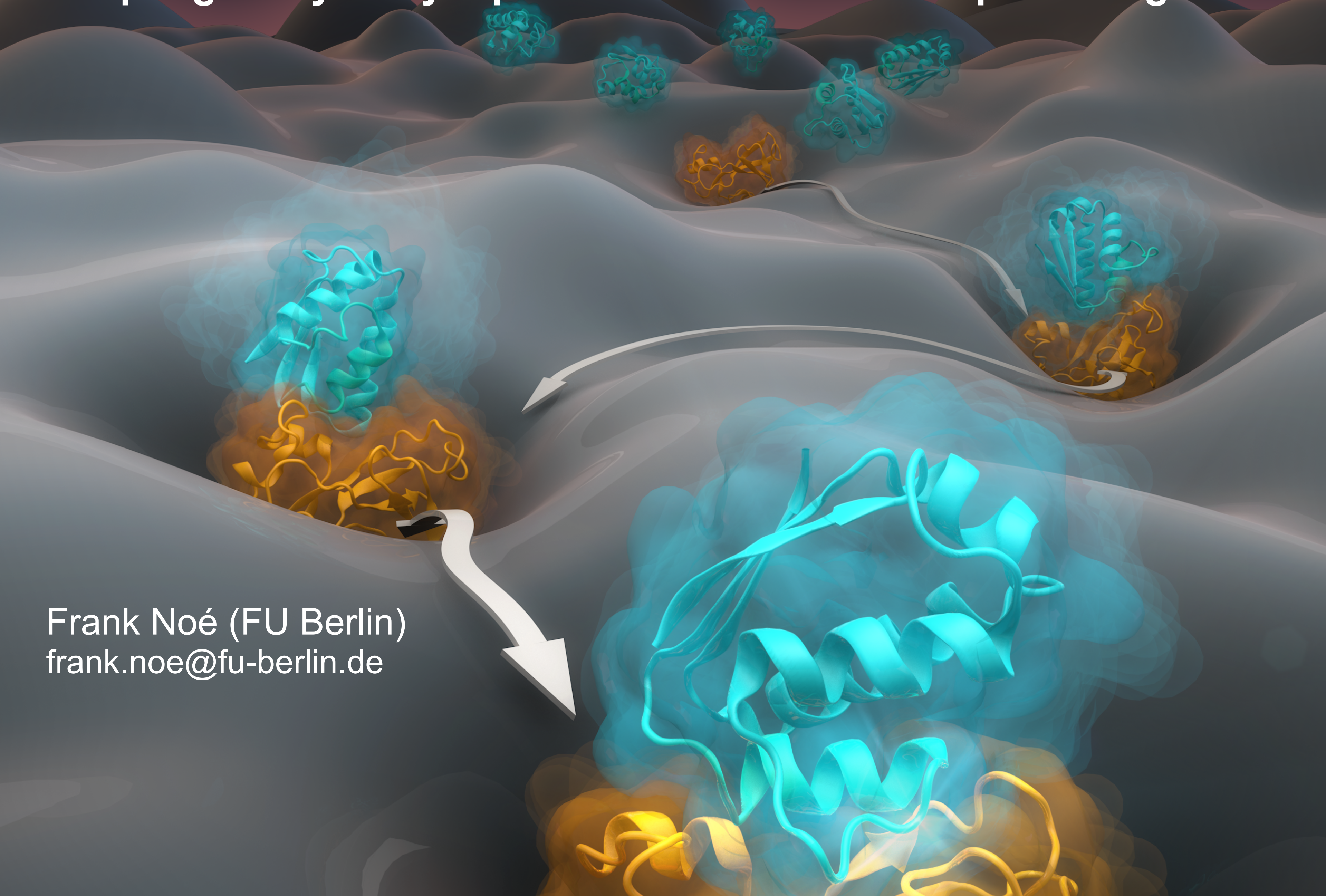
Boltzmann Generators:
sampling many-body equilibrium states with deep learning



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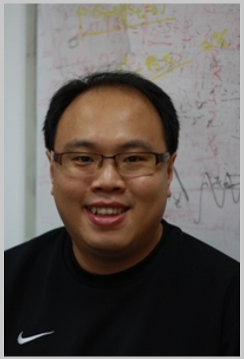
Thermodynamics **Sampling problem**

Boltzmann Generators
sampling equilibrium states of many-body systems with deep learning

Noé, Olsson, Köhler, Wu, **Science** 365: eaww1147 (2019)

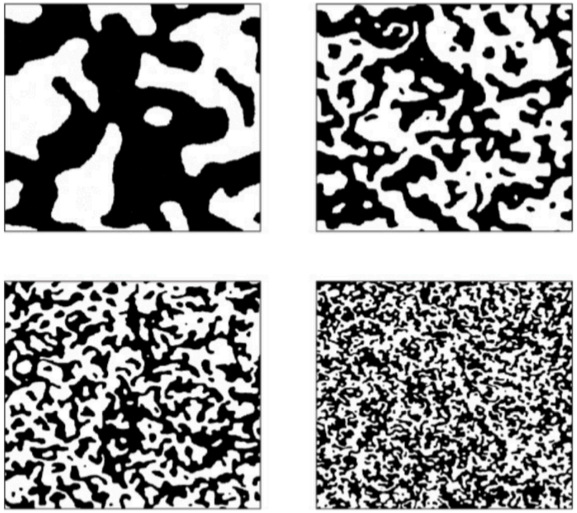
Simon Olsson

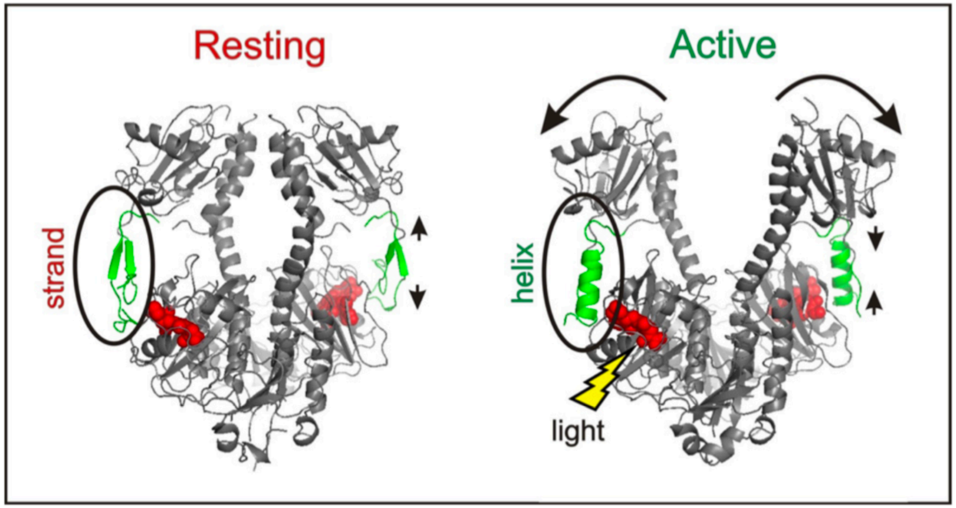
Jonas Köhler



Hao Wu

Boltzmann Generators



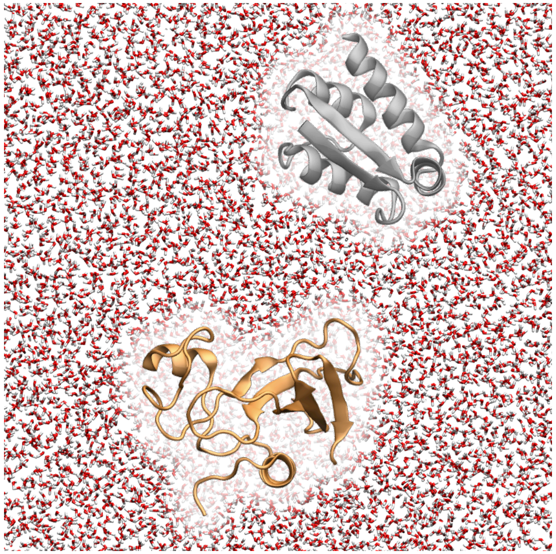


- **Input**: Reduced Potential Energy $u(\mathbf{x})$ in coordinates $\mathbf{x} \in \mathbb{R}^n$, e.g. $u(\mathbf{x}) = U(\mathbf{x})/k_B T$ (canonical ensemble).
- **Aim**: Generate *independent* Samples from Equilibrium Distribution.

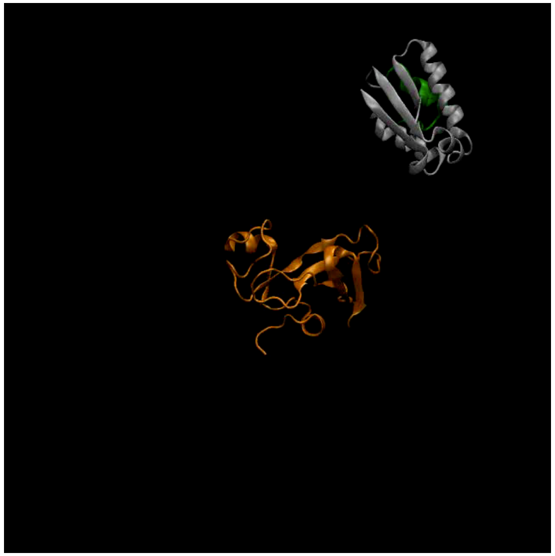
$$\mu(\mathbf{x}) \propto \mathrm{e}^{-u(\mathbf{x})}$$

- **Problem**:
  - Direct MC (proposal for all n degrees of freedom + rejection or reweighting) not available.
  - Standard approach: MD/MCMC with local moves $\rightarrow$ sampling problem.

W1: From passive to active - generative and reinforcement learning with physics



Microsecond
MD Trajectories

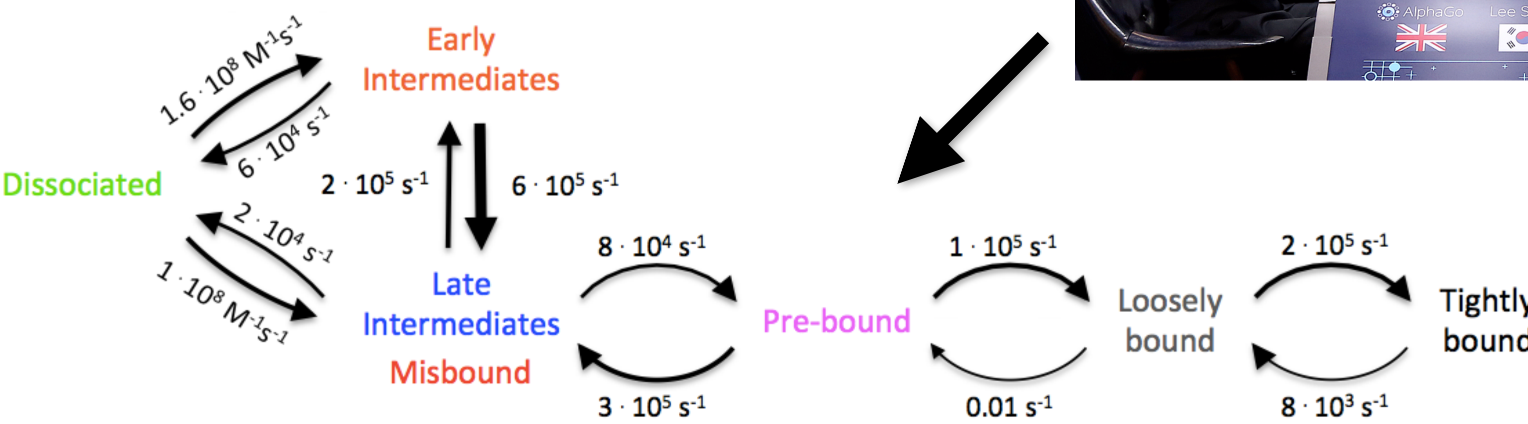


W1: From passive to active - generative and reinforcement learning with physics

Plattner, Doerr, De Fabritiis, Noé
Nature Chemistry 9, 1005 (2017)

