上海交通大学
材料科学与工程学院
School of Materials Science and Engineering, SJTU

MSE6701H, Multiscale Materials Modeling and Simulation

- ✓ Electronic DFT
- • **Atomistic MD**
- • Mesoscale PF

Lecture 10-P1

Molecular Dynamics under T, P constraints

Guisen Liu (刘桂森)

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Review

$$\dot{\mathbf{r}}_i = \mathbf{p}_i / m_i$$
$$\dot{\mathbf{p}}_i = m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i$$

- ✓ Solution to Newton's equation ➔ NVE
  - Basic MD run under NVE
  - However, isolated system with constant E is uncommon.
  - **In lab condition, control T or P is easier than control energy**
- ➢ **Physical ensembles**
  - ✓ **Biological reactions occur under constant Temperature: NVT**
    - **How to control T**
    - **How to analyze structure**
  - ▪ **Chemical reactions occur open to atmosphere (P): NPT**

Contents

- **Pressure control**
  - Berendsen
  - Andersen (Nose-Hoover)

- **Goals**
  - Apply P constraints to specific problems
  - Understand how pressure influences MD simulation results

Barostat: pressure in MD

- P for a classical *N*-body system
  - **Clausius virial theorem(note)**:

$$\langle P \rangle = \frac{1}{V} N k_B \langle T \rangle + \frac{1}{3V} \left\langle \sum_{i=1}^{N} \sum_{j>i}^{N} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \right\rangle$$

    - 1st term: pressure of an ideal gas (no interaction between molecules)
    - 2nd term: pairwise additive interactions

- **P** is a second order tensor (similar to stress)

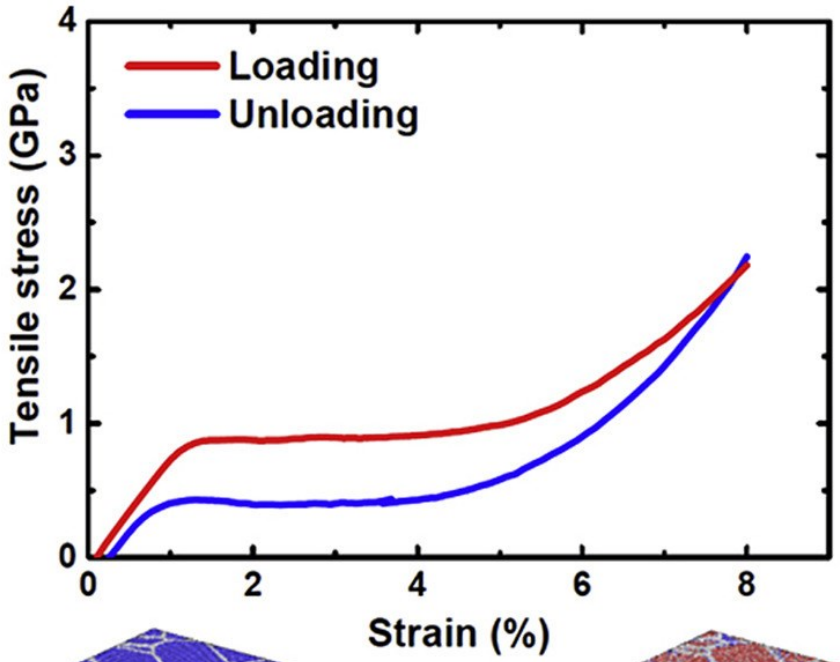
$$\mathbf{P} = \begin{pmatrix} \mathbf{P}_{xx} & \mathbf{P}_{xy} & \mathbf{P}_{xz} \\ \mathbf{P}_{yx} & \mathbf{P}_{yy} & \mathbf{P}_{yz} \\ \mathbf{P}_{zx} & \mathbf{P}_{zy} & \mathbf{P}_{zz} \end{pmatrix}$$

