Non-equilibrium MD based on Generalised Langevin Equation

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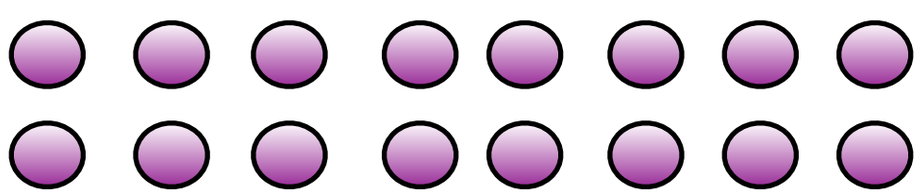
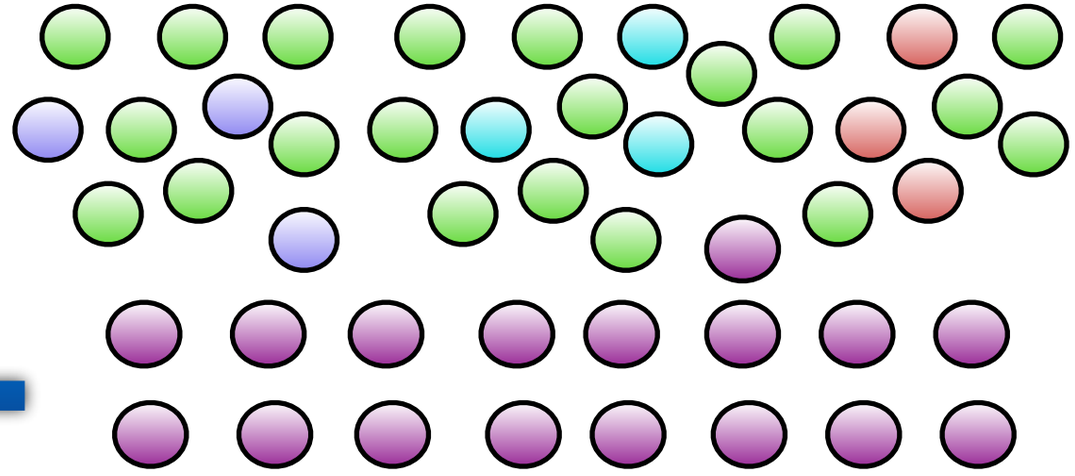
MD with exact thermostatting

- Many algorithms exist for equilibrium (e.g. canonical MD) thermostatting
- How would one run MD simulations at non-equilibrium?
- For instance, there is an energy transfer between different parts of the system
- and actual time scales of various processes are of interest?

