



# Entropy evaluation in atomistic simulations

Pavel Levashov

Joint Institute for High Temperatures RAS  
Moscow, Russia

**Workshop «Ab initio simulations of correlated fermions»  
devoted to the 60<sup>th</sup> anniversary of Prof. Michael Bonitz  
July 8-9, 2020**

# Classical MD (MC) simulations

- Classical interparticle potential  $\phi(r)$
- Interaction energy and pressure can be easily calculated:

$$E = E_{id} + \sum_{1 \leq i < j \leq N} \phi(r_{ij})$$

$$P = P_{id} - \frac{1}{3V} \left\langle \sum_{1 \leq i < j \leq N} r_{ij} \frac{d\phi(r)}{dr} \right\rangle$$

Entropy can not be calculated directly, one should apply special approaches.  
This is the problem for quantum computations.

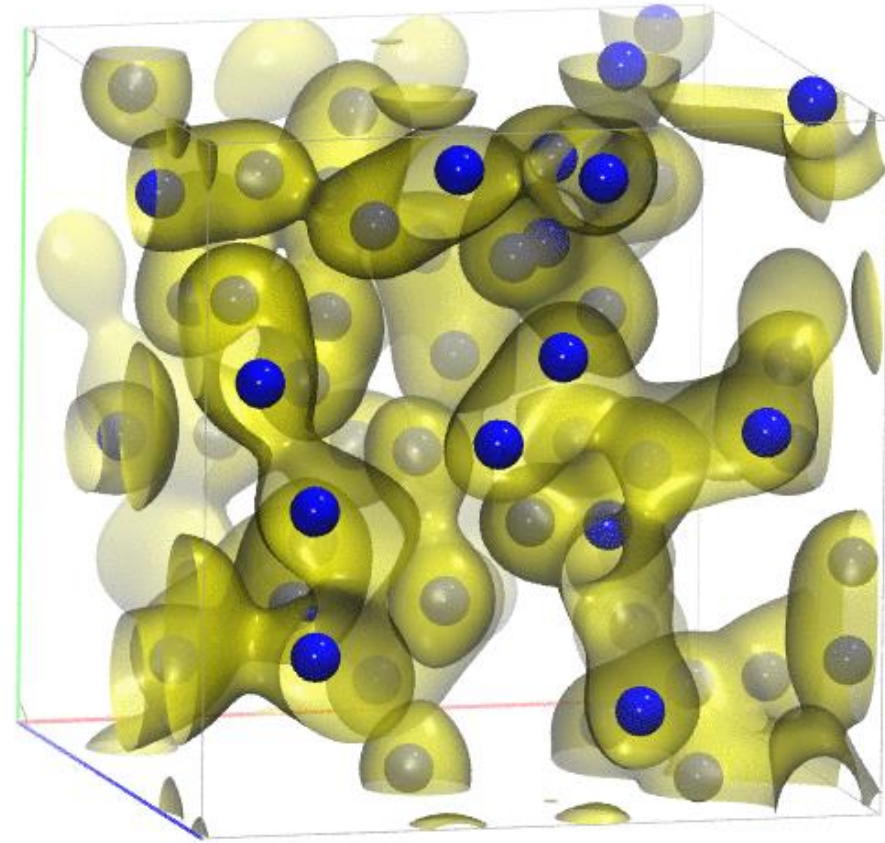
# Quantum molecular dynamics (QMD) simulation



- Adiabatic approximation
- Electrons are quantum and described by the density functional theory (DFT)
- Ions are classical and move under the forces from the electrons, described by Newton's equations

## Parameters of QMD calculations:

- GGA with PBE corrections for exchange-correlation functional
- PAW potentials with 6 valence electrons
- $\Gamma$ -point, Baldereschi, grids up to 4x4x4 were used to obtain convergence
- QMD simulations were performed for 54-128 atoms (W), NVT ensemble



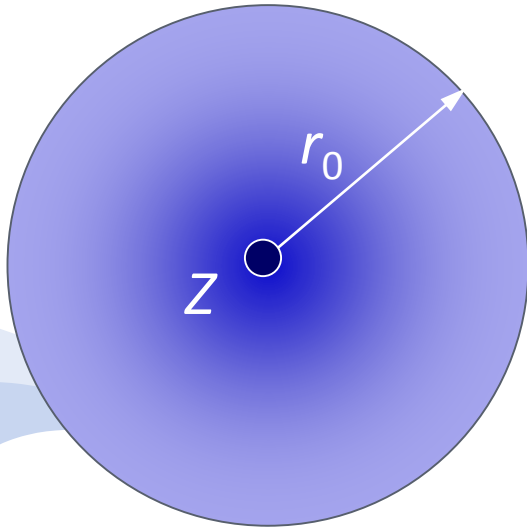
# Motivation and goal

**Paradoxical situation:** Entropy of a quantum system of interacting electrons is easier to calculate than entropy of a classical system!

**Motivation:** fast method of entropy evaluation of a classical system from a single MD (MC) run

**Goal:** Non-empirical calculation of phase diagrams of elements and compounds (melting and evaporation curves)

# Entropy in average atom models



Density:  $\frac{4}{3}\rho r_0^3 n = 1$

$T$  enters into Fermi-Dirac distribution

- Explicit expression for a thermodynamic potential (Helmholtz free energy or grand canonical)
  - Finite-temperature Thomas-Fermi (semiclassical)
  - Hartree-Fock-Slater (one-electron wave functions, occupancies,...)

$$S = - \left( \frac{\partial F}{\partial T} \right)_T ; S = - \left( \frac{\partial \Omega}{\partial T} \right)_V$$

- In some average atom model the expression for  $F$  or  $\Omega$  is inconsistent; in this case entropy is a key value ( $f_i$  – occupancies):

$$S = - \left[ \sum_i f_i \ln f_i + \sum_i (1 - f_i) \ln(1 - f_i) \right]$$

$P$  and  $E$  can be found through entropy

# Density functional theory: entropy

«First-principle» density functional theory is based on the Levy-Lieb formulation (1983). The theory is based on two assumptions (Kohn-Sham ansatz, [Kohn and Sham, 1965]):

- A system of interacting particles is replaced by a system of non-interacting particles with some effective potential. It is assumed, that the density of the ground state for both systems is the same.
- The Hamiltonian of a system of non-interacting particles contains a common operator of kinetic energy and a local potential, acting on the electron with spin at a point  $\mathbf{r}$ . The locality greatly simplifies calculations but is not necessary.
- There is a generalization for finite temperatures

Kohn-Sham functional:

$$E_{\text{KS}}[n] = \underbrace{T_s[n]}_{\text{non-inter. part.}} + \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) d\mathbf{r} + E_{\text{Hartree}}[n] + \underbrace{E_{xc}[n]}_{\text{ex.-corr. functional}}$$

$$E_0 = \min_n \min_{\psi \rightarrow n} \langle \psi | \hat{H} | \psi \rangle$$

At  $T > 0$  free energy functional is considered:  $F[n] = E_{\text{KS}}[n] - TS[n]$

# Density functional theory: entropy

Kohn-Sham equations: one-particle equations with a local potential:

$$\left( -\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{xc}(\mathbf{r}) - \varepsilon_i \right) \psi_i(\mathbf{r}) = 0$$

From the solution we obtain occupancies  $f_i$  and wave functions  $\psi_i(\mathbf{r})$ ,

$$n(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2$$

**Entropy** is calculated through one-particle occupancies:

$$S = - \left[ \sum_i f_i \ln f_i + \sum_i (1 - f_i) \ln(1 - f_i) \right]$$

**PIMC: currently no acceptable way of entropy estimation**



# Classical systems: crystals

For a crystal in the quasiharmonic approximation:

$$\ln Z = \int_0^{\infty} \ln q(\nu) F(\nu) d\nu,$$

harmonic oscillator

vibrational density of state

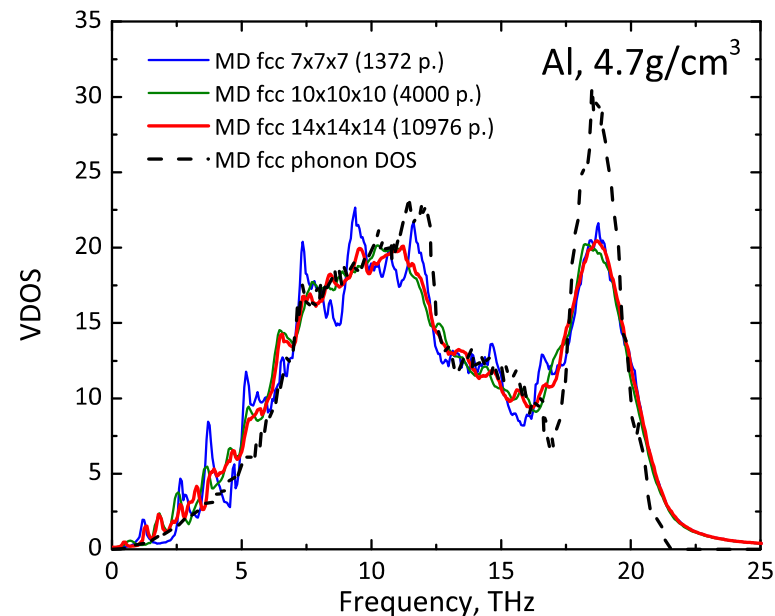
Entropy:

$$S = T \frac{\partial \ln Z}{\partial T} + \ln Z = \int_0^{\infty} W_S(\nu) F(\nu) d\nu$$

Weighting function:

$$W_S = \frac{\beta h \nu}{\exp(h\nu) - 1} - \ln[1 - \exp(-\beta h \nu)]$$

Typical vibrational DOS



# Widom's test particle method (1963)

- Applicable only for unordered systems
- Additional particle is inserted into the system and interaction energy of this particle with other particles is calculated
- Allows to calculate chemical potential of species  $i$ :

$$\mu_i = T \ln(\rho_i \lambda^3) - T \ln \left( \left\langle \exp \left( -\frac{\psi_i}{T} \right) \right\rangle \right) = \mu_{id} + \mu_{ex}$$

Here  $\psi_i$  – the interaction energy of an inserted particle with other particles

