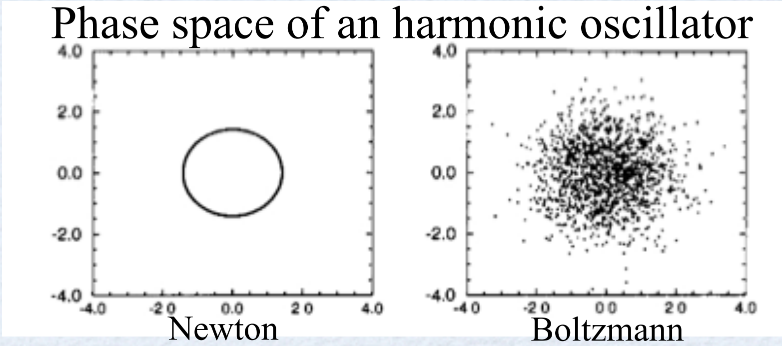
Under the hypothesis of ergodicity

$$\langle O(P_I, R_I) \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau dt O(P_I(t), R_I(t)) = \int dP_I dR_I O(P_I, R_I) P(P_I, R_I)$$

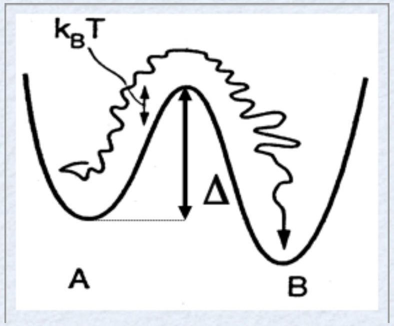
$$P(P_I, R_I) \propto \delta(H(P_I, R_I) - E) \qquad \langle K \rangle = \frac{3}{2} N k_B T$$

Problems with molecular dynamics

- ✳ Ergodicity



- ✳ Activated events



- ✳ Slow diffusion

Controlling the temperature

- From (NVE) to (NVT)

$$P(P_I, R_I) \propto \exp(-\beta H(P_I, R_I))$$

- A good thermostat should:
  - Sample the canonical distribution
  - Be ergodic
  - Be tunable
  - Not disturb the dynamics

Some popular thermostats

- Velocity-rescaling*
- Langevin dynamics* (Schneider and Stoll, PRB, 1978)
- Andersen* (JCP, 1980)
- Berendsen* *et al* (JCP, 1984)
- Nosé (JCP, 1984), Hoover (PRA, 1985)
- Nosé-Hoover chains (Martyna *et al*, JCP, 1992)
- ...

*stochastic thermostats, no conserved quantity

*the sampling is not canonical

Two simple but incorrect thermostats

Rescale the velocities so as to get the target kinetic energy value

$$\overline{K} = \frac{3}{2} N k_B T$$

Berensen's thermostat

$$dK = -\frac{K - \overline{K}}{\tau} dt$$

Make it stochastic

At every step draw the kinetic energy from the canonical distribution

$$P(K) \propto K^{\frac{3}{2}N-1} e^{-\beta K}$$

☺ Easy to code

☺ Samples the canonical distribution

☹ Leads to wrong dynamics

Make it smooth

Add a stochastic term

$$dK = -\frac{K - \overline{K}}{\tau} dt + 2\sqrt{\frac{K\overline{K}}{3N\tau}} dW$$

The limiting distribution of this stochastic process is

$$P(K) \propto K^{\frac{3}{2}N-1} e^{-\beta K}$$

A Monte Carlo perspective

Each step can be considered as a Monte Carlo move

The acceptance test can be written as

$$\min\left(1, \frac{M(x_i^* \leftarrow x_{i+1}^*)\bar{P}(x_{i+1}^*)}{M(x_{i+1} \leftarrow x_i)\bar{P}(x_i)}\right) \equiv \min\left(1, e^{-\frac{\Delta \bar{H}}{k_B T}}\right)$$

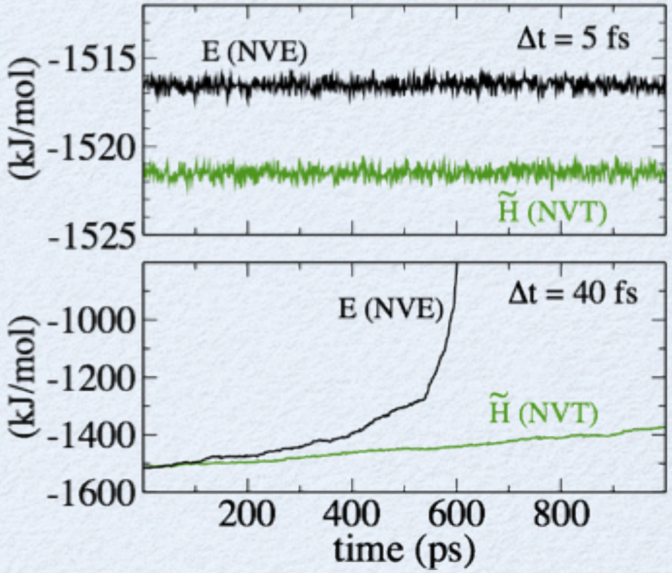
Use the effective energy as a measure of the accuracy

Orthokatanomy: a conserved quantity

$$\tilde{H} = H(x) - \int_0^t \frac{dt'}{\tau}(\bar{K} - K(t')) - 2\int_0^t \sqrt{\frac{K(t')\bar{K}}{N_f}} \frac{dW(t')}{\sqrt{\tau}}$$

Behaves like the energy in a MD run

Checking the integration time step



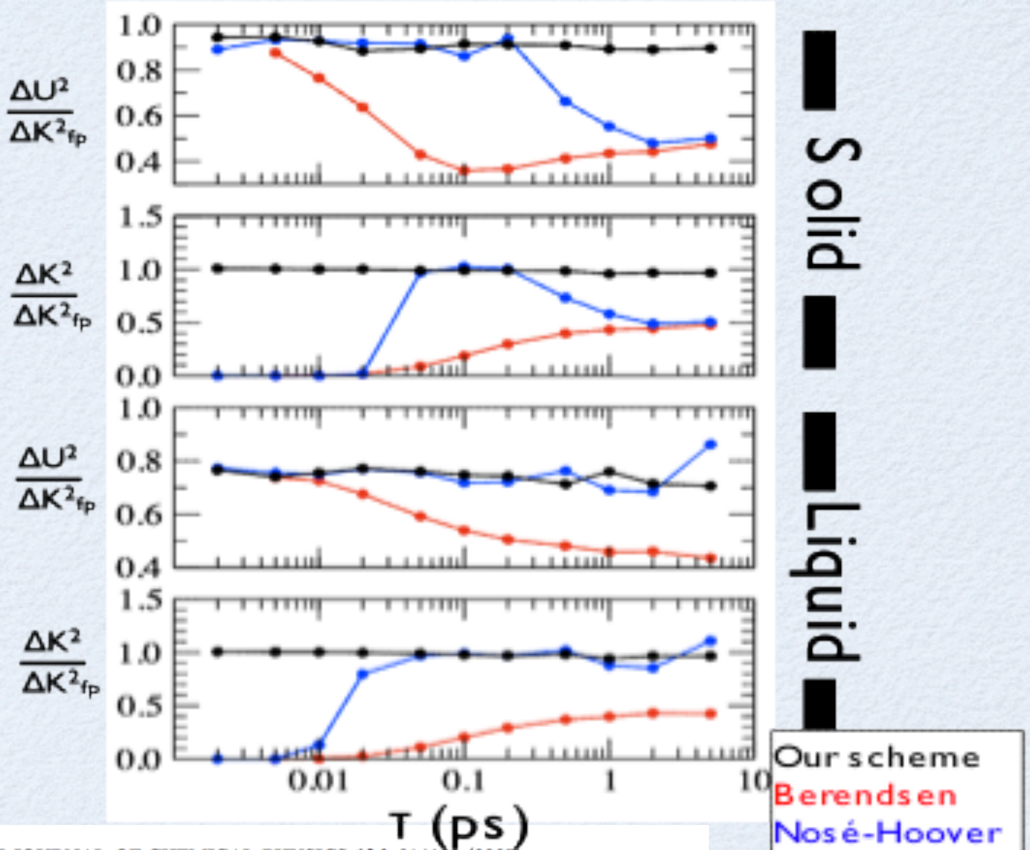
Similar ideas can be applied to the Langevin equation

An exellent thermostat

Lennard-Jones system

Berensen fails

Nose`-Hoover fails too



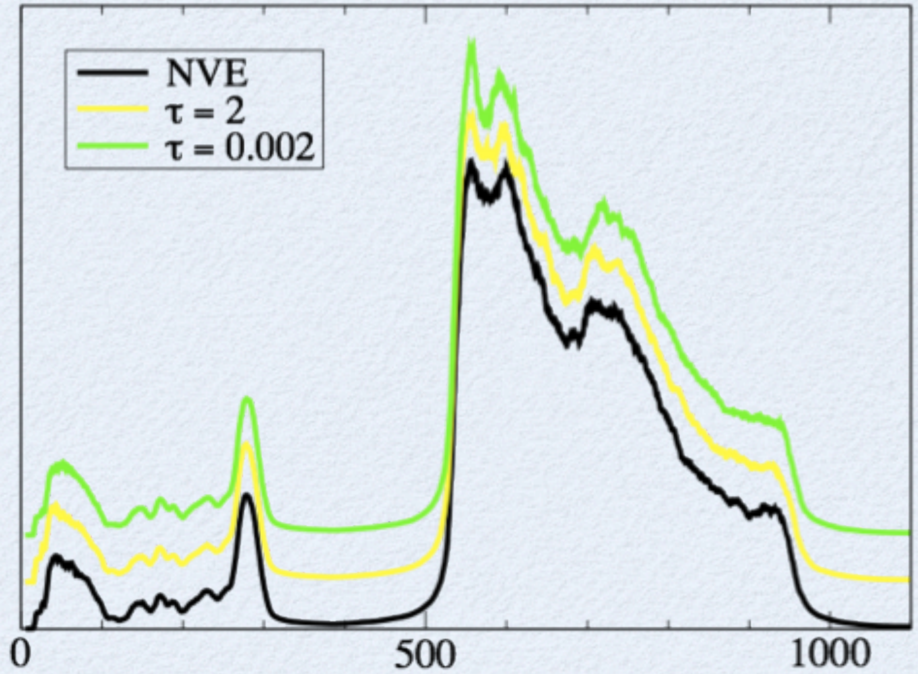
THE JOURNAL OF CHEMICAL PHYSICS **126**, 014101 (2007)