solid at T_2



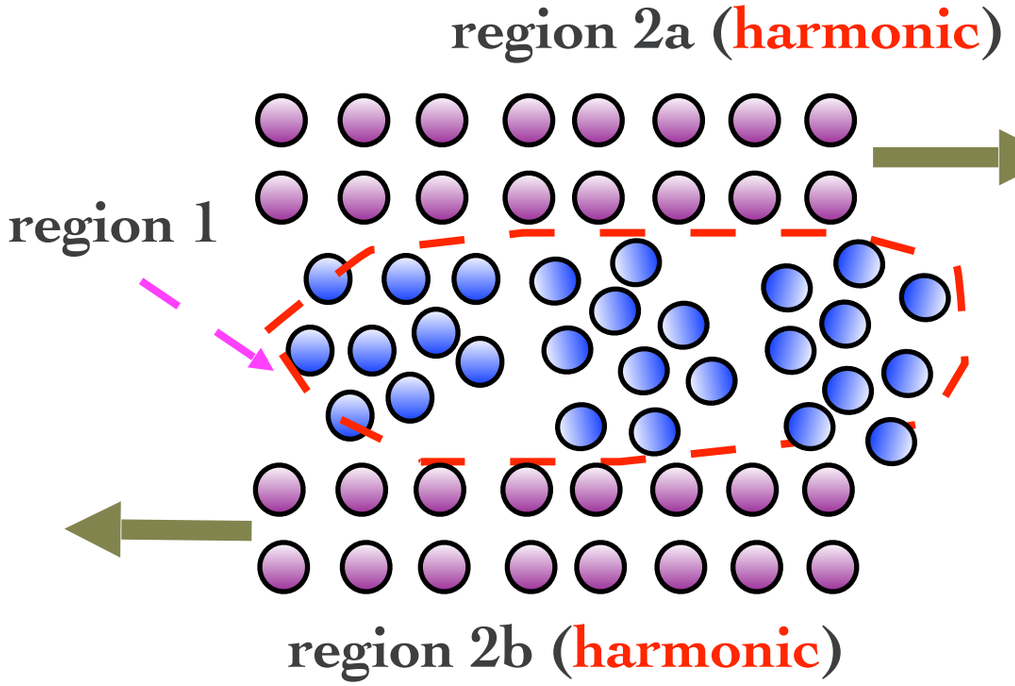
Tribology



Fluid at **T** it is supposed to be (likely, non-uniform)

solid at T_1

- If the atomistic **fluid is in contact with a harmonic solid** (solids) held at particular T (several T's), **an exact solution exists** based on the idea of **Generalised Langevin Equation (GLE)**
- Dissipation effects are accounted for exactly and happen at physically meaningful timescales → **natural thermostatting**



System's Hamiltonian

$$H = H_1 + H_2 + H_{12}$$ - system

$$H_2 = \frac{1}{2}\dot{u}_2^T m_2 \dot{u}_2 + \frac{1}{2}u_2^T \Phi_{22} u_2$$ - bath

$$H_{12} = h_2^T u_2$$ - their interaction

Equations of motion

$$\begin{cases} m_1\ddot{r}_1 = f_1 - \sum_{j\in 2} \dfrac{\partial h_j}{\partial r_1} u_j \\ m_2\ddot{u}_2 = -h_2(t) - \Phi_{22}u_2 \end{cases}$$

The bath atoms displacements can be calculated exactly:

$$x_2(t) = \dot{\Omega}_{22}(t)x_2(0) + \Omega_{22}(t)\dot{x}_2(0) - \int_0^t \Omega_{22}(t-\tau)V_2(\tau)d\tau$$

where

$$\Omega_{22}(t) = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda}\sin(\omega_\lambda t)$$

$$D_{22}e_\lambda = \omega_\lambda^2 e_\lambda$$

$$x_2 = m_2^{-1/2}u_2 \quad V_2 = h_2 m_2^{-1/2} \quad D_{22} = m_2^{-1/2}\Phi_{22}m_2^{-1/2}$$

Generalised Langevin Equation

$$m_1\ddot{r}_1 = \tilde{f}_1 + R_1 - \int_0^t \Gamma_{11}(t,t')\dot{r}_1(t')dt'$$

GLE

where $\tilde{f}_1 = f_1 + V_{12}(t)D_{22}^{-1}V_2(t)$ **- corrresponds to the instantaneous response of atoms in 2 on the positions of atoms in 1 ("pressure propagation" term)**

$\Gamma_{11}(t,\tau) = V_{12}(t)\Pi_{22}(t-\tau)V_{21}(\tau)$ **- this is the friction kernel depending on the "memory" of previous velocities of atoms in**

$$\Pi_{22}(t) = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2}\cos(\omega_\lambda t)$$

- matrix, related to the phonon G response F of the bath

Random force

$$R_1(t) = -V_{12}(t)\left[\dot{\Omega}_{22}(t)x_2(0) + \Omega_{22}(t)\dot{x}_2(0) + \Pi_{22}(t)V_2(0)\right]$$

$\rho_2(x_2,p_2) = Z^{-1}e^{-\beta(H_2+H_{12})}$ **- the bath is canonical**

$$\langle R_1(t)\rangle = 0$$
$$\langle R_1(t)R_1^T(t')\rangle = k_B T\,\Gamma(t,t')$$

- fluctuation-dissipation theorem

Implementation

$$m_1\ddot{r}_1 = \tilde{f}_1 + R_1 - \int_0^t \Gamma_{11}(t,t')\dot{r}_1(t')dt'$$