The method allows to restore thermodynamic potential and entropy

Problems:

- time-consuming;
- bad convergence for dense systems

# Thermodynamic integration

The method calculates the difference in free energy between two given states with potential energies  $U_A$  and  $U_B$ :

$$U(\lambda) = U_A + \lambda(U_B - U_A)$$

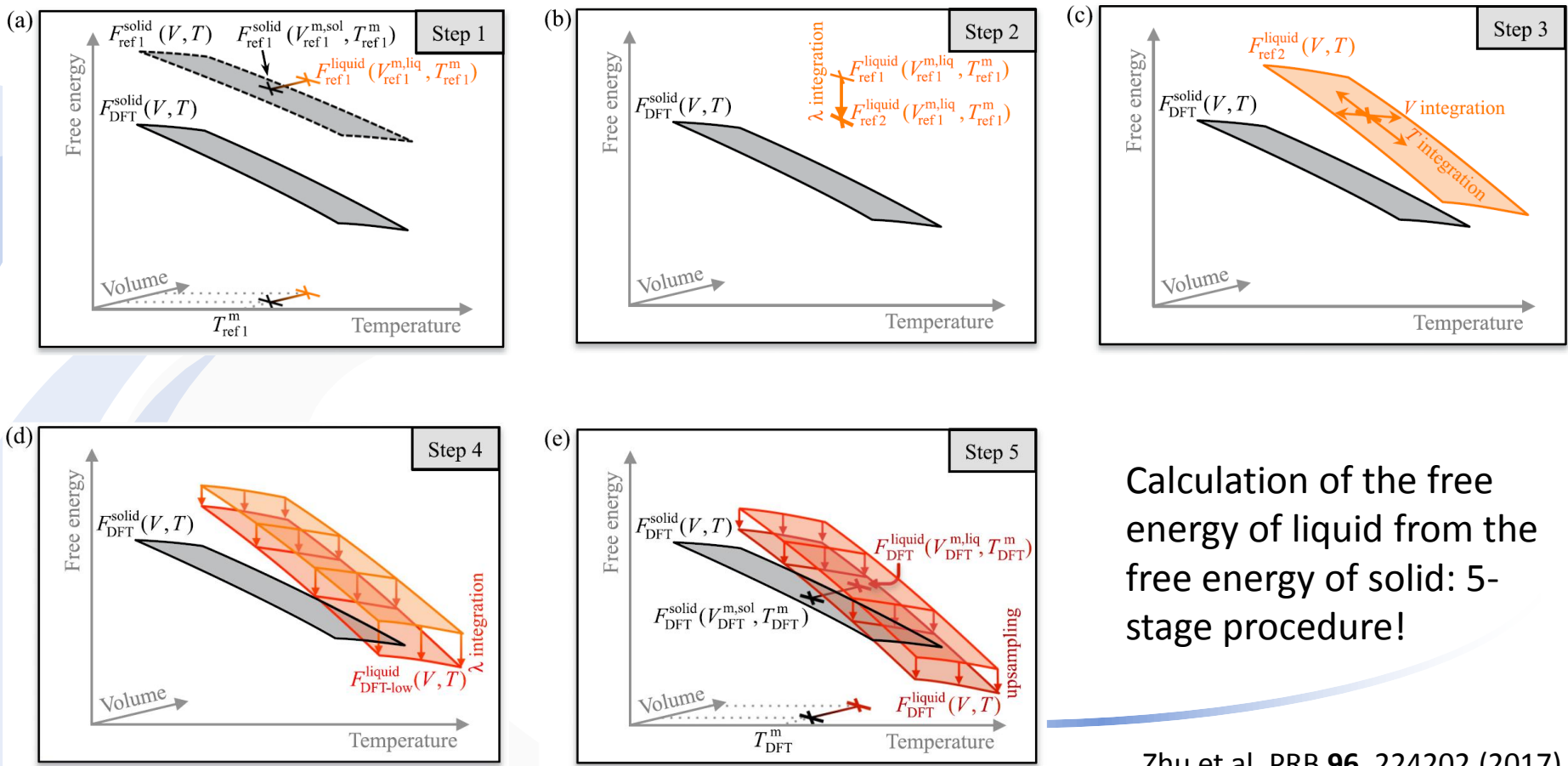
Free energy difference is calculated by integrating over ensemble-averaged enthalpy changes along the path between the states A and B:

$$\Delta F(A \rightarrow B) = \int_0^1 \left\langle \frac{\partial U_\lambda}{\partial \lambda} \right\rangle d\lambda$$

The method is exact but requires multiple simulations at each  $\lambda$   
Time-consuming for quantum computations  
Convergence should be checked

# Example: simulation of melting using thermodynamic integration

**Copper**, one point at the melting curve  
 DFT for the solid phase, QMD for the liquid  
 Two fitted EAM potentials (ref1 for solid, ref2 for liquid)



Calculation of the free energy of liquid from the free energy of solid: 5-stage procedure!

# Simulation of melting: Lindemann criterion

- Only solid phase is considered (DFT + phonons)
- Lindemann melting criterion:

$$\sqrt{\langle u^2(T_m) \rangle} = Ld_{nn}$$

$L$  – Lindemann parameter,

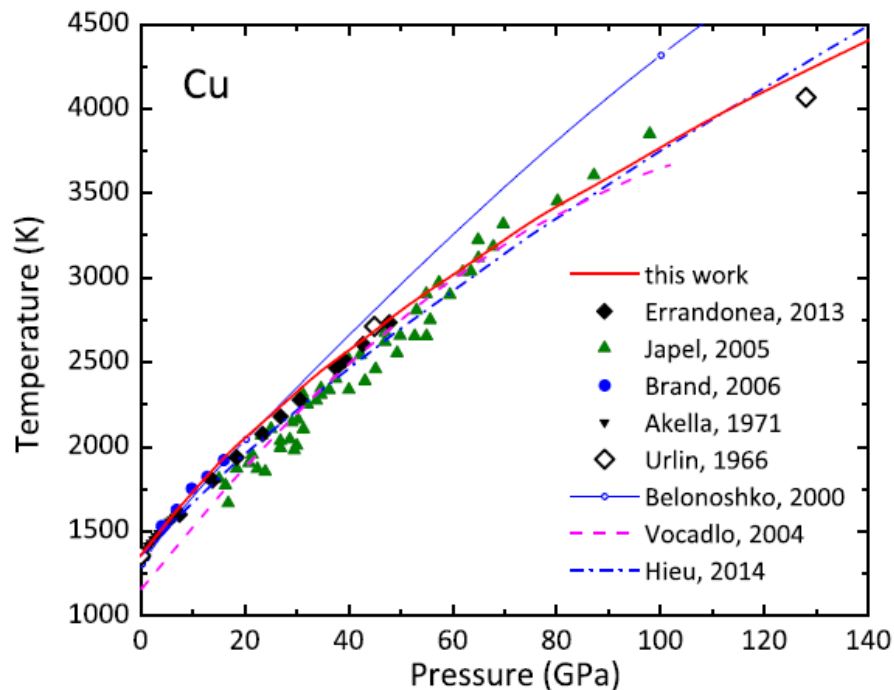
$d_{nn}$  – average interatomic distance

$u^2(T)$  – from phonon DOS  $g(\omega)$ :

$$\langle u^2(T) \rangle = \frac{\hbar}{2M_a} \int_0^\infty \frac{d\omega}{\omega} g(\omega) \coth \frac{\hbar\omega}{2T}$$

