

# Ensemble Lecture

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# References

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<http://lammps.sandia.gov/doc/Manual.html>
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[icme.hpc.msstate.edu/mediawiki/index.php/LAMMPS\\_tutorials](http://icme.hpc.msstate.edu/mediawiki/index.php/LAMMPS_tutorials)
- PLUMED manual  
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# Molecular Dynamics

You should also be aware that while MD is fairly simple to operate as a tool, the real skill comes from practice, experience and understanding of the underlying physics and statistical mechanics. You can compare it to say, a hammer and chisel: almost everybody can wield the hammer and split a piece of stone, but that doesn't automatically make you a sculptor.

- Axel Kohlmeyer

# Outline

- 1 Ensemble
- 2 Thermostats
- 3 Take Home Message

# Ensembles

# Definitions

- Micro-state: a system configuration uniquely defined by the atoms' positions and velocities and cell volume.
- Ensemble: assembly of all possible micro-states that are compatible with the macroscopic constraints.
- Thermodynamic observable: average of the microscopic value of a quantity, weighted by the probability of that micro-state to be visited within the defined ensemble.

# Ergodicity principle

In an isolated system, an infinitely long trajectory will visit every accessible micro-state with equal probability

$$\langle A \rangle = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t A(t') dt' \simeq \frac{1}{M} \sum_{i=1}^M A(t_i)$$

where  $M$  is the number of timesteps performed during the simulation. This is therefore the theoretical justification for using MD simulations to calculate and predict thermodynamic properties of materials.



# Thermodynamic ensembles

- An ensemble is uniquely defined by imposing any three of the following quantities: number of atoms ( $N$ ), chemical potential ( $\mu$ ), energy ( $E$  or  $H$ ), volume ( $V$ ), pressure ( $P$ ), external stress, ( $\sigma$ ) and temperature ( $T$ ).
- Microcanonical - ( $N, V, E$ )
- Canonical - ( $N, V, T$ )
- Isobaric - ( $N, P, H$ )
- Isothermal - isobaric ( $N, P, T$ )
- Isotension - ( $N, \sigma, H$ )
- Isothermal - isotension ( $N, \sigma, T$ )
- Grancanonical - ( $\mu, V, T$ )

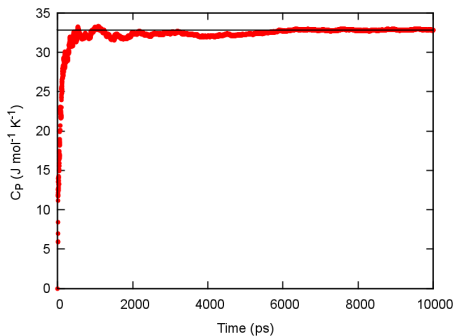
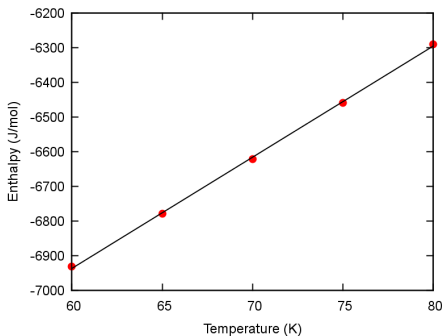
# Self diffusion coefficient of SPC/FW water @ 300K with a 25Å box

# Self diffusion coefficient of SPC/FW water @ 300K with a 25Å box

	D [ $10^{-5}$ cm <sup>2</sup> /s]
Experiment	2.30
NVE	2.45
NVT - CSVR	2.47
NVT - Nosé-Hoover	2.46
NPT - MTTK	2.44
NVT - Langevin	1.09*

# Ar specific heat @ 1atm and 70K

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P = \frac{\langle \delta H^2 \rangle_{NPT}}{k_B T^2}$$



# Ar specific heat @ 1atm and 70K

	slope	fluct.
Berendsen	31.98	4.36
Andersen	31.89	24.76
Langevin	32.16	34.83
Stochastic	32.07	32.80
Exp.	29.71	29.71

# Thermostats

# Temperature

- The microcanonical ensemble is of limited interest for most of the applications and therefore we need to control the microscopic quantities in such a way that the desired ensemble is reproduced.
- In analogy with the ideal gas, the instantaneous temperature of a system with  $N$  particles can be calculated from

$$K(t) = \frac{1}{2} \sum_{i=1}^N m_i v_i(t)^2 = \frac{1}{2} k_B T n_{dof}$$

where  $n_{dof}$  is the number of degrees of freedom.