- **Difficulties:** (a) colour noise
  (b) memory (the integral term) - impossible to run for long
- **Solution:**

- The FT of the actual **response function**

$$\Pi_{22}(t) = \sum_\lambda \frac{e_\lambda e_\lambda^\dagger}{\omega_\lambda^2}\cos(\omega_\lambda t) \quad \Longleftrightarrow \quad \Pi_{22}(\omega) = \frac{2}{|\omega|}\mathrm{Im}G_{22}(\omega^+)$$

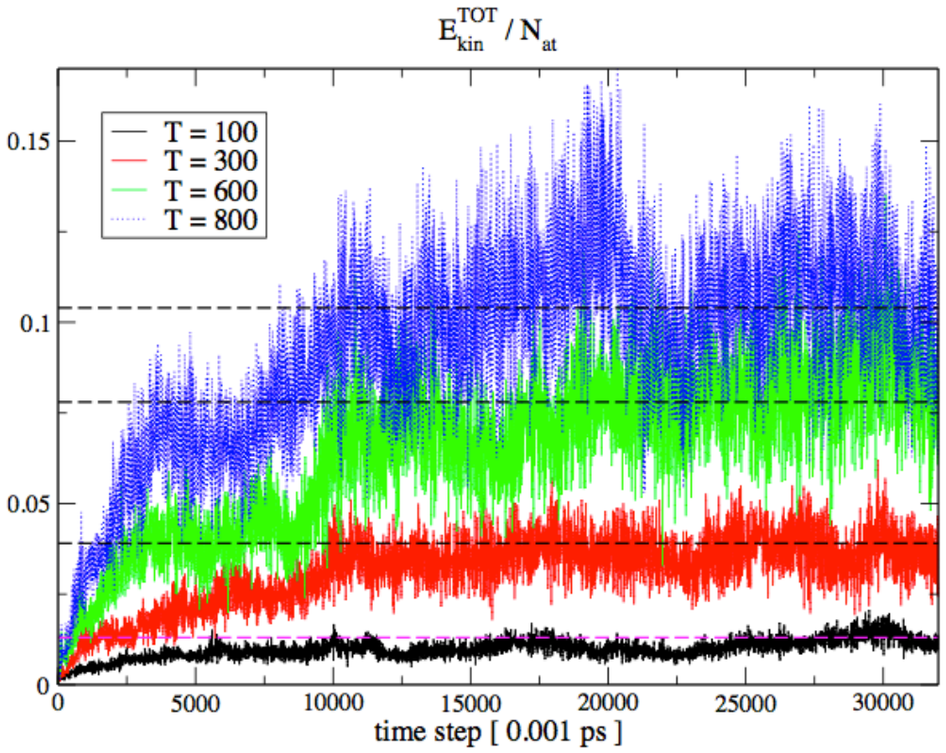
  is calculated from the **real bath** using its actual force field.

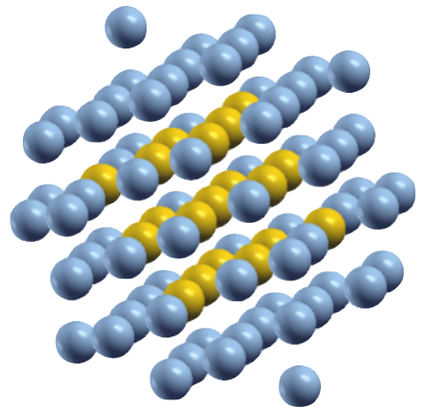
- The actual infinite bath(s) is(are) replaced by a **finite number of fictitious oscillators** as to provide an **exact mapping** of $\Pi_{22}(\omega)$ in the Fourier space.

