Weighted Langevin mechanics for potential escape problems

Ryosuke AKASHI (明石遼介)

Dept. of Physics, The Univ. of Tokyo

Collaborator: Yuri S. Nagornov. (UTokyo)

Ref. RA and Y. S. Nagornov, J. Phys. Soc. Jpn. **87**, 063801 (2018);
Y. S. Nagornov and RA, Physica A **528**, 121481 (2019);
Y. S. Nagornov and RA, arXiv:1907.11316.

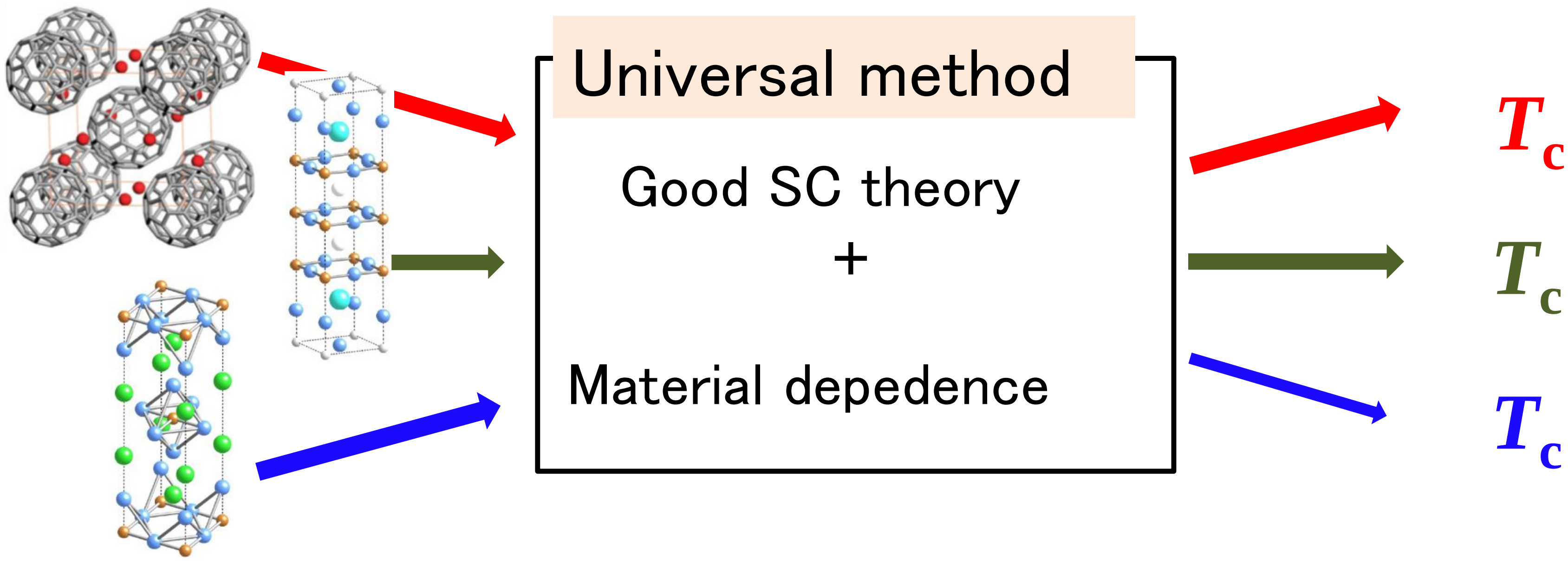
文部科学省　ポスト「京」萌芽的課題１　基礎科学のフロンティア—極限への挑戦
複合相関が織りなす極限マテリアル—原子スケールからのアプローチ

A bit on my background

03/2014	PhD of engineering, Univ. of Tokyo (Supervisor: Prof. Ryotaro Arita)
04/2014—08/2014	Postdoc at RIKEN-CEMS
09/2014—present	Assistant Prof. (助教), Univ. of Tokyo (Prof. Shinji Tsuneyuki's group)

Research interest

First-principle calculation for materials (especially for superconductors)



Universal method

Good SC theory

+

Material depedence

T_c

T_c

T_c

Aim: Prediction of new materials

Unambiguous explanation of HTC superconductors

A bit on my background

Main research subjects

First principles calculation of superconducting Tc

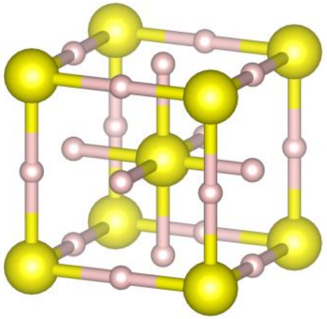
i, Development of density functional theory for superconductors

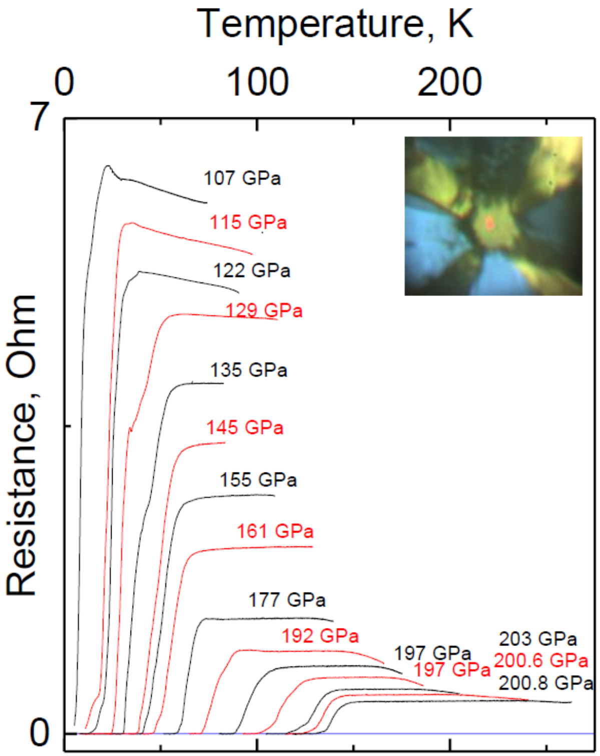
RA and R. Arita, PRL **111**, 057006 (2013)

ii, 200-kelvin superconductivity in compressed H_xS

RA, M. Kawamura, Y. Nomura, S. Tsuneyuki, and R. Arita, PRB **91**, 224513 (2015);
RA, W. Sano, R. Arita and S. Tsuneyuki, PRL **117**, 075503 (2016);
RA, arXiv;1909.02956

Sulfur (super)hydride
H_3S at extreme pressure





A bit on my background

Main research subjects

Development of DFT

i, with neural network

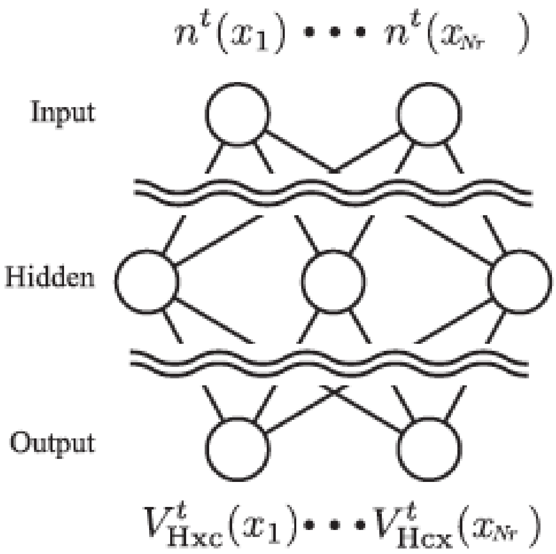
R. Nagai, RA, S. Sasaki and S. Tsuneyuki, J. Chem. Phys. **148**, 241737 (2018);
R. Nagai, RA, and O. Sugino, arXiv:1903.00238

ii, with relativistic corrections

T. Naito, RA, H.-Z. Liang, and S. Tsuneyuki, in prep.

iii, for nuclei

T. Naito, RA, and H.-Z. Liang, PRC **97**, 044319 (2018)



Reaction path search to the metastable structures

RA and Y. S. Nagornov, J. Phys. Soc. Jpn. **87**, 063801 (2018);
Y. S. Nagornov and RA, Physica A **528**, 121481 (2019);
Y. S. Nagornov and RA, arXiv:1907.11316;
https://github.com/ryosuke-akashi/AtomREM

🟥 hcp 🟩 fcc 🟦 bcc ⬜ other

A bit on my background

Main research subjects

Development of DFT

i, with neural network

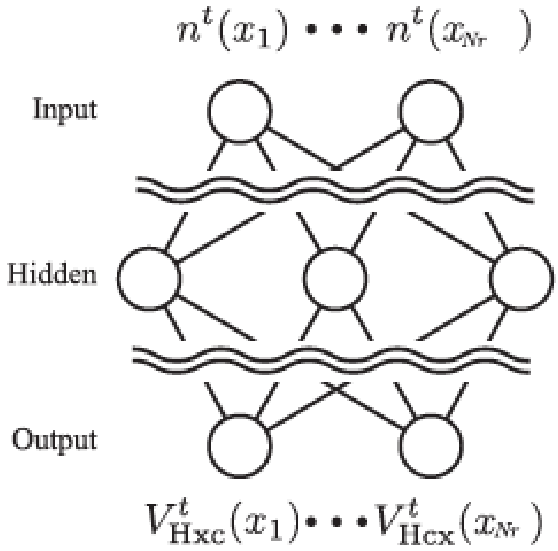
R. Nagai, RA, S. Sasaki and S. Tsuneyuki, J. Chem. Phys. **148**, 241737 (2018);
R. Nagai, RA, and O. Sugino, arXiv:1903.00238

ii, with relativistic corrections

T. Naito, RA, H.-Z. Liang, and S. Tsuneyuki, in prep.

iii, for nuclei

T. Naito, RA, and H.-Z. Liang, PRC **97**, 044319 (2018)



Reaction path search to the metastable structures

RA and Y. S. Nagornov, J. Phys. Soc. Jpn. **87**, 063801 (2018);
Y. S. Nagornov and RA, Physica A **528**, 121481 (2019);
Y. S. Nagornov and RA, arXiv:1907.11316;
https://github.com/ryosuke-akashi/AtomREM

🟥 hcp 🟩 fcc 🟦 bcc ⬜ other

This issue concerns an interdisciplinary problem.

Stochastic mechanics under thermal fluctuation

$$\dot{X} = \underline{-\partial U(X)} + \underline{W(X)}$$

Potential force

Random force(thremal fluctuation) $\propto\ T^{1/2}$

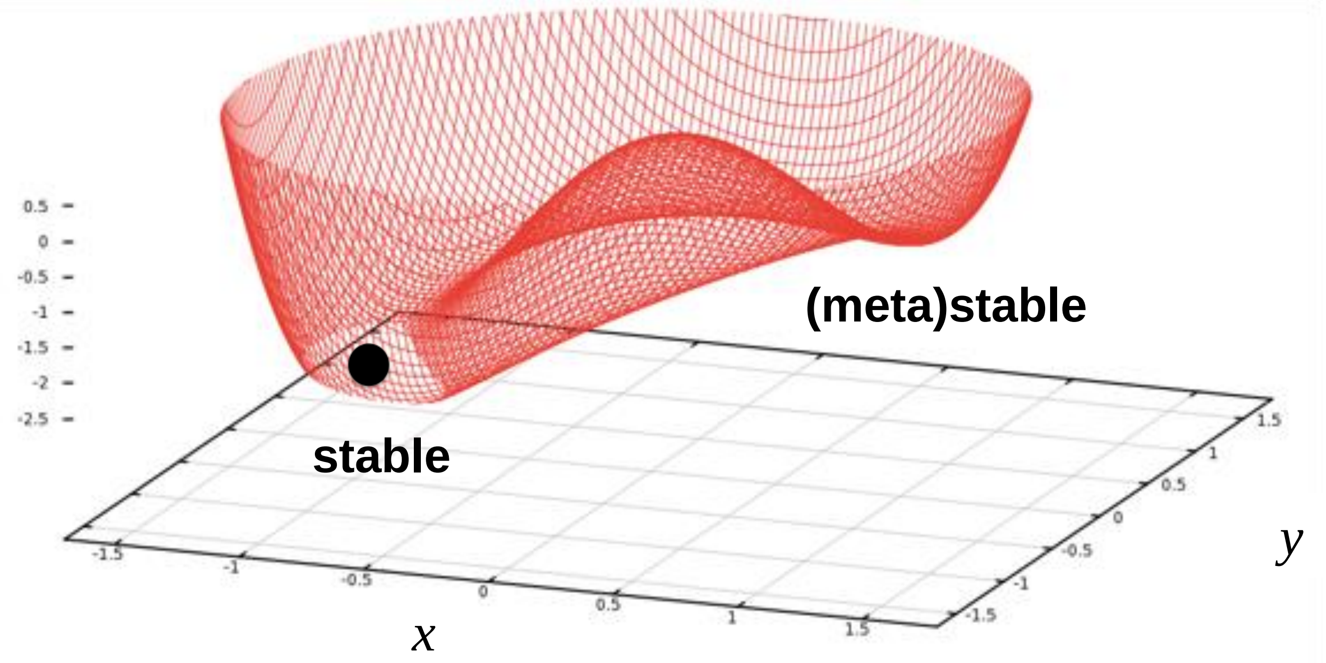
Stochastic mechanics under thermal fluctuation

