

# **Stat-mech on a computer: Simulating and sampling**

MSE 421 - Ceriotti

# Averages in the canonical ensemble

- The canonical ensemble describes a system in contact with a thermal reservoir at temperature  $T = 1/k_B\beta$
- Averages of observables can be computed as integrals over the canonical Boltzmann distribution

$$\langle A \rangle = \int d\mathbf{q} d\mathbf{p} P(\mathbf{p}, \mathbf{q}) A(\mathbf{p}, \mathbf{q}) \quad \langle A \rangle = \sum_{\nu} A_{\nu} P_{\nu}$$

- The goal of a simulation is to perform these averages/integrals by sampling **the states that have a non-negligible probability**

- Classical dynamics of a system of atoms with positions  $\mathbf{q}$  and momenta  $\mathbf{p}$ , described by the Hamiltonian

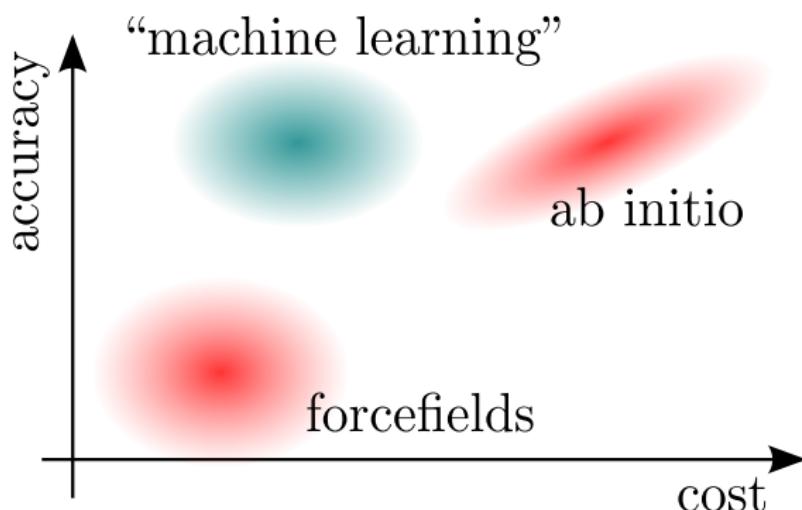
$$H(\mathbf{p}, \mathbf{q}) = K(\mathbf{p}) + V(\mathbf{q}) = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + V(\mathbf{q})$$

- We assume  $V$  is given (force fields, electronic structure calculation)
- In all cases, strictly Born-Oppenheimer
- Nuclei are treated as classical, distinguishable particles
- The configuration and momentum parts of  $P(\mathbf{p}, \mathbf{q})$  factor out, and the momentum part  $P(\mathbf{p})$  is trivial

$$P(\mathbf{p}, \mathbf{q}) = e^{-\beta H(\mathbf{p}, \mathbf{q})} = P(\mathbf{p}) \cdot P(\mathbf{q}) = \frac{e^{-\beta \sum_i \frac{\mathbf{p}_i^2}{2m_i}}}{\int d^{3N} \mathbf{p} e^{-\beta \sum_i \frac{\mathbf{p}_i^2}{2m_i}}} \cdot \frac{e^{-\beta V(\mathbf{q})}}{\int d^{3N} \mathbf{q} e^{-\beta V(\mathbf{q})}}$$

# Potentials, potentials, potentials!

- Actually, constructing a good model for  $V(\mathbf{q})$  is the most crucial step!  
Accuracy/cost trade-off



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- Actually, constructing a good model for  $V(\mathbf{q})$  is the most crucial step!  
Accuracy/cost trade-off
- Empirical forcefields try to represent interactions with “simple” functional forms. Time-consuming and error-prone fitting procedure, but then easy to use and inexpensive. A must for large systems

