

# C5.3 Statistical Mechanics

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Hilary Term 2022



Mathematical  
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Oxford  
Mathematics



# List of Lectures

- Lecture 1: Introduction
- Lecture 2: Temperature and Equilibrium (I)
- Lecture 3: Temperature and Equilibrium (II)
- Lecture 4: Phase Space Dynamics and Ergodicity
- Lecture 5: Entropy (I)
- Lecture 6: Entropy (II)
- Lecture 7: Free Energies (I)
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- Lecture 9: Derivation of the Boltzmann equation
- Lecture 10: Conservation laws and Boltzmann's  $H$ -theorem
- Lecture 11: A continuum limit: The Chapman-Enskog Method (I)
- Lecture 12: A continuum limit: The Chapman-Enskog Method (II) – The constitutive relations for stress and heat flux
- Lecture 13: The Ising Model (I) – Definition and Applications
- Lecture 14: The Ising Model (II) – Analytic and computational solutions
- Lecture 15: Phase Transitions

# Lecture 1: Introduction

# What is Statistical Mechanics?

What does it do?

# The approach of Statistical Mechanics

- Many systems too complex to analyse directly, e.g.
  - behaviour of all particles in a fluid;
  - or of all boulders in an earthquake fault;
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  - **Start** from microscopic description of phenomena
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- Key approach of **Statistical Mechanics (SM)**:
  - **Start** from microscopic description of phenomena
  - **Use** probabilistic (statistical) techniques.
  - **End** with macroscopic/collective description.
- The tools of SM are used throughout throughout science to study such situations

Let's look at a fundamental process that will already demonstrated the power of SM: Random walks and diffusion!

- Paths that take successive steps in random directions
- Arise as:
  - Partial sums of fluctuating quantities
  - Trajectories of particles undergoing repeated collisions
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## Partial sums of fluctuating quantities

- One often needs to compute sums of series of fluctuating quantities  $l_i$ ,

$$S_N = \sum_{i=1}^N l_i$$

- Sequence  $S_1, S_2, S_3, \dots$  gives 1D random walk

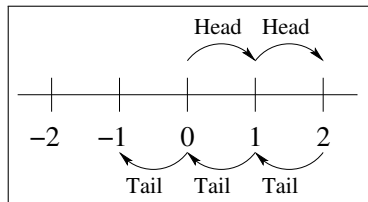
## Example: Coin Flip

$$l_i = \begin{cases} +1 & \text{heads} \\ -1 & \text{tails} \end{cases} \quad \Longrightarrow \quad S_N \equiv \sum_{i=1}^N l_i = \#\text{heads} - \#\text{tails}$$

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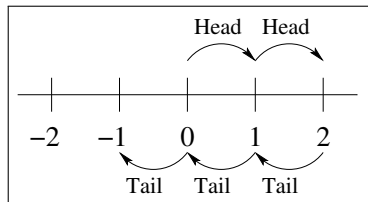
- Average value for an unbiased coin:

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- Unfortunately, the average is not very interesting.

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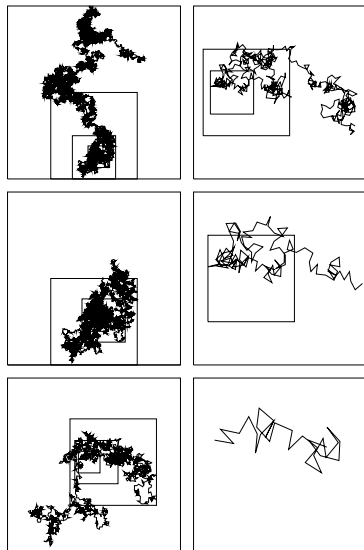
- **Higher dimensions, for example in 2D:**

- Flip 2 coins or drunkard's walk.

$$\mathbf{S}_N = \sum_{i=1}^N \mathbf{l}_i \quad \text{gives} \quad \sigma_s = \sqrt{\langle \mathbf{S}_N^2 \rangle} = \sqrt{N}L \quad \text{for step size } L$$

# Higher dimensional random walk (2D)

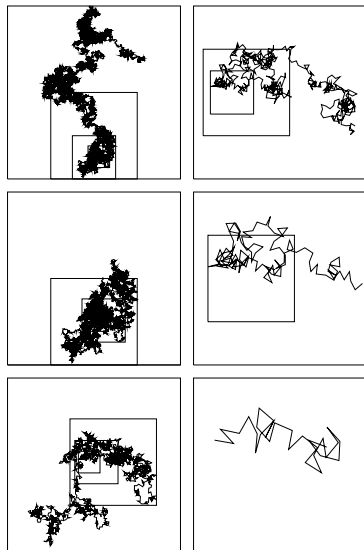
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Sethna, 2012

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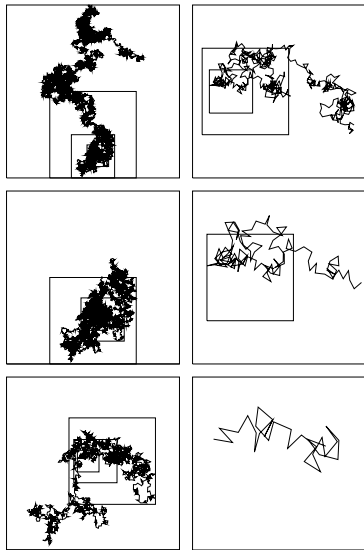


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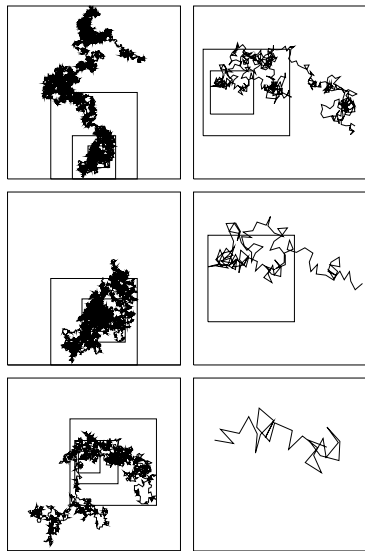
- Example of **Universality**:  
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- But: **Self avoiding random walks**  
(SAWs) have different type of  
behaviour

$$\sigma_s \sim N^\nu, \quad \nu > 1/2$$

for  $N \rightarrow \infty$  in dimensions 2, 3, or 4.  
SAWs are important for the  
modelling of **polymer chains**!



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## Question:

Given  $\rho(x, t)$  at time  $t$ , what is  $\rho(x, t + \Delta t)$  at time  $t + \Delta t$ ?

# Continuum limit of random walks in 1D (1)

## Assumptions

- Consider a general uncorrelated 1D random walk of a single particle.
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- Assume  $\chi$  is normalised to 1, mean 0 and standard derivation  $a$ , i.e.

$$\int \chi(l) dl = 1, \quad \int l\chi(l) dl = 0, \quad \int l^2\chi(l) dl = a^2.$$

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## Extensions and Remarks

- 1 Multi-dimensional version of derivation possible
- 2 Forced version of leads to the Einstein-Smoluchowski equation instead of (\*).



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## *Not covered:*

- **Quantum SM:** Provides underpinnings of astro- and condensed matter physics (properties of metals, lasers, stellar collapse).
- **Monte Carlo Methods:** Find averages of systems via computer simulations if analytical evaluation fails.

# The approach of Statistical Mechanics

Next and Next-Next steps

**What is Statistical Mechanics?**



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### Key examples for this lecture:

- 1 Start with vibrations of molecules and derive temperature, etc. (Next lectures: Fundamental notions of equilibrium SM such as temperature, entropy, etc.)

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## What is Statistical Mechanics?

A **probabilistic** approach to equilibrium **macroscopic properties** of systems with **large numbers** of degrees of freedom

### Key examples for this lecture:

- 1 Start with vibrations of molecules and derive temperature, etc. (Next lectures: Fundamental notions of equilibrium SM such as temperature, entropy, etc.)
- 2 Start with properties of individual particles and derive collective kinetic properties of fluids or solids. (The Boltzmann equation and its applications, from lecture 9 on.)

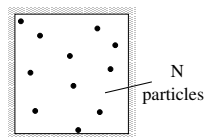
# Lecture 2: Temperature and Equilibrium (I)

# Equilibrium Statistical Mechanics and Ensembles

- Isolated system is said to approach **equilibrium** if and when it settles down at long time to a state **independent** of initial conditions (except for conserved quantities).
- The equilibrium is described as average over all states in phase space consistent with conservation laws.
- This collection of states is called an **ensemble**.
- There are many different types of ensembles, depending on the properties of the system being studied. The most popular are:
  - **Microcanonical Ensemble**: System is completely isolated so that no heat flow, mechanical work nor exchange of particles occurs.
  - **Canonical Ensemble**: System (only) exchanges heat with its environment and is kept at constant temperature.
  - **Grand Canonical Ensemble**: System (only) exchanges heat & particles with its environment at constant temperature and chemical potential.
- For now, we will only consider the **microcanonical ensemble**. For this ensemble, energy is conserved i.e. a constant.

# Microcanonical Ensemble

- Box of volume  $V$  with  $N$  classical particles
- Box's wall smooth and rigid  
 $\Rightarrow$  energy conserved when particles bounce off.



- **Configuration space:**  $3N$ -dimensional space of positions

$$\mathbf{q} = (x_1, y_1, z_1, \dots, x_N, y_N, z_N) = (\mathbf{q}_1, \dots, \mathbf{q}_N)$$

- **Momentum space:**  $3N$ -dimensional space of momenta

$$\mathbf{p} = (\mathbf{p}_1, \dots, \mathbf{p}_N)$$

- **Phase space:**  $6N$ -dimensional space of positions & momenta

$$(\mathbf{q}, \mathbf{p}) = (\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N).$$

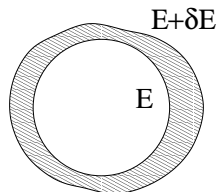
- $(\mathbf{q}(t), \mathbf{p}(t))$  is determined by Newton's laws and  $(\mathbf{q}(0), \mathbf{p}(0))$ , but:
  - $N$  is so large that computations are practically infeasible.
  - Most systems are chaotic:  
They show sensitive dependence on initial conditions.
  - We are interested in net effects of many particles (eg. pressure on wall)  
– **NOT** on tracking particles individually.

### **Question:**

How to extract simple meaningful predictions out of these complex trajectories?

## Microcanonical Ensemble (2)

- Chaotic time evolution (rapidly) scrambles knowledge of initial conditions except for conserved quantities
- For particles in a box, total energy is conserved.
- Let's hypothesize that energy is sufficient to describe the equilibrium state  
⇒ consider SM description of all possible states with energy  $E$ .  
This is the **microcanonical ensemble**
- Calculate the properties by averaging over states with energies in a shell  $(E, E + \delta E)$  in the limit  $\delta E \rightarrow 0$ .





# Microcanonical Ensemble (3)

- Phase space volume of energy shell

$$\mathcal{V}(E, \delta E) = \int_{H(\mathbf{p}, \mathbf{q}) \in (E, E + \delta E)} d\mathbf{q} d\mathbf{p}$$

where the **Hamiltonian**  $H$  represents the total energy

$$H = \frac{|\mathbf{p}|^2}{2m} + U(\mathbf{q}) = \underbrace{\sum_{i=1}^{3N} \frac{p_i^2}{2m}}_{\text{kinetic energy}} + \underbrace{U(q_1, \dots, q_{3N})}_{\text{potential energy}}$$

- Define

$$\Omega(E) \equiv \frac{\mathcal{V}(E, \delta E)}{\delta E} = \frac{1}{\delta E} \int_{H(\mathbf{p}, \mathbf{q}) \in (E, E + \delta E)} d\mathbf{q} d\mathbf{p}$$

in the limit  $\delta E \rightarrow 0$  (this limit will be implied from now on).

- Define the probability density of any state as  $\rho(\mathbf{p}, \mathbf{q}) = 1/\Omega(E)$ .  
Implicit assumption: All states with same energy are equally likely.
- Average of a property  $O$ :

$$\langle O \rangle_E = \frac{1}{\Omega(E)} \left[ \frac{1}{\delta E} \int_{H(\mathbf{p}, \mathbf{q}) \in (E, E + \delta E)} O(\mathbf{q}, \mathbf{p}) d\mathbf{q} d\mathbf{p} \right], \quad \delta E \rightarrow 0.$$

# Example: The Ideal Gas

- So far, the definitions are abstract and work for any microcanonical ensemble e.g. for a completely isolated system of any material.
- For the rest of this lecture, we will do concrete calculations for a specific material, a (mono-atomic) **ideal gas**.
  - For the ideal gas in a microcanonical ensemble, we will first consider the configuration space and then the momentum space
  - and end the lecture with some remarks that foreshadow ideas of future lectures.

# The Microcanonical Ideal Gas

- Gas in the limit where interactions between particles vanish,  $U = 0$ 
  - ⇒ Energy independent of  $\mathbf{q}$ ,
  - ⇒ Position and momenta can be considered separately when calculating  $\Omega$ .

Therefore, we will first discuss the configuration and then the momentum space.

- Example of monoatomic ideal gas: Helium at high temperature and low density.

# Configuration space

- $E$  independent of  $\mathbf{q} \implies$  all configurations have the same probability.
- What is the probability density  $\rho(\mathbf{q})$  that gas particles are in a particular configuration  $\mathbf{q} \in \mathbb{R}^{3N}$  in a box of volume  $V$ ?

$$\text{Answer: } \rho(\mathbf{q}) = \rho \text{ const, } \int_{(\text{Box})^N} \rho \, d\mathbf{q} = 1 \quad \Rightarrow \quad \rho = \frac{1}{V^N}$$

- $N$  is typically very large, on the order of  $N_A = 6 \times 10^{23}$ .
  - Consequence: Configurations which have almost exactly 50% of particles on right (and left) have much higher probability.
  - Let's check this by first asking:  
What is the probability  $P_m$  that for  $2N$  particles,  $N + m$  are in the right half of box?  
.. and then using the answer to calculate the sum  $\sum P_m$  over a range of small  $m$ .

# Calculation of $P_m$

- $2^{2N}$  ways for  $2N$  distinct particles to sit on 2 sides of box, equal probability  $1/2^{2N}$  for each of them.
- $\binom{2N}{N+m}$  have  $m$  extra particles in the right half

$$\implies P_m = 2^{-2N} \frac{(2N)!}{(N+m)!(N-m)!}$$

- Stirling's formula

$$n! \sim \left(\frac{n}{e}\right)^n \sqrt{2\pi n}$$

$$\begin{aligned}\implies P_m &\approx P_0 2^{-2N} \left(\frac{2N}{e}\right)^{2N} \left(\frac{N+m}{e}\right)^{-(N+m)} \left(\frac{N-m}{e}\right)^{-(N-m)} \\ &= P_0 \left(1 - \frac{m^2}{N^2}\right)^{-N} \left(1 + \frac{m}{N}\right)^{-m} \left(1 - \frac{m}{N}\right)^m \\ &\approx P_0 \exp\left(-\frac{m^2}{N}\right) \quad \text{since } N \gg |m|.\end{aligned}$$

(Notice we have absorbed the factor  $\sqrt{2\pi N}$  into coefficient  $P_0$ .)

## Calculation of $P_m$ (continued)

- Interim Result:  $P_m \approx P_0 \exp\left(-\frac{m^2}{N}\right)$
- Normalise  $1 = \sum_m P_m \approx \int_{-\infty}^{\infty} P_0 \exp\left(-\frac{m^2}{N}\right) dm = P_0 \sqrt{\pi N}$
- Result: Gaussian distribution with average 0, standard deviation  $\sigma = \sqrt{N/2}$ ,

$$P_m \approx \frac{1}{\sqrt{\pi N}} \exp\left(-\frac{m^2}{N}\right)$$

- With probability  $> 1 - (2 \times 10^{-9})$ , we have

$$-6\sigma \leq m \leq 6\sigma = 3\sqrt{2N}$$

$$\frac{|m|}{2N} \leq \frac{3}{\sqrt{2N}} \approx 10^{-12} \quad (N = N_A \approx 10^{24})$$

- Thus the  $\sum P_m$  over  $m \leq$  a tiny fraction of all particles is almost 1.
- In equilibrium SM, relative fluctuations of most quantities of interest are of size  $1/\sqrt{N}$  which is very, very small. Larger fluctuations are extremely unlikely.

# Momentum space

- Kinetic energy for interacting particles of same mass is

$$E = K = \sum_{i=1}^{3N} \frac{1}{2} m_i v_i^2 = \frac{|\mathbf{p}|^2}{2m}$$

- Microcanonical ensemble of system of particles of fixed energy  $E$

$$\frac{|\mathbf{p}|^2}{2m} = E \quad \Longrightarrow \quad |\mathbf{p}| = \sqrt{2mE}$$

$\Rightarrow \mathbf{p}$  lies on surface of sphere  $S_R^{3N-1}$  with radius  $R = \sqrt{2mE}$

- Assume  $\mathbf{p}$  of same energy are equally likely

$\Rightarrow$  probability density of a particular  $\mathbf{p}$  equals  $\rho(p) = 1/\tilde{\Omega}(E)$ , where

$$\tilde{\Omega}(E) = \frac{\text{Momentum space volume of thin shell } [E, E + \delta E]}{\delta E}$$

(reminder: in the limit  $\delta E \rightarrow 0$ )

- **Volume** of  $(l - 1)$ -dimensional sphere with radius  $R$ :

$$\mu(S_R^{l-1}) = \frac{\pi^{l/2} R^l}{(l/2)!} \quad [m! = \Gamma(m - 1) \quad \Gamma \text{ Gamma function}]$$

- Hence

$$\begin{aligned}\tilde{\Omega}(E) &= \lim_{\delta E \rightarrow 0} \frac{1}{\delta E} \left[ \mu \left( S_{\sqrt{2m(E+\delta E)}}^{3N-1} \right) - \mu \left( S_{\sqrt{2mE}}^{3N-1} \right) \right] \\ &= \frac{d}{dE} \mu \left( S_{\sqrt{2mE}}^{3N-1} \right) \\ &= \pi^{3N/2} (3Nm) (2mE)^{3N/2-1} / (3N/2)! \\ &= (3Nm) \pi^{3N/2} R^{3N-2} / (3N/2)! \\ \rho(p) &= 1/\tilde{\Omega}(E) \\ &= (3N/2)! / [(3Nm) \pi^{3N/2} R^{3N-2}]\end{aligned}$$



Determine the probability density  $\rho(p_1)$  that the  $x$ -component of the first particle is  $p_1$ .

# Determining $\rho(p_1)$

- $\rho(p_1) = \lim_{\delta E \rightarrow 0} \frac{\text{Annular area}}{\text{Shell volume}}$

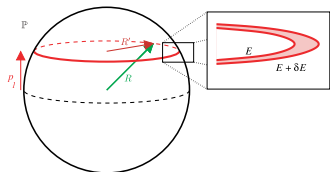
- $\frac{\text{Annular area}}{\delta E} = \frac{d}{dE} \mu(S_{R_1}^{3N-2}),$

with  $R_1 = \sqrt{R^2 - p_1^2}, \delta E \rightarrow 0.$

Chain rule: Annular area =  $\left( \frac{(3N-1)m\pi^{(3N-1)/2} R_1^{3N-3}}{(3N-1)/2!} \right) \delta E$

Recall: Shell volume =  $\left( \frac{(3Nm)\pi^{3N/2} R^{3N-2}}{(3N/2)!} \right) \delta E$

$$\Rightarrow \rho(p_1) \propto \left( \frac{R^2}{R_1^3} \right) \left( \frac{R_1}{R} \right)^{3N} = \underbrace{\frac{1}{R}}_{\approx \frac{1}{\sqrt{2mE}}} \underbrace{\left( \frac{R^3}{R_1^3} \right)}_{\approx 1} \underbrace{\left( 1 - \frac{p_1^2}{2mE} \right)^{3N/2}}_{\approx \exp\left(-\frac{p_1^2}{2mE}\right)}$$



(Sethna 2020)

## Determining $\rho(p_1)$ (cont'd)

- This gives

$$\rho(p_1) \propto \frac{1}{\sqrt{2mE}} \exp\left(\frac{3N}{2E} \frac{(-p_1^2)}{2E}\right)$$

- Normalising  $\int_{-\infty}^{+\infty} \rho(p_1) dp_1 = 1$  gives

$$\rho(p_1) = \frac{1}{\sqrt{2\pi m(2E/3N)}} \exp\left(\frac{3N}{2E} \frac{(-p_1^2)}{2m}\right)$$

- Notice: We have calculated  $\rho(p_1)$  in terms of  $E$  and  $N$  without considering any particular trajectories. This illustrates the power of SM.

# Summary

- So far, we've introduced the microcanonical ensemble and its probability density, and obtained specific expressions for it for the ideal gas (factored into the configuration and momentum space).
- In the next lecture, we will show how this can be used to define the temperature and the entropy (and further useful quantities)
- Application to the ideal gas will give us the equations well-known from school physics, and more.

- So far, we've introduced the microcanonical ensemble and its probability density, and obtained specific expressions for it for the ideal gas (factored into the configuration and momentum space).
- In the next lecture, we will show how this can be used to define the temperature and the entropy (and further useful quantities)
- Application to the ideal gas will give us the equations well-known from school physics, and more.
  
- The results in this lectures can be generalised to mixtures of several gases of different atomic masses. This gives an ellipsoid instead of a sphere, but the core argument remains the same.
- Let me conclude this lecture with two remarks, which anticipate general results that we will come back to later.

- ① Soon we'll show the following state equation for the ideal gas that you may now from school physics:

$$E = \frac{3N}{2} k_B T,$$

where  $k_B = 1.3807 \cdot 10^{-23} \text{ JK}^{-1}$  is **Boltzmann's constant**.  
Using this result, we obtain

$$\rho(p_1) = \frac{1}{\sqrt{2\pi m k_B T}} \exp\left(-\frac{E_1}{k_B T}\right), \quad (1)$$

where  $E_1 = p_1^2/(2m)$  is the energy contribution arising from  $p_1$  (the  $x$ -momentum of the first particle).

Equation (1) is our first example of a **Boltzmann distribution**:  
The probability of a small subsystem being in a state of energy  $E$  (say) is in general proportional to  $\exp(-E/k_B T)$ .

- 2 The mean kinetic energy resulting from the  $x$ -momentum component of a particle can easily be found from  $\rho(p_1)$ :

$$\langle E_1 \rangle = \left\langle \frac{p_1^2}{2m} \right\rangle = \int_{-\infty}^{\infty} \rho(p_1) \frac{p_1^2}{2m} dp_1 = \frac{k_B T}{2}$$

Notice this is the total energy divided by the degree of freedoms  $3N$ .

This is an example of the **Equipartition Theorem**:

“Each harmonic degree of freedom in a classical equilibrium system has average energy  $k_B T/2$ .”

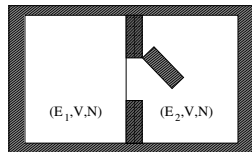
## Lecture 3: Temperature and Equilibrium (II)



# What is temperature?

Outline of our approach to answering this question

- Consider an isolated system with **fixed** total energy  $E$  and two subsystems (1 and 2) of fixed volume and number of particles.
- Assume they are only weakly connected energetically:
  - $E_1$  is independent of  $s_2$  (= state of subsys 2)
  - $E_2$  is independent of  $s_1$  (= state of subsys 1)
- **Question:** In equilibrium, how will the two systems divide up the total energy budget?
- **Answer (SM):** The split with the highest probability (or close to it)!
- Two steps:
  - **First step:** Determine the probability  $\rho(E_1)$  that subsystem 1 has energy  $E_1$ ;
  - **Second step:** Maximise this  $\rho(E_1)$ .
- This will allow us to define temperature (and introduce the concept of entropy)!



Two sub-systems that can exchange heat (but not particles) through the open door.

# First Step

Determine the probability density of subsys 1 having energy  $E_1$ , if total energy  $E$  is fixed

- The equilibrium behaviour of the total system is given by equal weighting of all states having total energy  $E = E_1 + E_2$ .

# First Step

Determine the probability density of subsys 1 having energy  $E_1$ , if total energy  $E$  is fixed

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- The probability density  $\rho(s_1)$  of a *particular state*  $s_1$  with energy  $E_1$  must be proportional to the number of states of sys 2 with energy  $E_2 = E - E_1$ , i.e.

$$\rho(s_1) \propto \Omega_2(E - E_1),$$

if  $\Omega_i(E_i)\delta E_i$  are the phase-space volumes of energy shells for subsys  $i$ .

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$$\rho(E_1) = \Omega_1(E_1)\Omega_2(E - E_1) / \int \Omega_1(E_1)\Omega_2(E - E_2) dE_1$$

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- **Question:** What is the normalisation  $\int \dots dE_1 = ?$ .

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- Normalisation:

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- **Intuition (and homework):**  $\int \cdots dE_1 = \int \Omega(E) dE$ .

# First Step: Result

$$\rho(E_1) = \frac{\Omega_1(E_1)\Omega_2(E - E_1)}{\Omega(E)}$$

Probability of subsystem 1 to have energy  $E_1$ .



