Simulating Materials at Constant Pressure Using Homogeneous Coordinates

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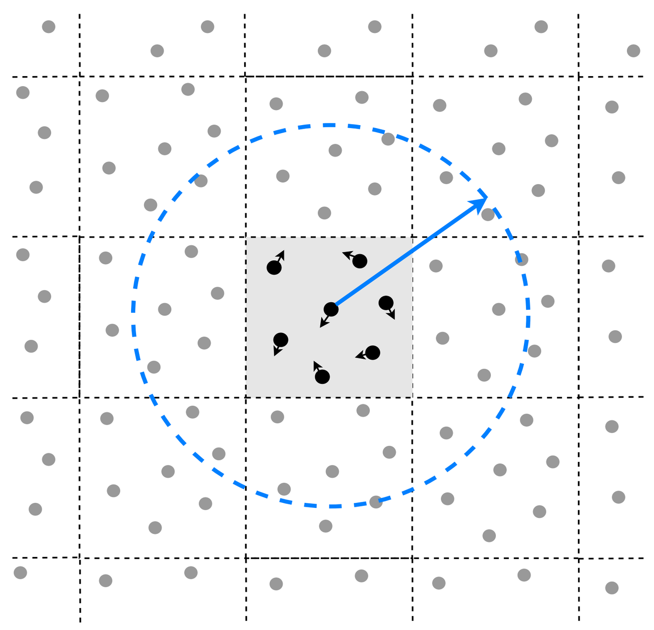
1. Molecular dynamics

Molecular dynamics (MD): the simulation of atoms as classical particles moving according to potential functions.

Periodic boundary conditions help us simulate the interior of materials without finite size effects.

Constant pressure simulation → variable volume [1]

How do we vary volume? → **Project aim:** devise an algorithm for dynamically scaling space in atomistic simulations.



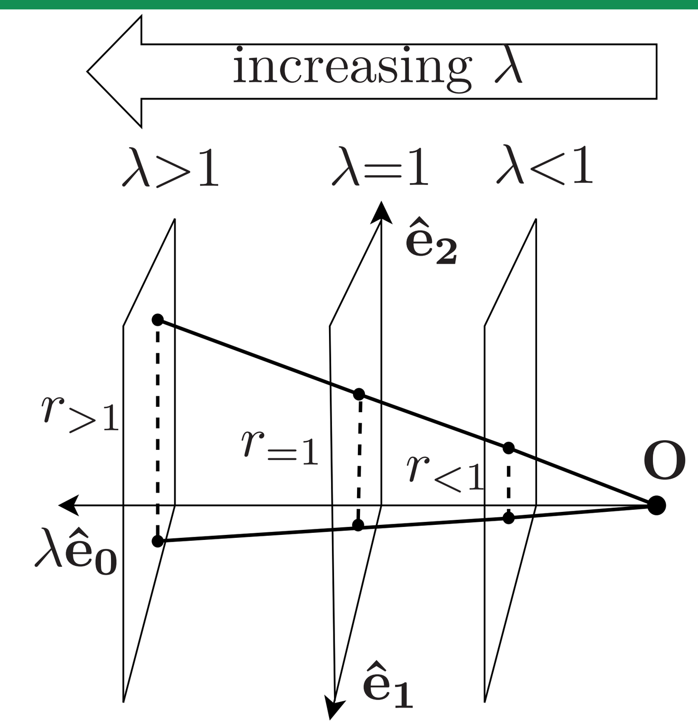
2. Uniform dilation with homogeneous coordinates

Uniform dilation by a factor of λ can be achieved with **homogeneous coordinates**. We add an **extra dimension** to Cartesian coordinates $\vec{r}$:

$$\vec{r} = (r^1, r^2, r^3) \rightarrow (\vec{s}, \lambda) = (s^1, s^2, s^3, \lambda)$$

Physical distances are now scaled by λ: $\vec{r} = \lambda\vec{s}$.

The diagram shows a plane moving along $\hat{\mathbf{e}}_0 \rightarrow \lambda$ increases → distance r increases.