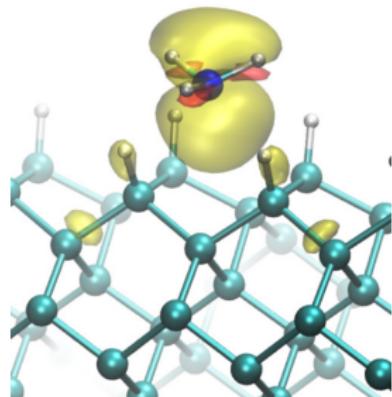
$$V(\mathbf{q}) \sim \underbrace{\sum_{ij} \frac{z_i z_j}{|\mathbf{q}_i - \mathbf{q}_j|}}_{\text{electrostatics}} + \underbrace{\sum_{\text{bonds}} k_i (\mathbf{q}_i - \mathbf{q}'_i)^2}_{\text{bonded terms}} - \underbrace{\sum_{ij} \frac{A_{ij}}{|\mathbf{q}_i - \mathbf{q}_j|^6}}_{\text{dispersion}} + \dots$$



# Potentials, potentials, potentials!

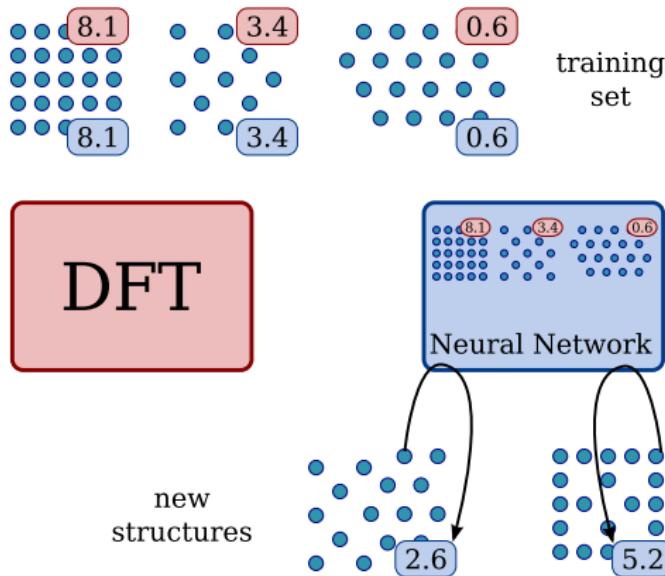
- Actually, constructing a good model for  $V(\mathbf{q})$  is the most crucial step!  
Accuracy/cost trade-off
- Ab initio calculations offer transferability and predictive power by solving on-the-fly the electronic structure problem: expensive! Typically limited to few 100's atoms

$$\hat{H}(\mathbf{q}) \Psi_{\text{electrons}} = E \Psi_{\text{electrons}} \quad \rightarrow \quad V(\mathbf{q}) \equiv E$$



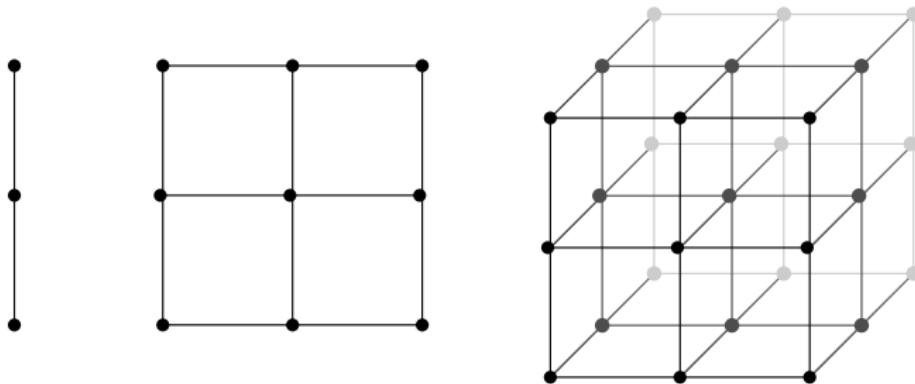
# Potentials, potentials, potentials!

