

# SI2520 - Nonequilibrium Statistical mechanics

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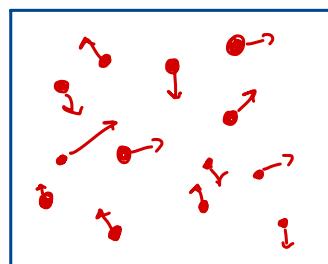
## Lecture 1 - Introduction and overview

This is a course on nonequilibrium statistical mechanics. What is that? There is no simple answer to this question. In some sense it is not one thing but rather a collection of phenomena and methods that share to some extend a philosophy and approach. But even that does not really capture everything. In fact, as opposed to, say, equilibrium statistical mechanics or quantum mechanics, where there is a set of core facts and methods, and therefore a courses on these topics will be similar in their material selection, two courses in nonequilibrium statistical mechanics given by two different lecturers may have no overlap in contents. This is also reflected in the lack of a single textbook in this course, which instead relies on multiple sources. The lecture notes aim to be self-contained, and recommendations for further reading will be given. A part of your challenge for this course, therefore, will be to seek out the information and knowledge that you personally need to master the course content. The required research should be thought of as a learning opportunity and a task.

We will cover many aspects of nonequilibrium physics in this course. In this first lecture I want to attempt to begin with providing some sort of overview and connections between the different parts of the course, which otherwise may seem a bit disconnected.

First, it is useful to remind us of the essence of statistical mechanics and its standing in the grand scheme of things.

Importantly, statistical mechanics describes equilibrium, and it is the microscopic underpinning for thermodynamics. To have something concrete in mind, think of a box of gas in equilibrium



### Thermodynamics:

Macroscopic variables  $T, V, P, N, \dots$

Entropy  $S$ , function of macroscopic variables

Empirical relations:

$$dU = TdS - PdV$$

$$dF = -SdT - PdV$$

$$dS \geq 0$$

### Statistical mechanics

Provides a microscopic description of thermodynamics. An essential assumption is that we do not need to know the detailed information about all particles in the gas to make verifiable predictions about the state of a system. This is in some sense a statement about typicality, there are many different possible microstates, call their number  $\Omega$ , that give the same macroscopic variables. And since all we measure,

at least in thermodynamics, are macroscopic variables, we don't need to (and in fact cannot) keep track of details of the microstate. Instead, we adopt a statistical description of the microscopic state. In equations, I assume this is known and familiar

Statistical mechanics :  $S = k \ln \Omega$

$$\Omega = \frac{1}{z} e^{-\beta H}$$

$$Z = \text{tr } \Omega$$

$$F = -\frac{1}{\beta} \ln Z \quad \text{etc.}$$

For example, instead of keeping track of the individual velocity of all particles in the gas, we ask about distribution of velocity. In an isotropic gas, for example, we get the Maxwell velocity distribution (in 3D)

$$P(v) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left( -\frac{mv^2}{2k_B T} \right)$$

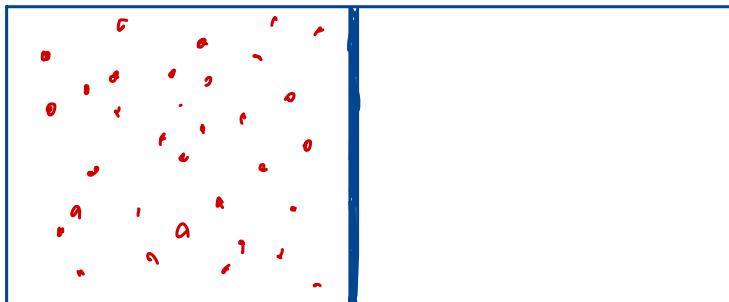
(we will need this later in the course).

By definition, an equilibrium state is a steady state, and if nothing breaks translation invariance, it is uniform. But not all steady states are in thermal equilibrium.