Canonical sampling through velocity rescaling

Giovanni Bussi,[a] Davide Donadio, and Michele Parrinello
Computational Science, Department of Chemistry and Applied Biosciences, ETH Zürich, USI Campus, Via Giuseppe Buffi 13, CH-6900 Lugano, Switzerland

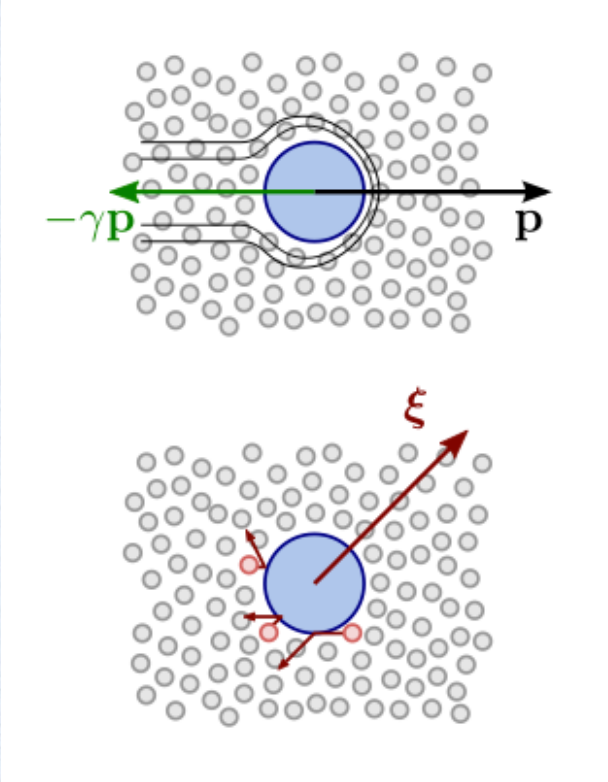
The right kind of dynamics

The vibrational spectrum of TIP4P water



Langevin equation

Brownian particle



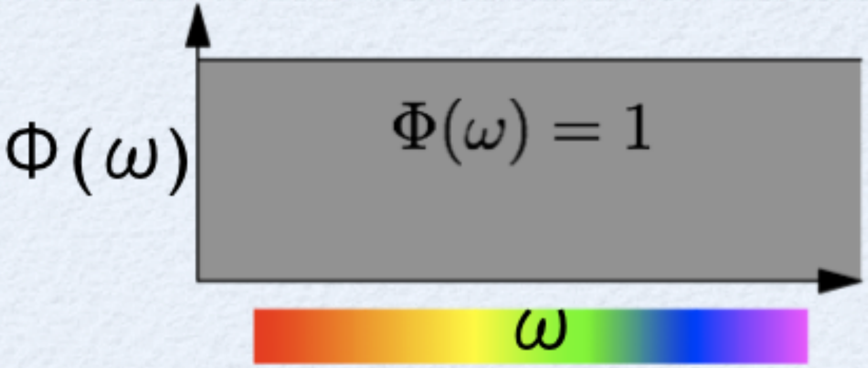
$$\dot{P} = -\gamma P + \xi$$

Langevin equation and statmech

$$\dot{R}_I = \frac{P_I}{M_I}$$

$$\dot{P}_I = F_I - \gamma P_I + \sqrt{2 M_I \gamma k_B T}\,\xi_I$$

$$\langle \xi_I(t)\xi_I(t')\rangle = \delta(t-t')$$



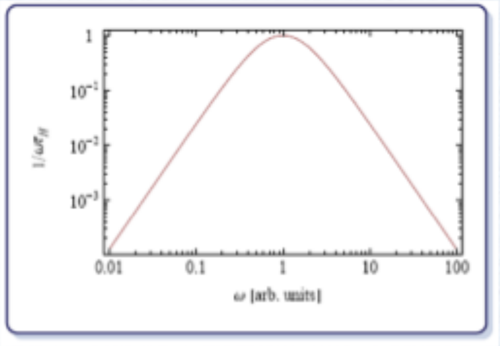
Canonical ensemble

$$P(P_I, R_I) \propto \exp(-\beta H(P_I, R_I))$$

How efficient is the sampling?

Given a mode of frequency ω, we choose the friction such that the energy relaxation time τ is optimal.

$$\omega\tau_{opt} = 1$$



For optimal sampling one chooses the reference frequency in the middle of the spectrum.

Generalized Langevin dynamics

$$\dot{R} = \frac{P}{M}$$

Memory function

$$\dot{P} = F - \int_0^t K(t-t')P(t')dt' + \sqrt{M k_B T}\,\zeta(t)$$

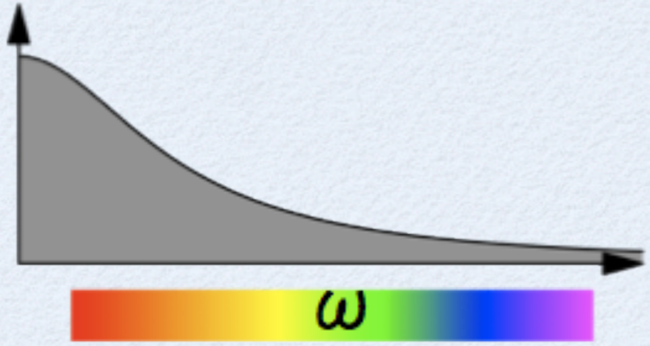
$$\langle \zeta(t)\zeta(t')\rangle = K(t-t')$$ → Colored noise

Mori-Zwanzig

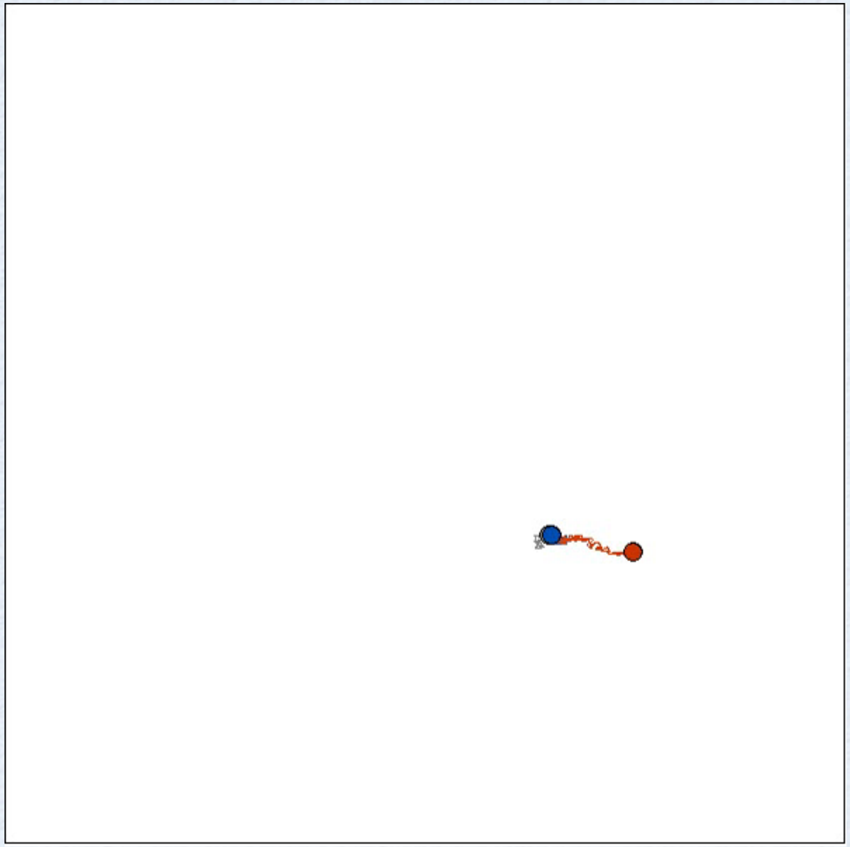
An elementary example

$$\langle \xi(t)\xi(t')\rangle = K(t-t') = \frac{1}{2\tau} e^{-\frac{|t-t'|}{\tau}}$$

$$K(\omega) = \frac{1}{1+(\omega\tau)^2}$$



The effect of different memory functions



Three particles

Same diffusion coefficient

Grey no memory

Blue fast memory

Red slow memory

Mission impossible?

Almost any memory function can be approximated by a Markov process in an extended space

$$\dot{R} = \frac{P}{M}$$

$$\begin{pmatrix} \dot{P} \\ \dot{s} \end{pmatrix} = \begin{pmatrix} F \\ 0 \end{pmatrix} - A \begin{pmatrix} P \\ s \end{pmatrix} + B\zeta(t)$$

$$\langle \zeta(t)\zeta(t') \rangle = \delta(t-t')$$

An elementary example

A non Markov process with a memory function of the type

$$K(t-t')=\frac{1}{2\tau}e^{-\frac{|t-t'|}{\tau}}$$

Is e equivalent to a Markov stochastic process in an extended space

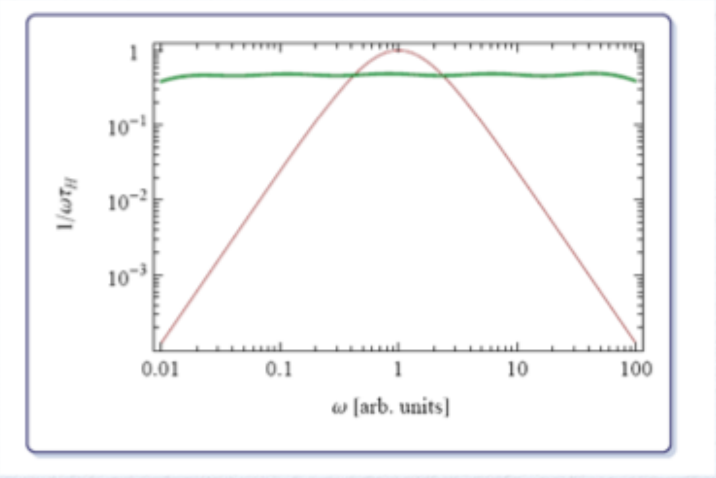
$$\begin{pmatrix} \dot{P} \\ \dot{s} \end{pmatrix} = \begin{pmatrix} F \\ 0 \end{pmatrix} - A\begin{pmatrix} P \\ s \end{pmatrix} + B\zeta(t)$$

with

$$A=\frac{1}{\tau}\begin{pmatrix} & \sqrt{\tau} \\ \sqrt{\tau} & 1 \end{pmatrix} \qquad B=\sqrt{\frac{Tm}{\tau}}\begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