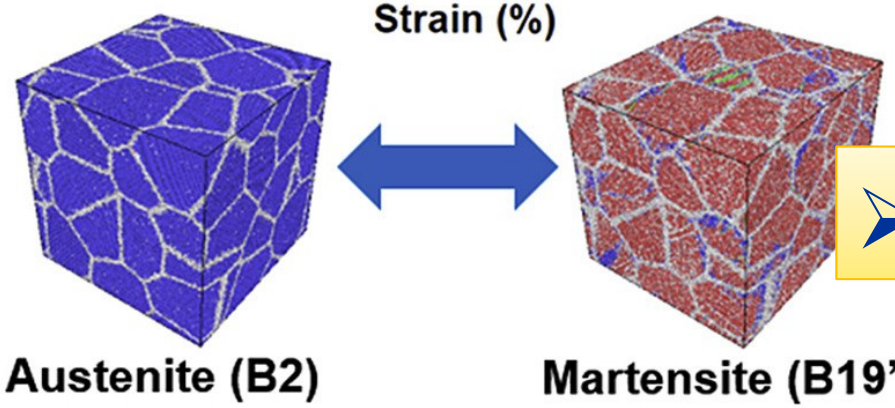
  - $\mathbf{P}xy$: force along y-axis acting on the surface whose normal is x-axis.

- **P** is usually anisotropic unless Pxx = Pyy = Pzz such as hydrostatic pressure.

Note: R. LeSar, Introduction to computational materials science: fundamentals to applications, Cambridge University Press2013. (Appendix G)

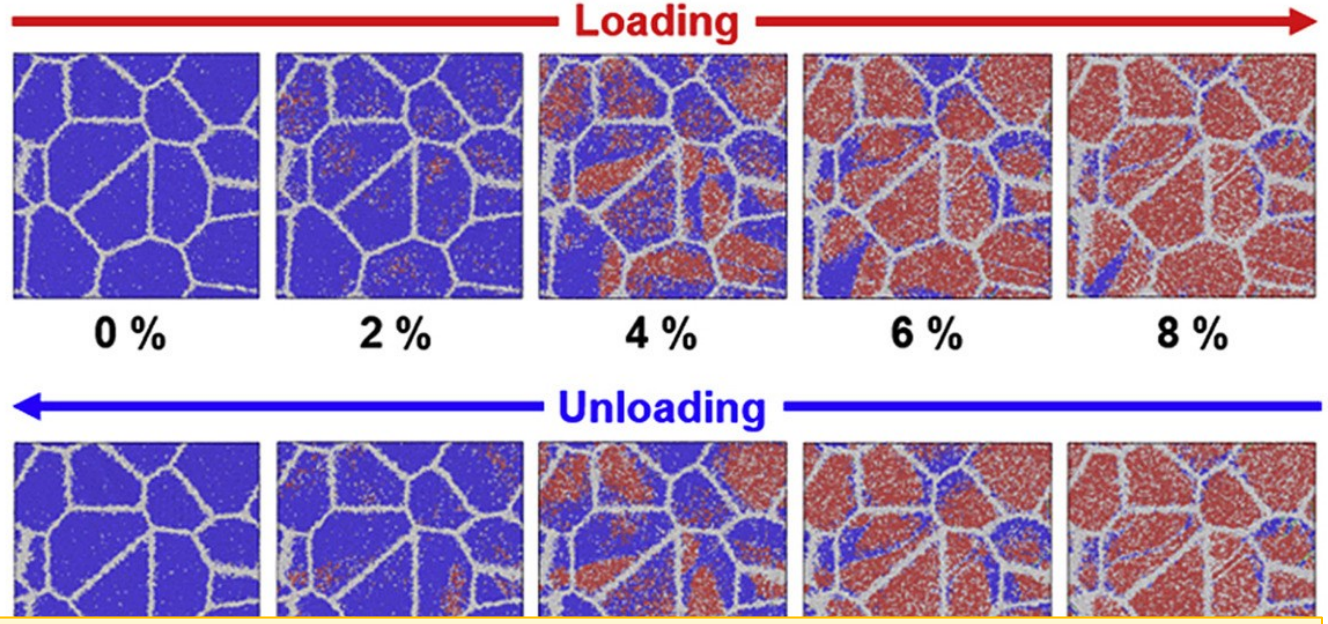
Phase Transformations in NiTi alloys





Austenite (B2) Martensite (B19')

- B19' phase nucleates at the grains' interior
- B19' phase grows towards the grain boundaries