Reinforcement learning

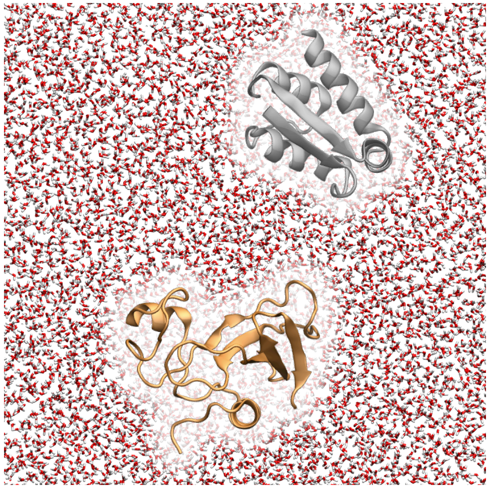
total 2 ms data



Adaptive Markov State Model — **seconds to hours kinetics**

Standard simulation methods in molecular physics are INSANELY expensive

Current approach



very long time

→

a lot of energy

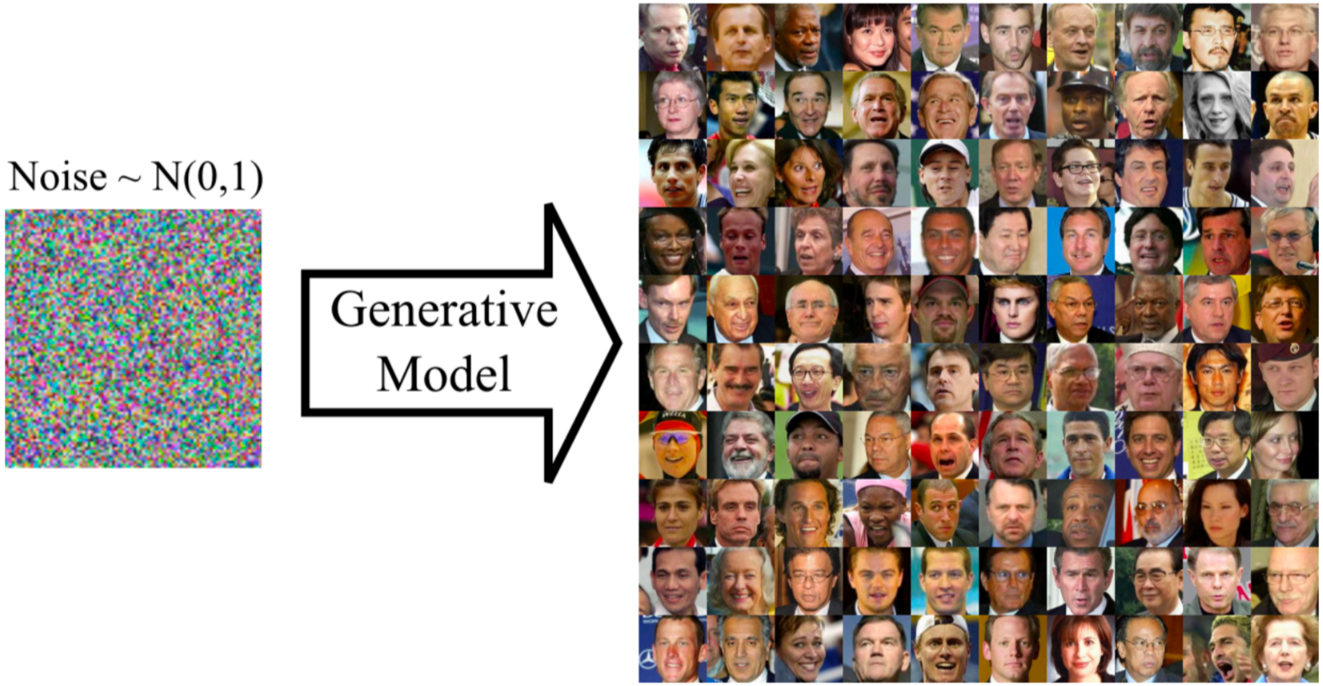
2 ms MD = 20,000 GPU days **500 gigajoule**

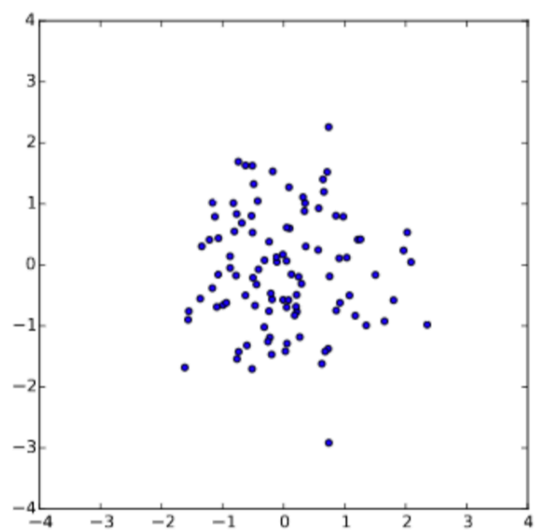
1 non-transferable model

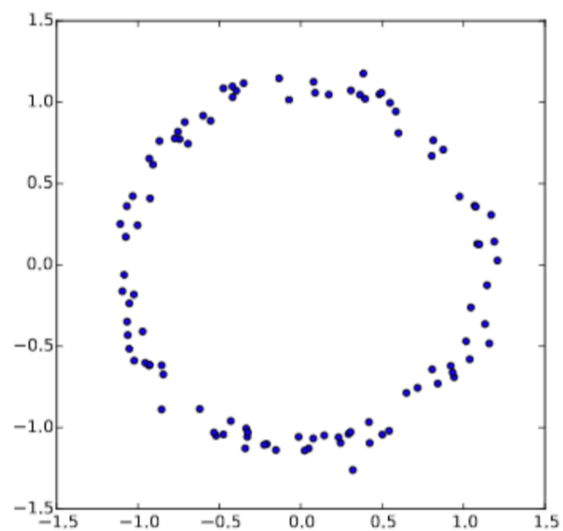
Burn a Saturn V rocket and deliver 50 ton payload to lunar orbit

1500 gigajoule

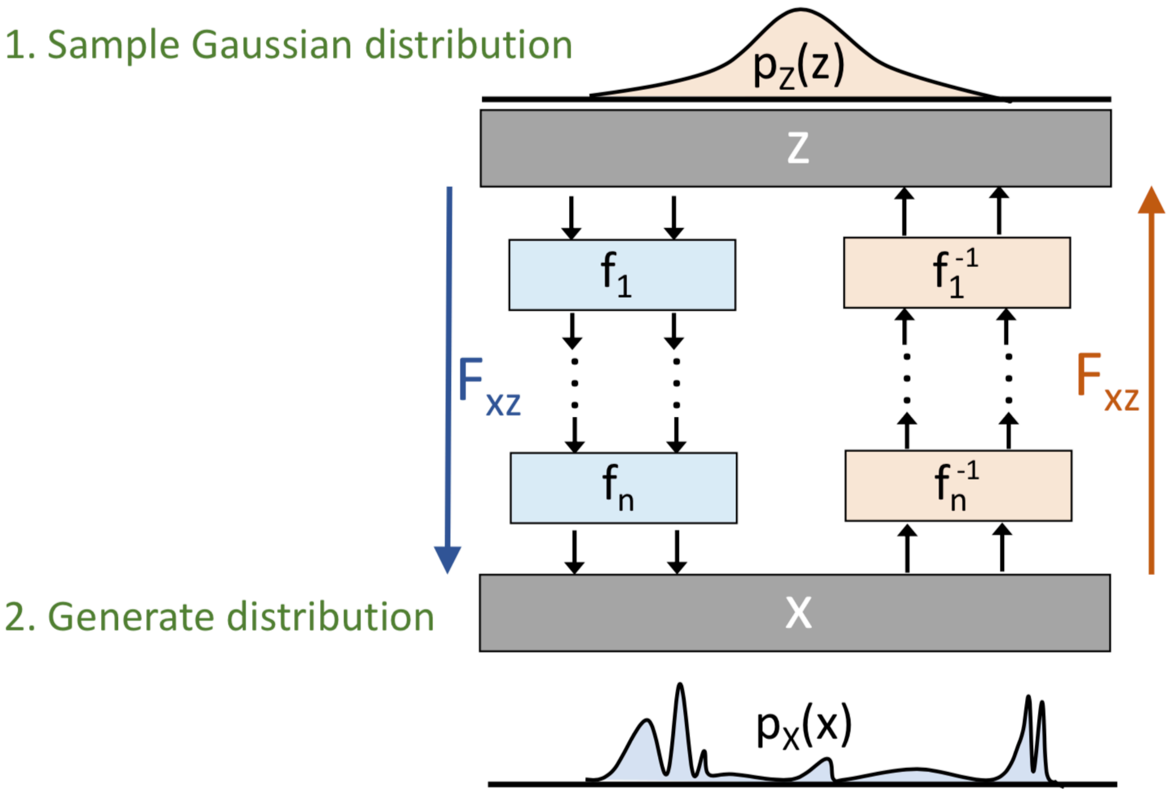
Boltzmann Generators







Flows and Normalizing Flows

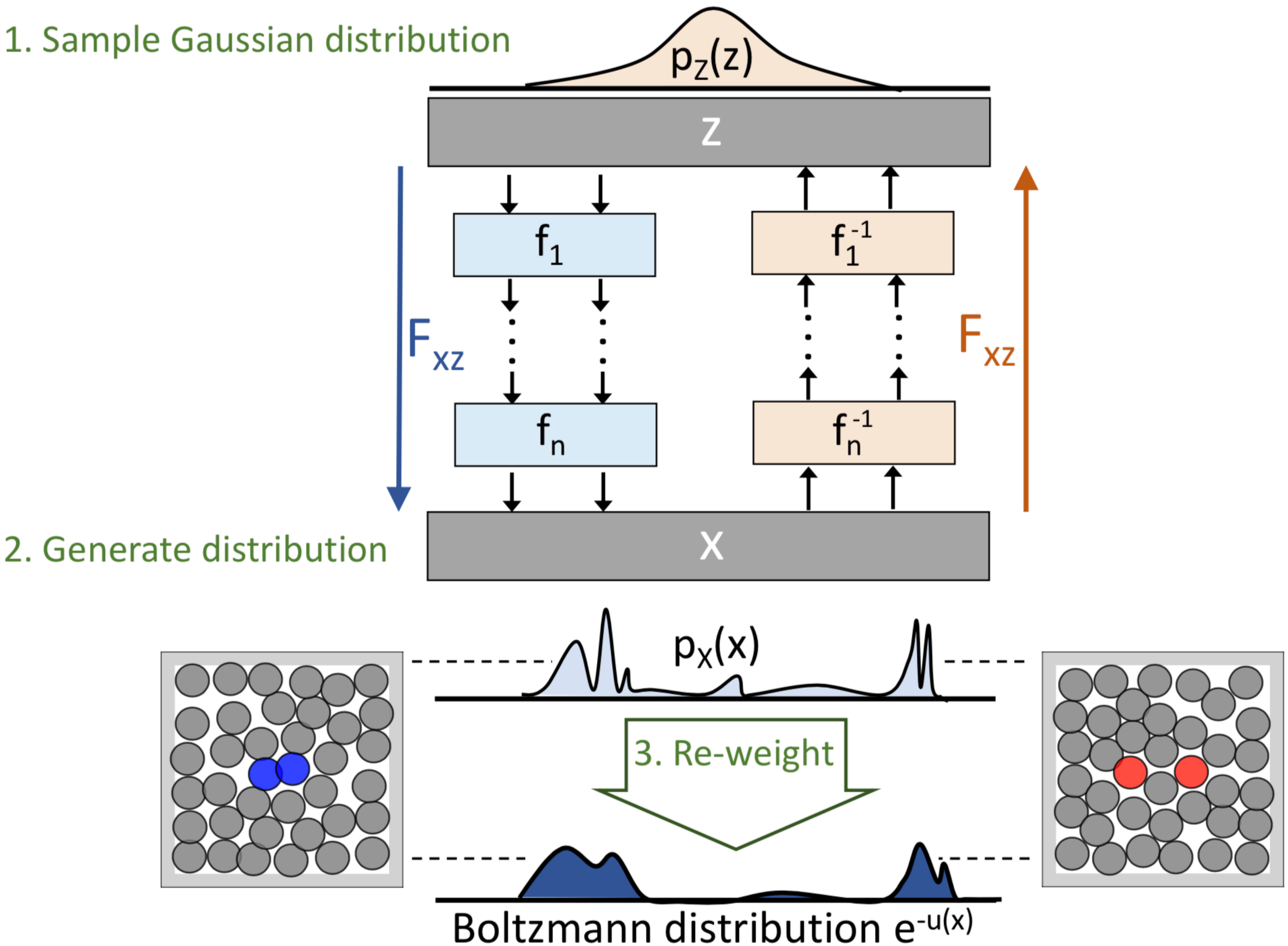


Main idea: Transformation of random variables for bijective transformations:

$$p_X(\mathbf{x}) = p_Z(f(\mathbf{x})) \left| \frac{\partial f(\mathbf{x})}{\partial \mathbf{x}^\top} \right|$$