$$\dot{X} = \underline{-\partial U(X)} + \underline{W(X)}$$

Potential force

Random force(thremal fluctuation) ∝ $T^{1/2}$

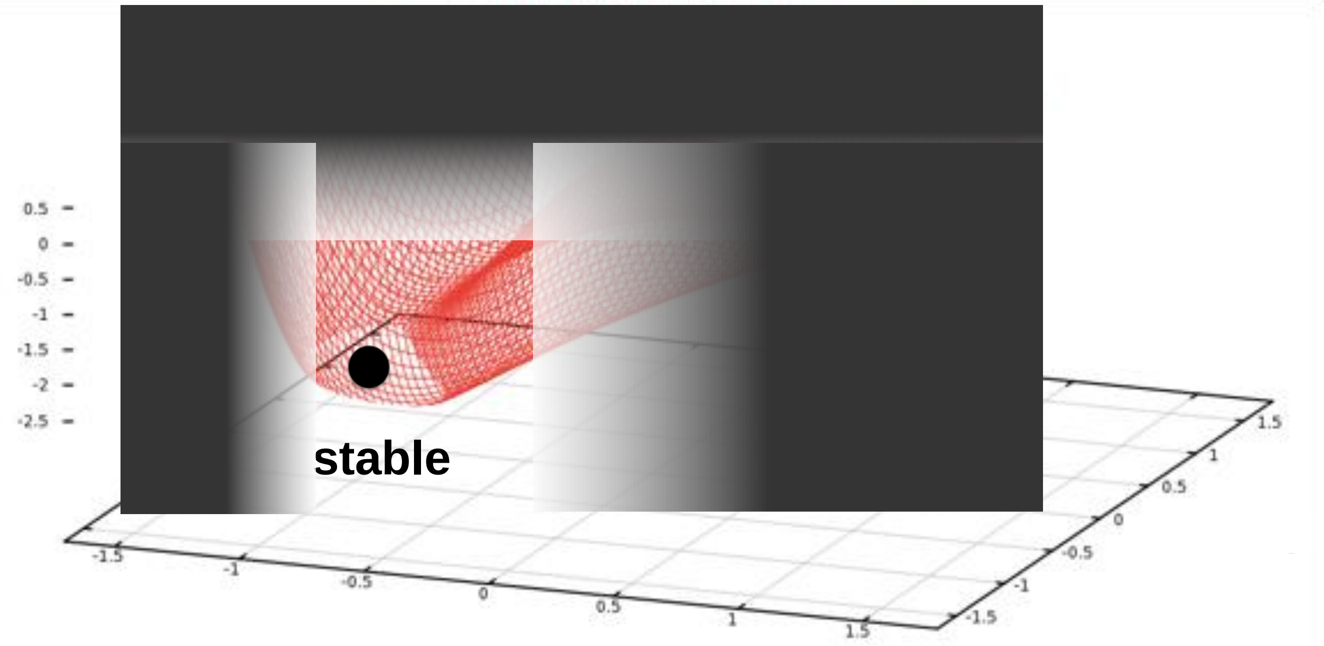
Potential surface $U(x, y)$



Task: Seek the most probable escape paths.

Stochastic mechanics under thermal fluctuation

In higher dimensions . . .



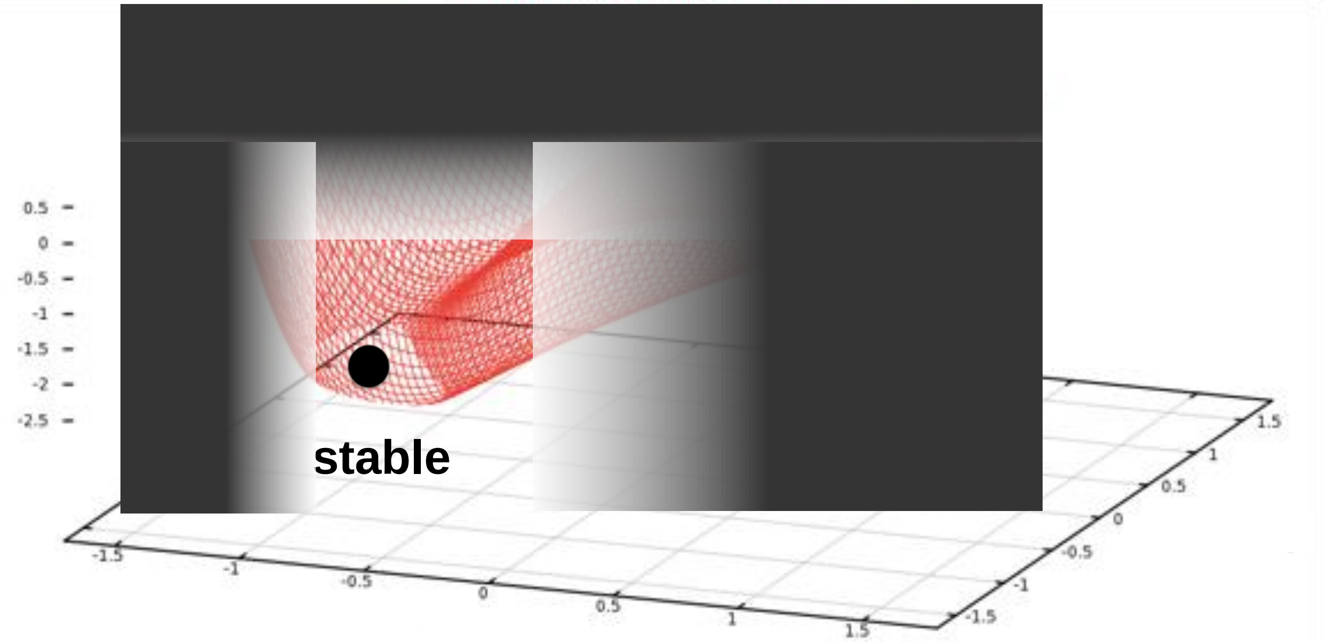
Stochastic mechanics under thermal fluctuation

In higher dimensions . . .

we usually cannot execute exhaustive search.

-Only local info of *U* is available.

-Even if we have analytic expression of *U*, we cannot locate the escape paths.



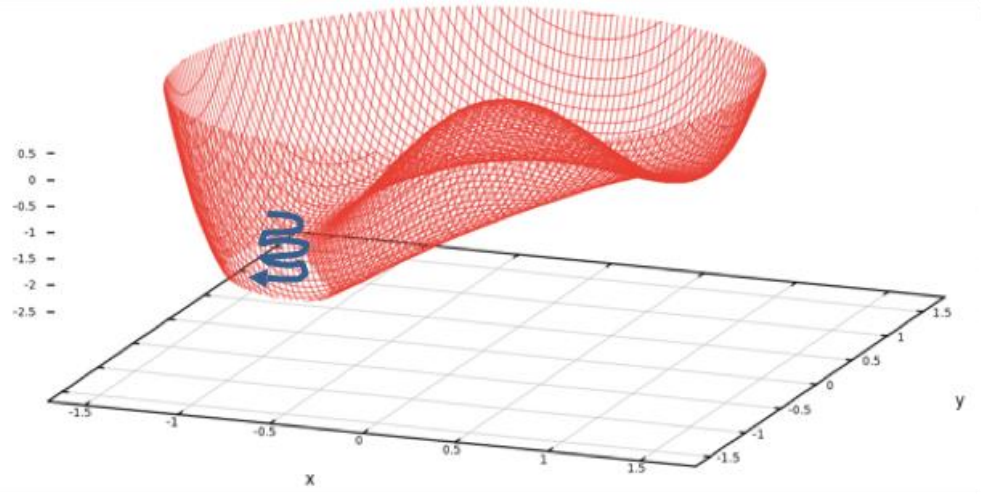
Thermally driven potential escape

$$\dot{X} = -\partial U(X) + W(X)$$

Numerical simulation of the Langevin mechanics

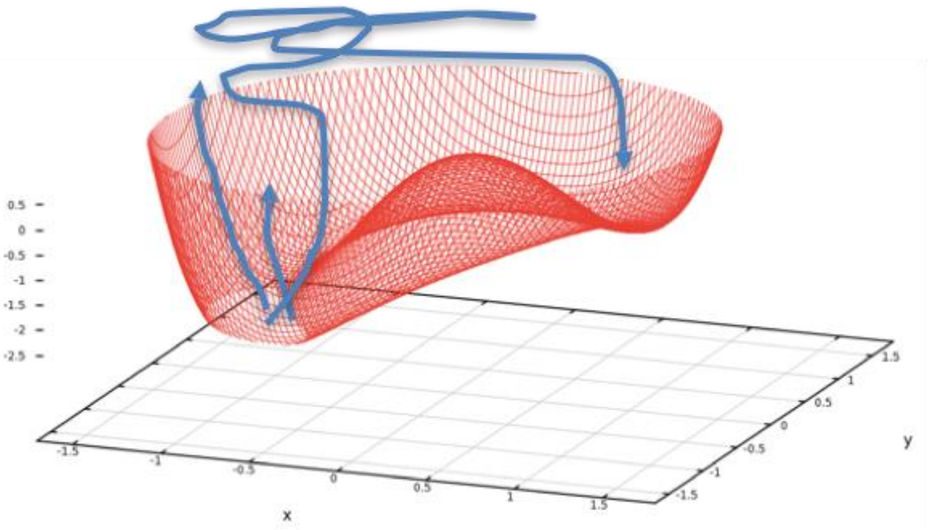
Low temperature (fluctuation)

Traverse rarely occurs.



High temperature

The system is broken, and/or the path information is lost.



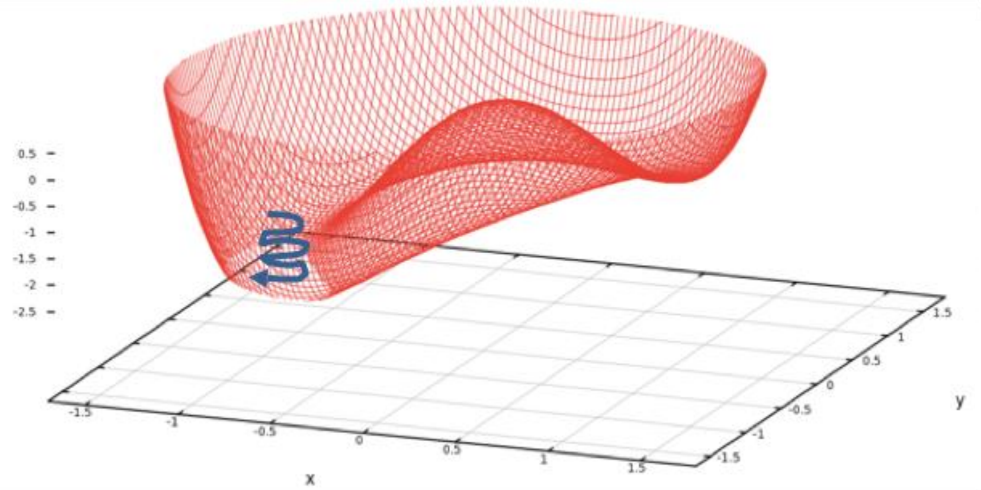
Thermally driven potential escape

$$\dot{X} = -\partial U(X) + W(X)$$

Numerical simulation of the Langevin mechanics

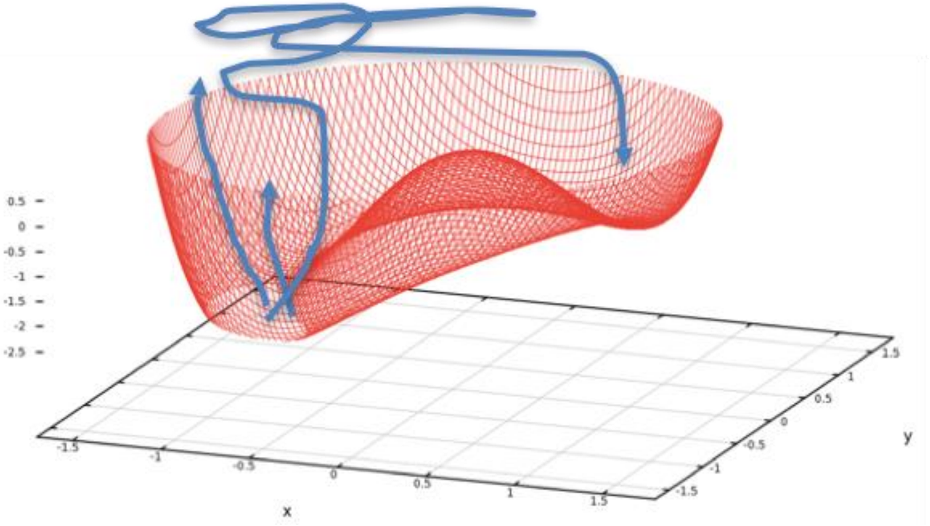
Low temperature (fluctuation)

Traverse rarely occurs.



