P.001

Kinetic or Dynamic Monte Carlo (KMC)

The "dynamics" in ordinary MC is just an artificial sequence of moves. In many cases, however, the actual physical dynamics can be coarse-grained to a Markov process, in particular, a sequence of transitions between coarse-grained states, at least approximately

e.g.

1. Diffusion represented via hopping events (defects in metals, lattice gas models)
2. Collisions between gas molecules (Kinetic theory)

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In KMC models, one needs to identify coarse-grained states and rules (probabilities or rates) for transitioning between them.

The Markov assumption is justified (sometimes formally) by the large separation of timescales between the typical waiting time between transitions (e.g. spin flips, atom jumps) and the duration of the actual transition (metastability).

→ Formally limit of zero temperature $k_B T \to 0$ [ACTIVATED dynamics]

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P.003

In material science two types of MCMC models are common:

(1) Continuous time discrete space (CTDS) Markov chains, e.g., lattice models such as the Ising model

(2) Continuous time continuous space (CTCS) MCs, e.g., continuum diffusion or collision dynamics

There is also mixed continuous-discrete space models (e.g., reaction-diffusion MC) The only difference is sums versus integrals

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The KMC or MCMC model is specified by the transition rates, which are assumed to be stationary:

$$p(x', t' \mid x, t) = p(x' \mid x ; \Delta t = t' - t)$$

$$p(x' \mid x ; dt) = dt \cdot w(x' \mid x) + \delta(x - x') \left[1 - \int d\tilde{x}\, w(\tilde{x} \mid x) \right]$$

Here $w(x' \mid x)$ is the transition rate, which is typically obtained using a transition state theory approximation.

P.005

The probability distribution for the chain to be in state x at time t obeys the Master Equation:

(for a jump process)

Usually TIME-INDEPENDENT

$$\partial_t p(x', t' \mid x, t) = \int d\tilde{x} \left[w(x' \mid \tilde{x}; t)\, p(\tilde{x}, t' \mid x, t) - w(\tilde{x} \mid x'; t)\, p(x', t' \mid x, t) \right]$$

incoming flux

outgoing flux

Differential version of the Chapman–Kolmogorov equation

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Equivalently, we can write a master equation for the probability density of observing the chain at x at time t:

$$\frac{\partial \mathbb{P}(x,t)}{\partial t} = \int d\tilde{x} \left[w(x|\tilde{x})\, \mathbb{P}(\tilde{x},t) - w(\tilde{x}|x)\, \mathbb{P}(x,t) \right]$$

The probability to <u>remain</u> in the same state during time Δt satisfies

$$\frac{\partial Q(y,\Delta t)}{\partial t} = -\left[\int dx \cdot w(x|y) \right] Q(y,\Delta t)$$

$$\Rightarrow Q(y,\Delta t) = \exp\left[-\lambda t \right] \quad \text{Poisson process}$$

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Where $\boxed{\lambda(y) = \int dx \cdot w(x|y)}$ is the total jump rate out of state y.

For discrete space $\boxed{\lambda_i = \sum_j P_{ij}}$

Each of the transitions out of the present state is a Poisson process, and the rates add up.

So simulating such a Markov chain is in principle very simple:

MC
1. Sample an exponentially distributed waiting time Δt using rate λ
2. Choose a new state with prob. $\frac{w(x,y)}{\lambda}$

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Side-note (for now)

If, in addition to the jump process, there is also a deterministic dynamics with drift rate $A(x,t)$:

$$\dot{x} = A[x(t), t]$$ e.g. Hamiltonian dynamics

this adds a divergence of a flux contribution to the Master Equation:

$$\partial_t p(x', t' | x, t) = -\nabla_{x'} \cdot \left[A(x', t') p(x', t' | x, t) \right]$$

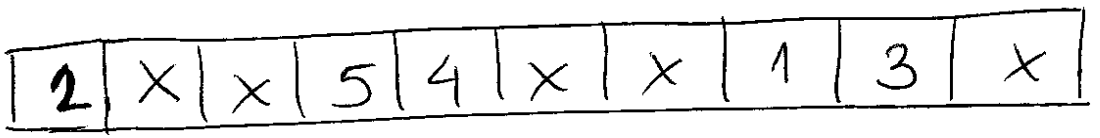
or

$$\partial_t \underline{P}(x,t) = -\nabla_x \cdot \left[A(x,t) \underline{P}(x,t) \right]$$

↖ Liouville's equation

P.009

For concreteness, let's focus on discrete spaces, e.g., a lattice model where particles occupy sites of a 1D lattice



← state with 5 particles and 10 sites.