- This results in a finite number of **1st order stochastic DEs** (MD equations) with white noises.
- These are solved by:
  (a) converting them into the corresponding Fokker-Planck equation
  (b) solving it for a small time step Δt
  (c) writing equivalent white noise stochastic discretised equations that is the required integration scheme

- **Implemented in LAMMPS (serial)**

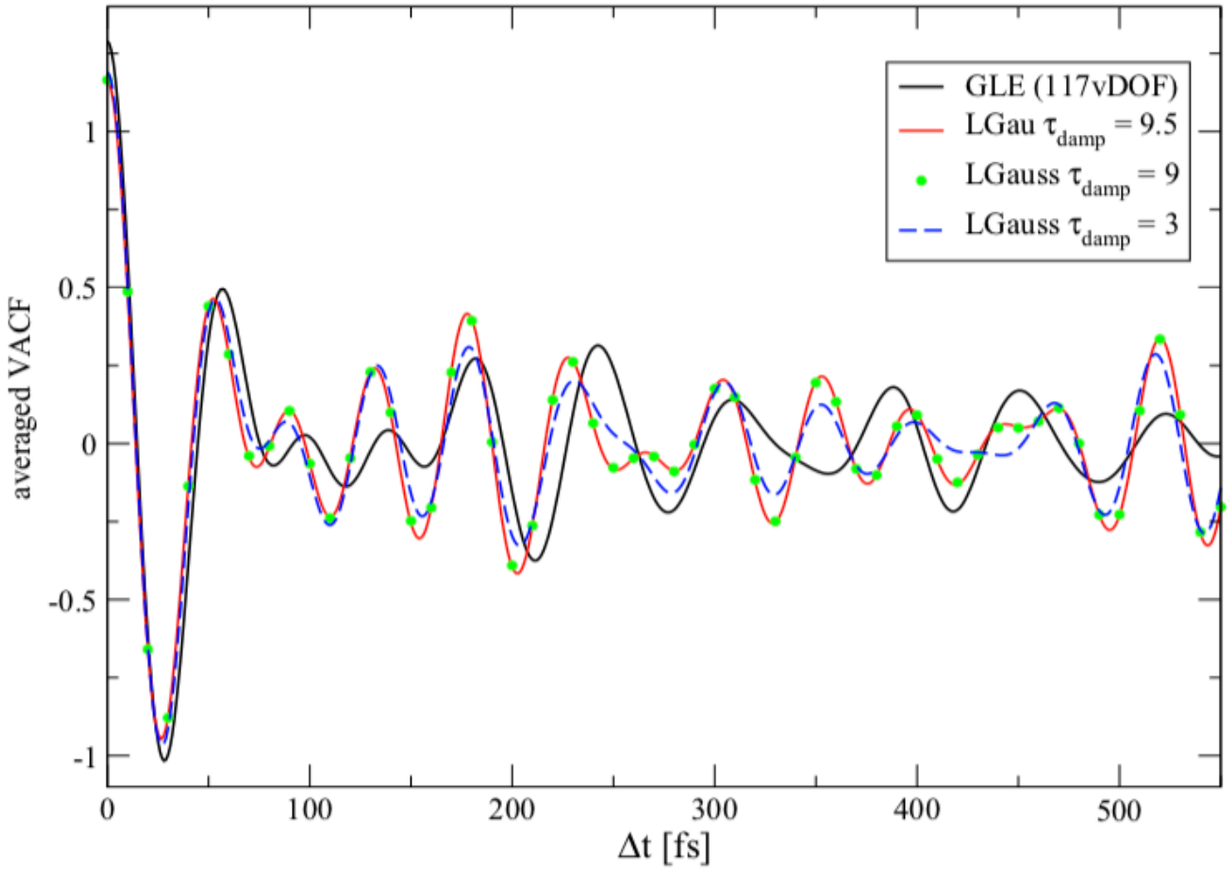
Thermalisation of a system



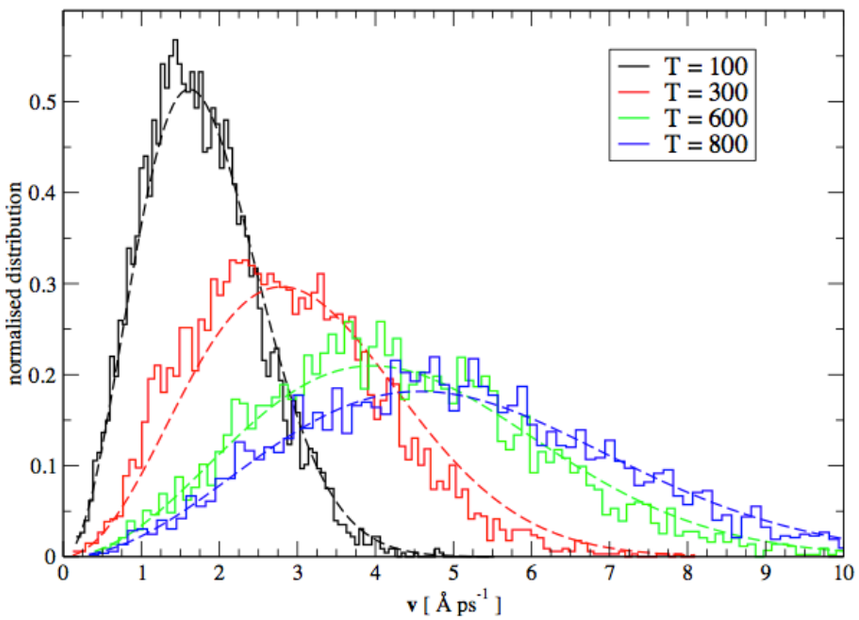


LJ solid

Velocity AC function (VACF)