Parametric PDE Flows: Tabak, Vanden-Eijnden (Commun. Math. Sci. 2010)
NICE: Dinh, Krueger Bengio (ICLR 2015)
RealNVP: Dinh, Sohl-Dickstein, Bengio (ICLR 2016)
Normalizing Flows: Rezende and Mohamed (ICML 2015)

Boltzmann Generators



Noé, Olsson, Köhler, Wu, **Science** 365: eaww1147 (2019). arXiv:1812.01729

- Invertible transformation:

$$\mathbf{z} = F_{xz}(\mathbf{x};\theta)$$
$$\mathbf{x} = F_{zx}(\mathbf{z};\theta).$$

- Jacobians:

$$\mathbf{J}_{zx}(\mathbf{z};\theta) = \left[\frac{\partial F_{zx}(\mathbf{z};\theta)}{\partial z_1}, \ldots, \frac{\partial F_{zx}(\mathbf{z};\theta)}{\partial z_n}\right]$$
$$\mathbf{J}_{xz}(\mathbf{x};\theta) = \left[\frac{dF_{xz}(\mathbf{x};\theta)}{dx_1}, \ldots, \frac{dF_{xz}(\mathbf{x};\theta)}{dx_n}\right]$$

- Transformation of random variables:

$$p_X(\mathbf{x}) = p_Z(T_{xz}(\mathbf{x}))\left|\det \mathbf{J}_{xz}(\mathbf{x})\right|$$
$$p_Z(\mathbf{z}) = p_X(T_{zx}(\mathbf{z}))\left|\det \mathbf{J}_{zx}(\mathbf{z})\right|$$

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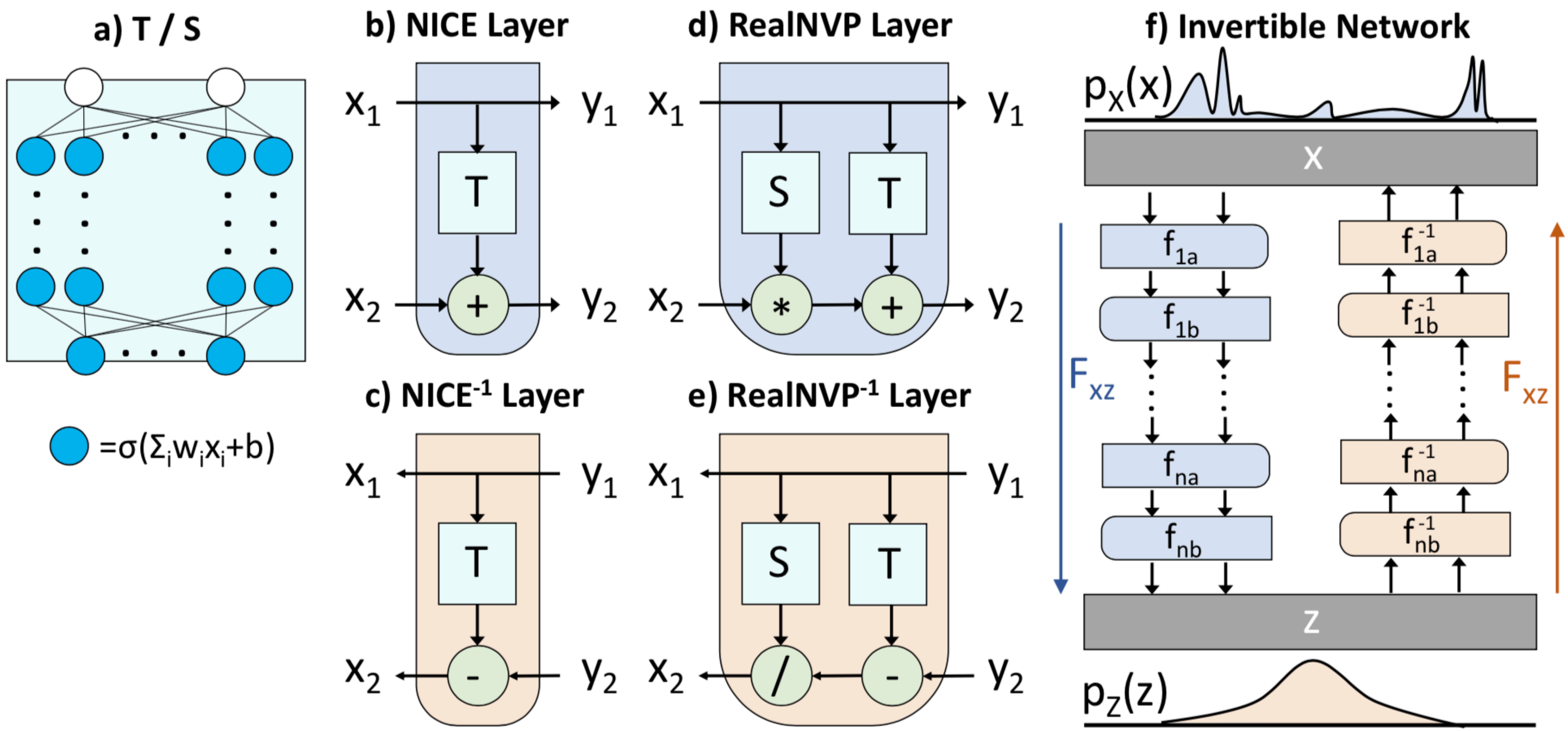
Boltzmann Generators



- **NICE**: Dinh, Krueger, Y. Bengio, ICLR 2015
- **RealNVP**: Dinh, Sohl-Dickstein, S. Bengio, ICLR 2017
- More advanced flow operations (e.g., normalizing flows)

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- **Distributions**:

$$\text{Prior} \quad \mu_Z(\mathbf{z}) \quad \xrightarrow{F_{zx}} \quad p_X(\mathbf{x}) \quad \text{generated}$$
$$\text{Boltzmann} \quad \mu_X(\mathbf{x}) \quad \xrightarrow{F_{xz}} \quad p_Z(\mathbf{z}) \quad \text{generated}$$

- **Aim**: sample configurations $\mathbf{x}$ from **Boltzmann distribution**

$$\mu_X(\mathbf{x}) = Z_X^{-1} \mathrm{e}^{-u(\mathbf{x})}$$

- **Prior distribution**: Sample input in $\mathbf{z}$ from isotropic Gaussian:

$$q_Z(\mathbf{z}) = \mathcal{N}(\mathbf{0}, \sigma^2 \mathbf{I}) = Z_Z^{-1} \mathrm{e}^{-\frac{1}{2}\|\mathbf{z}\|^2/\sigma^2},$$

Prior energy:

$$u_Z(\mathbf{z}) = -\log q_Z(\mathbf{z}) = \frac{1}{2\sigma^2}\|\mathbf{z}\|^2 + \text{const}$$

Boltzmann Generators

- Loss function:

$$J = \underbrace{w_{ML} J_{ML}}_{\text{max likelihood}} + \underbrace{w_{KL} J_{KL}}_{\text{Kullback–Leibler}} + \underbrace{w_{RC} J_{RC}}_{\text{reaction coordinate}}.$$

- KL divergence between generated $p_X(\mathbf{x})$ and Boltzmann distribution:

$$\begin{aligned} \mathrm{KL}_\theta\left[\mu_Z \,\|\, p_Z\right] &= \int \mu_Z(\mathbf{z}) \left[\log \mu_Z(\mathbf{z}) - \log p_Z(\mathbf{z};\theta)\right] \mathrm{d}\mathbf{z}, \\ &= \underbrace{-H_Z + \log Z_X}_{\text{const}} + \underbrace{\mathbb{E}_{\mathbf{z}\sim\mu_Z(\mathbf{z})}\left[u(F_{zx}(\mathbf{z};\theta)) - \log\left|\mathbf{J}_{zx}(\mathbf{z};\theta)\right|\right]}_{\text{free energy}} \end{aligned}$$

- KL loss:

$$J_{KL} = \mathbb{E}_{\mathbf{z}\sim\mu_Z(\mathbf{z})}\left[u(F_{zx}(\mathbf{z};\theta)) - \log\left|\mathbf{J}_{zx}(\mathbf{z};\theta)\right|\right]. \tag{5}$$

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Boltzmann Generators

- Loss function:

$$J = \underbrace{w_{ML} J_{ML}}_{\text{max likelihood}} + \underbrace{w_{KL} J_{KL}}_{\text{Kullback-Leibler}} + \underbrace{w_{RC} J_{RC}}_{\text{reaction coordinate}}.$$

- KL divergence between generated distribution $q_Z(\mathbf{z})$ and Gaussian:

$$\mathrm{KL}_\theta(\mu_X \parallel p_X) = -H_X - \int \mu_X(\mathbf{x}) \log p_X(\mathbf{x};\theta) \mathrm{d}\mathbf{x}$$
$$= \underbrace{-H_X + \log Z_Z}_{\text{const}} + \mathbb{E}_{\mathbf{x}\sim\mu(\mathbf{x})}\left[\frac{1}{\sigma^2}\left\|F_{xz}(\mathbf{x};\theta)\right\|^2 - \log\left|\mathbf{J}_{xz}(\mathbf{x};\theta)\right|\right]$$

Problem: sampling $\mathbf{x} \sim \mu(\mathbf{x})$ is difficult and our goal!

- **Maximum Likelihood** loss for initial data distribution $\rho(\mathbf{x})$:

$$J_{ML} = -\mathbb{E}_{\mathbf{x}\sim\rho(\mathbf{x})}\left[\log p_X(\mathbf{x};\theta)\right]$$
$$= \mathbb{E}_{\mathbf{x}\sim\rho(\mathbf{x})}\left[\frac{1}{\sigma^2}\left\|F_{xz}(\mathbf{x};\theta)\right\|^2 - \log\left|\mathbf{J}_{xz}(\mathbf{x};\theta)\right|\right]$$

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Boltzmann Generators

- Loss function:

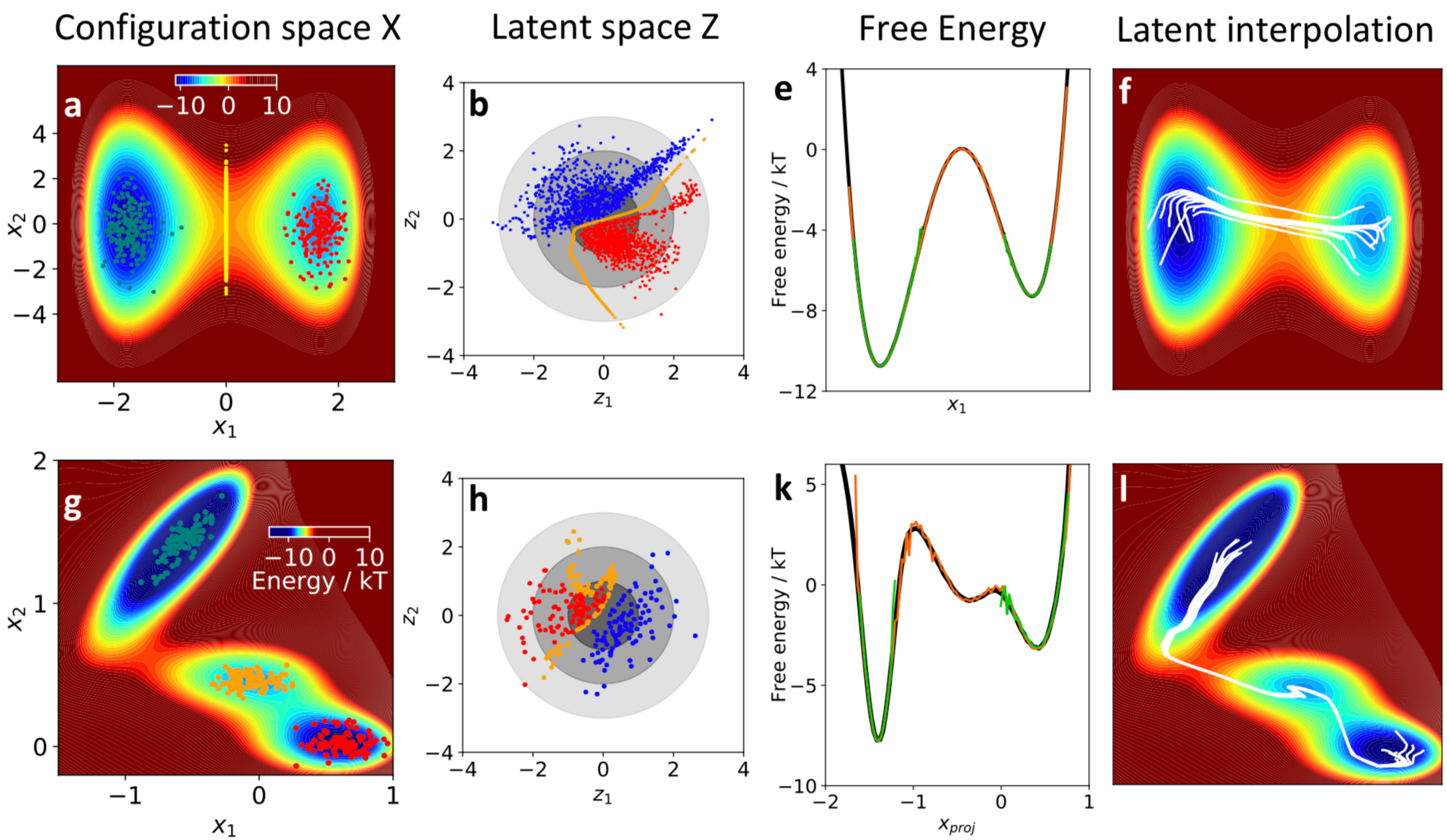
$$J = \underbrace{w_{ML} J_{ML}}_{\text{max likelihood}} + \underbrace{w_{KL} J_{KL}}_{\text{Kullback-Leibler}} + \underbrace{w_{RC} J_{RC}}_{\text{reaction coordinate}}.$$

- Reaction coordinate loss:

$$\begin{aligned} J_{RC} &= \int p(R(\mathbf{x})) \log p(R(\mathbf{x}))\, \mathrm{d}R(\mathbf{x}) \\ &= \mathbb{E}_{\mathbf{x} \sim p_X(\mathbf{x})} \log p(R(\mathbf{x})). \end{aligned}$$

- Implementation:
    - Reaction coordinate function R is user input
    - Min and max bounds are given
    - $p(R(\mathbf{x}))$ is computed as a batchwise kernel density estimate.

Boltzmann Generators: Double well and Mueller potential



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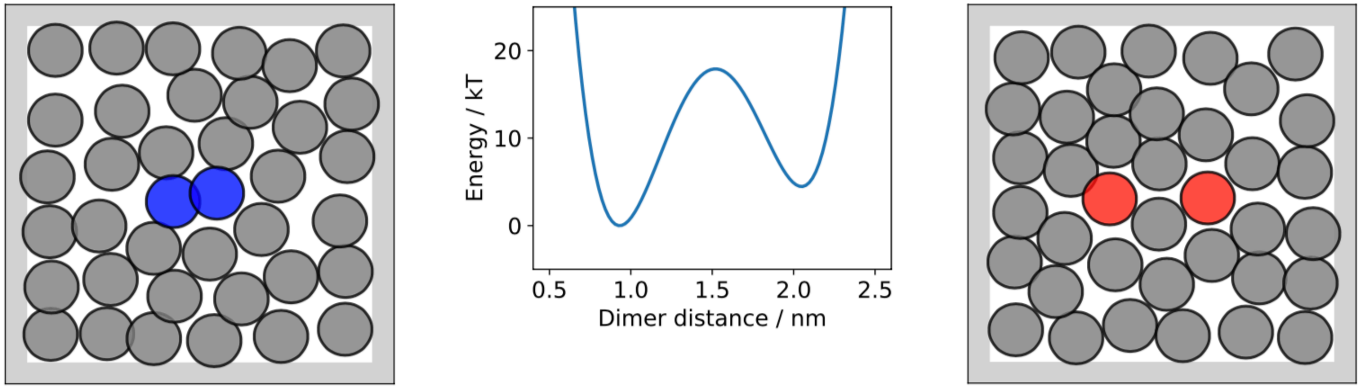
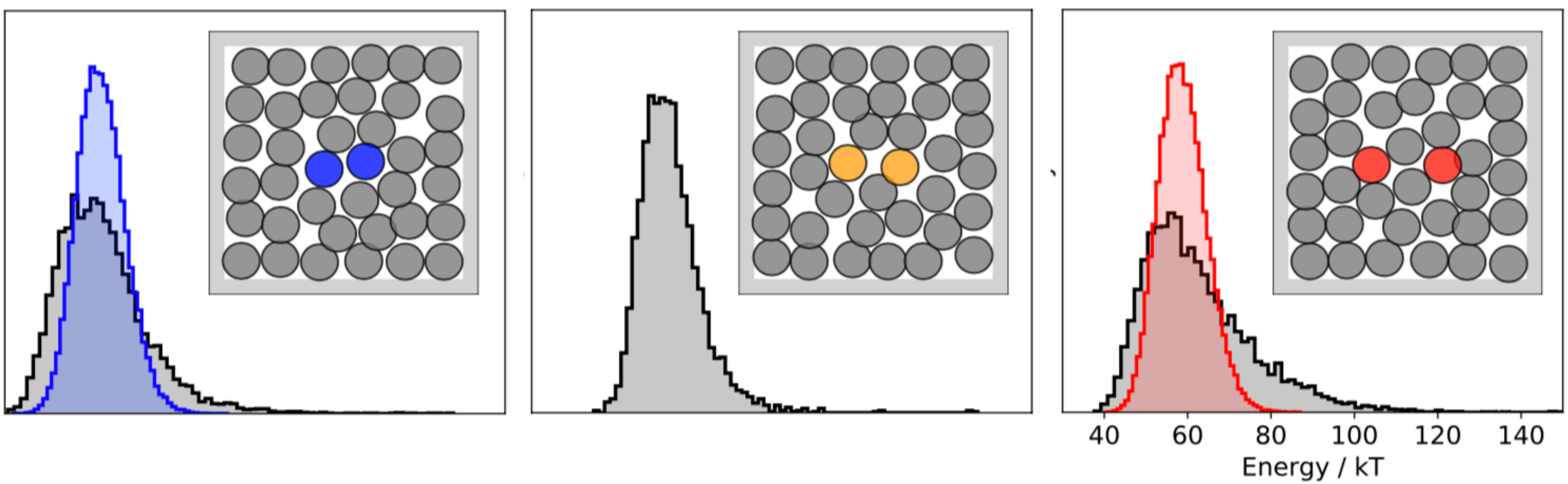
Boltzmann Generators: Bistable dimer in dense colloid solvent



Boltzmann-Generated samples:



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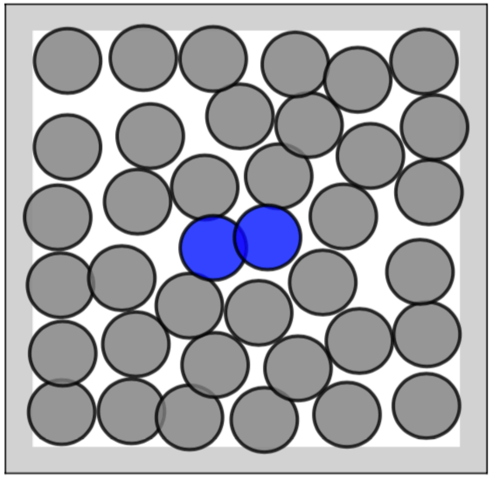
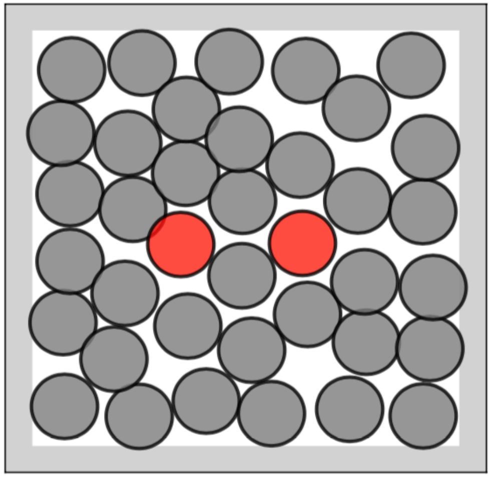
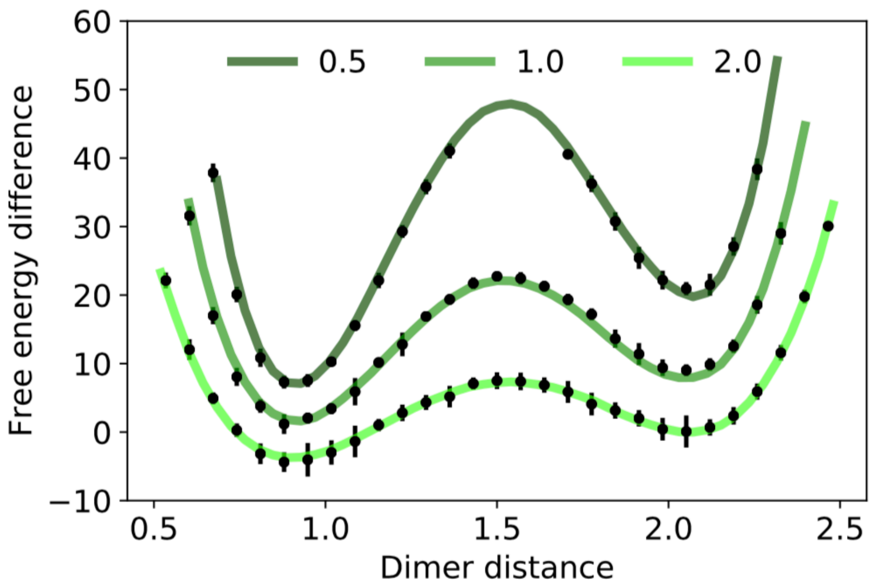
Boltzmann Generators: Bistable dimer in dense colloid solvent







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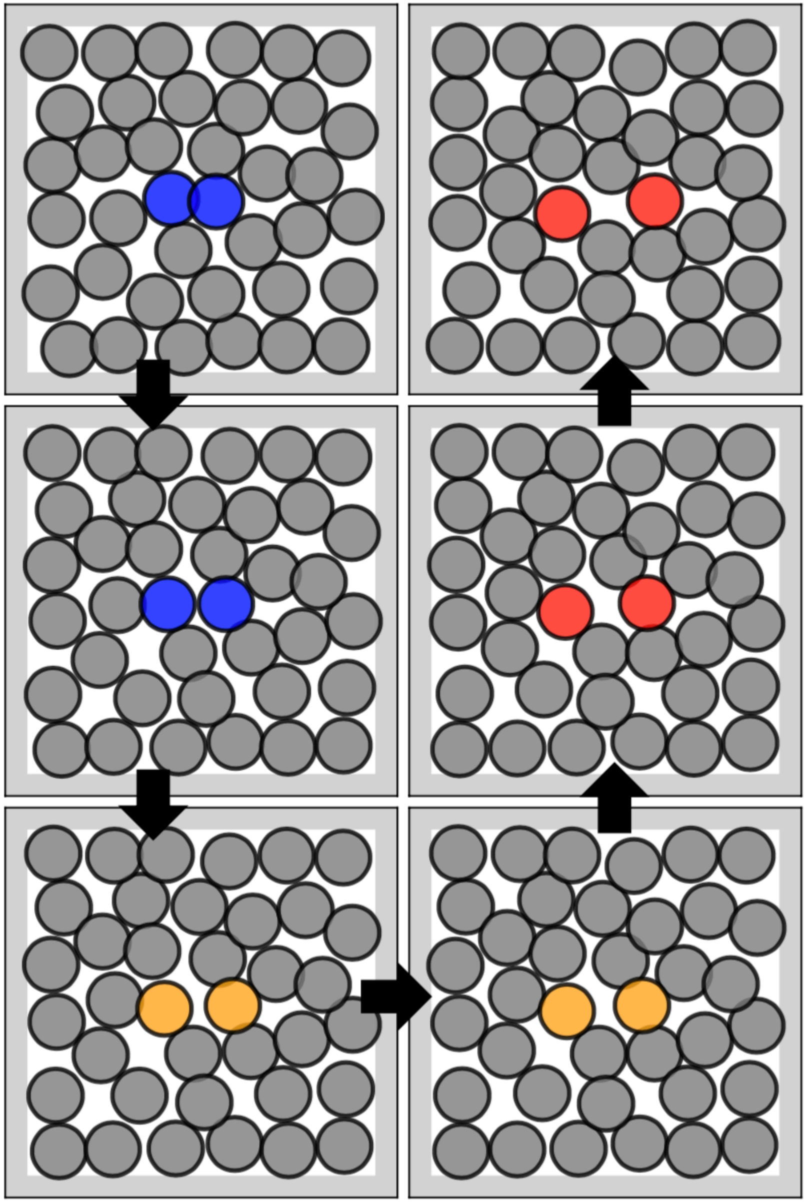
Boltzmann Generators: Bistable dimer in dense colloid solvent