3. Our Lagrangian

Express positions of atoms in homogeneous coordinates. Create fictitious dynamics with the following Lagrangian:

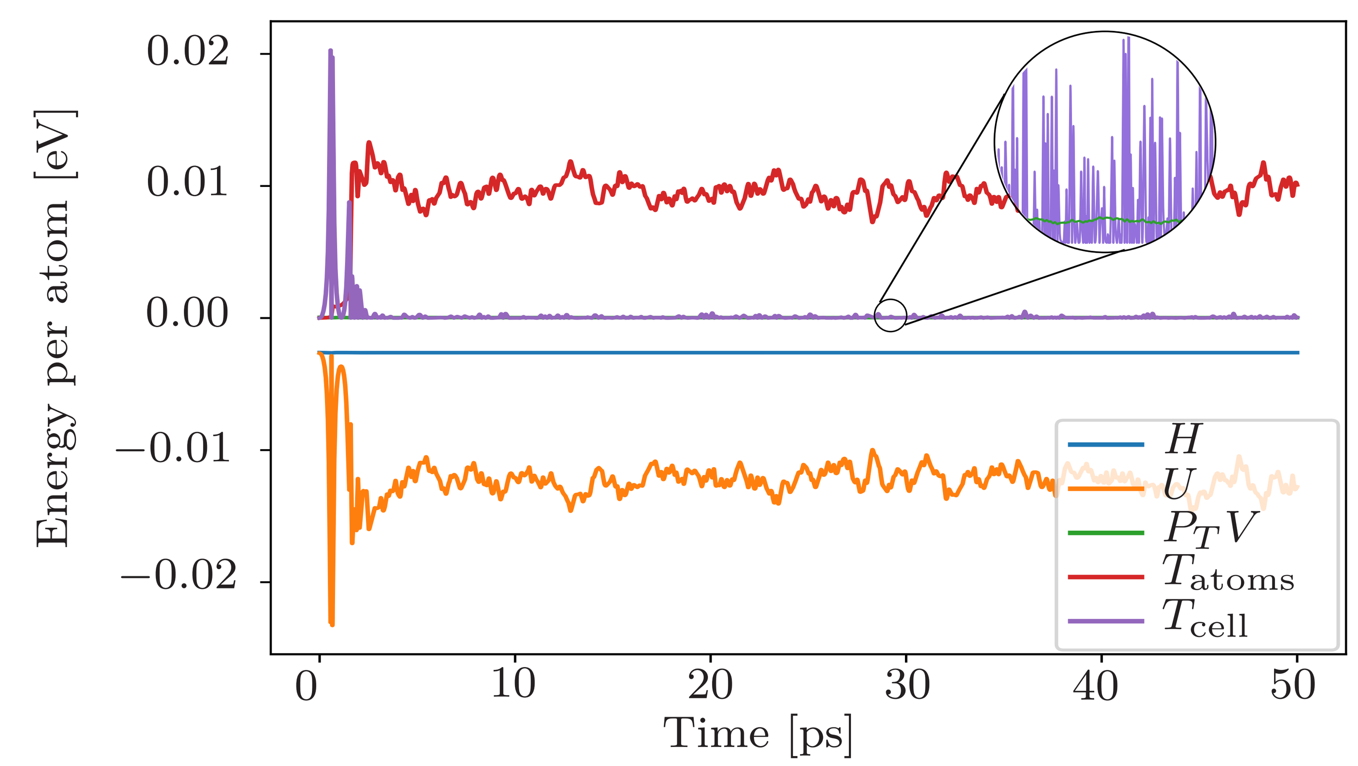
$$L = \underbrace{\sum_{i=1}^{N} \frac{1}{2} m \dot{\vec{s}}_i^{\,2}}_{T_{\text{atoms}}} + \underbrace{\frac{1}{2} W \dot{\lambda}^2}_{T_{\text{cell}}} - \underbrace{\left(U(\lambda, \{\vec{s}_i\}) + P_T V_0 \lambda^3 \right)}_{H_{\text{pot}}}$$