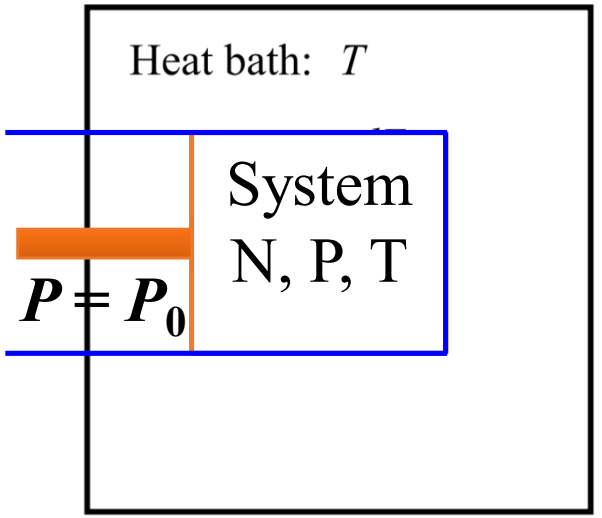
➢ **How to control stress in MD?**

- B2 phase nucleates at the grain and domain boundaries
- B2 phase grows towards the grains' interior

Atomic scale processes of phase transformations in nanocrystalline NiTi shape-memory alloys, Acta Mater 123 (2017) 90-101.

Control pressure in MD

- Modify equation of motion similar to control T
- Modify P in MD by scaling inter atomic distances $\mathbf{r}_{ij}$.



$$\langle P \rangle = \frac{1}{V} N k_B \langle T \rangle + \frac{1}{3V} \left\langle \sum_{i=1}^{N} \sum_{j>i}^{N} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \right\rangle$$

- NOT change box shape, but rescale box length
  1) **Berendsen** barostat. independent from thermostat, **weak** coupling
  2) **Andersen (Nose-Hoover)** barostat. **strong** coupling
- Change box shape
  3) **Parrinello-Rahman** barostat

1.1 The Berendsen barostat (1)

- **Rescale coordinates and box length** at each step

$$\mathbf{r}_i \rightarrow \mu \mathbf{r}_i, \quad L \rightarrow \mu L, \quad V \rightarrow \mu^3 V$$

- μ: rescale factor
- β: isothermal compressibility = 1/B
- P_0: desired pressure
- Δt: integrator time-step
- τ_p: time constant, rise time of the barostat

$$\mu = \left[1 + \frac{\beta \Delta t \left(P(t) - P_0 \right)}{\tau_p} \right]^{1/3}$$

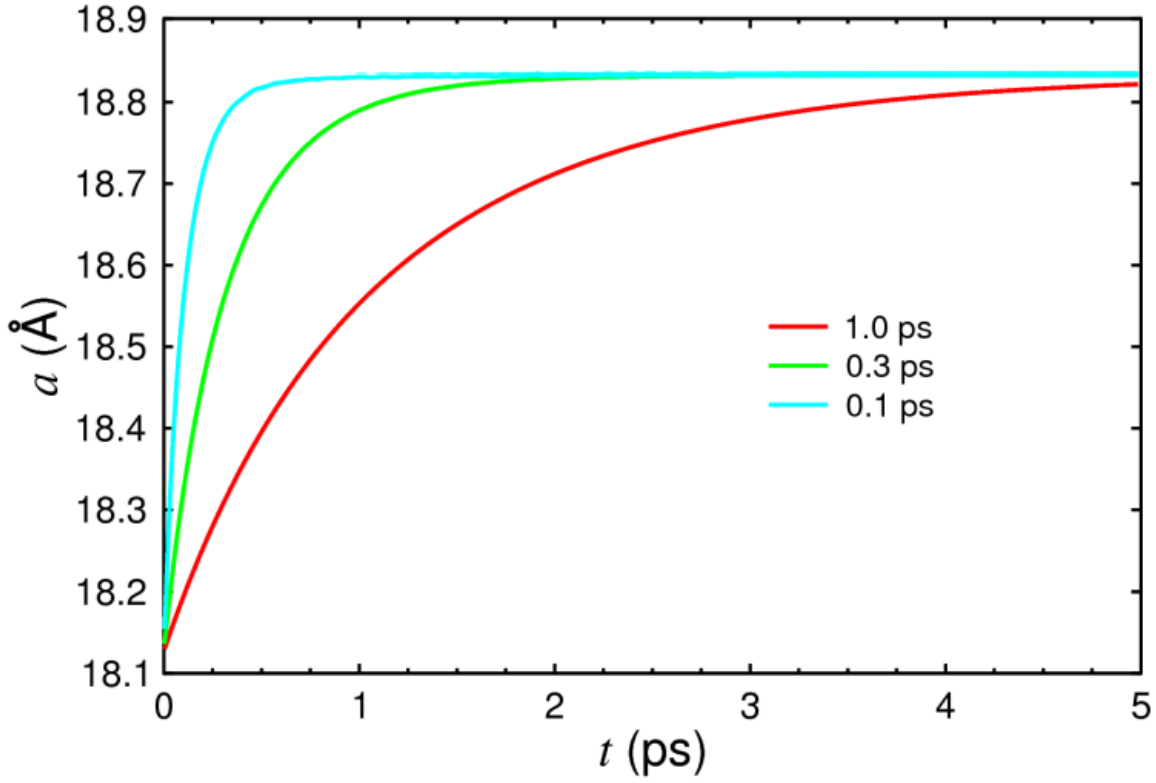
H. J. C. Berendsen, et al "Molecular dynamics with coupling to an external bath", Journal of Chemical Physics 81 pp. 3684-3690 (1984).