High temperature

The system is broken, and/or
the path information is lost.



Protein folding, molecular reaction,
impurity migration, collapse of metastable phases, . . .

Thermally driven potential escape

$$\dot{X} = -\partial U(X) + W(X)$$

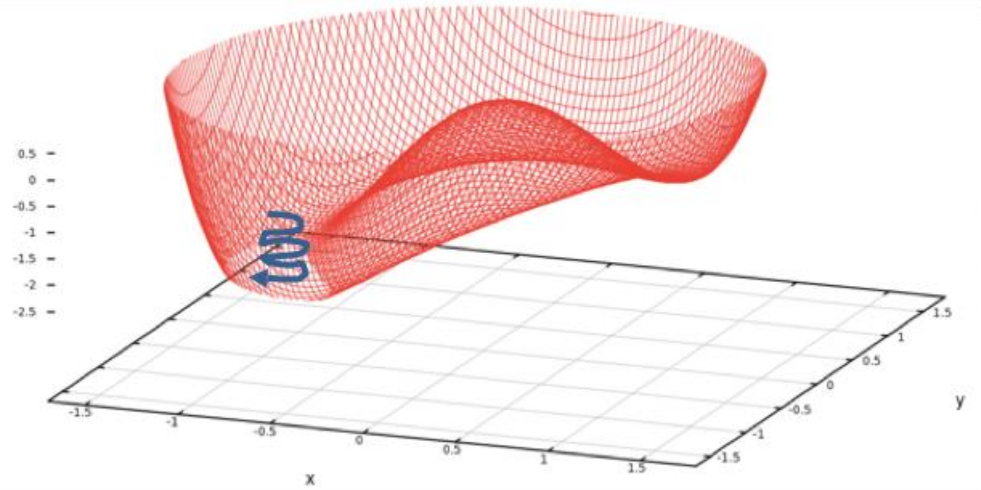
Numerical simulation of the Langevin mechanics

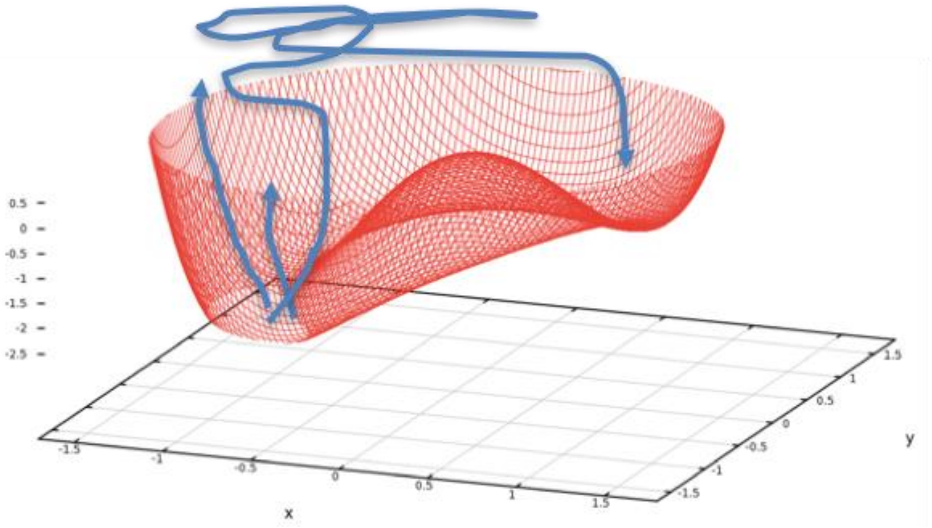
Low temperature (fluctuation)

Traverse rarely occurs.

High temperature

The system is broken, and/or
the path information is lost.





Protein folding, molecular reaction,
*impurity migration, collapse of metastable phases, . . ., **and also nuclear fission**.*

A common thread

Fission dynamics by stochastic treatment

Y. Abe *et al*., Phys. Rep. **275**, 49 (1996)

$$\dot{X} = -\partial U(X) + \underbrace{W(X)}_{\text{Diffusion force (from internal particles)}}$$

$$U = U(\underbrace{\chi_1, \chi_2, \chi_3, \ldots}_{\text{Macroscopic shape parameters}})$$

A common thread

Fission dynamics by stochastic treatment

Y. Abe *et al.*, Phys. Rep. **275**, 49 (1996)

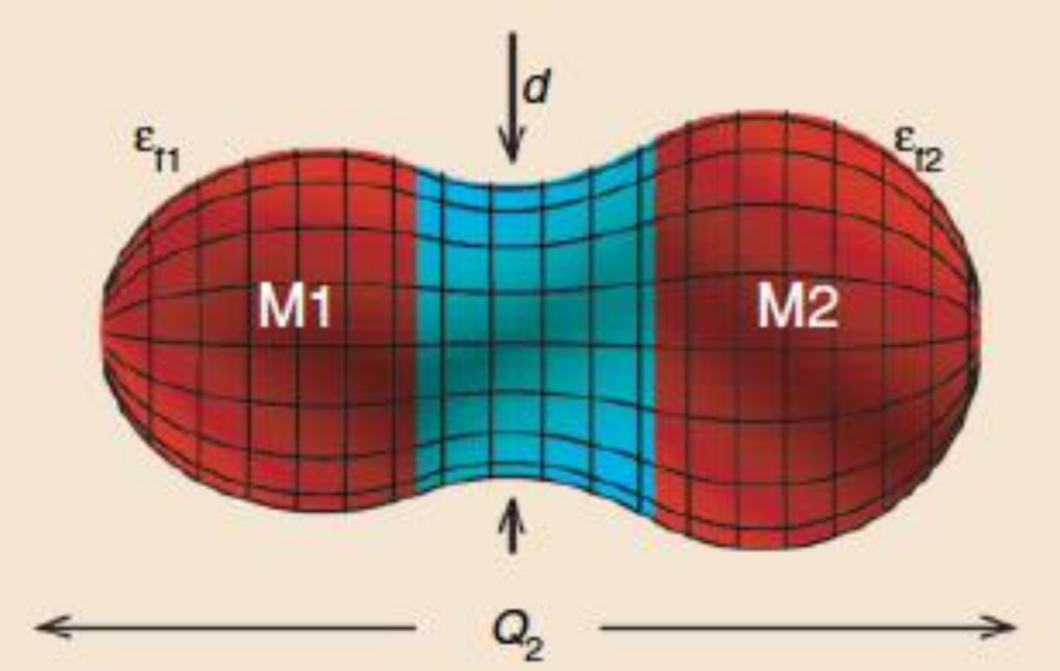
$$\dot{X} = -\partial U(X) + \underline{W(X)}$$

Diffusion force (from internal particles)

$$U = U(\underline{\chi_1, \chi_2, \chi_3, \cdots})$$

Macroscopic shape parameters

P. Moeller *et al.*, PRC **79**, 064304 (2009);
J. Randrup and P. Moeller, PRL **106**, 132503(2011).

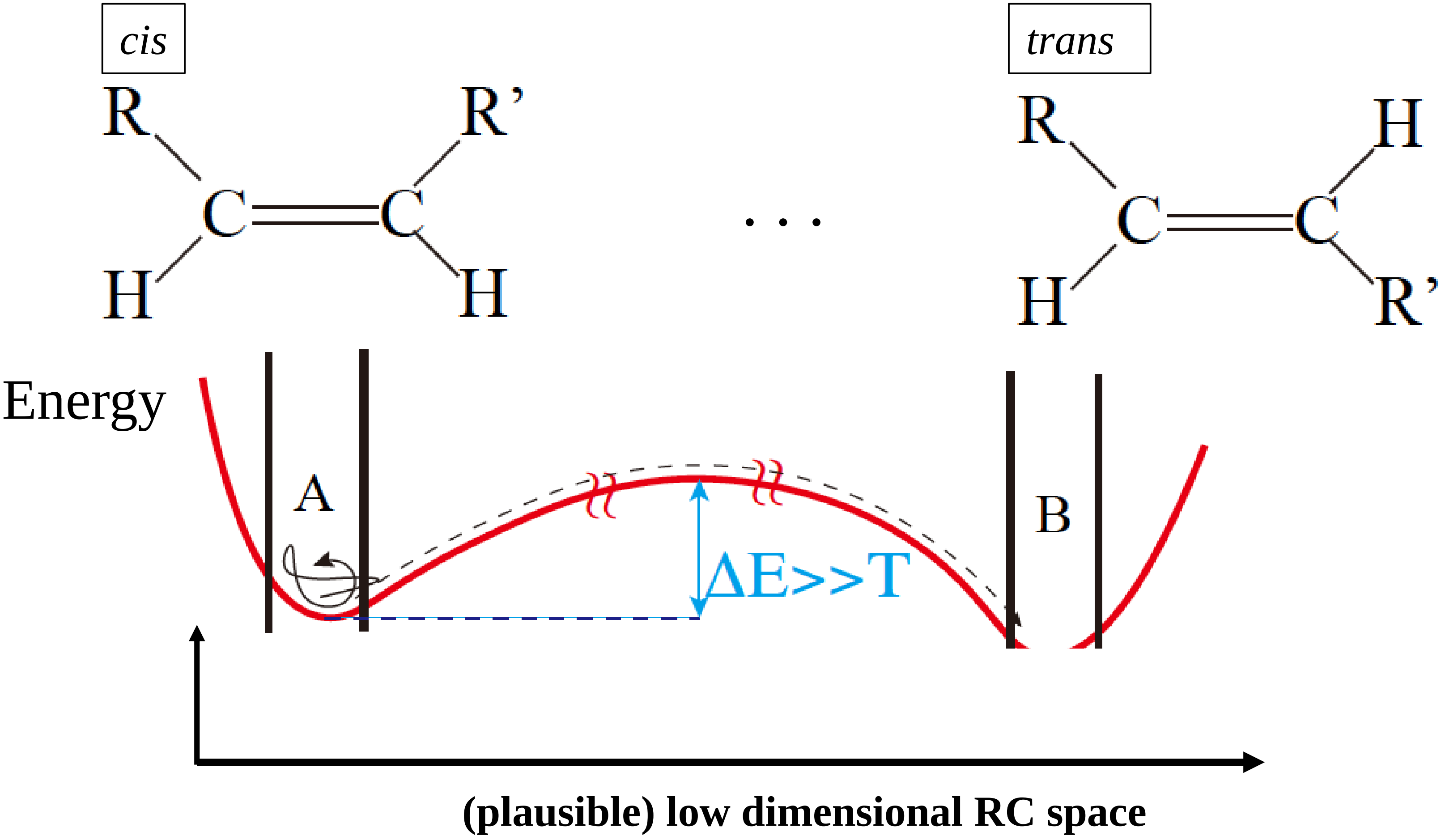


Q_2 ~ Elongation (fission direction)
α_g ~ (M1-M2)/(M1+M2) Mass asymmetry
ε_{f1} ~ Left fragment deformation
ε_{f2} ~ Right fragment deformation
d ~ Neck

Thermally driven potential escape

Typical strategy:

Define reaction coordinate (RC) and execute any biased dynamics



Thermally driven potential escape

Typical strategy:

Define reaction coordinate (RC) and execute any biased dynamics

Potential bias:
Add artificial potential as a function of RCs
-Umbrella sampling G. Torrie and J. Valleau: J. Comput. Phys. **23** (1977) 187
-Metadynamics A. Laio and M. Parrinello: Proc. Natl. Acad. Sci. USA **99** (2002) 12562
-Hyperdynamics A. F. Voter: J. Chem. Phys. **106** (1997) 4665
-Anharmonic downward distortion following O. Maeda et al., Chem. Phys. Lett., **384**, 277 (2004).
- . . .

Sampling bias:
Selectively accept the trials which proceed in the desired RC direction
-Forward flux sampling R. J. Allen et al. : Phys. Rev. Lett. **94** (2005) 018104
-Parallel cascade sampling R. Harada and A. Kitao: J. Chem. Phys. **139** (2013) 035103
-. . .

Problems:
-Warping of the trajectory due to the artificial potential
-Unintuitive appropriate RCs

Thermally driven potential escape

Typical strategy:

Define reaction coordinate (RC) and execute any biased dynamics

Potential bias:
Add artificial potential as a function of RCs

- -Umbrella sampling G. Torrie and J. Valleau: J. Comput. Phys. **23** (1977) 187
- -Metadynamics A. Laio and M. Parrinello: Proc. Natl. Acad. Sci. USA **99** (2002) 12562
- -Hyperdynamics A. F. Voter: J. Chem. Phys. **106** (1997) 4665
- -Anharmonic downward distortion following O. Maeda et al., Chem. Phys. Lett., **384**, 277 (2004).
- - . . .

