

Application:

Diffusion over a barrier

time units: slow (from Langevin)

$$+\gamma v = -\frac{1}{m} f'(x) + \frac{1}{m} f''(x)$$

$$\Rightarrow K^{(1)} = -\frac{1}{\gamma m} f'(x) \quad f(x): \text{pot}$$

$$= -\frac{D}{kT} f'(x) (-1)$$

$$K^{(2)} = \left(\frac{1}{\gamma m}\right)^2 \frac{\pi}{2} = \frac{kT}{2m} - D$$

classical problem in many fields!!

eg. transport on rough surfaces or complex landscapes, chemical reactions ...!

Consider:

$$\frac{\partial P(x,t)}{\partial t} = \hat{L}_{FP} P(x,t) \quad \text{prefactor set to 1 for simplicity (see Risken)}$$

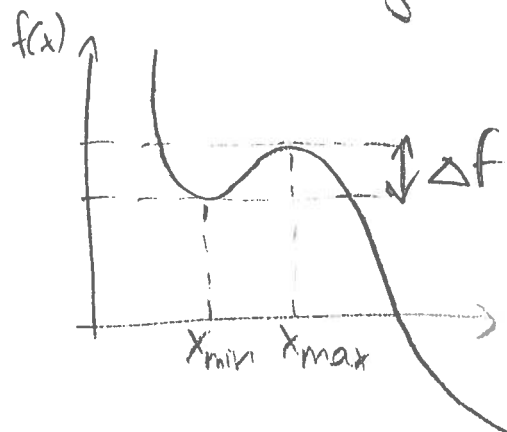
where $\hat{L}_{FP} = \frac{\partial}{\partial x} f'(x) + D \frac{\partial^2}{\partial x^2}$

$$\Rightarrow K^{(1)}(x) = -f'(x)$$

can be interpreted as a force (i.e., $f(x)$ is a potential)

$$\Rightarrow K^{(2)}(x) = D = \text{const}$$

assume that $f(x)$ has the following form:



question: What is the "escape rate" ??

(related question:

What is the probability that the particles escapes the valley ??)

Definition of the escape rate:
(dimension: inverse time!)

$p.r. = j$ ← current density

↑
total probability to find the particles close to the potential minima

analogous to classical current
 $j = \frac{N}{A \cdot t} = \frac{N}{V} \cdot \frac{\Delta x}{\Delta t}$
area (volume)

starting point: Consider the current density

$$J(x,t) = -f'(x) - D \frac{\partial}{\partial x} P(x,t)$$

this can be written as ^{derivative} (not shown here!)

⊛ $J(x,t) = -D e^{-f(x)/D} \frac{\partial}{\partial x} [e^{f(x)/D} P(x,t)]$

We now assume that

$\frac{\Delta f}{D}$ is very large (⇔ barrier is very high!)

$$\Rightarrow \frac{\partial}{\partial t} P(x,t) \approx 0$$

$$\Rightarrow J(x,t) \approx \text{const} = J$$

current density

constant in space and time!

("quasi-stationary state")

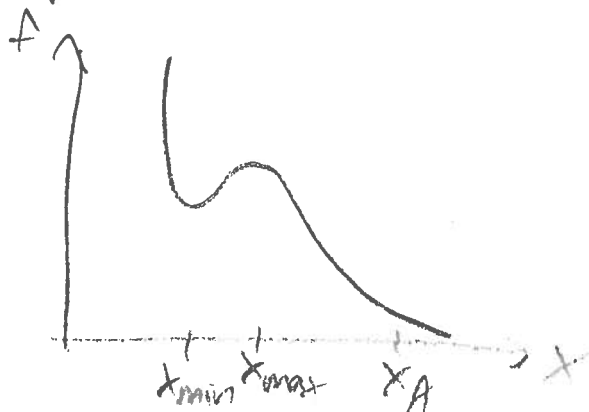
note: we do not assume $J=0$, since there is no true equilibrium in this restricted portion of space!