1.1 The Berendsen barostat (2)

- **Effect of parameter** τ_p(time constant)

$$\mu = \left[1 + \frac{\beta \Delta t \left(P(t) - P_0 \right)}{\tau_p} \right]^{1/3}$$

  - If $P > P_0$, increase dimension
  - If $P < P_0$, decrease dimension



- P, T, V and U_{pot} all fluctuate
- ✓ In equilibrium with large τ_p, Berendsen gives realistic fluctuations in T & P.

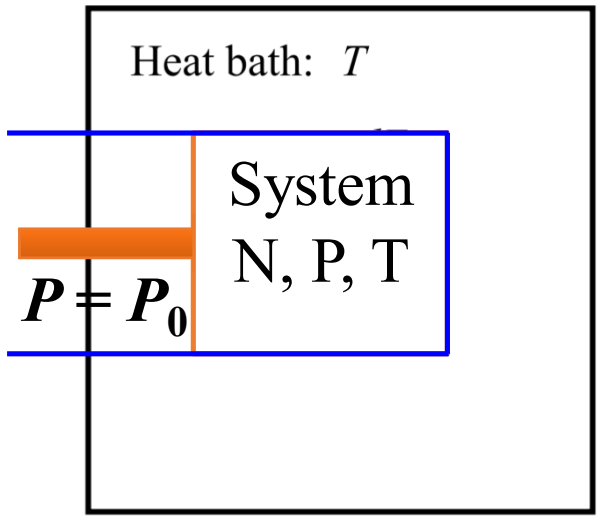
H. J. C. Berendsen, et al "Molecular dynamics with coupling to an external bath", Journal of Chemical Physics 81 pp. 3684-3690 (1984).

1.2 The Andersen barostat (1)

- The system volume V varies with the position of a fictional piston (mass Q)
- The piston has kinetic and potential energy

$$E_k^{pis} = \frac{1}{2} Q \dot{V}^2, \quad E_p^{pis} = P_0 V$$

- Atom positions and velocities in reduced coordinates $\mathbf{s}$ $\quad \mathbf{r}_i = V^{1/3}\mathbf{s}_i, \quad \mathbf{v}_i = V^{1/3}\dot{\mathbf{s}}_i$



- Modified equation of motion $\ddot{\mathbf{s}}_i = \frac{\mathbf{F}_i}{m_i V^{1/3}} - \frac{2}{3}\frac{\dot{\mathbf{s}}_i \dot{V}}{V}, \quad \ddot{V} = \frac{P(t) - P_0}{Q}$

- Energy of the extended system ($\tilde{H}$) is conserved

$$\tilde{H} = \sum_{i=1}^{N} \frac{1}{2} m_i |\mathbf{v}_i|^2 + U(\{\mathbf{r}_i\}) + E_k^{pis} + E_p^{pis}$$

H. C. Andersén, J. Chem. Phys. 72, 2384 (1980)
W. G. Hoover. Phys. Rev. A 31 (1986), 1695 G. J.

1.2 The Andersen barostat (2)

$$\ddot{\mathbf{s}}_i = \frac{\mathbf{F}_i}{m_i V^{1/3}} - \frac{2}{3}\frac{\dot{V}}{V}\dot{\mathbf{s}}_i, \quad \ddot{V} = \frac{P(t) - P_0}{Q}$$