Application #1:optimal sampling

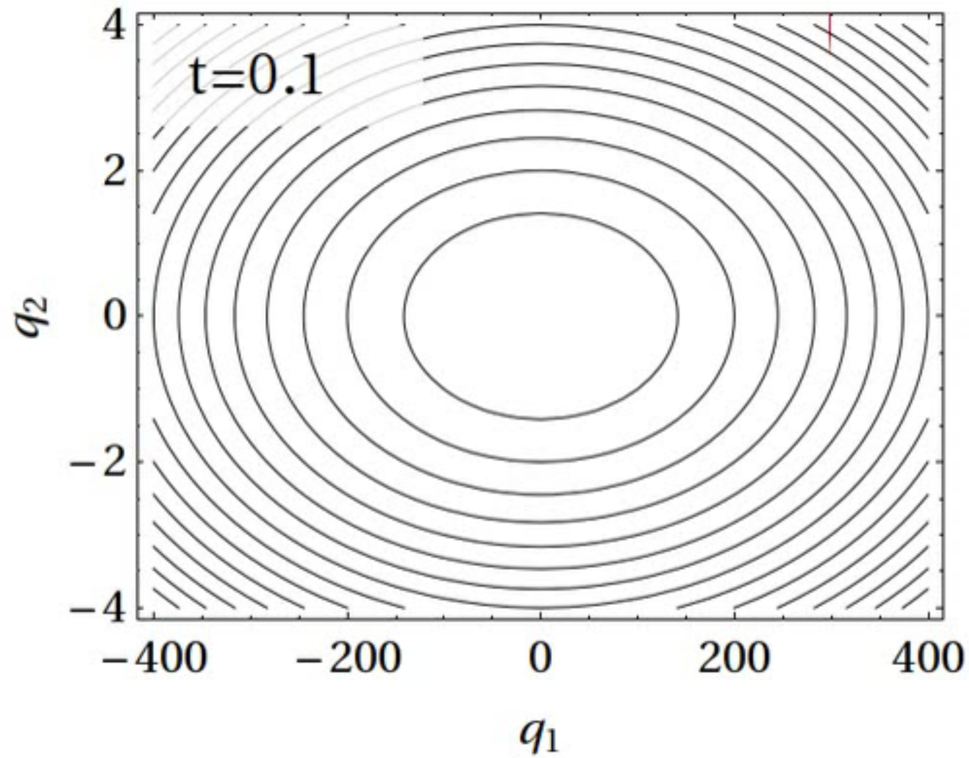
Design τ(ω) such that τ(ω)~ ω^{-1} in the relevant frequency range

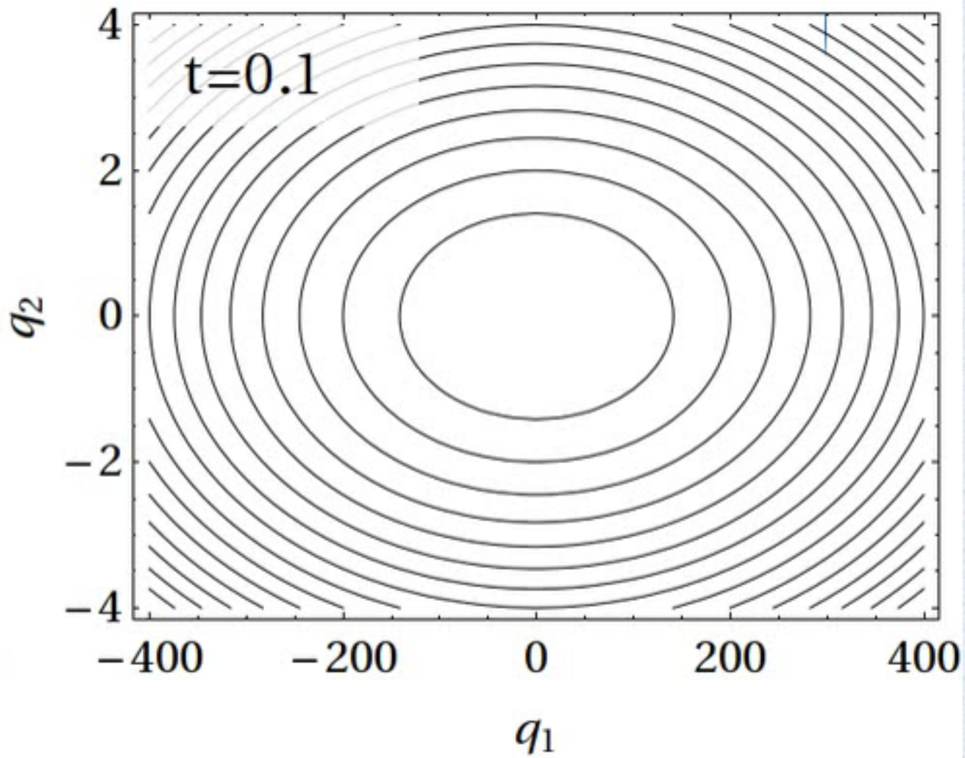


Optimal

Standard

Optimal sampling at work

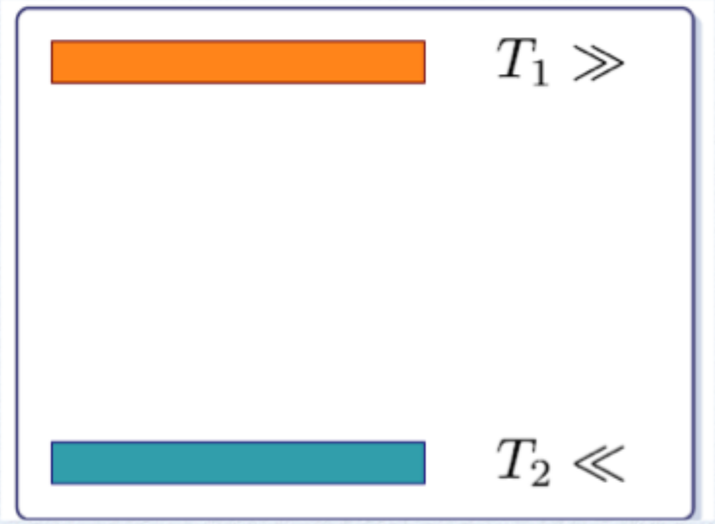




Standard

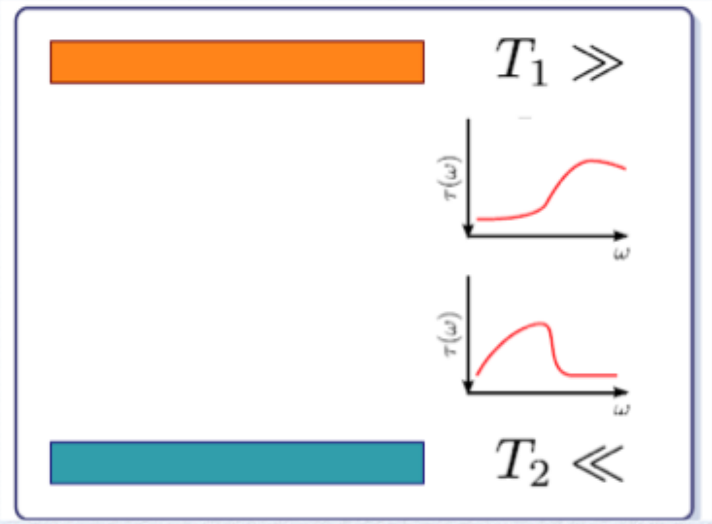
Optimal

#2: different strokes for different folks



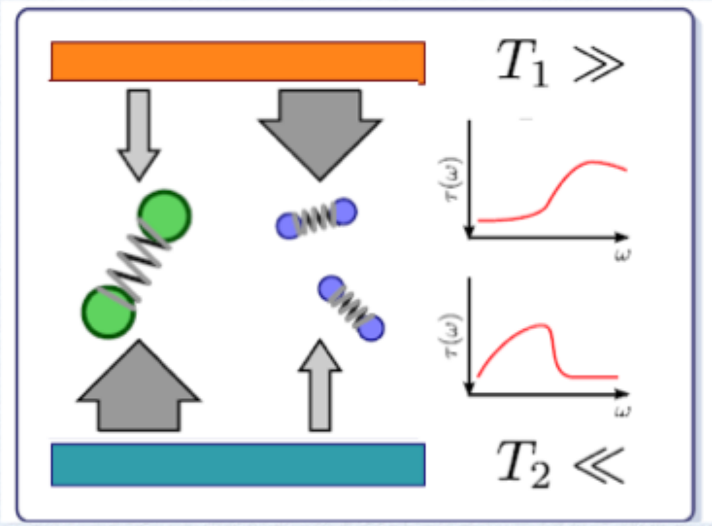
Two thermostats at different temperatures

#2: different strokes for different folks



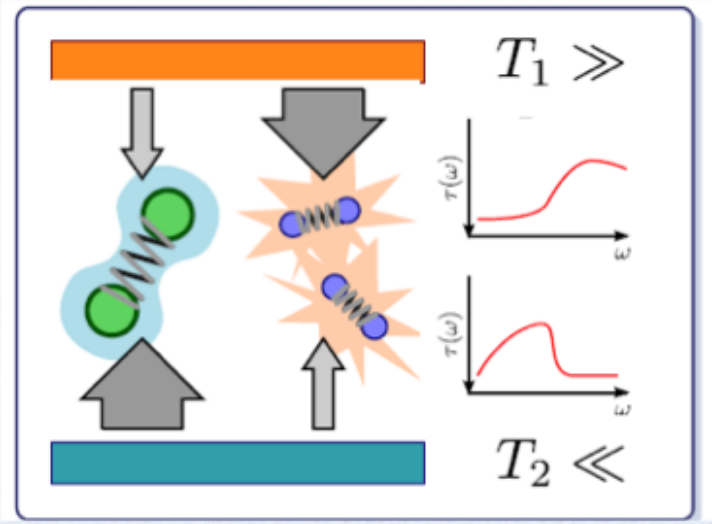
Impose different responses

#2: different strokes for different folks



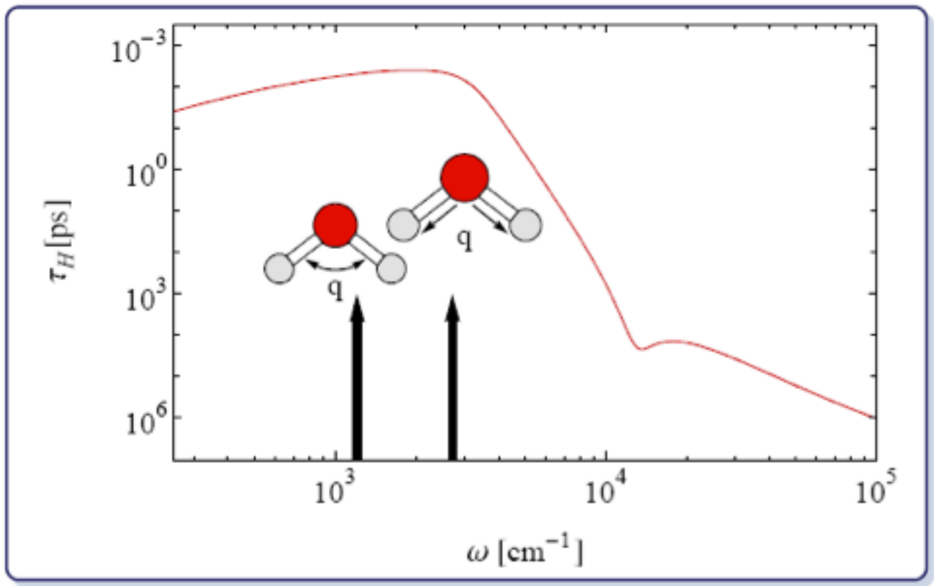
The thermostats will act differently on different modes