Since the number of states is too large, solving the full master Equation requires, in principle, computing the exponential of the transition matrix of size N_{states}^2 (infeasible!)

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$$\partial_t P_i(t) = \sum_j w_{ji} P_j(t) - \left[\sum_j w_{ij}\right] P_i(t)$$

$$\partial_t \vec{P}(t) = W \cdot \vec{P}(t)$$

W: transition matrix

$$\Rightarrow \boxed{\vec{P}(t) = e^{Wt} \cdot \vec{P}(0)}$$

e^{Wt}: matrix exponential

Instead of trying to compute the full $\vec{P}(t)$, however, we can just generate a lot of <u>sample trajectories</u> by <u>simulating</u> the Markov chain, and then compute expectation values as averages

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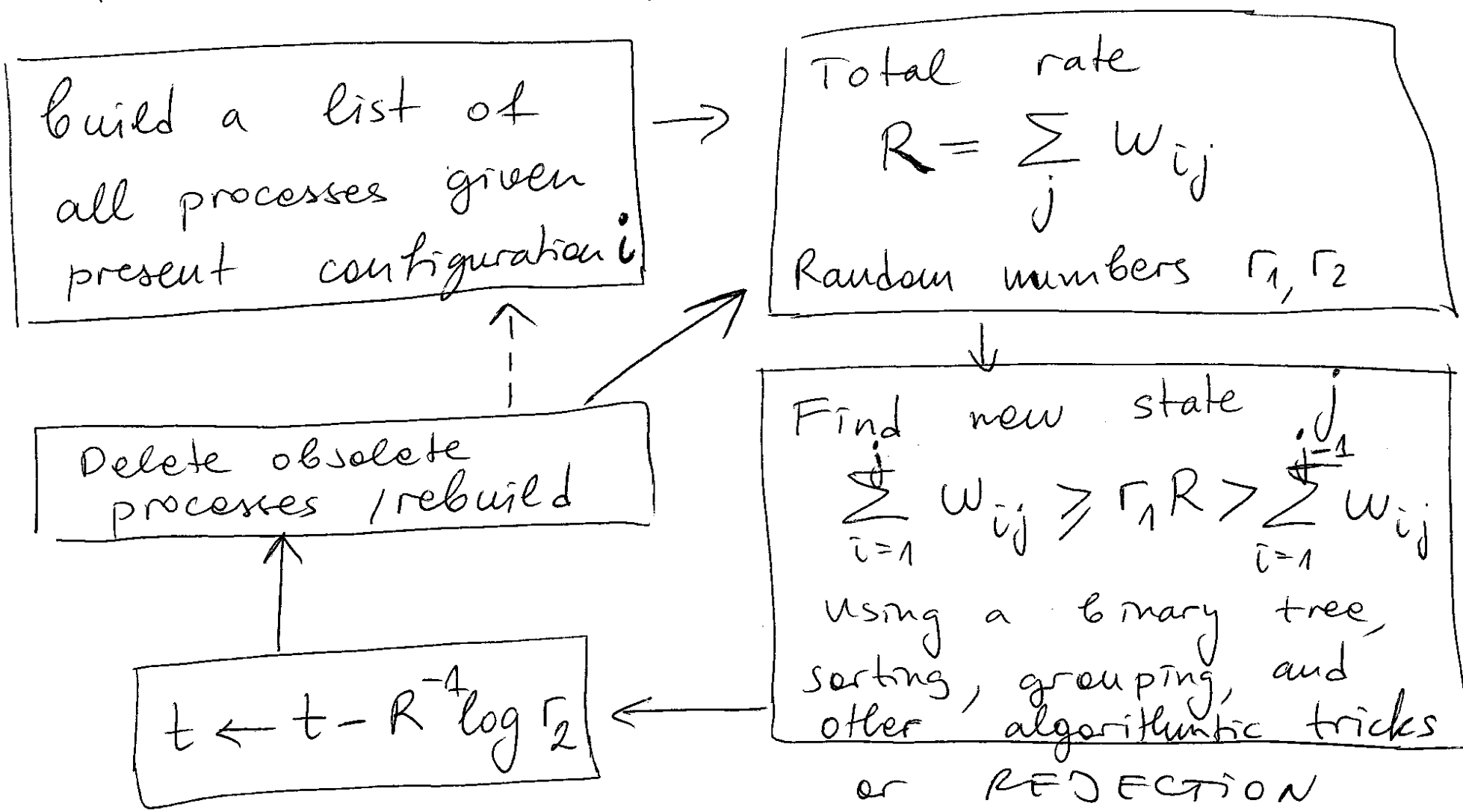
KMC algorithm done via a process list (synchronous KMC):



(see Review article by Kratzer)

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The key to efficient synchronous KMC is the effective use of data structures:

→ How to quickly select which transition to execute?