Reference melting temperature is required to determine  $L$

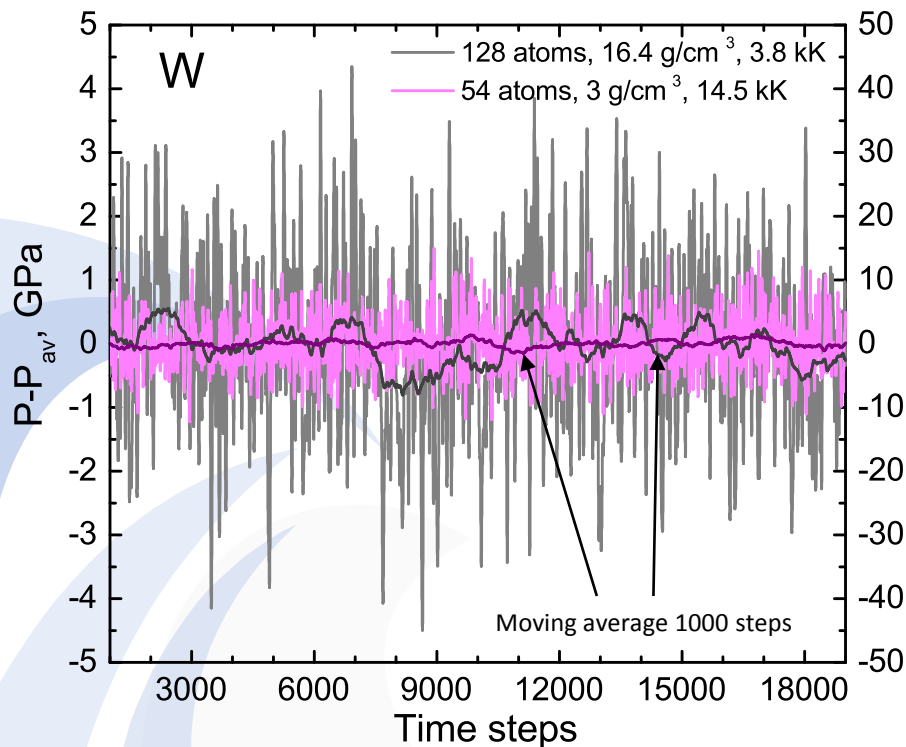
Melting curve of copper



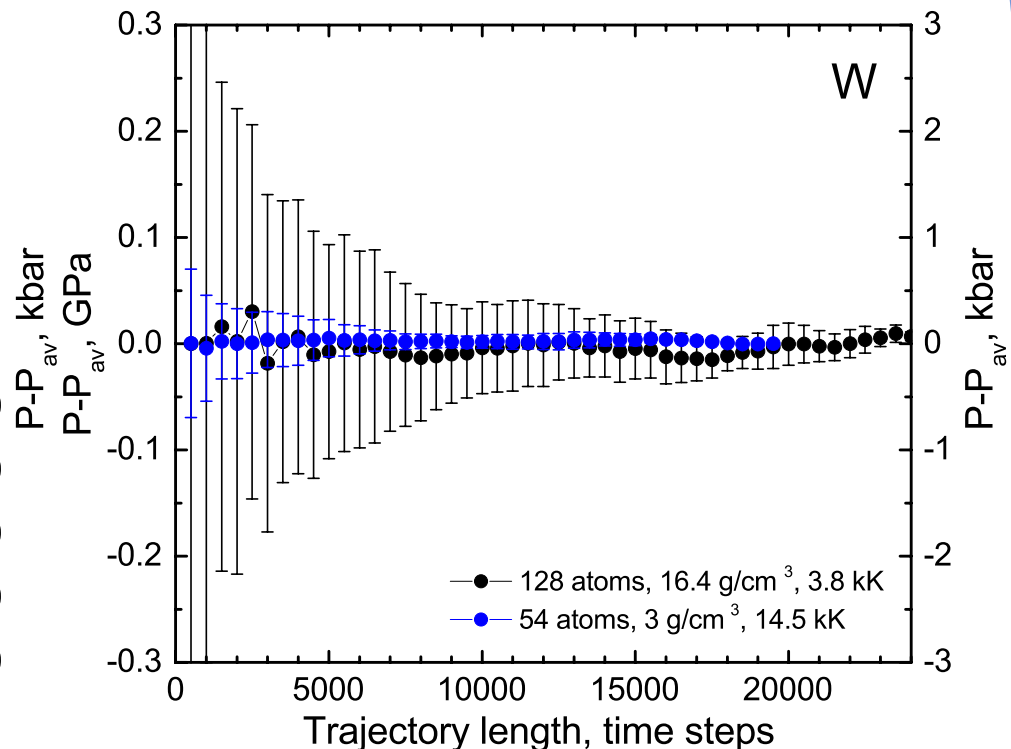
Method is inapplicable for compounds

# Estimation of evaporation curve

## Evolution of pressure in QMD



## Statistical error of average pressure



- We used **128 atoms** for  $\rho > 7 \text{ g/cm}^3$  and **54 atoms** for  $\rho < 7 \text{ g/cm}^3$
- Trajectory length was chosen to provide the statistical error for pressure less than 1 kbar (5000-10000 steps)

Monte-Carlo procedure (2 000+ tries):

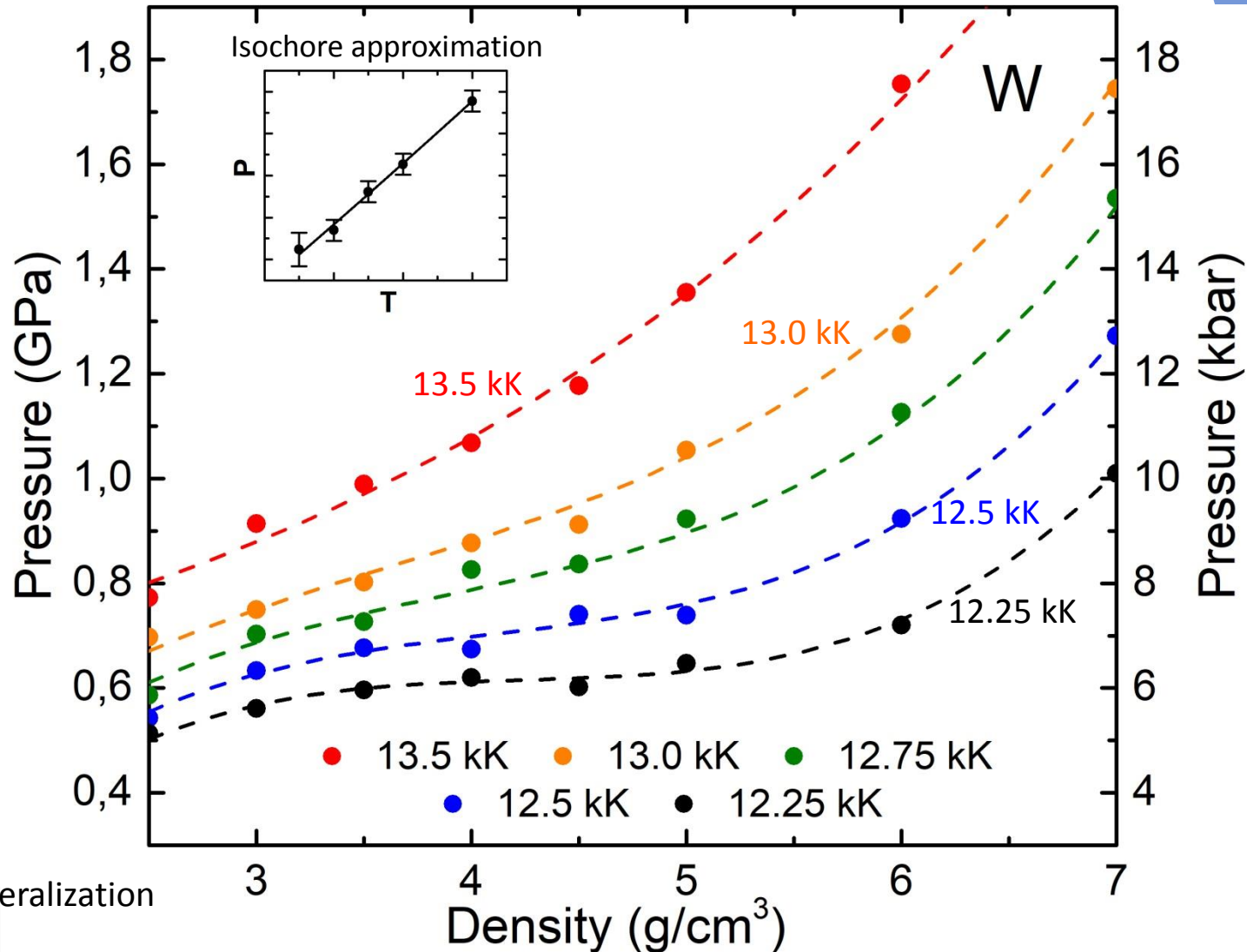
- approximation of isochores taking into account statistical error
- Calculations of isotherms, search for the inflection point:

$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0,$$

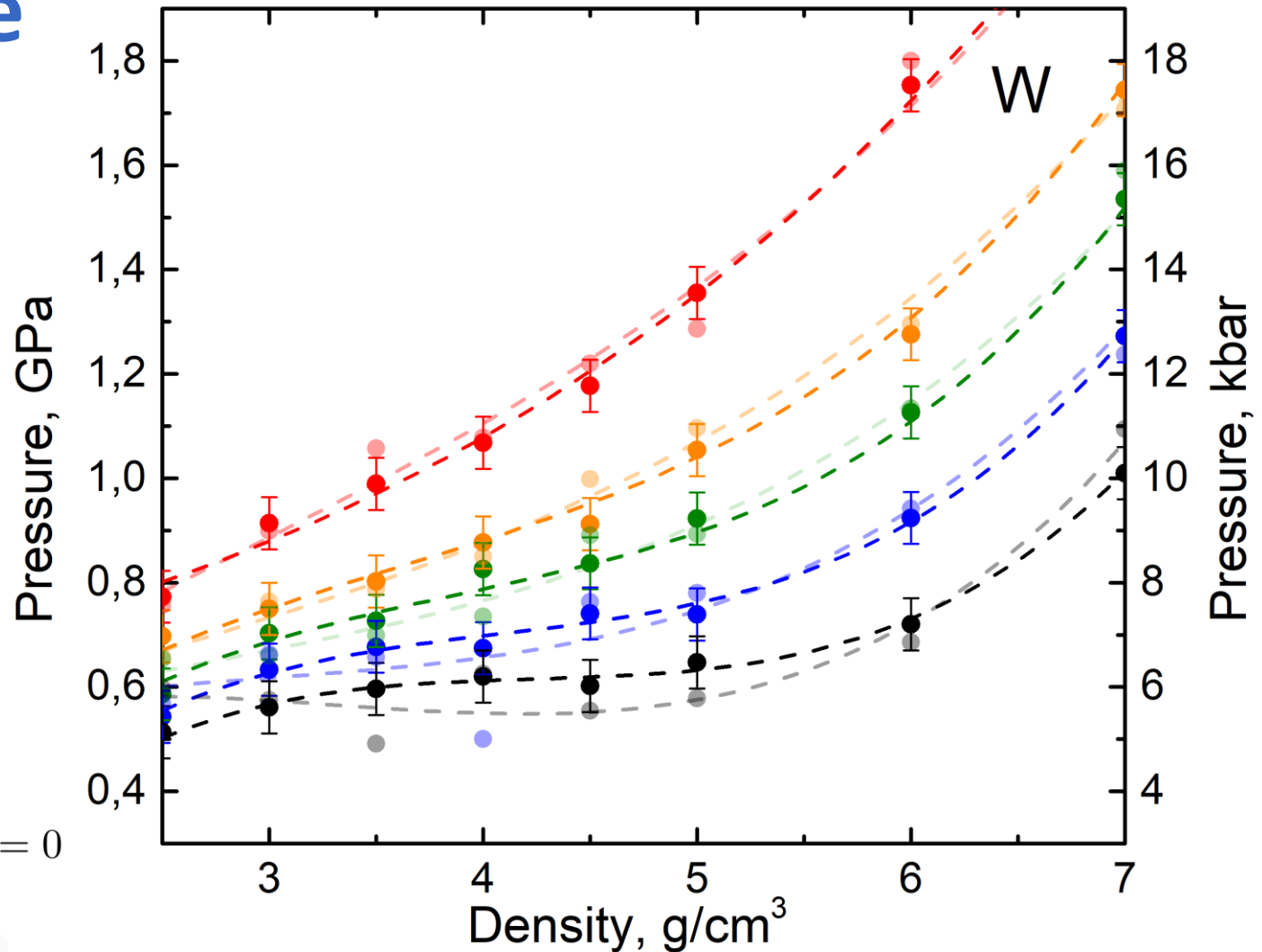
$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$$