## Nonequilibrium

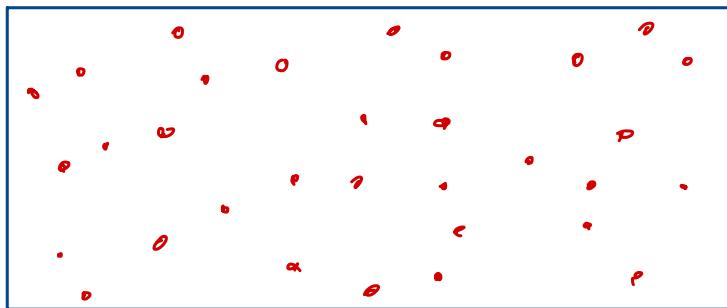
So far, we only summarized basic notions of equilibrium physics, thermodynamics and its relation to statistical mechanics. In the nonequilibrium case a system is somehow driven out of equilibrium, perhaps by acting on it by some forces or fields, and then evolves in time. If the perturbation is turned off the system may (or may not) reach a thermal steady state at long times, or if the perturbation is kept on reach a nonequilibrium steady state with currents flowing. As a simple to discuss example, imagine we start with a box with a partition and gas only in the left half:

$t=0$

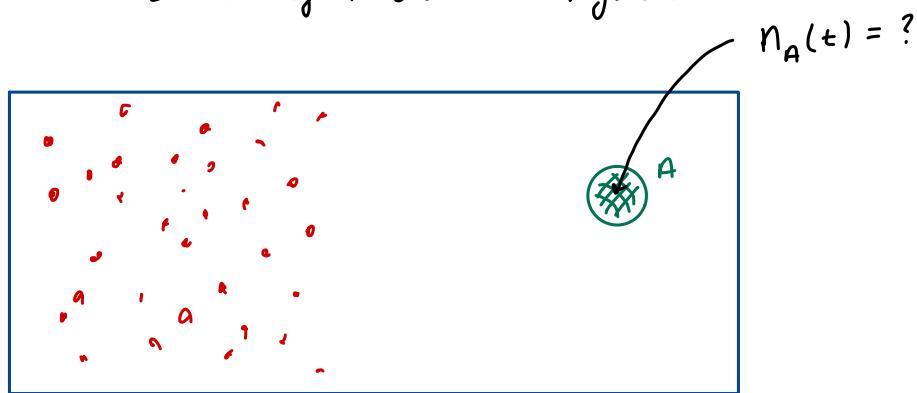


If we remove the partition the gas will start to flow to the right and according to our intuition after some time it is uniformly distributed over the whole box

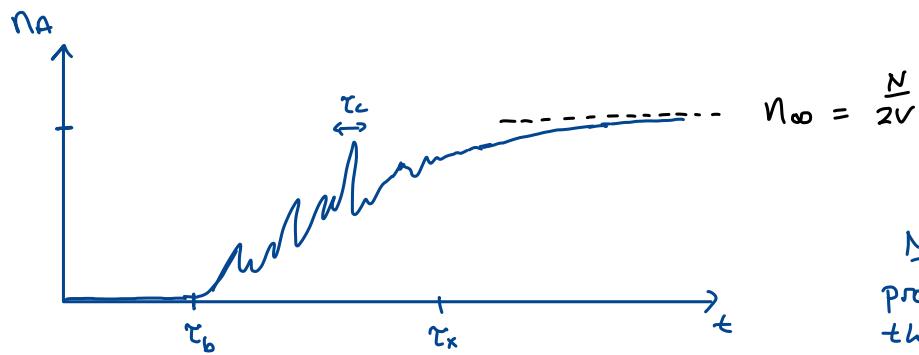
$t=\infty$



This, of course, is a setup familiar to you from thermodynamics, and we can use thermodynamics to calculate properties of the initial and final state, with some assumptions about the dynamics, including that the final state is thermal. These assumptions are probably justified in this particular case, but it is not always obvious that they are. But suppose we are interested in how the system reaches its final state, what do we expect? Let's, for example, imagine we can measure the particle density in a small region on the right:



How would  $n_A(t)$  look like? (Discuss!)



Note: The real curve will probably not look exactly like this, but that's ok, we just want to get a feeling for what to roughly expect.