- Actually, constructing a good model for  $V(\mathbf{q})$  is the most crucial step!  
Accuracy/cost trade-off
- Recent developments try to “machine-learn” ab initio energies, trying to get nearly as accurate with much less effort



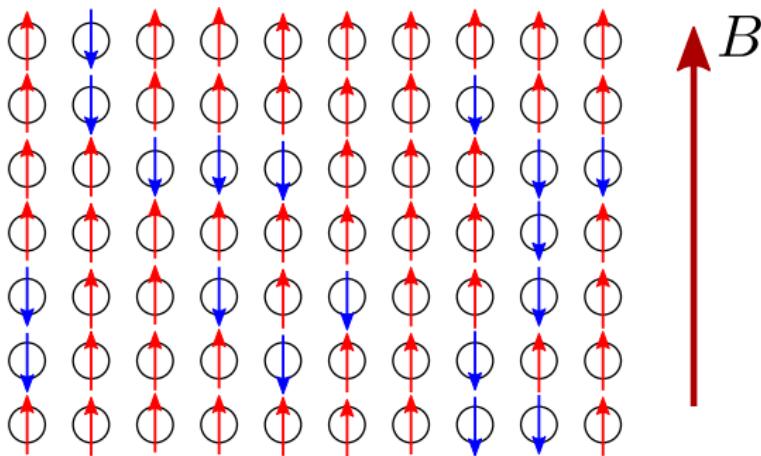
# The curse of dimensionality

- Statistical averaging is basically just integration. Should be easy to do numerically....
- Performing the integral by quadrature is impractical, because the number of grid points grows **exponentially** with dimensionality



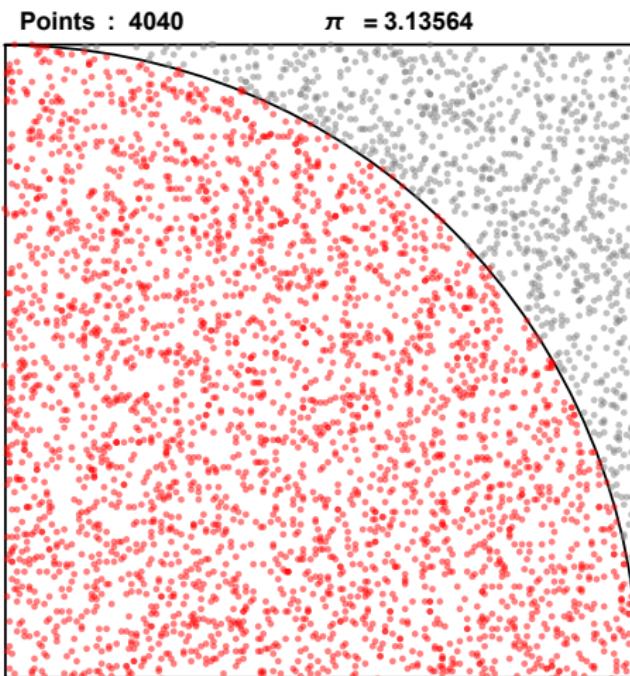
# Sampling by enumeration

- Now think about computing averages for a spin lattice with  $N$  sites. Enumeration of all possible spin states also grows exponentially:  $2^N$  possible configurations must be traversed to cover all possibilities!
- What saves us is (1) that often just a small fraction of microstates have  $P_\nu \gg 0$  and (2) that we don't need to sample *all* states, only a representative fraction