The procedure is the generalization of the method from

Miljacic L. et al. *Calphad* **51**, 133 (2015)



# Demonstration of Monte-Carlo procedure



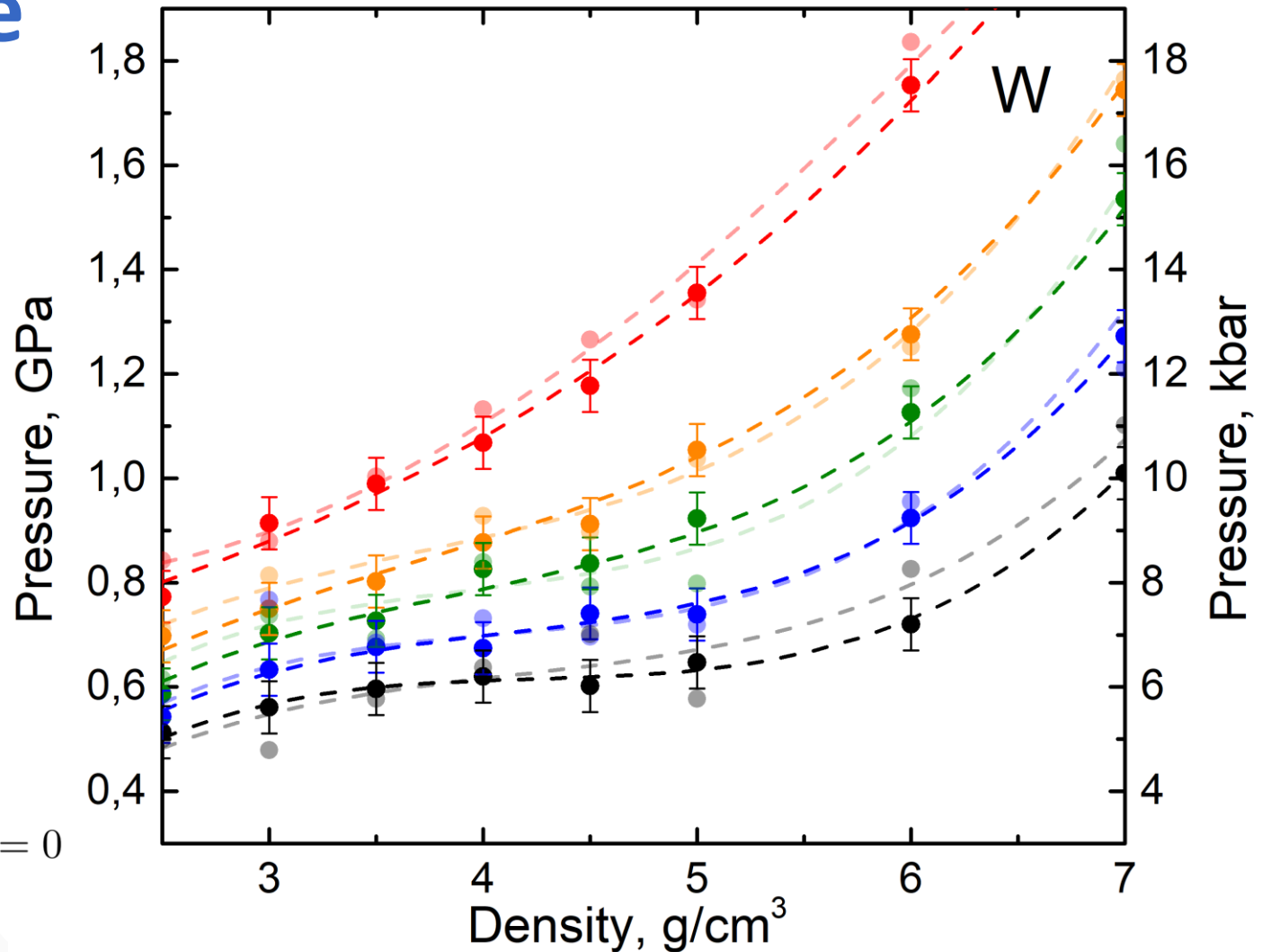
$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$$

Monte-Carlo procedure (2 000+ tries):

- Approximation of isochores taking into account statistical error
- Calculations of isotherms, search for inflection point



## procedure

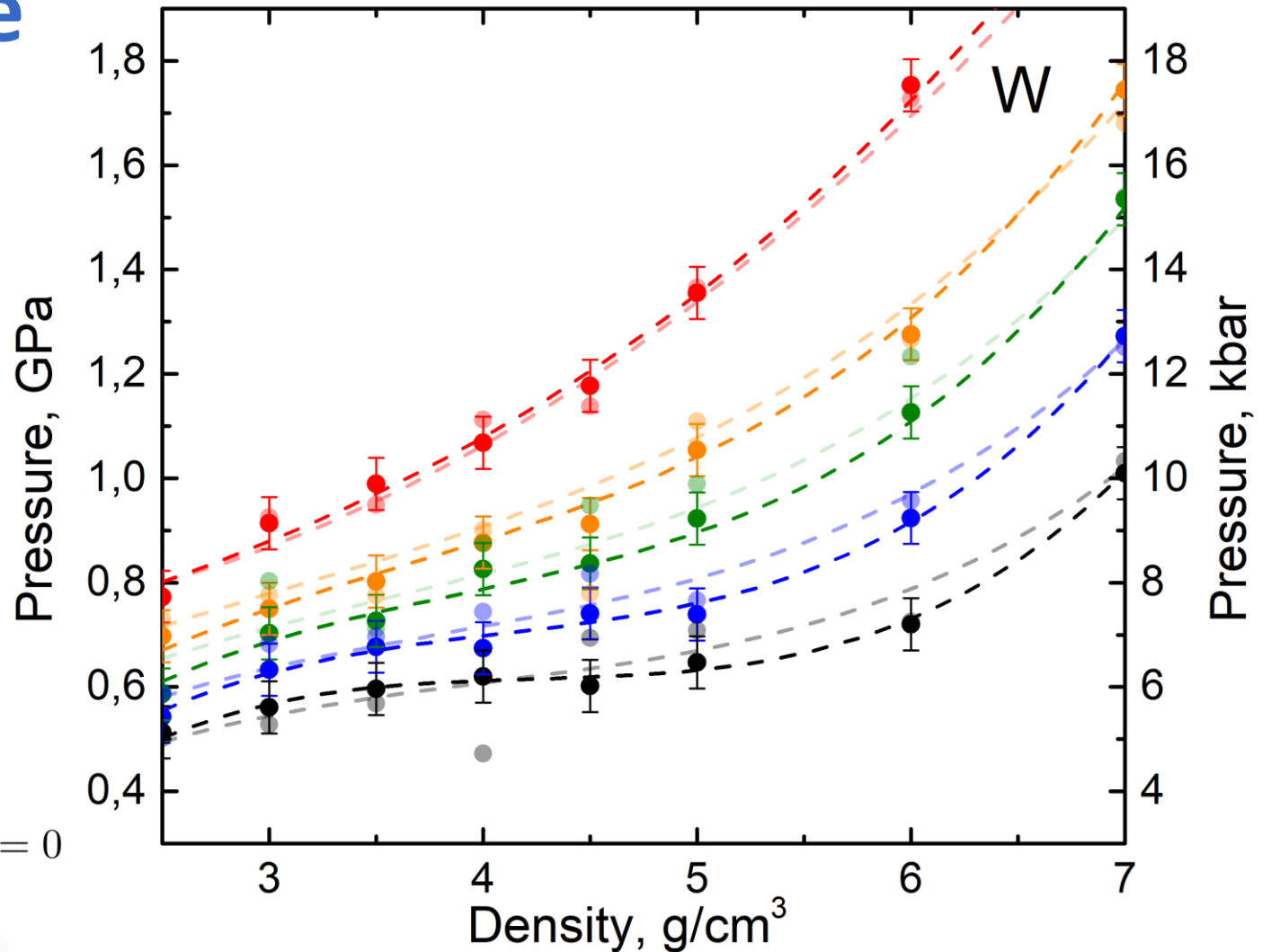


$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$$

Monte-Carlo procedure (2 000+ tries):

- Approximation of isochores taking into account statistical error
- Calculations of isotherms, search for inflection point