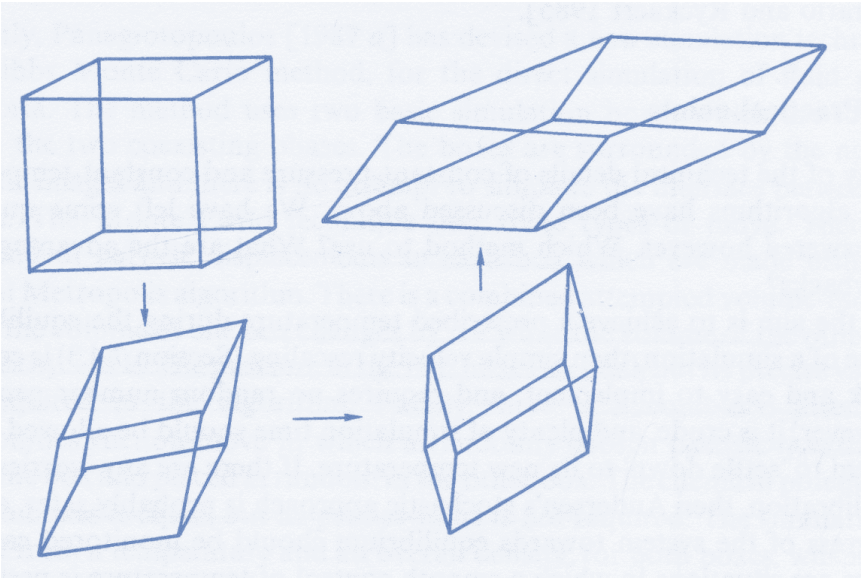
$$\ddot{\mathbf{r}}_i = \frac{\mathbf{F}_i}{m_i} - \lambda \dot{\mathbf{r}}_i, \quad \dot{\lambda} = \frac{T(t) - T_0}{M_s}$$

- If $P >$ desired P_0, increase V, expand the volume
- If $P <$ desired P_0, decrease V, shrink the volume
- Mass of the piston Q
  - Large Q: slow convergence
  - Small Q: wide oscillations
- Nose-Hoover barostat is based on Andersen method

H. C. Andersén, J. Chem. Phys. 72, 2384 (1980)
W. G. Hoover. Phys. Rev. A 31 (1986), 1695 G. J.

1.3 The Parrinello-Rahman barostat

- Allow dynamic change of size and **shape**
  - Cell size and shape: $\mathbf{H} = \{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$
  - Scaled coordinates: $\mathbf{s}_i = \mathbf{H}^{-1}\mathbf{r}_i$
  - Modify EOM, with fictional mass Q



$$\ddot{\mathbf{s}} = \mathbf{H}^{-1}\mathbf{F}_i / m_i - \mathbf{G}^{-1}\dot{\mathbf{G}}\dot{\mathbf{s}}, \text{ with } \mathbf{G} = \mathbf{H}^T\mathbf{H}$$

$$\ddot{\mathbf{H}} = \frac{\mathbf{P} - p\mathbf{I}}{Q} V \left(\mathbf{H}^{-1}\right)^T - \mathbf{H}\boldsymbol{\Sigma}, \text{ with hydrostatic } p = \frac{P_{11} + P_{22} + P_{33}}{3}$$

$$\boldsymbol{\Sigma} = \mathbf{H}_0^{-1}\left(\mathbf{S} - p\mathbf{I}\right)\left(\mathbf{H}_0^{-1}\right)^T V_0, \mathbf{S} \text{ is external pressure tensor}$$

  - Mass Q controls the rate of change of the pressure

✓ **solid phase transformation**

M. Parrinello and A. Rahman: Phys. Rev. Lett. 45 (1980) 1196;
J. Appl. Phys. 52 (1981) 7182; J. Chem. Phys. 76 (1982) 2662.