\Rightarrow from (*)

$$J e^{f(x)/D} = -D \frac{\partial}{\partial x} \left(e^{f(x)/D} \underbrace{P(x)}_{\text{assumed to be independent of } t!} \right)$$

integrate from x_{\min} to a point x_A outside the barrier

— and assume that $P(x_A) \approx 0$, since the particles are essentially trapped in the valley!!



$$\Rightarrow J = D e^{f(x_{\min})/D} \cdot P(x_{\min}) \cdot \left[\int_{x_{\min}}^{x_A} dx' e^{f(x')/D} \right]^{-1}$$

Consider now the probability density:

note: We have already assumed that we can work in the stationary limit!!

$$\rightarrow P(x) \rightarrow P^{\text{stat}}(x) = e^{-\Phi(x)}$$

where $\Phi(x) = f(x)/D$

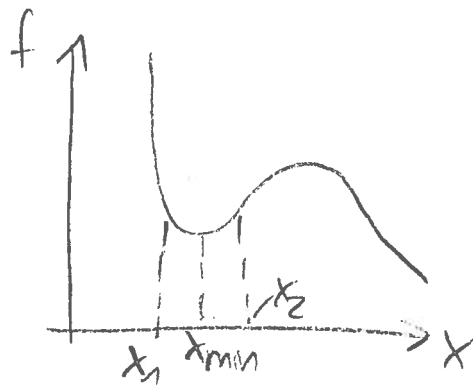
$$\Rightarrow \frac{P(x)}{P(x_{\text{min}})} = e^{-[f(x) - f(x_{\text{min}})]/D} \quad \text{for any point } x \text{ in the valley}$$

integrate to get the total probability to find the particle within the valley

$$\rho = \int_{x_1}^{x_2} dx P(x)$$

$$= P(x_{\text{min}}) e$$

$$\frac{f(x_{\text{min}})/D}{\int_{x_1}^{x_2} dx e^{-f(x)/D}}$$



Combine this with our result for the current:

$\Rightarrow -d\tilde{w}(t)|_{x'} = -dt \int_{x_1}^{x_2} dx \frac{\partial}{\partial t} P(x,t|x',0)$ is the probability that the particles reaches the border in the interval $(t, t+dt)$

$$\Rightarrow \underbrace{w(T)|_{x'}}_{\substack{\text{probability density,} \\ \text{that the particle} \\ \text{leaves the borders} \\ \text{at time } T}} = - \frac{d\tilde{w}(T)|_{x'}}{dT} = - \int_{x_1}^{x_2} \frac{d}{dt} P(x,T|x',0) \Big|_{t=T} dx$$

From this we can calculate the mean first passage time:

$$\bar{T} = \int_0^{\infty} dt T w(T)$$

For a potential of the form one finds:

$$T = \frac{1}{\nu_{\text{right}} + \nu_{\text{left}}}$$



Remarks to our result for the Kramers rate

1) we have chosen units according to the book of Risken

Taking true units (i.e. $\hat{L}_{FP} = D \frac{\partial^2}{\partial x^2} + \frac{D}{k_B T} \frac{\partial}{\partial x} f'(x)$)

we obtain:

$$r = \frac{D}{2\pi k_B T} \sqrt{\frac{f''(x_{min})}{f''(x_{max})}} e^{-\Delta f / k_B T}$$

2) Relation to the so-called "mean first passage time"

define first the first passage time T

\Rightarrow time at which a stochastic variable (in our case the Brownian particle) leaves a given domain $[x_1, x_2]$

The distribution of these times T can be calculated as follows. Consider first:

$$\tilde{w}(t)_{x'} = \int_{x_1}^{x_2} dx P(x, t | x', 0)$$

probability of processes which have started at x' for $t=0$ and have not yet reached the boundary at time t \rightarrow (otherwise the integration limits must be revised)

escape rate:

$$\frac{1}{N} = \frac{P}{J} = \dots = \frac{1}{D} \int_{x_1}^{x_2} e^{-f(x)/D} dx \left(\int_{x_{\min}}^{x_A} dx' e^{-f(x')/D} \right)$$

to obtain an analytical formula we expand the (potential) function $f(x)$

- 1st integral: contributions come only from the vicinity of x_{\min}
- 2nd integral: contributions only from the vicinity of x_{\max}

expand up to second order \rightarrow Gauss integrals ...
one finally obtains:

$$N = \frac{1}{2\pi} \sqrt{\frac{f''(x_{\min})}{f''(x_{\max})}} e^{-\Delta f/D}$$

where $\Delta f = f_{\max} - f_{\min}$ and $D = \frac{k_B T}{\gamma m}$

\checkmark typical of an activated process! (Arrhenius)

Fokker-Planck equation for interacting particles

starting point:

Langevin equations for system of overdamped Brownian particles with potential energy

$$U(\underline{r}^N, t)$$

assume that all particles experience same friction

$$\underline{r}^N = \underline{r}_1, \dots, \underline{r}_N$$

$$m \ddot{\underline{r}}_i \approx 0 = -\gamma \dot{\underline{r}}_i + \frac{1}{m} \underline{F}_i(\underline{r}^N, t) + \underline{f}_i(t)$$

$$\text{and } \underline{F}_i = -\nabla_{\underline{r}_i} U(\underline{r}^N, t)$$

$$\langle \underline{f}_i(t) \underline{f}_j(t') \rangle = \delta_{ij} \frac{D}{2} \delta(t-t')$$

set $T_i = 1/\gamma$

$$\Rightarrow \dot{\underline{r}}_i = -\frac{1}{\gamma m} \nabla_{\underline{r}_i} U(\underline{r}^N, t) + \frac{1}{\gamma m} \underline{f}_i(t)$$

$$\Rightarrow K_i^{(1)} = -\frac{1}{\gamma m} \nabla_{\underline{r}_i} U = -\frac{D}{k_B T} \nabla_{\underline{r}_i} U(\underline{r}^N, t) \quad \text{force} = \frac{D}{k_B T} \underline{F}_i(\underline{r}^N, t)$$

$$K_{ij}^{(2)} = \frac{1}{\gamma^2 m^2} \frac{D}{2} \delta_{ij} = D \delta_{ij}$$

$$\Rightarrow \dot{\underline{r}}_i = -\frac{D}{k_B T} \nabla_{\underline{r}_i} U(\underline{r}^N, t) + \underline{\Phi}_i(t)$$

$$\Rightarrow \frac{\partial}{\partial t} P(\underline{r}^N, t) = \left[-\sum_{i=1}^N \frac{\partial}{\partial r_i} k_i^{(a)} (\underline{r}^N, t) + \sum_{i,j} \frac{\partial^2}{\partial r_i \partial r_j} k_{ij}^{(r)} \right] P(\underline{r}^N, t)$$

or

$$\frac{\partial}{\partial t} P(\underline{r}^N, t) = -D \sum_{i=1}^N \nabla_i \left(\nabla_i + \beta \nabla_i U(\underline{r}^N, t) \right) P(\underline{r}^N, t)$$

acts only on U!!

⊛

This is often called the Smoluchowski equation!!

where $\beta = \frac{1}{k_B T}$

consider briefly the equilibrium limit:

$$\frac{\partial}{\partial t} P(\underline{r}^N, t) = 0$$

in this case, ⊛ is solved by $P^{eq} \sim e^{-\beta U(\underline{r}^N)}$!
Boltzmann factor!!

because:

$$\nabla_i (\nabla_i P^{eq}) = \nabla_i \left(e^{-\beta U} (-\beta \nabla_i U) \right) = e^{-\beta U} (-\beta \nabla_i U)^2 + e^{-\beta U} (-\beta \nabla_i^2 U)$$

$$\nabla_i (\beta \nabla_i U) P^{eq} = \beta \nabla_i^2 U P^{eq} + \beta \nabla_i U \nabla_i P^{eq} = -\nabla_i (\nabla_i P^{eq})$$

q.e.d.!

V. Dynamical density functional theory

Idea: start from the Fokker-Planck (Smoluchowski) equation, but consider instead of the many-particle probability density $P(\underline{r}_N^M, t)$ rather the one-particle ("singlet")-density

\Rightarrow map onto an effective one-particle problem!!

statistical
Definition of the (one-particle) density:

$$g(\underline{r}, t) = \left\langle \sum_{i=1}^N \delta(\underline{r}_i(t) - \underline{r}) \right\rangle$$

definition via the many-particle density:

$$g(\underline{r}, t) = N \int d\underline{r}_2 \dots \int d\underline{r}_N P(\underline{r}_N^M, t)$$

Question: How does $g(\underline{r}, t)$ depend on time?

\Rightarrow integrate the FP equation!

$$\begin{aligned} \Rightarrow \int d\underline{r}_2 \dots \int d\underline{r}_N \frac{\partial}{\partial t} P(\underline{r}_N^M, t) & \quad \text{acts only on } \underline{r}! \\ = D \int d\underline{r}_2 \dots \int d\underline{r}_N \sum_{i=1}^N \nabla_i \cdot (\nabla_i + \beta \nabla_i u) P(\underline{r}_N^M, t) & \quad \downarrow \end{aligned}$$