# Demonstration of Monte-Carlo procedure

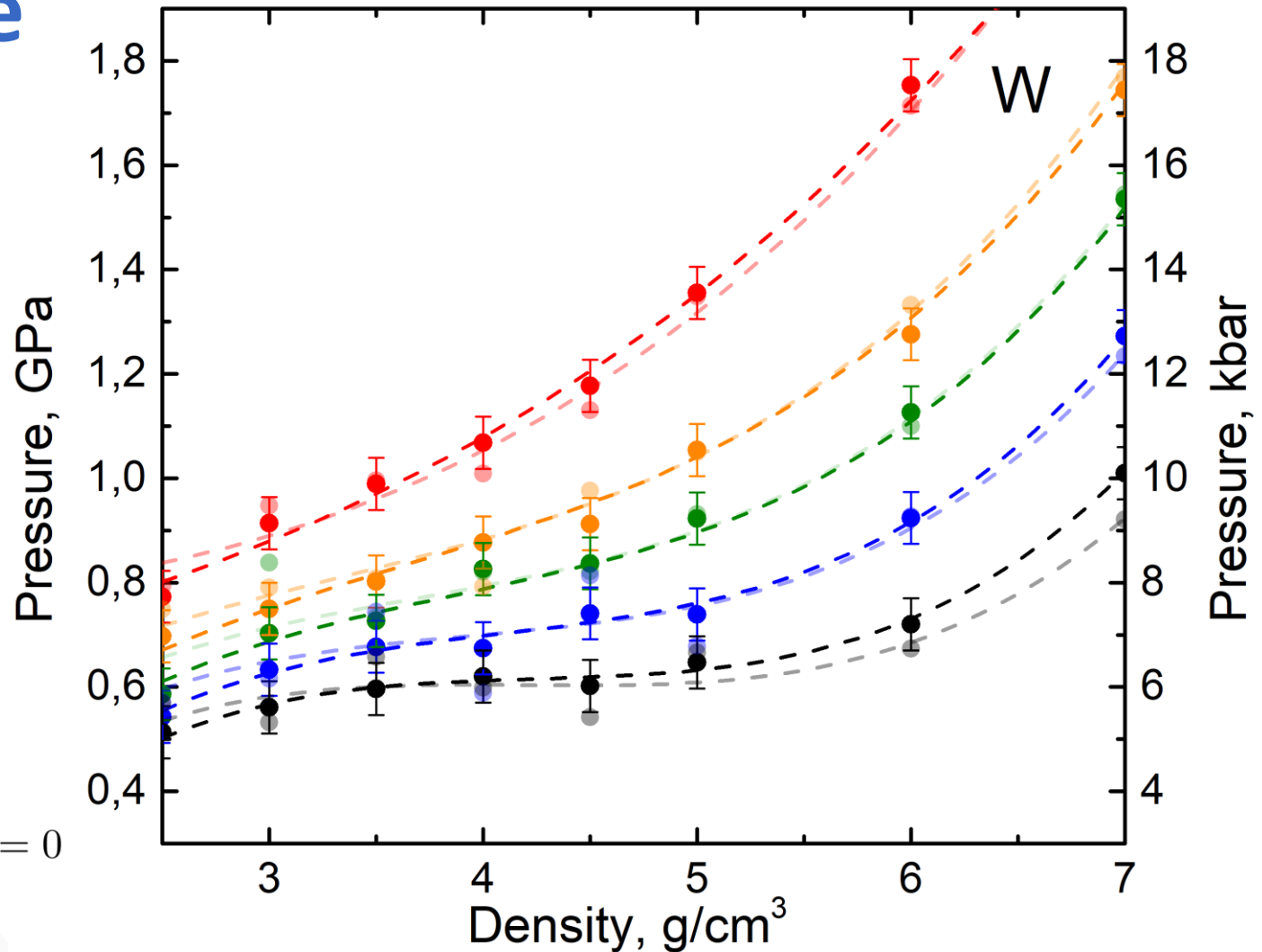


$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$$

Monte-Carlo procedure (2 000+ tries):

- Approximation of isochores taking into account statistical error
- Calculations of isotherms, search for inflection point

# Demonstration of Monte-Carlo procedure



$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$$

Monte-Carlo procedure (2 000+ tries):

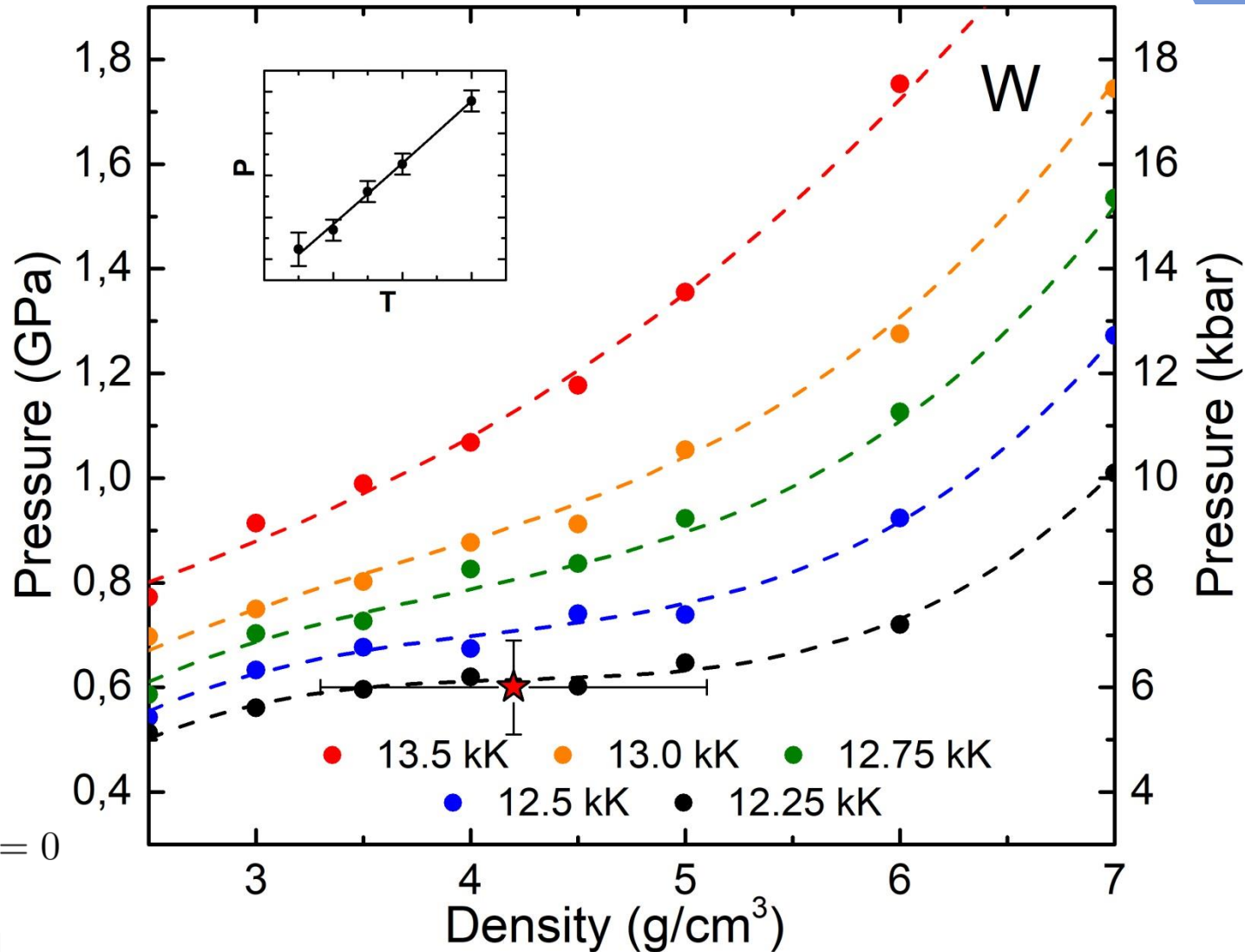
- Approximation of isochores taking into account statistical error
- Calculations of isotherms, search for inflection point

# Estimation of critical point parameters

## Critical point:

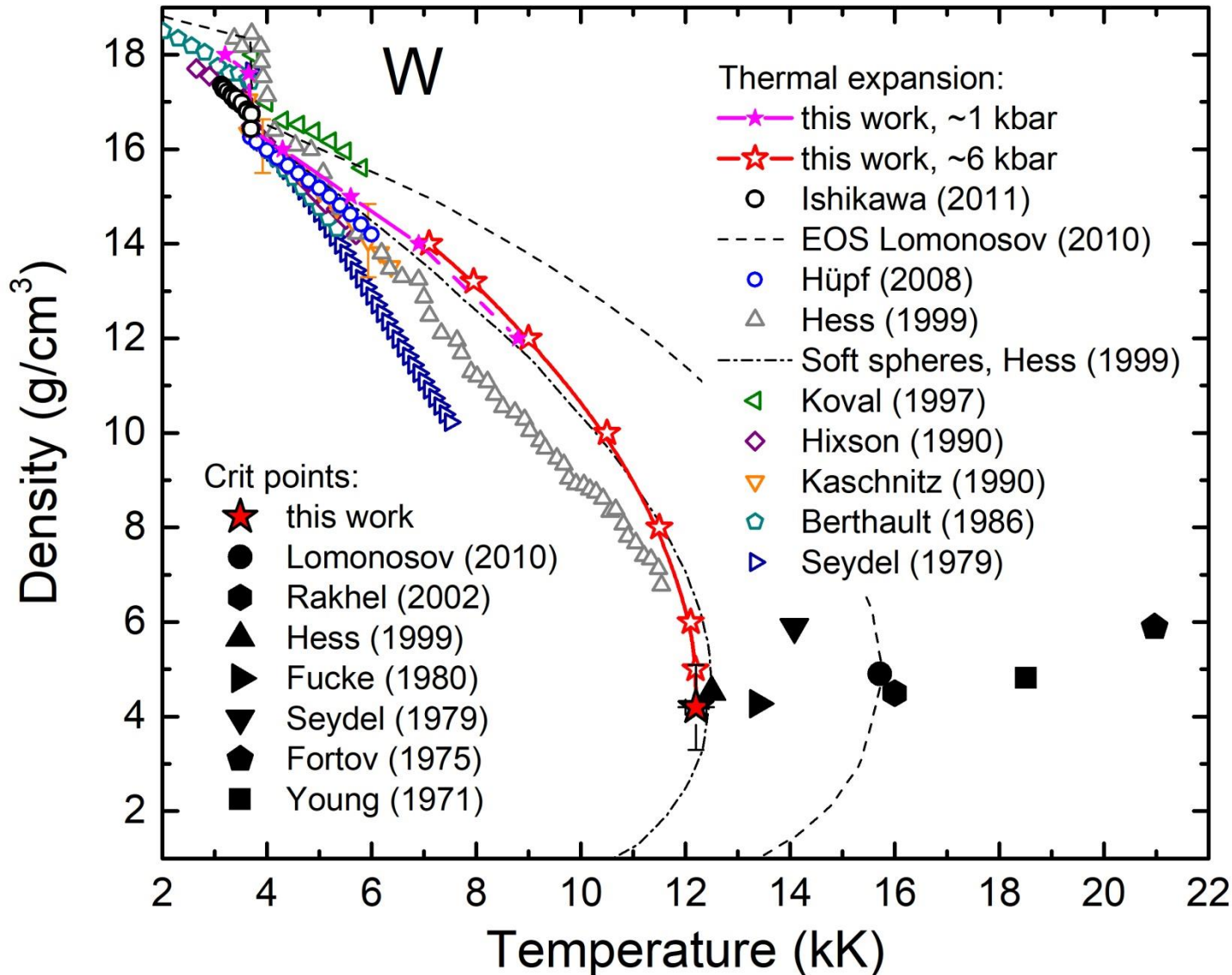
$T_c = 12.2 \pm 0.2$  kK;  
 $P_c = 6.0 \pm 0.9$  kbar;  
 $\rho_c = 4.2 \pm 0.9$  g/cm<sup>3</sup>;  
 $Z_c = 0.26 \pm 0.7$  g/cm<sup>3</sup>