## Second Step

Maximise  $\rho(E_1)$

- $\rho(E_1)$  has a sharply peaked maximum  $E_1^*$  (Homework).

$$\frac{d}{dE_1}\rho(E_1) = 0 \quad \Longrightarrow \quad \frac{1}{\Omega_1} \left. \frac{d\Omega_1}{dE_1} \right|_{E_1=E_1^*} = \frac{1}{\Omega_2} \left. \frac{d\Omega_2}{dE_2} \right|_{E_2=E-E_1^*}$$

- Equality of  $(1/\Omega)(d\Omega/dE)$  characterises two systems which only exchange energy to be in equilibrium with each other. This is what we call temperature in real life!
- Not so fast! Temperature and temperature scales were invented before SM, physical laws were formulated in terms of them. To be *quantitatively* consistent with a pre-existing scale (the Kelvin scale), we need to choose

$$\frac{1}{T} \equiv k_B \left. \frac{1}{\Omega} \frac{d\Omega}{dE} \right|_{V,N}$$

where we have emphasized the fixed volume and number of particles. (Other choices would lead to equivalent but different formulations of, e.g., the equation of state for an ideal gas etc.)

## Second Step (2)

### Definition of entropy

- The **equilibrium entropy** for each system is defined by

$$S_{\text{equil}}(E) = k_B \log(\Omega(E)).$$

- Then, the definition of temperature becomes

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{V,N}.$$

- The equilibrium condition becomes

$$\left. \frac{dS_1}{dE_1} \right|_{E_1=E_1^*} - \left. \frac{dS_2}{dE_2} \right|_{E_2=E-E_1^*} = 0$$

that is, **the total entropy**  $S_1(E_1) + S_2(E - E_1)$  **is maximised**.

- 1 The equilibrium behaviour of System (System 1) only depends on the temperature of the external world (=System 2) and not what material it is made of.
- 2 Some terminology:
  - **Intensive** quantity: Stays constant as system grows  
E.G.: Temperature or pressure
  - **Extensive** Scales linearly with the size of the system.  
E.G.: Energy, volume, number of particles
- 3 Entropy is extensive.  
(Doubling the size of a system squares the phase space volume. Hence taking the log guarantees that entropy scales linearly with system size like energy, volume, number of particles etc.)
- 4 **Entropy** is the cost of buying **energy** from the rest of the world:

$$\delta S = \left. \frac{\partial S}{\partial E} \right|_{V,N} \delta E = \frac{\delta E}{T}$$

One must accept the entropy  $\delta E/T$  when buying  $\delta E$  (heat) energy from the heat bath (= external world) at temperature  $T$ .

# Equilibria between systems with other types of interactions

What happens if we allow the system to exchange volume or particles?

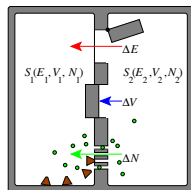
Do other useful quantities arise from this (in terms of derivatives of the entropy)?

**YES!**

# Pressure and chemical potential

Consider two subsystems that can exchange energy, volume or particles.

How does the entropy change as  $\Delta T$ ,  $\Delta V$  or  $\Delta N$  move from subsystem 1 to subsystem 2?



$$\begin{aligned}\Delta S &= \left( \left. \frac{\partial S_1}{\partial E_1} \right|_{V,N} - \left. \frac{\partial S_2}{\partial E_2} \right|_{V,N} \right) \Delta E + \left( \left. \frac{\partial S_1}{\partial V_1} \right|_{E,N} - \left. \frac{\partial S_2}{\partial V_2} \right|_{E,N} \right) \Delta V \\ &\quad + \left( \left. \frac{\partial S_1}{\partial N_1} \right|_{E,V} - \left. \frac{\partial S_2}{\partial N_2} \right|_{E,V} \right) \Delta N \\ &= \textcircled{1} \Delta E + \textcircled{2} \Delta V + \textcircled{3} \Delta N.\end{aligned}$$

Equilibrium is achieved, when the entropy is maximal, that is, a small exchange of energy, volume or particles does not change it:

$$\Delta S = 0.$$

## Pressure and chemical potential (2)

- ① = 0: Maximising entropy with respect to energy exchange sets  $\partial S/\partial E|_{V,N}$  equal. This led us to the definition of temperature

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{V,N}$$

- ② = 0: Maximising entropy with respect to volume exchange sets  $\partial S/\partial V|_{E,N}$  equal. Hence define pressure via

$$\frac{P}{T} = \left. \frac{\partial S}{\partial V} \right|_{E,N}.$$

- ③ = 0: Maximising entropy with respect to particle exchange sets  $\partial S/\partial N|_{E,V}$  equal. Hence define chemical potential via

$$-\frac{\mu}{T} = \left. \frac{\partial S}{\partial N} \right|_{E,V}.$$

- These definitions are often summarized as

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN.$$

# Entropy as a thermodynamic potential $S(E, V, N)$

A lot of information can be obtained/recovered from

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN. \quad (*)$$

- It tells you that the state of the system can be described by only three independent variables,  $E$ ,  $V$  and  $N$ . This is a consequence of allowing only these three quantities to be exchanged with the system/between systems.
- In particular, it implies that  $S$  is a function of these three variables  $S = S(E, V, N)$ , or equivalently, that integration of the right hand side of (\*) is independent of the path of integration.
- Furthermore,  $S$  being a function of  $(E, V, N)$  implies (by differentiation)

$$dS = \left. \frac{\partial S}{\partial E} \right|_{V,N} dE + \left. \frac{\partial S}{\partial V} \right|_{E,N} dV + \left. \frac{\partial S}{\partial N} \right|_{E,V} dN$$

Then, from comparison with (\*), we recover our previous relations

$$\frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{V,N}, \quad \frac{P}{T} = \left. \frac{\partial S}{\partial V} \right|_{E,N}, \quad -\frac{\mu}{T} = \left. \frac{\partial S}{\partial N} \right|_{E,V}.$$

- $S(E, V, N)$  is an example of a **thermodynamic potential (or free energy)**.

# The (inner) energy $E$ as a thermodynamic potential

$E$  can also be seen as a free energy. Rearranging (\*) gives

$$dE = T dS - P dV + \mu dN.$$

This tells you that:

- The state of the system can be described in terms of  $S$ ,  $V$  and  $N$ .
- $E$  can be considered as function of these three independent variables.
- Then

$$dE = \left. \frac{\partial E}{\partial S} \right|_{V,N} dS + \left. \frac{\partial E}{\partial V} \right|_{S,N} dV + \left. \frac{\partial E}{\partial N} \right|_{S,V} dN$$

- Thus

$$\left. \frac{\partial E}{\partial S} \right|_{V,N} = T, \quad \left. \frac{\partial E}{\partial V} \right|_{S,N} = -P, \quad \left. \frac{\partial E}{\partial N} \right|_{S,V} = \mu.$$

This shows that the pressure and the chemical potential are the “forces” associated with volume increase and particle number change, respectively.



# Other ways to find derivatives

- Useful mathematical identities for  $f = f(x, y)$

- $\frac{\partial f}{\partial x} \Big|_y = \frac{1}{\frac{\partial x}{\partial f} \Big|_y}$

- $\frac{\partial f}{\partial x} \Big|_y \frac{\partial x}{\partial y} \Big|_f \frac{\partial y}{\partial f} \Big|_x = -1$  NOT = +1!

- Find  $\partial E / \partial V \Big|_{S,N}$ :

$$-1 = \frac{\partial S}{\partial V} \Big|_{E,N} \frac{\partial V}{\partial E} \Big|_{S,N} \frac{\partial E}{\partial S} \Big|_{V,N} \quad \text{(Second identity)}$$

$$= \frac{\partial S}{\partial V} \Big|_{E,N} \frac{1}{\partial E / \partial V \Big|_{S,N}} \frac{1}{\partial S / \partial E \Big|_{V,N}} \quad \text{(First identity)}$$

$$= \frac{P}{T} \frac{1}{\partial E / \partial V \Big|_{S,N}} T \quad \text{(See above)}$$

Thus  $\frac{\partial E}{\partial V} \Big|_{S,N} = -P.$  “Force” associated with volume increase.

## Other ways to find derivatives (2)

- Another example:  $\partial E / \partial N|_{S,V}$ :

$$\begin{aligned} -1 &= \left. \frac{\partial S}{\partial N} \right|_{E,V} \left. \frac{\partial N}{\partial E} \right|_{S,V} \left. \frac{\partial E}{\partial S} \right|_{V,N} && \text{(Second identity)} \\ &= -\frac{\mu}{T} \frac{1}{\partial E / \partial N|_{S,V}} T && \text{(First identity \& see above)} \end{aligned}$$

Thus  $\boxed{\left. \frac{\partial E}{\partial N} \right|_{S,V} = \mu.}$  “Force” associated with # of particles.

# Entropy of an ideal gas

- So far, we have defined the entropy and other quantities abstractly for the general case. We haven't obtained them yet for any specific example system.
- Now, we will do this for the case of an ideal (monoatomic) gas
- Let's find the entropy, temperature, pressure for a volume of an ideal gas using the microcanonical ensemble
- From “highschool physics”:
  - $E = (3/2)Nk_B T$
  - $PV = Nk_B T$  equation of state for an ideal gas (aka ideal gas law).

# Entropy of an ideal gas

... and pressure and temperature

- Recall

$$\Omega_{\text{crude}} = \frac{V^N (2N/3E) \pi^{3N/2} (2mE)^{3N/2}}{(3N/2)!} \approx \frac{V^N \pi^{3N/2} (2mE)^{3N/2}}{(3N/2)!}$$

- Thus

$$\begin{aligned} S_{\text{crude}} &= k_B \log(\Omega_{\text{crude}}) \\ &= Nk_B \log V + (3Nk_B)/2 \log(2\pi mE) - k_B \log((3N/2)!). \end{aligned}$$

- Thus

$$\begin{aligned} \frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{V,N} &= \frac{3Nk_B}{2E} \implies E = \frac{3}{2} Nk_B T, \quad \checkmark \\ \frac{P}{T} = \left. \frac{\partial S}{\partial V} \right|_{E,N} &= \frac{Nk_B}{V} \implies PV = Nk_B T. \quad \checkmark \end{aligned}$$

## Refinement #1

**Divide energy shell volume by  $\hbar^{3N}$**  ( $\hbar$ =Planck's constant)

This removes dimensions from  $\Omega$  and set entropy to zero at absolute temperature 0, consistent with Quantum Mechanics.

## Refinement #2

**Divide energy shell volume by  $N!$  to account for undistinguished particles**

- E.g. for two particles, phase space positions  $((p_A, q_A), (p_B, q_B))$  and  $((p_B, q_B), (p_A, q_A))$  should not be counted as separate configurations, so need to divide by 2.
- Without  $1/N!$  factor, entropy of joining two containers of undistinguishable gas particles increases substantially. (This is only OK for containers with two gases of distinguishable (different) particles.)

# Entropy of an ideal gas – final version

- $\Omega(E) = \left(\frac{V^N}{N!}\right) \frac{\pi^{3N/2} (2mE)^{3N/2}}{(3N/2)!} \left(\frac{1}{\hbar}\right)^{3N}$
- $S(E) = Nk_B \log \left( V \hbar^{-3} (2\pi m E)^{3/2} \right) - k_B \log (N! (3N/2)!)$
- Stirling:  $\log(N!) \approx N \log N - N$  gives at large  $N$ :

$$S(E, V, N) = \frac{5}{2} Nk_B + Nk_B \log \left[ \frac{V}{N \hbar^3} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right]$$

This is the standard formula for the entropy of an ideal gas.

- Introduce  $\rho = N/V$  particle density  
 $\lambda = \hbar / \sqrt{4\pi m E / 3N}$  thermal de Broglie wavelength.

$$S = Nk_B \left( \frac{5}{2} - \log(\rho \lambda^3) \right)$$

# Summary

- 1 We introduced the phase space volume and the probability density for a microcanonical ensemble, and used this to define the entropy of a system.
- 2 We argued that system that exchange energy, volume or particles will tend to be in their most probable states and hence maximise their combined entropy. We used this to define temperature, pressure and chemical potential.
- 3 We explicitly calculated these quantities for the ideal gas, recovering well-known physical laws.

Final comment:

The thermodynamic definition of pressure we gave in this lecture keeps entropy constant, while the mechanical one assume slow, adiabatic volume changes. It is not immediately obvious the two are the same. Read Sethna, section 3.4.1, for a detailed discussion.

# Lecture 4: Phase Space Dynamics and Ergodicity



# Central question and outline of this lecture

**Question:** Why do so many systems actually reach equilibrium? Why is this equilibrium (that is, the equilibrium values of relevant properties) captured by the statistics of the microcanonical ensemble?

- We justified the microcanonical ensemble by suggesting that energy conservation implies that we average over all states of fixed energy with equal weight.
- **Now** we will outline more convincing arguments for the microcanonical ensemble and its statistics. We will do this in two steps, using two different tools:
- **Liouville's theorem:** Volume in phase space is conserved, relative weights of different parts of surface is not changed as energy surface is mixed in time.
- **Ergodic system:** System where energy surface is well mixed.

**Liouville + Ergodicity**  $\implies$  Microcanonical ensemble's gives long time behaviour (values) that we call equilibrium behaviour (values).

# Hamilton's equations

The laws of motion for  $N$  particles without dissipation are given by

$$\begin{aligned}\dot{q}_\alpha &\equiv \frac{dq_\alpha}{dt} = \frac{\partial \mathcal{H}}{\partial p_\alpha} \\ \dot{p}_\alpha &\equiv \frac{dp_\alpha}{dt} = -\frac{\partial \mathcal{H}}{\partial q_\alpha}, \quad \alpha = 1, \dots, 3N,\end{aligned}$$

where the **Hamiltonian**  $\mathcal{H}$  typically is the total energy of the particles.

**Example:**  $N$  particles with potential energy  $U = U(q_1, \dots, q_N)$ .

$$H(\mathbf{q}, \mathbf{p}) = \sum_{\alpha=1}^N \frac{p_\alpha^2}{2m_\alpha} + U(q_1, \dots, q_{3N}).$$

This gives

$$\begin{aligned}\dot{q}_\alpha &= \frac{p_\alpha}{m_\alpha}, \\ \dot{p}_\alpha &= -\frac{\partial U}{\partial q_\alpha} \equiv f_\alpha(q_1, \dots, q_{3N}), \quad f_\alpha: \text{force on coordinate } \alpha,\end{aligned}$$

Combined:  $m_\alpha \ddot{q}_\alpha = f_\alpha$ , Newton's (second) law!

# Local conservation of probability density

- Consider the probability density  $\rho$  in phase space,

$$\rho = \rho(\mathbf{q}, \mathbf{p}, t) = \rho(q_1, \dots, q_{3N}, p_1, \dots, p_{3N}, t).$$

Vaguely, think of the integral of  $\rho$  over a region  $D$  of the phase space as giving the “fraction of the members of the ensemble” (each of which is represented by a point in phase space) that lie in this region.

- Define  $\phi(\cdot, \cdot, t) : (\mathbf{p}_0, \mathbf{q}_0) \mapsto (\mathbf{p}, \mathbf{q}) = (\mathbf{p}(\mathbf{p}_0, \mathbf{q}_0, t), \mathbf{q}(\mathbf{p}_0, \mathbf{q}_0, t))^T$  represent the flow in phase space, i.e.  $\mathbf{p}(t)$  and  $\mathbf{q}(t)$  satisfy Hamilton's equations and  $\mathbf{p}(0) = \mathbf{p}_0$ ,  $\mathbf{q}(0) = \mathbf{q}_0$ ,
- $\rho$  is *locally conserved*, that is, the integral of  $\rho$  over a region  $D(t)$  that is convected with the flow,  $D(t) = \phi(D(0), t)$ , remains constant:

$$\frac{d}{dt} \int_{D(t)} \rho(\mathbf{p}, \mathbf{q}, t) dq_1 \dots dq_{3N} dp_1 \dots dp_{3N} = 0$$

- Reynolds' transport theorem gives (dropping the '(t)' from  $D(t)$ )

$$\int_D \frac{\partial \rho}{\partial t} \prod_{\alpha} dq_{\alpha} dp_{\alpha} + \int_{\partial D} (\rho \dot{\mathbf{q}}, \rho \dot{\mathbf{p}}) \cdot d\mathbf{S}(\mathbf{p}, \mathbf{q}) = 0$$

## Local conservation of probability density (2)

- ... carrying over from the previous slide

$$\int_D \frac{\partial \rho}{\partial t} \prod_{\alpha} dq_{\alpha} dp_{\alpha} + \int_{\partial D} (\rho \dot{\mathbf{q}}, \rho \dot{\mathbf{p}}) \cdot d\mathbf{S}(\mathbf{p}, \mathbf{q}) = 0$$

- The divergence theorem implies

$$\int_D [\rho_t + \operatorname{div}(\rho \dot{\mathbf{q}}, \rho \dot{\mathbf{p}})] \prod_{\alpha} dq_{\alpha} dp_{\alpha} = 0 \quad \forall D$$

- Hence

$$\rho_t + \operatorname{div}(\rho \dot{\mathbf{q}}, \rho \dot{\mathbf{p}}) = 0.$$

or in components

$$\rho_t = - \sum_{\alpha=1}^{3N} \frac{\partial (\rho \dot{q}_{\alpha})}{\partial q_{\alpha}} + \frac{\partial (\rho \dot{p}_{\alpha})}{\partial p_{\alpha}}$$

# Liouville's theorem

Starting from local probability conservation and expanding,

$$\rho_t = - \sum_{\alpha=1}^{3N} \left( \frac{\partial \rho}{\partial q_\alpha} \dot{q}_\alpha + \rho \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \rho}{\partial p_\alpha} \dot{p}_\alpha + \rho \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} \right).$$

Applying Hamilton's equations,

$$\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} = \frac{\partial}{\partial q_\alpha} \left( \frac{\partial \mathcal{H}}{\partial p_\alpha} \right) = \frac{\partial}{\partial p_\alpha} \left( \frac{\partial \mathcal{H}}{\partial q_\alpha} \right) = - \frac{\partial \dot{p}_\alpha}{\partial p_\alpha}.$$

the 2<sup>nd</sup> and 4<sup>th</sup> terms (blue) in cancel.

$$\Rightarrow \frac{d\rho}{dt} \equiv \frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left( \frac{\partial \rho}{\partial q_\alpha} \dot{q}_\alpha + \frac{\partial \rho}{\partial p_\alpha} \dot{p}_\alpha \right) = 0$$

**Liouville's  
theorem**

## Liouville's theorem (2)

- The left hand side of the previous is the **total derivative of  $\rho$** , so the short form of Liouville's theorem is:

$$\frac{d\rho}{dt} = 0.$$

- This means that locally,  $\rho$  does not change if one moves with the flow in phase space.
- The local probability conservation assumption we started says the “fraction of members” in the ensemble that lie in a region of the phase space that is convected by the flow does not change.
- Liouville's theorem says that in addition, because the flow is Hamiltonian, the volume of the region does not change even as it is twisted and distorted by the flow. In other words, **the flow is incompressible**.
- Therefore the **probability density  $\rho$**  does not change as it is convected along with the flow.

## Liouville's theorem (3)

Another formulation of Liouville's theorem uses the **Poisson bracket**, defined for two functions  $A, B$  in phase space as

$$\{A, B\} \equiv \sum_{\alpha=1}^{3N} \left( \frac{\partial A}{\partial q_{\alpha}} \frac{\partial B}{\partial p_{\alpha}} - \frac{\partial A}{\partial p_{\alpha}} \frac{\partial B}{\partial q_{\alpha}} \right).$$

Thus, using Hamilton's equations

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= - \sum_{\alpha=1}^{3N} \left( \frac{\partial \rho}{\partial q_{\alpha}} \dot{q}_{\alpha} + \frac{\partial \rho}{\partial p_{\alpha}} \dot{p}_{\alpha} \right) \\ &= - \sum_{\alpha=1}^{3N} \left( \frac{\partial \rho}{\partial q_{\alpha}} \frac{\partial \mathcal{H}}{\partial p_{\alpha}} - \frac{\partial \rho}{\partial p_{\alpha}} \frac{\partial \mathcal{H}}{\partial q_{\alpha}} \right) = -\{\rho, \mathcal{H}\}. \end{aligned}$$

Thus,  $\rho$  is stationary ( $\rho_t = 0$ ), iff  $\{\rho, \mathcal{H}\} = 0$  at any time. The latter is the case, for example, if  $\rho$  can be written as a function of  $\mathcal{H}$ , which, for the microcanonical ensemble, is equivalent to saying that  $\rho$  is uniform along the energy surface.

# Liouville's theorem: Summary

- ①  $d\rho/dt = 0$ , as a result of the **the flow in phase space being incompressible**: Small elements of phase space move along with the flow, twisting and extending, but they do not change their density and hence their volume.
- ② **Microcanonical ensembles are time independent.** An initially uniform probability density  $\rho$  over the energy surface remains uniform. (Thus we can replace the assumption made in previous lectures of uniformity at all times by the weaker and more plausible assumption of uniformity at an initial time, from which the general property follows.)
- ③ **There are no attractors.** The system cannot settle down into a single state like for example the phase space for a damped pendulum. Hence equilibration of phase space in SM happens by a completely different mechanism!



Averaging over energy in the microcanonical ensemble requires the hypothesis that **the energy surface is thoroughly stirred**  $\equiv$  **ergodic**.

## Definition 1

In an ergodic system, the trajectory of almost every point on the constant energy surface in phase space eventually passes arbitrarily close to every other point on this surface.

- Intuitively: A trajectory covers the whole energy surface, hence the average of any property  $O(\mathbf{q}(t), \mathbf{p}(t))$  over time must be the same as the average over the energy surface.
- This definition is hard to work with. It is easier to use a different definition of ergodicity.

## Definition 2

Define an **ergodic component**  $R$  of a set  $S$  (e.g. an energy surface) to be a subset that remains invariant under the flow, i.e.

$$r(0) \in R \implies r(t) \in R \quad \forall t.$$

A time evolution in  $S$  is **ergodic** iff all of the ergodic components of  $S$  either have zero volume (zero measure) or have volume equal to  $S$ .

- Intuitive explanation of equivalence of these two definitions: See Sethna p. 66 & 67.

# Ensemble average equals time average

## Definition of the time average starting at $(\mathbf{p}(0), \mathbf{q}(0))$

$$\overline{O(\mathbf{p}(0), \mathbf{q}(0))} \equiv \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T O(\mathbf{q}(\tau), \mathbf{p}(\tau)) d\tau.$$

## Definition of the microcanonical ensemble average

Let  $S$  denote the energy surface.

$$\langle O \rangle_S = \int_S \rho(\mathbf{p}, \mathbf{q}, t) O(\mathbf{p}, \mathbf{q}) dq_1 \dots dq_{3N} dp_1 \dots dp_{3N}.$$

(Strictly speaking, the integral over  $S$  should be stated in terms of a limit over the energy shell, but see Sethna p.63 footnote 2.)

### **Claim:**

For an observable  $O$  the microcanonical average equals the time average

$$\overline{O(\mathbf{p}(0), \mathbf{q}(0))} = \langle O \rangle_S.$$

almost anywhere on the energy surface  $S$ , if  $\rho$  is stationary.

This claim is established in three steps.

# Ensemble average equals time average: Step 1

## Step 1. Time averages are constant along trajectories

Sketch of a proof:

The claim states that if the two points  $(\mathbf{p}(0), \mathbf{q}(0))$  and  $(\mathbf{p}(t), \mathbf{q}(t))$ , are crossed at time 0 and  $t$  (say), then the averages

$$\overline{O(\mathbf{p}(0), \mathbf{q}(0))} = \overline{O(\mathbf{p}(t), \mathbf{q}(t))}$$

should be equal. Applying the definition to both averages, we have

$$\overline{O(\mathbf{p}(0), \mathbf{q}(0))} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T O(\mathbf{q}(\tau), \mathbf{p}(\tau)) d\tau,$$

$$\overline{O(\mathbf{p}(t), \mathbf{q}(t))} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T O(\mathbf{q}(t + \tau), \mathbf{p}(t + \tau)) d\tau$$

$$= \lim_{T \rightarrow \infty} \frac{1}{T + t} \int_t^{T+t} O(\mathbf{q}(\tau), \mathbf{p}(\tau)) d\tau$$

$$= \lim_{\tilde{T} \rightarrow \infty} \frac{1}{\tilde{T}} \int_t^{\tilde{T}} O(\mathbf{q}(\tau), \mathbf{p}(\tau)) d\tau.$$

As the integrals only differ by a finite value (for well-behaved  $O$ ), the two limits should be equal.

## Ensemble average equals time average: Step 2

**Step 2.** *Time averages are constant almost anywhere on the energy surface  $S$ .*

Sketch of a proof:

Let  $R_a \equiv \{(\mathbf{q}(0), \mathbf{p}(0)) \in S; \overline{O(\mathbf{p}(0), \mathbf{q}(0))} < a\}$ .

If  $(\mathbf{q}(0), \mathbf{p}(0)) \in R_a$ , then  $(\mathbf{q}(t), \mathbf{p}(t)) \in R_a$  for all  $t$ , since the time average is constant along a trajectory.

$\implies R_a$  is an ergodic component

$\implies$  Either  $\text{vol}(R_a) = 0$  or  $\text{vol}(R_a) = \text{vol}(S)$ .

Thus,  $\overline{O(\mathbf{p}(0), \mathbf{q}(0))}$  is equal to  $a^* = \inf\{a; \text{vol}(R_a) > 0\}$  for almost any  $(\mathbf{q}(0), \mathbf{p}(0))$  on the energy surface  $S$ .