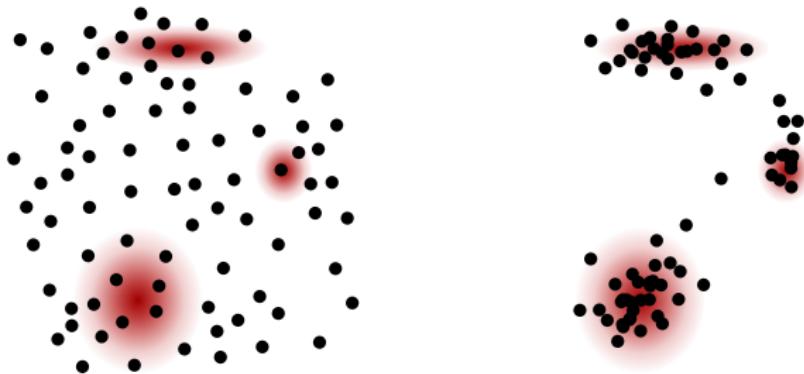
# Monte Carlo integration

- To compute integrals without a grid, we could just generate uniformly distributed random values, and compute the value of the function there
- For instance, one can use this to compute the area of a circle relative to an enclosing square by tossing random values on a square, and counting how many have  $x^2 + y^2 < 1$  [the fraction converges to  $\pi/4$ ]



# Integration by importance sampling

- We can compute  $\int f(x) dx$  as  $\text{area} \times \sum_i f(x_i) / N$
- One could think of using the same trick: randomly-distributed points  $\mathbf{q}_i$ , and computing  $\langle A \rangle \approx \sum_i P(\mathbf{q}_i) A(\mathbf{q}_i) / \sum_i P(\mathbf{q}_i)$ . But  $P(\mathbf{q})$  is often very irregular and most points do not contribute to the integral
- Ideally, one would want to generate  $\mathbf{q}_i$ 's distributed as  $P(\mathbf{q})$ , and compute  $\langle A \rangle \approx \frac{1}{M} \sum_i A(\mathbf{q}_i)$ . This is **importance sampling**.



# Ergodicity of sampling

- Underlying assumption behind all of this is **ergodicity**:

$$\lim_{M \rightarrow \infty} \frac{1}{M} \sum_i A(\mathbf{q}_i) = \int d\mathbf{q} P(\mathbf{q}) A(\mathbf{q})$$

- This is an additional condition, that is very hard to prove in practice.
- We always have a finite  $M$ , so the question is: *how much* ergodic is the trajectory? How can we “measure” ergodicity?
- As we saw, this is closely related to the statistical error on  $\langle A \rangle$
- The key tool to assess the ergodicity of a trajectory for computing  $\langle A \rangle$  is the autocorrelation function

$$c_{AA}(t) = \langle A(0) A(t) \rangle$$

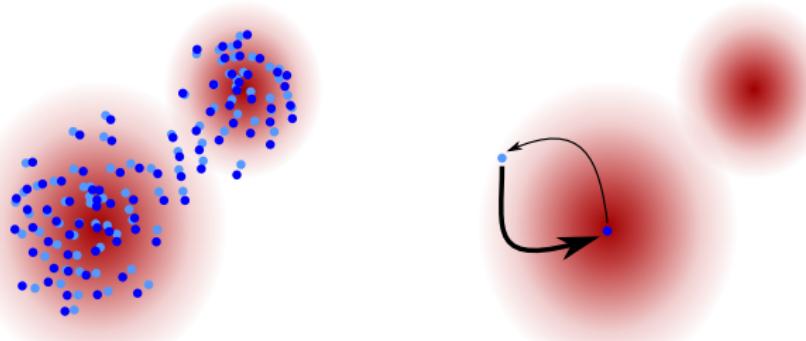
# Using Monte Carlo for importance sampling

- How to generate a sequence of points distributed as  $P(\mathbf{q})$ ?
  - Monte Carlo moves  $\mathbf{q} \rightarrow \mathbf{q}'$  that generate a new point given a previous point consistent with  $P$ .
  - The move (typically) contains some randomness: probability  $p(\mathbf{q} \rightarrow \mathbf{q}')$
- **Necessary** (& “sufficient”) condition:  $P$  invariant under the move

$$\int d\mathbf{q} P(\mathbf{q}) p(\mathbf{q} \rightarrow \mathbf{q}') = P(\mathbf{q}')$$