#2: different strokes for different folks

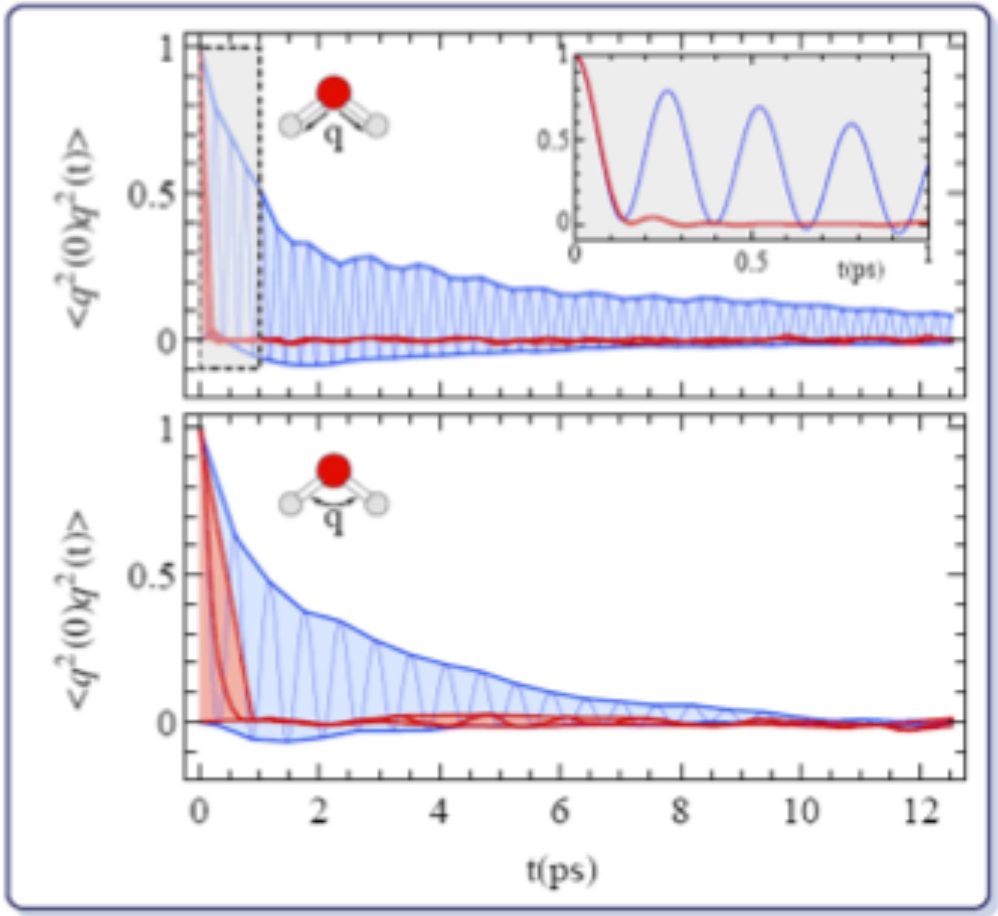


Note: one can impose a frequency dependent temperature
without having to calculate the second derivatives

Car-Parrinello



More efficient then Nose'-Hoover



#3: Quantum effects

Enforce a quantum distribution for momenta and positions for each oscillator

$$\left\langle \boldsymbol{P}^2 \right\rangle = \omega^2 \left\langle \boldsymbol{R}^2 \right\rangle = \hbar\omega \,\mathbf{coth}\left(\frac{\hbar\omega}{\boldsymbol{k}_B \boldsymbol{T}} \right)$$

Correct in the harmonic and classical limit
in between it interpolates

No need to know the harmonic spectrum!

Harmonic oscillator

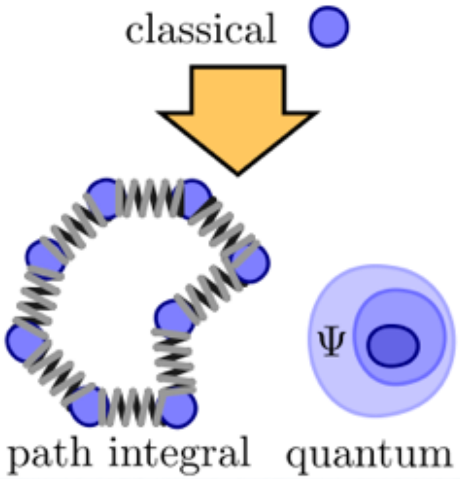
$$\rho(x) \propto \exp - \frac{1}{\frac{\hbar\omega}{2}\coth\beta\frac{\hbar\omega}{2}}\left(\frac{1}{2}m\omega^2x^2\right) = \exp - \beta^*(\omega)\left(\frac{1}{2}m\omega^2x^2\right)$$

The position (and momentum) distribution of a quantum harmonic oscillator is like that of a classical one at the temperature

$$\beta^*(\omega)^{-1} = \frac{\hbar\omega}{2}\coth\frac{\beta\hbar\omega}{2}$$

Why bother?

$$Z = \mathrm{Tr}\left[e^{-\frac{\beta}{P}\mathbf{H}}\right]^P = \int \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_P \langle \mathbf{r}_1 | e^{-\frac{\beta}{P}\mathbf{H}} | \mathbf{r}_2 \rangle \ldots \langle \mathbf{r}_P | e^{-\frac{\beta}{P}\mathbf{H}} | \mathbf{r}_1 \rangle$$

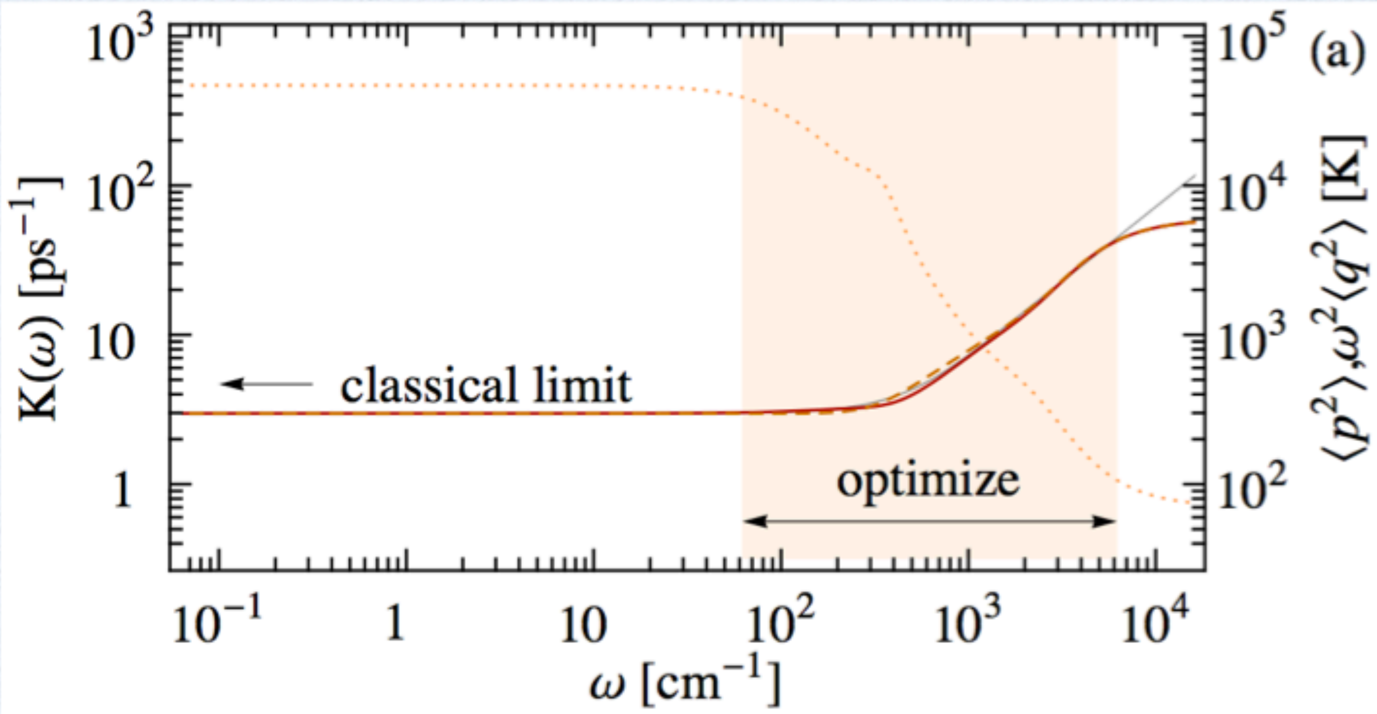


$$\langle \mathbf{r}_1 | e^{-\frac{\beta}{P}\mathbf{H}} | \mathbf{r}_2 \rangle \approx$$