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Boltzmann Generators: Exploration

1. Sample batch $\{\mathbf{x}_1, ..., \mathbf{x}_B\}$ from X.

2. Update Boltzmann Generator parameters $\boldsymbol{\theta}$ by training on batch.

3. For each $\mathbf{x}$ in batch, propose a Metropolis Monte Carlo step in latent space with step-size s:

$$\mathbf{z}' = T_{xz}(\mathbf{x}) + s\mathcal{N}(\mathbf{0}, \mathbf{I}).$$

4. Accept or reject proposal with probability $\min\{1, \exp(-\Delta E)\}$ using the energy difference:

$$\Delta E = u(T_{zx}(\mathbf{z}')) - u(\mathbf{x}) - \log R_{zx}(\mathbf{z}'; \boldsymbol{\theta}) + \log R_{xz}(\mathbf{x}; \boldsymbol{\theta})$$

   For the accepted samples, replace $\mathbf{x}$ by $\mathbf{x}' = T_{zx}(\mathbf{z}')$.

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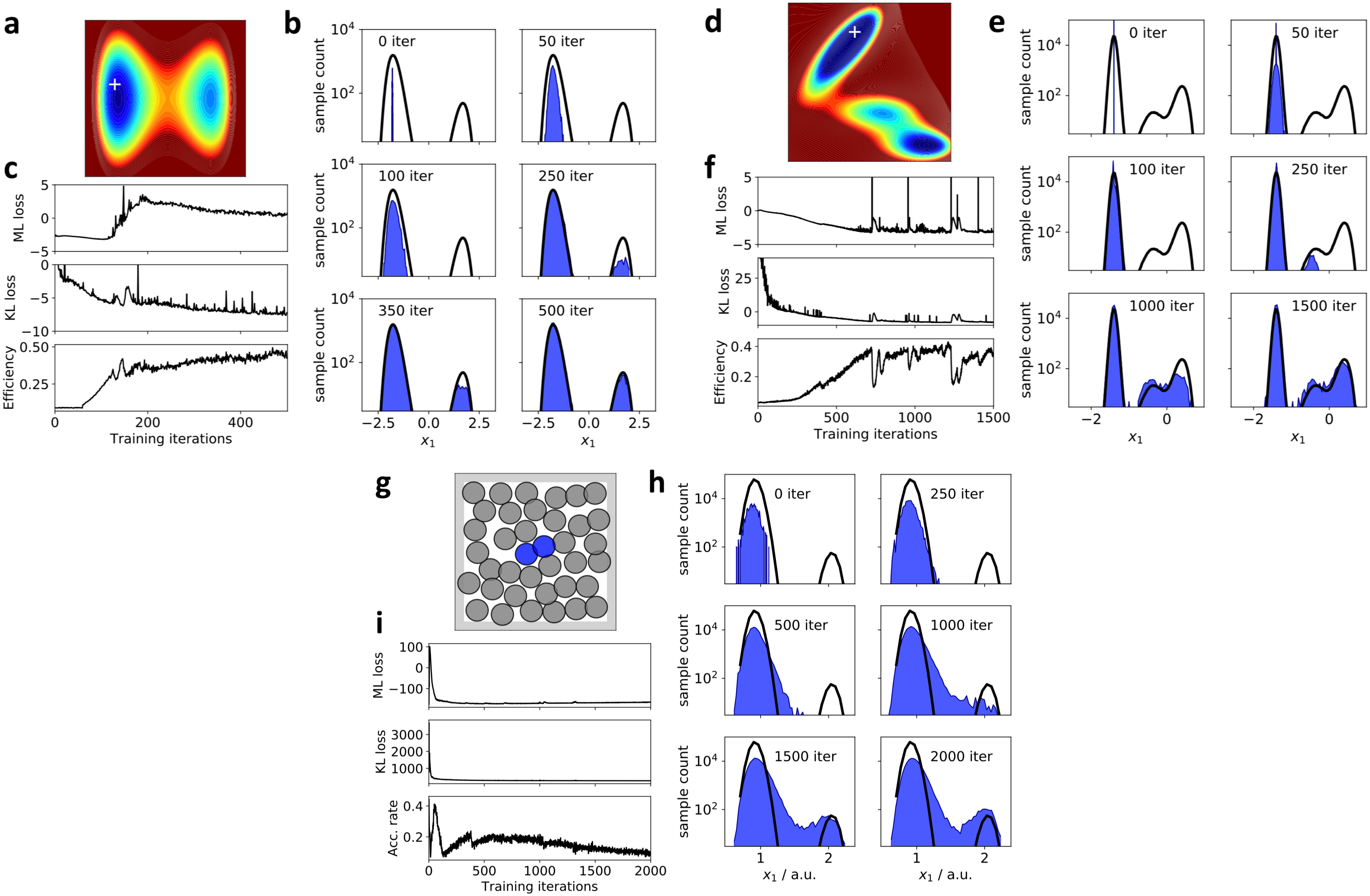
Boltzmann Generators: Exploration



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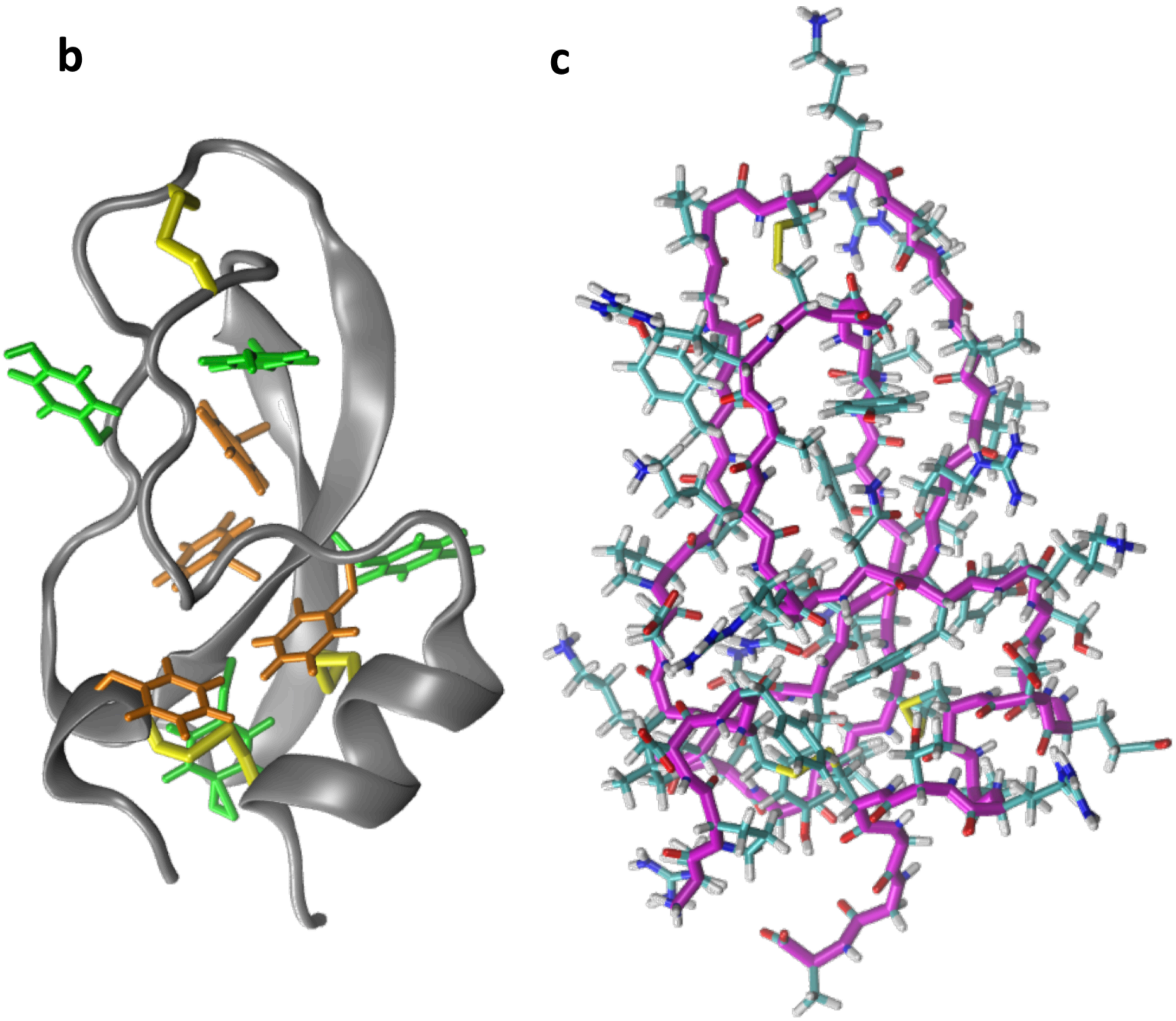
Boltzmann Generators: towards proteins



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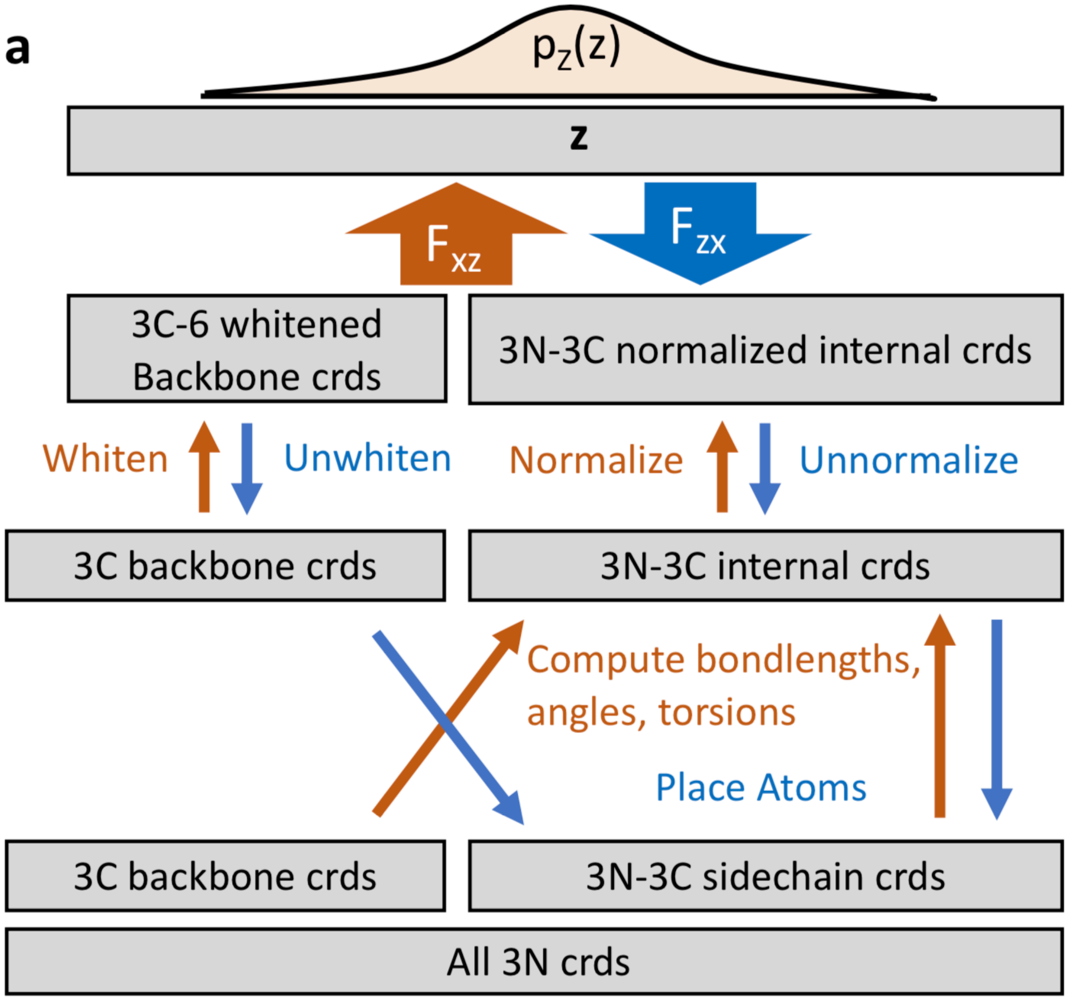
Boltzmann Generators: proteins