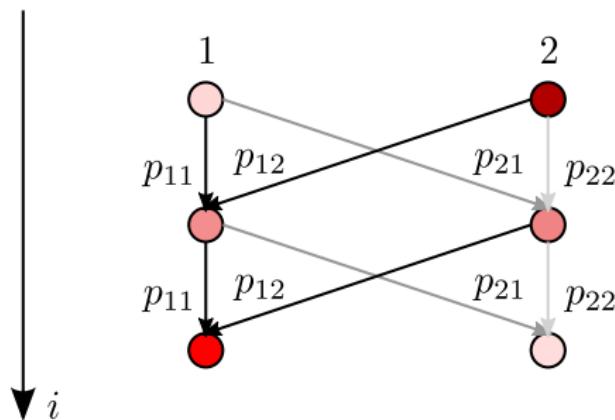
- **Sufficient** condition: **detailed balance**

$$P(\mathbf{q}) p(\mathbf{q} \rightarrow \mathbf{q}') = P(\mathbf{q}') p(\mathbf{q}' \rightarrow \mathbf{q})$$



# “Equilibration”

- Detailed balance guarantees that the target distribution  $P(\mathbf{q})$  is *conserved*. What if we start from the wrong distribution? Example: two-state problem, with equilibrium distribution  $P_1 = 0.1$ ,  $P_2 = 0.9$ .
  - ➊ Take  $p(1 \rightarrow 2) = 0.45$ ,  $p(2 \rightarrow 1) = 0.05$ ,  $p(1 \rightarrow 1) = 0.55$ ,  $p(2 \rightarrow 2) = 0.95$ .
  - ➋ Say we are in state 1 with prob.  $x_1$  and in 2 with prob.  $x_2$ . Let  $p_{ij} = p(j \rightarrow i)$ . One MC step is equivalent to a matrix-vector product  $\mathbf{x}' \leftarrow \mathbf{p} \mathbf{x}$
  - ➌ Repeat application of  $\mathbf{p}$  corresponds to  $\mathbf{p}^N$ , that we can characterize in terms of the  $N$ -th powers of its eigenvalues. Let's see what are the eigenvalues and eigenvectors of  $\mathbf{p}$



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$$\mathbf{p} = \begin{pmatrix} 0.8 & 0.3 & 0.5 \\ 0.1 & 0.3 & 0.1 \\ 0.1 & 0.4 & 0.4 \end{pmatrix}$$

- One can build a transition matrix that violates detailed balance, still it has a well-defined stationary distribution!

# Accept/reject: Metropolis moves

- A simple way to generate moves consistent with detailed balance. Split the move in two steps: generation/acceptance

$$p(\mathbf{q} \rightarrow \mathbf{q}') = g(\mathbf{q} \rightarrow \mathbf{q}') a(\mathbf{q} \rightarrow \mathbf{q}')$$

- Generate a new configuration with a criterion that is symmetric:

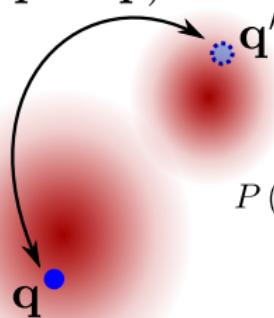
$$g(\mathbf{q} \rightarrow \mathbf{q}') = g(\mathbf{q}' \rightarrow \mathbf{q})$$

- Accept the new configuration with probability

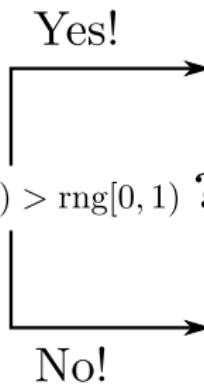
$$a(\mathbf{q} \rightarrow \mathbf{q}') = \min [1, P(\mathbf{q}') / P(\mathbf{q})] = \min \left[ 1, e^{-\beta [V(\mathbf{q}') - V(\mathbf{q})]} \right].$$

