

Fluctuating hydrodynamics

Denote the coarse-grained free energy as $F(x)$, where x are the selected coarse-grained variables, and recall the SDE obtained in the Markovian approx.:

$$\left\{ \begin{aligned} \partial_t x &= -N \cdot \frac{\partial F}{\partial x} + \sqrt{2k_B T} B \cdot W(t) \\ & \quad \left(\text{Ito} \right) + \left(k_B T \right) \frac{\partial}{\partial x} \cdot N^* \end{aligned} \right.$$

where $B B^* = \frac{1}{2} (N + N^*)$

We now consider the case when $x \equiv x(r, t)$ is a hydrodynamic field, formally infinite-dimensional but not really, since we assume $x(r, t)$ is smooth on the scale of the microscopic dynamics (particles).

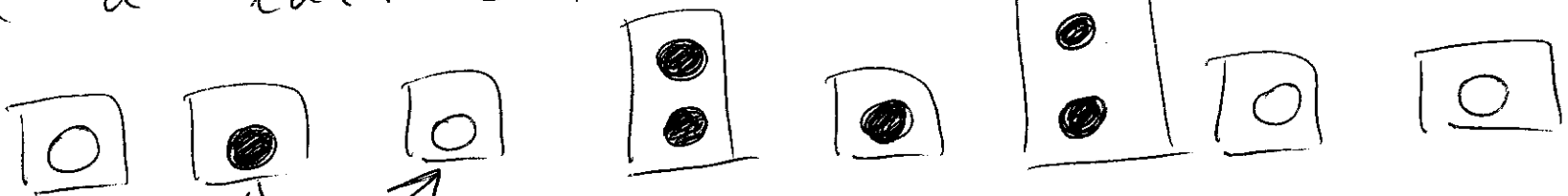
First, we need a formula for the free energy functional

$$F[x(r, t)] \equiv F(x)$$

We consider simple particle models:

Random walk models for particles on a lattice:

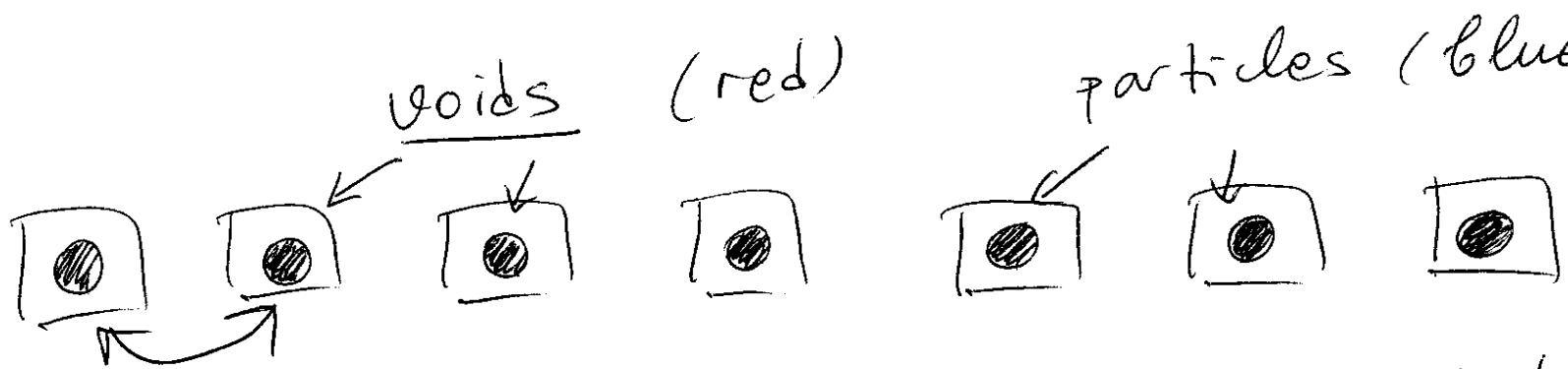
(1)



Markov chain hopping process

simple diffusion

(2)



Markov chain exchange process (Kawasaki spin dynamics)

excluded random walk diffusion

In both cases, the total number of particles is conserved, which leads us to believe that the density of particles (# per unit length)