Sampling bias:
Selectively accept the trials which proceed in the desired RC direction

- -Forward flux sampling R. J. Allen et al. : Phys. Rev. Lett. **94** (2005) 018104
- -Parallel cascade sampling R. Harada and A. Kitao: J. Chem. Phys. **139** (2013) 035103
- -. . .

Is any RC- and artificial potential-free algorithm possible?

Why is the escape rare?

Langevin molecular mechanics (overdamped)

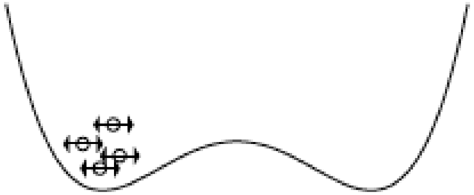
$$\dot{X} = \underline{-\partial U(X)} + \underline{W(X)}$$

Potential force

Random force(thremal fluctuation) $\propto$ $T^{1/2}$

Why is the escape rare?

Langevin description: Eq. of motion of variables with stochastic force

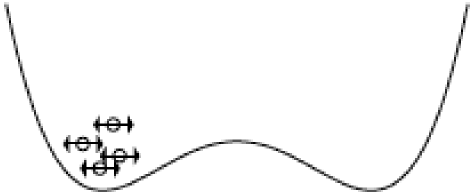


$$\dot{X} = -\partial U(X) + W(X)$$

Strong force is rarely exerted such that the potential barrier is overcome

Why is the escape rare?

Langevin description: Eq. of motion of variables with stochastic force

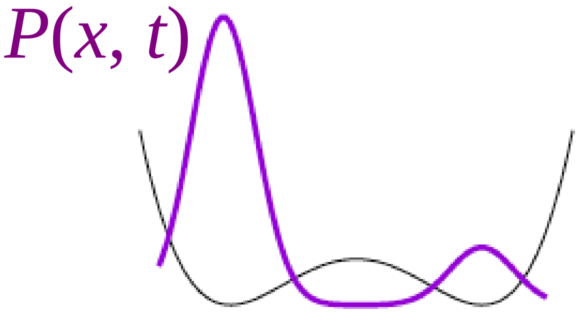


$$\dot{X} = -\partial U(X) + W(X)$$

Equiv.

Strong force is rarely exerted such that the potential barrier is overcome

Fokker–Planck description: Deterministic Eq. of motion of distribution of variables



$$\partial_t P(X,t) = \hat{L} P(X,t)$$

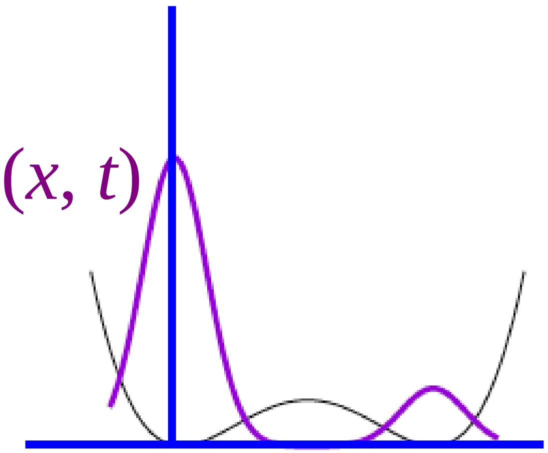
Distribution amplitude is infinitesimally small near the potential barrier

Ref. C. Gardiner, “Stochastic Methods (4th ed.)” (Springer)

Why is the escape rare?

Fokker–Planck description: Deterministic Eq. of motion of distribution of variables

$P(\mathrm{x},\,0)=\delta(x\text{-}x_0)$

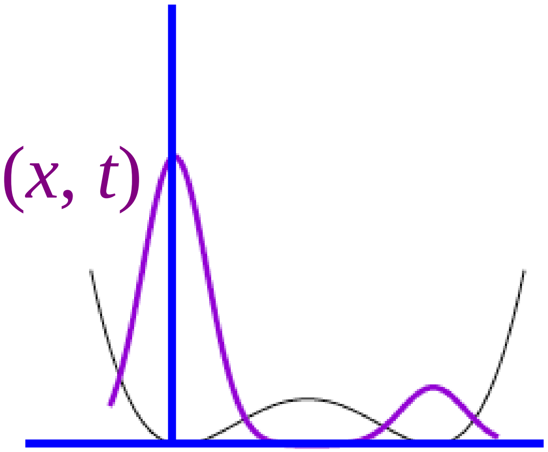


Why is the escape rare?

Fokker–Planck description: Deterministic Eq. of motion of distribution of variables

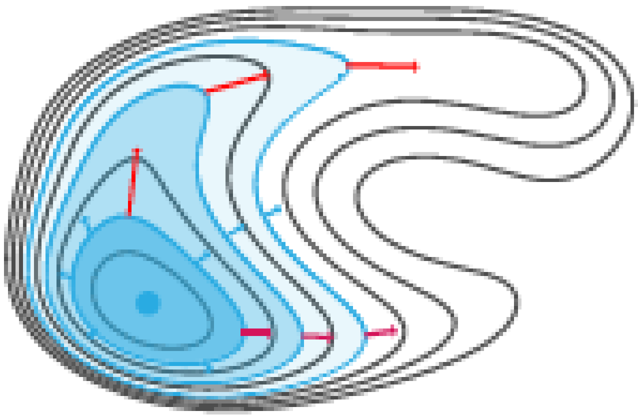
$P(\mathrm{x}, 0)=\delta(x\text{-}x_0)$

$P(x, t)$



Long time limit

$$\boxed{P(X, t \to \infty) \propto \exp(-\beta U(X))}$$

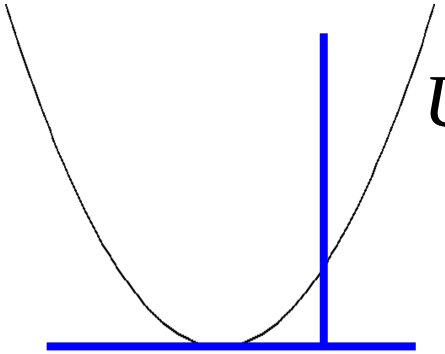


Nonzero component up the potential
→extract it!

Ornstein-Uhlenbeck process

$$\boxed{\partial_t p(x,t) = \frac{1}{\Gamma}\partial_x(\alpha x + k_B T\partial_x)p(x,t)}$$

$P(x, 0)=\delta(x-x_0)$

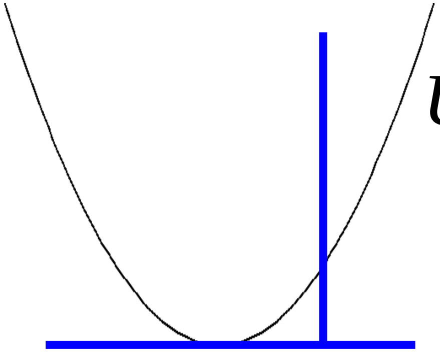


$U(x)=\alpha x^2/2$

Ornstein-Uhlenbeck process

$$\boxed{\partial_t p(x,t) = \frac{1}{\Gamma}\partial_x(\alpha x + k_B T\partial_x)p(x,t)}$$

$P(x,\ 0)=\delta(x\text{-}x_0)$



General solution

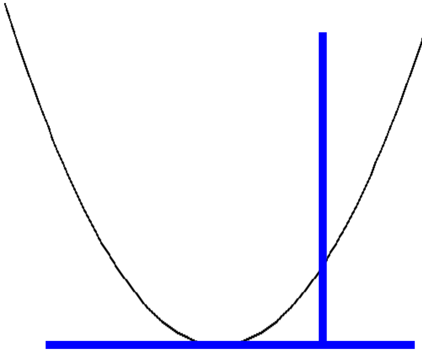
$$\boxed{p(x,t) = \sqrt{\frac{\alpha}{2\pi k_{\mathrm{B}} T(1-s^2)}}\exp\left[-\frac{\alpha(x-sx_0)^2}{2k_{\mathrm{B}}T(1-s^2)}\right]}$$

$$s \equiv s(t) = \exp(-\alpha t/\Gamma)$$

Ornstein-Uhlenbeck process

$$\boxed{\partial_t p(x,t) = \frac{1}{\Gamma}\partial_x(\alpha x + k_B T \partial_x) p(x,t)}$$

$P(x, 0)=\delta(x-x_0)$



$U(x)=\alpha x^2/2$

Distribution center
~O(t)

General solution

$$\boxed{p(x,t) = \sqrt{\frac{\alpha}{2\pi k_\mathrm{B} T(1-s^2)}}\exp\left[-\frac{\alpha(x-sx_0)^2}{2k_\mathrm{B}T(1-s^2)}\right]}$$

$$s \equiv s(t) = \exp(-\alpha t/\Gamma)$$

Distribution width
~O($t^{1/2}$)

In small t diffusion >> potential drift = leakage of $p(x,t)$ up the potential $U(x)$

Ornstein-Uhlenbeck process

Center~O(t)

General solution

$$p(x,t) = \sqrt{\frac{\alpha}{2\pi k_\mathrm{B}T(1-s^2)}}\exp\left[-\frac{\alpha(x-sx_0)^2}{2k_\mathrm{B}T(1-s^2)}\right]$$

$$s \equiv s(t) = \exp(-\alpha t/\Gamma)$$

Width~O($t^{1/2}$)

In small t diffusion >> potential drift = leakage of $p(x,t)$ up the potential $U(x)$

Ornstein-Uhlenbeck process

Center~O(t)

General solution

$$\boxed{p(x,t) = \sqrt{\frac{\alpha}{2\pi k_{\mathrm{B}} T(1-s^2)}} \exp\left[-\frac{\alpha(x-sx_0)^2}{2k_{\mathrm{B}}T(1-s^2)}\right]}$$

$$s \equiv s(t) = \exp(-\alpha t/\Gamma)$$

Width~O($t^{1/2}$)

In small t diffusion >> potential drift = leakage of $p(x,t)$ up the potential $U(x)$

$$\Rightarrow p(x,t) \;\propto\; p_{\mathrm{eq}}(x)\boxed{q(x,t)}$$

Large at large-$U(x)$ region,
small at small-$U(x)$ region.

Ornstein-Uhlenbeck process

General solution

$$\boxed{p(x,t) = \sqrt{\frac{\alpha}{2\pi k_{\mathrm{B}} T(1-s^2)}} \exp\left[-\frac{\alpha(x-sx_0)^2}{2k_{\mathrm{B}}T(1-s^2)}\right]}$$

$$s \equiv s(t) = \exp(-\alpha t/\Gamma)$$

$$\boxed{p(x,t) = \exp[-(1-\delta)U(x)/k_{\mathrm{B}}T]q(x,t)}$$

Ornstein-Uhlenbeck process

General solution

$$\boxed{p(x,t) = \sqrt{\frac{\alpha}{2\pi k_{\rm B}T(1-s^2)}}\exp\left[-\frac{\alpha(x-sx_0)^2}{2k_{\rm B}T(1-s^2)}\right]}$$

$$s \equiv s(t) = \exp(-\alpha t/\Gamma)$$

$$\boxed{p(x,t) = \exp[-(1-\delta)U(x)/k_{\rm B}T]q(x,t)}$$

$$\boxed{q(x,t) = C(t)\exp\left[-\frac{\{x-x_{max}(\delta,s)\}^2}{2\sigma^2(\delta,s)}\right]}$$

q−center

$$x_{max}(\delta,s) = x_0\frac{s}{\delta+(1-\delta)s^2}$$

q−width

$$\sigma^2(\delta,s) = \frac{k_{\rm B}T}{\alpha}\frac{1-s^2}{\delta+(1-\delta)s^2}$$

Ornstein-Uhlenbeck process

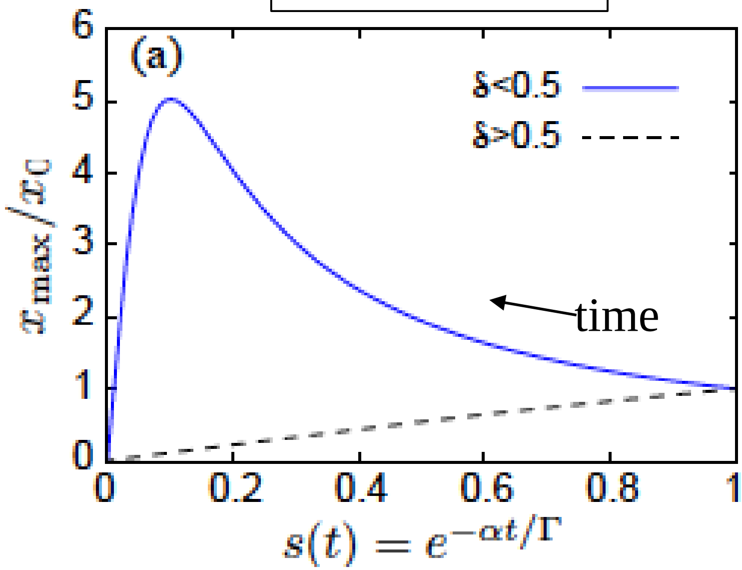
General solution

$$\boxed{p(x,t) = \sqrt{\frac{\alpha}{2\pi k_\mathrm{B}T(1-s^2)}}\exp\left[-\frac{\alpha(x-sx_0)^2}{2k_\mathrm{B}T(1-s^2)}\right]}$$