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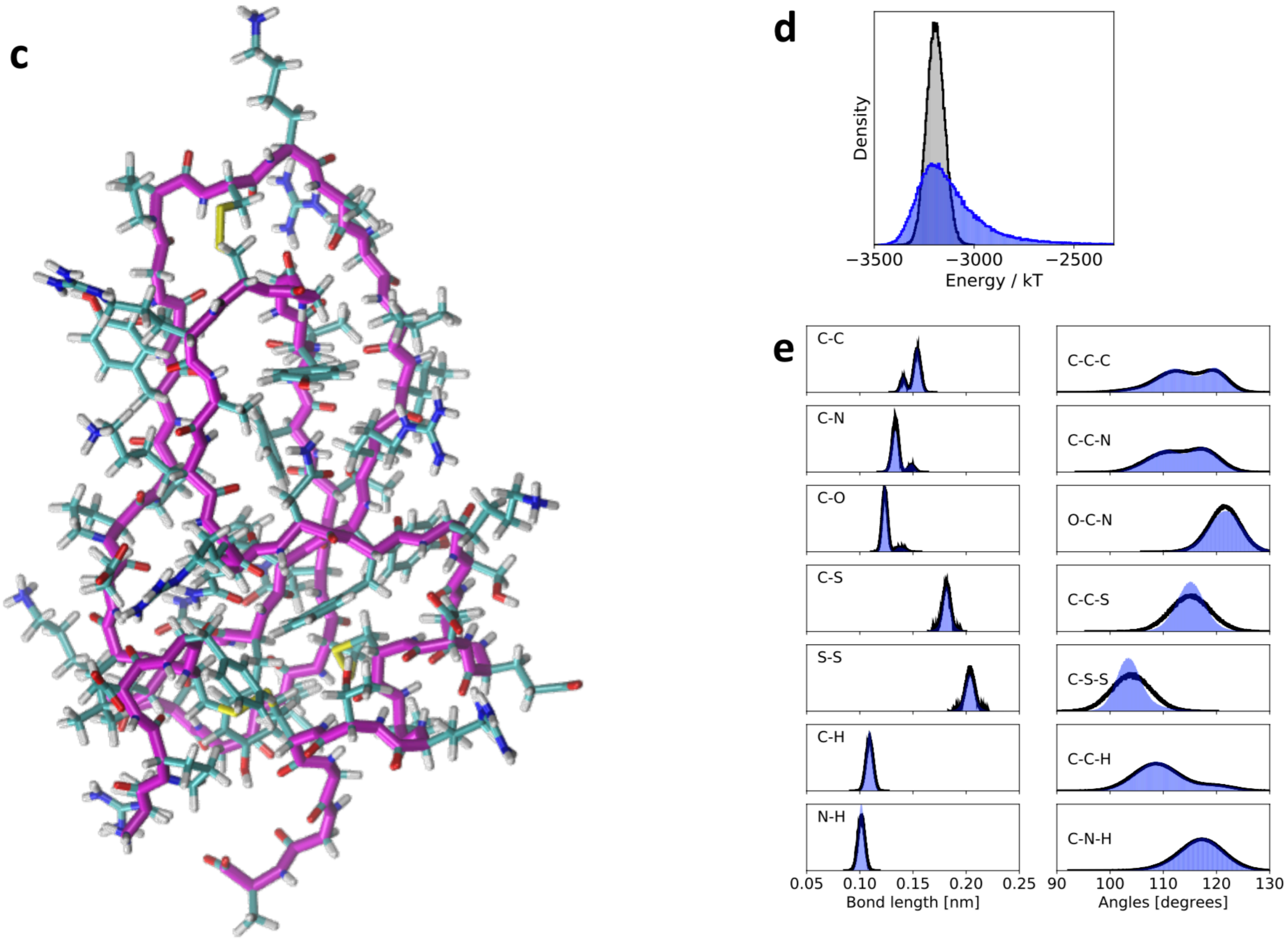
Boltzmann Generators: proteins



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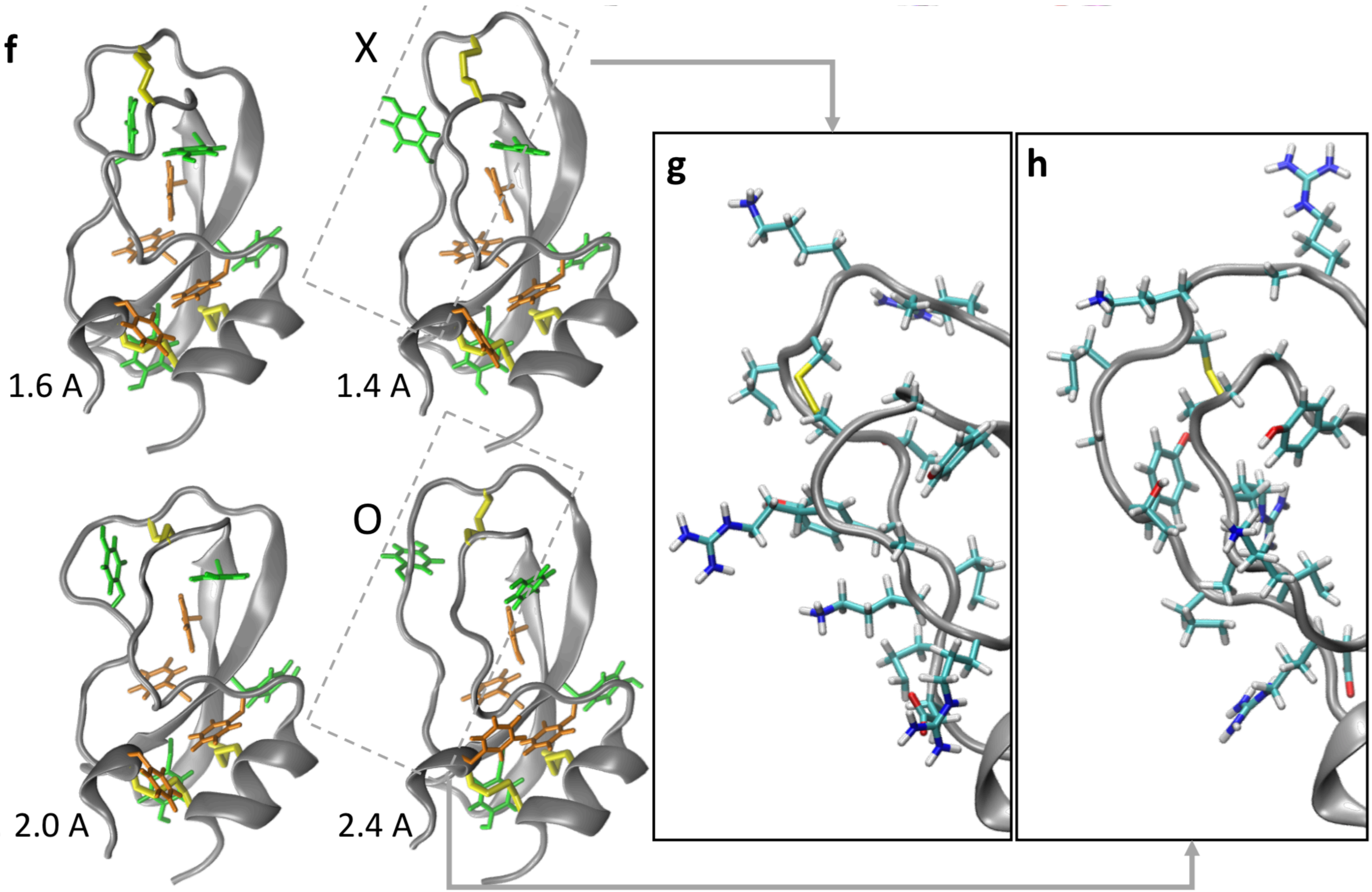
Boltzmann Generators: proteins



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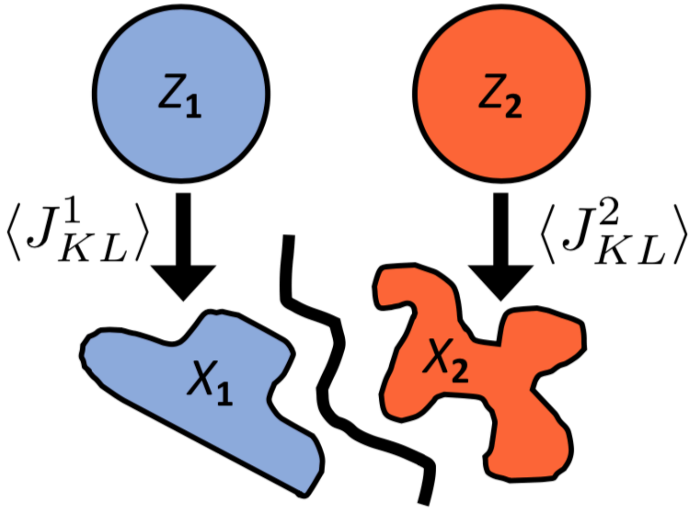
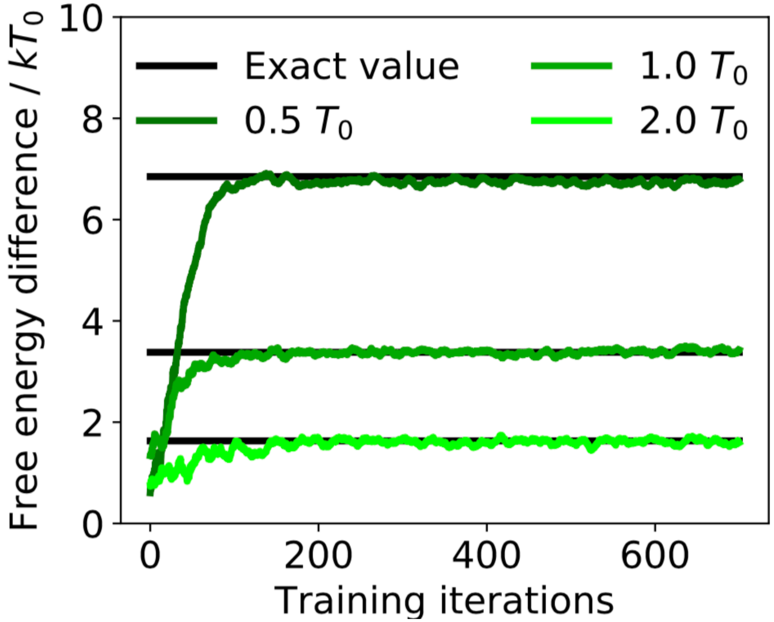
Boltzmann Generators: free energy differences