## Ensemble average equals time average: Step 3

**Step 3.** *If the ensemble is time independent ( $\rho_t = 0$ ), then*

$$\overline{O(\mathbf{p}(0), \mathbf{q}(0))} = \langle O \rangle_S$$

*for  $O(\mathbf{p}(0), \mathbf{q}(0))$  almost everywhere on the energy surface  $S$ .*

Remark: Recall that from our discussion of Liouville's theorem, we can assume that  $\rho$  is stationary and uniform on the energy surface.

Sketch of a proof:

For stationary solutions, the ensemble average is time independent,

$$\frac{d}{dt} \langle O \rangle_S = \int_S \rho_t(\mathbf{p}, \mathbf{q}, t) O(\mathbf{p}, \mathbf{q}) dq_1 \dots dq_{3N} dp_1 \dots dp_{3N} = 0.$$

Thus

$$\langle O \rangle_S = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \langle O \rangle_s dt$$

## Ensemble average equals time average: Step 3 (cont'd)

$$\langle O \rangle_S = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \int_S \rho(\mathbf{p}, \mathbf{q}, t) O(\mathbf{p}, \mathbf{q}) dq_1 \dots dq_{3N} dp_1 \dots dp_{3N} dt,$$

since  $\phi(S, t) = S$ ,

$$= \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \int_{\phi(S, t)} \rho(\mathbf{p}, \mathbf{q}, t) O(\mathbf{p}, \mathbf{q}) dq_1 \dots dq_{3N} dp_1 \dots dp_{3N} dt$$

$$= \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \int_S \rho(\phi(\mathbf{p}(0), \mathbf{q}(0), t), t) O(\phi(\mathbf{p}(0), \mathbf{q}(0), t)) dq_1(0) \dots [..]$$

and since  $\rho$  is constant along trajectories,

$$= \int_S \rho(\mathbf{p}(0), \mathbf{q}(0), 0) \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T O(\phi(\mathbf{p}(0), \mathbf{q}(0), t)) dt dq_1(0) \dots [..]$$

$$= \langle \overline{O(\mathbf{p}(0), \mathbf{q}(0))} \rangle_S$$

$$= a^*,$$

which is equal to  $\overline{O(\mathbf{p}(0), \mathbf{q}(0))}$  almost everywhere on  $S$ .

- Ergodic behaviour hard to prove for given microscopic dynamics.
  - Proven for collision of hard spheres
  - Proven for geodesic motion on manifolds with constant curvature
  - Often easier to “see” ergodicity on a computer.
- Some very fundamental problems involve systems that are not ergodic, e.g.:
  - 1 KAM theory in Hamiltonian systems (mixed dynamics rather than ergodic dynamics)
  - 2 Fermi-Pasta-Ulam paradox.
  - 3 Broken symmetry phases  
Magnets, crystals, liquid crystals only explore one of a variety of equal energy ground states
  - 4 Glasses fall out of equilibrium as they cool and oscillate about one of many metastable states



# Lecture 5: Entropy (I)

- Entropy is the most influential concept to come from Statistical Mechanics
- We will explore 3 definitions of entropy:
  - Measure of **irreversible changes** in a system;
  - Measure of **disorder** in a system;
  - Measure of **ignorance** about a system.

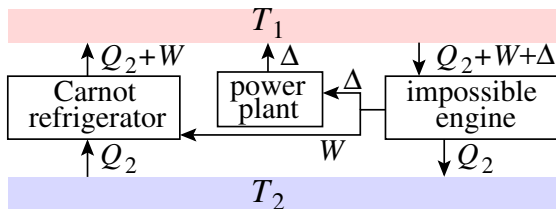
## Definition 1: Entropy as irreversibility

- Energy conservation not the only restriction on generating useful work from heat
  - Work cannot be generated from a “hot” material without dumping some energy as heat into a cold sink (e.g. from only a hot stone alone, that is, without a second, colder stone.)
  - Energy divided between hot steam and a cold lake is more useful than water at intermediate temperature
- Moreover, the equilibration of a hot and cold body in contact in an isolated system is **irreversible**: The return to the old state requires input of work.

# Reversible Processes

- A process that, after it has taken place, can be reversed and returns the system and its surroundings to their original states.
- The most efficient engine is a reversible one
  - Combining a reversible engine with a more efficient machine would return the system to the original state **AND** do useful work on the way.
  - Efficiency of an engine, e.g. for engine on the right:

$$\varepsilon = \frac{\text{work done}}{\text{heat input}} = \begin{cases} \frac{W+\Delta}{Q_2+W+\Delta} & \text{"impossible" engine} \\ \frac{W}{W+Q_2} & \text{Carnot (i.e. reversible) engine} \end{cases}$$



A reversible engine and perpetual motion with heat baths  $T_1 > T_2$  (Sethna 2020)

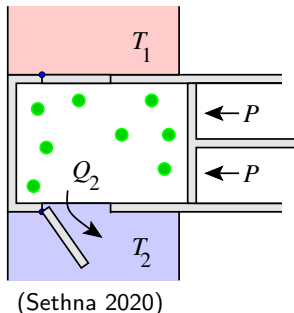
- All reversible engines (for the same  $T_1, T_2$ ) have the same efficiency.

# Carnot engines

The **Carnot engine** is a **prototypical reversible heat engine** that we will describe in more detail.

## Construction of the engine

- Piston with external pressure  $P$
- Heat baths at  $T_1 > T_2$ .
- Gas in cylinder
- In each cycle, heat  $Q_1$  flows out of the hot bath,  $Q_2$  into the cold bath.
- The net work done by the piston on the outside world is  $W = Q_1 - Q_2$



# Requirements for reversibility

- ① Hot things cannot touch cold things
- ② Frictionless operation (e.g. between piston and cylinder walls)
- ③ Walls of container (piston) must not move too quickly.
- ④ Systems at high pressure cannot expand into systems of low pressure

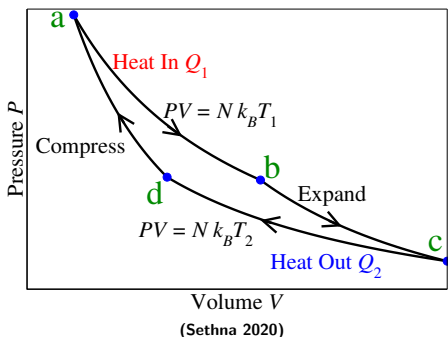
# The Carnot Cycle

**Step 1:** ( $a \rightarrow b$ ). The cylinder with the compressed gas is connected to the hot bath. Piston moves out at decreasing pressure, heat  $Q_1$  flows in to maintain gas at temperature  $T_1$ .

**Step 2:** ( $b \rightarrow c$ ). The cylinder is disconnected from baths. The piston expands further, cooling gas down to temperature  $T_2$ .

**Step 3:** ( $c \rightarrow d$ ). The cylinder with the expanded gas is connected to the cold bath and compressed. Heat  $Q_2$  flows out, maintaining the gas at temperature  $T_2$ .

**Step 4:** ( $d \rightarrow a$ ). The cylinder is disconnected again, the gas compressed further, until the temperature is at  $T_1$ , returning the cylinder to its original state.





# Energy balance for the Carnot Cycle

- Work  $W$  done on outside world is:

$$\begin{aligned}W &= \oint F dx = \int \frac{F}{A} A dx = \oint P dV \\ &= \text{area inside } PV\text{-loop.}\end{aligned}$$

- From energy conservation we know:

$$W = Q_1 - Q_2.$$

- All reversible heat engines with the same  $T_1$  and  $T_2$  produce the same amount of work  $W$  for a given heat input  $Q_1$  (they have the same efficiency  $W/Q_1!$ ).  
 $\implies$  use simplest material as work medium: a mono-atomic ideal gas.
- Reminder regarding mono-atomic ideal gasses:
  - Equation of state:  $PV = Nk_B T$
  - Equipartition theorem:  $E = \text{kinetic energy} = (3/2)Nk_B T$ .

# Detailed analysis of the Carnot cycle (Steps 1 & 3)

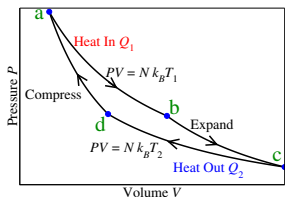
- $(a \rightarrow b)$ : From energy conservation,

$$\begin{aligned}Q_1 &= E_b - E_a + W_{ab} \\&= \frac{3}{2}Nk_B T_1 - \frac{3}{2}Nk_B T_1 + \int_a^b P dV \\&= \int_a^b \frac{3}{2}Nk_B T \frac{1}{V} dV,\end{aligned}$$

Thus we have:

$$Q_1 = Nk_B T_1 \log\left(\frac{V_b}{V_a}\right).$$

- $(c \rightarrow d)$ : Similarly,  $Q_2 = Nk_B T_2 \log\left(\frac{V_c}{V_d}\right).$



# Detailed analysis of the Carnot cycle (Steps 2 & 4)

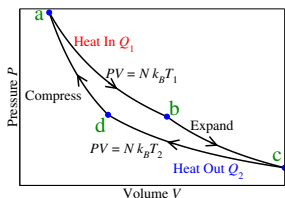
- $(b \rightarrow c)$ : We need to determine the ideal gas behaviour under expansion/compression without any heat in- or outflow (“adiabatic” expansion or compression).

- Energy conservation  $dE = -P dV$
- Using  $E = (3/2)Nk_B T$  and  $P = Nk_B T/V$  gives

$$\frac{3}{2} \frac{dT}{T} = -\frac{dV}{V}.$$

- Integrating from  $b$  to  $c$  gives  $\frac{V_c}{V_b} = \left(\frac{T_1}{T_2}\right)^{3/2}$

- $(d \rightarrow a)$ : Similarly  $\frac{V_d}{V_a} = \left(\frac{T_1}{T_2}\right)^{3/2} \implies \boxed{\frac{V_c}{V_d} = \frac{V_b}{V_a}}$



# Detailed analysis of the Carnot cycle: Results

- $\frac{Q_1}{T_1} \stackrel{\text{Step 1}}{=} Nk_B \log\left(\frac{V_b}{V_a}\right) \stackrel{\text{Step 2\&4}}{=} Nk_b \log\left(\frac{V_c}{V_d}\right) \stackrel{\text{Step 3}}{=} \frac{Q_2}{T_2}$ .

- Efficiency of a reversible engine:

$$\varepsilon_R = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

- Recall that for *any* engine

$$\varepsilon \leq \varepsilon_R.$$

- In fact, for a *real* engine, the strict inequality holds!

# Implications for the change of entropy

- Define thermodynamic entropy change induced by heat flux  $Q$  at temperature  $T$  as

$$\Delta S_{\text{th}} = \frac{Q}{T}.$$

This is consistent with our previous definition  $1/T = \partial S / \partial E$  (at fixed  $V$  and  $N$ )

i.e.  $\Delta S = \Delta E / T = Q / T!$

- Thus, for the Carnot engine,

$$\Delta S_{\text{tot}} = \Delta S_{\text{out}} - \Delta S_{\text{in}} = \frac{Q_2}{T_2} - \frac{Q_1}{T_1} = 0.$$

- For a general engine with efficiency  $\varepsilon = (Q_1 - Q_2) / Q_1$

$$\Delta S_{\text{tot}} = \frac{Q_2}{T_2} - \frac{Q_1}{T_1} = \frac{Q_1}{T_2} \left( 1 - \frac{T_2}{T_1} - \frac{Q_1 - Q_2}{Q_1} \right) = \frac{Q_1}{T_2} (\varepsilon_R - \varepsilon) \geq 0.$$

- For real engines:  $\Delta S_{\text{tot}} > 0$ .**
- Macroscopic behaviour provides “arrow of time”, while microscopic laws are time-invariant!

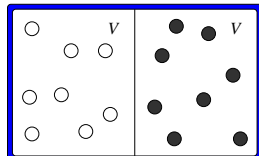
## Definition 2: Entropy as disorder

# Entropy as disorder

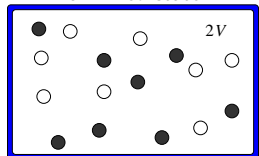
- Partitioned box with  $N/2$  undistinguished white particles left,  $N/2$  undistinguished black particles right.
- Unmixed configurational entropy

$$S_u = 2k_B \log \left( \frac{V^{N/2}}{(N/2)!} \right).$$

- Removal of partition does not change  $T$  and  $P$ , so process is reversible **except** for mixing.  $\Rightarrow$  **All entropy change is due to the mixing of particles.**



unmixed state



mixed state  
(Sethna 2020)

- The entropy of the mixed state is:

$$S_m = 2k_B \log \left( \frac{(2V)^{N/2}}{(N/2)!} \right).$$

- $\Rightarrow$  The entropy change (=mixing entropy) is

$$\Delta S = S_m - S_u = Nk_B \log 2.$$

## Entropy as disorder (continued)

- We gain entropy of  $k_B \log 2$  every time we place a particle into one of the gases without knowing which box to chose.
- Another way of writing the formula on the previous slide:  
$$\Delta S = k_B \log(2^N)$$
- More generally:

$$S_{\text{counting}} = k_B \log(\#\text{configurations}).$$



# Gibb's paradox

Suppose we now have  $N/2$  black particles on either side of the partition i.e. the particles on the right and left cannot be distinguished from each other.

- The unmixed entropy  $S_u$  is the same as before.
- The mixed entropy has changed:

$$S_m = k_B \log \left( \frac{(2V)^N}{N!} \right).$$

- Subtracting and then using Stirling's approximation:

$$\begin{aligned} \frac{\Delta S}{k_B} &= 2 \log((N/2)!) - \log(N!) + N \log 2 \\ &= 2(N/2) \log(N/2) - 2(N/2) - N \log N + N + N \log 2 + o(N) \\ &= o(N) \ll N \end{aligned}$$

i.e. no change of entropy to leading order as  $N \rightarrow \infty$ .

- Without  $N!$  in the definition of the entropy, entropy of mixing would change to leading order – **Gibb's paradox!**

- **Osmotic pressure**

Can entropy of mixing generate useful work, thus connecting the “entropy as disorder” concept with the thermodynamic definition of entropy?

YES!!!

Allowing only one species of particles in a 2-species mixture to cross a semipermeable membrane creates a pressure difference that can drive a piston.

- **Maxwell's demon**

A demon operates a small door between two containers. He only opens the door if black particles appear from left or white from the right. This re-segregates the system and lowers the entropy of the system.

However: Running a demon produces entropy so laws of thermodynamics are not violated.

## Lecture 6: Entropy (II)

### Definition 3: Entropy as ignorance

# Entropy as ignorance: Information and memory

- Most general (and powerful) interpretation of entropy.
- E.G.: For system in equilibrium, we have lost *all* information about initial conditions and hence of details of system except conserved quantities i.e. our ignorance of the system (= entropy) is maximal.
- Property of our knowledge of a system rather than of the system itself.
- The measurement of a detailed configuration reduces entropy. The detailed knowledge of a system can be used to extract useful work not available before the measurement.

# Non-equilibrium entropy (Discrete case)

- The entropy of  $M$  equally likely states (see 2<sup>nd</sup> definition of entropy) is

$$S(M) = k_B \log M = -k_B \log p_i,$$

where  $p_i \equiv 1/M$  is the probability of each state.

- If  $p_i$  is non-uniform (i.e. when the system is *not* in equilibrium), we generalise to

$$S_{\text{discrete}} = -k_B \langle \log p_i \rangle = -k_B \sum_i p_i \log p_i.$$

# Non-equilibrium entropy (Continuum distributions)

- Non-equilibrium state of classical Hamiltonian system can be described with probability density  $\rho(q, p)$  on phase-space.
- Non-equilibrium entropy becomes

$$\begin{aligned} S_{\text{noneq}} &= -k_B \langle \log \rho \rangle = -k_B \int \rho \log \rho \, d\rho \\ &= -\frac{k_B}{\hbar^{3N}} \int_{H(\mathbf{q}, \mathbf{p}) \in (E, E+\delta E)} \rho(\mathbf{q}, \mathbf{p}) \log(\rho(\mathbf{q}, \mathbf{p})) \, d\mathbf{q} \, d\mathbf{p}. \end{aligned}$$

- For the micro-canonical ensemble, where

$$\begin{aligned} \rho_{\text{eq}} &= \frac{1}{\text{shell volume}} = \frac{1}{\Omega(E)\delta E} \\ \implies S_{\text{micro}} &= k_B \log(\Omega(E)\delta E) \end{aligned}$$

- Comparison with previous equilibrium values (see ch.3):

$$S_{\text{equil}} = k_B \log \Omega(E).$$

The difference is negligible: It is  $(k_B/N) \log(\delta E)$  per particle.

(It is connected with the choice of zero for entropy, which is arbitrary for classical systems)

# Information entropy: Shannon entropy

- Shannon entropy  $S_S =$  information entropy  $\equiv -k_S \sum_i p_i \log p_i$ .
- Choose  $k_S = 1/\log 2$  (does not require temperature, which is not needed in general in information theory)

$$\implies S_S = - \sum_i p_i \log_2 p_i.$$

- $S_S$  measures the entropy in **bits**.
  - Let's assume we consider 10-digit binary numbers, and weight each of the  $2^{10} = 1024$  possible states with equal probability  $p_i = 2^{-10}$
  - Then, the Shannon entropy is

$$S_S = - \sum_i p_i \log_2 p_i = - \sum_i 2^{-10} (-10) = 10,$$

as you would expect.

- $S_S$  puts a fundamental limit on the amount by which data can be compressed.



# Information entropy $S_i(p_1, \dots, p_M)$ : Axiomatic definition

## Axioms

Let  $p_i$  be the probability of state  $i = 1, \dots, M$  and  $M$  the # of states. The information entropy  $S_I$  satisfies three axioms:

- The entropy is maximal for equal probabilities

$$S_I\left(\frac{1}{M}, \dots, \frac{1}{M}\right) > S_I(p_1, \dots, p_M)$$

unless  $p_i = 1/M$  for all  $i$ .

- The entropy is unaffected by states of zero probability

$$S_I(p_1, \dots, p_{M-1}, 0) = S_I(p_1, \dots, p_{M-1})$$

- The entropy change for conditional probabilities  
This requires some definitions and notation, given on the next page.

## Information entropy definition: Third Axiom

- For two sets of events,

$$A = \{A_k\} \text{ with } |A| = M, \quad B = \{B_l\} \text{ with } |B| = N,$$

let  $S_I(A) \equiv S_I(p_1, \dots, p_M)$ ,  $S_I(B) \equiv S_I(q_1, \dots, q_N)$ .

- Define

$$r_{kl} \equiv P(A_k \text{ and } B_l), \quad q_l \equiv P(B_l), \quad c_{kl} \equiv P(A_k|B_l) = \frac{r_{kl}}{q_l}.$$

( $c_{kl}$  is the conditional probability of  $A_k$  after  $B_l$  has happened. Note:  $\sum_k c_{kl} = 1$ .)

- Define

$$S_I(AB) \equiv S_I(r_{11}, r_{12}, \dots, r_{1N}, r_{21}, \dots, r_{MN}) = S_I(c_{11}q_1, \dots, \dots);$$

$$S_I(A|B_l) \equiv S_I(c_{l1}, \dots, c_{lM}).$$

$$\langle S_I(A|B_l) \rangle_B = \sum_l q_l S_I(A|B_l)$$

- Then we require  $\boxed{\langle S_I(A|B_l) \rangle_B = S_I(AB) - S_I(B)}$  (\*)

## Additivity and the third axiom

- If  $A$  and  $B$  are uncorrelated,  $S_I(A|B_l) = S_I(A)$ , then

$$\langle S_I(A|B_l) \rangle_B = S_I(A)$$

and the property (\*) implies

$$S_I(AB) = S_I(A) + S_I(B)$$

i.e. the entropy for uncoupled systems is **additive**, hence  $S$  is extensive.

## The Shannon entropy and the definition of the information entropy

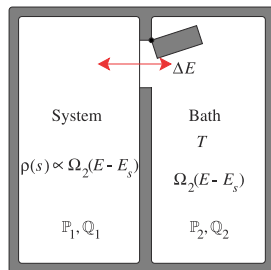
- The Shannon entropy satisfies all three axioms  
[If  $p \log p|_{p=0} \equiv \lim_{p \rightarrow 0} (p \log p) = 0$ ]
- In fact, the Shannon entropy is **uniquely** characterised by these three properties (up to an overall constant).

# Lecture 7: Free Energies (I)

- Now we turn to studying parts of statistical mechanical systems.
  - We ignore parts of a system, and embody the rest in a new statistical ensemble and its free energy.
- We want to *ignore the external world* (aka as the “heat bath”)
  - Most systems are coupled to the external world (they can exchange e.g. heat or particles), **BUT** if the system of interest is only weakly coupled to the external world, we can remove it.
  - This introduces new ensembles and free energies
  - The **canonical ensemble** and the **Helmholtz free energy** arise from a heat bath that can exchange energy with the system of interest.
  - The **grand canonical ensemble** and **grand free energy** arise from a bath which can exchange particles at a fixed chemical potential.
- We want to *ignore unimportant internal degrees of freedom*.
  - Introduce e.g. friction and noise in mechanical system, ignoring details of movement of individual atoms.
  - Introduce reaction rate theory in chemical reactions.
- We want to *coarse-grain*.

# The canonical ensemble (I)

- The canonical ensemble governs the equilibrium behaviour of system at **fixed temperature**.
- In L2&3, we derived “temperature” by considering an isolated system consisting of 2 weakly coupled subsystems that could exchange energy.
- Now: Focus on one of these parts (“**the system**”) and assume the other part (“**the bath**”) is large.
- From L3: The probability density that the system is in a particular state  $s$  (with energy  $E_s$ ) is proportional to the volume of the energy shell for the heat bath at energy  $E - E_s$ :



(Sethna 2020)

$$\rho(s) \propto \Omega_2(E - E_s) = \exp\left(\frac{S_2(E - E_s)}{k_B}\right).$$

## The canonical ensemble (II)

- Consider two states  $A$  and  $B$  of the (fluctuating) system in equilibrium. The fluctuations are small and the heat bath is large,

$$\begin{aligned}\implies \frac{1}{T_2} &= \frac{\partial S_2}{\partial E_2} \approx \text{const.} \quad \text{in } (E - E_A, E - E_B) \\ \frac{\rho(s_B)}{\rho(s_A)} &= \frac{\Omega_2(E - E_B)}{\Omega_2(E - E_A)} \\ &= \exp \left[ \frac{1}{k_B} (S_2(E - E_B) - S_2(E - E_A)) \right] \\ &\approx \exp \left[ \frac{E_A - E_B}{k_B} \frac{\partial S_2}{\partial E} \right] = \exp \left( \frac{E_A - E_B}{k_B T_2} \right).\end{aligned}$$

- Letting  $s \equiv s_B$ , we get the **Boltzmann distribution**

$$\rho(s) \propto \exp \left( -\frac{E_S}{k_B T_2} \right).$$

# The canonical ensemble (III)

- Normalisation

$$\rho(s) = \frac{\exp\left(-\frac{E_S}{k_B T_2}\right)}{Z} \quad (*)$$

where the normalisation factor  $Z$  – also called the **partition function** – is given by

$$Z = \sum_n \exp\left(-\frac{E_n}{k_B T_2}\right) = \frac{1}{h^{3N_1}} \int \exp\left(-\frac{H_1(\mathbf{q}_1, \mathbf{p}_1)}{k_B T}\right) d\mathbf{q}_1 d\mathbf{p}_1.$$

- Eqn. (\*) is the definition of the canonical ensemble. It can be derived more formally by using the partial trace to remove the bath degrees of freedom from the micro-canonical ensemble.
- **Note:** Most quantities of interest can be calculated in two ways:
  - Via an explicit sum over states;
  - In terms of derivatives of  $Z$  (which is essentially a generating function).
- (From now on, we will write  $N \equiv N_1$  for the number of particles in “the system”).



## Example: The average internal energy

The average internal energy  $\langle E \rangle$ , where  $\langle \rangle$  denotes the canonical average, is given by

$$\begin{aligned}\langle E \rangle &= \sum_n E_n P_n \\ &= \frac{1}{Z} \sum_n E_n \exp(-\beta E_n) && (\beta \equiv 1/k_B T) \\ &= -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_n \exp(-\beta E_n) \\ &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \\ &= -\frac{\partial \log Z}{\partial \beta}\end{aligned}$$

## Example: The specific heat

- The specific heat per particle  $c_v \equiv \partial \langle E \rangle / \partial T / N$  at constant volume (of the system) can be calculated via

$$Nc_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \langle E \rangle}{\partial \beta} \frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial \langle E \rangle}{\partial \beta}$$

$$\implies Nc_v = -\frac{1}{k_B T^2} \frac{\partial^2 \log Z}{\partial \beta^2}$$

- On the other hand

$$\begin{aligned} Nc_v &= -\frac{1}{k_B T^2} \frac{\partial}{\partial \beta} \left[ \frac{\sum E_n \exp(-\beta E_n)}{\sum \exp(-\beta E_n)} \right] \\ &= -\frac{1}{k_B T^2} \left[ \frac{\left( \sum E_n \exp(-\beta E_n) \right)^2}{Z^2} - \frac{\sum E_n^2 \exp(-\beta E_n)}{Z} \right] \\ &= \frac{1}{k_B T^2} \left[ \langle E^2 \rangle - \langle E \rangle^2 \right] = \frac{\sigma_E^2}{k_B T^2}, \end{aligned}$$

where  $\sigma_E \equiv \left[ \left( \langle E^2 \rangle - \langle E \rangle^2 \right) / k_B T^2 \right]^{1/2}$  is the root-mean-square fluctuation of the energy.