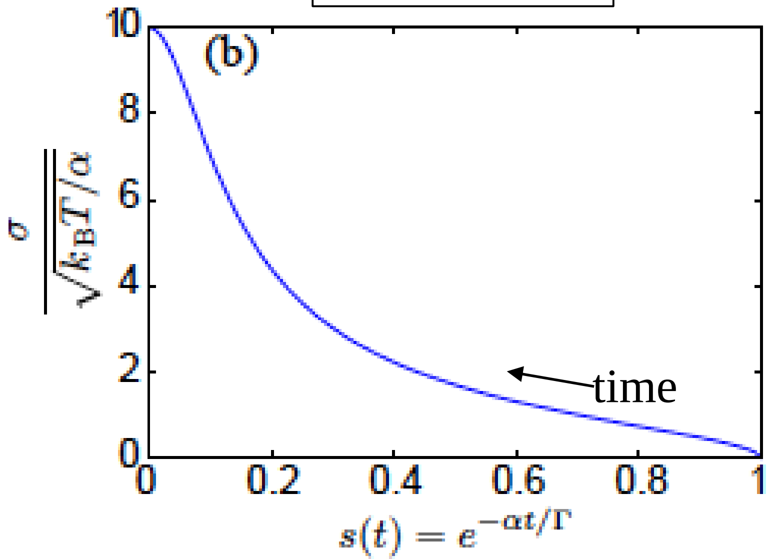
$$s \equiv s(t) = \exp(-\alpha t/\Gamma)$$

$$\boxed{p(x,t) = \exp[-(1-\delta)U(x)/k_\mathrm{B}T]q(x,t)}$$

***q*-center**

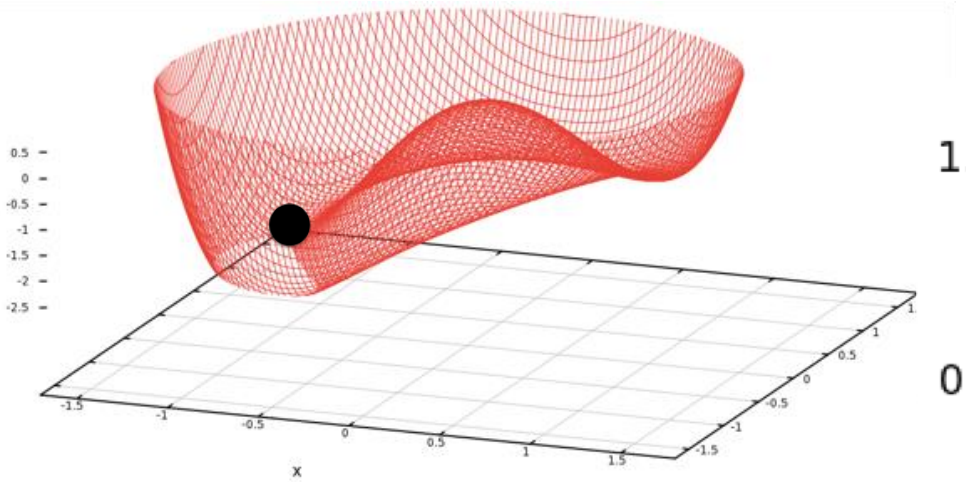


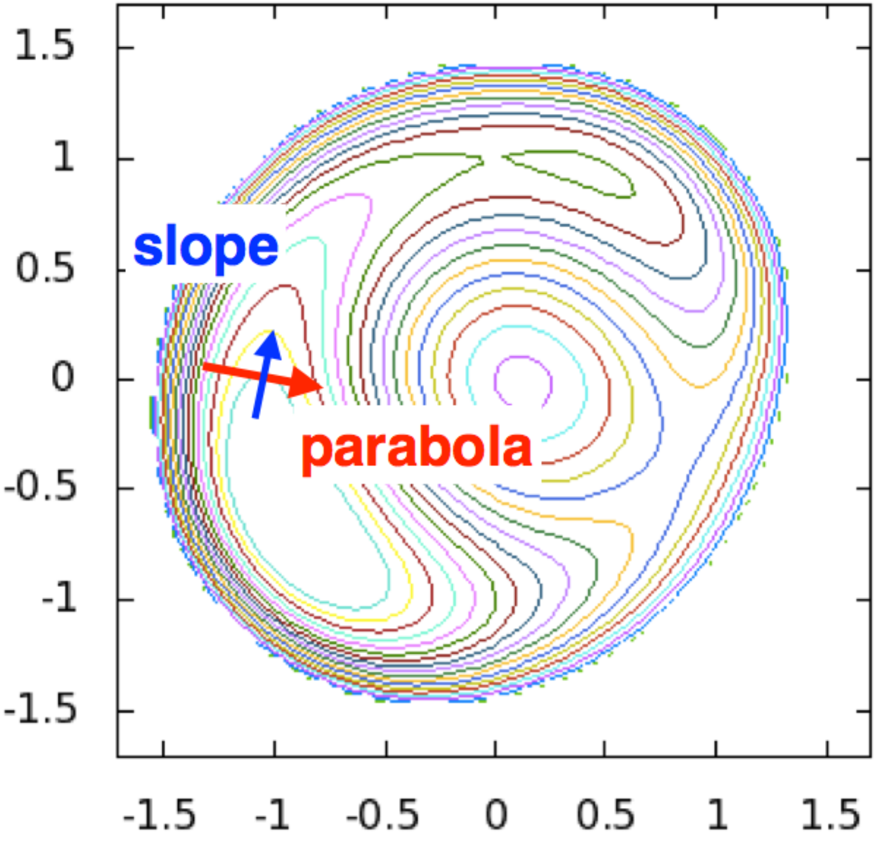
***q*-width**



***q* goes up the surface if $x_0>>T^{1/2}$**

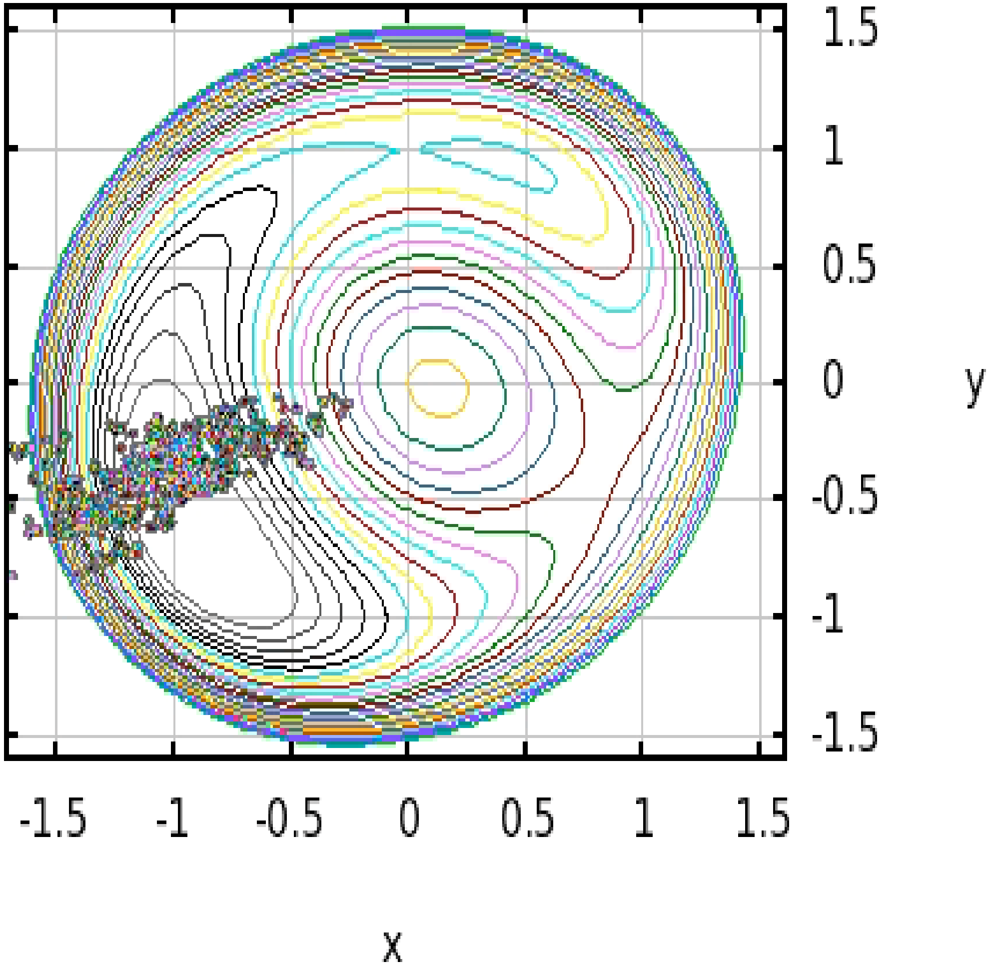
q(x, t) on high dimensional potential surfaces





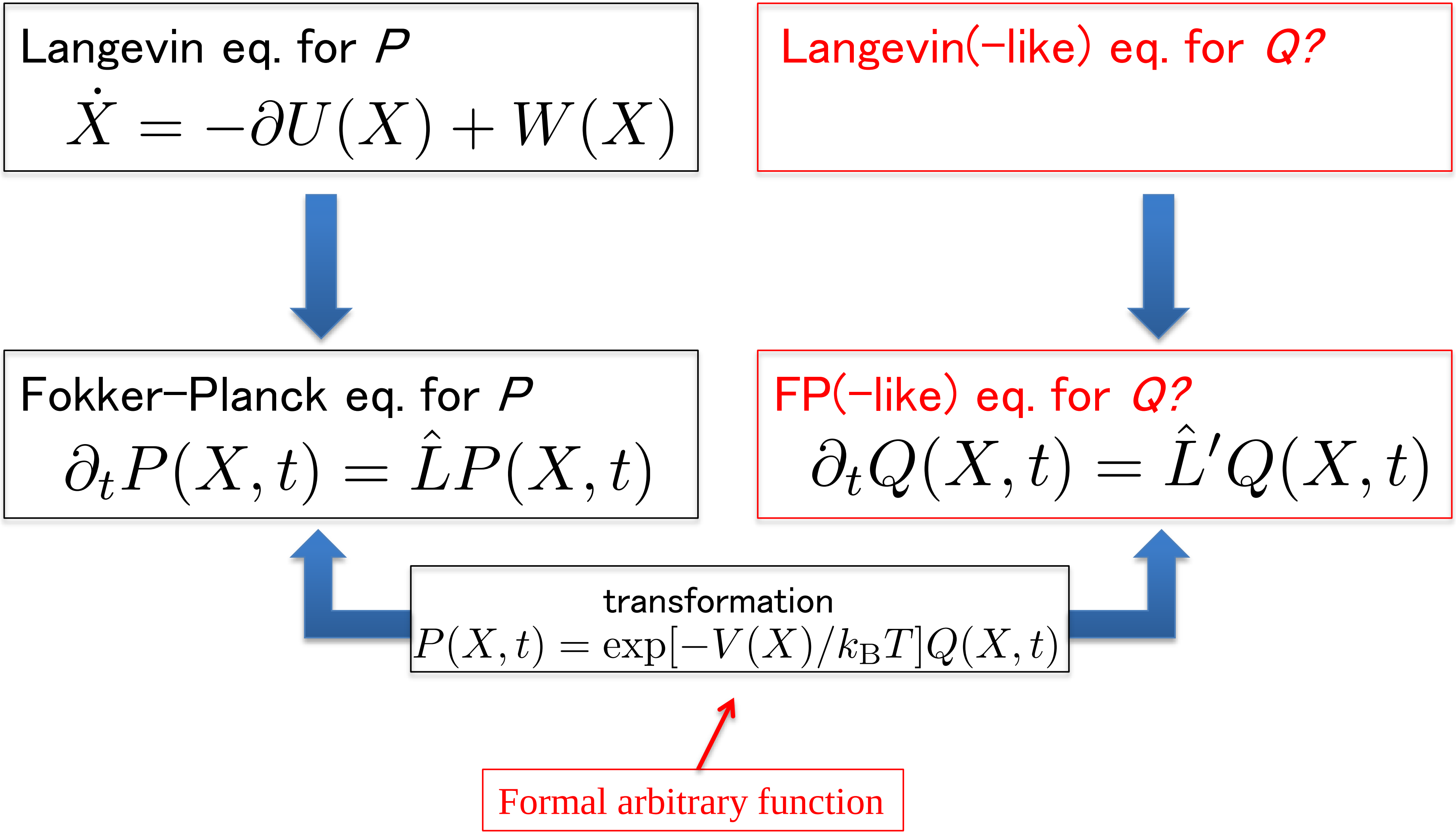
Slope direction : go up;
Parabolic direction: spread

Put at the “valley line”, *q* goes upward the valley→optimum escape to the saddle point?