$t_b$ : minimum time for particles to reach A

$t_x$ : local equilibrium time

$t_c$ : collision time

At long times  $t \geq t_x \gg t_c, t_b$  the system may reach local equilibrium such that we can coarse grain and for example introduce a local macroscopic density  $n(\vec{r}, t)$  given by local equilibrium. Just from symmetries and conservation laws alone (the total number of particles is conserved) we would expect that a hydrodynamic description would be accurate, and this would result in the continuity equation

$$\frac{\partial n}{\partial t} + \vec{\nabla} \cdot \vec{j} = 0$$

The particle current arises from variation in density and close to equilibrium, this will be small. We can therefore expand to obtain

$$\vec{j}(\vec{r}, t) = -D \vec{\nabla} n(\vec{r}, t) \quad (\text{Fick's law})$$

$\uparrow D > 0$ , diffusion constant

Plugging this into the continuity equation, we obtain the diffusion equation

$$\boxed{\frac{\partial n(\vec{r}, t)}{\partial t} = D \vec{\nabla}^2 n(\vec{r}, t)}$$

Solve with Fourier transform

$$\frac{\partial n(\vec{k}, t)}{\partial t} = -D k^2 n(\vec{k}, t)$$

$$\Rightarrow n(\vec{x}, t) = \int \frac{d^d k}{(2\pi)^d} n(\vec{k}, t_0) e^{-D k^2 (t-t_0)} e^{i \vec{k} \cdot \vec{x}}$$

$$\text{if } n(\vec{x}, t_0) = \delta(\vec{x} - \vec{x}_0) \quad \text{then} \quad n(\vec{k}, t_0) = e^{-i \vec{k} \cdot \vec{x}_0}$$

$$\text{and} \quad n(\vec{x}, t) = (4\pi D |t-t_0|)^{-d/2} \exp\left(-\frac{(\vec{x}-\vec{x}_0)^2}{4D|t-t_0|}\right)$$

(See e.g. Daniel Arovas lecture notes on Non eq. stat. Phys)

Note: When one is close to equilibrium one can also use irreversible thermodynamics, which assumes one can define a smooth entropy function. See appendix to this lecture for more details.

So, essentially from symmetries alone we have argued that diffusion should emerge in a nonequilibrium at long times. This leaves many questions unanswered. Does diffusion always emerge? In other words, can  $D=0$ ? And what determines the value of  $D$  anyway. What happens before we enter the diffusive regime, and are there other universal behaviors that can emerge?

Generally, in a complex many-body system we have no hope of solving the many-body dynamics exactly. What and why and how we can still model such situations, with applications to almost all of physics, is what this course is about. There are several different approaches one can take, and these correspond roughly to the three main parts of this course:

### Part 1 - stochastic dynamics

The main idea here is to take inspiration from statistical mechanics and introduce a statistical approach. I can not hope to model the dynamics of all particles, and I also don't need to. If I can write down dynamical equations that give me the statistics of possible outcomes or behaviors, this is anyway all we are

interested in, and is all we can hope to measure. By keeping this general we will obtain systematic approaches that are widely applicable. In particular we will study:

- Langevin equation  $\rightarrow$  prototypical stochastic differential equation
  - Master equation
  - Fokker-Planck equation
  - One-step stochastic processes
- } Markov processes and time evolution of their probability processes

### Part 2 - microscopic "perturbation theory"

We will try to solve dynamics in a more microscopic approach, but to make progress requires making some simplifying assumptions.

- kinetic theory & Boltzmann equation
- ( - linear response
- Fluctuation-dissipation theorem ) only optional lecture notes, no lectures.

### Part 3 - Open quantum systems

Most of part 1+2 ignore quantum coherences, but are still applicable to quantum systems when this is a good approximation. In this last part we will discuss how one includes quantum effects in so-called quantum master equations and, if time allows, will discuss how a form of quantum typicality leads to the emergence of statistical mechanics from quantum mechanics. More specifically, we will cover:

- Quantum quenches
- Lindblad equation
- Eigenstate thermalization hypothesis
- Random circuits

### Random walk and the arrow of time

For the rest of this lecture let us start getting a flavor of our work in parts 1 and 2. Perhaps the simplest stochastic description of motion is the random walk:

### Random Walk



See python simulation

Position  $x(t)$  only measured at discrete times  $t_n = n \Delta t$

$$x(t + \Delta t) = x(t) + \underbrace{\Delta x_n}_{\text{random variable drawn from some distribution } P(\Delta x)}$$

Assume  $\Delta x_n$  are independent, identically distributed

$$\langle \Delta x_n \rangle = 0 \quad \text{and} \quad \langle (\Delta x_n)^2 \rangle = \sigma^2 < \infty$$

then  $x(t_n) = \Delta x_0 + \Delta x_1 + \dots + \Delta x_{n-1} = \sum_{k=0}^{n-1} \Delta x_k$

## Probability theory-reminder

$\underline{X} = \{x_1, x_2, \dots, x_N\}$  set of events.

Probability of  $x$  is  $P(x)$

Expectation value of a function  $f = f(x)$

$$\langle f \rangle = \sum_x f(x) P(x)$$

$$\text{In particular } \langle 1 \rangle = \sum_x P(x)$$

Variance of  $f$

$$\langle (\delta f)^2 \rangle = \langle (f - \langle f \rangle)^2 \rangle = \langle f^2 \rangle - \langle f \rangle^2$$

Covariance of  $f_i$  and  $f_j$

$$\langle_{ij} \equiv \langle \delta f_i \delta f_j \rangle = \langle (f_i - \langle f_i \rangle)(f_j - \langle f_j \rangle) \rangle$$

$$= \langle f_i f_j \rangle - \langle f_i \rangle \langle f_j \rangle$$

When the set  $\underline{X}$  becomes continuous sums are replaced by integrals:

$$\langle f \rangle = \int_{\underline{X}} dx f(x) P(x)$$

etc.

$x(t)$  sum of large number of independent identically distributed random variables

$\Rightarrow x(t)$  normally distributed for large  $t$

↑ central limit theorem (see digression next two pages)

$$P(x) = \frac{1}{\sqrt{2\pi\sigma_x^2}} e^{-\frac{1}{2\sigma_x^2}(x-\mu_x)^2}$$

Let's calculate  $\mu_x$  and  $\sigma_x^2$

$$\mu_x = \langle x(t) \rangle = \sum_k \langle \Delta x_k \rangle = 0$$

$$\sigma_x^2 = \langle x^2(t) \rangle = \sum_{k,l} \langle \Delta x_k \Delta x_l \rangle$$

$$= \underbrace{\sum_k \langle (\Delta x_k)^2 \rangle}_{\sigma^2} + \underbrace{\sum_{k \neq l} \langle \Delta x_k \Delta x_l \rangle}_{= \langle \Delta x_k \rangle \langle \Delta x_l \rangle = 0 \text{ since } \Delta x_k \text{ and } \Delta x_l \text{ independent}}$$

$$= n \sigma^2 = \frac{\sigma^2 t}{n t} \equiv 2 D t$$

with diffusion coefficient  $D = \frac{\sigma^2}{2nt}$

$$\Rightarrow P(x, t) = \frac{1}{\sqrt{4\pi D t}} e^{-\frac{x^2}{4Dt}}$$

Solution of diffusion equation

Assumptions: no interaction between particles  $\Rightarrow$  low density

- $\Delta x_k$  independent  $\Rightarrow \Delta t \gg \tau_{\text{mic}}$  collision time

## Central limit theorem (small digression)

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Assume  $x_i \quad i \in 1, \dots, N$  a set of identically distributed random variables with mean  $\mu = \langle x_i \rangle$  and standard deviation  $\sigma^2 = \langle (\sum x_i)^2 \rangle = \langle (x - \langle x_i \rangle)^2 \rangle$ .