- In case of reject *add again  $\mathbf{q}$  to the list of samples!*

$$g(\mathbf{q} \rightarrow \mathbf{q}')$$



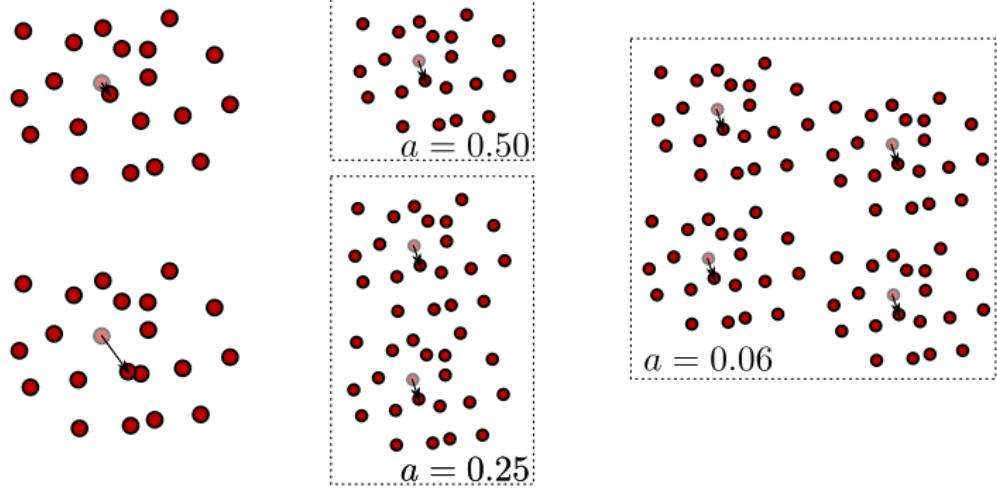
$$P(\mathbf{q}') / P(\mathbf{q}) > \text{rng}[0, 1] ?$$



Metropolis et al., J. Chem. Phys 1953

# Problems with Monte Carlo

- Must find a balance between having high acceptance, and making things happen!
- Fundamental problem: size-extensive changes in energy upon “global” moves reduce dramatically the acceptance
- One should develop “smart” moves, hard to generalize to arbitrary problems



# Sampling by molecular dynamics

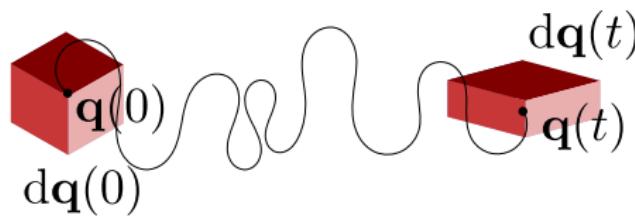
- An alternative: use Hamilton's equations to generate a trajectory

$$\dot{\mathbf{p}} = -\partial V / \partial \mathbf{q}, \quad \dot{\mathbf{q}} = \mathbf{p} / m$$

- Does not obey detailed balance (but a generalization of it).
- Does fulfill the *necessary*, "global" condition: could prove cleanly with a Liouville operator formalism. The ingredients are:
  - Conservation of probability density

$$\frac{dP}{dt} \propto e^{-\beta H} \frac{dH}{dt}, \quad \frac{dH}{dt} = \frac{\partial H}{\partial \mathbf{p}} \cdot \dot{\mathbf{p}} + \frac{\partial H}{\partial \mathbf{q}} \cdot \dot{\mathbf{q}} = -\frac{\partial H}{\partial \mathbf{p}} \cdot \frac{\partial H}{\partial \mathbf{q}} + \frac{\partial H}{\partial \mathbf{q}} \cdot \frac{\partial H}{\partial \mathbf{p}} = 0$$