T_{atoms} - kinetic energy of atoms in three dimensions

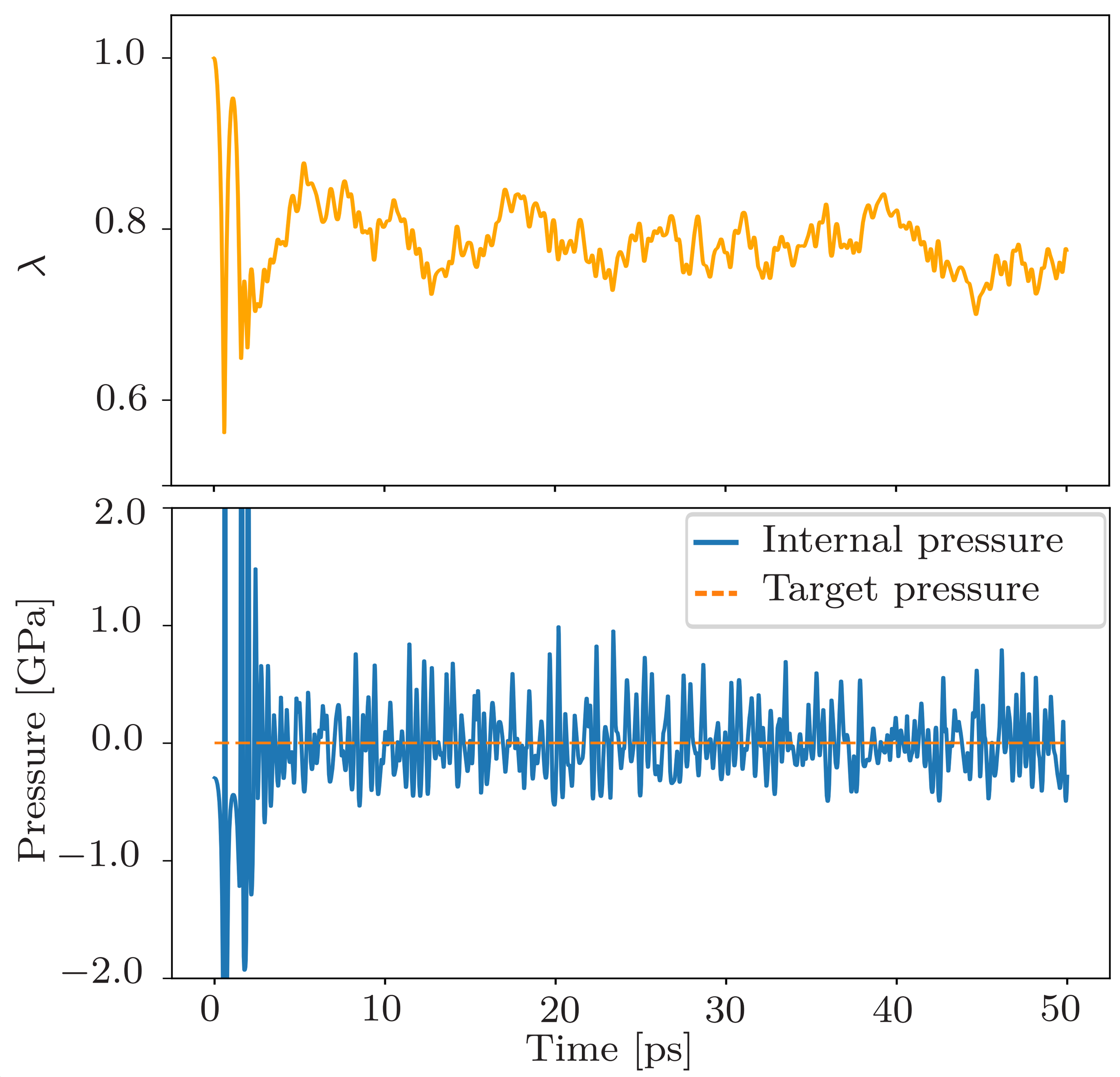
T_{cell} - kinetic energy of cell, correction for the fourth dimension
W - cell mass, inertia associated with fourth dimension

H_{pot} - enthalpic potential: $H_{\text{pot}} = U + P_T V$
U - potential energy, P_T - target pressure

The **conserved quantity** is enthalpy: $H = T_{\text{atoms}} + T_{\text{cell}} + H_{\text{pot}}$



4. Results



Equations of motion for our system:

$$m\ddot{s}_i^k = F_i^k \lambda, \quad \text{and} \quad W\ddot{\lambda} = \frac{3V}{\lambda}(P_{\text{int}} - P_T)$$

$F_i^k = -\dfrac{\partial U}{\partial s_i^k}$ - component k of force on i due to other atoms

$P_{\text{int}} = -\dfrac{\partial U}{\partial V}$ - internal pressure

Wrote MD code to numerically integrate system using the **velocity Verlet algorithm**, with Lennard-Jones potential for Argon.

- Enthalpy is **conserved**.
- When $P_{\text{int}} \neq P_T$, λ is accelerated. Scale volume in response to pressure differential → **barostat**.

5. Conclusions

Introducing **homogeneous coordinates** allows volume and positions to be decoupled while **conserving enthalpy** and stabilising at **target pressure**.

Further work: generalise algorithm to anisotropic stresses using Clifford Algebra [2].

6. References

[1] Hans C Andersen. Molecular dynamics simulations at constant pressure and/or temperature. *The Journal of chemical physics*, 72(4):2384–2393, 1980.

[2] C. Doran, D. Hestenes, F. Sommen, and N. Van Acker. Lie groups as spin groups. *Journal of Mathematical Physics*, 34(8):3642–3669, August 1993.