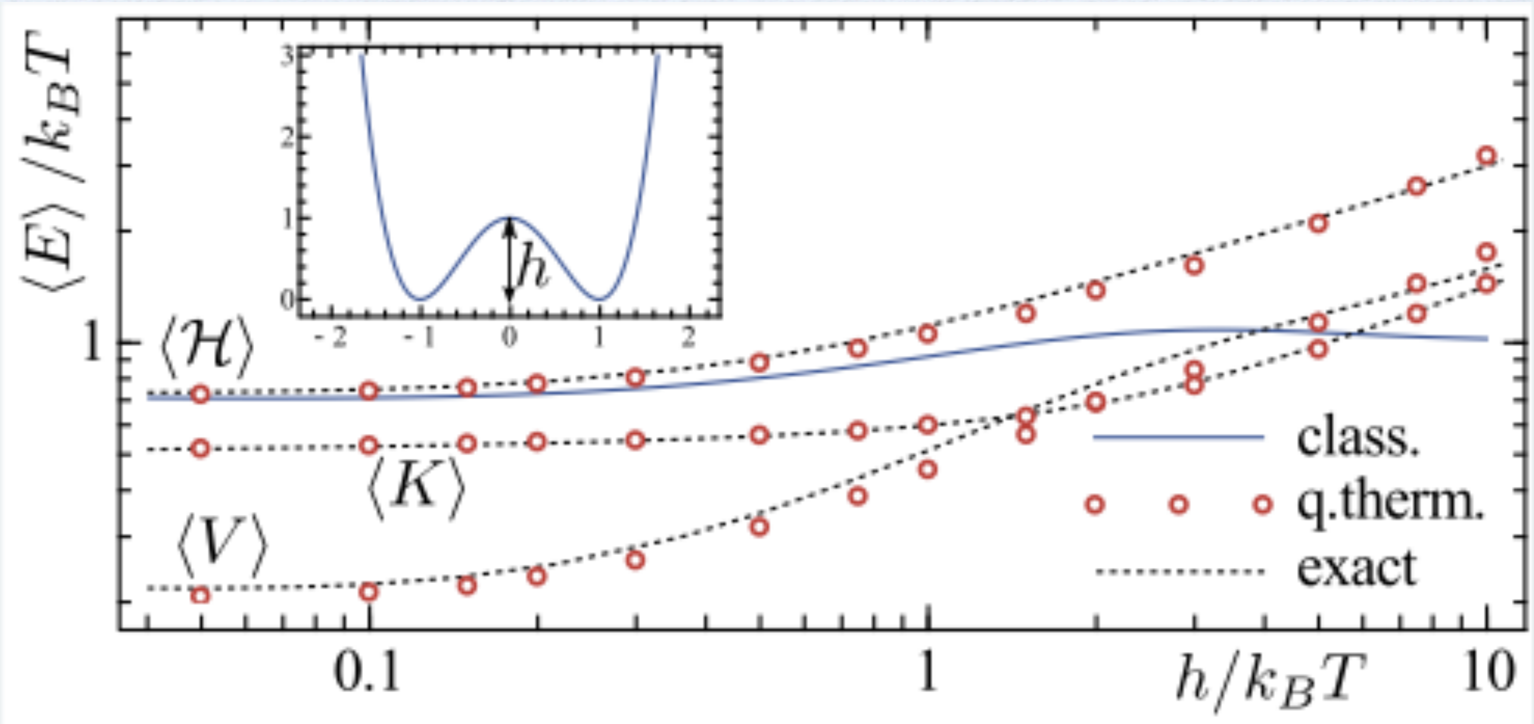
$$\exp\left[-\frac{\beta}{P}\left(\frac{V(\mathbf{r}_1)+V(\mathbf{r}_2)}{2} + \frac{1}{2} m \omega_P^2 (\mathbf{r}_1 - \mathbf{r}_2)^2\right)\right]$$