- Conservation of phase-space volume



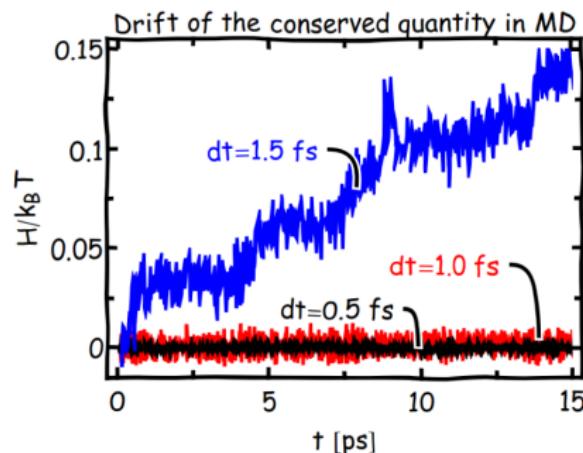
# Integrating the equations of motion

- MD requires discrete time step  $dt$  integration of Hamilton's equations
- Many integrators exist. My favourite: symmetric-split velocity Verlet
  - Time-reversible, **symplectic**, simple implementation, easy to extend
  - Monitor total energy fluctuations and drift to get a grip of the integration error

$$\mathbf{p} \leftarrow \mathbf{p} - \frac{\partial V}{\partial \mathbf{q}} \frac{dt}{2}$$

$$\mathbf{q} \leftarrow \mathbf{q} + \frac{\mathbf{p}}{m} dt$$

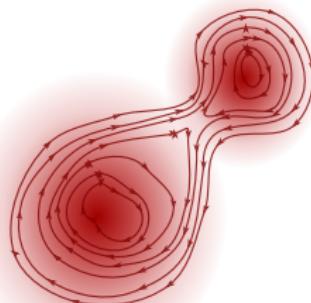
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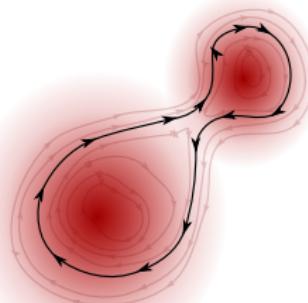
- Integration error leads to (small) departure from the (micro)canonical ensemble, but no problem with system size: MD assumes the error is split evenly across the system

# Conserved energy in Hamiltonian MD

- The probability distribution is conserved *globally*, i.e. if we started many trajectories from the canonical ensemble, we would sample the whole of it
- However, individual trajectories conserve the total energy  $H(\mathbf{p}, \mathbf{q})$ , and so only sample partially the canonical distribution
- We have an **ergodicity** problem with MD



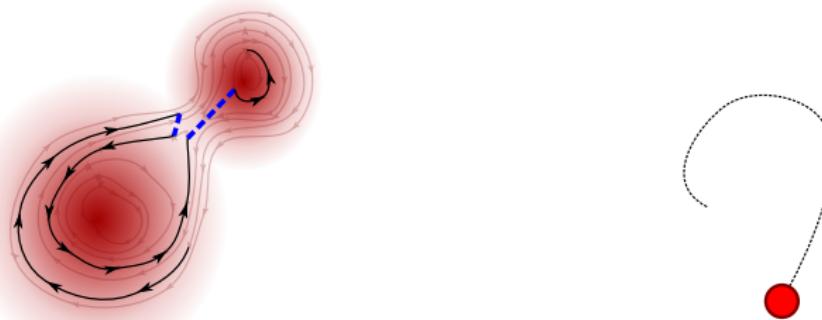
$$dP/dt = 0$$



$$dH/dt = 0$$

# Constant-temperature molecular dynamics

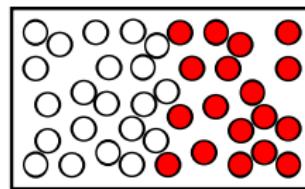
- Plain, Hamiltonian MD conserves energy and is not ergodic
- Must modify the dynamics to model the interaction with a heat bath (**thermostats**)
- Andersen thermostat: randomize atomic velocities every now and then
  - Exploits factorization of the canonical partition function
  - Simple, physically sound and effective



