

Statistical mechanics for molecular

①

simulations (2015)

Lecture 7

Non-equilibrium systems II :

These are quite advanced topics!!

fluctuation-dissipation & chemical kinetics

* regression theorem

* time-correlation functions

* chemical kinetics & simulation of rare events.

So in the last lecture we studied the

with a focus on chemical kinetics as the example

Brownian dynamics and briefly touched on the subject of fluctuation-dissipation theorem that plays a key role in ^{the foundation of} non-equilibrium statistical

mechanics. This lecture, the final one, I will talk about how this allows us to calculate various system responses using ~~the~~ ^{equilibrium ensemble} simulations. **timeless**

Lars Onsager: 1968 Nobel Prize. (2)

* Regression theorem

"The relaxation of macroscopic non-equilibrium disturbances is governed by the same law as the regression of spontaneous microscopic fluctuations in an equilibrium system"

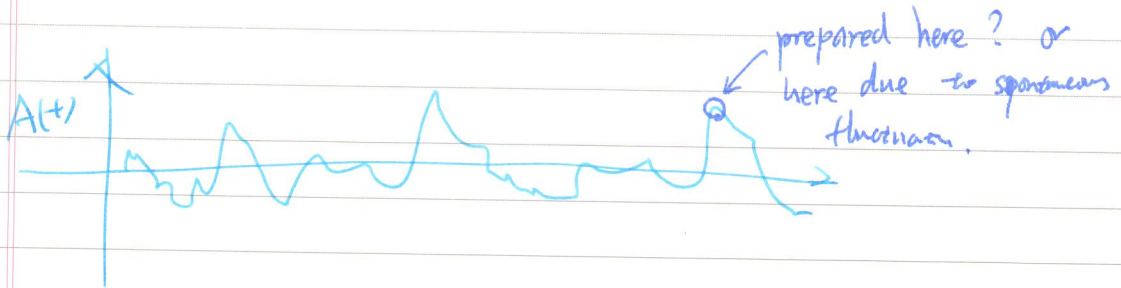
regression:
back to
"mean" equilibrium
behavior.

system" \leftarrow a single statement worth a Nobel prize!!

Physically, this theorem depends on the fact that the system, in an non-equilibrium state, on average, does not know how it reached the non-equilibrium state.

know how it reached the non-equilibrium

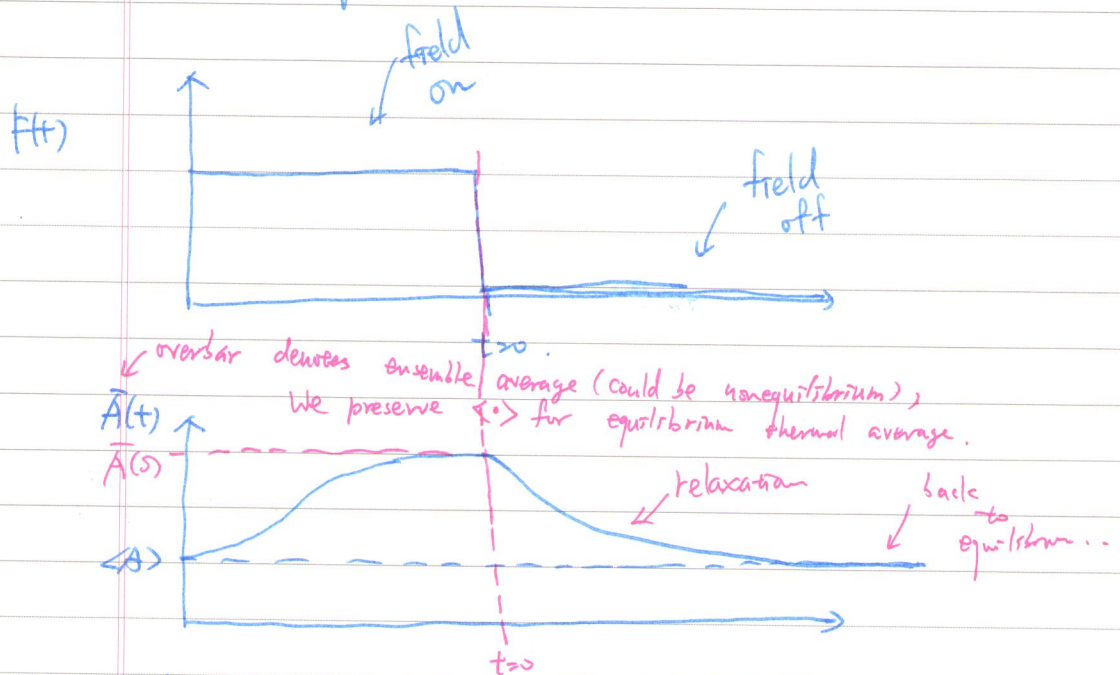
state:



How it is prepared is not important, the underlying Hamiltonian is the same, so the dynamics are the same!! timeless

In a "non-equilibrium" experiment, an external field is often used to prepare the system in a nonequilibrium state, and the relaxation back to equilibrium is then studied:

For example:



relaxation measured by $\bar{A}(t) - \langle A \rangle$

They follow the same Hamiltonian

The regression theorem states that a quantitative relation between the relaxation of the non-equilibrium system after the field is turned off ($\bar{A}(t) @ t > 0$) and the regression of fluctuations can be established:

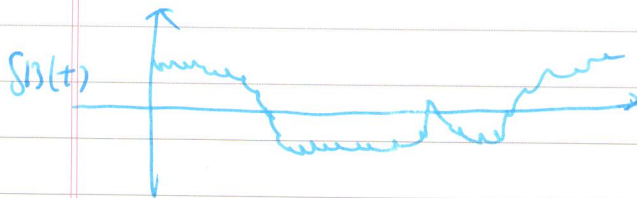
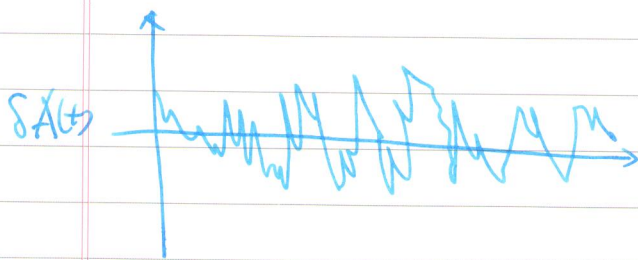
$$\frac{\bar{A}(t) - \langle A \rangle}{\bar{A}(0) - \langle A \rangle} = \frac{\langle \delta A(0) \delta A(t) \rangle}{\langle \delta A^2 \rangle}$$

timeless

Now, how do we measure the "regression" of fluctuations??

Before we can introduce the quantitative formula of the regression theorem, we need to first be able to quantify "regression" of spontaneous fluctuation.

For this we introduce the tool of time-correlation function. Let's consider dynamical ^{fluctuation} of classical observables:



Do these two ^{observables} ~~variables~~ "regress" differently? How can we capture the difference dynamics?

timeless

* Time-correlation function

Let's consider a fluctuation in an observable

$$\delta A(t) = A(t) - \langle A \rangle$$

This is governed by the classical mechanics, so

$A(t)$ depends on the phase-space point.

$$\delta A(t) = \delta A(t; \underbrace{r^N, p^N}_{\text{initial condition}}) = \delta A(r^N(t), p^N(t))$$

Note that $\langle \delta A(t) \rangle = 0$ is uninteresting, what

can be used to describe the fluctuating

dynamics is the conditional "correlation" of

fluctuations at two different time points.

Consider the correlation between $\delta A(t)$ at t_1 &

t_2 :

$$C(t_1, t_2) = \langle \delta A(t_1) \delta A(t_2) \rangle \stackrel{\text{ensemble average.}}{=} \langle A(t_1) A(t_2) \rangle - \langle A \rangle^2$$

⑥ ⑧

This is the time-correlation function.

It has many useful properties:

① time-shifting invariance.

Since $C(t_1, t_2)$ captures \swarrow property of equilibrium ensemble.

$$\begin{aligned} \text{We write } C(t_1, t_2) &= \langle \delta A(t_1) \delta A(t_2) \rangle \quad \swarrow \text{independent of time "0"} \\ &= \langle \delta A(t_1 + \tau) \delta A(t_2 + \tau) \rangle \quad \swarrow \text{set } \tau = -t_1 \\ &= \langle \delta A(0) \delta A(t_2 - t_1) \rangle \\ &= \langle \delta A(0) \delta A(t) \rangle = C(t). \end{aligned}$$

② $C(0) = \langle \delta A^2 \rangle$ is the variance of the fluctuations, recall $\langle \delta A^2 \rangle \sim \frac{1}{N}$ for an extensive variable.