$$\omega_P = P/\beta\hbar$$

Some popular thermostats

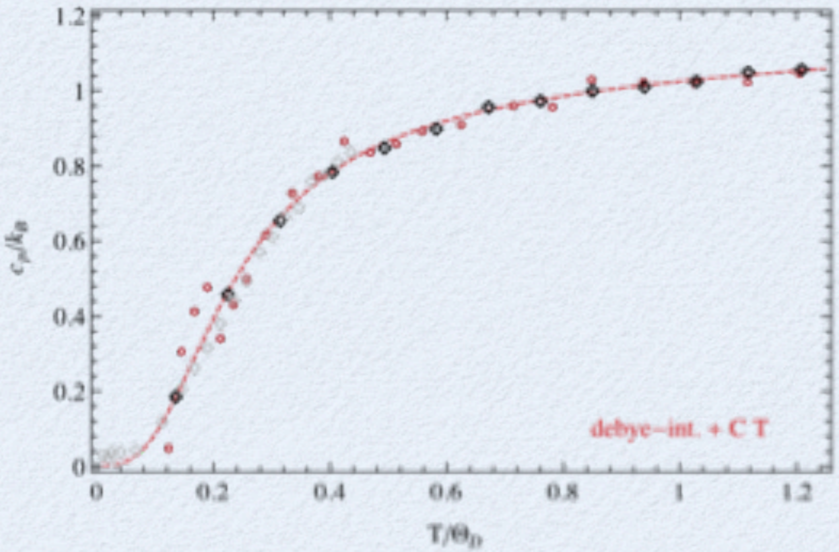


A double well

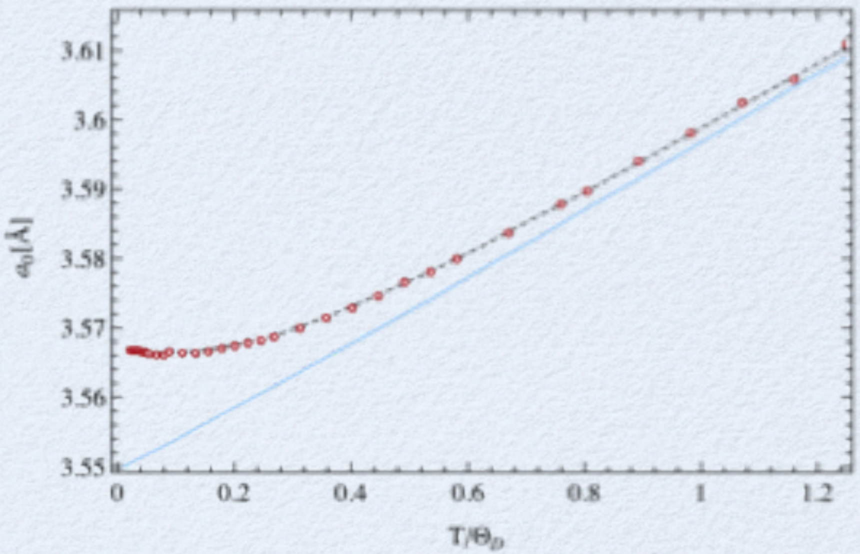


A quantum solid: diamond

Specific heat

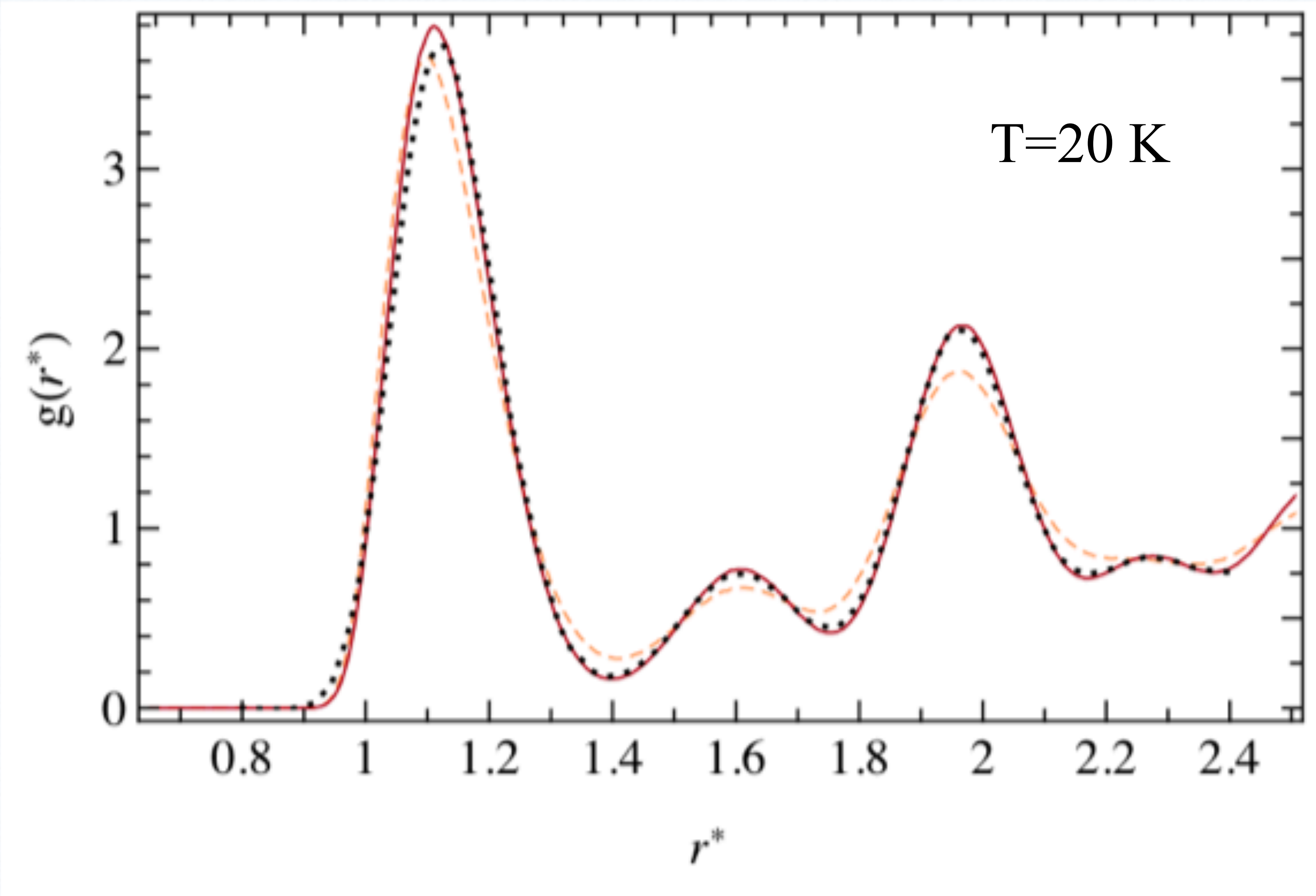


Lattice constant

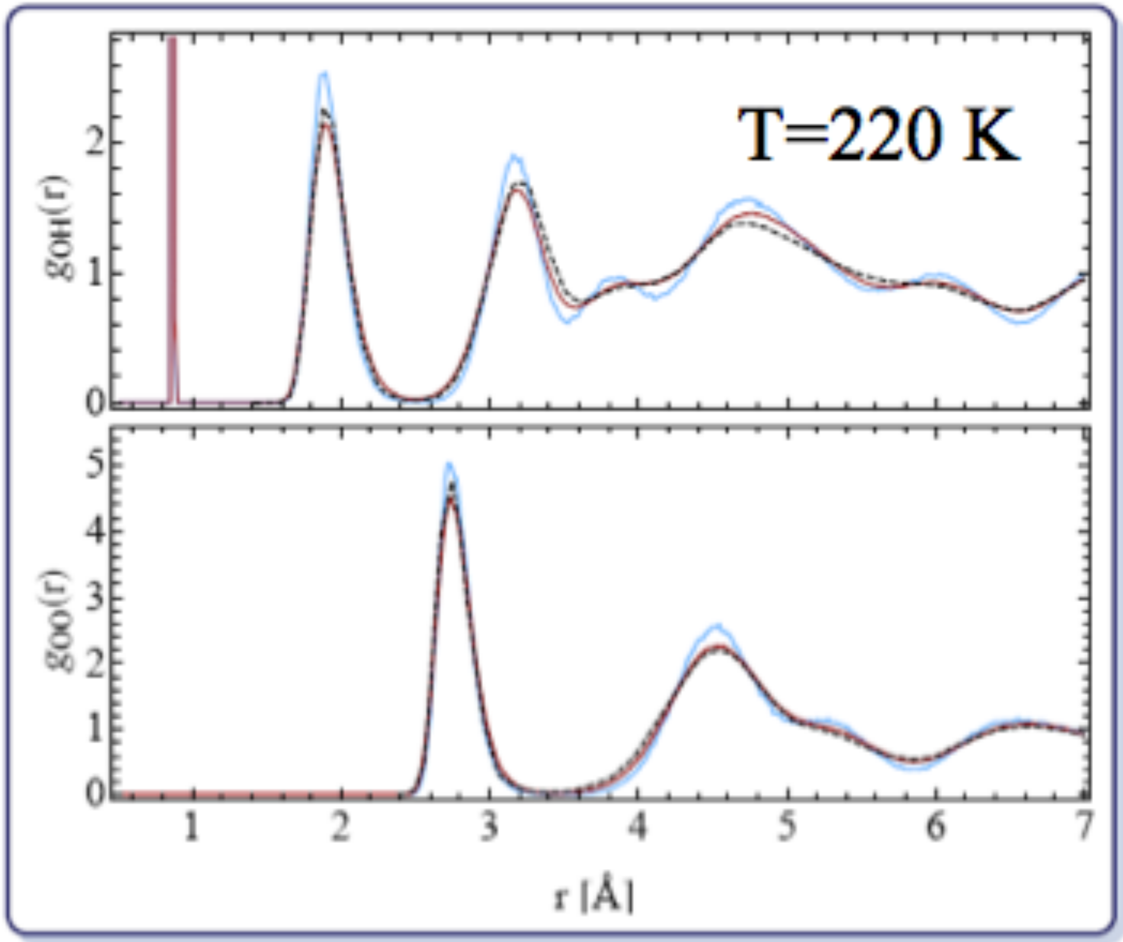


Path integral Quantum thermostat Classical

Neon



Ice (TIP4P)

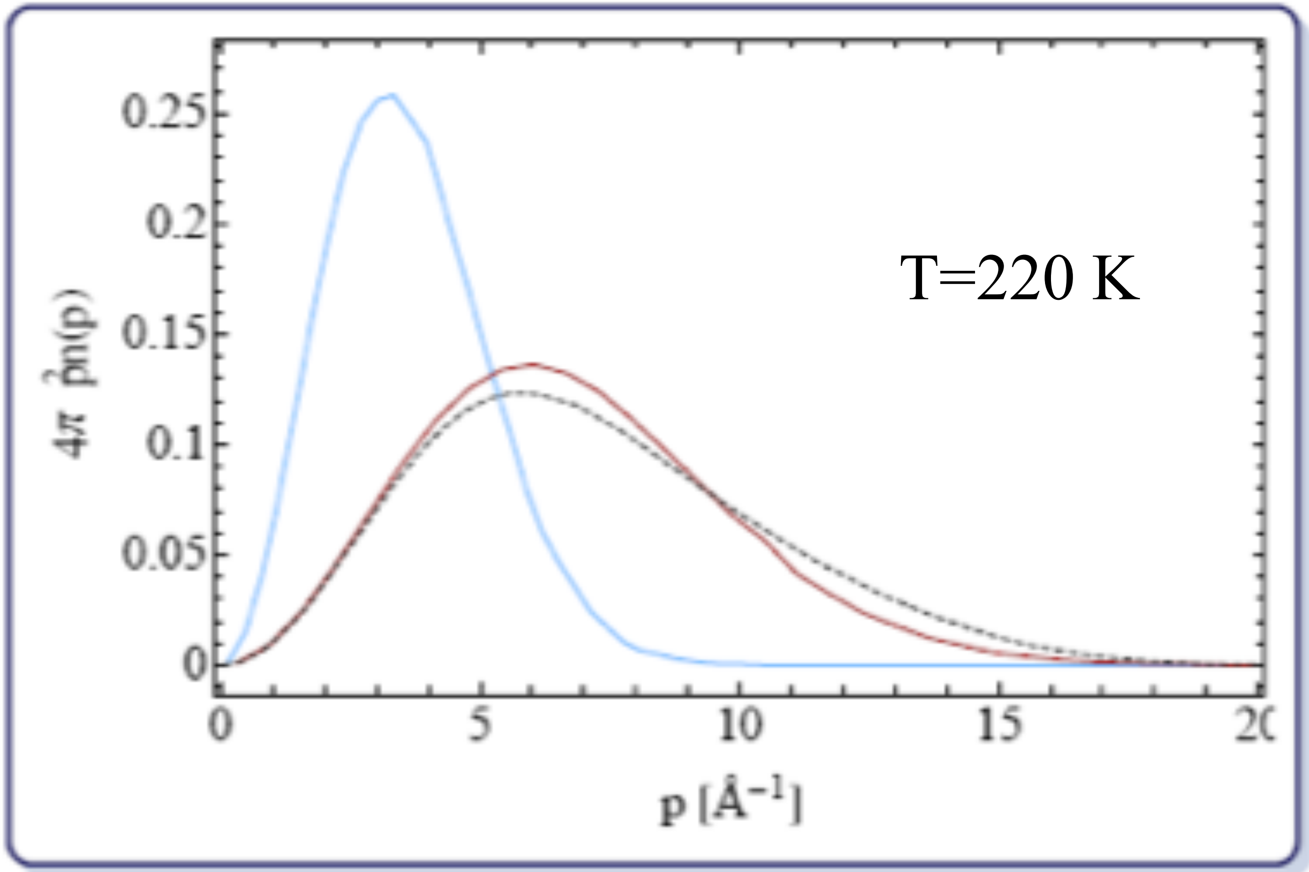


Path integral

Quantum thermostat

Classical

Ice momentum distribution



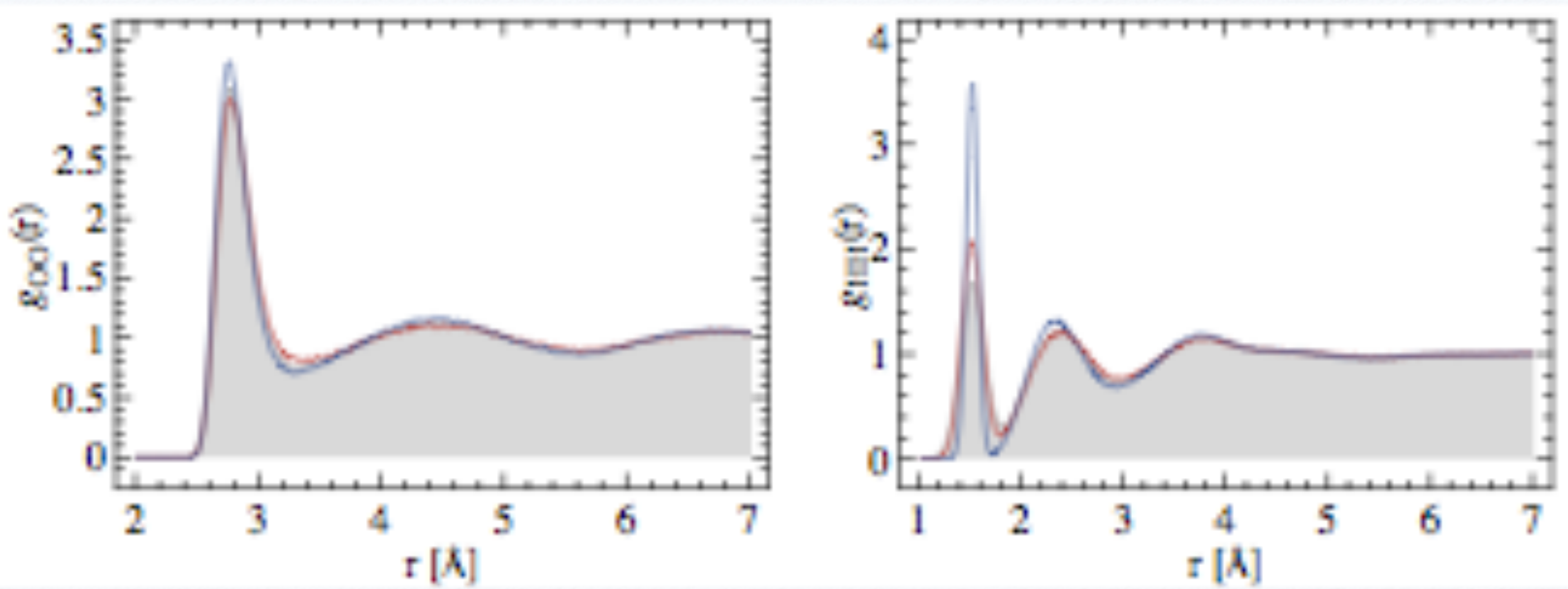
Experiment

Quantum thermostat

Classical

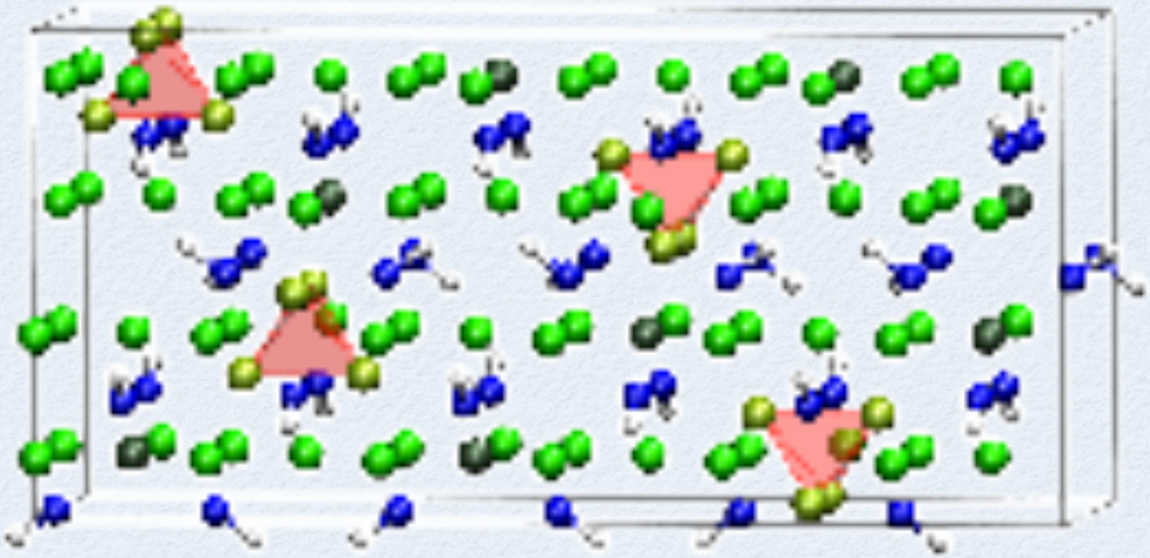
G. Reiter et al., Braz. J. Phys. **34**, 142 (2004)