Andersen, J. Chem. Phys. 1980

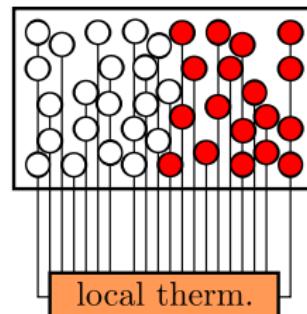
# Local and global thermostats

- “Global” thermostats enforce the correct distribution of the *total* kinetic energy (Berendsen, Nosé-Hoover, Bussi)
  - Gentle on the dynamics, but rely on the intrinsic Hamiltonian dynamics to relax internal degrees of freedom
- “Local” thermostats enforce the correct distribution of *each component* of the momentum (Andersen, Langevin, massive NHC)
  - More aggressive, slower collective dynamics, but also effective for poorly ergodic systems (e.g. crystals)



global therm.

$$P(K) \propto K^{3N/2-1} e^{-\beta K}$$



$$P(\mathbf{p}) \propto e^{-\beta \mathbf{p}^2/2m}$$

# Deterministic and stochastic thermostats

- Nosé-Hoover thermostat: extended-Lagrangian approach, **deterministic** equations of motion

$$\dot{q} = \frac{p}{m}, \quad \dot{p} = -\frac{\partial V}{\partial q} - p \frac{p_s}{Q}, \quad \dot{p}_s = \frac{p^2}{m} - \frac{1}{\beta}, \quad \dot{s} = \frac{p_s}{Q}$$

- Not ergodic, must introduce chains to make the dynamics chaotic
- The local version is not rotationally invariant
- Integration is not straightforward, must use multiple time step
- Langevin-style thermostats: intrinsically **stochastic** dynamic

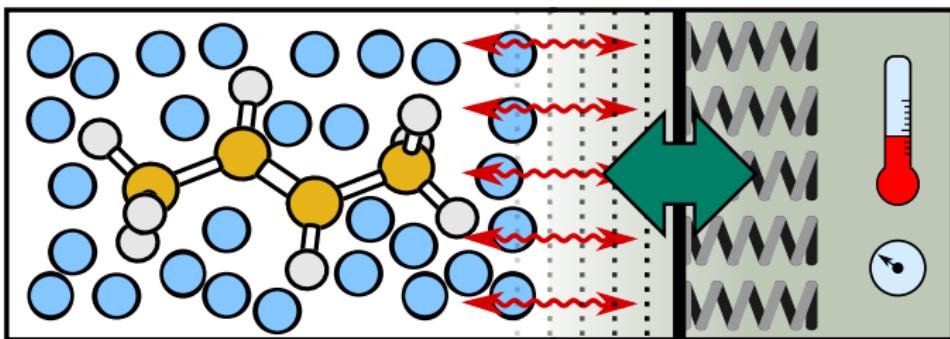
$$\dot{q} = \frac{p}{m}, \quad \dot{p} = -\frac{\partial V}{\partial q} - \gamma p + \sqrt{2m\gamma/\beta}\xi, \quad \langle \xi(t) \xi(0) \rangle = \delta(t)$$

- Ergodic, very natural model for coupling to a heat bath
- Linear equations, very stable and easy to integrate
- Require some care with the random number generator (parallelism!)

Nosé, J. Chem. Phys. 1984; Hoover, Phys. Rev. A 1985; Schneider & Stoll, Phys. Rev. B 1978

## Other ensembles

- It is possible to modify the equations that underlie MD (or MC!) to sample several different ensembles
- ① Plain Hamilton's equations sample the microcanonical ensemble
- ② A thermostat allows for energy fluctuations and enables canonical sampling
- ③ It is also possible to introduce a *barostat*, equations that allow for volume fluctuations to sample an isobaric/isothermal ensemble



$$P \propto e^{-\beta E} e^{-\beta pV}$$