$\rho(x)$ is a slowly-evolving coarse variable since it only changes due to boundary events (fluxes through the boundary). We expect deterministically,

$$\partial_t \rho = D \partial_{xx} \rho$$

← Diffusion PDE
← Diffusion coefficient

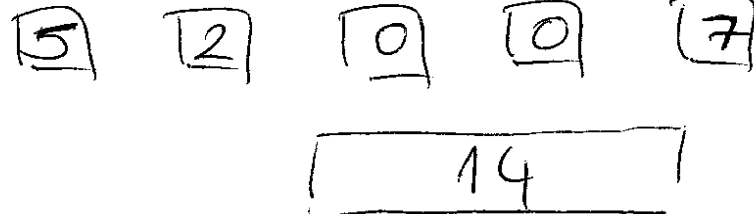
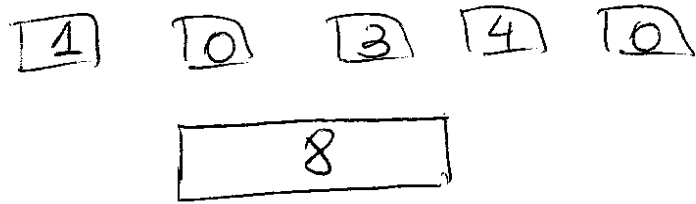
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Lecture 7

(5)

microscopic configuration



Z

X

N_s sites per
hydrodynamic cell

macroscopic or
coarse-grained
configuration

The coarse-grained variable is now
a vector of integer occupation numbers

$$x \equiv \vec{s} = \{ s_1, s_2, \dots, s_{N_c} \}$$

N_c
↑
number of
hydro cells

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Recall definition of free energy

$\Omega(x) = \left\{ \begin{array}{l} \text{number of micro states} \\ \text{compatible with a macro state } x \end{array} \right.$

$$F = -k_B T \ln \Omega$$

Since the particles are non-interacting here we do not include any weighting (energies) of the micro states and just count (entropy). Also, different hydrodynamic cells are independent (non-interacting), so we have the

Local equilibrium (assumption in reality):

$$F(\vec{S}) = \sum_{i=1}^{N_c} F_i(S_i)$$

Since $\Omega(\vec{S}) = \prod_{i=1}^{N_c} \Omega_i(S_i)$

So all we need to do is figure out the entropy associated with placing N_p particles on a lattice of N_s sites. This is now combinatorics.

① Simple (non-excluded) diffusion:

$$\Omega_{N_S}^{N_P} = \frac{N_S^{N_P}}{N_P!}$$

$$\ln \Omega = N_P \ln N_S - \ln(N_P!)$$

$$= N_S \left[s - s \ln s \right] + \underline{\text{constants}}$$

where $\left[s = \frac{N_P}{N_S} \right]$ (concentration or occupation fraction)

and we used Stirling's approximation
 $\ln(n!) \approx n [\ln(n) - 1]$

② Excluded random walk:

$$\ln \Omega = \ln \binom{N_S}{N_P} = \ln \left(\frac{N_S!}{N_P! (N_S - N_P)!} \right)$$

$$\ln \Omega \approx N_S \left[g \ln g + (1-g) \ln(1-g) \right]$$

where again $g = \frac{N_P}{N_S}$

$$F_i(g_i) = - (k_B T) N_S \begin{cases} g - g \ln g & \text{(simple)} \\ g \ln g + (1-g) \ln(1-g) & \text{(excluded)} \end{cases}$$

These are correct results but they do not account for the boundary conditions, which determine the proper ensemble. Since we care a lot about the equilibrium distribution of the coarse-grained variables

$$P_{eq}(\vec{S}) \sim \exp \left[-\tilde{F}(\vec{S}) / k_B T \right]$$

it is worth-while to write down $\tilde{F}(\vec{S})$ that takes into account externally-imposed constraints.

The BCs fix the average density or total number of particles:

$$\left\{ \begin{array}{l} \tilde{F}(\vec{S}) = \min \sum_{i=1}^{N_c} F(S_i) \\ \text{s.t. } \sum_{i=1}^N S_i = N_c \cdot \bar{S} \leftarrow \text{constraint} \end{array} \right.$$

Use a Lagrange multiplier (called chemical potential in physics):

$$\frac{\partial}{\partial S_i} \left[\sum F(S_i) + \lambda \left(\sum S_i - N_c \bar{S} \right) \right] = 0$$

①

$$\frac{\partial F}{\partial g_i} = -\lambda = -(\ln k_B T) N_S \ln g_i \leftarrow \begin{array}{l} \text{non-} \\ \text{excluded} \\ \text{walk} \end{array}$$

\Rightarrow All $g_i = \bar{g}$ at equilibrium
(minimum free energy)

and

$$\lambda = (\ln k_B T) N_S \ln \bar{g}$$

 \Rightarrow

$$\tilde{F}(\vec{g}) = -(\ln k_B T) N_S \sum_{i=1}^{N_C} g_i \left(1 + \ln \frac{\bar{g}}{g_i} \right)$$

for simple diffusion + constants

② For excluded walk:

$$\frac{\partial F}{\partial s_i} = -\lambda = -(\ln_B T) N_S \ln \frac{s_i}{1-s_i}$$

$$\Rightarrow \lambda = -(\ln_B T) N_S \ln \frac{\bar{s}}{1-\bar{s}}$$

$$\tilde{F}(\vec{s}) = -(\ln_B T) N_S \sum_{i=1}^{N_C} \left\{ s \left[\ln \frac{s}{\bar{s}} - \ln \frac{1-s}{1-\bar{s}} \right] + \ln(1-s) \right\}$$

excluded walk

For the coarse-grained evolution, what really matters is the gradient of the free energy (the thermodynamic force):

$$\frac{\partial \tilde{F}}{\partial \vec{S}_i} = - (k_B T) N_S \left\{ \begin{array}{l} \ln \frac{S_i}{\bar{S}} \\ \ln \frac{S_i}{\bar{S}} - \ln \frac{(1-S_i)}{(1-\bar{S})} \end{array} \right.$$