## Fluctuation-response relations

- The relation

$$\underbrace{Nc_v}_{\substack{\text{macroscopic susceptibility} \\ \text{aka linear response}}} = \underbrace{\frac{\sigma_E^2}{k_B T^2}}_{\text{microscopic fluctuations}}$$

is an example of a **fluctuation-response** relation.

## The thermodynamic limit

- **Question:**

Are the results calculated using the canonical ensemble the same as those calculated using the microcanonical ensemble?

- Energy fluctuations per particle tend to zero in the thermodynamic limit:

$$\frac{\sigma_E}{N} = \frac{1}{\sqrt{N}} \sqrt{k_B c_v T} = O(N^{-1/2}) \rightarrow 0 \quad \text{as } N \rightarrow \infty.$$

- Thus: tiny fluctuations will not change the properties of the macroscopic system, so the two ensembles predict the same behaviour.

## Part 2: The Helmholtz free energy

$$\begin{aligned} S &= -k_B \sum P_n \log P_n = -k_B \sum \frac{\exp(-\beta E_n)}{Z} \log \left( \frac{\exp(-\beta E_n)}{Z} \right) \\ &= k_B \beta \langle E \rangle + k_B \log(Z) \frac{\sum \exp(-\beta E_n)}{Z} \\ &= \frac{\langle E \rangle}{T} + k_B \log Z \end{aligned}$$

- Note: The formulae for  $\langle E \rangle$ ,  $c_V$  and  $S$  all involve  $\log Z$  and its derivatives. Hence it is an important quantity.
- Thus define the **Helmholtz free energy** for the canonical ensemble as

$$A(T, V, N) \equiv -k_B T \log Z = \langle E \rangle - TS$$

# The Helmholtz free energy $A = E - TS$ (continued)

- $A$  is the energy that is free to do useful work:  
An engine that draws  $E = Q_1$  from a hot bath and releases  $S = Q_2/T$  into a cold bath can do work

$$W = Q_1 - Q_2 = E - TS = A$$

- We can obtain the entropy from  $A$  via

$$\begin{aligned}\left. \frac{\partial A}{\partial T} \right|_{N,V} &= -\frac{\partial}{\partial T} (k_B T \log Z) = -k_B \log Z - k_B T \frac{\partial \log Z}{\partial \beta} \frac{\partial \beta}{\partial T} \\ &= -k_B \log Z - k_B T \langle E \rangle \frac{1}{k_B T^2} = -k_B \log Z - \frac{\langle E \rangle}{T} \\ &= -S\end{aligned}$$

- Notice that it follows (directly from our definition of  $A$ ) that

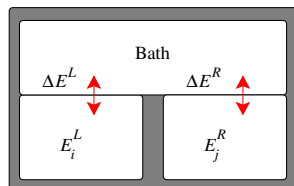
$$Z = \exp\left(-\frac{A(T, V, N)}{k_B T}\right)$$

# Uncoupled systems and canonical ensembles

- The canonical ensemble is often convenient, because when the Hamiltonian decouples, the partition function  $Z$  factors into pieces that can be computed separately.
- Consider subsystems  $L$  and  $R$  that interact weakly via a bath at  $\beta = 1/k_B T$ .

$$\begin{aligned} Z &= \sum_{i,j} e^{-\beta(E_i^L + E_j^R)} \\ &= \left( \sum_i e^{-\beta E_i^L} \right) \left( \sum_j e^{-\beta E_j^R} \right) = Z^L Z^R \end{aligned}$$

$$\begin{aligned} \Rightarrow A &= -k_B T \log Z = -k_B T \log(Z^L Z^R) \\ &= A^L + A^R. \end{aligned}$$



(Sethna 2020)

- The calculation for the micro-canonical ensemble is much harder. The energy  $m$  of the subsystems must sum up to given  $E$  so finding the energy of one subsystem requires us to deal with all other subsystems.

## Example: An ideal gas at temperature $T$

- The particles of an ideal gas are uncoupled. Thus, the partition function for  $N$  distinguishable particles of mass  $m$  in volume  $V = l^3$  is

$$Z_{\text{ideal}}^{\text{dist}} = \prod_{\alpha=1}^{3N} \underbrace{\frac{1}{h} \int_0^l dq_{\alpha} \int_{-\infty}^{\infty} dp_{\alpha} \exp\left(-\frac{\beta p_{\alpha}^2}{2m}\right)}_{\text{Partition function for one particle}}$$
$$= \left(\frac{l}{h} \sqrt{\frac{2\pi m}{\beta}}\right)^{3N} = \left(\frac{l}{\lambda}\right)^{3N},$$

where  $\lambda$  is the thermal de Broglie wavelength (defined earlier in the course).

- The mean internal energy of an ideal gas is

$$\langle E \rangle = \frac{\partial \log Z_{\text{ideal}}^{\text{dist}}}{\partial \beta} = -\frac{\partial}{\partial \beta} \log(\beta^{-3N/2})$$
$$= \frac{3N}{2\beta} = \frac{3}{2} N k_B T.$$



## Example: An ideal gas with indistinguishable particles

- For **indistinguishable** particles:  $Z_{\text{ideal}}^{\text{undist}} = \frac{(l/\lambda)^{3N}}{N!}$ .

- $\langle E \rangle$  doesn't change, but  $A$  does

$$A_{\text{ideal}}^{\text{undist}} = -k_B T \log \left( \frac{(l/\lambda)^{3N}}{N!} \right) = -Nk_B T \log \left( \frac{V}{\lambda^3} \right) + k_B T \log(N!)$$

$$\sim -Nk_B T \log \left( \frac{V}{\lambda^3} \right) + k_B T (N \log(N) - N) \quad (\text{Stirling})$$

$$= -Nk_B T \left[ \log \left( \frac{V}{N\lambda^3} \right) + 1 \right]$$

$$= Nk_B T \left( \log(\rho\lambda^3) - 1 \right), \quad (\rho = N/V).$$

$$\Rightarrow S^{\text{undist}} = -\frac{\partial A_{\text{ideal}}^{\text{undist}}}{\partial T} = -Nk_B \left( \log(\rho\lambda^3) - 1 \right) - Nk_B T \frac{\partial \log(T^{-3/2})}{\partial T}$$

$$= Nk_B \left( \frac{5}{2} - \log(\rho\lambda^3) \right).$$

derived earlier, with more effort, using the microcanonical ensemble.

- **Classical harmonic oscillators.** (Sethna p. 111)

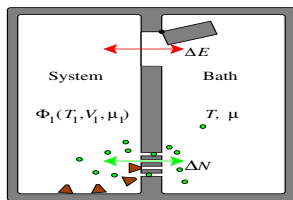
**Note:** Electromagnetic radiation, vibrations of atoms in solids, excitations of many other systems near equilibria can be approximately described as a set of uncoupled harmonic oscillators.

- **Classical velocity distributions.**

- Both for the ideal gas and for harmonic oscillators each component of the momentum contributes a factor of  $\sqrt{2\pi m/\beta}$  to  $Z$ .
- This is true for any classical system in which momenta are uncoupled to positions, that is, where the momentum parts are of standard form  $\sum_{\alpha} p_{\alpha}^2/(2m_{\alpha})$ .

## Lecture 8: Free Energies (II)

# Grand Canonical Ensemble



(Sethna 2020)

- **Grand canonical ensemble** allows one to decouple the calculations of systems that can exchange both energy and particles w/ the environment.
- System in state  $s$  with energy  $E_1$  and a number  $N_1$  of particles.
- Bath with energy  $E_2 = E - E_1$  and  $N_2 = N - N_1$  particles.
- Probability density that system is in state  $s$  is

$$\begin{aligned}\rho(s) &\propto \Omega_2(E - E_1, N - N_1) = e^{\frac{S_2(E - E_1, N - N_1)}{k_B}} \quad [E_1 \ll E, N_1 \ll N] \\ &\propto e^{\frac{-E_1}{k_B T} - N_1 \frac{\partial S_2}{\partial N}} = e^{\frac{-E_1}{k_B T} + \frac{N_1 \mu}{k_B T}} = e^{\frac{-(E_1 - \mu N_1)}{k_B T}},\end{aligned}$$

where  $\mu = -T \frac{\partial S_2}{\partial N}$  is the chemical potential.

# Grand Canonical Ensemble (2)

- Using  $dE = TdS - PdV + \mu dN$  shows that  $\mu = \left. \frac{\partial E}{\partial N} \right|_{S,V}$  is precisely the energy change needed to add an additional particle (adiabatically) and keep the  $(N + 1)$ -particle system in equilibrium.
- At low temp., a system fills w/ particles until energy needed to jam in another particles reaches  $\mu$ , and it then exhibits thermal number fluctuations about that filling.
- Analogously to canonical ensemble, there is a normalization factor called the **grand partition function**:

$$\Xi(T, V, \mu) = \sum_n e^{-\frac{(E_n - \mu N_n)}{k_B T}} \quad (2)$$

It normalizes the prob. dens. & is a generating function.

- Prob. density of state  $s_i$  is  $\rho(s_i) = e^{-\frac{E_i - \mu N_i}{k_B T}} / \Xi$
- The **grand free energy** is  $\Phi(T, V, \mu) \equiv -k_B T \log(\Xi) = \langle E \rangle - TS - \mu N$
- Note: Euler relation:  $E = TS - PV + \mu N$  can be derived and used to show that  $\Phi(T, V, \mu) = -PV$ .

# Grand Canonical Ensemble (3)

- **Partial traces:** the grand canonical partition function can be written as a sum over canonical partition functions.

Split sum over the  $\{s\}$  states into a double sum  $\sum_M \sum_{\ell_M}$ .

Inner sum traces over all states  $l_M$  with  $M$  particles.

$M$  - # particles in subset;  $\ell_M$  - internal label of a state within subset

$s_{M,\ell_M}$  - Corresponding label in  $\{s\}$ ;  $E_{M,\ell_M} = E_{s_{M,\ell_M}}$  - its energy.

$$\begin{aligned}\Xi(T, V, \mu) &= \sum_M \sum_{\ell_M} e^{-\frac{(E_{\ell_M, M} - \mu M)}{k_B T}} = \sum_M \left( \sum_{\ell_M} e^{-\frac{E_{\ell_M, M}}{k_B T}} \right) e^{\frac{\mu M}{k_B T}} \\ &= \sum_M Z(T, V, M) e^{\frac{\mu M}{k_B T}} = \sum_M e^{-\frac{1}{k_B T} (A(T, V, M) - \mu M)}\end{aligned}$$

- Note:  $e^{-\frac{E_n}{k_B T}}$  is prob. of a system being in a particular state  $n$ , and  $e^{-\frac{A(T, V, M)}{k_B T}}$  is prob. of the system having any state w/  $M$  particles.

# Grand Canonical Ensemble (4)

- The grand canonical ensemble is useful for non-interacting quantum systems. A closely related ensemble arises in chemical reactions.
- Average (expected) number of particles in system  $N$  is

$$\langle N \rangle = \frac{\sum_m N_m e^{-\frac{1}{k_B T}(E_m - \mu N_m)}}{\sum_m e^{-\frac{1}{k_B T}(E_m - \mu N_m)}} = \frac{k_B T}{\Xi} \frac{\partial \Xi}{\partial \mu} = - \frac{\partial \Phi}{\partial \mu}$$

- Determine **number fluctuations** around this average. Try derivative

$$\begin{aligned} \frac{\partial \langle N \rangle}{\partial \mu} &= \frac{\partial}{\partial \mu} \left( \frac{\sum_m N_m e^{-\frac{1}{k_B T}(E_m - \mu N_m)}}{\Xi} \right) \\ &= - \frac{1}{\Xi^2} \frac{(\sum_m N_m e^{-\frac{1}{k_B T}(E_m - \mu N_m)})^2}{k_B T} + \frac{1}{\Xi} \frac{(\sum_m N_m^2 e^{-\frac{1}{k_B T}(E_m - \mu N_m)})}{k_B T} \\ &= \frac{\langle N^2 \rangle - \langle N \rangle^2}{k_B T} = \frac{\langle (N - \langle N \rangle)^2 \rangle}{k_B T} = [\text{rms of fluctuations of } N]^2 \end{aligned}$$

## Lecture 8, Part 2



# What is Thermodynamics?

- Thermodynamics is the theory (in the context of physical particles) that emerges from SM in the limit of large systems.
  - It is derived from SM in the thermodynamic limit ( $N \rightarrow \infty$ )
  - Thermodynamics is then the macroscopic theory of near-equilib. systems when fluctuations are ignored; SM is the microscopic theory used to derive it.
- Note: the purview of SM is much broader than just deriving thermodynamics from first principles; it is fundamental for fields like information theory, dynamical systems, complex systems and networks.

# What is Thermodynamics? (2)

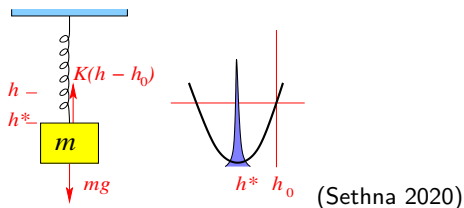
- **Axioms 'laws' of thermodynamics**

- ① Transitivity of equilibria: if 2 systems are in equilib. w/ a 3<sup>rd</sup> one, then they are in equilib. w/ each other.
- ② Conservation of energy: the total energy of an isolated system (including heat energy) is constant.
- ③ Entropy always increases (in isolated systems): (more correctly, it is non-decrease of entropy): An isolated system can undergo irreversible processes whose effects can be measured by a state function called entropy.
- ④ Entropy goes to zero at absolute zero: the entropy per particle of any two large equilib. systems approaches the same value as temp. approaches absolute 0.

# What is Thermodynamics? (3)

- Notes:
  - ① is the basis for defining temp.; our SM derivation of temp. provides the microscopic justification of this law.
  - ② is a fundamental principle of physics and thermodynamics. Thermodynamics inherits it from its truth in the microscopic description.
  - ③ we discussed this at length in chapter 5.
  - ④  $S \rightarrow 0$  as temp  $\rightarrow 0K$  comes from measuring phase-space volume in units of  $h^{3N}$  (see earlier discussion).
- **Reading homework:** Read discussion on (Sethna, pg. 115-116) and note definition of Legendre transform, Gibbs free energy (for systems at const. temp. and pressure, such as most biological and chemical systems), enthalpy (a free energy for systems at const. entropy and pressure).

# Mechanics: Friction and Fluctuations



- Mass on a spring; at  $h^*$  the forces balance and energy is minimized.
- Now we are going to explain why the mass appears to minimize energy (... rather than conserving it).

## Mechanics: Friction and Fluctuations (2)

The system (mass+spring) is coupled to a large number  $N$  of internal DOF (their atomic constituents are part of the environment).

- Oscillation of mass is coupled to the other DOF (via friction) and shares energy w/ them.
- Spring potential energy is quadratic, so we can use equipartition theorem: in equilib.,  $\frac{1}{2}K(h - h^*)^2 = \frac{1}{2}k_B T$ .
- If  $K = 10 \frac{N}{m}$  at room temp. ( $k_B T \approx 4 \times 10^{-21} J$ ), then the fluctuations have size

$$\sqrt{\langle (h - h^*)^2 \rangle} = \sqrt{\frac{k_B T}{K}} \approx 2 \times 10^{-11} \text{ m} = 0.2 \text{ \AA},$$

so the position minimizes energy up to thermal fluctuations smaller than an atomic radius.

- To connect this SM picture to the friction coefficient of the damped harmonic oscillator, one derives a so called Langevin equation using a careful SM treatment (see chapter 10 in Sethna for more info.):

$$\ddot{h} = -\frac{K}{m}(h - h^*) - \gamma\dot{h} + \xi(t),$$

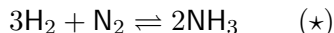
where  $\gamma$  represents friction (or dissipation), and  $\xi(t)$  is a random noise force coming from internal vibrational DOF of the system.

- The strength of noise  $\xi$  depends on dissipation and temp  $T$  so as to guarantee a Boltzmann distribution at steady state.

## Lecture 8, Part 3: Chemical Reactions

# Chemical Equilibria and Reaction Rates

- For chemical reactions, one is often interested in number of molecules as a function of time and **IS NOT** interested in properties that depend on position and momenta of molecules.
- Hence we will develop a coarse grain formulation with a **free energy** to derive in particular the **law of mass action**.
- Chemical reactions change one type of molecules into another, e.g.:



- In chemical equilibrium, the concentrations  $X_i = [x_i]$  of the various molecules satisfy the law of mass action
  - The general reaction: Let the stoichiometries  $\nu_i$  give the number of molecules  $X_i$  changed during reaction ( $\nu_i < 0$  for reactants and  $\nu_i > 0$  for products).
  - The law of mass action is: 
$$\prod_i [X_i]^{\nu_i} = K_{\text{eq}}(T) \quad (\star\star)$$
- For  $(\star)$ , this gives  $\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = K_{\text{eq}}(T)$ .
- There is a naive but unconvincing argument for  $(\star\star)$ , so let's derive it properly from SM:



# Chemical Equilibria and Reaction Rates (2)

- We seek a free energy formulation of our system for fixed  $V$  and  $T$ :  
The Helmholtz free energy is the natural choice:

$$A = A(T, V, N_{H_2}, N_{N_2}, N_{NH_3}).$$

- When the chemical reaction takes place, we have

$$\begin{aligned}\Delta A &= \frac{\partial A}{\partial N_{H_2}} \Delta N_{H_2} + \frac{\partial A}{\partial N_{N_2}} \Delta N_{N_2} + \frac{\partial A}{\partial N_{NH_3}} \Delta N_{NH_3} \\ &= (3\mu_{H_2} + \mu_{N_2} - 2\mu_{NH_3}) \Delta N_{N_2},\end{aligned}$$

where  $\mu_X$  is the chemical potential of molecule  $X$ .

- Reaction proceeds until  $A$  is at a min, so

$$-3\mu_{H_2} - \mu_{N_2} + 2\mu_{NH_3} = 0 \quad (\star \star \star) \quad \text{in equilib.}$$

# Chemical Equilibria and Reaction Rates (3)

- To derive the law of mass action, we assume that the molecules are uncorrelated in space
  - ⇒ each molecular species is a separate ideal gas.
  - ⇒ for each gas,

$$A(N, V, T) = Nk_B T \left[ \log \left( \frac{N}{V} \lambda^3 \right) - 1 \right] + NF_0,$$

where

$$\left\{ \begin{array}{l} \lambda = \frac{h}{\sqrt{2\pi m k_B T}} \\ NF_0 \end{array} \right. \quad \begin{array}{l} \text{is the thermal de Broglie wavelength} \\ \text{comes from internal free energy of the molecules,} \\ \text{see footnote 31 on (Sethna, pg. 119)} \end{array}$$

$$\begin{aligned} \Rightarrow \quad \mu(N, V, T) &= \frac{\partial A}{\partial N} \\ &= k_B T \log(N/V) + k_B T \log(\lambda^3) + F_0. \quad (\star \star \star) \end{aligned}$$

# Chemical Equilibria and Reaction Rates (4)

- insert (\*\*\*\*) into (\*\*\*) , divide by  $k_B T$ , and write  $[X] = \frac{N_X}{V}$  to get the laws of mass action:

$$\begin{aligned} -3 \log[H_2] - \log[N_2] + 2 \log[NH_3] &= \log[K_{eq}] \\ \Rightarrow \frac{[NH_3]^2}{[H_2]^3 [N_2]} &= K_{eq} \end{aligned}$$

where

$$K_{eq} = K_0 e^{\frac{-\Delta F_{net}}{k_B T}},$$

and

$$\begin{aligned} \Delta F_{net} &= -3F_0^{H_2} - F_0^{N_2} + 2F_0^{NH_3}, \\ K_0 &= \frac{\lambda_{H_2}^9 \lambda_{N_2}^3}{\lambda_{NH_3}^6} = \frac{h^6 m_{NH_3}^3}{8\pi^3 k_B^3 T^3 m_{H_2}^{3/2} m_{N_2}^{3/2}} \propto T^{-3} \end{aligned}$$

The Boltzmann factor favours a final state with molecular free energy lower than the initial state.

- **Read end of section 6.6 in Sethna (pp. 119-120)** on e.g. **transition states** & the **Arrhenius law** of thermally-activated reaction rates.

**Lecture 8, Part 4**  
**An example of coarse graining**  
**The free energy density of the ideal gas**

# Free Energy Density for the Ideal Gas

- Want to see how diffusion eq. is connected w/ free energies and ensembles.
- Inhomogeneous systems out of equilibrium can be described by SM, if the gradients in space and time are small enough s.t. the system is close to a local equilib.; we can then represent the local state of the system by order parameters fields- one field for each property (density, temperature, magnetization) needed to characterize the state of a uniform, macroscopic body.
- We can describe a spatially varying, inhomogeneous system that is nearly in equilib. using a free energy density (which typically depends on order parameters and their derivatives).
- Recall that for **Helmholtz free energy**

$$A(N, V, T) = Nk_B T [\log(\rho \lambda^3) - 1]$$

$\Rightarrow$  Free energy density for  $n_i = \rho(\vec{x}_i) \Delta V$  particles in a small volume is

$$\mathcal{F}^{\text{ideal}}(\rho(\vec{x}_j), t) = \frac{A(n_j, \Delta V, T)}{\Delta V} = \rho(\vec{x}_j) k_B T [\log(\rho(\vec{x}_j) \lambda^3) - 1]$$

## Free Energy Density for the Ideal Gas (2)

- The probability for a given particle density  $\rho(\vec{x})$  is

$$P\{\rho\} = \frac{e^{-\beta \int \mathcal{F}^{\text{ideal}}(\rho(\vec{x})) d\vec{x}}}{Z} \quad (\beta=1/k_B T)$$

- As usual, free energy  $F\{\rho\} = \int \mathcal{F}^{\text{ideal}}(\rho(\vec{x})) d\vec{x}$  acts just like the energy in the Boltzmann dist.
  - We have 'integrated out' the microscopic DOF (i.e., the positions and velocities of individual particles) and replaced them w/ coarsed-grained field  $\rho(x)$ .
- Can use  $\mathcal{F}$  to determine any equilibrium property that can be written in terms of  $\rho(x)$  e.g., correlation functions  $\langle \rho(x)\rho(x') \rangle$ ; .
- Also provides framework for discussing evolution laws for non-uniform densities e.g.  $\rho(x, t)$ .
  - If system is close to equilib in each small volume  $\Delta V$ , then time evolution of  $\rho(x, t)$  can be studied w/ equilib. SM even though system is not globally in equilib.

## Free Energy Density for the Ideal Gas (3)

- Non-uniform density has a force that pushes it towards uniformity; the total free energy decreases when particles flow from regions of (high) particle density to those of low density.
- One can then use  $\mathcal{F}$  to calculate this force, and then derive laws for the time evolution.
- Chemical potential for a uniform system is

$$\mu = \frac{\partial A}{\partial N} = \frac{\partial A/V}{\partial N/V} = \frac{\text{change in free energy density}}{\text{change in average density}} = \frac{\partial \mathcal{F}}{\partial \rho}$$

- Generalisation: For a non-uniform system, the total chemical potential at  $x$  is the 1<sup>st</sup> Variation of  $\mathcal{F}$  w.r.t  $\rho$

$$\mu(x) = \frac{\delta \mathcal{F}}{\delta \rho}$$

- For the ideal-gas free energy, which has no gradient term of  $\rho$ , we get

$$\Rightarrow \mu(x) = \frac{\delta \mathcal{F}^{\text{ideal}}}{\delta \rho} = \frac{\partial}{\partial \rho} (\rho k_B T [\log(\rho \lambda^3) - 1]) = k_B T \log(\rho \lambda^3)$$

## Free Energy Density for the Ideal Gas (4)

- A particle can lower the free energy by moving from regions with high chemical potential to regions with low chemical potential.
- $-\frac{\partial\mu}{\partial x}$  acts much like a pressure gradient in that it provides a statistical mechanical force on a particle.
- **Example:** Small amount of perfume in a large body of still air
  - Particle density is locally conserved, but momentum is strongly damped (as perfume particles can scatter off of air molecules).
  - Velocity of the particles,  $\vec{v} = -\gamma\frac{\partial\mu}{\partial x}$ , where  $\gamma = \text{const.} = \text{"mobility"}$ .
  - This is an example of linear response (i.e., current  $\propto$  gradient of property).



# Free Energy Density for the Ideal Gas (5)

- $\Rightarrow$  particle current

$$\begin{aligned}\vec{J} &= \rho \vec{v} = \rho(x) \left(-\gamma \frac{\partial \mu}{\partial x}\right) \\ &= -\rho(x) \frac{\partial}{\partial x} [\gamma k_B T \log(\rho \lambda^3)] = -\rho(x) \frac{\gamma k_B T}{\rho} \frac{\partial \rho}{\partial x} = -\gamma k_B T \frac{\partial \rho}{\partial x}\end{aligned}$$

- Combine this with conservation of  $\rho$ ,

$$\begin{aligned}\Rightarrow \quad \frac{\partial \rho}{\partial \tau} &= -\vec{\nabla} \cdot \vec{J} \\ &= \gamma k_B T \frac{\partial^2 \rho}{\partial x^2} \\ &= \text{our friend the diffusion equation!}\end{aligned}$$

- The diffusion coefficient is given by the Einstein relation  $D = \gamma k_B T$ .