Even water

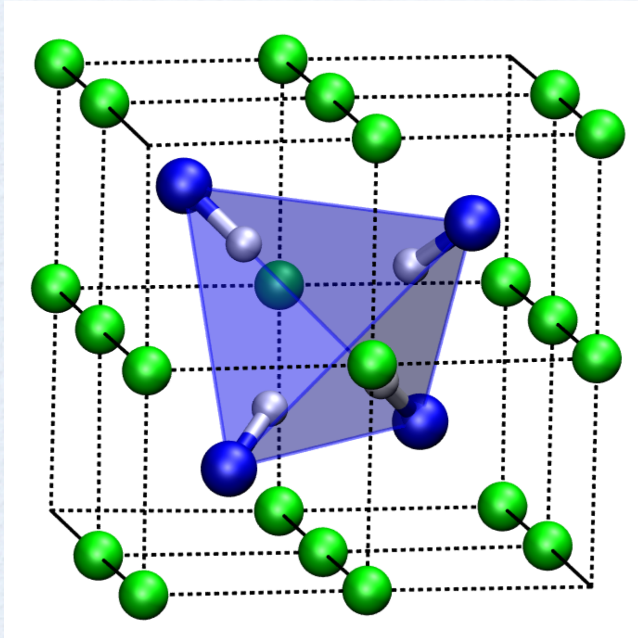


An interesting material: Li_2NH

Belongs to a class of materials being investigated for hydrogen storage



A complex antifluorite structure (Fm$\underline{3}$m) not yet fully resolved



Tetrahedral arrangement of the NH groups around a Li vacancy

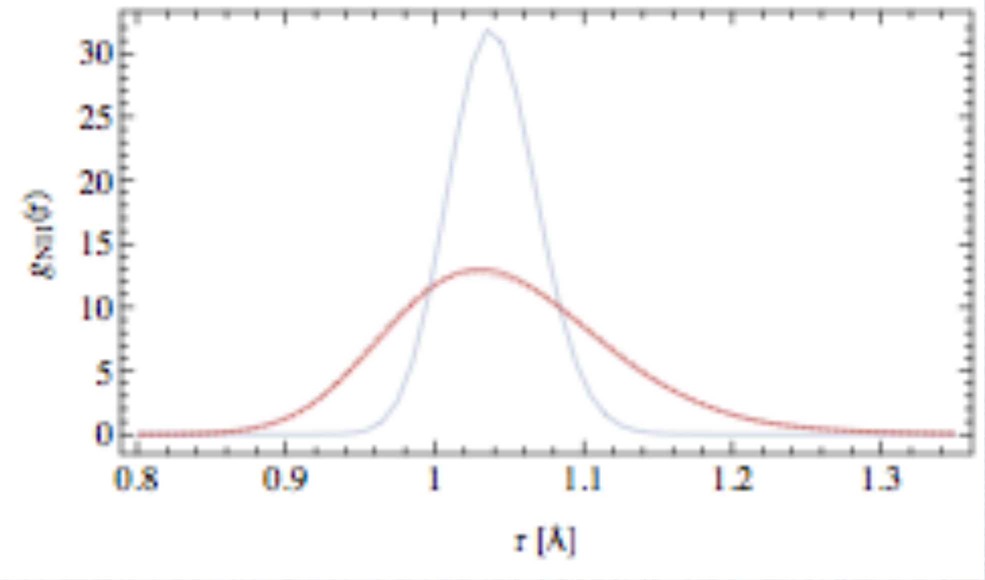
Ab-initio quantum simulation

128 atoms supercell

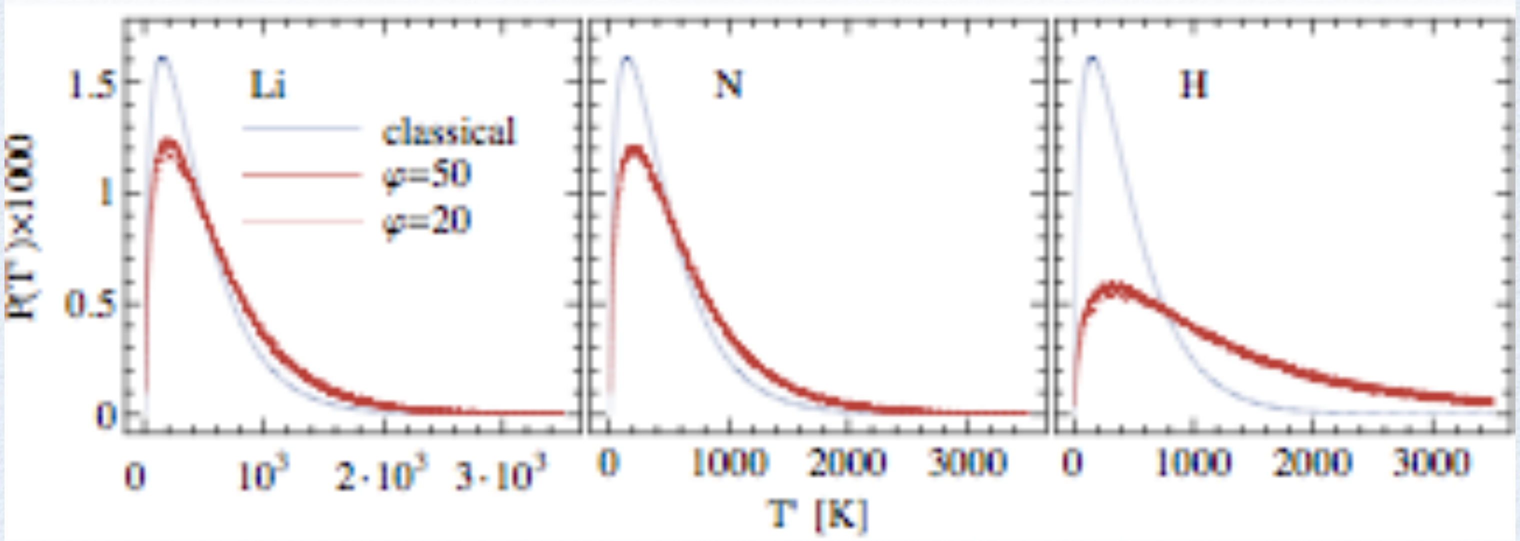
PDE exchange and correlation

Quantum thermostats

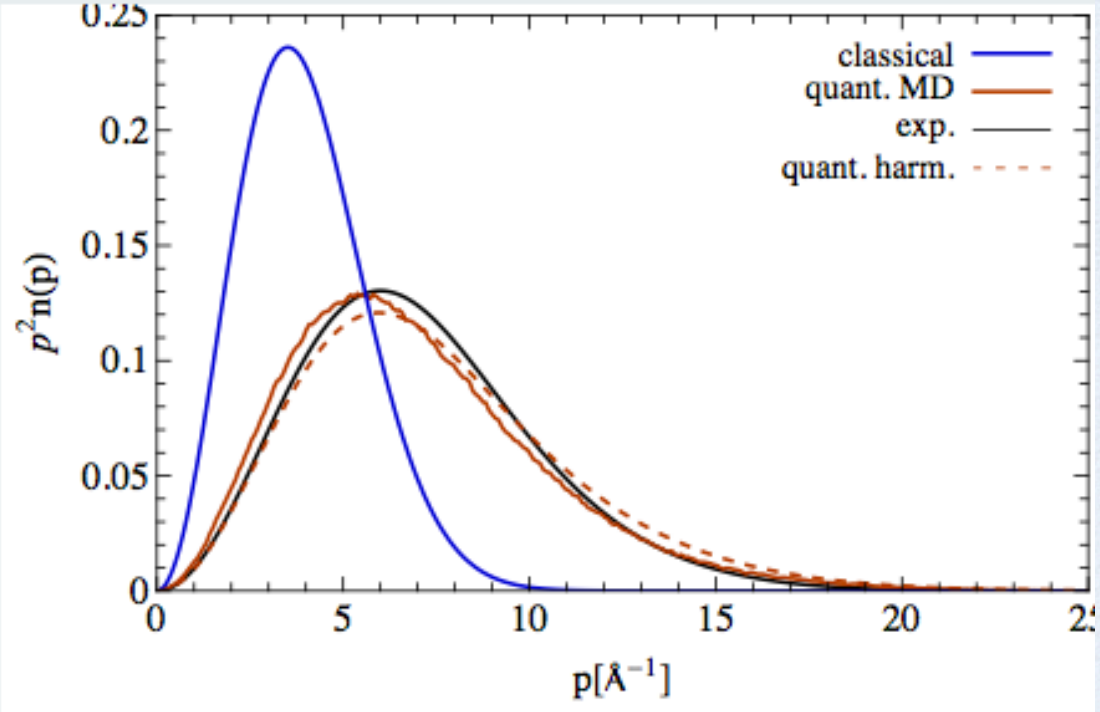
T=300 K



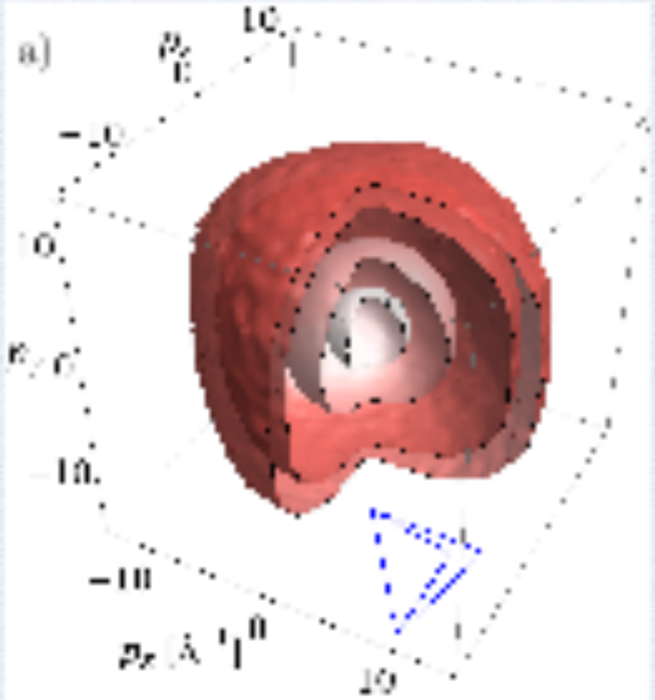
Effective temperature distributions



Momentum distribution: Theory and Experiment