Left side:

exchange time derivative and spatial integration

$$\Rightarrow \frac{\partial}{\partial t} \frac{1}{N} \rho(\mathbf{r}^N, t) = -D \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N \sum_{i=1}^N \nabla_i (\nabla_i P + \beta P \nabla_i U) \quad (**)$$

rewrite right hand side in terms of currents

(recall: $\frac{\partial}{\partial t} P = -\nabla \cdot \underline{J}$)

here $\underline{J} = \begin{pmatrix} J_1 \\ \vdots \\ J_N \end{pmatrix}$ where $J_i = J_i(\mathbf{r}^N, U) = -D \nabla_i (\nabla_i P + \beta P \nabla_i U)$

then we get from (**):

$$\frac{1}{N} \frac{\partial}{\partial t} \rho(\mathbf{r}^N, t) = \nabla_1 \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N J_1(\mathbf{r}^N, t) \quad \textcircled{1}$$

$$+ \int d\mathbf{r}_2 \dots \int d\mathbf{r}_N \sum_{i=2}^N \nabla_i \cdot J_i(\mathbf{r}^N, t) \quad \textcircled{2}$$

Consider first $\textcircled{2}$

for each of the $(N-1)$ terms in the sum, we can evaluate one integral via the law of Gauss!

e.g. $\int d\mathbf{r}_2 \dots \int d\mathbf{r}_N \nabla_2 \cdot J_2(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \int d\mathbf{r}_3 \dots \int d\mathbf{r}_N J_2(\mathbf{r}_1, \mathbf{r}_2 |_{-\infty}^{\infty}, \mathbf{r}_3, \dots, \mathbf{r}_N)$ where J_2 is calculated on the boundary of the volume.

now use the conservation law for the probability

$$\frac{\partial}{\partial t} \underbrace{\int d\underline{r}^N P(\underline{r}^N, t)}_{=1} = 0 \quad \sum_{i=1}^N \nabla_i \cdot \underline{J}_i$$

$$= - \int d\underline{r}^N \nabla \cdot \underline{J} = - \int_{\text{boundary}} \underline{J}$$

→ (total) current must vanish at the boundary $\underline{J}_{\text{surface}} = 0$

This should hold for each particle (since each particle should be somewhere in the volume)

$$\Rightarrow \underline{J}_i \Big|_{\text{boundary}} = 0$$

⇒ Term ② in ③ is zero!

Consider now term ①

$$\nabla_1 \int_{\underline{r}_2} \dots \int_{\underline{r}_N} \underline{J}_1(\underline{r}^N, t) \quad \leftarrow \text{insert expression for } \underline{J}_1$$

$$= \nabla_1 (-1) D \int_{\underline{r}_2} \dots \int_{\underline{r}_N} (\nabla_1 P + \beta P \nabla_1 U)$$

$$= -D \nabla_1^2 \int_{\underline{r}_2} \dots \int_{\underline{r}_N} P(\underline{r}^N, t)$$

$$- D \beta \nabla_1 \int_{\underline{r}_2} \dots \int_{\underline{r}_N} P \nabla_1 U(\underline{r}^N, t)$$

Ansatz for the potential energy of the system:

$$U(\underline{r}^N, t) = \sum_{i=1}^N \underbrace{\Phi^{\text{ext}}(\underline{r}_i, t)}_{\text{external potential}} + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N u(\underline{r}_i, \underline{r}_j)$$

typically symmetric!

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insert expression
for u

$$\Rightarrow \textcircled{1} = -N^{-1} D \nabla_1^2 \rho(\underline{r}_1, t)$$

$$- \beta D \nabla_1 \int d\underline{r}_2 \dots \int d\underline{r}_N P \nabla_1 \Phi^{\text{ext}}(\underline{r}_1, t)$$

other external terms vanish!

$$- \beta D \nabla_1 \int d\underline{r}_2 \dots \int d\underline{r}_N P \nabla_1 \sum_{j=1}^N u(\underline{r}_1, \underline{r}_j)$$

N-1 terms, each of which should give the same contribution in a homogeneous system!

$$= -N^{-1} D \nabla_1^2 \rho(\underline{r}_1, t)$$

$$- N^{-1} D \beta \nabla_1 \rho(\underline{r}_1, t) \nabla_1 \Phi^{\text{ext}}(\underline{r}_1, t)$$

$$- (N-1) \beta D \nabla_1 \int d\underline{r}_2 \dots \int d\underline{r}_N P \nabla_1 u(\underline{r}_1, \underline{r}_2)$$

now use the definition of the time-dependent two-particle density:

$$\rho^{(2)}(\underline{r}_1, \underline{r}_2, t) = N(N-1) \int d\underline{r}_3 \dots \int d\underline{r}_N P(d\underline{r}^N, t)$$

$$\Rightarrow \textcircled{1} = -N^{-1} D \left(\nabla_1^2 \rho(\underline{r}_1, t) + \beta \nabla_1 \rho(\underline{r}_1, t) \nabla_1 \Phi^{\text{ext}}(\underline{r}_1, t) \right)$$

$$+ \beta \nabla_1 \int d\underline{r}_2 \rho^{(2)}(\underline{r}_1, \underline{r}_2, t) \nabla_1 u(\underline{r}_1, \underline{r}_2)$$