Define a new random variable

$$y = \sum_{i=1}^N x_i$$

Then the probability distribution of  $y$  is

$$p(y) = \langle \delta(y - \sum x_i) \rangle = \int dx_1 \dots dx_N p(x_1) \dots p(x_N) \delta(y - \sum x_i)$$

Now use that  $\delta(y - y_0) = \int dk e^{ik(y-y_0)}$

$$p(y) = \prod_i \int dx_i p(x_i) \int dk e^{-ik(y-x_i)} \int dk e^{-iky} \prod_i \int dx_i p(x_i) e^{ikx_i}$$

$$= \int dk \exp(N \ln \int dx p(x) e^{ikx_i} - iky)$$

$$= \int dk \exp(N \ln g(k) - iky)$$

where  $g(k) = \langle e^{ikx} \rangle$  is the generating function of  $p(x)$

such that

$$\ln g(k) = \sum_n \frac{(kx)^n}{n!} \langle \langle x^n \rangle \rangle = \sum_n \frac{(ik)^n}{n!} \langle \langle x^n \rangle \rangle$$

$\Rightarrow$  the cumulant generating function

$$\langle \langle x \rangle \rangle = \langle x \rangle = \mu$$

$$\langle \langle x^2 \rangle \rangle = \langle x^2 \rangle - \langle x \rangle^2 = \sigma^2 \text{ etc.}$$

This then gives

$$\begin{aligned}
 p(y) &= \int dk \exp\left(-ik(y - \mu_N) - \frac{Nk^2}{2}\sigma^2\right) + \int dk e^{N \sum_{n>2} \frac{(ik)^n}{n!} \langle\langle x^n \rangle\rangle} \\
 &= \frac{1}{\sqrt{2\pi N\sigma^2}} \exp\left(\frac{(y - N\mu)^2}{2N\sigma^2}\right) + O\left(\frac{1}{N^2}\right)
 \end{aligned}$$

which is Gaussian distributed with

$$\mu_y = N\mu$$

$$\sigma_y^2 = N\sigma^2$$

## The arrow of time

OK, we wrote down the stochastic process of a random walk and observed that in the right limit we get diffusion. This is nice, but Note that the diffusion equation is not time reversal symmetric. It describes an irreversible process, consistent with the second law of thermodynamics, which for isolated systems reads

$$\cancel{ds \geq 0}$$

The same is true for other macroscopic laws we might write down, such as heat conduction, friction etc.

That's good, right?

Well, yes, it means we have an arrow of time as we are used to (splattering eggs etc.).

But, the microscopic equations of motion are time reversal symmetric:

$$m \ddot{x} = -\vec{\nabla} u \quad \text{Newton}$$

$$i\hbar \partial_t |\psi(t)\rangle = \hat{H} |\psi(t)\rangle \quad \text{Schrödinger} \quad (T = K!)$$

etc. ↑  
complex conjugation

Therefore, if entropy increases forward in time, it should also increase backwards in time!

How does the arrow of time, or irreversible dynamics, emerge from time reversal symmetric dynamics?

(Boltzmann, Maxwell, ... )

### Intuition

Container with two compartments, initially filled with gas on only one side.



$$\frac{\Omega_{\text{final}}}{\Omega_{\text{initial}}} = 2^N$$

$\Rightarrow$  Probability of spontaneous fluctuation back to initial state  $2^{-N} \sim 2^{-23} \lllll 1$

Irreversibility = evolution from less probable to more probable.

## Increase of entropy

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Let's try to calculate the increase of entropy using classical mechanics.

This will reveal interesting physics and serve as an example of the more microscopic approaches we will explore in part 2 of the course.

First question: which entropy?

Let's use the statistical entropy

$$S = - \sum_n p_n \ln p_n$$

Where does this formula come from? It was introduced by Shannon in famous papers from 1948 titled "A mathematical theory of communication." Shannon argued that this formula gives the expected amount of information for a measurement of a probability distribution. It may be interesting to look up Shannons arguments but here let us just give an argument motivating the form.

Imagine we have a discrete probability distribution  $p_1, p_2, \dots$

We draw from that distribution  $n$  times and then expect to get outcome 1  $n_1 = p_1 n$  times, outcome 2  $n_2 = p_2 n$  times etc.

However, we don't know in what order these outcomes come.

The total number of possible outcomes is

$$\Omega = \frac{n!}{n_1! n_2! n_3! \dots}$$

Using the Stirling approximation  $\ln n! \approx n \ln n - n$  for  $n \rightarrow \infty$  we get that

$$\ln \Omega = n \ln n - n - \sum_j n_j \ln n_j + \underbrace{\sum_j n_j}_{=n}$$

$$\ln \Omega = n \ln n - \sum_j p_j n (\ln p_j + \ln n)$$

$$= n \ln n - n \ln n \underbrace{\sum_j p_j}_{=1} - n \sum_j p_j \ln p_j = -n \sum_j p_j \ln p_j$$

So, indeed  $S = \sum_j p_j \ln p_j$  measures somehow the average entropy or amount of information one obtains from a measurement of a probability distribution  $P(x)$ .