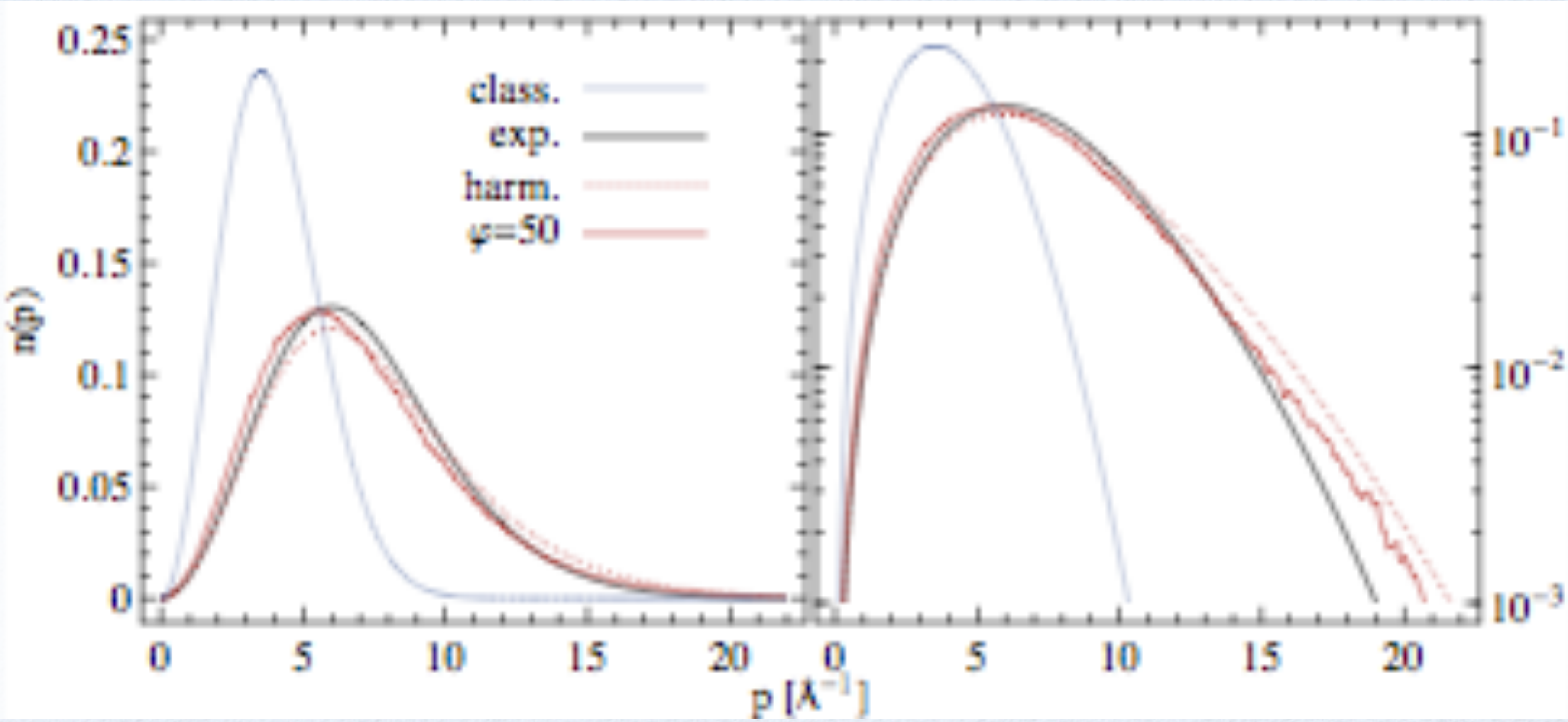


Spherical average

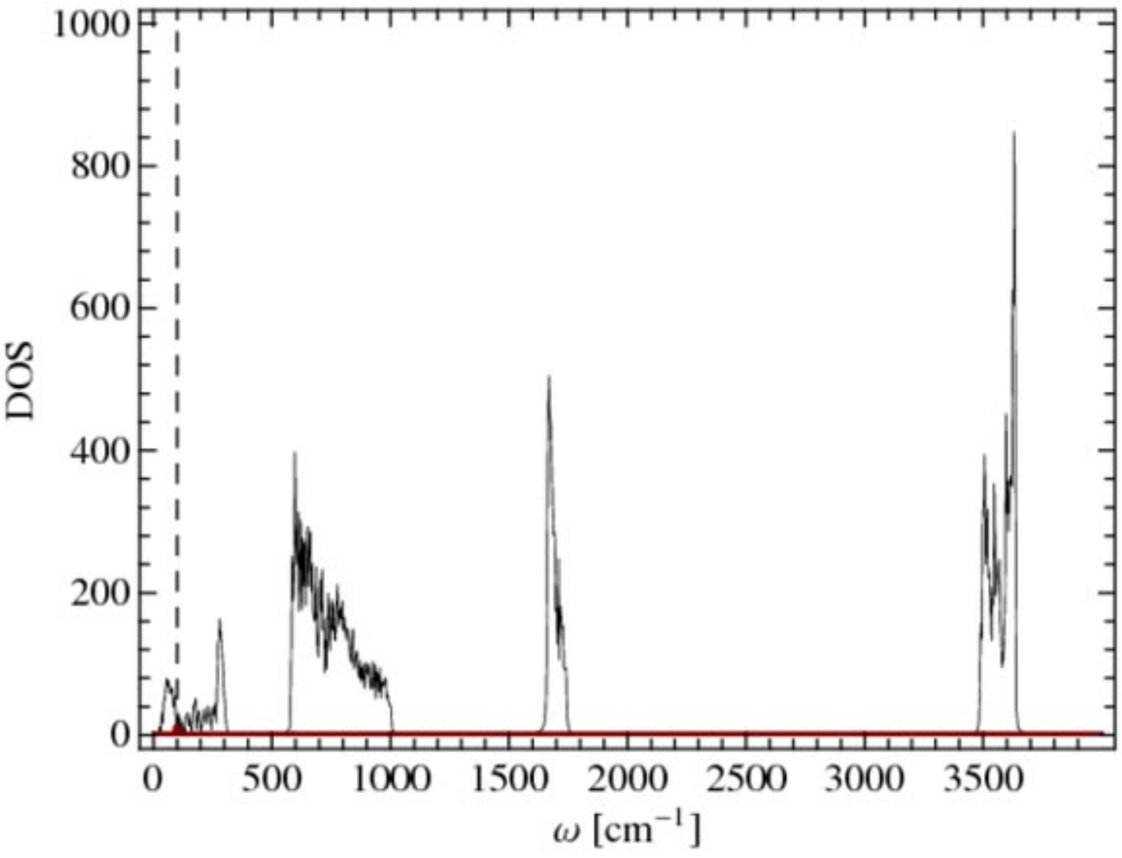


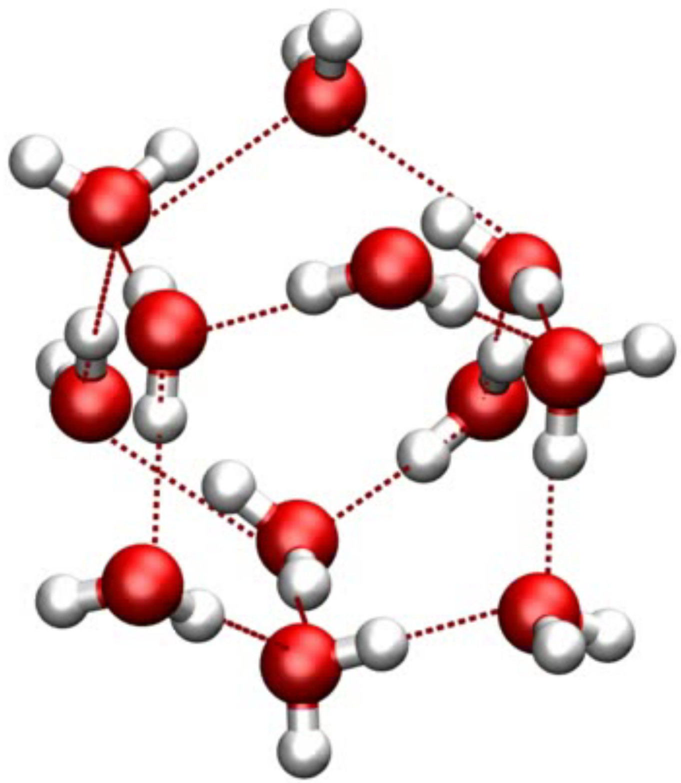
Angularly resolved

Spherical average



#4 δ-like excitation





Exciting selectively the vibrational modes of ice

#5 The best has yet to come

Collaborators

For the thermostats

G. Bussi, SISSA (Trieste)

M. Ceriotti, ETH (Lugano)

D. Donadio, MPI (Mainz)

For Li_2NH

Theory

M. Ceriotti, ETH (Lugano)
G. Miceli, Bicocca (Milano)
M. Bernasconi, Bicocca (Milano)

Experiment

A. Pietropaolo, Tor Vergata (Roma)
D. Colognesi, Bicocca (Milano)
M. Catti, Bicocca (Milano)
A. C. Nale, Bicocca (Milano

The end

Thank you for your attention