→ How to quickly update the list of possible transitions and rates (if "on the fly" KMC then a less coarse grained method is used to do this carefully)

In simple models of lattice gases the best one can usually do is $O(\log N)$ per step

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An alternative KMC algorithm is a time-ordered list KMC or asynchronous algorithm

1. For each possible event, assign randomly an exponential waiting time and thus a tentative event time t_k.
2. Sort these times in an event queue (heap)
3. Execute the earliest (first) event in the queue
4. Update the event queue and go back to 2

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Go through several examples on board:

(1) Simple non-interacting diffusion (hopping) with multiple species
   - Distinguishable particles
   - Indistinguishable particles (rejection) or sorting

(2) Excluded random walk [also boundaries]
   - Rejection based
   - Rejection-free
   - Relation to Ising-type models

(3) Repulsion-driven random walk
   - Particle identity matters (DSMC)
   - Reactive collisions

(4) Chemical reaction networks

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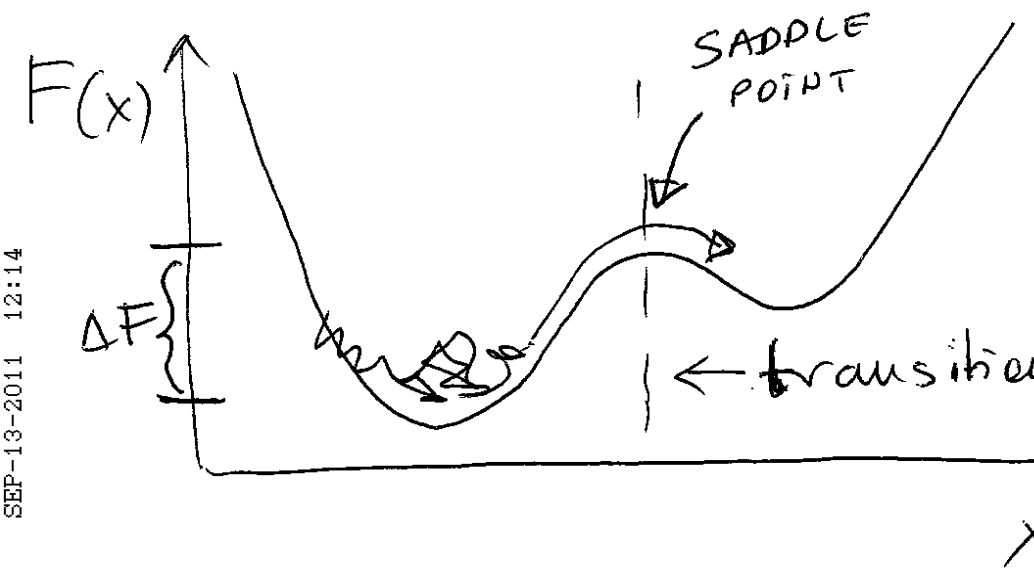
Briefly: Where do the transition rates come from?

Answer: Transition State Theory, which is based on Large Deviation Theory

→ SPECIAL GUEST LECTURE OCT. 5TH by Prof. Eric Vanden-Eijnden



Formally a weak noise limit, maybe also overdamped

$k_B T \to 0$

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TST-like rate equation:

$$w_{ij} \approx \frac{k_B T}{h} \exp\left[- \frac{\Delta F_{ij}}{k_B T} \right]$$

ΔF_{ij} is an activation free energy

$$F = \mathcal{U} - T \cdot S$$

$\mathcal{U}$: internal energy; S: entropy

$$\Delta F_{ij} \approx k_B \log\left[\frac{\mathcal{Z}_i}{\mathcal{Z}_{ij}^{TS}} \right]$$

$\mathcal{Z}_i$: partition function

Constrained "free-energy", hard to calculate

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TOTAL P.017

Often the entropic contribution or vibrational free energy is approximated

$$W_{ij} \approx W_0 \exp\left[-\frac{\Delta E_{ij}}{k_B T}\right]$$

W_0: attempt frequency prefactor

ΔE_{ij}: activation energy

where ΔE_{ij} is also approximated, for example, using "bond counting".

satisfies detailed balance

$$\rightarrow \frac{W_{ij}}{W_{ji}} = \frac{\exp\left[-\beta E^{TS} + \beta E_i\right]}{\exp\left[-\beta E^{TS} + \beta E_j\right]} = \frac{\exp(-\beta E_j)}{\exp(-\beta E_i)}$$

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