# Lecture 9: Derivation of the Boltzmann equation

# Background

- The Boltzmann equation bridges the microscopic description of many particle system at the level of individual particle with the macroscopic behaviour of the system as a whole.
- It describes the evolution of nonequilibrium systems.  
Classical example: Systems that experience heat flow due to temperature gradients.
- In the limit of small **mean free path** one obtains continuum equations.  
Formal procedure: **Chapman-Enskog** method for small **Knudsen number** (=mean free path/macroscopic length scale)
- On the other hand of course the Boltzmann equation is valid for rarefied gases, where the mean free path is large.
- There are many other applications and modifications of the Boltzmann equation.
- Our first task will be to see how the Boltzmann equation is obtained from the microscopic system, that is, from Liouville's equation.

# Plan for the lectures about the Boltzmann equation

- ① We will first derive the Boltzmann equation, starting with Liouville's equation.
- ② We will derive conservation laws for averaged quantities of Boltzmann's equation and prove the H-theorem that effectively shows the irreversible evolution into equilibrium. This connects the Boltzmann equation with fundamental macroscopic laws: Conservation laws and the second law of thermodynamics & entropy.
- ③ We then carry out the Chapman-Enskog expansion in the small Knudsen number to derive the continuum equations (e.g. Fourier's law for the heat flux).

Thus, we bridge the entire spectrum of length scales from the particle physics to the continuum description.

Derivations of Boltzmann's equation, in three steps:

- Heuristic derivation of the form of the equation
- Derivation of the **(BBGKY) hierarchy** (attributed to Bogoliubov, Born, Green, Kirkwood and Yvon). These describe the evolution of the velocity distribution function including collisions, between two particles using the two-particle distribution function, which in turn satisfies the next equation in the hierarchy that requires the three particle distribution function, etc.
- Truncation of the BBGKY hierarchy and derivation of the approximate **Boltzmann collision term** from first principles.

# The velocity distribution function $f$

- Fluid consists of a large number  $N$  of molecules, whose position and velocity fluctuate in time
- Molecules interact through the action of short range forces which in effect can be conceived of as enabling collisions.
- Define a **velocity distribution function**  $f(\mathbf{r}, \mathbf{v}, t)$
- $f$  is expected number density function of molecules at position  $\mathbf{r}$  and velocity  $\mathbf{v}$ . Hence we have 6 dimensions for  $(\mathbf{r}, \mathbf{v})$  (rather than  $6N$ )
- More precisely,

$$f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v} d\mathbf{r} \quad (3)$$

is the expected number of molecules in the six-dimensional hypervolume element  $d\mathbf{v} d\mathbf{r}$  centred at  $(\mathbf{r}, \mathbf{v})$ ,

- $d\mathbf{v}$  is a (positive) volume element in velocity space,
- $d\mathbf{r}$  is a volume element in physical space.

# Heuristic Derivation

- Track  $f$  in time along phase space trajectories
- Collisionless case
  - Let  $\mathcal{F}$  represent the (exclusively external) forces

$$f(\mathbf{r} + \mathbf{v}\Delta t, \mathbf{v} + \frac{\mathcal{F}}{m}\Delta t, t + \Delta t) d\mathbf{v} d\mathbf{r} = f(\mathbf{r}, \mathbf{v}, t) d\mathbf{v} d\mathbf{r}$$

- Liouville justifies the use of the same infinitesimals on both sides (they are not scaled as we move in phase space). Cancelling the infinitesimals gives

$$f(\mathbf{r} + \mathbf{v}\Delta t, \mathbf{v} + \frac{\mathcal{F}}{m}\Delta t, t + \Delta t) = f(\mathbf{r}, \mathbf{v}, t)$$

- Upon Taylor-expanding and taking the limit  $\Delta t \rightarrow 0$ , one obtains

$$f_t + \nabla f \cdot v + \nabla_v f \cdot \frac{\mathcal{F}}{m} = 0$$

Notice the left hand side is the total derivative  $df/dt$ .

- Collision included: Liouville in  $6N$  phase space still applies, but the additional forces introduce an additional term  $(\partial f/\partial t)_{\text{col}}$  on the right hand side of all the above equations.

Now let's go for the systematic approach .. starting from Liouville's equation.



# Connection between $f$ and Liouville density

- Liouville density  $\rho$  describes the density of an ensemble of trajectories in the  $6N$ -dimensional phase space  $\Gamma$ .
- Then the  **$s$ -particle probability density** is defined as

$$\rho_s = \int_{\Gamma_{s+1}} \rho d\Gamma_{s+1}, \quad d\Gamma_{s+1} = \prod_{s+1}^N d\gamma_k, \quad d\gamma_k = d\mathbf{q}_k d\mathbf{p}_k, \quad (4)$$

where  $\mathbf{p}_k = m\mathbf{v}_k$ ,  $\mathbf{q}_k = \mathbf{r}_k$ .

- Define the  **$s$ -particle distribution function**  $f_s(\gamma_1, \dots, \gamma_s)$  as the expectation value of finding any  $s$  (of the total of  $N$ ) particles at positions  $(\gamma_1, \dots, \gamma_s)$ .

$$f_s(\gamma_1, \dots, \gamma_s) = \frac{N!}{(N-s)!} \rho_s(\gamma_1, \dots, \gamma_s). \quad (5)$$

# The BBGKY hierarchy

The distribution functions  $f_s$  we just constructed satisfy the following equations that you will derive from Liouville's equation  $\rho_t + \{\rho, H\} = 0$  on your problem sheet:

$$\frac{\partial f_s}{\partial t} + \{f_s, H_s\} = \int_P \sum_{i=1}^s \frac{\partial f_{s+1}}{\partial \mathbf{p}_i} \cdot \frac{\partial W_{i,s+1}}{\partial \mathbf{q}_i} d\gamma_{s+1}, \quad (6)$$

where

- $\{f_s, H_s\}$  is the Poisson bracket,
- $W_{ij} = W(|\mathbf{r}_i - \mathbf{r}_j|)$  is the inter-particle potential;
- $P = V \times U$  is the position-velocity space inhabited by each particle.
- $H$  and  $H_s$  are the  $N$  and the  $s$  particle Hamiltonians.

# The BBGKY hierarchy (2)

- Define  $\mathbf{a}_{ij} = -\frac{1}{m} \nabla_{\mathbf{r}_i} W_{ij}$  (not summed) as the force per unit mass on particle  $i$  due to particle  $j$ . ( $\nabla_{\mathbf{r}_i}$  is gradient with respect to  $\mathbf{r}_i$ .)
- Assume  $\mathbf{g}$  is the external force per unit mass acting on the particles.
- Then BBGKY equations become

$$\frac{\partial f_s}{\partial t} + \sum_{i=1}^s \left[ \mathbf{v}_i \cdot \nabla_{\mathbf{r}_i} f_s + \left\{ \mathbf{g} + \sum_{j=1}^s \mathbf{a}_{ij} \right\} \cdot \nabla_{\mathbf{v}_i} f_s \right] \quad (7)$$

$$= - \sum_{i=1}^s \int_P \mathbf{a}_{i,s+1} \cdot \nabla_{\mathbf{v}_i} f_{s+1} d\gamma_{s+1}. \quad (8)$$

- In particular, the one particle velocity distribution function  $f = f_1$  satisfies

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} f + \mathbf{g} \cdot \nabla_{\mathbf{v}} f = - \int_P \mathbf{a}_{12} \cdot \nabla_{\mathbf{v}} f_2 d\gamma_2. \quad (9)$$

- Details covered in homework (problem sheet).

# The BBGKY hierarchy (3)

- We assume that
  - $N$  is large
  - The joint probability density function

$$\rho_2(\mathbf{r}, \mathbf{v}; \mathbf{s}, \mathbf{w}, t) = \rho_1(\mathbf{r}, \mathbf{v}, t)\rho_1(\mathbf{s}, \mathbf{w}, t).$$

This is reasonable assumption for a hard-sphere gas.

- On the problem sheet, you will show that the collision term takes the form

$$Q = - \int_P \mathbf{a}(\mathbf{r} - \mathbf{s}) \cdot \nabla_{\mathbf{v}} f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{s}, \mathbf{w}, t) ds d\mathbf{w}. \quad (10)$$

- You will show that for short range forces,

$$Q = -\mathbf{A} \cdot \nabla_{\mathbf{v}} f, \quad \mathbf{A} = K \nabla n, \quad (n(\mathbf{r}, t) \text{ is number density}). \quad (11)$$

Derivations of Boltzmann's equation, in three steps:

- Heuristic derivation of the form of the equation
- Derivation of the **(BBGKY) hierarchy** (attributed to Bogoliubov, Born, Green, Kirkwood and Yvon). These describe the evolution of the velocity distribution function including collisions, between two particles using the two-particle distribution function, which in turn satisfies the next equation in the hierarchy that requires the three particle distribution function, etc.
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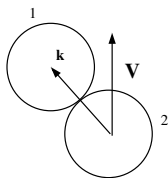
# The collision integral

- The previous equation does not have the form which the Boltzmann equation usually takes.
- We now derive an alternative expression for  $Q$  from first principles for a collection
  - of hard elastic spheres or with intermolecular forces are conservative and short range
  - and where the collisions are very rapid.
- Contributions to  $Q$  occur
  - via losses (collisions remove particles from the neighbourhood in  $\mathbf{v}$ )
  - via gains, whereby collisions beyond  $d\mathbf{r} d\mathbf{v}$  cause production of particles with velocities near  $\mathbf{v}$ .
- Hence we separate  $Q$  into two components,

$$Q = Q_+ - Q_-, \quad (12)$$

where  $Q_+$  and  $Q_-$  are the gain and loss from collisions, respectively.

# Impact of two spheres



- Consider the collision of molecule 1 and 2 with velocities  $\mathbf{v}$  and  $\mathbf{w}$  (same masses and diameters). Collisions of more particles are rare.
- Let  $\mathbf{k}$  denote the unit vector from centre 2 to centre 1 at impact.
- Let  $\mathbf{V} = \mathbf{w} - \mathbf{v}$  denote the relative velocity.
- Collision requires  $\mathbf{V} \cdot \mathbf{k} > 0$ .
- Post impact quantities are denoted by primes.
- Momentum conservation implies

$$\mathbf{v} + \mathbf{w} = \mathbf{v}' + \mathbf{w}' \quad (*)$$

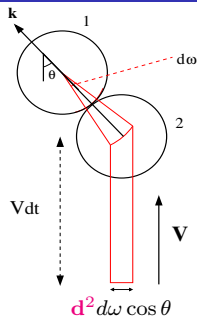
- For elastic impact:

$$-\mathbf{V} \cdot \mathbf{k} = \mathbf{V}' \cdot \mathbf{k}, \quad \mathbf{V} - (\mathbf{V} \cdot \mathbf{k})\mathbf{k} = \mathbf{V}' - (\mathbf{V}' \cdot \mathbf{k})\mathbf{k}. \quad (**)$$

- Combining (\*) and (\*\*) gives

$$\mathbf{v}' = \mathbf{v} + (\mathbf{V} \cdot \mathbf{k})\mathbf{k}, \quad \mathbf{w}' = \mathbf{w} - (\mathbf{V} \cdot \mathbf{k})\mathbf{k}. \quad (13)$$

# Impact frequency



- The number of molecules in the vicinity of  $\mathbf{r}, \mathbf{v}$  is  $f(\mathbf{r}, \mathbf{v}, t) d\mathbf{r} d\mathbf{v}$ .
- The number of impacts in time  $dt$  within a solid angle  $d\omega(\mathbf{k})$  at the point of contact in direction  $\mathbf{k}$  of molecule 1 with molecules moving at relative speed  $\mathbf{V}$  is  $f(\mathbf{r} - \mathbf{d}\mathbf{k}, \mathbf{w}, t) dV_{\text{cyl}} d\mathbf{w}$ ;
- $\mathbf{d}$  is the molecular diameter, and  $dV_{\text{cyl}}$  is the volume of the cylinder,
 
$$dV_{\text{cyl}} = \mathbf{d}^2 \mathbf{k} \cdot \mathbf{V} d\omega(\mathbf{k}) dt. \quad (14)$$
- $(-\mathbf{d}\mathbf{k})$  represents the offset between the centre of the molecules, but is small and will be ignored in the argument of  $f$ .



## Impact frequency (2)

- Thus:  $Q_- d\mathbf{r} d\mathbf{v} dt = f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{w}, t) d^2\mathbf{k} \cdot \mathbf{V} d\omega(\mathbf{k}) d\mathbf{w} d\mathbf{r} d\mathbf{v} dt$ ;
- Integrating over  $\mathbf{V}$  and  $\mathbf{k}$  such that  $\mathbf{V} \cdot \mathbf{k} > 0$ , we have

$$Q_- = \int_U \int_{\Omega_+} f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{w}, t) d\Omega d\mathbf{w}, \quad (15)$$

where  $\Omega_+ = \{\mathbf{k} \mid \mathbf{V} \cdot \mathbf{k} > 0\}$ ,  $d\Omega = d^2\mathbf{k} \cdot \mathbf{V} d\omega(\mathbf{k})$ .

- Recall that  $\mathbf{V} \cdot \mathbf{k} > 0$  is required for particle impact, and  $d\omega(\mathbf{k})$  is the solid angle around  $\mathbf{k}$ .

# Calculation of the collision integral

- For the source term we relabel  $\mathbf{v} \leftrightarrow \mathbf{v}'$  and  $\mathbf{w} \leftrightarrow \mathbf{w}'$ .
- Since the collision is reversible, the change in velocity formulae remain valid, and the source term is

$$Q_+ d\mathbf{r} d\mathbf{v} dt = f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r}, \mathbf{w}', t) d^2\mathbf{k}' \cdot \mathbf{V}' d\omega(\mathbf{k}') d\mathbf{w}' d\mathbf{r} d\mathbf{v}' dt; \quad (16)$$

note the primes on the velocities and the corresponding volume elements on the right hand side.

- We have also written the direction vector as  $\mathbf{k}'$ , which is cosmetic, but useful, as we now show. As a consequence, the formulae apply with  $\mathbf{k}$  replaced by  $\mathbf{k}'$ , so that a collision requires  $\mathbf{V}' \cdot \mathbf{k}' > 0$  that is  $\mathbf{V} \cdot \mathbf{k}' < 0$ .
- Now write  $\mathbf{k}' = -\mathbf{k}$ , so that  $\mathbf{V} \cdot \mathbf{k} > 0$  as before.

## Calculation of the collision integral (2)

- Finally, we want to change variables on the right hand side of (16) from  $\mathbf{v}'$ ,  $\mathbf{w}'$  to  $\mathbf{v}$ ,  $\mathbf{w}$  so that we can carry out the same division by the hypervolume  $d\mathbf{r} d\mathbf{v} dt$  to find  $Q_+$ .
- The transformation (13) is linear, and the change of variable yields

$$d\mathbf{v}' d\mathbf{w}' = J d\mathbf{v} d\mathbf{w}, \quad (17)$$

where  $J$  is the Jacobian of the transformation,

$$J = \left| \frac{\partial(\mathbf{v}', \mathbf{w}')}{\partial(\mathbf{v}, \mathbf{w})} \right|. \quad (18)$$

- Evaluating the coefficients, we find

$$J = \begin{vmatrix} I - K & K \\ K & I - K \end{vmatrix}, \quad (19)$$

where  $I \in \mathbb{R}^{3,3}$  identity matrix, and  $K \in \mathbb{R}^{3,3}$  is the orthogonal matrix

$$K_{ij} = k_i k_j. \quad (20)$$

The  $k_i$  are the components of  $\mathbf{k}$ .

## Calculation of the collision integral (3)

- Note that  $K\mathbf{k} = \mathbf{k}$ , and  $K\mathbf{m} = K\mathbf{n} = \mathbf{0}$  if  $\mathbf{m}$  and  $\mathbf{n}$  are independently orthogonal to  $\mathbf{k}$ . By direct calculation, the following vectors are eigenvectors of the matrix underlying  $J$ :

$$\begin{pmatrix} \mathbf{m} \\ \mathbf{0} \end{pmatrix}, \begin{pmatrix} \mathbf{n} \\ \mathbf{0} \end{pmatrix}, \begin{pmatrix} \mathbf{0} \\ \mathbf{m} \end{pmatrix}, \begin{pmatrix} \mathbf{0} \\ \mathbf{n} \end{pmatrix}, \begin{pmatrix} \mathbf{k} \\ \mathbf{k} \end{pmatrix}, \begin{pmatrix} \mathbf{k} \\ -\mathbf{k} \end{pmatrix}, \quad (21)$$

with respective eigenvalues  $1, 1, 1, 1, 1, -1$ ; thus  $J = 1$ .

- Hence

$$d\mathbf{v}' d\mathbf{w}' = d\mathbf{v} d\mathbf{w} \quad (22)$$

in (16).

## Calculation of the collision integral (4)

Dividing by the hypervolume element and noting that

$$\mathbf{k}' \cdot \mathbf{V}' = \mathbf{k} \cdot \mathbf{V}, \quad (23)$$

we obtain the source term  $Q_+$  in the form

$$Q_+ = \int_U \int_{\Omega_+} f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r}, \mathbf{w}', t) d\Omega d\mathbf{w}, \quad (24)$$

and the collision term takes the final form

$$Q = \int_U \int_{\Omega_+} [f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r}, \mathbf{w}', t) - f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{w}, t)] d\Omega d\mathbf{w}, \quad (25)$$

in which  $\mathbf{v}'$  and  $\mathbf{w}'$  are given by (13).

- Result from 1<sup>st</sup> principles calculation (**Boltzmann collision integral**):

$$Q = \int_U \int_{\Omega_+} [f(\mathbf{r}, \mathbf{v}', t)f(\mathbf{r}, \mathbf{w}', t) - f(\mathbf{r}, \mathbf{v}, t)f(\mathbf{r}, \mathbf{w}, t)] d\Omega d\mathbf{w}, \quad (26)$$

- Result from BBGKY hierarchy:

$$Q = - \int_P \mathbf{a}(\mathbf{r} - \mathbf{s}) \cdot \nabla_{\mathbf{v}} f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{s}, \mathbf{w}, t) d\mathbf{s} d\mathbf{w}. \quad (27)$$

and after combination with the hard-sphere approximation:

$$Q = -\mathbf{A} \cdot \nabla_{\mathbf{v}} f, \quad \mathbf{A} = K \nabla n. \quad (28)$$

- The expressions are qualitatively different:
  - *The BBGKY/hard sphere  $Q$ 's are time reversible, while the Boltzmann collision integral changes sign when  $t \leftrightarrow -t$ .*
  - The BBGKY  $Q$  is exact, and the hard sphere approximation is very reasonable.
- Why is the (inexact) Boltzmann collision integral the one to go with? This has much to do with entropy and the 2nd law of thermodynamics, which is reflected in the H-Theorem, proved in the next lecture.

# Lecture 10: Conservation laws and Boltzmann's *H*-theorem

# Conservation laws

**Goal:** Derive macroscopic conservation laws for mass, momentum and energy for the solutions of the Boltzmann equation.

- **Why are we interested in conservation laws?**
  - Conservation laws are central building blocks for macroscopic continuum models
  - Together with the constitutive equations, they give rise to the governing equations.
- Example: Conservation of momentum for a fluid has the form

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = \nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{g},$$

where  $\rho$  and  $\mathbf{u}$  are the fluid density and momentum,  $\mathbf{g}$  the external force (e.g. gravity), and  $\boldsymbol{\sigma}$  the stress tensor.

- Constitutive equation for  $\boldsymbol{\sigma}$  for a Newtonian fluid ( $\mu$  viscosity,  $p$  pressure):

$$\sigma_{ij} = -p\delta_{ij} + \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$

The constitutive equations will also be derived from Boltzmann (later)!



Claim: Microscopic conservation of particle number, momentum and energy imply conservation laws for the macroscopic mass, momentum and energy density.

Three Steps:

- 1 Define averages  $\bar{\psi}$  and show that if

$$I = \int_U \psi(\mathbf{v}) Q d\mathbf{v} = 0. \quad (29)$$

is satisfied, then  $\bar{\psi}$  (to be defined) satisfies the conservation law

$$\frac{\partial(\rho\bar{\psi})}{\partial t} + \nabla \cdot (\rho\bar{\psi}\mathbf{u}) + \nabla \cdot \mathbf{J}_\psi = \overline{\rho\mathbf{g} \cdot \nabla_{\mathbf{v}}\psi}. \quad (30)$$

- 2 If (and only if)  $\psi(v)$  is **summational** or **collision invariant**,

$$\psi(\mathbf{v}') + \psi(\mathbf{w}') = \psi(\mathbf{v}) + \psi(\mathbf{w}) \quad (*),$$

(29) is satisfied.

- 3 For the three quantities  $\psi(\mathbf{v}) = 1$ ,  $\mathbf{v}$ ,  $\frac{1}{2}v^2$ , which satisfy (\*), the resulting (macroscopic) conservation laws are those for mass, momentum and energy.

# Step 1

## Averages over velocity space

- We define the number density of molecules  $n$  at a point in physical space to be

$$n = \int_U f d\mathbf{v}, \quad (31)$$

where we suppose  $f \rightarrow 0$  as  $|\mathbf{v}| \rightarrow \infty$ .

- If the molecules have mass  $m$ , then the density is defined as

$$\rho = mn. \quad (32)$$

- We also define the mean velocity by

$$n\mathbf{u} = \int_U f\mathbf{v} d\mathbf{v}, \quad (33)$$

- More generally, the mean  $\bar{\psi}$  of a quantity  $\psi$  is defined by

$$n\bar{\psi} = \int_U f\psi d\mathbf{v}. \quad (34)$$

# Step 1

## Evolution of the averages (1)

- We have the following identity:

$$\begin{aligned} \int_U \left[ \frac{\partial(f\psi)}{\partial t} + \nabla_{\mathbf{r}} \cdot (f\psi\mathbf{v}) + \nabla_{\mathbf{v}} \cdot (f\psi\mathbf{g}) \right] d\mathbf{v} = \\ \int_U \psi \left[ \frac{\partial f}{\partial t} + \nabla_{\mathbf{r}} \cdot (f\mathbf{v}) + \nabla_{\mathbf{v}} \cdot (f\mathbf{g}) \right] d\mathbf{v} \\ + \int_U f \left[ \frac{\partial \psi}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} \psi + \mathbf{g} \cdot \nabla_{\mathbf{v}} \psi \right] d\mathbf{v}. \quad (35) \end{aligned}$$

- On the left hand side, we remove the  $t$  and  $\mathbf{r}$  derivatives outside the integral, and apply the divergence theorem to the  $\mathbf{v}$  derivative, together with the (necessary) assumption  $f \rightarrow 0$  as  $|\mathbf{v}| \rightarrow \infty$ .
- If the body force per unit mass  $\mathbf{g} = \mathbf{g}(\mathbf{r})$  is independent of  $\mathbf{v}$ , the Boltzmann equation takes the form

$$\frac{\partial f}{\partial t} + \nabla_{\mathbf{r}} \cdot (f\mathbf{v}) + \nabla_{\mathbf{v}} \cdot (f\mathbf{g}) = Q, \quad (36)$$

which we apply to the first integral on the RHS of (35).

# Step 1

## Evolution of the averages (1)

- From this and (35) we obtain (after multiplying by  $m$ )

$$\frac{\partial(\rho\bar{\psi})}{\partial t} + \nabla \cdot (\rho\bar{\psi}\mathbf{u}) + \nabla \cdot \mathbf{J}_\psi = \int_U m\psi Q d\mathbf{v} + \rho \left[ \overline{\psi_t + \mathbf{v} \cdot \nabla \psi + \mathbf{g} \cdot \nabla_{\mathbf{v}} \psi} \right], \quad (37)$$

where

$$\mathbf{J}_\psi = \rho \overline{\psi \mathbf{u}'}, \quad (38)$$

is the molecular flux of  $\psi$ , the velocity fluctuations  $\mathbf{u}'$  are defined by

$$\mathbf{u}' = \mathbf{v} - \mathbf{u}, \quad (39)$$

and we have written  $\nabla = \nabla_{\mathbf{r}}$ .

- The averaged term on the right hand side is simplified if we suppose  $\psi$  depends only on  $\mathbf{v}$ , since then  $\psi_t = \nabla \psi = 0$ .
- This has the proper form for a conservation law for  $\psi$ , if the term containing  $Q$  vanishes.