- Analogously we can also define that the system has reached thermal equilibrium if the velocity distribution function,  $P(v)$ , is the Maxwell-Boltzmann function (for every species)

$$P_T(v) = 4\pi N v^2 \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}}$$

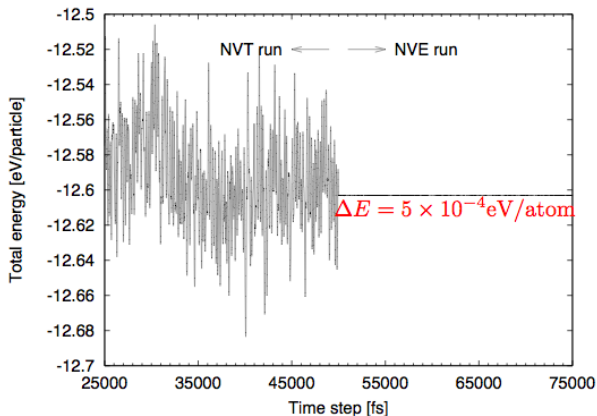
# Thermostats I

- The instantaneous temperature depends only on the atoms' velocities.
- Several algorithms have been proposed to modify the atoms' velocities to control the temperature but not all of them give the right sampling of the canonical ensemble.
  - Velocity rescaling
  - Berendsen
  - Andersen
  - Langevin
  - Nosé–Hoover
  - Stochastic rescaling
- Desirable features are robustness and preservation of the correlations



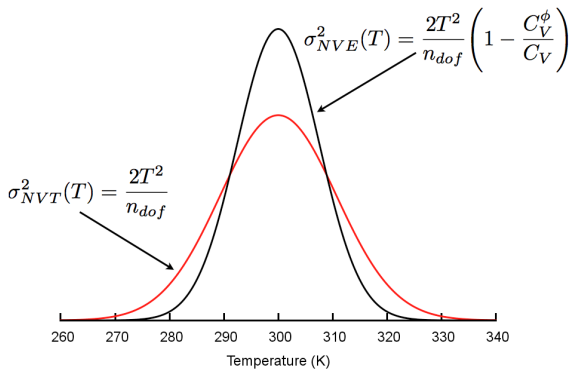
# Thermostats II

## Comparison between a *NVT* and *NVE* simulations



# Thermostats III

In the canonical ensemble (NVT) the temperature is not constant but it has a well defined distribution



# Velocity rescaling I

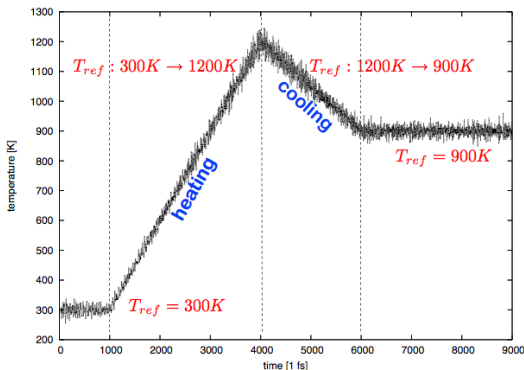
- Let's define  $T_{ref}$  the reference temperature at which we want to perform the simulation.
- At every cycle of the integration of the equation of motion we can rescale the atoms' velocities by a factor  $\xi$  to obtain the desired temperature

$$\xi = \sqrt{\frac{T_{ref}}{T(t)}}$$

# Velocity rescaling II

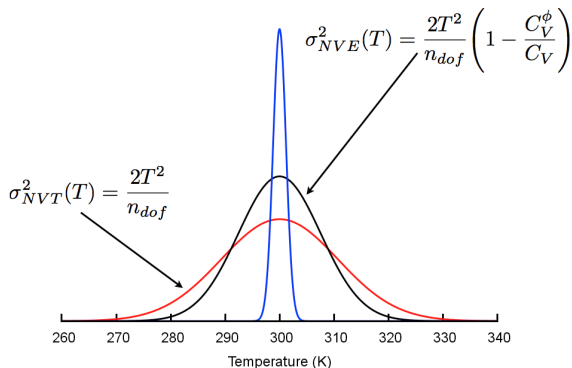
- By changing the reference temperature with time, we can easily heat/cool the system

$$\xi = \sqrt{\frac{T_{ref}(t)}{T(t)}}$$



# Velocity rescaling III

- This method is extremely robust and always work, but it does NOT produce the right sampling of the canonical ensemble!