Summary of T & P constraint methods

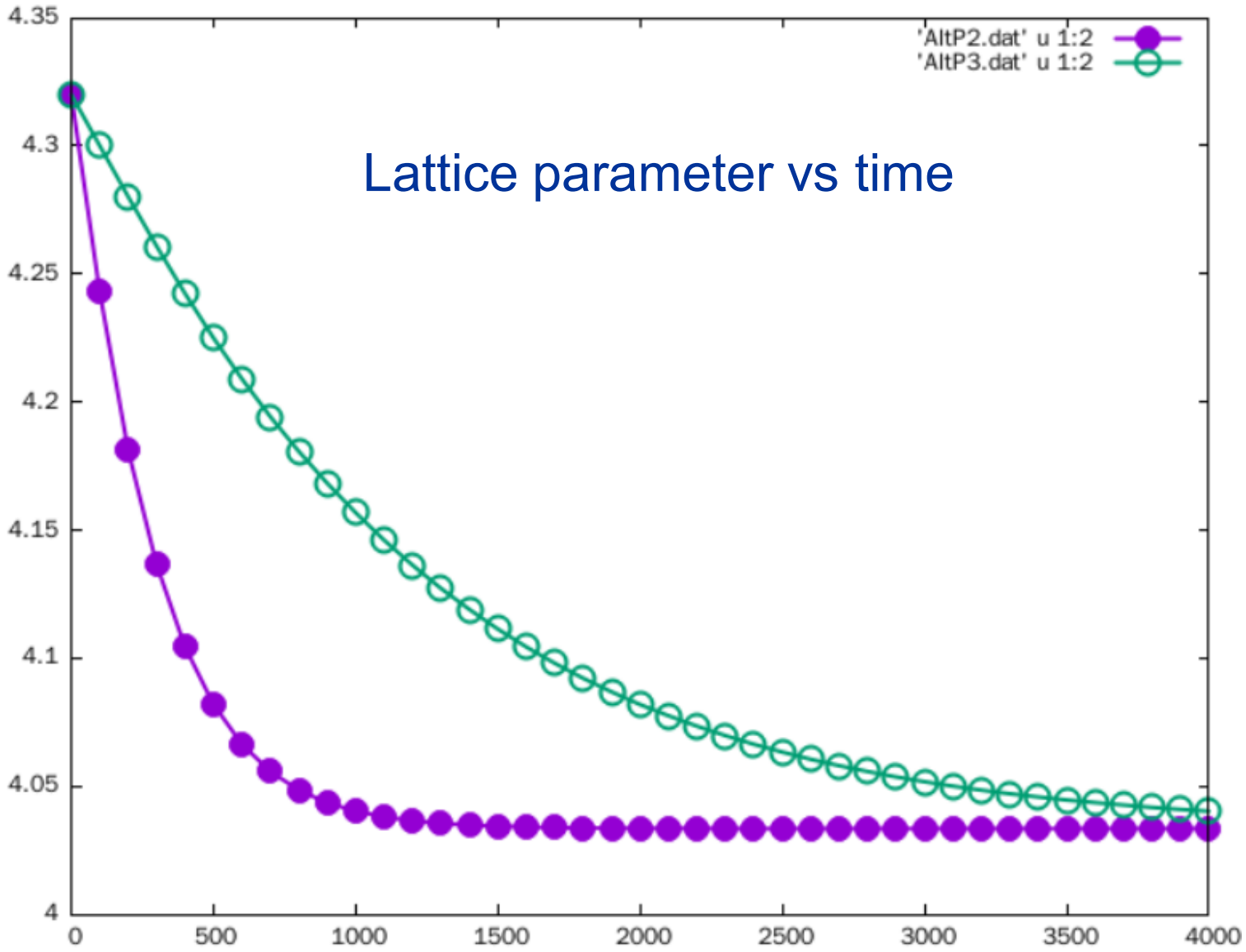
method	pros	cons
Berendsen P Andersen T	• Fast, smooth first-order approach to equilibrium	Less reliable for simulation at equilibrium
Nosé-Hoover T & P Parinello-Rahman P	• Maintain NVT, or NPT • Most reliable for a. equilibrium simulation b. thermodynamic properties	Slow, second-order approach to equilibrium

Choose proper ones for your specific problem/simulation conditions!