## Step 2

Claim in Step 2:

We want to show (29) that the contribution from the collision term

$$I = \int_U \psi(\mathbf{v}) Q d\mathbf{v} = 0.$$

vanishes for all velocity distribution functions  $f$  if and only if  $\psi$  is a summational or collision invariant

$$\psi(\mathbf{v}') + \psi(\mathbf{w}') = \psi(\mathbf{v}) + \psi(\mathbf{w}),$$

## Step 2

### The collision term and summational invariants (1)

- Split  $I = I_+ - I_-$ , corresponding to  $Q = Q_+ - Q_-$ . Then

$$I_+ \equiv \int_U \psi(\mathbf{v}) Q_+ d\mathbf{v} = \int_{\Sigma} \psi(\mathbf{v}) f(\mathbf{v}'(\mathbf{v}, \mathbf{w})) f(\mathbf{w}'(\mathbf{v}, \mathbf{w})) d\Sigma, \quad (40)$$

where

$$f(\mathbf{v}) \equiv f(\mathbf{r}, \mathbf{v}, t), \quad \Sigma = U^2 \times \Omega_+, \quad \Omega_+ = \{\mathbf{k} \mid \mathbf{V} \cdot \mathbf{k} > 0\},$$

$$d\Sigma = d\Omega d\mathbf{w} d\mathbf{v}, \quad d\Omega = d^2\mathbf{k} \cdot \mathbf{V} d\omega(\mathbf{k}),$$

$$\mathbf{v}' = \mathbf{v} + (\mathbf{V} \cdot \mathbf{k})\mathbf{k}, \quad \mathbf{w}' = \mathbf{w} - (\mathbf{V} \cdot \mathbf{k})\mathbf{k}, \quad \mathbf{V} = \mathbf{w} - \mathbf{v}.$$

- We change variables from  $\mathbf{v}, \mathbf{w}$  to  $\mathbf{v}', \mathbf{w}'$  and define  $\mathbf{k}' = -\mathbf{k}$ .

Jacobian is one as earlier, recall  $\mathbf{V}' = \mathbf{w}' - \mathbf{v}'$  and  $\mathbf{V}' \cdot \mathbf{k} = -\mathbf{V} \cdot \mathbf{k}$ .

$$I_+ = \int_{U^2} \int_{\mathbf{V}' \cdot \mathbf{k}' > 0} \psi(\mathbf{v}(\mathbf{v}', \mathbf{w}')) f(\mathbf{v}') f(\mathbf{w}') d^2\mathbf{k}' \cdot \mathbf{V}' d\omega(\mathbf{k}') d\mathbf{w}' d\mathbf{v}',$$

where  $\mathbf{v} = \mathbf{v}' - (\mathbf{V} \cdot \mathbf{k})\mathbf{k} = \mathbf{v}' + (\mathbf{V}' \cdot \mathbf{k}')\mathbf{k}'$

- Relabelling  $\mathbf{v}'$  as  $\mathbf{v}$  and  $\mathbf{w}'$  as  $\mathbf{w}$  we get

$$I_+ = \int_{\Sigma} \psi(\mathbf{v}') f(\mathbf{v}) f(\mathbf{w}) d\Sigma. \quad (41)$$

## Step 2

### The collision term and summational invariants (2)

- Since  $I_- = \int_U \psi(\mathbf{v}) Q_- d\mathbf{v} = \int_\Sigma \psi(\mathbf{v}) f(\mathbf{v}) f(\mathbf{w})$ , we have
$$I = I_+ - I_- = \int_\Sigma [\psi(\mathbf{v}') - \psi(\mathbf{v})] f(\mathbf{v}) f(\mathbf{w}) d\Sigma. \quad (42)$$

- In (42), we now relabel  $\mathbf{v}$  as  $\mathbf{w}$  and vice-versa, and define  $\mathbf{k}' = -\mathbf{k}$ . Then  $\mathbf{v}' = \mathbf{v} + ((\mathbf{v} - \mathbf{w}) \cdot \mathbf{k})\mathbf{k}$  becomes  $\mathbf{w} + ((\mathbf{w} - \mathbf{v}) \cdot \mathbf{k})\mathbf{k}$  which is (cf. (13))  $\mathbf{w}'$ . Thus

$$I = \int_{U^2} \int_{\mathbf{V} \cdot \mathbf{k}' > 0} [\psi(\mathbf{w}') - \psi(\mathbf{w})] f(\mathbf{v}) f(\mathbf{w}) d^2\mathbf{k}' \cdot \mathbf{V} d\omega d\mathbf{w} d\mathbf{v}. \quad (43)$$

- Adding the two expressions (noting that  $\mathbf{k}'$  is a dummy variable),

$$2I = \int_\Sigma [\psi(\mathbf{v}') + \psi(\mathbf{w}') - \psi(\mathbf{v}) - \psi(\mathbf{w})] f(\mathbf{v}) f(\mathbf{w}) d\Sigma. \quad (44)$$

- It follows from this that (29), that is,  $I = 0$ , is satisfied identically if

$$\psi(\mathbf{v}') + \psi(\mathbf{w}') = \psi(\mathbf{v}) + \psi(\mathbf{w}), \quad (45)$$

Such  $\psi$  are called **summational** or **collision invariants**.

## Step 2

### The collision term and summational invariants (3)

It is also possible to show the reverse: if  $I = 0$  for all  $f$ , then  $\psi$  is a summational invariant.

- Define  $K(f, g)$  more generally as

$$K(f, g) = \frac{1}{2} \int_{\Sigma} [\psi(\mathbf{v}') + \psi(\mathbf{w}') - \psi(\mathbf{v}) - \psi(\mathbf{w})] f(\mathbf{v}) g(\mathbf{w}) d\Sigma.$$

- Obviously,  $K(f, f) = I = 0$  for all  $f$ , and  $K(f, g) = K(g, f)$ . Thus

$$0 = K(f+g, f+g) - K(f, f) - K(g, g) = K(f, g) + K(g, f) = 2K(g, f)$$

for all  $f, g$ .

- Taking now for example  $f$  and  $g$  to be e.g.  $\delta$ -functions, we see that  $[\psi(\mathbf{v}') + \dots]$  must be pointwise zero, and equation (45) follows.



# Step 3

Conservation laws for mass, momentum and energy.

It is straightforward to see that

$$\psi = 1, \mathbf{v}, \frac{1}{2}v^2. \quad (46)$$

are summational invariants. These and their linear combinations are in fact the only ones (shown later if time permits).

- For  $\psi = 1$ , we obtain the **conservation of mass** equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0. \quad (47)$$

- For  $\psi = \mathbf{v}$ , we obtain **conservation of momentum** in the form

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = \nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{g}, \quad (48)$$

$$\text{where the stress tensor is defined by } \boldsymbol{\sigma} = -\rho \overline{\mathbf{u}' \mathbf{u}'}, \quad (49)$$

- For  $\psi = \frac{1}{2}v^2$ , we obtain **energy conservation:**

$$\frac{\partial}{\partial t} \left( \frac{1}{2} \rho u^2 + \rho e \right) + \nabla \cdot \left[ \left( \frac{1}{2} \rho u^2 + \rho e \right) \mathbf{u} \right] = -\nabla \cdot \mathbf{q} + \nabla \cdot (\boldsymbol{\sigma} \cdot \mathbf{u}) + \rho \mathbf{g} \cdot \mathbf{u}, \quad (50)$$

$$\text{where the internal energy/unit mass is defined by } e = \frac{1}{2} \overline{u'^2}, \quad (51)$$

$$\text{and the conductive heat flux is } \mathbf{q} = \frac{1}{2} \rho \overline{u'^2 \mathbf{u}'}. \quad (52)$$

# A note on the kinetic theory of gases

- Derivation of the collision integral assumes that between molecules,  $l \gg d$ , the molecular diameter, as in **gases**. (For **liquids**: The collision integral is different and internal energy needs to include contribution of intermolecular forces.)
- Internal energy per molecule is related to the temperature by

$$\frac{1}{2}m\overline{u'^2} = \frac{3}{2}kT, \quad (53)$$

where  $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$  is Boltzmann's constant.

- In addition, we define the pressure in the usual way as

$$p = -\frac{1}{3}\sigma_{kk} = \frac{1}{3}\rho\overline{u'^2}, \quad (54)$$

- From this, we can derive the ideal gas law

$$p = nkT = \frac{\rho RT}{M}, \quad (55)$$

where the ideal gas constant & the molecular weight are defined by, resp.,

$$R = kA, \quad M = Am, \quad (56)$$

( $A = 6 \times 10^{23}$  Avogadro's number.)

# Lecture 10, Part 2

## The H-theorem

- Why is Boltzmann's famous  $H$ -theorem so central?
- It shows that

$$H = \int_U f \ln f d\mathbf{v}.$$

is *non-increasing* over time.

- The form and role of this quantity strongly resembles the entropy in thermodynamics/equilibrium statistical mechanics. (Entropy is non-decreasing due to a different sign convention.)
- In particular, it fixes the arrow of time and shows that the system of particles relaxes to an equilibrium distribution, the **Maxwell distribution**.

# Derivation of Boltzmann's $H$ -theorem

- Now suppose that  $f$  is slowly varying in  $\mathbf{r}$ , but may depend on  $t$ .

$$\text{Define } H = \int_U f \ln f \, d\mathbf{v}. \quad (57)$$

- Using the identity (35) with  $\psi = \ln f$  gives

$$\int_U \left[ \frac{\partial(f \ln f)}{\partial t} + \nabla_{\mathbf{r}} \cdot (f \ln f \mathbf{v}) + \nabla_{\mathbf{v}} \cdot (f \ln f \mathbf{g}) \right] d\mathbf{v} = \\ \int_U Q \ln f \, d\mathbf{v} + \int_U f \left[ \frac{\partial \ln f}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} \ln f + \mathbf{g} \cdot \nabla_{\mathbf{v}} \ln f \right] d\mathbf{v}.$$

- Evaluating the derivatives of  $\ln$  in the last integral gives  $\int_U Q$ . Other  $\mathbf{r}$  derivatives are dropped. The term in the first integral involving  $\mathbf{g}$  vanishes identically by an application of

$$\int_U \nabla_{\mathbf{v}} G \, d\mathbf{v} = \int_{\partial U} G \mathbf{n} \, dS = 0, \quad \text{if } G \rightarrow 0 \text{ as } |\mathbf{v}| \rightarrow \infty. \quad (58)$$

- Thus

$$\dot{H} = \int_U (1 + \ln f) Q \, d\mathbf{v} \quad (59)$$

## Derivation of Boltzmann's $H$ -theorem (2)

Note the last integral has the form  $\int_U \psi \ln f d\mathbf{v}$ ,  $\psi = (1 + \ln f)$ . We go back to (44), which we write in the form

$$\int_U \psi(\mathbf{v})Q d\mathbf{v} = \frac{1}{2} \int_{\Sigma} \Delta\psi(\mathbf{v}, \mathbf{w})f(\mathbf{v})f(\mathbf{w}) d\Sigma, \quad (60)$$

where

$$\Delta\psi \equiv \psi(\mathbf{v}') + \psi(\mathbf{w}') - \psi(\mathbf{v}) - \psi(\mathbf{w}). \quad (61)$$

In the integral, we change variables from  $\mathbf{v}, \mathbf{w}$  to  $\mathbf{v}', \mathbf{w}'$ , and in addition we define  $\mathbf{k}' = -\mathbf{k}$ . We then change the dummy labelling between the primed and unprimed variables, noting (13) and its inverses; the result is

$$\int_U \psi(\mathbf{v})Q d\mathbf{v} = -\frac{1}{2} \int_{\Sigma} \Delta\psi(\mathbf{v}, \mathbf{w})f(\mathbf{v}')f(\mathbf{w}') d\Sigma. \quad (62)$$

Adding the two results, we obtain

$$\int_U \psi(\mathbf{v})Q d\mathbf{v} = \frac{1}{4} \int_{\Sigma} \Delta\psi(\mathbf{v}, \mathbf{w})[f(\mathbf{v})f(\mathbf{w}) - f(\mathbf{v}')f(\mathbf{w}')] d\Sigma. \quad (63)$$

## Derivation of Boltzmann's $H$ -theorem (3)

- Applying (63) gives

$$\dot{H} = \frac{1}{4} \int_{\Sigma} \ln \left[ \frac{f(\mathbf{v}')f(\mathbf{w}')}{f(\mathbf{v})f(\mathbf{w})} \right] [f(\mathbf{v})f(\mathbf{w}) - f(\mathbf{v}')f(\mathbf{w}')] d\Sigma. \quad (64)$$

- Since  $f > 0$  and  $(1 - \zeta) \ln \zeta \leq 0$ , it follows that  $\dot{H} \leq 0$ .
- In addition,  $H$  is bounded from below, and thus  $H \rightarrow \text{const}$ , i.e.  $\dot{H} \rightarrow 0$ .
- For  $\dot{H} = 0$ , since the integrand is always  $\leq 0$  and vanishes only if  $f(\mathbf{v})f(\mathbf{w}) = f(\mathbf{v}')f(\mathbf{w}')$ , we necessarily have

$$\Delta \ln f = 0. \quad (65)$$

This defines the equilibrium state to which  $f$  converges.

This is **Boltzmann's  $H$ -theorem**.

- The state  $\dot{H} = 0$  defines an equilibrium distribution, called the **Maxwellian distribution**.

# Maxwellian distribution

- (65) means that  $\ln f$  is a summational invariant, thus  $\ln f$  must be a linear combination of the three summational invariants in (46), i. e.,

$$f = A \exp[\mathbf{B} \cdot \mathbf{v} - \frac{1}{2} C v^2], \quad (66)$$

or equivalently, completing the square,

$$f = \hat{A} \exp[-\frac{1}{2} C |\mathbf{v} - \hat{\mathbf{v}}|^2]. \quad (67)$$

- We can now determine the constants in terms of the mean number density, velocity, and temperature, defined, using (31), (33) and (53), by

$$n = \int_U f d\mathbf{v}, \quad n\mathbf{u} = \int_U f \mathbf{v} d\mathbf{v}, \quad \frac{nkT}{m} = \frac{1}{3} \int_U f |\mathbf{v} - \mathbf{u}|^2 d\mathbf{v}. \quad (68)$$

- Carrying out the calculations, we find

$$\hat{\mathbf{v}} = \mathbf{u}, \quad C = \frac{m}{kT}, \quad \hat{A} = n \left( \frac{m}{2\pi kT} \right)^{3/2}. \quad (69)$$



## Maxwellian distribution (2)

Thus

$$f = n \left( \frac{m}{2\pi kT} \right)^{3/2} \exp \left[ -\frac{m u'^2}{2kT} \right]. \quad (70)$$

This is the Maxwellian distribution, a Gaussian in the velocity fluctuation  $\mathbf{u}'$ . Note that (70) can be written in the form

$$f = \frac{n}{(2\pi c^2)^{3/2}} \exp \left[ -\frac{u'^2}{2c^2} \right], \quad (71)$$

where

$$c = \sqrt{\frac{kT}{m}} = \sqrt{\frac{RT}{M}} = \sqrt{\frac{\bar{p}}{\rho}} \quad (72)$$

is the isothermal sound speed.

# Lecture 11: A continuum limit: The Chapman-Enskog Method (I)

- Derive constitutive relations from the Boltzmann equation.
- Derive expressions for the viscosity and thermal conductivity.

- The terms in the conservation of mass, momentum and energy equations which need to be specified are the stress tensor and the conductive heat flux.
- Recall from (49) and (52) that these are

$$\boldsymbol{\sigma} = -\overline{\rho \mathbf{u}' \mathbf{u}'}, \quad \mathbf{q} = \frac{1}{2} \overline{\rho u'^2 \mathbf{u}'}. \quad (73)$$

- If we use the Maxwellian distribution for  $f$  to provide expressions for these, we find

$$\boldsymbol{\sigma} = -p\mathbf{I}, \quad \mathbf{q} = \mathbf{0}; \quad (74)$$

hardly surprising, since our assumption of spatial independence implies uniform temperature and velocity.

# The approach

- Thus in order to compute viscosity and thermal conductivity, we must consider corrections to the equilibrium Maxwellian distribution due to variation of  $f$  with  $\mathbf{r}$
- Assume that the **mean free path**  $l_f$  is much smaller than the typical macroscopic size  $L$  of the system (e.g. the “box”).

Systematic approach through the **Chapman–Enskog method**:  
Expand in terms of  $\varepsilon = \text{Kn} = l_f/L$ .  $\text{Kn}$  is the **Knudsen-number**.

Obtaining corrections to the Maxwellian equilibrium distribution in the small mean free path limit will be done in the following steps:

- Part 1 (this part): Nondimensionalisation.
- Part 1 (this part): Expansion in terms of the Knudsen number giving to leading order a slowly varying Maxwellian distribution.
- Part 2: Derivation of the first order correction to the Maxwellian distribution.

In **Lecture 12**: Derivation of the constitutive relations for the stress and the heat flux using the first order correction of the Maxwellian.

# Non-dimensionalisation – Estimates

- Let the typical scales for the macroscopic variables  $n$ ,  $T$  be  $n_0$ ,  $T_0$
- The typical fluctuation velocity scale  $v_0$  for  $u$  is given by

$$v_0 = \sqrt{\frac{kT_0}{m}}. \quad (75)$$

- The particle number density scale  $n_0$  defines a mean inter-particle distance

$$l = \frac{1}{n_0^{1/3}}. \quad (76)$$

- The intermolecular potential varies over an interaction distance which we may take to be the molecular diameter  $d$ . The hard sphere gas assumption presumes  $d \ll l$ .

## Non-dimensionalisation – Estimates (2)

- The inter-particle length  $l$  is much less than the **mean free path**  $l_f$ , which is the typical distance a particle progresses between collisions.
- A single particle travelling in its domain of cross-sectional area  $l^2$  encounters another particle every distance  $l$ , but typically not in the same position. Looking ahead of itself, it needs to encounter  $\sim (l/d)^2$  particles (which thus cover the cross section), before it is likely to collide with one. The mean free path is thus

$$l_f \sim \frac{l^3}{d^2} = \frac{1}{n_0 d^2}. \quad (77)$$

[Chapman and Cowling (1970, p. 88) use a more elaborate calculation to show that  $l_f = \frac{1}{\pi\sqrt{2}n_0d^2}$ .]

- We can also define a corresponding mean free time between collisions,

$$t_f = \frac{l_f}{v_0}, \quad (78)$$

and a mean collision time

$$t_c = \frac{d}{v_0}. \quad (79)$$



# Non-dimensionalisation – The resulting scalings

- We non-dimensionalise the variables as

$$\begin{aligned}n &\sim n_0, & f &\sim \frac{n_0}{v_0^3}, & Q &\sim \frac{n_0^2 d^2}{v_0^2}, & \mathbf{r} &\sim L, \\ \mathbf{v} &\sim v_0, & \mathbf{g} &\sim g, & t &\sim \frac{L}{v_0}, & T &\sim T_0,\end{aligned}\tag{80}$$

- The Boltzmann equation (36) with (25) takes the dimensionless form

$$\begin{aligned}\varepsilon \left[ \frac{\partial f}{\partial t} + \nabla_{\mathbf{r}} \cdot (f \mathbf{v}) + \frac{1}{F^2} \nabla_{\mathbf{v}} \cdot (f \mathbf{g}) \right] &= Q, \\ Q = \int_U \int_{\Omega_+} [f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r}, \mathbf{w}', t) - f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{w}, t)] d\Omega d\mathbf{w}.\end{aligned}\tag{81}$$

- Here

$$F = \frac{v_0}{\sqrt{gL}}, \quad \varepsilon = \frac{l_f}{L} = \frac{1}{n_0 d^2 L}.\tag{82}$$

- $F \gg 1$  is a kind of Froude number (Mach number  $\times$  Froude number)
- The parameter  $\varepsilon \ll 1$  is known as the Knudsen number  $Kn$ .  
 $\implies$  Develop a perturbative solution when  $f$  also depends on  $\mathbf{r}$ .

# A multi-scale expansion

- We write the material derivative of  $f$  in  $P = V \times U$  as  $\dot{f}$ , so that the dimensionless Boltzmann equation in (81) is just

$$\varepsilon \dot{f} = Q(f, f). \quad (83)$$

- Here it is now useful to define the collision integral  $Q$  in terms of the symmetric bilinear operator

$$Q(f, g)(\mathbf{v}) = \frac{1}{2} \int_U \int_{\Omega_+} [f(\mathbf{v}')g(\mathbf{w}') + f(\mathbf{w}')g(\mathbf{v}') - f(\mathbf{v})g(\mathbf{w}) - f(\mathbf{w})g(\mathbf{v})] d\Omega d\mathbf{w}. \quad (84)$$

- By putting

$$f = e^\Phi, \quad (85)$$

(83) can be written in the form

$$\varepsilon \dot{\Phi} = \int_U \int_{\Omega_+} [\exp(\Delta\Phi) - 1] f(\mathbf{w}) d\Omega d\mathbf{w}. \quad (86)$$

# A multi-scale expansion – The leading order solution

- We expand the solution as

$$\Phi = \Phi_0 + \varepsilon\phi + \dots \quad (87)$$

- To leading order

$$0 = \int_U \int_{\Omega_+} [\exp(\Delta\Phi_0) - 1] f(\mathbf{w}) d\Omega d\mathbf{w}.$$

or 
$$0 = Q(f_0, f_0), \quad f_0 \equiv \exp(\Phi_0).$$

- Treating the latter as in the  $H$ -theorem, gives (64) but with out the time derivative and with  $f_0$  instead of  $f$ .

Thus, to leading order,  $\Delta\Phi_0 = 0$ , i.e.  $f_0$ =Maxwellian.

- This gives the Maxwellian distribution  $f_0$  in dimensionless form , so that

$$\Phi_0 = \ln \left[ \frac{n^*}{(2\pi T^*)^{3/2}} \right] - \frac{u'^2}{2T^*}, \quad \mathbf{u}' = \mathbf{v} - \mathbf{u}, \quad (88)$$

where  $n^*$ ,  $T^*$  and  $\mathbf{u}$  can now depend on  $t$  and  $\mathbf{r}$  (but not on  $\mathbf{v}$ ).

**Lecture 11, Part 2**  
**Derivation of the first order correction to the Maxwellian  
distribution.**

## Reminder of the problem setting

$$\varepsilon \dot{f} = Q(f, f). \quad (\text{cf. 83})$$

By putting

$$f = e^\Phi, \quad (\text{cf. 85})$$

(83) can be written in the form

$$\varepsilon \dot{\Phi} = \int_U \int_{\Omega_+} [\exp(\Delta \Phi) - 1] f(\mathbf{w}) d\Omega d\mathbf{w}. \quad (\text{cf. 86})$$

We expand the solution as

$$\Phi = \Phi_0 + \varepsilon \phi + \dots \quad (\text{cf. 87})$$

# Formulation of the next order correction problem

- To next order, we have the linear equation

$$\mathcal{L}\phi = \dot{\Phi}_0, \quad (89)$$

where we define the linear integral operator

$$\mathcal{L}\phi = \int_U \int_{\Omega_+} f_0(\mathbf{w}) \Delta\phi \, d\Omega \, d\mathbf{w}, \quad (90)$$

where here  $f_0 = e^{\Phi_0}$  is the Maxwellian.

- (89) is a linear Fredholm integral equation, and can be treated using standard methods, which we do now.
- Alternatively, by direct calculation from (83),

$$\dot{\Phi}_0 \exp(\Phi_0) = 2Q(f_0, f_0\phi), \quad \text{thus } \mathcal{L}\phi = \frac{2}{f_0}Q(f_0, f_0\phi). \quad (91)$$

# Overview (of solution steps)

We want to solve

$$\mathcal{L}\phi = \dot{\Phi}_0. \quad [\text{see (89)}]$$

- 1 We define an inner product as (overbar denote c.c.)

$$\langle \phi, \psi \rangle = \int_U f_0(\mathbf{v}) \phi(\mathbf{v}) \bar{\psi}(\mathbf{v}) d\mathbf{v}$$

and show that  $\mathcal{L}$  is self adjoint with respect to  $\langle \cdot, \cdot \rangle$

- 2 The null space of  $\mathcal{L}$  is  $\mathcal{N} = \text{span}\{1, \mathbf{v}, \frac{1}{2}v^2\}$ .
- 3 Therefore the integral equation (89) only has solutions if

$$\langle \dot{\Phi}_0, \eta \rangle = 0 \quad (92)$$

for all  $\eta \in \mathcal{N}$  of  $\mathcal{L}$  (Fredholm Alternative). Applying (92) recovers the conservation laws.

- 4 We can now find the solution(s)  $\phi$  of (89).

# Overview (of solution steps)

We want to solve

$$\mathcal{L}\phi = \dot{\Phi}_0. \quad [\text{see (89)}]$$

- 1 We define an inner product as (overbar denote c.c.)

$$\langle \phi, \psi \rangle = \int_U f_0(\mathbf{v}) \phi(\mathbf{v}) \bar{\psi}(\mathbf{v}) d\mathbf{v}$$

and show that  $\mathcal{L}$  is self adjoint with respect to  $\langle \cdot, \cdot \rangle$

- 2 The null space of  $\mathcal{L}$  is  $\mathcal{N} = \text{span}\{1, \mathbf{v}, \frac{1}{2}v^2\}$ .
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$$\langle \dot{\Phi}_0, \eta \rangle = 0 \quad (92)$$

for all  $\eta \in \mathcal{N}$  of  $\mathcal{L}$  (Fredholm Alternative). Applying (92) recovers the conservation laws.

- 4 We can now find the solution(s)  $\phi$  of (89).



# Proof that $\mathcal{L}$ is self adjoint

- Consider the integral

$$I = \int_U \psi(\mathbf{v}) Q(f, g)(\mathbf{v}) d\mathbf{v}, \quad (93)$$

using the definition of  $Q$  in (84).