RA and Y. S. Nagornov, J. Phys. Soc. Jpn. **87**, 063801 (2018);

Stochastic equation of x for *q*(x,t)



Langevin eq. for *P*

$$\dot{X} = -\partial U(X) + W(X)$$

Langevin(−like) eq. for *Q?*

Fokker−Planck eq. for *P*

$$\partial_t P(X,t) = \hat{L} P(X,t)$$

FP(−like) eq. for *Q?*

$$\partial_t Q(X,t) = \hat{L}' Q(X,t)$$

transformation

$$P(X,t) = \exp[-V(X)/k_{\mathrm{B}}T]Q(X,t)$$

Formal arbitrary function

Master equation for *q*(x,t)

Giardina, Kurchan, Lecomte, and Tailleur, J. Stat. Phys. **145** (2011) 787

N-dim Fokker-Planck (Smoluchowski) equation

$$\boxed{\partial_t p(\mathbf{x},t) = \frac{1}{\Gamma}\left[\partial_i(\partial_i U(\mathbf{x})) + k_{\mathrm{B}} T \partial_i^2\right] p(\mathbf{x},t)}$$

Master equation for *q*(x,t)

Giardina, Kurchan, Lecomte, and Tailleur, J. Stat. Phys. **145** (2011) 787

N-dim Fokker-Planck (Smoluchowski) equation

$$\boxed{\partial_t p(\mathbf{x},t) = \frac{1}{\Gamma}\left[\partial_i(\partial_i U(\mathbf{x})) + k_\mathrm{B} T \partial_i^2\right] p(\mathbf{x},t)}$$

$$p(\mathbf{x},t) = \underline{C(t)}\exp[-\underline{V}(\mathbf{x})/k_\mathrm{B}T]\underline{q(\mathbf{x},t)}$$

Normalization factor

Biasing potential
(generalization of *U*)

biased distribution
(by def. positive definite)

Master equation for *q*(x,t)

Giardina, Kurchan, Lecomte, and Tailleur, J. Stat. Phys. **145** (2011) 787

N-dim Fokker-Planck (Smoluchowski) equation

$$\partial_t p(\mathbf{x},t) = \frac{1}{\Gamma}\left[\partial_i(\partial_i U(\mathbf{x})) + k_\mathrm{B}T\partial_i^2\right] p(\mathbf{x},t)$$

$$p(\mathbf{x},t) = \underline{C(t)}\exp[-\underline{V(\mathbf{x})}/k_\mathrm{B}T]\underline{q(\mathbf{x},t)}$$

Normalization factor

Biasing potential
(generalization of *U*)

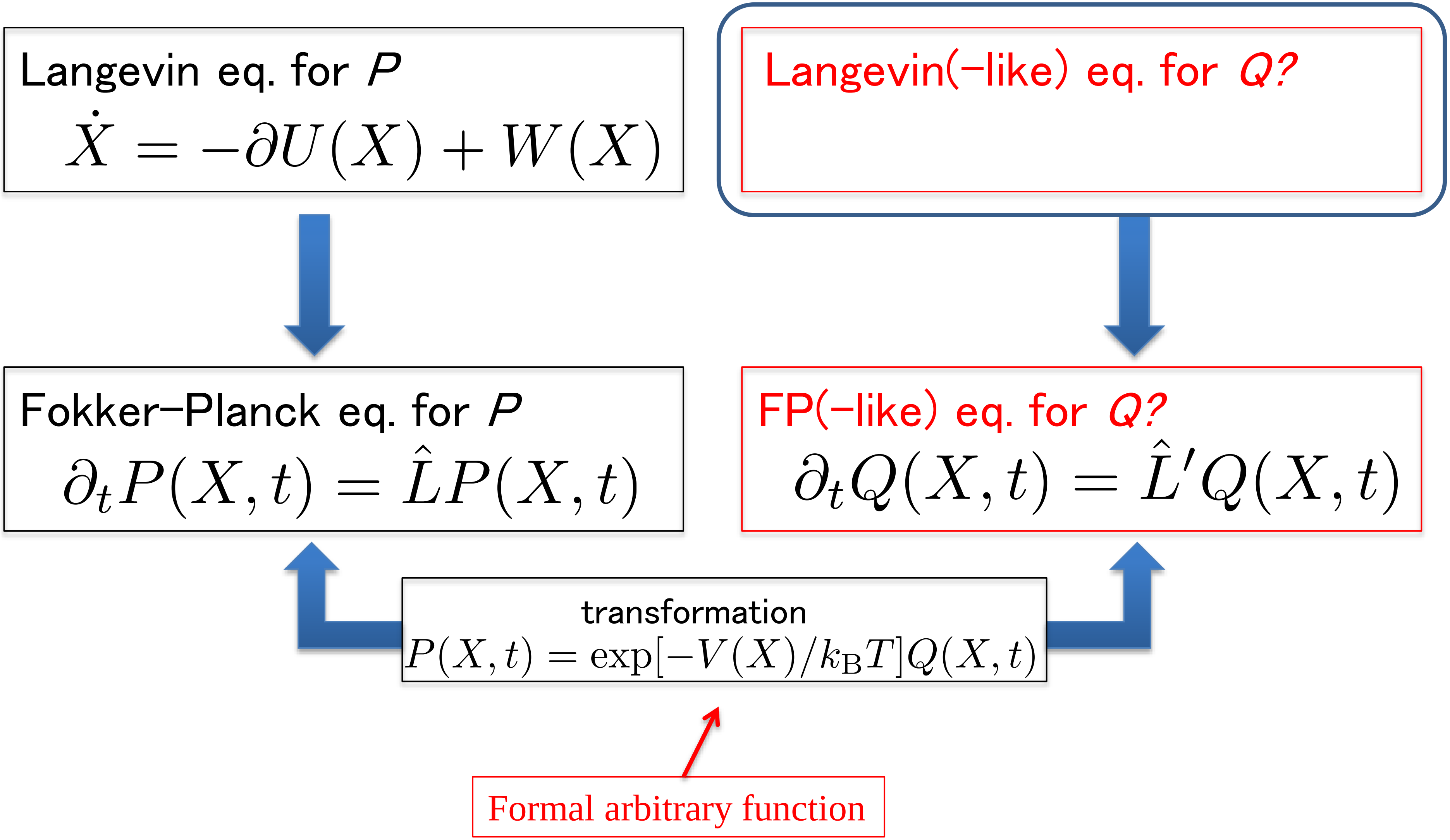
biased distribution
(by def. positive definite)

Master equation for *q*

$$\partial_t q(\mathbf{x},t) = \frac{1}{\Gamma}\left\{\partial_i[\partial_i(U(\mathbf{x}) - 2V(\mathbf{x}))] + k_\mathrm{B}T\partial_i^2\right\} q(\mathbf{x},t) + \frac{1}{\Gamma}\left(F(\mathbf{x}) - \langle F\rangle_q\right) q(\mathbf{x},t)$$

$$F(\mathbf{x}) = \partial_i^2 V - \beta(\partial_i V)(\partial_i(U - V)) \qquad \langle F\rangle_q = \int \mathrm{d}\mathbf{x}F(\mathbf{x})q(\mathbf{x},t) \qquad \partial_t \ln C(t) = \langle F\rangle_q$$

Stochastic equation of x for $q(x,t)$



Langevin eq. for *P*

$$\dot{X} = -\partial U(X) + W(X)$$

Langevin(–like) eq. for *Q?*

Fokker–Planck eq. for *P*

$$\partial_t P(X,t) = \hat{L} P(X,t)$$

FP(–like) eq. for *Q?*

$$\partial_t Q(X,t) = \hat{L}' Q(X,t)$$

transformation

$$P(X,t) = \exp[-V(X)/k_{\mathrm{B}}T] Q(X,t)$$

Formal arbitrary function

Stochastic equation of x for *q*(x,t)

Langevin—Fokker-Planck correspondence

L.

$$dx_i = -\frac{\partial_i U(\mathbf{x})}{\Gamma} dt + \sqrt{\frac{2k_{\mathrm{B}} T dt}{\Gamma}} W_i$$

Random value from
normal regular distribution

Stochastic equation of x for *q*(x,t)

Langevin—Fokker-Planck correspondence

L.

$$dx_i = -\frac{\partial_i U(\mathbf{x})}{\Gamma} dt + \sqrt{\frac{2k_\mathrm{B} T dt}{\Gamma}} W_i$$

Random value from normal regular distribution

Exactly derived

F.–P.

$$\partial_t p(\mathbf{x},t) = \hat{L} p(\mathbf{x},t), \ \hat{L} = \frac{1}{\Gamma}\partial_i \left[(\partial_i U(\mathbf{x})) + k_\mathrm{B} T \right]$$

$$\Leftrightarrow p(\mathbf{x}, t+dt) = \exp[\hat{L} dt] p(\mathbf{x},t) \quad \text{(integral form)}$$

Stochastic equation of x for *q*(x,t)

Langevin—Fokker-Planck correspondence

L.

$$dx_i = -\frac{\partial_i U(\mathbf{x})}{\Gamma} dt + \sqrt{\frac{2k_{\mathrm{B}}Tdt}{\Gamma}} W_i$$

Random value from
normal regular distribution

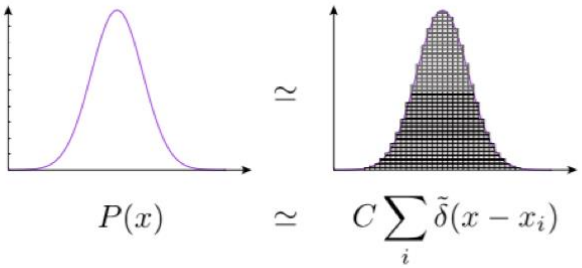
Exactly derived

F.–P.

$$\partial_t p(\mathbf{x},t) = \hat{L} p(\mathbf{x},t),\ \hat{L} = \frac{1}{\Gamma}\partial_i \left[(\partial_i U(\mathbf{x})) + k_{\mathrm{B}}T\right]$$

$$\Leftrightarrow p(\mathbf{x}, t+dt) = \boxed{\exp[\hat{L}dt]} p(\mathbf{x},t) \quad \text{(Integral form)}$$

Operation on *p*
=Evolution of walkers with property x
with the Langevin equation



Stochastic equation of x for *q*(x,t)

Master equation for q

$$\partial_t q(\mathbf{x},t) = \frac{1}{\Gamma}\left\{\partial_i[\partial_i(U(\mathbf{x}) - 2V(\mathbf{x}))] + k_{\mathrm{B}}T\partial_i^2\right\} q(\mathbf{x},t) + \frac{1}{\Gamma}\left(F(\mathbf{x}) - \langle F\rangle_q\right) q(\mathbf{x},t)$$

$$F(\mathbf{x}) = \partial_i^2 V - \beta(\partial_i V)(\partial_i(U-V)) \qquad \langle F\rangle_q = \int d\mathbf{x}F(\mathbf{x})q(\mathbf{x},t) \qquad \partial_t \ln C(t) = \langle F\rangle_q$$

$$\boxed{\partial_t q(\mathbf{x},t) = [\hat{L}' + \hat{R}]q(\mathbf{x},t)}$$

Stochastic equation of x for *q*(x,t)

Master equation for q

$$\partial_t q(\mathbf{x},t) = \underline{\frac{1}{\Gamma}\left\{\partial_i[\partial_i(U(\mathbf{x})-2V(\mathbf{x}))]+k_{\mathrm{B}}T\partial_i^2\right\}}\, q(\mathbf{x},t) + \underline{\frac{1}{\Gamma}\left(F(\mathbf{x})-\langle F\rangle_q\right)}\, q(\mathbf{x},t)$$

$$F(\mathbf{x}) = \partial_i^2 V - \beta(\partial_i V)(\partial_i(U-V)) \qquad \langle F\rangle_q = \int d\mathbf{x}F(\mathbf{x})q(\mathbf{x},t) \qquad \partial_t \mathrm{ln}C(t) = \langle F\rangle_q$$

Multiply scalar $\frac{1}{\Gamma}\{F(\mathbf{x})-\langle F\rangle\}$

$$\boxed{\partial_t q(\mathbf{x},t) = [\boxed{\hat{L}'}+\boxed{\hat{R}}]q(\mathbf{x},t)}$$

$\hat{L}$ with $U \to U-2V$

Stochastic equation of x for q(x,t)