# Berendsen thermostat I

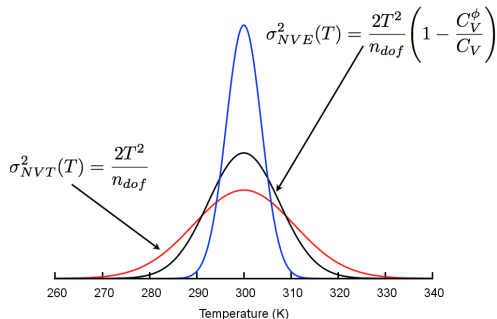
- An algorithm which is less harsh on the system is the **Berendsen thermostat**
- Here the temperature is gradually brought to the reference value.
- The velocity of this drag is determined by a parameter,  $\tau_T$ , which is usually called the **thermostat relaxation time**.

$$\xi = \left[ 1 + \frac{\delta t}{\tau_T} \left( \frac{T_{ref}}{T(t)} - 1 \right) \right]^{\frac{1}{2}}$$

- Is evident that in the limit of  $\tau_T = \delta t$  this reduces to the velocity rescaling and in the limit of  $\tau_T \rightarrow \infty$  this reduces a microcanonical simulation.

# Berendsen thermostat II

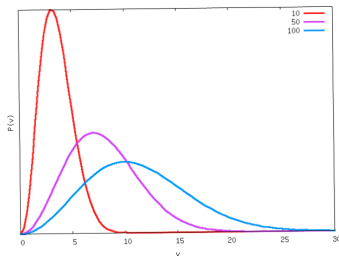
- Like the velocity rescaling, the Berendsen thermostat does NOT produce the right sampling of the canonical ensemble!



- The width of the distribution depends on  $\tau_T$ , but at most will resemble the microcanonical distribution.

# Andersen thermostat I

- The velocities equilibrium distribution for a system in thermal equilibrium at a given temperature is known analytically and this information to design an algorithm that produces the right sampling of the canonical ensemble.
- We can do this by randomly selecting a particle of the system and reassigning its velocity according to the Maxwell-Boltzmann distribution.



$$P_T(v) = 4\pi v^2 \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}}$$



# Andersen thermostat II

- This thermostat can be imagined as a sequence of random collisions between the atoms of the system with fictitious particles of the “heat-bath”.
- Andersen demonstrated that to achieve the right sampling of the canonical ensemble the frequency of these collisions has to be

$$\omega \propto \frac{2\eta}{3k_B\rho^{1/3}N^{2/3}}$$

where  $\eta$  is the thermal conductivity of the material and  $\rho$  its number density. He also showed that after such collisions each component of the atom's velocity should be taken from

$$p(v_{ix}) = \left( \frac{m}{2\pi k_B T} \right)^{1/2} e^{-\frac{mv_{ix}^2}{2k_B T}}$$

# Andersen thermostat III

- Advantages of this method are:
  - Easy implementation.
  - It gives the right ensemble averages.
- Disadvantages of this method are:
  - It doesn't conserve the system momentum.
  - It decorrelates the velocities making the trajectory unphysical.
  - The definition of the frequency of the collisions is not straightforward.

# Langevin thermostat I

- This thermostat mimics the presence of a fictitious "heat bath particles" that constantly collide with the atoms in the simulation.
- The presence of the "heat bath particles" causes a viscous damping on the velocities plus random changes in direction and magnitude

$$\dot{v}_i = \frac{v_i(\delta t) - v_i(0)}{\delta t} = \frac{f_i}{m_i} - \gamma v_i(0) + R_i$$

where  $\gamma$  is the friction coefficient and  $R$  a random number.

# Langevin thermostat II

- If we manipulate a bit this equation we get

$$v_i(\delta t) = \frac{f_i}{m_i} \delta t + c_1 v_i(0) + c_2 \Gamma$$

where  $\Gamma$  is a random number from a Gaussian distribution with variance 1.

- It can then be demonstrated that if we take

$$\begin{aligned} c_1 &= e^{-\gamma \delta t} \\ c_2 &= \sqrt{\frac{(1-c_1)^2 k_B T}{m_i}} \end{aligned}$$

we reproduce the correct canonical ensemble.

- It's interesting to analyse the limits of this thermostat:
  - For  $\gamma \rightarrow 0$  we recover the NVE equations of motion
  - For  $\gamma \rightarrow \infty$  we have a "Brownian Dynamics" simulation

# Nosé–Hoover I

- The Nosé–Hoover thermostat uses the same idea of the velocity rescaling of having a rescaling coefficient that is used to keep the temperature constant
- This is done in a rigorous way by explicitly treating the ”thermostat” as an extra ”particle” and solving the equation of motion for its degrees of freedom
- The Hamiltonian of the system is then written as

$$\mathcal{H}_{\mathcal{NH}} = \sum_{i=1}^N \frac{m_i \mathbf{v}_i^2}{2} + U(\mathbf{x}^N) + \frac{Q\xi^2}{2} + 3Nk_B T \ln s$$