- By relabelling the arguments in (93), and adding the results, we obtain the relation

$$I = \frac{1}{8} \int_{\Sigma} \Delta\psi [f(\mathbf{v})g(\mathbf{w}) + f(\mathbf{w})g(\mathbf{v}) - f(\mathbf{v}')g(\mathbf{w}') - f(\mathbf{w}')g(\mathbf{v}')] d\Sigma.$$

- Now we plug  $f = f_0$ ,  $g = f_0\phi$  into this (and use (91)) to get

$$\int_U f_0(\mathbf{v})\psi(\mathbf{v})\mathcal{L}\phi(\mathbf{v}) d\mathbf{v} = -\frac{1}{4} \int_{\Sigma} f_0(\mathbf{v})f_0(\mathbf{w})\Delta\psi\Delta\phi d\Sigma, \quad (94)$$

and because of the symmetry of this last expression, we also have

$$\int_U f_0(\mathbf{v})\psi(\mathbf{v})\mathcal{L}\phi(\mathbf{v}) d\mathbf{v} = \int_U f_0(\mathbf{v})\phi(\mathbf{v})\mathcal{L}\psi(\mathbf{v}) d\mathbf{v}, \quad (95)$$

$$\text{i.e.} \quad \langle \psi, \mathcal{L}\phi \rangle = \langle \mathcal{L}\psi, \phi \rangle \quad (96)$$

- $\mathcal{L}$  is self-adjoint!

# Overview (of solution steps)

We want to solve

$$\mathcal{L}\phi = \dot{\Phi}_0. \quad [\text{see (89)}]$$

- 1 We define an inner product as (overbar denote c.c.)

$$\langle \phi, \psi \rangle = \int_U f_0(\mathbf{v}) \phi(\mathbf{v}) \bar{\psi}(\mathbf{v}) d\mathbf{v}$$

and show that  $\mathcal{L}$  is self adjoint with respect to  $\langle \cdot, \cdot \rangle$

- 2 **The null space of  $\mathcal{L}$  is  $\mathcal{N} = \text{span}\{1, \mathbf{v}, \frac{1}{2}v^2\}$ .**
- 3 Therefore the integral equation (89) only has solutions if

$$\langle \dot{\Phi}_0, \eta \rangle = 0 \quad (*)$$

for all  $\eta \in \mathcal{N}$  of  $\mathcal{L}$  (Fredholm Alternative). Applying (\*) recovers the conservation laws.

- 4 We can now find the solution(s)  $\phi$  of (89).

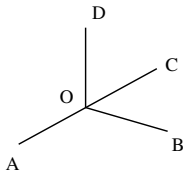
## Determining the null space of $\mathcal{L}$ .

- We now show that  $\mathcal{N} \equiv \{\eta : \mathcal{L}\eta = 0\} = \text{span}\{1, \mathbf{v}, \frac{1}{2}v^2\} \equiv \mathcal{S}$ .
- If  $\phi \in \mathcal{S}$ , then we know (from Lecture 10) that  $\Delta\phi = 0$ . Then from the first definition of  $\mathcal{L}$  (in (90)) we know  $\mathcal{L}\phi = 0$ , that is,  $\phi \in \mathcal{N}$ .
- The main task is to show the reverse inclusion: That  $\mathcal{S}$  already contains ALL the null space of  $\mathcal{L}$ :  $\mathcal{N} \subset \mathcal{S}$ .
- First, in view of (94), we see that

$$\langle \phi, \mathcal{L}\phi \rangle \leq 0, \quad (97)$$

- Equality holds in (97) if and only if  $\Delta\phi = 0$ , i.e. if  $\phi$  is a summational invariant.
- Implication: If  $\phi \in \mathcal{N}$ , then  $\phi$  is a summational invariant. Therefore, all we need to show is that  $\mathcal{S}$  contains all summational invariants i.e. any  $\phi$  that satisfies  $\Delta\phi = 0$ .
- In doing this, we also fulfill a promise we made in Lecture 10: That all summational invariants are contained in  $\text{span}\{1, \mathbf{v}, \frac{1}{2}v^2\}$ .

## Determining the null space of $\mathcal{L}$ (2)



- Suppose  $\phi$  is a summational invariant with  $\phi = 0$  on the five points  $O: (0, 0, 0)$ ,  $A: (0, -1, 0)$ ,  $B: (1, 0, 0)$ ,  $C: (0, 1, 0)$  and  $D: (0, 0, 1)$
- Since  $\phi = 0$  on three points of the square spanned by  $OBC$ , then  $\phi = 0$  on the fourth, that is at  $(1, 1)$  (say  $\equiv E$ ). Suppressing the third coordinate, let  $\mathbf{v} = (1, 0) = B$  and  $\mathbf{w} = (0, 1) = C$ . For  $\mathbf{k} = (1, 0)$  we get

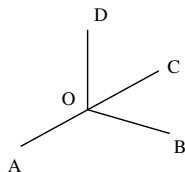
$$\mathbf{v}' = (1, 0) + [(-1, 1) \cdot \mathbf{k}] \mathbf{k} = (0, 0) = O,$$

$$\mathbf{w}' = (0, 1) - [(-1, 1) \cdot \mathbf{k}] \mathbf{k} = (1, 1) = E,$$

thus  $\phi(E) = \phi(\mathbf{w}') = -\phi(\mathbf{v}') + \phi(\mathbf{v}) + \phi(\mathbf{w}) = 0$ .

- Thus, repeating for further squares, we get  $\phi = 0$  on all points of the cuboid spanned by  $OABCD$ .

## Determining the null space of $\mathcal{L}$ (3)



- Let  $\mathbf{v} = A = (0, -1)$ ,  $\mathbf{w} = C = (0, 1)$ , and  $\mathbf{k} = (-1, -1)/\sqrt{2}$ . Then

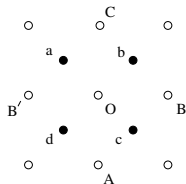
$$\mathbf{v}' = (0, -1) + [(0, 2) \cdot \mathbf{k}] \mathbf{k} = (1, 0) = B,$$

$$\mathbf{w}' = (0, -1) - [(0, 2) \cdot \mathbf{k}] \mathbf{k} = (-1, 0) = -B,$$

Thus, if  $B' \equiv -B$ , we have  $\phi(B') = \phi(A) + \phi(C) - \phi(B) = 0$ .

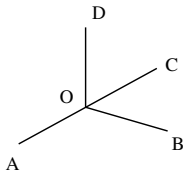
- Using the argument of the previous slide, we can now conclude  $\phi = 0$  on the reflected cuboid spanned by  $OAB'CD$ .
- Repeating reflections shows that  $\phi = 0$  on  $\mathbb{Z} \times \mathbb{Z} \times \mathbb{Z}$ .

## Determining the null space of $\mathcal{L}$ (4)



- Next we consider a square grid as shown in the figure, with an interior square  $abcd$ .
- We then have  $\phi_a + \phi_b = 0$  (by consideration of the square  $OaCb$ ), and similarly  $\phi_b + \phi_c = 0$ ,  $\phi_c + \phi_d = 0$ ,  $\phi_a + \phi_d = 0$ .
- Thus  $\phi = 0$  at all four points, and hence at all points of the subdivided grid in  $U$ .
- The subdivision can be iterated indefinitely, with the consequence that if  $\phi$  is continuous, then it is identically zero.

# Determining the null space of $\mathcal{L}$ (5)



- Finally, suppose that  $\phi$  is summational and continuous.
- We can uniquely choose (five) coefficients  $a$ ,  $\mathbf{b}$  and  $c$  so that the function

$$\psi = a + \mathbf{b} \cdot \mathbf{v} + \frac{1}{2}cv^2 \in \mathcal{S} \quad (98)$$

is equal to  $\phi$  at  $O$ ,  $A$ ,  $B$ ,  $C$  and  $D$ .

- Then  $\phi - \psi$  is summational, and  $\phi - \psi = 0$  at the five points.
- Thus, from the previous  $\phi - \psi = 0$  everywhere, therefore  $\phi = \psi \in \mathcal{S}$ .
- Notice that in showing that  $\mathcal{S}$  contains all summational invariants, we have fulfilled our promise in Lecture 10 (below eqn. (45)).

# Overview (of solution steps)

We want to solve

$$\mathcal{L}\phi = \dot{\Phi}_0. \quad [\text{see (89)}]$$

- ① We define an inner product as (overbar denote c.c.)

$$\langle \phi, \psi \rangle = \int_U f_0(\mathbf{v}) \phi(\mathbf{v}) \bar{\psi}(\mathbf{v}) d\mathbf{v} \quad (99)$$

and show that  $\mathcal{L}$  is self adjoint with respect to  $\langle \cdot, \cdot \rangle$

- ② The null space of  $\mathcal{L}$  is  $\mathcal{N} = \text{span}\{1, \mathbf{v}, \frac{1}{2}v^2\}$ .

- ③ **Therefore the integral equation (89) only has solutions if**

$$\langle \dot{\Phi}_0, \eta \rangle = 0 \quad (*)$$

**for all  $\eta \in \mathcal{N}$  of  $\mathcal{L}$  (Fredholm Alternative). Applying (\*) recovers the conservation laws.**

- ④ We can now find the solution(s)  $\phi$  of (89).



# Applying the solvability condition

- We now calculate  $\dot{\Phi}_0$ , and split it into contributions from  $\mathcal{N}$  and  $\mathcal{N}_\perp$ .
- From (88), we have that

$$\Phi_0 = A - \frac{1}{2}Cu'^2, \quad \mathbf{u}' = \mathbf{v} - \mathbf{u}, \quad (100)$$

where

$$A = \ln \left[ \frac{n^*}{(2\pi T^*)^{3/2}} \right], \quad C = \frac{1}{T^*}, \quad \mathbf{u}, \quad (101)$$

are functions of  $\mathbf{r}$  and  $t$  but not of  $\mathbf{v}$ .

- The calculation then yields

$$\dot{\Phi}_0 = \Phi_{\mathcal{N}} - \mathbf{W} \cdot \nabla C + CU_{ij} \frac{\partial u_i}{\partial x_j}, \quad (102)$$

where

$$\Phi_{\mathcal{N}} = \frac{dA}{dt} + \mathbf{u}' \cdot \left[ \nabla A - \frac{C\mathbf{g}}{F^2} + C \frac{d\mathbf{u}}{dt} - \frac{5}{2}T^* \nabla C \right]$$
$$+ \frac{1}{2}u'^2 \left[ \frac{2}{3}C \nabla \cdot \mathbf{u} - \frac{dC}{dt} \right],$$

and

$$\mathbf{W} = \left( \frac{1}{2}u'^2 - \frac{5}{2}T^* \right) \mathbf{u}', \quad U_{ij} = u'_i u'_j - \frac{1}{3}u'^2 \delta_{ij}. \quad (103)$$

- Note that

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla, \quad \dot{\Phi}_0 = \frac{\partial \Phi_0}{\partial t} + \mathbf{v} \cdot \nabla \Phi_0 + \frac{g \cdot \nabla_{\mathbf{v}} \Phi_0}{F^2}.$$

## Applying the solvability condition (2)

Reminder: The previous equations are

$$\dot{\Phi}_0 = \Phi_{\mathcal{N}} - \mathbf{W} \cdot \nabla C + CU_{ij} \frac{\partial u_i}{\partial x_j}, \quad (\text{cf. 102})$$

$$\Phi_{\mathcal{N}} = \frac{dA}{dt} + \mathbf{u}' \cdot \left[ \nabla A - \frac{C\mathbf{g}}{F^2} + C \frac{d\mathbf{u}}{dt} - \frac{5}{2} T^* \nabla C \right] \\ + \frac{1}{2} u'^2 \left[ \frac{2}{3} C \nabla \cdot \mathbf{u} - \frac{dC}{dt} \right],$$

$$\mathbf{W} = \left( \frac{1}{2} u'^2 - \frac{5}{2} T^* \right) \mathbf{u}', \quad U_{ij} = u'_i u'_j - \frac{1}{3} u'^2 \delta_{ij}. \quad (\text{cf. 103})$$

- 
- The term  $\Phi_{\mathcal{N}}$  lies in the null space of  $\mathcal{L}$
  - One can show that  $\mathbf{W}$  and  $\mathbf{U}$  are orthogonal to  $\mathcal{N}$  & to each other.
  - Therefore the solvability condition  $\langle \dot{\Phi}_0, \eta \rangle = 0$  (see (92)) requires  $\Phi_{\mathcal{N}} = 0$ .
  - One can show that this, in fact, recovers the conservation laws derived in Lecture 10.

# Overview (of solution steps)

We want to solve

$$\mathcal{L}\phi = \dot{\Phi}_0. \quad [\text{see (89)}]$$

- 1 We define an inner product as (overbar denote c.c.)

$$\langle \phi, \psi \rangle = \int_U f_0(\mathbf{v}) \phi(\mathbf{v}) \bar{\psi}(\mathbf{v}) d\mathbf{v}$$

and show that  $\mathcal{L}$  is self adjoint with respect to  $\langle \cdot, \cdot \rangle$

- 2 The null space of  $\mathcal{L}$  is  $\mathcal{N} = \text{span}\{1, \mathbf{v}, \frac{1}{2}v^2\}$ .
- 3 Therefore the integral equation (89) only has solutions if

$$\langle \dot{\Phi}_0, \eta \rangle = 0 \quad (*)$$

for all  $\eta \in \mathcal{N}$  of  $\mathcal{L}$  (Fredholm Alternative). Applying (\*) recovers the conservation laws.

- 4 **We can now find the solution(s)  $\phi$  of (89).**

# Solution for $\phi$

- A particular solution we seek of

$$\mathcal{L}\phi = -\mathbf{W} \cdot \nabla C + CU_{ij} \frac{\partial u_i}{\partial x_j}. \quad (89)$$

can be written as

$$\phi = -\boldsymbol{\xi} \cdot \nabla C + C\boldsymbol{\eta} : \nabla \mathbf{u}, \quad (104)$$

where

$$\mathcal{L}\boldsymbol{\xi} = \mathbf{W}, \quad \mathcal{L}\boldsymbol{\eta} = \mathbf{U}. \quad (105)$$

- The solutions of (105) have the form

$$\boldsymbol{\xi} = -F(u')\mathbf{u}', \quad \boldsymbol{\eta} = -G(u')\mathbf{U}. \quad (106)$$

- Without loss of generality we may choose  $\boldsymbol{\xi}, \boldsymbol{\eta} \perp \mathcal{N}$  (which thus specifies them uniquely), as contributions of elements from  $\mathcal{N}$  to  $\phi$  can always be moved to  $\Phi_0$ .
- One can find approximate expressions for  $F$  and  $G$ , but we do not pursue that here.
- A derivation of (106) will be sketched next.

# Derivation of the form (106) for $\xi$ and $\eta$

For the problem (see (105), (105))

$$\mathcal{L}\xi = \mathbf{W} = \left(\frac{1}{2}u'^2 - \frac{5}{2}T^*\right) \mathbf{u}'$$

we will now discuss our claim that the solution has the form

$$\xi = -F(u')\mathbf{u}'. \quad (\text{cf. 106})$$

- The justification of (106) is not so easy to deduce. It relies on a certain rotational invariance of the operator  $\mathcal{L}$ .
- We write (90) in the form

$$\mathcal{L}\phi = \int_U f_0(w) \left[ \int_{\Omega_+} \Delta\phi(\mathbf{v}, \mathbf{w}, \mathbf{\Omega}) d\Omega \right] d\mathbf{w}, \quad (107)$$

which recognises that the Maxwellian is a function of the magnitude of  $\mathbf{w}$ , and that  $\Delta\phi$  is a function of both  $\mathbf{v}$  and  $\mathbf{w}$ , which together define the sphere spanned by  $\mathbf{\Omega}$ , as well as the direction element  $\mathbf{\Omega}$ .

- Now suppose that

$$\phi = g(v)\mathbf{v}; \quad (108)$$

thus  $\mathcal{L}\phi$  is a vector.

## Derivation of the form (106) for $\xi$ and $\eta$ (continued)

- Let us consider the effect of a rotation about the  $\mathbf{v}$  axis on  $\mathcal{L}\phi$ , that is, we multiply  $\mathcal{L}\phi$  by a matrix  $R$  which is orthogonal, and which satisfies  $R\mathbf{v} = \mathbf{v}$  (hence also  $\mathbf{v} = R^T\mathbf{v}$ ).

- If we define

$$\mathbf{w} = R^T \mathbf{w}^*, \quad \mathbf{k} = R^T \mathbf{k}^*, \quad (109)$$

then

$$\mathbf{v}' = R^T \mathbf{v}^{*'}, \quad \mathbf{w}' = R^T \mathbf{w}^{*'}, \quad (110)$$

and thus

$$\Delta\phi(\mathbf{v}, \mathbf{w}, \Omega) = \Delta\phi(\mathbf{v}, R^T \mathbf{w}^*, R^T \Omega^*) = R^T \Delta\phi(\mathbf{v}, \mathbf{w}^*, \Omega^*), \quad (111)$$

where  $\Omega^*$  is the direction element associated with  $\mathbf{k}^*$ .

- The direction sphere  $\Omega_+$  is unaffected by the transformation, since  $\mathbf{V} \cdot \mathbf{k} = \mathbf{V}^* \cdot \mathbf{k}^*$ , as are the volume element and the Maxwellian.
- It then follows that if we change variable to  $\mathbf{w}^*$  in (107),

$$R\mathcal{L}\phi = \mathcal{L}\phi, \quad (112)$$

## Derivation of the form (106) for $\xi$ and $\eta$ (end)

- Letting  $\mathbf{u} = \mathcal{L}\phi$ , then it follows from (112) that  $R\mathbf{u} = \mathbf{u}$  for any rotation which leaves (only)  $\mathbf{v}$  invariant, thus  $\mathbf{u} \parallel \mathbf{v}$ .
- Thus we have shown that

$$\mathcal{L}[g(v)\mathbf{v}] = h(v)\mathbf{v}, \quad (113)$$

where  $h$  must be a function only of  $v = |\mathbf{v}|$ .

- We see that if  $\xi = -F(u')\mathbf{u}'$ , then  $\mathcal{L}\xi$  has the correct form to match the given  $\mathbf{W} = \left(\frac{1}{2}u'^2 - \frac{5}{2}T^*\right)\mathbf{u}$ .
- Finding a suitable  $F(u')$  requires solving an inhomogeneous Fredholm integral equation with a RHS that is orthogonal to the null space of the integral operator, so this has a solution.
- That the solutions then must be of the form of (106) follows from the fact that they are unique (if in  $\mathcal{N}_\perp$ ).
- Similar reasoning (involving tensors) can be applied to show the form for  $\eta$  in (106).

# Lecture 12: A continuum limit: The Chapman-Enskog Method (II) – The constitutive relations for stress and heat flux



- Derive the constitutive law for the stresses including an expression for the viscosity  $\mu$
- Derive the constitutive law for the heat flux including an expression for the thermal conductivity  $k$ .
- Establish positivity of  $\mu$  and  $k$
- Calculate numerical values for  $\mu$  and  $k$ .

# Stress tensor and viscosity

- We return to the definition of the stress tensor in terms of the fluctuations.

- In dimensionless coordinates, these are (since  $\phi \perp \frac{1}{2}u'^2$ )

$$\sigma_{ij} = -p\delta_{ij} + \tau_{ij}, \quad \tau_{ij} = -\frac{kT_0}{d^2L} \langle \phi, u'_i u'_j \rangle = -\frac{kT_0}{d^2L} \langle \phi, U_{ij} \rangle. \quad (114)$$

- Now note that  $\mathbf{u}'\mathbf{u}'$  is orthogonal to  $\boldsymbol{\xi} = -F(u')\mathbf{u}'$ , (see (106)), and so only the  $\boldsymbol{\eta}$  term of

$$\phi = -\boldsymbol{\xi} \cdot \nabla C + C\boldsymbol{\eta} : \nabla \mathbf{u}, \quad (\text{cf. 104})$$

contributes to (114). Now recall  $\boldsymbol{\eta} = -G(u')\mathbf{U}$ .

- This gives (in dimensional form, and using the summation convention)

$$\tau_{ij} = \frac{\sqrt{mkT}}{d^2} \beta_{ijkl} \frac{\partial u_k}{\partial x_l}, \quad (115)$$

where

$$\beta_{ijkl} = \frac{1}{T^{*3/2}} \langle GU_{kl}, U_{ij} \rangle. \quad (116)$$

- Symmetry considerations show that all  $\beta_{ijkl} = 0$  unless  $(k, l) = (i, j)$  or  $(j, i)$ . There are then two cases,  $i \neq j$  and  $i = j$ .

# Calculating $\beta_{ijkl}$

(Case  $i \neq j$ )

- We have

$$\tau_{ij} = 2\mu\dot{\epsilon}_{ij}, \quad (117)$$

where

$$\dot{\epsilon}_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad (118)$$

is the strain rate tensor, and the viscosity is ( $i, j$  not summed)

$$\mu = \frac{\sqrt{mkT}}{d^2} \mu^*, \quad \mu^* = \frac{1}{T^{*3/2}} \langle GU_{ij}, u'_i u'_j \rangle. \quad (119)$$

- Evidently  $\mu$  is independent of the particular choice of  $i$  and  $j$ ; in fact, we have also

$$\mu^* = \frac{1}{T^{*3/2}} \langle GU_{ij}, U_{ij} \rangle = \frac{1}{T^{*3/2}} \langle Gu_i'^2, u_j'^2 \rangle \Big|_{i \neq j}. \quad (120)$$

# Calculating $\beta_{ijkl}$

(Case  $i = j$ )

- We have

$$\tau_{ii} = \frac{\sqrt{mkT}}{d^2} \sum_k \frac{1}{T^{*3/2}} \langle GU_{kk}, u_i'^2 \rangle \frac{\partial u_k}{\partial x_k}, \quad (121)$$

and for each value of  $k$ , we find

$$\langle GU_{kk}, u_i'^2 \rangle = \langle Gu_k'^2, u_i'^2 \rangle - \left(\frac{1}{3}G_1 + \frac{2}{3}G_2\right), \quad (122)$$

where

$$G_1 = \langle Gu_i'^2, u_i'^2 \rangle, \quad G_2 = \langle Gu_i'^2, u_j'^2 \rangle \Big|_{i \neq j} \quad (123)$$

- As in the previous case, these are independent of  $i, j$ .
- By direct calculation, we have, putting  $\mathbf{u}' = \sqrt{T^*}(x, y, z) = \sqrt{T^*}\mathbf{r}$ ,

$$\begin{aligned} G_1 &= \frac{n^*T^{*2}}{(2\pi)^{3/2}} \int_U G(r) e^{-\frac{1}{2}r^2} x^4 dV = \frac{n^*T^{*2}}{4} \sqrt{\frac{2}{\pi}} \int_0^\infty G(r) r^6 e^{-\frac{1}{2}r^2} dr, \\ G_2 &= \frac{n^*T^{*2}}{(2\pi)^{3/2}} \int_U G(r) e^{-\frac{1}{2}r^2} x^2 y^2 dV = \frac{1}{3}G_1. \end{aligned} \quad (124)$$

# Final form for $\mu^*$

- It follows from (121) that [sum over  $k$  only]

$$\tau_{ii} = 2\mu \left[ \frac{\partial u_i}{\partial x_i} - \frac{1}{3} \dot{\epsilon}_{kk} \right] \quad (125)$$

- Together with (117), this yields the general formula

$$\tau_{ij} = 2\mu (\dot{\epsilon}_{ij} - \frac{1}{3} \dot{\epsilon}_{kk} \delta_{ij}). \quad (126)$$

- From (120) and (124), we have

$$\mu = \frac{\sqrt{mkT}}{d^2} \mu^*,$$
$$\mu^* = \frac{G_2}{T^{*3/2}} = \frac{1}{12} \sqrt{\frac{2}{\pi}} \int_0^\infty G^*(r) r^6 e^{-\frac{1}{2}r^2} dr, \quad (127)$$

where we have written  $G = G^*/n^*T^{*1/2}$

# Heat flux and thermal conductivity

The heat flux is calculated in the same way. From its definition in (52), we find

$$q_i = \frac{1}{d^2 L} \sqrt{\frac{k^3 T_0^3}{m}} \langle \phi, \frac{1}{2} u'^2 u'_i \rangle. \quad (128)$$

To calculate the inner product, note that since  $\phi \perp \mathcal{N}$ ,

$$\langle \phi, \frac{1}{2} u'^2 u'_i \rangle = \langle \phi, W_i \rangle, \quad (129)$$

and in view of (104) and the fact that  $\mathbf{U} \perp \mathbf{W}$ , we have

$$\langle \phi, \frac{1}{2} u'^2 u'_i \rangle = -\langle \xi_j, W_i \rangle \frac{\partial C}{\partial x_j}, \quad (130)$$

summed over  $j$ . Since both  $\xi$  and  $\mathbf{W}$  are proportional to  $\mathbf{u}'$ , it follows that  $\langle \xi_j, W_i \rangle = 0$  if  $i \neq j$ , and thus

$$\langle \phi, \frac{1}{2} u'^2 u'_i \rangle = -\frac{1}{T^{*2}} \langle \xi_i, W_i \rangle \frac{\partial T^*}{\partial x_i} \quad (131)$$

(not summed).