Master equation for q

$$\partial_t q(\mathbf{x},t) = \underline{\frac{1}{\Gamma}\left\{\partial_i[\partial_i(U(\mathbf{x})-2V(\mathbf{x}))] + k_{\mathrm{B}}T\partial_i^2\right\}} q(\mathbf{x},t) + \underline{\frac{1}{\Gamma}\left(F(\mathbf{x}) - \langle F\rangle_q\right)} q(\mathbf{x},t)$$

$$F(\mathbf{x}) = \partial_i^2 V - \beta(\partial_i V)(\partial_i(U-V)) \qquad \langle F\rangle_q = \int d\mathbf{x} F(\mathbf{x}) q(\mathbf{x},t) \qquad \partial_t \ln C(t) = \langle F\rangle_q$$

Multiply scalar $\frac{1}{\Gamma}\{F(\mathbf{x}) - \langle F\rangle\}$

$$\partial_t q(\mathbf{x},t) = [\boxed{\hat{L}'}+\boxed{\hat{R}}]q(\mathbf{x},t)$$

$\hat{L}$ with $U \to U-2V$

$$\Leftrightarrow q(\mathbf{x},t+dt) = \exp\left[(\hat{L}'+\hat{R})dt\right] q(\mathbf{x},t)$$

Stochastic equation of x for *q*(x,t)

Master equation for q

$$\partial_t q(\mathbf{x},t) = \underline{\frac{1}{\Gamma}\left\{\partial_i[\partial_i(U(\mathbf{x})-2V(\mathbf{x}))]+k_{\mathrm{B}}T\partial_i^2\right\}}\, q(\mathbf{x},t) + \underline{\frac{1}{\Gamma}\left(F(\mathbf{x})-\langle F\rangle_q\right)}\, q(\mathbf{x},t)$$

$$F(\mathbf{x}) = \partial_i^2 V - \beta(\partial_i V)(\partial_i(U-V)) \qquad \langle F\rangle_q = \int d\mathbf{x}F(\mathbf{x})q(\mathbf{x},t) \qquad \partial_t \ln C(t) = \langle F\rangle_q$$

Multiply scalar $\frac{1}{\Gamma}\{F(\mathbf{x})-\langle F\rangle\}$

$$\boxed{\partial_t q(\mathbf{x},t) = [\boxed{\hat{L}'}+\boxed{\hat{R}}]q(\mathbf{x},t)}$$

$\hat{L}$ with $U \to U-2V$

$$\Leftrightarrow q(\mathbf{x},t+dt) = \exp\left[(\hat{L}'+\hat{R})dt\right] q(\mathbf{x},t)$$

$$\approx \underline{\exp\left[\hat{L}'\frac{dt}{2}\right]}\;\underline{\exp\left[\hat{R}dt\right]}\;\underline{\exp\left[\hat{L}'\frac{dt}{2}\right]}\, q(\mathbf{x},t) + O(dt^3)$$

Suzuki−Trotter decomposition

Stochastic equation of x for *q*(x,t)

Master equation for q

$$\partial_t q(\mathbf{x},t) = \underline{\frac{1}{\Gamma}\left\{\partial_i[\partial_i(U(\mathbf{x})-2V(\mathbf{x}))] + k_{\mathrm{B}}T\partial_i^2\right\}}\, q(\mathbf{x},t) + \underline{\frac{1}{\Gamma}\left(F(\mathbf{x})-\langle F\rangle_q\right)}\, q(\mathbf{x},t)$$

$$F(\mathbf{x}) = \partial_i^2 V - \beta(\partial_i V)(\partial_i(U-V)) \qquad \langle F\rangle_q = \int d\mathbf{x}F(\mathbf{x})q(\mathbf{x},t) \qquad \partial_t \ln C(t) = \langle F\rangle_q$$

Multiply scalar $\frac{1}{\Gamma}\{F(\mathbf{x})-\langle F\rangle\}$

$$\boxed{\partial_t q(\mathbf{x},t) = [\boxed{\hat{L}'} + \boxed{\hat{R}}]\, q(\mathbf{x},t)}$$

$\hat{L}$ with $U \rightarrow U-2V$

$$\Leftrightarrow q(\mathbf{x},t+dt) = \exp\left[(\hat{L}'+\hat{R})dt\right] q(\mathbf{x},t)$$

$$\approx \underline{\exp\left[\hat{L}'\frac{dt}{2}\right]}\, \underline{\exp\left[\hat{R}dt\right]}\, \underline{\exp\left[\hat{L}'\frac{dt}{2}\right]}\, q(\mathbf{x},t) + O(dt^3)$$

Suzuki-Trotter decomposition

Evolve the walkers by the modified Langevin eq.

Multiply exp[R(x)dt] to the weight of the walkers

The algorithm

RA and Y. S. Nagornov, J. Phys. Soc. Jpn. **87**, 063801 (2018).

Initial distribution

"Entrance" to the potential valley

$$q(\mathbf{x}, t=0) = \delta(\mathbf{x} - \mathbf{x}_0)$$

Time evolution

$$q(\mathbf{x}, t+dt) \approx \exp\left[\hat{L}'\frac{dt}{2}\right] \exp\left[\hat{R}dt\right] \exp\left[\hat{L}'\frac{dt}{2}\right] q(\mathbf{x}, t) + O(dt^3)$$

with $V=(1-\delta)U$ and $\delta<0.5$

The algorithm

RA and Y. S. Nagornov, J. Phys. Soc. Jpn. **87**, 063801 (2018).

Initial distribution

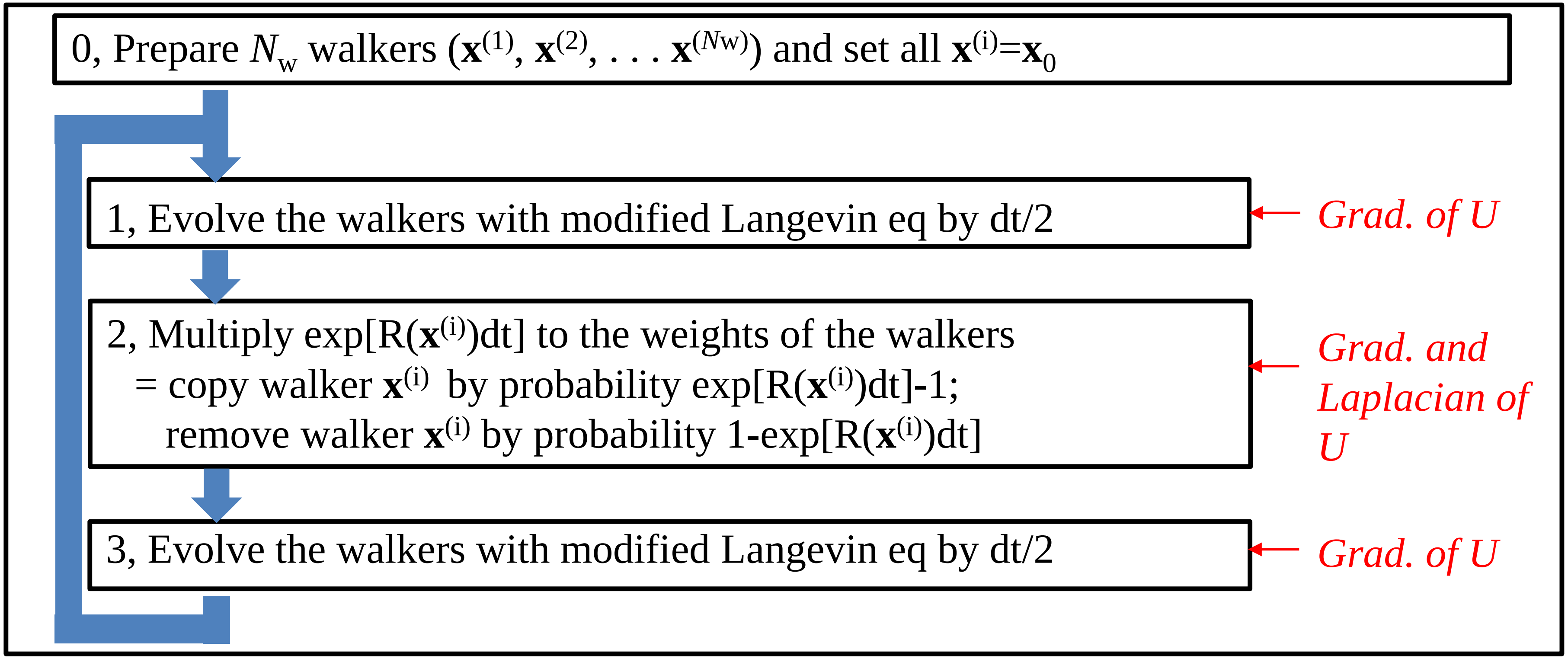
“Entrance” to the potential valley

$$q(\mathbf{x}, t = 0) = \delta(\mathbf{x} - \mathbf{x}_0)$$

Time evolution

$$q(\mathbf{x}, t + dt) \approx \exp\left[\hat{L}'\frac{dt}{2}\right] \exp\left[\hat{R}dt\right] \exp\left[\hat{L}'\frac{dt}{2}\right] q(\mathbf{x}, t) + O(dt^3)$$

with $V=(1-\delta)U$ and $\delta<0.5$



0, Prepare N_w walkers ($\mathbf{x}^{(1)}$, $\mathbf{x}^{(2)}$, . . . $\mathbf{x}^{(N\mathrm{w})}$) and set all $\mathbf{x}^{(\mathrm{i})}=\mathbf{x}_0$

1, Evolve the walkers with modified Langevin eq by dt/2 ← *Grad. of U*

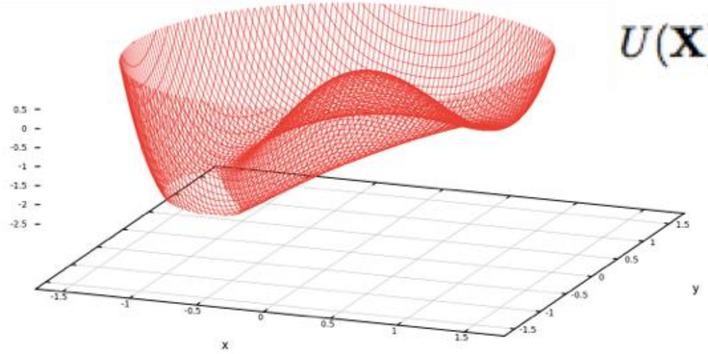
2, Multiply exp[R($\mathbf{x}^{(\mathrm{i})}$)dt] to the weights of the walkers
= copy walker $\mathbf{x}^{(\mathrm{i})}$ by probability exp[R($\mathbf{x}^{(\mathrm{i})}$)dt]-1;
remove walker $\mathbf{x}^{(\mathrm{i})}$ by probability 1-exp[R($\mathbf{x}^{(\mathrm{i})}$)dt] ← *Grad. and Laplacian of U*

3, Evolve the walkers with modified Langevin eq by dt/2 ← *Grad. of U*

Collection of the walkers forms *q* tracking up the potential valley

Example: two dimensions

RA and Y. S. Nagornov, J. Phys. Soc. Jpn. **87**, 063801 (2018).

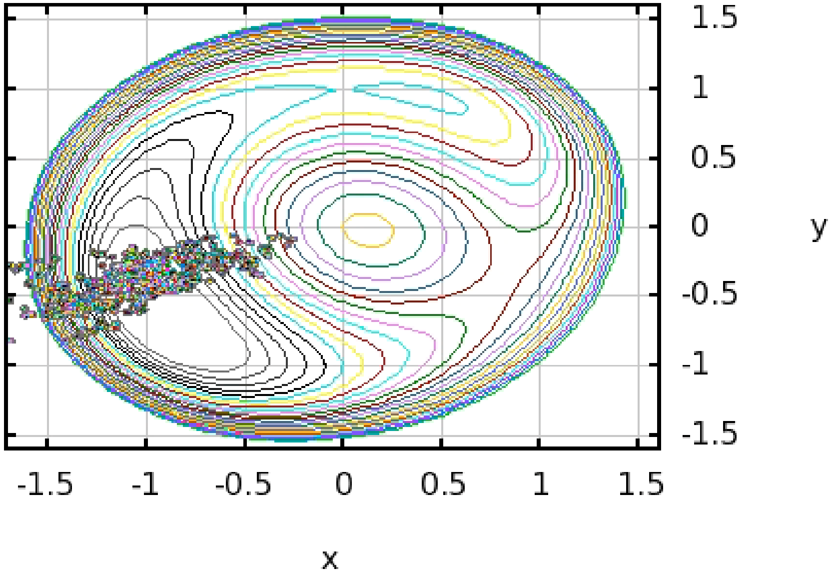


$$U(\mathbf{X}) = A\left(x^2+y^2\right)\left[(x^2-1)+(y^2-1)\right] + B\exp(-x^2y^2) + x - xy$$

(A=2.0, B=0.5)