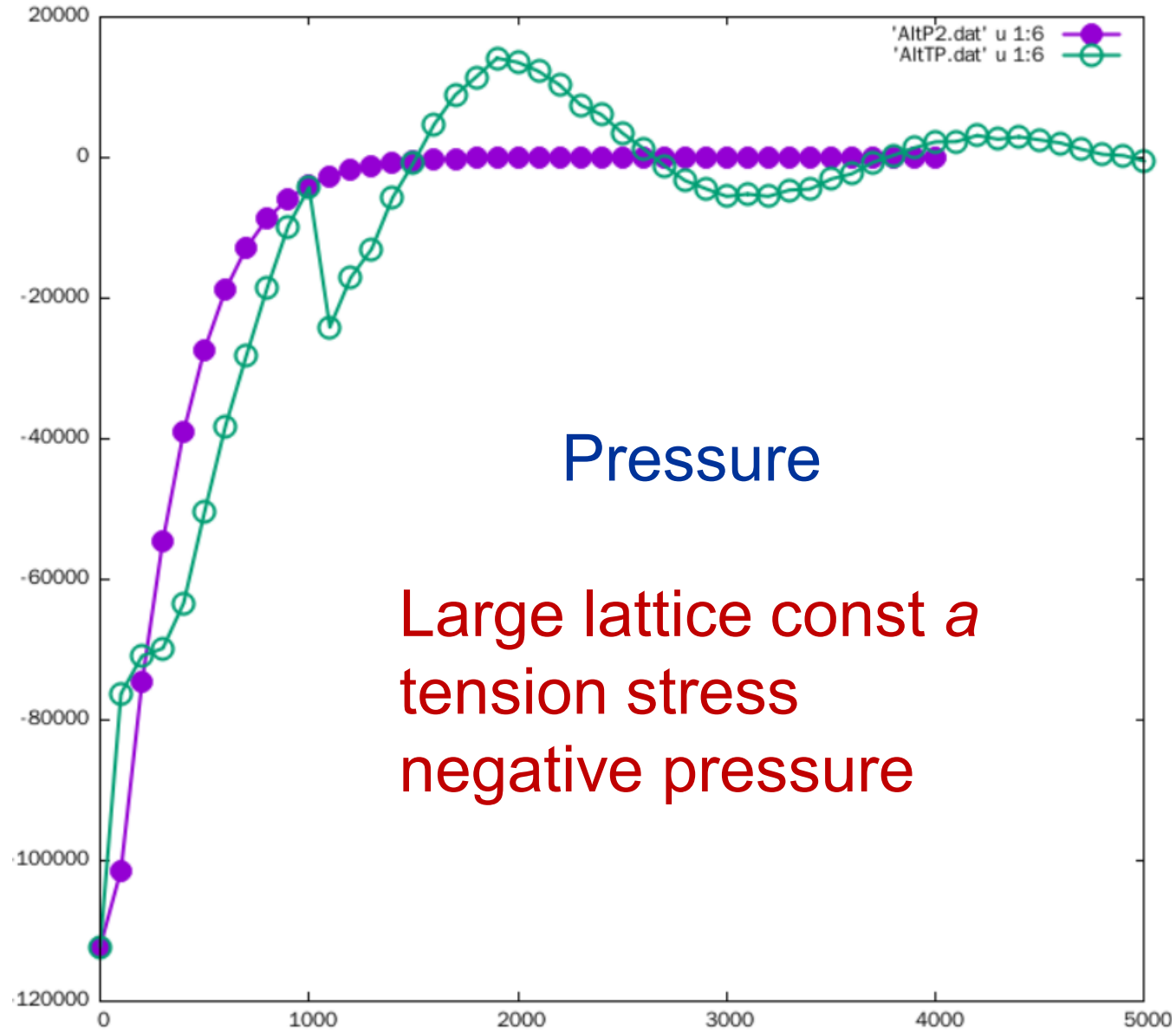
Comments on thermostat and barostat

- **Do not use any trivial quenching scaling methods**, which ***suppress fluctuations***, and do not provide physical ensembles.
- General approach
  - Start with weak coupling, rapidly relax the system to the desired temperature or pressure we are interested in (relatively large fluctuation).
  - Continue with strong coupling (small fluctuation) to obtain the equilibrium properties we desired.
  - If equilibration time is not too long (near equilibration), use strong coupling.
- Which one to use?
  - Thermostat: Andersen is fast. Nose-Hoover is more accurate.
  - Barostat
    - Orthogonal: Berendsen is fast. Andersen (Nose-Hoover) is proper.
    - Shear pressure or crystal structure change: use Parrinello-Rahman