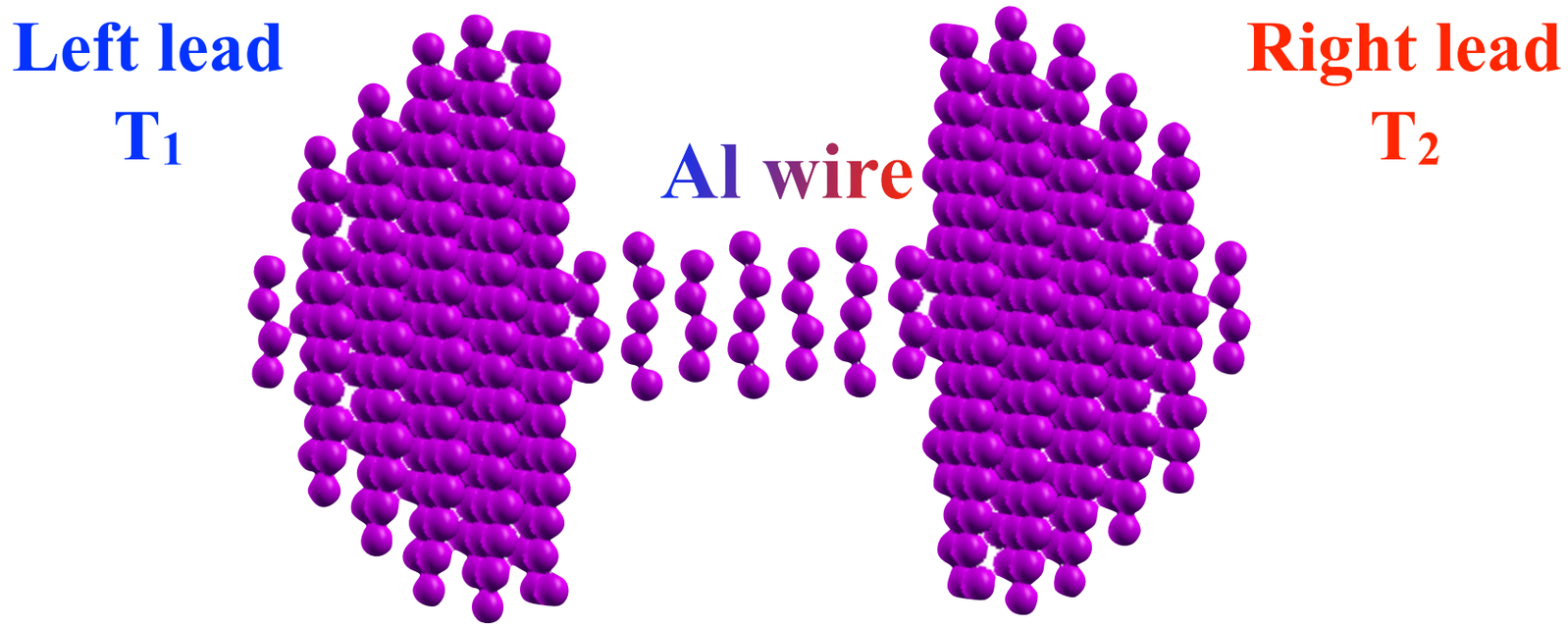
Distribution of atomic velocities



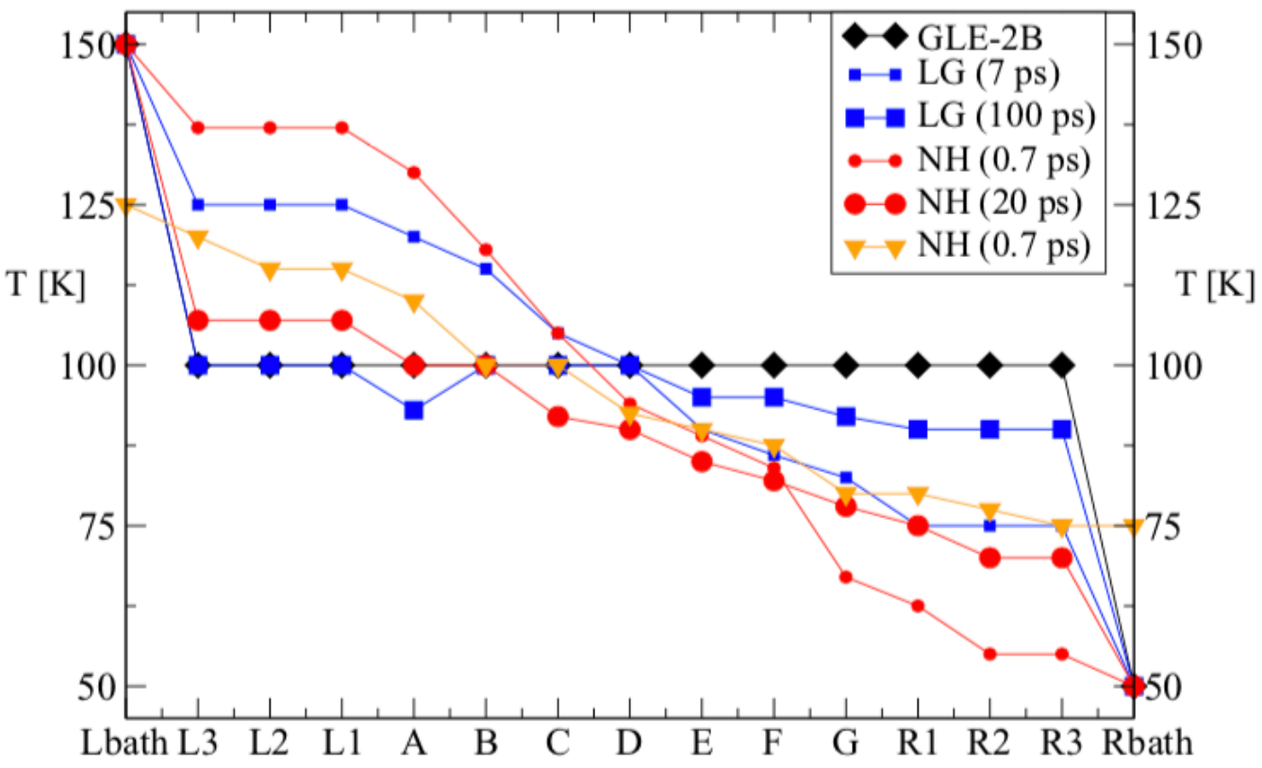
$$f(v) = \left(\frac{m\beta}{2m}\right)^{3/2} 4\pi v^2 e^{-\beta m v^2/2}$$

Conventional Langevin dynamics requires priory knowledge of the friction constant; our method is *ab initio* in nature.