Combine everything

from $\textcircled{*}$
 \Rightarrow

$$\textcircled{*} \quad \frac{\partial}{\partial t} \rho(\underline{r}_1, t) = D \left(\nabla_1^2 \rho(\underline{r}_1, t) \right) + \beta \nabla_1 \rho(\underline{r}_1, t) \nabla_1 \Phi^{\text{ext}}(\underline{r}_1, t) \\ + \beta \nabla_1 \int d\underline{r}_2 \rho^{(2)}(\underline{r}_1, \underline{r}_2, t) \nabla_1 u(\underline{r}_1, \underline{r}_2)$$

Note:

so far everything is exact!!

(direct consequence of the Fokker-Planck-equation)
 (Smoluchowski)

But: How shall we treat the time-dependent correlation function?

Idea: "Adiabatic" approximation

$$\Leftrightarrow \text{set } \rho^{(2)}(\underline{r}_1, \underline{r}_2, t) = \rho^{(2)}(\underline{r}_1, \underline{r}_2)$$

two-particle correlation function of an equilibrium system with density $\rho(\underline{r}_1, t)$!!

interpretation:

In each time step, the system is in a "local equilibrium" determined by the instantaneous value of the density field

Then: use an equilibrium sum rule
 (from classical density functional theory) (exact!!)

$$\left| \int d\underline{r}_2 g^{(2)}(\underline{r}_1, \underline{r}_2) \nabla U(\underline{r}_1, \underline{r}_2) \right. \\ \left. = -k_B T g(\underline{r}_1) \nabla_1 c^{(2)}(\underline{r}_1) \right|$$

where $c^{(2)}(\underline{r}_1) = -\beta \frac{\delta F^{ex}[\rho]}{\delta g(\underline{r}_1)}$

Functional derivative of the excess (i.e. interaction) contribution to the Free energy!

background:

The total free energy in equilibrium can be written

as $F[\rho] = k_B T \int d\underline{r}_1 g(\underline{r}_1) \ln(-\beta g(\underline{r}_1))^{-1}$
 $+ F^{ex}[\rho] + \int d\underline{r}_1 g(\underline{r}_1) \Phi^{ext}(\underline{r}_1)$

Inserting these expressions into $\textcircled{4}$, we obtain:

$$\frac{\partial}{\partial t} \rho(\underline{r}_1, t) = D \left[\nabla_1^2 \rho(\underline{r}_1, t) + \beta \nabla_1 \rho(\underline{r}_1, t) \nabla_1 \phi^{\text{ext}}(\underline{r}_1, t) + \beta \nabla_1 \rho(\underline{r}_1, t) \nabla_1 \frac{\delta F^{\text{ex}}[\rho]}{\delta \rho(\underline{r}_1, t)} \right]$$

note: the first terms on the right-hand side can also be expressed via the (total) free energy

$$\rightarrow \frac{\partial}{\partial t} \rho(\underline{r}_1, t) = D \nabla_1 \rho(\underline{r}_1, t) \nabla_1 \frac{\delta F[\rho]}{\delta \rho(\underline{r}_1, t)}$$

Key equation of the so-called
"dynamical density functional theory"
(DDFT)

!!

Remarks

- The DDT equation can be written as

$$\frac{\partial}{\partial t} \rho(\underline{r}, t) + \nabla \cdot \mathbf{j} = 0$$

$$\text{where } \mathbf{j} = D \rho(\underline{r}, t) \nabla \frac{dF[\rho]}{d\rho}$$

$$= D \rho(\underline{r}, t) \nabla \mu(\underline{r}, t)$$

chemical
potential

Interpretation:

changes of ρ in time are driven by inhomogeneities in the chemical potential!

- For the special case

$$F^{\text{ex}}[\rho] = 0 \quad (\text{i.e. no interactions}) \quad \text{and} \quad \phi^{\text{ext}} = 0$$

the DDT reduces to the diffusion equation.

$$\frac{\partial}{\partial t} \rho(\underline{r}, t) = D \nabla^2 \rho(\underline{r}, t)$$