$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0, \quad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$$



Monte-Carlo procedure (2 000+ tries):

- Approximation of isochores taking into account statistical error
- Calculations of isotherms, search for inflection point



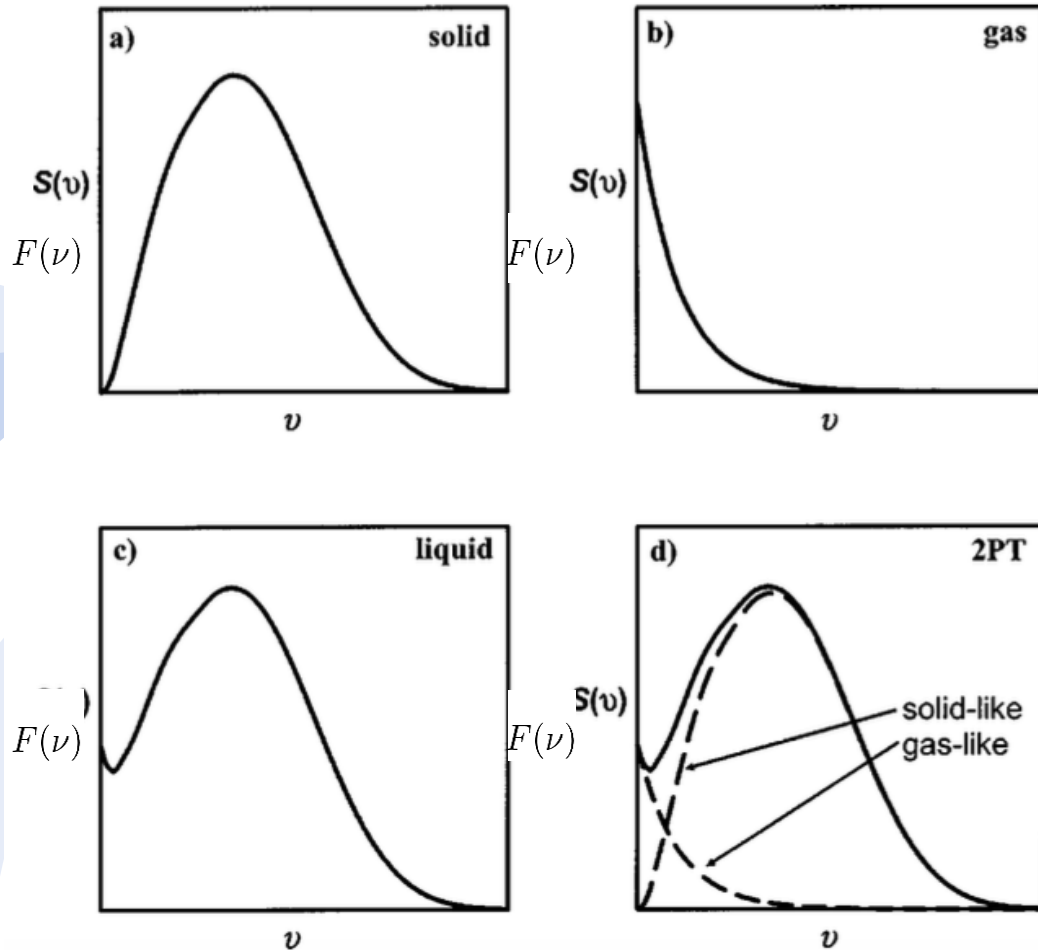
Our calculations are close to the data by by

- Seydel and Berthault in the solid phase
- by Hüpf and Hess in the liquid phase

Our critical parameters are close to the prediction made from Likalter's similarity relation,  
[PRB \*\*53\*\*, 4386 \(1996\)](#)

**Problem: we need an (approximate) method of entropy estimation from one MD (or MC) run**

# Two-phase model. Vibrational DOS decomposition



$N$  particles

Gas phase has  $3fN$  degrees of freedom, crystal phase -  $3(1 - f)N$

Vibrational DOS is represented as a sum gas a solid contributions:

$$F(\nu) = F^s(\nu) + F^g(\nu)$$

$F^g(0)$  is connected with the self-diffusion coefficient

# Hard-spheres model for the gas phase

Velocity autocorrelation function for hard spheres:

$$c^{\text{HS}}(t) = c^{\text{HS}}(0) \exp(-\alpha t) = \frac{3kT}{m} \exp(-\alpha t)$$

$\alpha$  - Enskog friction coefficient

$$F^{\text{HS}}(\nu) = \frac{4}{kT} \int_0^\infty \sum_{j=1}^{N^g} \sum_{k=1}^3 m_j c_j^k(t) \cos(2\pi\nu t) dt$$

$f$  – fraction of gas phase

$$= \frac{4}{kT} \int_0^\infty 3N^g kT \exp(-\alpha t) \cos(2\pi\nu t) dt$$



$$F^{\text{HS}}(0) = \frac{12fN}{\alpha} = F(0)$$

$$= \frac{12N^g \alpha}{\alpha^2 + 4\pi^2\nu^2},$$



$$F^{\text{HS}}(\nu) = \frac{F(0)}{1 + \left[ \frac{\pi F(0)\nu}{6fN} \right]^2}$$

$N^g = fN$  - number of hard spheres



# Entropy calculation

Weighted sum of solid and gas contributions:

$$S_{ionic} = S_s + S_g$$

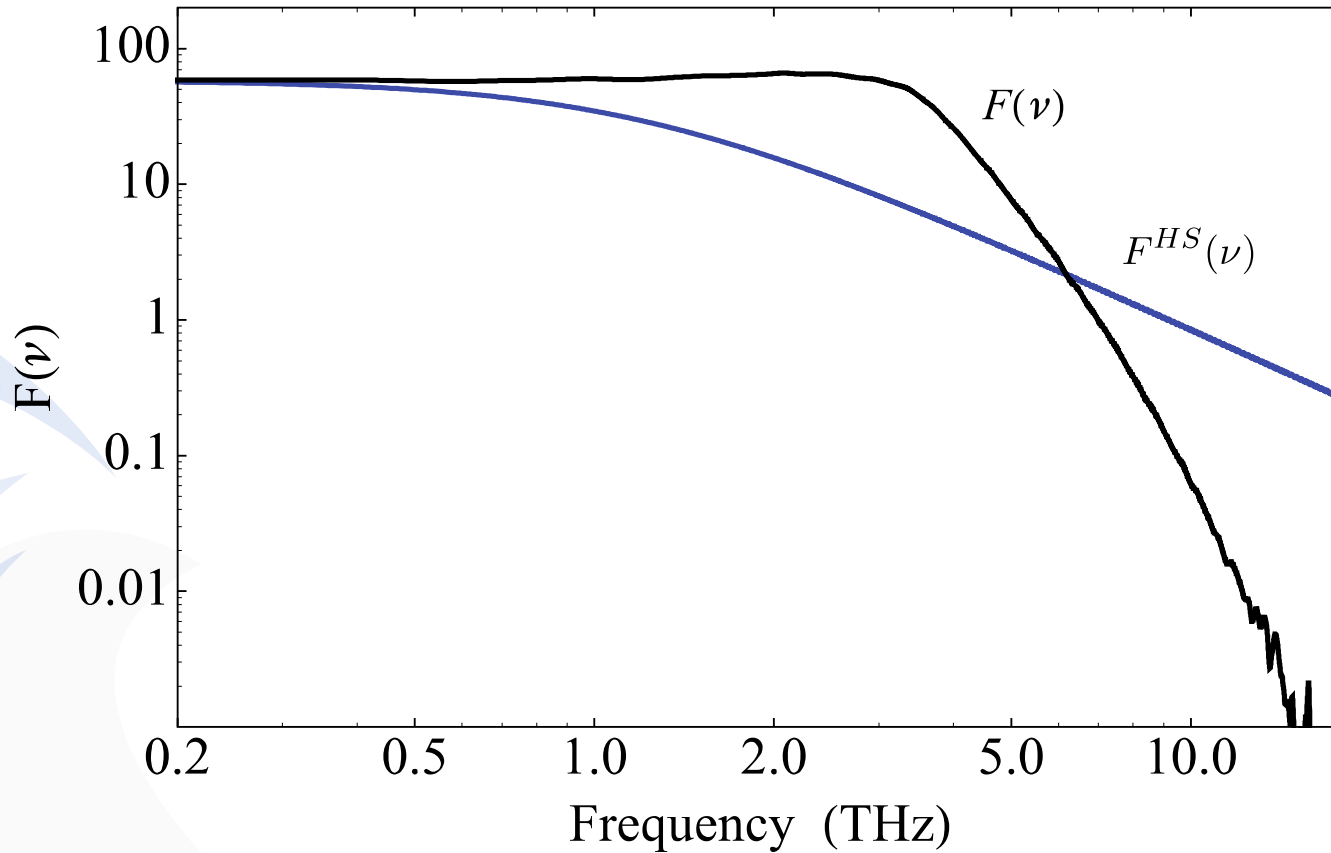
$$S_s = k_B \int_0^{\infty} (F(\nu) - F^{HS}(\nu)) W_s(\nu) d\nu, \quad F^{HS}(\nu) = \frac{F(0)}{1 + \left[ \frac{\pi F(0)\nu}{6fN} \right]^2}$$

$$S_g = k_B \int_0^{\infty} F^{HS}(\nu) W_g^{HS}(\nu) d\nu,$$

$$S_e = -k \langle \sum_i [f_i \ln f_i + (1 - f_i) \ln(1 - f_i)] \rangle$$

# Comparison of VDOS for Na

Vibrational DOS for Na at  $T = 723$  K and normal pressure



The slope of the VDOS tail is incorrect



# Velocity autocorrelation function as a memory function

$$\frac{d\Phi_g(t)}{dt} = - \int_0^t K_g(\tau) \Phi_g(t - \tau) d\tau \quad \text{- velocity autocorrelation function}$$

$$\Phi(t) = \sum_{n=0}^{\infty} (-1)^n \frac{M_{2n}}{(2n)!} t^{2n} \quad \text{- temporal series expansion (moments)}$$

$$F_g(\nu) = \frac{1}{2} \left[ \frac{1}{\hat{K}_g(i2\pi\nu) + i2\pi\nu} + \frac{1}{\hat{K}_g(-i2\pi\nu) - i2\pi\nu} \right] \quad \text{Complementary error function}$$