If  $P(x)$  is continuous the natural generalization of the above formula is

$$S = - \int dx P(x) \ln P(x).$$

Note: In information theory  $S$  is often denoted with  $H$ .

Getting back to our problem, we use the Shannon entropy but using for  $P(x)$  the probability density in phase space. We define the probability density in phase space

$$\rho(\bar{q}, \bar{p}, t) \quad \text{where} \quad \begin{cases} \bar{q} = (q_1, \dots, q_n) \\ \bar{p} = (p_1, \dots, p_n) \end{cases} \quad \left. \right\} \bar{x} = (\bar{q}, \bar{p})$$

Then the Gibbs entropy

$$S = -k_B \int dx \rho(x) \ln \rho(x)$$

equals the thermodynamic entropy in equilibrium.

What about the time evolution?

Liouville equation:

$$\frac{\partial \rho}{\partial t} = \{ H, \rho \} = \sum_i \frac{\partial H}{\partial q_i} \frac{\partial \rho}{\partial p_i} - \frac{\partial H}{\partial p_i} \frac{\partial \rho}{\partial q_i} = -h \rho$$

$\uparrow$   
Poisson bracket

$$\text{Defining } \vec{v} = \left( \frac{\partial H}{\partial p_i}, -\frac{\partial H}{\partial q_i} \right) = (\dot{q}, \dot{p}) = \dot{\vec{x}}$$

↑ Hamilton's equations  
of motion

$$\frac{\partial \rho}{\partial t} = -\vec{v} \cdot \nabla_{\vec{x}} \rho = -\nabla_{\vec{x}}(\rho \vec{v}) + \cancel{\rho \nabla_{\vec{x}} \cdot \vec{v}}$$

~~0~~

$$\text{since: } \nabla_{\vec{x}} \cdot \vec{v} = \frac{\partial^3 H}{\partial p \partial p} - \frac{\partial^3 H}{\partial p \partial q} = 0$$

$\Rightarrow$  continuity equation

$$\frac{\partial \rho}{\partial t} = -\nabla_{\vec{x}}(\rho \vec{v})$$

i.e., the flow in phase space is incompressible

Now (put  $k_B = 1$ )

$$\frac{\partial S}{\partial t} = - \int dx \left( \dot{\rho} \ln \rho + \dot{\rho} \right)$$

$$= \int dx \nabla_{\vec{x}}(\rho \vec{v}) (\ln \rho + 1)$$

$$= - \int dx \rho \vec{v} \frac{1}{\rho} \nabla_{\vec{x}} \rho$$

↑ integration by parts and drop surface terms  
since system is isolated.

$$= - \int dx \vec{v} \cdot \nabla_{\vec{x}} \rho = - \int dx \vec{\nabla}_{\vec{x}}(\rho \vec{v}) = 0 !$$

The Gibbs entropy is a constant of motion!

Why does the Gibbs entropy not increase?

Being the statistical entropy, it measures our lack of information about the system. This remains constant during the Hamiltonian evolution, since it is reversible and in the derivation we kept track of all degrees of freedom.

In a macroscopic description, we only keep track of a few relevant variables (the amount of gas in left container) but disregard (out of necessity) irrelevant variables (complicated velocity correlations etc.). During the evolution information flows from the relevant variables to the irrelevant, thereby increasing the disorder in the relevant variables.

One can define a relevant entropy or Boltzmann entropy, which maximizes the statistical entropy with the constraints that the relevant variables  $\langle A_i(t) \rangle = \bar{A}_i(t)$

$\Rightarrow$  obtain density matrix

$$\rho_B(t) = \frac{1}{Z(t)} e^{-\sum_i \gamma_i A_i} = e^{-\psi - \sum_i \gamma_i A_i}$$

see Balian, Am. J. Phys. 67 1078 (1999) for details.