Example: Berendsen method

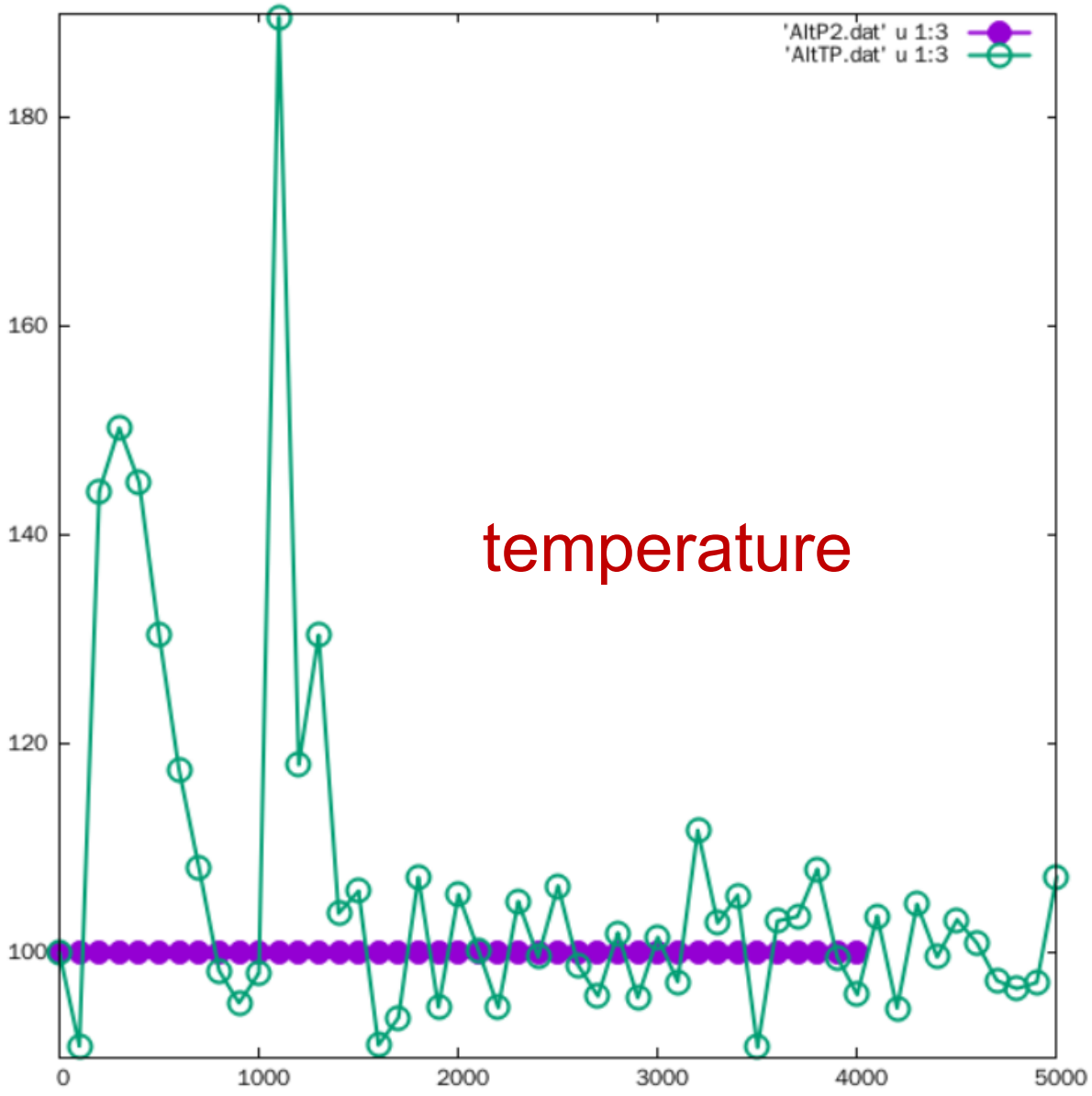


Example: NPT ensemble



Pressure

Large lattice const *a*
tension stress
negative pressure



temperature

MD: overall flow chart