③ for independent case $\langle AB \rangle = \langle A \rangle \langle B \rangle$
So when $t \rightarrow \infty$, $C(t) = \langle \delta A(0) \delta A(t) \rangle \rightarrow 0$.

$$\lim_{t \rightarrow 0} C(t) = 0.$$

④ $C(t) = C(-t)$ \Leftarrow for classical systems, not true for Q.M.

timeless

⑤ for ergodic systems

$$\langle \delta A(0) \delta A(t) \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt \cdot \delta A(t_1) \delta A(t_2), \quad t = t_2 - t_1$$

With the definition of $C(t)$, we

can present the mathematical formula for

the regression theorem:

Overbar: ensemble average, the ensemble can be non-equilibrium

relaxation of $\bar{A}(t)$

regression of fluctuations

bracket: thermal average

$$\frac{\overline{\bar{A}(t) - \langle A \rangle}}{\overline{\bar{A}(0) - \langle A \rangle}} = \frac{\langle \delta A(0) \delta A(t) \rangle}{\langle \delta A^2 \rangle}$$

← thermal average

valid in the so-called linear response regime.

If the system is prepared in a ^{non-equilibrium} state such that the observable expectation $\langle \bar{A}(0) \rangle = \bar{A}(0)$

A rigorous proof of this \rightarrow linear response theory.

Note that the over-bar denotes the ~~non-ensemble~~ average over an non-equilibrium ensemble.

We will illustrate the usage of this next time.

Now we do not have time to illustrate more properties of time-correlation functions, but I hope you do note that it is a very important tool in statistical mechanics. It is an equilibrium property of a system/ensemble, but various non-equilibrium responses are calculated from time correlations:

* Infrared (resonance): $I(\omega) = \int_{-\infty}^{\infty} dt. e^{i\omega t} \langle \mu(t) \mu(0) \rangle$ ↙ μ : molecular dipole -

* Transport coefficient: $\kappa = \int_0^{\infty} \langle \dot{A}(t) \dot{A}(0) \rangle dt$ ↙ heat, electricity...

or $L = \beta \cdot V \int_0^{\infty} ds \langle J(s) J(0) \rangle$ ↙ zero bias ↙ flux

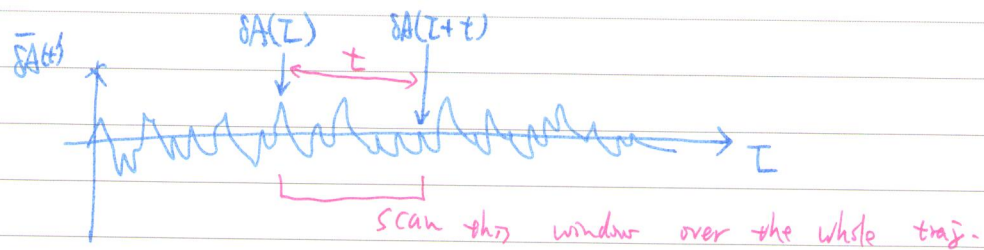
e.g. heat flux ~

Note that these time-correlation functions can be calculated from simulations.

In principle, the time-correlation function can be calculated from a ^{long} trajectory if the system's ^{dynamics} is ergodic:

~~$$\langle \delta A(t) \delta A(t') \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt' \delta A(t'+t) \delta A(t')$$~~

$$\langle \delta A(t) \delta A(t') \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt \delta A(t) \delta A(t+t)$$



This is the ideal case in which the sampling is sufficiently well. However, for many problems the sampling is difficult \Rightarrow barrier crossing \sim .

We will illustrate how the regression theorem can be used to calculate reaction rates!

* Chemical kinetics.