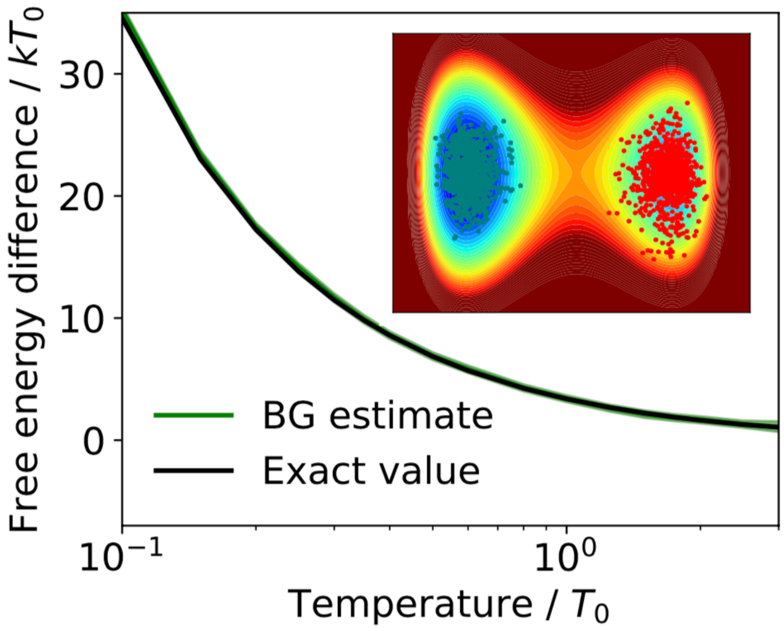
$$J_{KL} = \mathbb{E}_{\mathbf{z}}\left[u(F_{zx}(\mathbf{z})) - \log R_{zx}(\mathbf{z})\right]$$

Free Energy difference from two independent Boltzmann Generators

$$\Delta A_{12} = \langle J_{KL}^2 \rangle - \langle J_{KL}^1 \rangle$$







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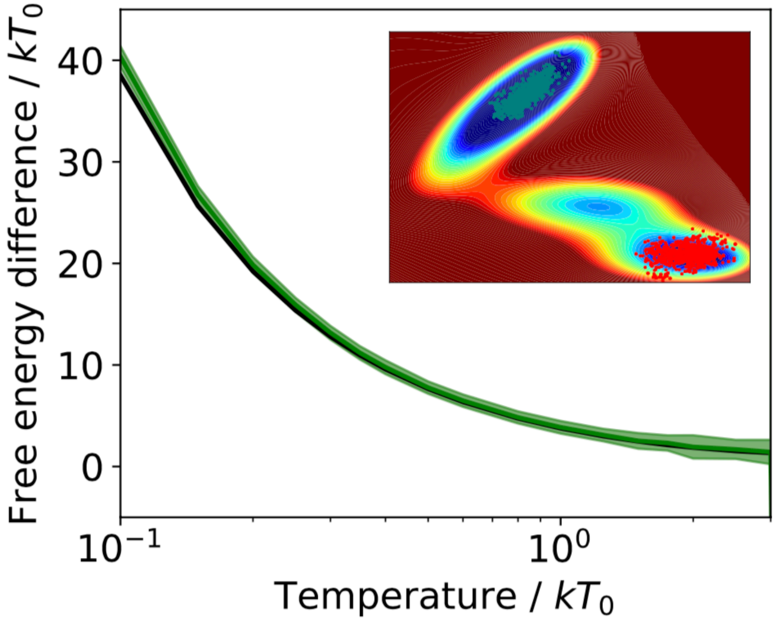
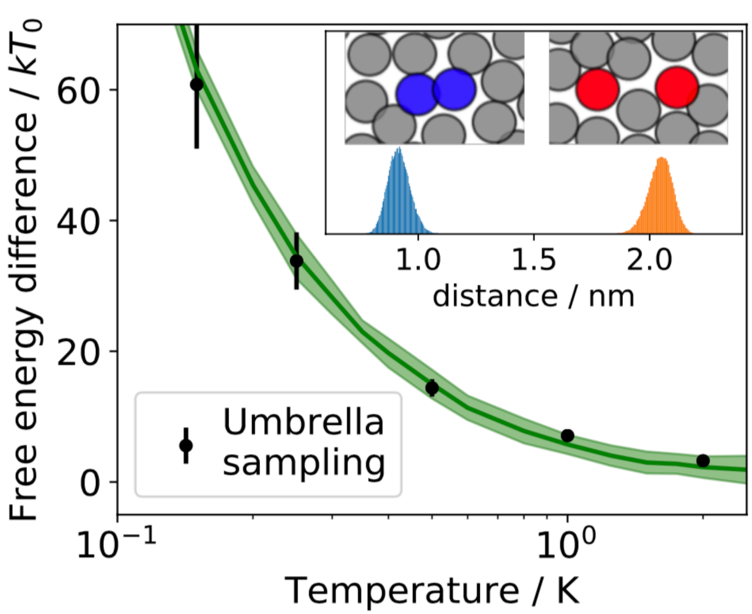
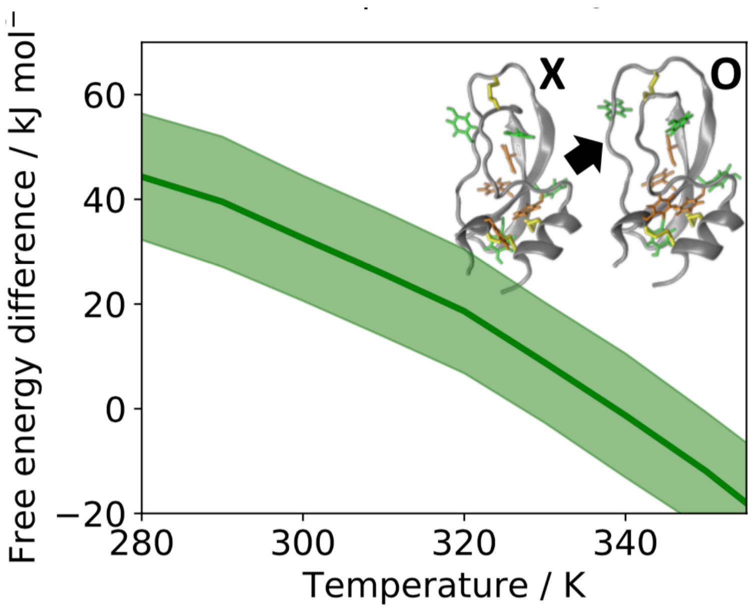
Boltzmann Generators: free energy differences







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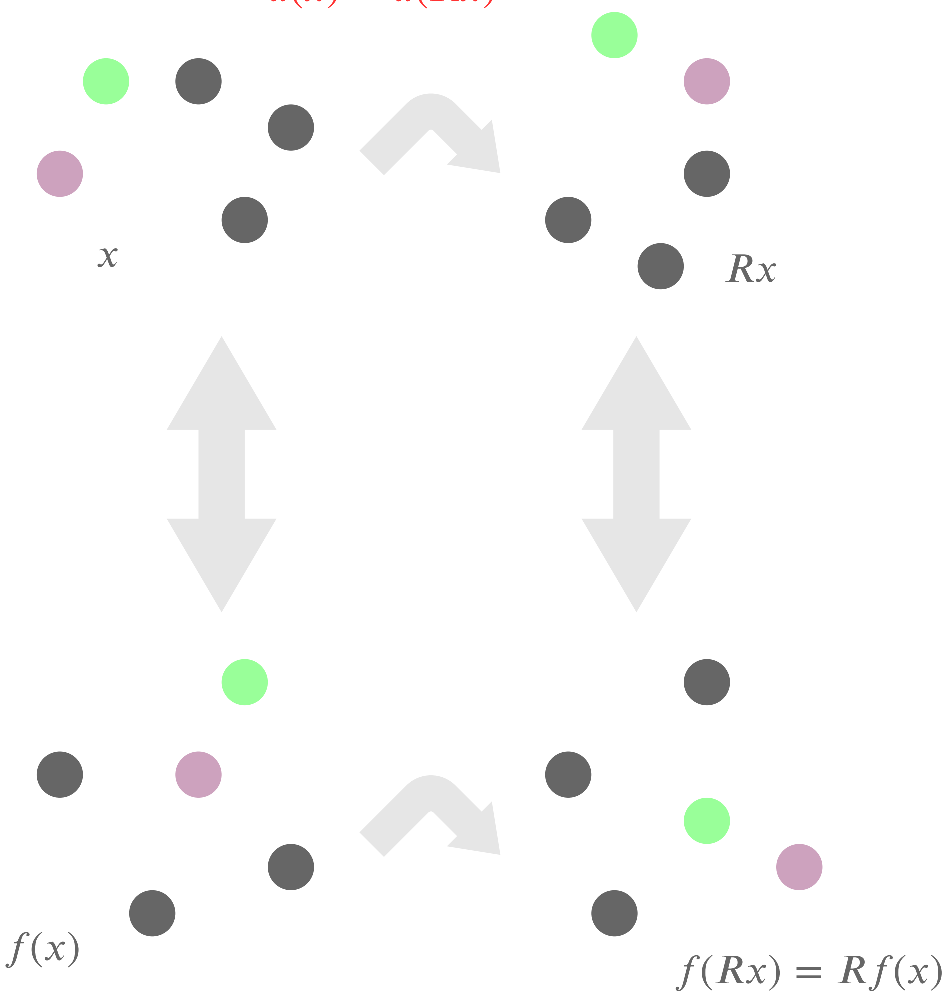
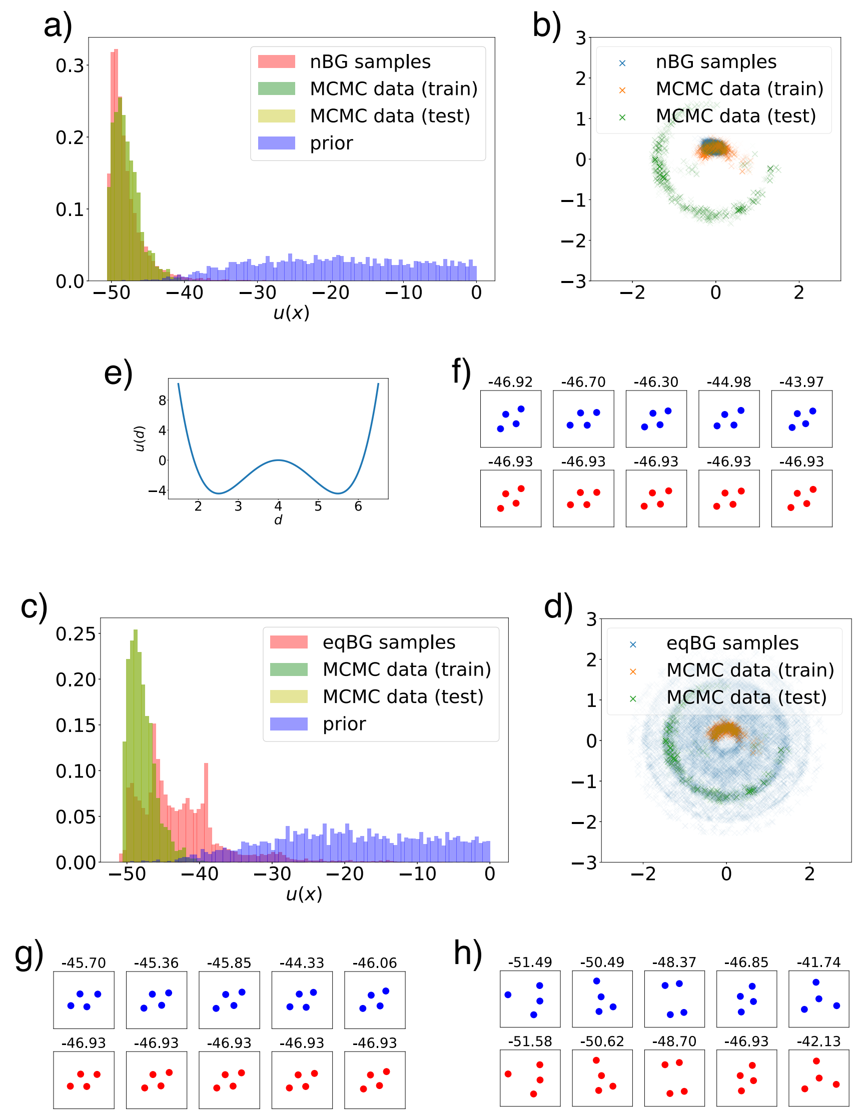
Equivariant Boltzmann Generators

$u(x) = u(Rx)$





$\log p(f(x) = \log p(f(Rx)) = \log p(R(fx))$

Köhler, Klein, Noé, **in prep.**

PauliNet: Deep neural network solution of the electronic Schrödinger equation

Jan Hermann, Zeno Schätzle and Frank Noé
arXiv:1909.08423

September 22, 2019

Freie Universität Berlin

- **Electronic Schrödinger Equation**:

$$\hat{H}\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N) = E\psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$$

  - $\mathbf{r} = (\mathbf{r}_1,\ldots,\mathbf{r}_N)^\top \in \mathbb{R}^{3N}$ spatial electron coordinates
  - E electronic energy, ψ electronic wave function.