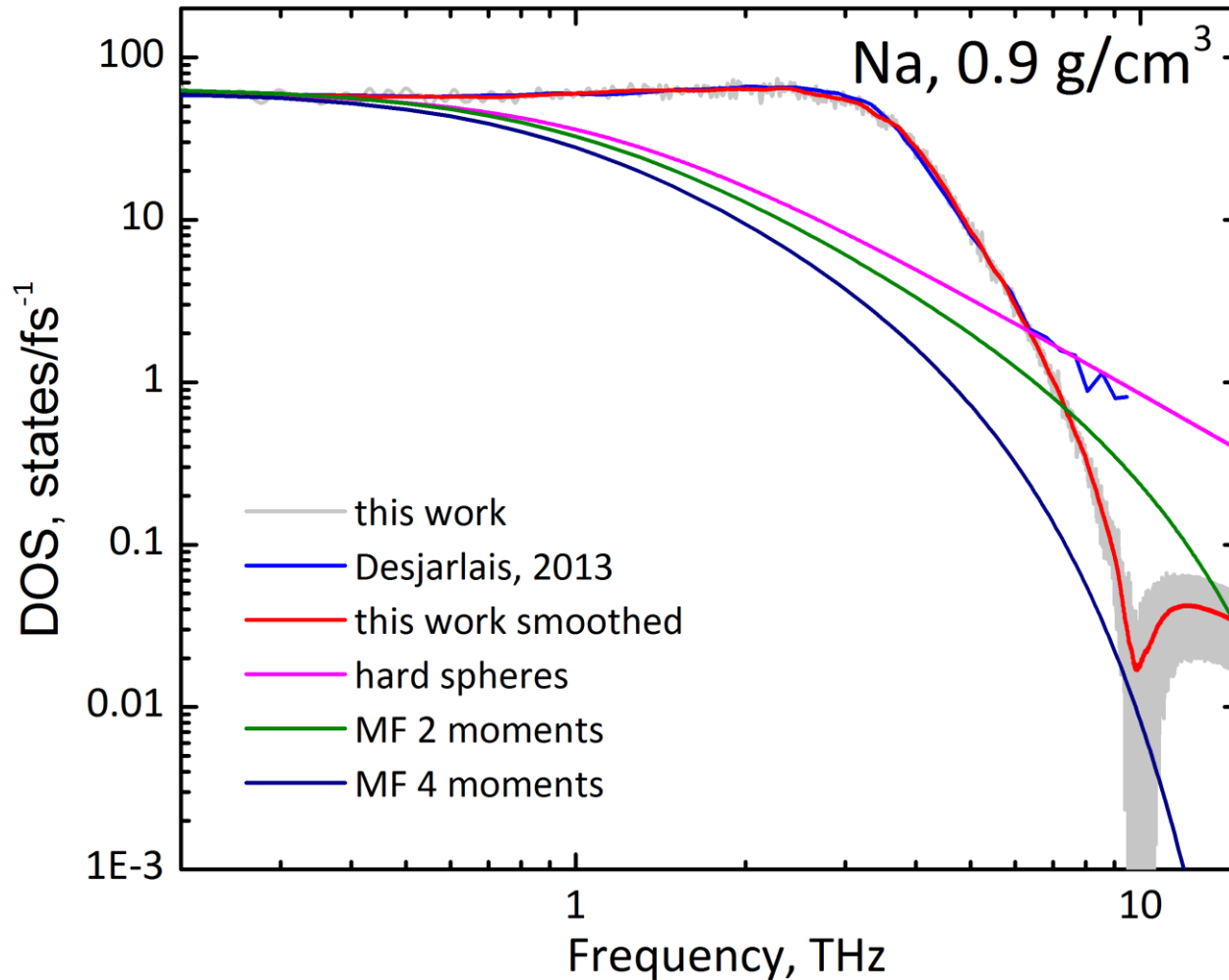
$$K_g(\tau) = A_g e^{-B_g \tau^2} \quad \hat{K}_g(s) = A_g \sqrt{\frac{\pi}{4B_g}} \exp\left[\frac{s^2}{4B_g}\right] \text{Erfc}\left[\frac{s}{2\sqrt{B_g}}\right]$$

Laplace transform

$$F_g(0) = \frac{1}{\hat{K}_g(0)} = \frac{1}{A_g} \sqrt{\frac{4B_g}{\pi}} = \frac{F(0)}{f_g}$$

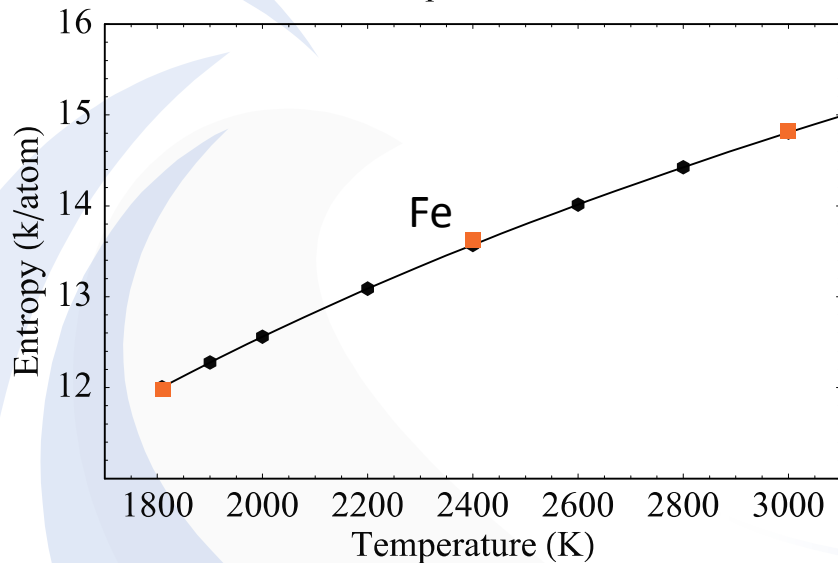
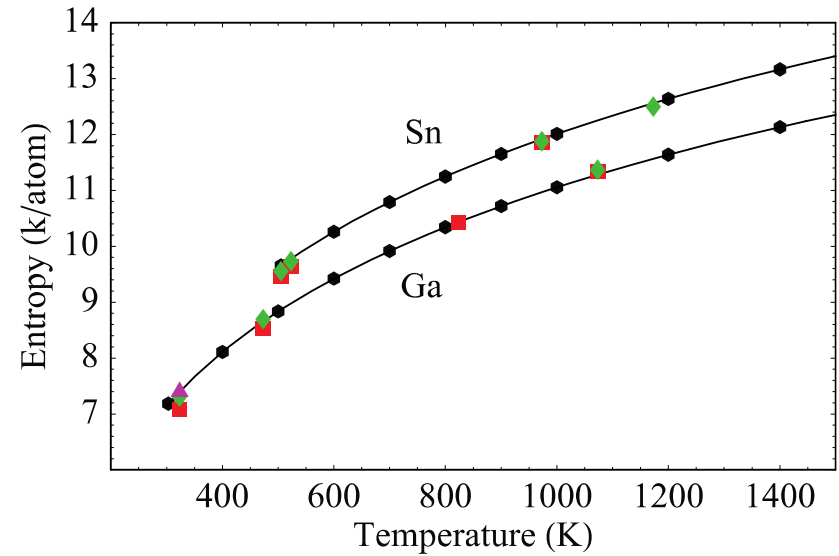
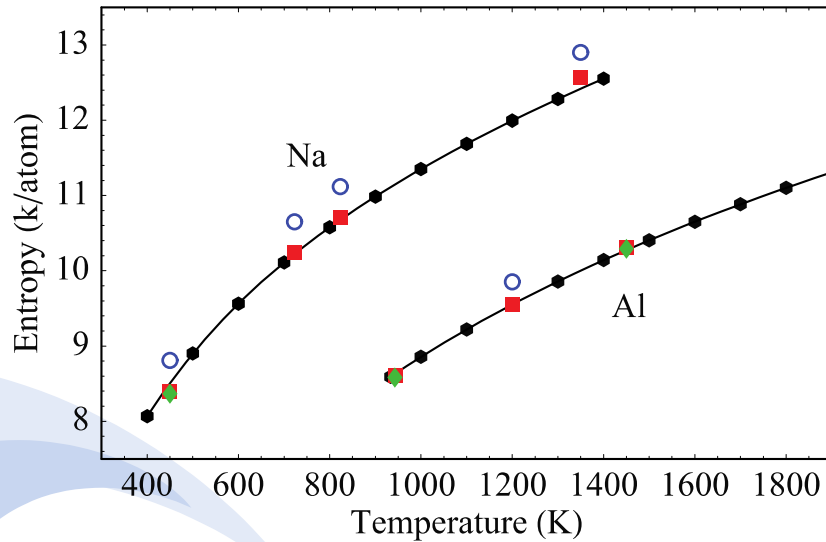
$$A_g = 4B_g / \left[ 2 + \sqrt{\pi(1 + 4B_g/\alpha^2)} \right] \quad \text{Agreement with hard-sphere model at low } \nu$$

# Memory function vs. hard spheres



Memory function with 2 or 4 moments changes the slope of the tail

# Entropy for liquid metals: comparison



$$S_{\text{mag}} = k \ln \left[ 1 + \langle \delta m_s^2 \rangle^{1/2} \right],$$

Problems:

- hard-sphere potential has only one fitting parameter;
- memory function can give several solutions;
- Bad results for refractory metals

# Soft-sphere potential for entropy evaluation

$$\phi(r) = \varepsilon \left( \frac{\sigma}{r} \right)^n - \text{soft-sphere potential}$$