Now we will consider the application of the theory to treat chemical kinetics to illustrate its powerfulness. Let's consider a simple chemical equation.



macroscopic theory

The rate equation is

$$\frac{dC_A(t)}{dt} = -k_{B \leftarrow A} C_A(t) + k_{A \leftarrow B} C_B(t)$$

$$\frac{dC_B(t)}{dt} = k_{B \leftarrow A} C_A(t) - k_{A \leftarrow B} C_B(t)$$

In equilibrium, we have $\frac{dC_A(t)}{dt} = \frac{dC_B(t)}{dt} = 0$

$$\therefore \frac{\langle C_A \rangle}{\langle C_B \rangle} = \frac{k_{A \leftarrow B}}{k_{B \leftarrow A}}$$

← detailed balance condition

If we make a small perturbation

$$C_A(t) = \langle C_A \rangle + \Delta C_A(t), \quad C_B(t) = \langle C_B \rangle - \Delta C_B(t)$$

$$\frac{d\Delta C_A(t)}{dt} = -k_{A \rightarrow B} \cdot \Delta C_A(t) - k_{B \rightarrow A} \cdot \Delta C_B(t)$$

$$\therefore \Delta C_A(t) = \Delta C_A(0) \cdot e^{-(k_{B \rightarrow A} + k_{A \rightarrow B}) \cdot t}$$

$$= \Delta C_A(0) \cdot e^{-t/\tau}$$

where the decay rate $\tau = \frac{1}{k_{A \rightarrow B} + k_{B \rightarrow A}}$

$$= \frac{1}{k_{A \rightarrow B}} \times \frac{1}{1 + \frac{\langle C_A \rangle}{\langle C_B \rangle}} = \frac{\chi_{B \rightarrow A}}{k_{A \rightarrow B}}$$

↑ forward rate

where the mole fraction

$$\chi_{B \rightarrow A} = \frac{C_B}{C_A + C_B}$$

microscopic
fluctuation!
↓

Now the number density fluctuation should be

related to the concentration:

$$\bar{n}_A(t) \propto C_A(t)$$

So according to the regression theorem

$$\frac{\Delta C_A(t)}{\Delta C_A(0)} = \frac{\langle \delta n_A(0) \delta n_A(t) \rangle}{\langle (\delta n_A)^2 \rangle}$$

$$\Rightarrow e^{-t/\tau} = \langle \delta n_A(0) \delta n_A(t) \rangle / \langle \delta n_A^2 \rangle \quad \text{--- (1)}$$

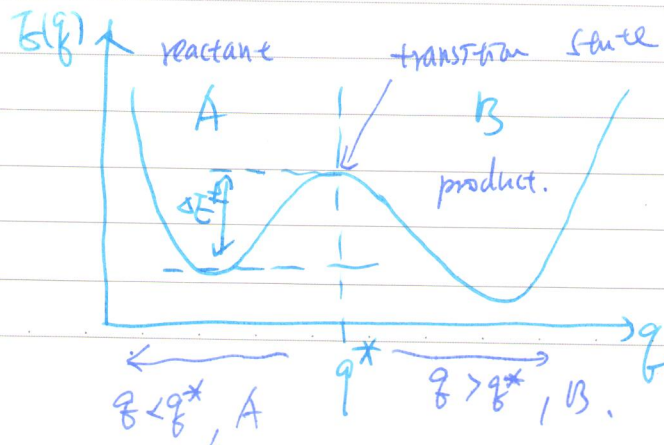
the microscopic particle number fluctuation is

related to the microscopic relaxation time!!

Now in order to further characterize the number fluctuation, we need a microscopic

way to define τ_A !!

Assume a single rxn coordinate:



timeless

So the simple chemical dynamics is

effectively the diffusion of one

particle in the PES \rightarrow we use particle

position $z(t)$ to determine whether it is A or B.

By tagging one particle:

$$N_A(t) = H_A[z(t)] = \begin{cases} 1 & \text{if } z(t) < z^* \\ 0 & \text{if } z(t) > z^* \end{cases}$$

position of the particle at time t.