Note $\frac{\partial \tilde{F}}{\partial \vec{S}_i}(\bar{S}) = 0$ as it should

The equilibrium distribution is

$$P_{eq} = \exp[-\tilde{F}/h_b T] = \prod_{i=1}^{N_c} e^{-\tilde{F}(g_i)/h_b T}$$

For small deviations from equilibrium

$$\delta g_i = g_i - \bar{g}$$

we can approximate

$$\tilde{F}(g_i) = \tilde{F}(\bar{g}) + \frac{1}{2} \tilde{F}''(\bar{g}) (\delta g_i)^2$$

so that P_{eq} is a multivariable Gaussian distribution with a diagonal covariance matrix

$$C_{ij} = \langle (\delta S)_i (\delta S)_j \rangle = \frac{k_B T}{F''(\bar{S})} \delta^{ij}$$

↑
covariance matrix is a multiple of the identity

fluctuations in different cells are uncorrelated at true thermodynamic equilibrium

coarse-graining scale

$$\langle (\delta S)^2 \rangle = \begin{cases} \bar{S}/N_S & \text{for simple} \\ \frac{\bar{S}(1-\bar{S})}{N_S} & \text{for excluded} \end{cases}$$

For these simple models we can actually rigorously derive the equilibrium distribution. For simple diffusion

$$\textcircled{1} \left\{ \begin{array}{l} P(N_P) \text{ is } \underline{\text{Poisson}} \text{ with mean } \bar{N}_P = \bar{S} N_S \\ \Rightarrow \langle (\delta S)^2 \rangle = \frac{\langle \delta N_P^2 \rangle}{N_S^2} = \frac{\bar{S}}{N_S} \text{ as we obtained} \end{array} \right.$$

(this is simply a central theorem result)

$$\textcircled{2} \left\{ \begin{array}{l} P(N_P) \text{ is a } \underline{\text{binomial}} \text{ distribution} \\ \text{for excluded walk} \\ \text{mean} = \bar{S} N_S \\ \text{variance} = N_S \bar{S} (1 - \bar{S}) \end{array} \right.$$

How do we now obtain the mobility operator so as to construct

$$S_t = -N \cdot \frac{\partial F}{\partial g} + \text{fluctuations} ?$$

One way is to use Mori-Zwanzig formalism and remain in a discrete setting, where a particular coarse-graining length scale

N_s is fixed. Instead, we will follow a non-rigorous alternative for passing to a continuous limit.

$$F(\vec{g}) = \sum_{i=1}^{N_c} F(g_i) \quad (\text{function})$$

FORMAL! \Downarrow free-energy functional

$$\mathcal{F}[g(r)] = \int F(g(r)) dr$$

$$\frac{\partial F}{\partial \vec{g}} \rightarrow \frac{\delta \mathcal{F}}{\delta g} = F'(g) \leftarrow \text{field}$$

functional
derivative

Now $N[g(r)]$ will be a linear
differential operator.

In the asymptotic limit $N_S \rightarrow \infty$ one can rigorously derive a deterministic equation for the density field $\rho(r, t)$.

[see work by Raghun Varadhan]

Here we take an intuitive but hand-waving approach.

We know that $\rho(r, t)$ follows a conservation law

$$\partial_t \rho = - \nabla \cdot [j(\rho)]$$

"current" or "flux"

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The free energy evolves as :

$$\frac{\partial F}{\partial t} = \int F'(s) (\partial_t s) dr$$

$$= - \int F' (\nabla \cdot j) dr \quad (\text{integration by parts ignoring boundaries})$$

$$= \int j \cdot [\nabla F'(s)] dr$$

Diffusion should strictly lower the free energy (purely dissipative), so

assume
Fick's law

$$j = - \tilde{D} \nabla \left(\frac{\partial F}{\partial s} \right)$$

$$\tilde{D} \geq 0$$

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$$\partial_t \rho = N \cdot \frac{\partial F}{\partial \rho} = \underbrace{\nabla \cdot \tilde{D}}_{\text{diffusive generator}} \nabla \left(\frac{\partial F}{\partial \rho} \right)$$

diffusive generator \rightarrow
$$N = \frac{\partial}{\partial r} \cdot \tilde{D} \frac{\partial}{\partial r}$$