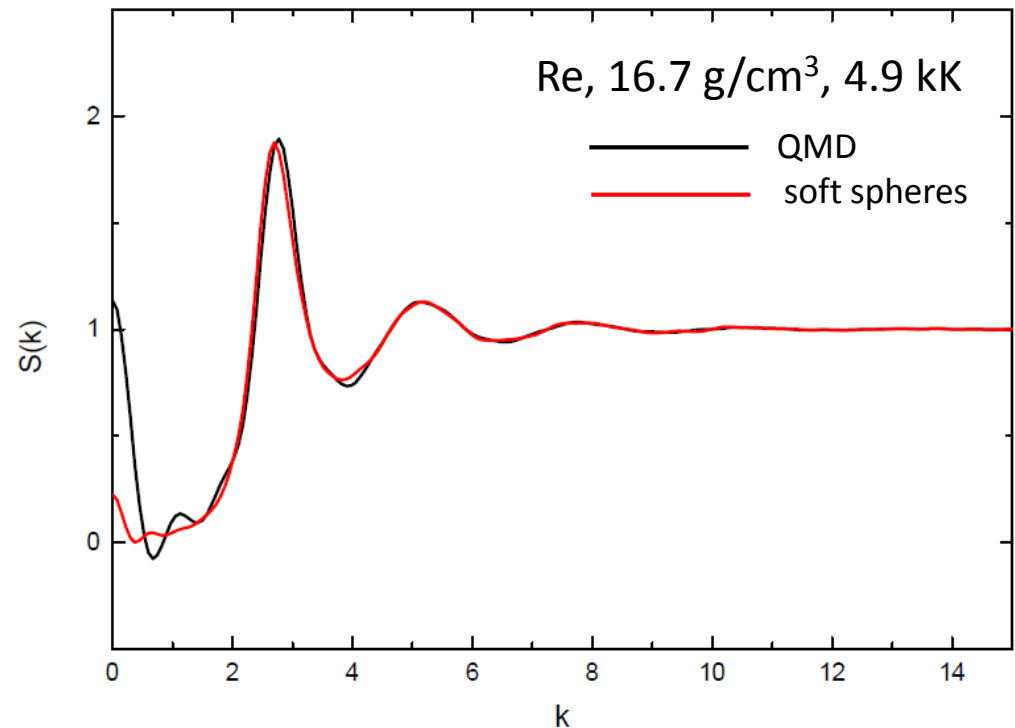
Uniform potential, all properties depend only on one parameter:

$$\zeta = \frac{\pi}{6} \left( \frac{\varepsilon^{3/n}}{T} \rho \sigma^3 \right)$$

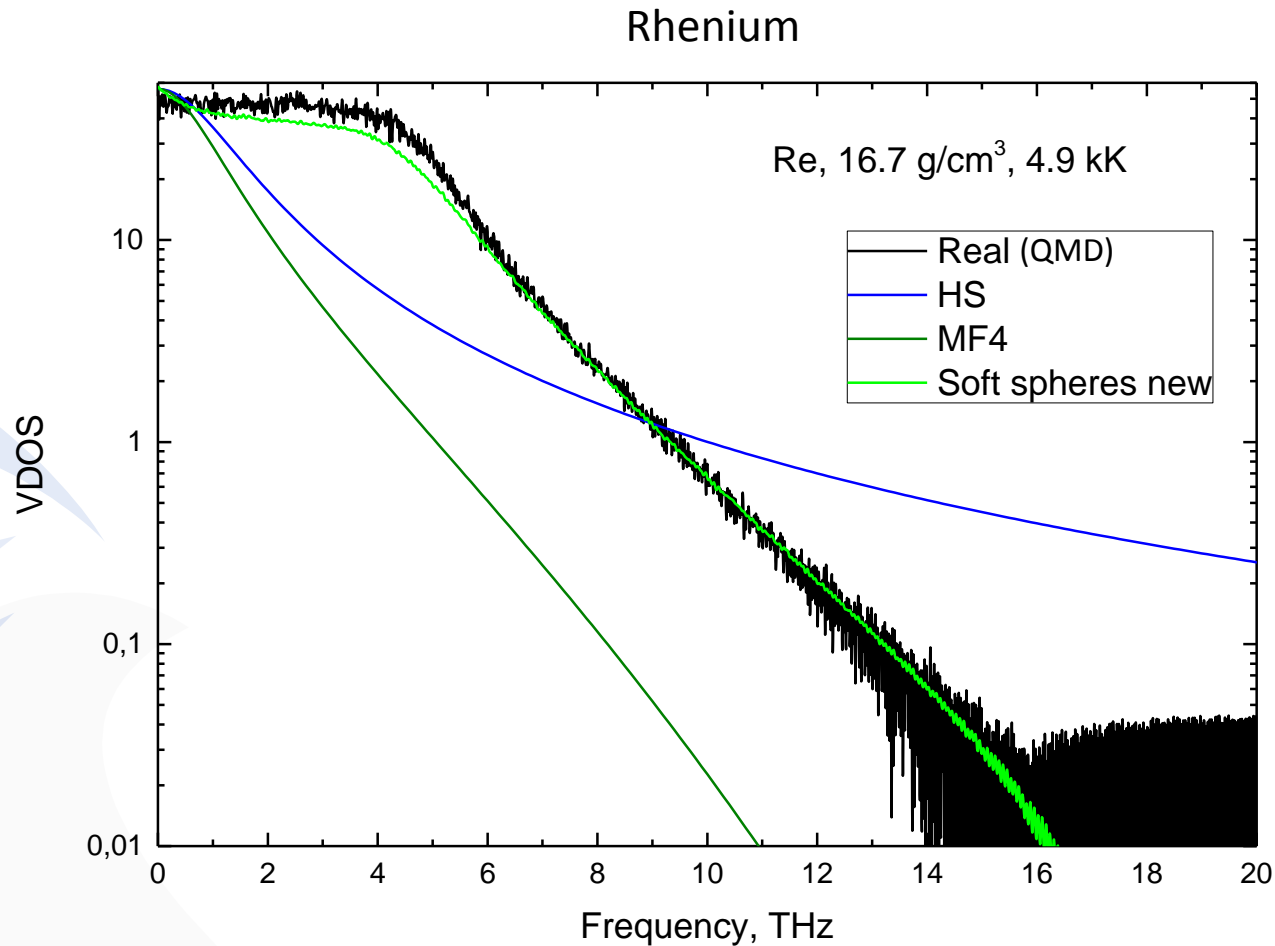
Potential parameters  $\varepsilon$ ,  $\sigma$ ,  $n$  are determined from structure factor fitting at given  $T$  and  $\rho$ :

$$S(k) = 1 + 4\pi\rho \int_0^{\infty} [g(r) - 1] r \frac{\sin(kr)}{k} dr$$

Structure factor for rhenium

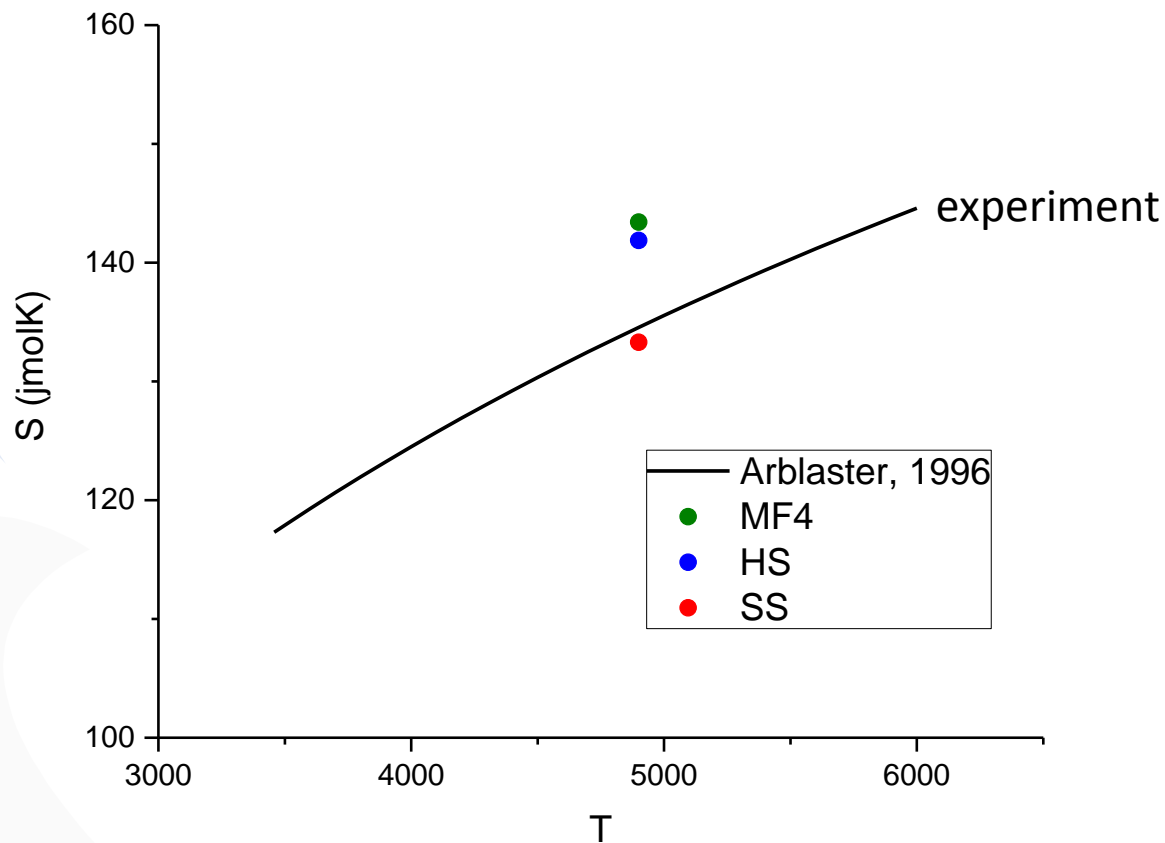


# Vibrational density of states, comparison



Soft-sphere potential gives better agreement with QMD VDOS tail

# Entropy for rhenium, comparison



Soft-sphere potential gives promising results for entropy



# Conclusions

- Method of entropy estimation of a classical system from a single MD (MC) run is still needed
- Two-phase approach is approximate and have limitations
- New approaches based upon microcanonical ensemble (Jarzynski equality, density of states estimation) should be checked
- Entropy calculation in PIMC is still missing – very important for liquid-liquid phase transition
- My best wishes to Michael!