Simulation of the walkers

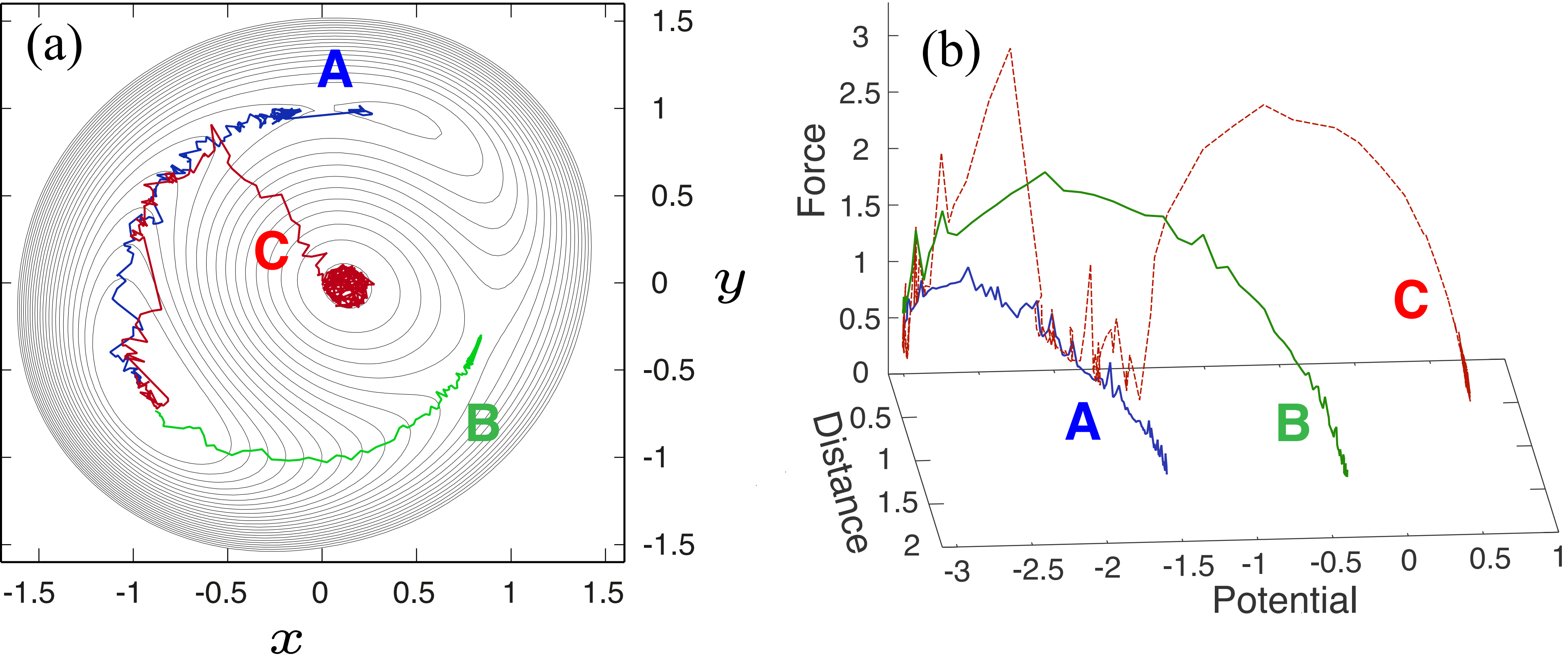
N_w=~1000



Example: two dimensions

RA and Y. S. Nagornov, J. Phys. Soc. Jpn. **87**, 063801 (2018).

Time series of the walker average of (x, y)



−Paths depend on the initial position

−Accidental departure ends up to the maximum

→Practically, parameter tuning is mandatory.

N_w, δ, T, dt

Application: Lennerd-Jones clusters

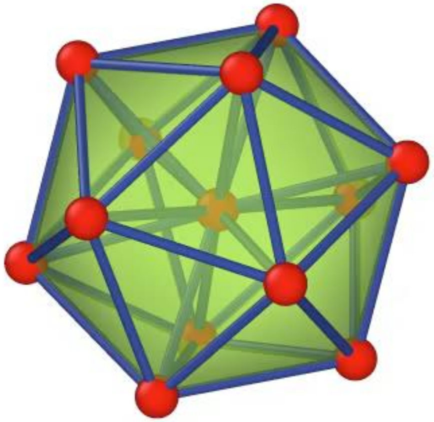
Y. S. Nagornov and RA, Physica A **528**, 121481 (2019).

$$U = \epsilon \sum_{\langle ij \rangle} \left[-\frac{\sigma^6}{r_{ij}^6} + \frac{\sigma^{12}}{r_{ij}^{12}} \right] \qquad \epsilon = 6.684; \sigma = 3.4$$

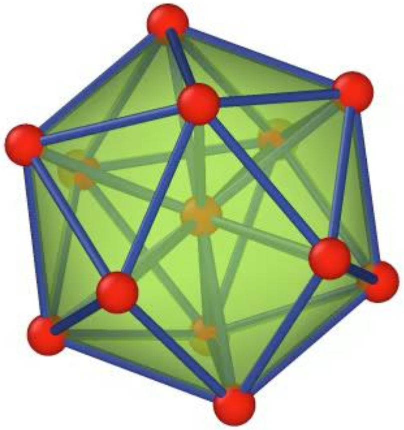
Visualize the mean value of the walker positions.
Execute the usual Langevin equation after reaching the saddle point.

LJ$_{13}$(39dim.) N_w=3200; δ=0.48; T=0.001; dt=0.0005. 32000 timestep

Reaction 1: Twist



Reaction 2: Cap–vacancy formation



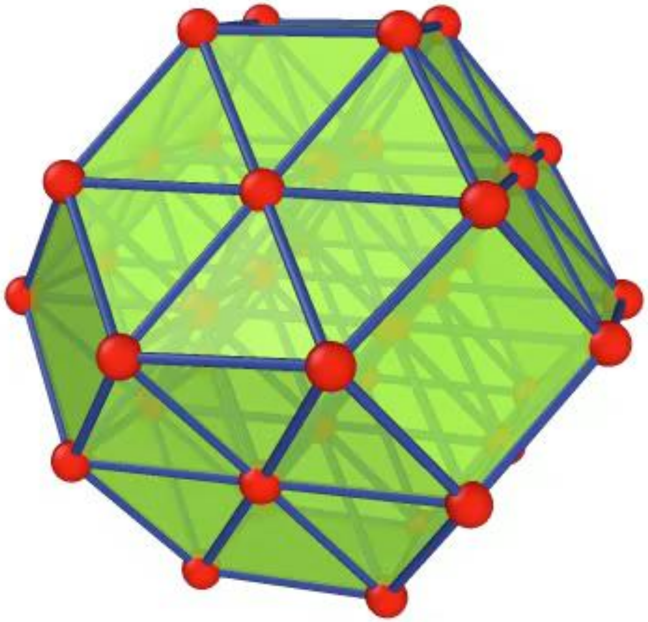
Application: Lennerd-Jones clusters

Y. S. Nagornov and RA, Physica A **528**, 121481 (2019).

$$U = \epsilon \sum_{\langle ij \rangle} \left[-\frac{\sigma^6}{r_{ij}^6} + \frac{\sigma^{12}}{r_{ij}^{12}} \right]$$

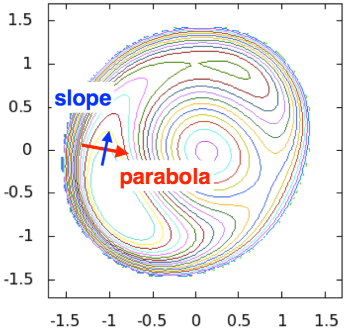
LJ_{38}(114 dim.) N_w=3200; δ~0.48; T=0.0002; dt=0.0005. ~70000step

Cap-vacancy formation



Summary

RA and Y. S. Nagornov, J. Phys. Soc. Jpn. **87**, 063801 (2018);
Y. S. Nagornov and RA, Physica A **528**, 121481 (2019).

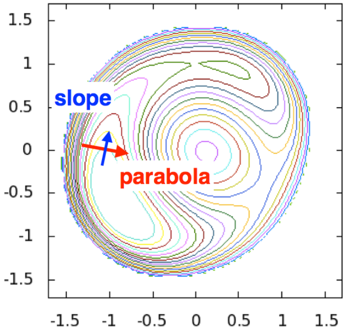


Transformation of the Fokker-Planck eq.
→Reaction coordinate free escape method

$$\boxed{P(X,t) = C(t)\exp[-\beta(1-\delta)U(X)]Q(X,t)}$$

Summary

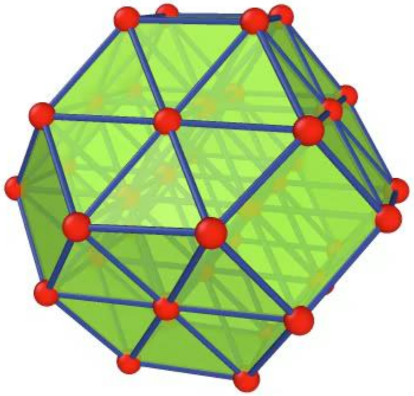
RA and Y. S. Nagornov, J. Phys. Soc. Jpn. **87**, 063801 (2018);
Y. S. Nagornov and RA, Physica A **528**, 121481 (2019).



Transformation of the Fokker–Planck eq.
→Reaction coordinate free escape method

$$\boxed{P(X,t)=C(t)\exp[-\beta(1-\delta)U(X)]Q(X,t)}$$

Successful search of escape paths in more than 100 dimensions



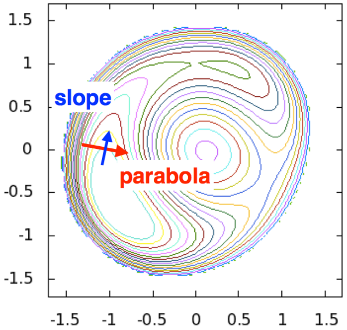
文部科学省　ポスト「京」萌芽的課題１　基礎科学のフロンティアー極限への挑戦
複合相関が織りなす極限マテリアル—原子スケールからのアプローチ

Summary

RA and Y. S. Nagornov, J. Phys. Soc. Jpn. **87**, 063801 (2018);
Y. S. Nagornov and RA, Physica A **528**, 121481 (2019).

Transformation of the Fokker–Planck eq.
→Reaction coordinate free escape method

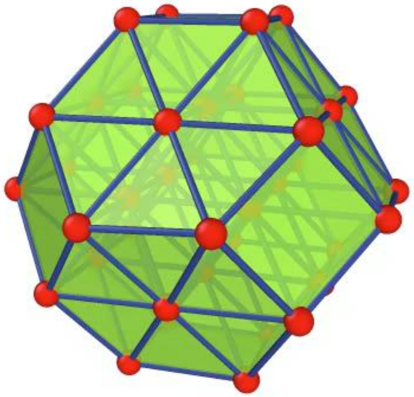
$$\boxed{P(X,t) = C(t)\exp[-\beta(1-\delta)U(X)]Q(X,t)}$$



Successful search of escape paths in more than 100 dimensions

Code "Atomistic rare event manager (AtomREM)" is available.

Y. S. Nagornov and RA, arXiv:1907.13316;
https://github.com/ryosuke-akashi/AtomREM.



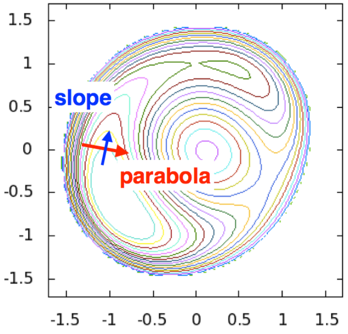
文部科学省　ポスト「京」萌芽的課題 1　基礎科学のフロンティア—極限への挑戦
複合相関が織りなす極限マテリアル—原子スケールからのアプローチ

Summary

RA and Y. S. Nagornov, J. Phys. Soc. Jpn. **87**, 063801 (2018);
Y. S. Nagornov and RA, Physica A **528**, 121481 (2019).

Transformation of the Fokker–Planck eq.
→Reaction coordinate free escape method

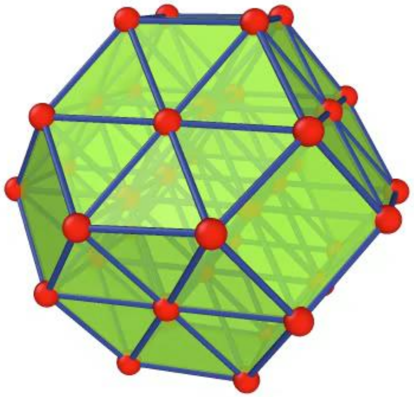
$$\boxed{P(X,t) = C(t)\exp[-\beta(1-\delta)U(X)]Q(X,t)}$$



Successful search of escape paths in more than 100 dimensions

Code "Atomistic rare event manager (AtomREM)" is available.

Y. S. Nagornov and RA, arXiv:1907.13316;
https://github.com/ryosuke-akashi/AtomREM.



Perspectives

- **Free energy surfaces**
- **Non empirical extraction of good RCs**
- **. . .**

文部科学省　ポスト「京」萌芽的課題 1　基礎科学のフロンティア―極限への挑戦

複合相関が織りなす極限マテリアル―原子スケールからのアプローチ