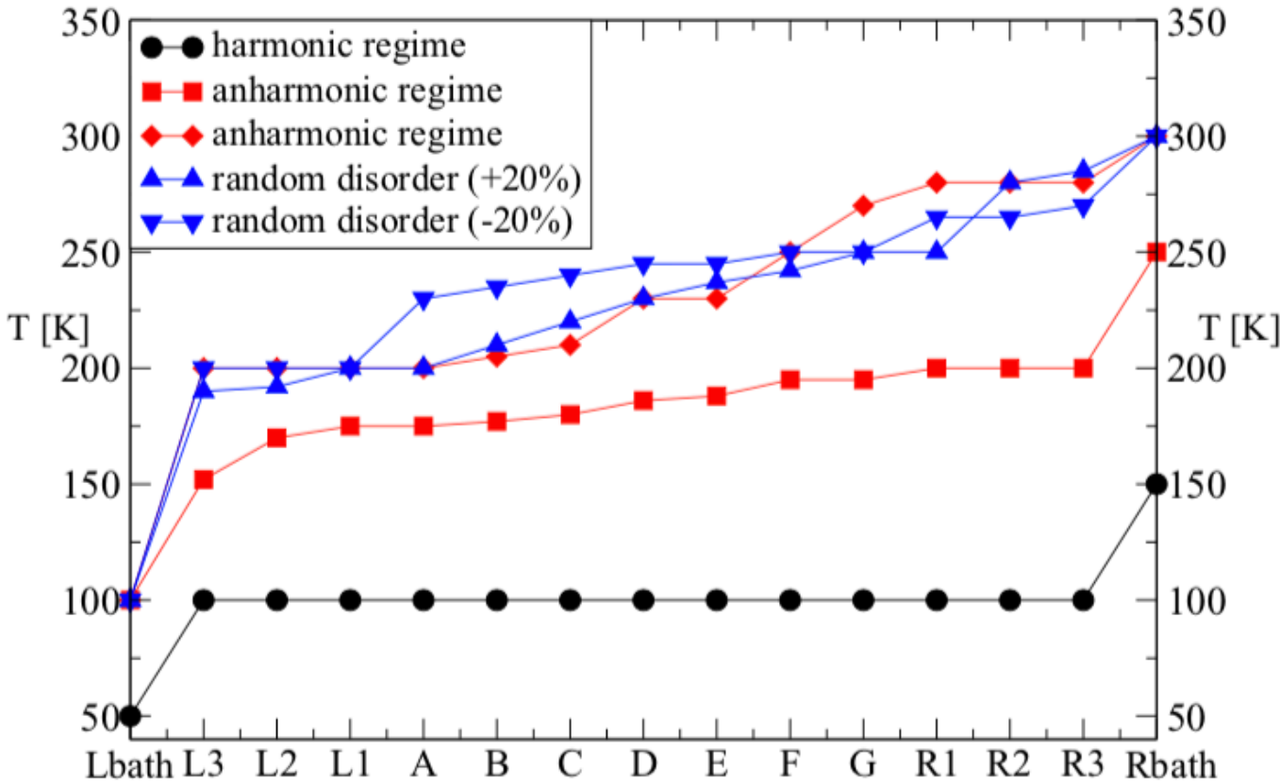
Thermal transport



Low T gradients



Large T gradients



Conclusions

- GLE opens a way to perform physically meaningful thermostatting in MD simulations
- It is applicable both to equilibrium and non-equilibrium
- The structure of the central system could be arbitrary (e.g. liquid molecules)
- LAMMPS implementation already exists; DFT implementation is not, but can be easily created

Main publications

L. Kantorovich - Phys. Rev. B, v. 78, No. 094304 (2008).

L. Kantorovich and N. Rompotis - Phys. Rev. B, v. 78, No. 094305 (2008).

L. Stella, C. D. Lorenz, and L. Kantorovich - Phys. Rev. B, v. 89, 134303 (2014)

H. Ness, L. Stella, C.D. Lorenz, and L. Kantorovich - Phys. Rev. B 91, 014301 (2015).

H. Ness, A. Genina, L. Stella, C.D. Lorenz, and L. Kantorovich - Phys. Rev. B, v. 93, 174303 (2016)

H. Ness, L. Stella, C. D. Lorenz, and L. Kantorovich - J. Chem. Phys. 146, 164103 (2017)