- **Hamiltonian** operator:

$$\hat{H} := \sum_i \left(-\tfrac{1}{2}\nabla^2_{\mathbf{r}_i} - \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right) + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

  - Z_I nuclear charges
  - $\mathbf{R}_I$ fixed nuclear coordinates (Born--Oppenheimer approximation).

- **Electronic spins** $s_i \in \{\uparrow,\downarrow\}$.
  ψ must be antisymmetric wrt exchange of equal-spin electrons

$$\psi(\ldots,\mathbf{r}_i,\ldots,\mathbf{r}_j,\ldots) = -\psi(\ldots,\mathbf{r}_j,\ldots,\mathbf{r}_i,\ldots)$$

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Variational Monte Carlo

- **Variational Approach** (used in Hartree-Fock, DMRG, QMC)

$$E_0 = \min_{\psi} E[\psi] \leq \min_{\theta} E[\psi(\mathbf{r};\theta)] \qquad E[\psi] = \int \mathrm{d}\mathbf{r}\, \psi(\mathbf{r}) \hat{H} \psi(\mathbf{r})$$

- **VMC**: Variational Quantum Monte Carlo:

$$E[\psi;\theta] = \mathbb{E}_{\mathbf{r}\sim|\psi|^2}\left[E_{\mathrm{loc}}[\psi](\mathbf{r};\theta)\right] \qquad E_{\mathrm{loc}}[\psi](\mathbf{r};\theta) = \hat{H}\psi(\mathbf{r};\theta)/\psi(\mathbf{r};\theta)$$

- **Deep VMC idea**: use deep neural network to represent $\psi(\mathbf{r};\theta)$, minimize variational energy $E[\psi;\theta]$ over θ.
  - G. Carleo, M. Troyer, Science 355:602-606 (2017): Discrete lattice systems, Restricted Boltzmann Machines.
  - **DeepWF**: J. Han et al, arXiv:1807.07014 (2018): Atoms+Molecules, Poor accuracy, moderate computational cost.
  - **FermiNet**: D. Pfau et al, arXiv:1909.02487 (Sept 2019): Atoms+Molecules, highest accuracy, insane computational cost.
  - **PauliNet**: This work, arXiv:1909.08423 (Sept 2019): Atoms+Molecules, high accuracy, moderate computational cost.

Variational Monte Carlo

- **Variational Approach** (used in Hartree-Fock, DMRG, QMC)

$$E_0 = \min_{\psi} E[\psi] \leq \min_{\theta} E[\psi(\mathbf{r};\theta)] \qquad E[\psi] = \int \mathrm{d}\mathbf{r}\, \psi(\mathbf{r}) \hat{H} \psi(\mathbf{r})$$

- **VMC**: Variational Quantum Monte Carlo:

$$E[\psi;\theta] = \mathbb{E}_{\mathbf{r}\sim|\psi|^2}\left[E_{\mathrm{loc}}[\psi](\mathbf{r};\theta)\right] \qquad E_{\mathrm{loc}}[\psi](\mathbf{r};\theta) = \hat{H}\psi(\mathbf{r};\theta)/\psi(\mathbf{r};\theta)$$

- **Deep VMC idea**: use deep neural network to represent $\psi(\mathbf{r};\theta)$, minimize variational energy $E[\psi;\theta]$ over θ.
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Hermann, Schätzle, Noé, **arXiv:1909.08423** (2019).
Deep neural network solution of the electronic Schrödinger equation.

$$\psi(\mathbf{r};\theta) = \det[\varphi_\mu(\mathbf{r}_i^\uparrow) f_{\mu i}(\mathbf{r};\theta)] \det[\varphi_\mu(\mathbf{r}_i^\downarrow) f_{\mu i}(\mathbf{r};\theta)] \mathrm{e}^{\gamma(\mathbf{r})+J(\mathbf{r};\theta)}$$

with:

- $\varphi_\mu(\mathbf{r}_i)$: one-electron molecular orbitals (fixed)
- $J(\mathbf{r};\theta)$: Jastrow factor neural network (trainable)
- $\mathbf{f}(\mathbf{r};\theta)$: Backflow neural network (trainable)
- $\gamma(\mathbf{r})$: Asymptotics (fixed)

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- Assign electrons to $\uparrow$ and $\downarrow$ sets.

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- **Antisymmetry** for **single-electron** functions: Slater determinants.

$$\psi_{\mathrm{HF}}(\mathbf{r}) := \det[\varphi_\mu(\mathbf{r}_i^\uparrow)] \det[\varphi_\mu(\mathbf{r}_i^\downarrow)]$$

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[2] D. Luo, B. K. Clark. *Phys. Rev. Lett.* 122:226401 (2019)
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PauliNet – Physics 1: Antisymmetry

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PauliNet – Physics 2: HF Baseline

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- Use fixed Hartree-Fock (HF) orbitals $\varphi_\mu(\mathbf{r}_i^\uparrow)$
- $\varphi_\mu(\mathbf{r}_i^\uparrow)$: linear combination of basis functions centered on atomic nuclei, coefficients optimized variationally.
- Pro: HF fast, captures physics of atoms and molecules qualitatively
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- Exploit the flexibility of deep learning to achieve **higher accuracy**!

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PauliNet – Physics 3: Beyond HF

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- **Cusp conditions**:

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- **PauliNet**:
  - Nuclear cusps are built into $\varphi_\mu(\mathbf{r}_i)$[7].
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$$\gamma(\mathbf{r}) := \sum_{i<j} -\frac{c_{ij}}{1 + |\mathbf{r}_i - \mathbf{r}_j|} \qquad c_{ij} = \begin{cases} \frac{1}{4} & s_i = s_j \\ \frac{1}{2} & s_i \neq s_j \end{cases}$$

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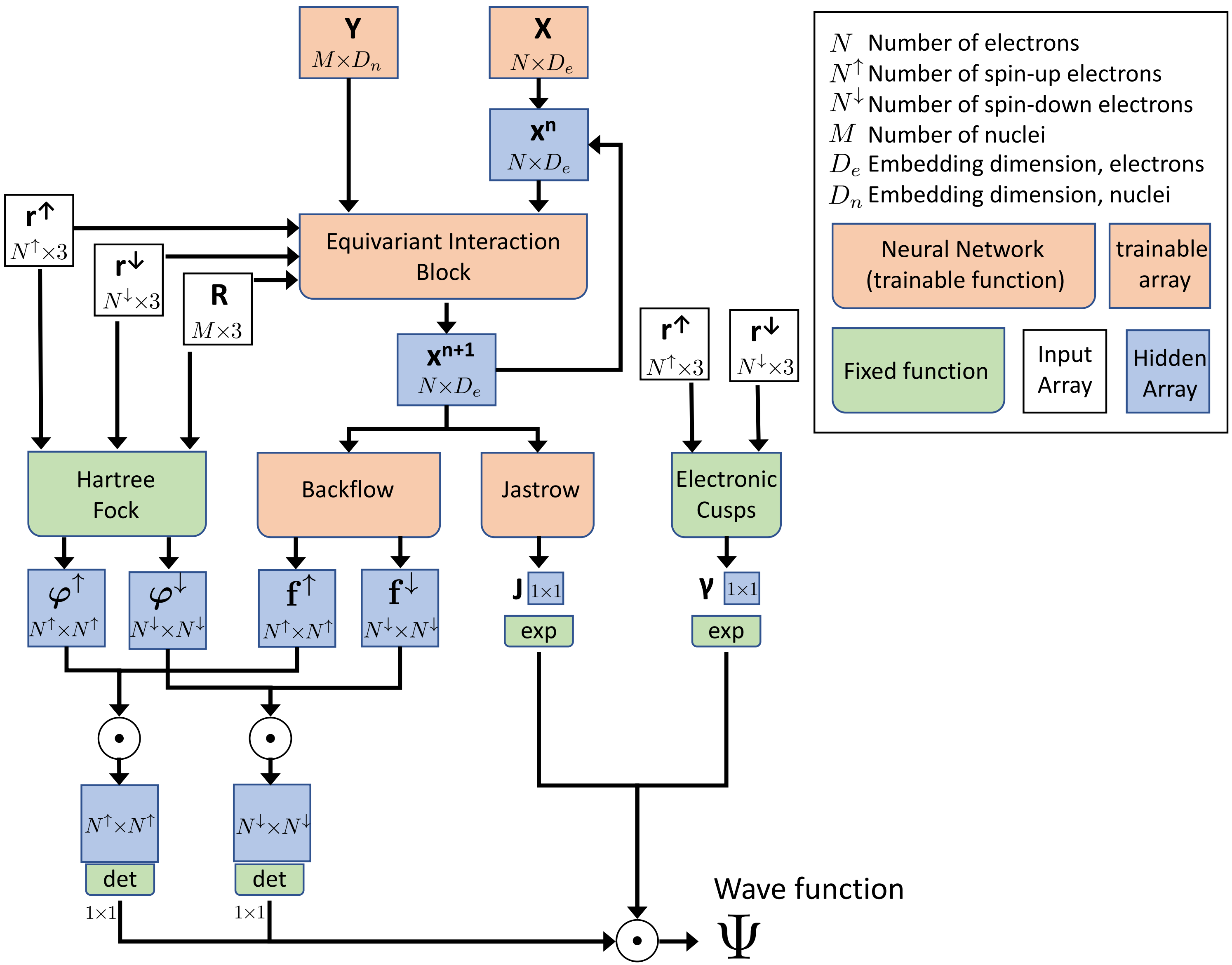
PauliNet



Hermann, Schätzle, Noé, **arXiv:1909.08423** (2019).
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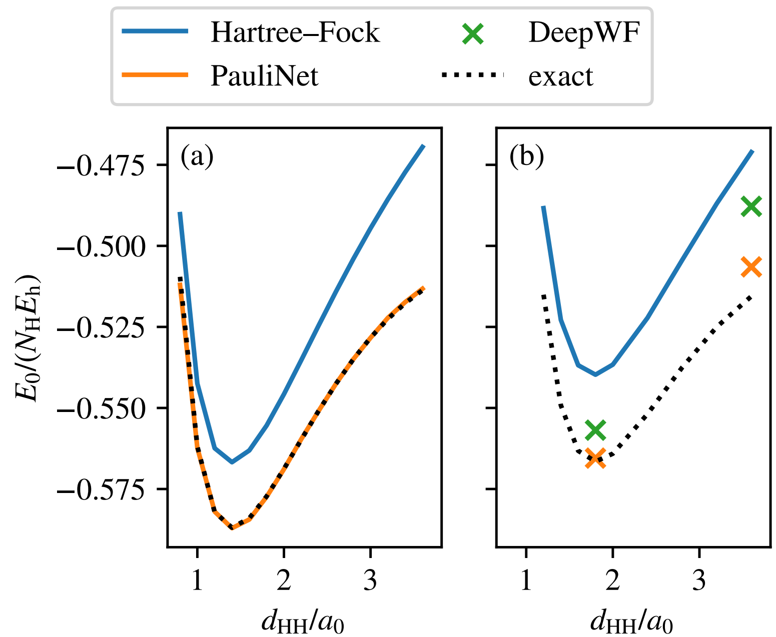
PauliNet: Results

system[a]	VMC		DMC		DeepWF		PauliNet	
	E_0/E_h ($\%\ E_{corr}$)							
H_2[b]					−1.1738	98.4%	−1.174 37(6)	99.7%
LiH[c]	−8.0635[f]	91.5%	−8.0703[f]	99.7%	−7.8732	[g]	−8.0690(3)	98.1%
Be[d]	−14.6311[d]	61.6%	−14.6572[d]	89.2%	−14.6141	43.6%	−14.6546(7)	86.5%
B[d]	−24.6056[d]	60.0%	−24.6398[d]	88.3%	−24.2124	[g]	−24.634(2)	83.5%
H_{10}[e]					−5.5685	63.8%	−5.655(2)	96.0%



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Cecilia Clementi (Rice University)
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Gianni de Fabritiis (Barcelona)

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