Note that

$$\langle H_A \rangle = \chi_A = \frac{C_A}{C_A + C_B}$$

H_A is either 1 or 0.

$$\langle H_A^2 \rangle = \langle H_A \rangle = \chi_A$$

Therefore

$$\begin{aligned} \langle (H_A)^2 \rangle &= \langle H_A^2 \rangle - \langle H_A \rangle^2 = \chi_A - \chi_A^2 \\ &= \chi_A (1 - \chi_A) \\ &= \chi_A \cdot \chi_B \end{aligned}$$

Therefore Eq. ① becomes $\langle H_A(t) \rangle = H_A(q(t))$

$$e^{-\frac{t}{\tau}} = \frac{\langle \delta H_A(s) \delta H_A(t) \rangle}{\langle \delta H_A^2 \rangle} = \frac{\langle H_A(s) H_A(t) \rangle - \langle H_A \rangle^2}{\chi_A \chi_s}$$

To derive an expression for τ , we take time derivative of both sides:

$$-\frac{1}{\tau} \cdot e^{-\frac{t}{\tau}} = \frac{d}{dt} \frac{\langle H_A(s) H_A(t) \rangle}{\chi_A \chi_s}$$

Note $H_B(q) = 1 - H_A(q)$
 $\langle \dot{q}(s) \delta[q(s) - q^*] \rangle = 0$
↑ odd ↑ even
 So $-\langle H_A(s) H_A(t) \rangle = -\langle \dot{q}(s) \delta[q(s) - q^*] H_A(q(t)) \rangle$
 $= \langle \dot{q}(s) \delta[q(s) - q^*] H_B(q(t)) \rangle$

Note that

$$\frac{d}{dt} \langle H_A(s) H_A(t) \rangle = \frac{d}{dt} \langle H_A(-t) H_A(0) \rangle$$

$$= -\langle \dot{H}_A(-t) H_A(0) \rangle$$

$$= -\langle \dot{H}_A(0) H_A(t) \rangle$$

Dirac delta

$$\dot{H}_A(0) = \dot{H}_A(q(0)) = \dot{q} \cdot \frac{d}{dq} H_A(q) = -\dot{q} \cdot \delta(q - q^*)$$

Therefore $\frac{1}{\tau} \cdot e^{-\frac{t}{\tau}} = \frac{\langle \dot{q}(s) \cdot \delta[q(s) - q^*] H_A(q(t)) \rangle}{\chi_A \chi_s}$

see box. on top of barrier. (only $q(s) \approx q^*$ particles affect $H_A(t)$)

timeless

* Transition state theory.

① at short times: $t \ll \tau$, $e^{-\frac{t}{\tau}} \approx 1$

② $\chi_A = \langle \Theta(q - q^*) \rangle$ step function.

Assume T.S. population is in ~~static~~ thermal equilibrium with χ_A on the bottom of well (i.e. δB large).

this
page
see
slides

* Bennete - Chandler approach.

The problem of TSS is also clearly illustrated by the derivation above!

More in
Chapter 16. of
Frankel &
Smiré !!

* neglect of re-crossing events

* knowledge of the precise location of TS required.

* factorization of the thermal average terms.

As a result, TST only provides an upper bound to the transition rate. To better estimate the rate, Bennete and Chandler both proposed to evaluate the rate using "shooting" MD trajectories. (JCP 68, 2959 (1978)). The idea is quite straightforward.

(7)

We consider to calculate using a "none-precise" $g^* = g$,

$$R_{B \leftarrow A} = \frac{\langle \dot{g}(0) \cdot \delta[g(0) - g_1] \cdot H_0(g(t)) \rangle}{\chi_A}$$

Note that in this case, the TST rate is

$$R_{B \leftarrow A}^{TST} = \frac{1}{2} \langle |\dot{g}(0)| \rangle \frac{e^{-PE(g_1)}}{\int_{-\infty}^{g_1} dg e^{-PE(g)}}$$

average initial velocity.

Therefore if we define a transmission coefficient,

$$K(t) = \frac{R_{B \leftarrow A}(t)}{R_{B \leftarrow A}^{TST}} = \frac{\langle \dot{g}(0) \delta[g(0) - g_1] \cdot \Theta(g(t) - g_1) \rangle}{\frac{1}{2} \langle |\dot{g}(0)| \rangle}$$

no need to simulate, this is $\frac{2k_B T}{\chi_A m}$

then we can calculate $K(t)$ using MD simulation,

and apply it to correct the TST result!!

can be evaluated

by shooting MD trajectories from g_1 .

The transmission coefficient can be seen as a

"conditional probability" of asking if the particle is

initially at g_1 , then what's the prob. of finding

the particle on the B side at time t , weighted by the initial velocity!!

average over sampled velocities \rightarrow timeless