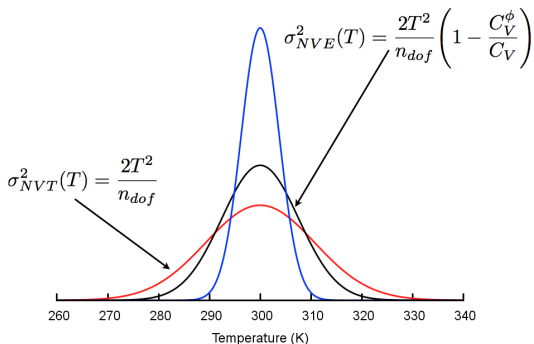
- $Q$  corresponds to the ”mass” of the thermostat and  $s$  to its ”position”

# Nosé–Hoover II

- The Nosé–Hoover thermostat was the first one to have all the good properties:
  - It gives the right ensemble
  - It preserves the correlations
- It works fine for most of the systems but there are some pathological cases where it fails and for those a "chain of thermostats" has to be used.
- The thermostat "mass" has to be chosen carefully in order to prevent artefacts
- A "chain" of thermostats can solve most of the problems.

# Stochastic rescaling I

- This is so simple that I always wonder why it took more than 50 years of MD simulation to come up with it
- Let's recall the Berendsen thermostat and why it is not giving the right temperature distribution



# Stochastic rescaling II

- An intuitive way to solve this problem is to randomly take the reference temperature at every timestep from a Gaussian distribution centred on the desired temperature and with the canonical width
- A small disadvantage of this thermostat is that there's no true "conserved" quantity. However, a bookkeeping term can be defined for the purpose of controlling the accuracy of the integration of the equation of motion.



# Stochastic rescaling III

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## Canonical sampling through velocity rescaling

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TABLE I. The diffusion coefficient  $D$  of water at 300 K, as a function of the relaxation time  $\tau$  of the thermostat. For a comparison, also the value obtained from an  $NVE$  trajectory is shown.

$\tau$ (ps)	$D$ ( $10^{-5}$ cm <sup>2</sup> /s)
0.002	$3.63 \pm 0.01$
0.02	$3.44 \pm 0.06$
0.2	$3.51 \pm 0.05$
2.0	$3.53 \pm 0.01$
$NVE$	$3.47 \pm 0.03$

# Take Home Message

# Take home message I

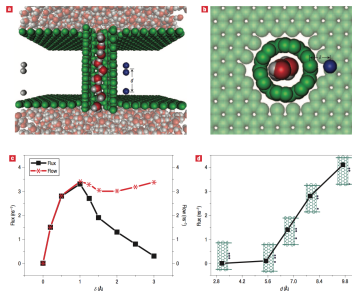
- The set up can grossly affect the results of your simulations
  - System size / starting configuration
  - Simulation length
  - ...
- Always check whether the thermostat / barostat settings do not affect the results of your calculations
- Every code has bugs, always check your results against known answers or **preferably** classical/statistical thermodynamics

# Take home message II

## LETTERS

### A charge-driven molecular water pump

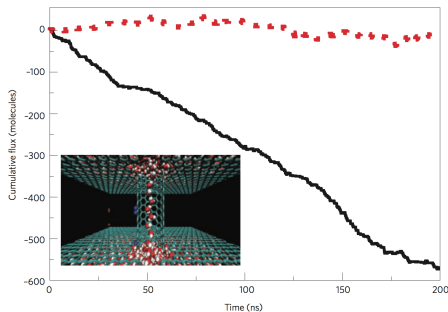
XIAOJING GONG<sup>1,2</sup>, JINGYUAN LI<sup>3</sup>, HANGJUN LU<sup>1,2,4</sup>, RONGZHENG WAN<sup>1</sup>, JICHEN LI<sup>5</sup>, JUN HU<sup>1,6\*</sup>  
AND HAIPING FANG<sup>1\*</sup>



**Figure 1** Introduction to the main system and the flows and fluxes for different charge arrangements in the main system. **a**, Side view of the main system. The green spheres are the carbon atoms of the nanotube and the grey/blue arrows (note that the figure is not drawn to scale). The blue points are the positive charges (0.5e, 0.5e and 1.0e, from top to bottom), and the grey ones are negative charges to neutralize the positive charges near the channel. Water molecules are shown in sphere representation with oxygen in red and hydrogen in grey. **b**, Top view of the same arrangement. **c**, Flow and flux for different radial distance  $\delta$  for  $\delta = 7.0$  Å. **d**, Flux with respect to  $\delta$  for  $\delta = 0.5$  Å.

# Take home message III

Static charges cannot drive a continuous flow of water molecules through a carbon nanotube



Default settings for:

- Charged groups
- Berendsen thermostat
- Neighbours list update

- Gong *et al.*; *Nature Nanotech.* 2007, **2**, 709-712.
- Wong-ekkabut; *Nature Nanotech.* 2010, **5**, 555-557.