Denote :

$$\mu = \frac{\partial F}{\partial \rho} = \mu(\rho) \quad \text{chemical potential}$$

Then

$$\frac{\partial}{\partial r} \left(\frac{\partial F}{\partial \rho} \right) = \frac{\partial}{\partial r} \mu(\rho(r)) = \left(\frac{\partial \mu}{\partial \rho} \right) \frac{\partial \rho}{\partial r}$$

So we get the PDE

$$\partial_t S = \frac{\partial}{\partial r} \cdot \left[\tilde{D} \left(\frac{\partial \mu}{\partial s} \right) \frac{\partial s}{\partial r} \right]$$

compare to Fick's law:

$$\partial_t S = \nabla \cdot \left(\underset{\substack{\uparrow \\ \text{diffusion coefficient}}}{D} \nabla S \right)$$

DETERMINISTIC
EQUATION

$$\Rightarrow D = \tilde{D} \left(\frac{\partial \mu}{\partial s} \right)$$

Note that $\begin{cases} N = N^* \\ N \geq 0 \end{cases}$ is self-adjoint and positive-semi-definite

The dynamics including fluctuations involves B.W., where

$$\left\{ \begin{aligned} BB^* &= N = \frac{\partial}{\partial r} \cdot \tilde{D} \frac{\partial}{\partial r} \\ &= \text{Div} \cdot \tilde{D} \cdot \text{Grad} \end{aligned} \right.$$

Observing that $(\text{Div})^* = -\text{Grad}$, one intuitive choice for B is

$$B = \frac{\partial}{\partial r} \cdot \tilde{D}^{1/2}$$

which makes B.W. a divergence of a stochastic flux, ensuring conservation.

Putting everything together, we obtain the stochastic PDE of the stochastic diffusion equation form:

$$\partial_t \mathcal{S} = \nabla \cdot \left\{ D \nabla \mathcal{S} + \left[2k_B T D / \left(\frac{\partial \mathcal{M}}{\partial \mathcal{S}} \right) \right]^{1/2} W(r, t) \right\}$$

spatio-temporal
white noise

$$\langle W(r, t) W(r', t') \rangle = \delta(r - r') \delta(t - t')$$

random Gaussian field (Brownian sheet)

Now let's obtain explicit equations for the simple and excluded random walks:

We should be careful with units.

$F(g)$ is now free-energy per unit length (volume).

Define physical density

$$\rho_i = \frac{m N_P}{(\Delta x) N_S}$$

m = particle mass

Δx = crystal lattice spacing

$$\Rightarrow \frac{N_P}{N_S} = \frac{\Delta x \cdot \rho_i}{m}$$

$$\Rightarrow F(g) = \frac{\tilde{F}\left(\frac{\Delta x \cdot \rho}{m}\right)}{(\Delta x) \cdot N_S}$$

discrete free energy

With proper units

$$\frac{\partial F(\rho)}{\partial \rho} = \left(\frac{k_B T}{m}\right) \begin{cases} \ln \rho/\bar{\rho} \\ \ln \rho/\bar{\rho} - \ln \frac{1-\rho}{1-\bar{\rho}} \end{cases} = \mu(\rho)$$

$$\Rightarrow \frac{\partial \mu}{\partial \rho} = \left(\frac{k_B T}{m}\right) \begin{cases} \rho^{-1} & \text{simple} \\ \left[\frac{\rho(1-\rho)}{\bar{\rho}}\right]^{-1} & \text{excluded} \end{cases}$$

$$\Rightarrow \partial_t \rho = \nabla \cdot \left\{ D \nabla \rho + \left(2mD\bar{\rho}\right)^{1/2} W(\rho, t) \right\}$$

Put $\rho(1 - \frac{\rho}{\bar{\rho}})$ for excluded

Addendum to page 8

On page 8 there was a wrong counting result

$$\Omega_{N_S}(N_P) = \frac{N_S^{N_P}}{N_P!} \quad (\text{not integer})$$

However, the result for the free energy was correct.

Here is one way to derive it, noting that the Poisson distribution is a limit of a binomial distribution

The simple random walk is indistinguishable from an excluded walk at small density

$$s \ll 1 \Rightarrow (1-s) \ln(1-s) \approx -s$$

and so $F_i(s) = - (k_B T) N_s [s \ln s - s]$
as derived (wrongly!) before

In fact, our coarse-grained free energy was exact, knowing that $P(N_p)$ is Poisson:

$$F = - (k_B T) \ln [P(N_p)] = - (k_B T) \ln \left[\frac{\overline{N_p}^{N_p} e^{-\overline{N_p}}}{N_p!} \right]$$

$$= - (k_B T) N_s [s \ln \overline{S}/s + s]$$