## Heat flux and thermal conductivity (2)

Converting the temperature gradient to dimensional units, we find

$$\mathbf{q} = -k_T \nabla T, \quad (132)$$

where the thermal conductivity is

$$k_T = \frac{k^*}{d^2} \left( \frac{k^3 T}{m} \right)^{1/2}, \quad (133)$$

$$\text{and } k^* = \frac{1}{T^{*5/2}} \langle \xi_i, W_i \rangle = \frac{1}{T^{*5/2}} \langle F u'_i, (\frac{1}{2} u'^2 - \frac{5}{2} T^*) u'_i \rangle \left. \vphantom{\frac{1}{T^{*5/2}}} \right\} \quad (134)$$
$$= \frac{1}{3 T^{*5/2}} \langle F, (\frac{1}{2} u'^2 - \frac{5}{2} T^*) u'^2 \rangle.$$

Making the substitution  $u' = r \sqrt{T^*}$  and writing

$$F = \frac{T^{*1/2} F^*(r)}{n^*}, \quad (135)$$

this last integral can be explicitly written as

$$k^* = \frac{4\pi}{3} \int_0^\infty e^{-\frac{1}{2} r^2} F^*(r) \left( \frac{1}{2} r^2 - \frac{5}{2} \right) r^4 dr. \quad (136)$$

# Viscosity and thermal conductivity are positive

- Remaining task: Show that  $\mu$  and  $k_T$  are positive.
- From (99) and (94), we see that  $\mathcal{L}$  is negative definite on  $\mathcal{N}_\perp$ : For  $\psi \notin \mathcal{N}$ , we have  $\Delta\psi \neq 0$  thus

$$\langle \psi, \mathcal{L}\psi \rangle = -\frac{1}{4} \int_{\Sigma} f_0(\mathbf{v}) f_0(\mathbf{w}) (\Delta\psi)^2 d\Sigma < 0. \quad (137)$$

- It follows that (137) applies for  $\psi = \boldsymbol{\xi}, \boldsymbol{\eta}$ , and thus from (105)

$$\langle \boldsymbol{\xi}, \mathbf{W} \rangle > 0, \quad \langle G(u')\mathbf{U}, \mathbf{U} \rangle > 0, \quad (138)$$

where the inequalities apply separately to each component of the inner products.

- From (120) and (134), it follows that

$$\mu^* = \frac{1}{T^{*3/2}} \langle GU_{ij}, U_{ij} \rangle > 0 \quad \text{and} \quad k^* = \frac{1}{T^{*5/2}} \langle \xi_i, W_i \rangle > 0.$$



# Putting in numbers

- Explicit expressions for  $\mu^*$  and  $k^*$  are given in (127) and online notes. Chapman and Cowling (1970, page 168) evaluate after solving for  $F$  and  $G$ ,

$$\mu^* = \frac{5}{16\sqrt{\pi}} \approx 0.176, \quad k^* = \frac{75}{64\sqrt{\pi}} \approx 0.661. \quad (139)$$

- It is of interest to compare the corresponding dimensional values

$$\mu \sim \frac{0.18\sqrt{mkT}}{d^2}, \quad k_T \sim \frac{0.66}{d^2} \left( \frac{k^3 T}{m} \right)^{1/2}, \quad (140)$$

with actual measured values. We take as **representative values for air**:

$$m \sim 5 \times 10^{-26} \text{ kg}, \quad k = 1.38 \times 10^{-23} \text{ J K}^{-1}, \\ d \sim 3.6 \times 10^{-10} \text{ m}, \quad T \sim 300 \text{ K} \quad (141)$$

- These give  $\mu \sim 1.8 \times 10^{-5} \text{ Pa s}$  and  $k_T \sim 0.08 \text{ W m}^{-1} \text{ K}^{-1}$ .
- The first is about right, whereas the actual value of  $k_T$  is about  $3\times$  lower. The agreement of the viscosity is slightly illusory, since in effect one can estimate the molecular 'diameter' from the viscosity; however, the fact that the resultant thermal conductivity is close to the actual value provides an independent confirmation of the theory.

# Lecture 13: The Ising Model (I) – Definition and Applications

- A big thing in SM is models on networks and lattices.
- Such models have a variable at each site of some sort of networks (e.g., a regular grid) and a Hamiltonian or evolution law for each variable.
- Ising model has been used for many physical systems, including: **magnetism**, **binary alloys**, and **liquid-gas transition**.
  - It is the most extensively studied lattice model in physics.
  - Useful for lots of things (see preview Sethna p. 217).
- Simple system at the micro-level to study behaviour of large systems
- Work horse of statistical mechanics that also drove the development of renormalisation group theory (based on the observation that at coarser levels, the structure of e.g. the Ising model reproduces itself).

# Definition of the Ising model(s)

- A network (e.g., a lattice) of  $N$  sites  $i$  with a single 2-state DOF  $s_i \in \{-1, 1\}$  on each site:

- Hamiltonian is  $\mathcal{H} = - \sum_{ij} J_{ij} s_i s_j - h \sum_i s_i$

- $(J_{ij})$  is the **coupling matrix**:

- $J_{ij} = 0$ : sites  $i$  and  $j$  are **not interacting**;
- $J_{ij} > 0$ : interaction is **ferromagnetic**;
- $J_{ij} < 0$ : interaction is **anti-ferromagnetic**.

- **Nearest neighbour interaction (only)**

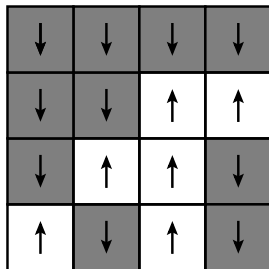
$$\begin{cases} J_{ij} = J = \text{const.}, & \text{if } i \text{ and } j \text{ are nearest neighbours} \\ 0, & \text{otherwise} \end{cases}$$

$$\Rightarrow \mathcal{H} = \sum_{\langle ij \rangle} J s_i s_j - h \sum_i s_i,$$

where  $\langle ij \rangle$  means that  $i$  and  $j$  are nearest neighbours.

- Example: Ising model on a 2D lattice (next page)

## Example: 2D Lattice



**Figure:**  $\uparrow \equiv +1 \equiv \text{light}$ ,  $\downarrow \equiv -1 \equiv \text{dark}$

- 4 centre squares have 4 nearest neighbours each;
- Non-corner edge ones have 3, and corner ones have 2.
- In finite systems, one can use periodic BCs so every square has 4 nearest neighbours.

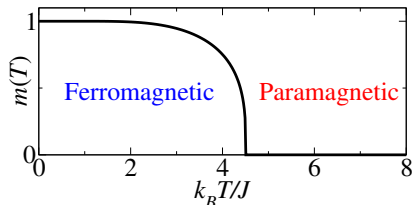
- Original use of Ising model.
- Each  $s_i$  is called a **spin**,  $h$  is the **external field**, and  $M := \sum_i s_i$  is the **magnetization**.
- This is where ferromagnetic ( $J_{ij} > 0$ ) and antiferromagnetic ( $J_{ij} < 0$ ) terminology comes from.
- Energy  $J_{ij}s_i s_j$  of 2 neighbouring spins is
  - $-J_{ij}$  if the spins are **parallel** (both  $+1$  or both  $-1$ )
  - $+J_{ij}$  if they are **antiparallel** (one  $+1$  and one  $-1$ ).

## Magnetism (2)

- Consider the nearest neighbour coupling matrix with

$$\begin{cases} J_{ij} = J, & \text{nearest neighbours} \\ 0, & \text{else} \end{cases}$$

- $J > 0$  favours parallel spins and these will mostly point in one direction [ferromagnetic phase];
- $J < 0$  favours anti-parallel spins and these will mostly orient themselves in a checkerboard pattern [anti-ferromagnetic phase];
- At high temperatures (for both signs of  $J$ ), we expect entropy to dominate: spins fluctuate wildly in a **paramagnetic phase** and the magnetization per spin  $m(T) \equiv \frac{M(T)}{N} \approx 0$ .
- There is a **phase transition** at a **critical temperature**  $T_c \approx 4.5$ .



Ising magnetization in a 3D cubic lattice Ising model.

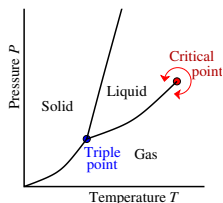
(Sethna 2020)

- Consider square lattice of atoms of type  $A$  and  $B$  ( $A = +1, B = -1$ ) of numbers  $N_A$  and  $N_B$  ( $N := N_A + N_B$ ).
- Interaction energies (i.e., bond strengths) are  $E_{AA}, E_{BB}, E_{AB}$ , and the numbers of such bonds are  $N_{AA}, N_{BB}, N_{AB}$ .
  - $\Rightarrow \mathcal{H} = -E_{AA}N_{AA} - E_{BB}N_{BB} - E_{AB}N_{AB}$ .
  - This is the nearest-neighbour Ising model with  $J = \frac{1}{4}(E_{AA} + E_{BB} - 2E_{AB})$  and  $h = E_{AA} - E_{BB}$  (see footnote 8 on (Sethna, pg.165)).
- A phase transition occurs from a high-temperature state (where the species freely interchange their positions) to a low-temperature stage (species are organised in an 'antiferromagnetic' i.e. 'checkerboard' style). For brass (1:1 Copper:Zinc) the transition is at  $733^\circ\text{C}$ .
- Can generalize by
  - including atomic relaxation effects
  - incorporating thermal fluctuations into  $\mathcal{H}$  to make it a free energy (see footnote 9 on (Sethna, pg. 165)),
  - or by considering more elaborate coupling such as large-range interactions.

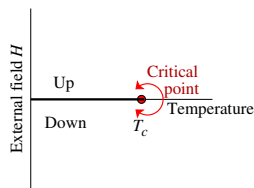


- Ising model is also used to study liquid-gas transition.
  - In this **lattice gas** interpretation,  $s_i = +1$  for sites of atoms and  $s_i = -1$  for sites w/o atoms.
  - The gas has mostly  $s_i = -1$  spins (negative 'magnetization') and the liquid phase has mostly  $s_i = +1$ .
- Near gas phase, seems ok; but in "liquid" phase, it is really more like a crystal, so it is not a good model there.
- But Ising model is good for probing behaviour near a **critical point**.

# The critical point



$P$ - $T$  Phase diagram aka bifurcation diagram for a typical material (Sethna 2020)



$P$ - $T$  phase diagram for the Ising model (Sethna 2020)

- (1) solid/liquid boundary amounts to a change in symmetry and cannot end
- (2) gas/liquid boundary typically **does** end  
(One can go **continuously** from liquid phase to gas phase by increasing pressure above  $P_c$ , increasing temp. above  $T_c$ , then lowering  $P$  again.)
- The behaviour near the critical points in these two situations (realistic one above and model one below) is remarkably similar; this leads to the notion of **universality** [See chapter 12 of Sethna]. In many ways the behaviour at the liquid-gas critical point is described **exactly** by the 3D Ising model.

# Lecture 14: The Ising Model (II) – Analytic and computational solutions

# How to solve the Ising Model?

- 1 1D case can be solved analytically.
- 2 Be very clever: Onsager solved a 2D version (very technical) for square lattices; 3D is open even in square lattice.  
(For a treatment of the 2D version, see for example: M. L. Glasser (Am. J. Phys. 38, 1033 (1970)).)
- 3 Monte Carlo computational techniques.

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- 3 Monte Carlo computational techniques.

# Ising 1D-Model – Transfer-Matrix Method

Ising Model with periodic boundary conditions

$$H(\sigma) = -J \sum_i s_i s_{i+1} - \frac{B}{2} \sum_i (s_i + s_{i+1}) \quad m(\sigma) = \frac{1}{N} \sum_{i=1}^N s_i$$

Transfer-Matrix Notation:

$$S_i = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{if } s_i = +1, \quad S_i = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{if } s_i = -1,$$

$$T(s_i, s_{i+1}) = \exp \left[ \beta J s_i s_{i+1} + \frac{\beta}{2} B (s_i + s_{i+1}) \right] = S_i^t \underbrace{\begin{pmatrix} e^{\beta(J+B)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-B)} \end{pmatrix}}_{\equiv \hat{T}} S_{i+1}.$$

Partition function:

$$\begin{aligned} Z(\beta) &= \sum_{\sigma \in \Sigma} e^{-\beta H(\sigma)} = \sum_{s_1=\pm 1} \dots \sum_{s_N=\pm 1} \prod_{i=1}^N T(s_i, s_{i+1}) \\ &= \sum_{s_1=\pm 1} \dots \sum_{s_N=\pm 1} S_1^t \hat{T} (S_2 S_2^t) \hat{T} \dots S_N^t \hat{T} S_1 \\ &= \sum_{s_1=\pm 1} S_1^t \hat{T}^N S_1 = \text{trace } \hat{T}^N = \Lambda_+^N + \Lambda_-^N \end{aligned}$$

Eigenvalues:

$$\Lambda_{\pm} = e^{\beta J} \left( \cosh(\beta B) \pm \sqrt{\sinh^2(\beta B) + e^{-4\beta J}} \right)$$

Average magnetisation

$$\mathbb{E}_{\beta, B}(m) = \frac{1}{N} \frac{\partial \ln(Z)}{\partial B} \longrightarrow \frac{\partial \ln(\Lambda_+)}{\partial B} = \frac{\sinh(\beta B)}{\sqrt{\sinh^2(\beta B) + e^{-4\beta J}}}$$

for  $N \rightarrow \infty$ .

# How to solve the Ising Model?

- 1 1D case can be solved analytically.
- 2 Be very clever: Onsager solved a 2D version (very technical) for square lattices; 3D is open even in square lattice.  
(For a treatment of the 2D version, see for example: M. L. Glasser (Am. J. Phys. 38, 1033 (1970)).)
- 3 **Monte Carlo computational techniques.**  
Some material courtesy Dirk Peschka

Homework: Read section 8.2 in Sethna.



How to compute the average

$$\mathbb{E}(f) = \sum_{\sigma} f(\sigma)p(\sigma)$$

of a random variable  $f$  with the probability distribution

$$p(\sigma) = \frac{\exp(-\beta H(\sigma))}{Z}$$

numerically?

**Problem:** Too many microstates!

**Ansatz:** Replace

$$\sum_{\sigma} f(\sigma)p(\sigma) \Rightarrow \frac{1}{N_{\text{mc}}} \sum_{n=1}^{N_{\text{mc}}} f(\sigma_n)$$

with the Markov chain  $\sigma_n$  transition rate  $p_{N,N-1} = P(\sigma_N|\sigma_{N-1})$ .

**Requirement:** The transition rate must lead to the distribution

$$p(\sigma) = Z^{-1} \exp(-\beta H).$$

**How to:** Metropolis Algorithm<sup>1</sup>

$$p_{N,N-1}(\sigma) = \min\left(1, \exp(-\beta\Delta H(\sigma))\right) \quad \Delta H(\sigma) = H(\sigma_N) - H(\sigma_{N-1})$$

Notice: Subsequently, the realisation  $f(\sigma_n)$  will be called a measurement.

---

<sup>1</sup>N. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller und E. Teller: Equation of State Calculations by Fast Computing Machines. (doi:10.1063/1.1699114)

# The Monte-Carlo Method: The heat bath algorithm

2D-Case – 1D very similar.

- Pick a site  $i = (x, y)$  at random
- Check how many neighbour spins are pointing up:

$$m_i = \sum_{j:\langle ij \rangle} s_j = 4, 2, 0, -2, -4$$

for 4, 3, 2, 1, 0 neighbours up, respectively.

- Calculate  $E_+ = -Jm_i - H$  and  $E_- = Jm_i + H$ , the energy for the spin  $i$  to be  $+1$  or  $-1$  given its current environment.
- Set spin  $i$  up with probability (reminder: Here and earlier,  $\beta = 1/k_B T$ )

$$\frac{\exp(-\beta \mathbf{E}_+)}{\exp(-\beta E_+) + \exp(-\beta E_-)}$$

and down with probability.

$$\frac{\exp(-\beta \mathbf{E}_-)}{\exp(-\beta E_+) + \exp(-\beta E_-)}$$

# Numerics 1D – Code

```
% ising1d.m
nx          = 50; % N
monte_carlo_steps = 100; % N_mc
monte_carlo_substeps = 100;

beta = 0.5; % 1/(k*T)
j     = 1.0; % Coupling parameter
B     = 0.1; % external field

s=2*round(rand(nx, 1))-1;
for n1=1:monte_carlo_steps
    for n2=1:monte_carlo_substeps
        s=mc1d(s,j,B,beta,nx );
    end
    m(n1)=mean(s(:));
end
plot(m)

% Function: mc1d.m
% Markov step P(n+1,n)
% 1D linear mesh, length nx

function s=mc1d(s,j,B,beta,nx )

for x=1:nx

    % neighbouring positions
    xm1 = mod(x-2+nx,nx)+1;
    xp1 = mod(x,nx)+1;

    % neighbouring spins
    s1=s(xm1 );    s2=s(xp1 );

    % heat bath algorithm for p = exp(-beta*H):
    % set s=+1 if rand < w=exp(bA)/(exp(bA)+exp(-bA))
    % otherwise s=-1
    A=j*(s1+s2 )+B;
    w=exp(beta*A)/(exp(beta*A)+exp(-beta*A));
    s(x )=(rand(1)<w)*2-1;

end
```

# Numerics 2D – Code

```
% ising2d.m
nx          = 50; % N
ny          = 50;
monte_carlo_steps = 100; % N_mc
monte_carlo_substeps = 100;
```

```
beta = 0.5; % 1/(k*T)
j     = 1.0; % Coupling parameter
B     = 0.1; % external field
```

```
s=2*round(rand(nx,ny))-1;
for n1=1:monte_carlo_steps
    for n2=1:monte_carlo_substeps
        s=mc2d(s,j,B,beta,nx,ny);
    end
    m(n1)=mean(s(:));
end
plot(m)
```

```
% Function: mc2d.m
% Markov Step P(n+1,n)
% 2D mesh size (nx) x (ny)
```

```
function s=mc2d(s,j,B,beta,nx,ny)
```

```
for x=1:nx
    for y=1:ny
```

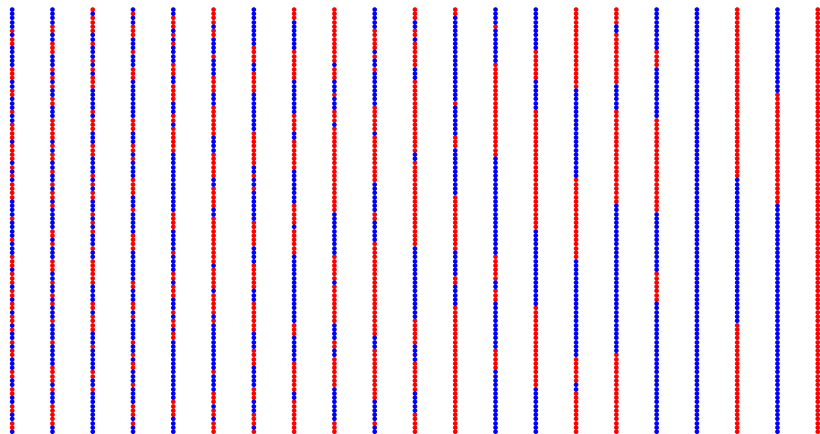
```
        % neighbouring positions
        xm1 = mod(x-2+nx,nx)+1;
        xp1 = mod(x,nx)+1;
        ym1 = mod(y-2+ny,ny)+1;
        yp1 = mod(y,ny)+1;
```

```
        % neighbouring spins
        s1=s(xm1,y );    s2=s(xp1,y );
        s3=s(x ,ym1);    s4=s(x ,yp1);
```

```
        % heat bath algorithm for p = exp(-beta*H):
        % set s=+1 if rand < w=exp(bA)/(exp(bA)+exp(-bA))
        % otherwise s=-1
        A=j*(s1+s2+s3+s4)+B;
        w=exp(beta*A)/(exp(beta*A)+exp(-beta*A));
        s(x,y)=(rand(1)<w)*2-1;
```

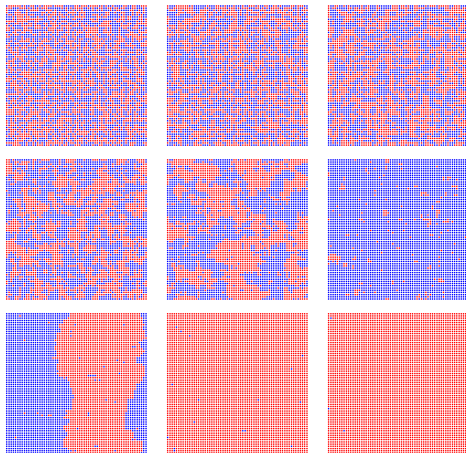
```
    end
end
```

# Numerics 1D – Typical micro states



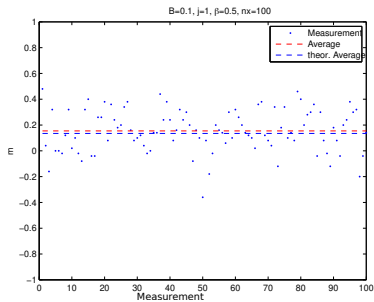
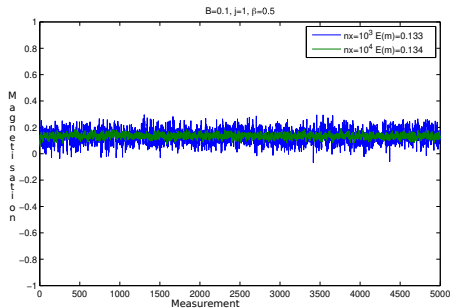
Typical states with  $\beta = 0.0, \beta = 0.1, \dots, \beta = 1.9, \beta = 2.0$   
( $\beta = 1/(k_B T)$ )

# Numerics 2D – Typical micro states



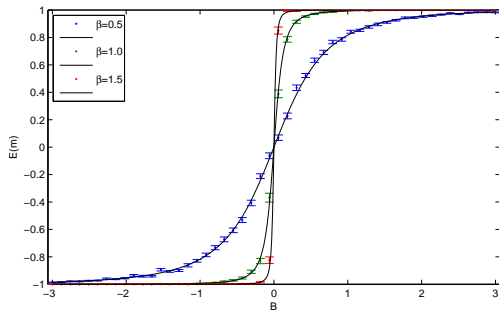
Typical states with  $\beta = 0.0, \dots, \beta = 0.8$

# Numerics 1D – The magnetisation as a random variable



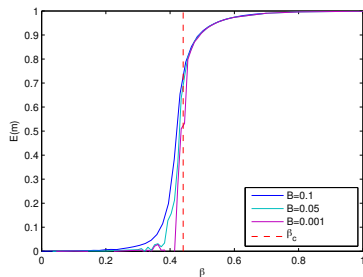


# Numerics 1D – dependence on $B$ and $\beta$

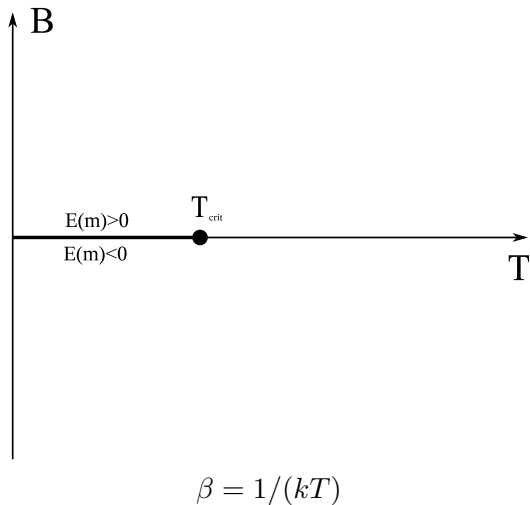


$$\mathbb{E}_{\beta, B}(m) = \frac{\sinh(\beta B)}{\sqrt{\sinh^2(\beta B) + e^{-4\beta J}}}$$

# Numerics 2D – The magnetisation as a random variable.



# Phase Diagram



# Lecture 15: Phase Transitions

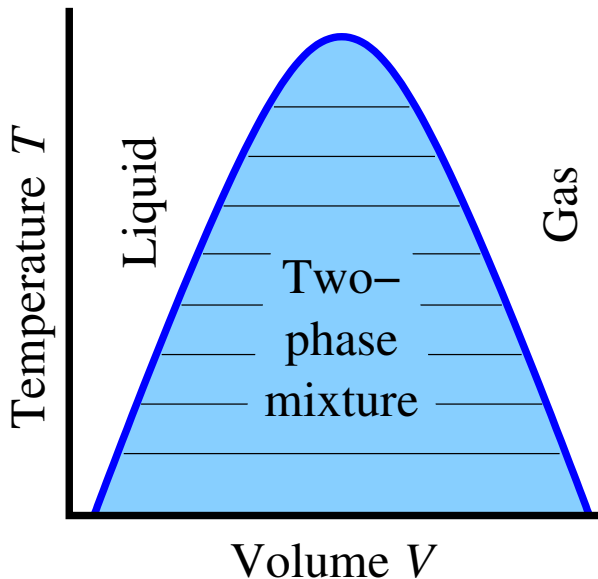
# Illustration of abrupt phase transitions

- Most phase transitions are abrupt; at the transition, the system has discontinuities in most physical properties
- Also, in most cases, these transitions happen with no indication that a change is about to occur: Pure water turns directly to ice- not to slush first and then to ice.

## Illustration of abrupt phase transitions (continued)

- However, boiling away a pan of water is not abrupt- this is because one is not controlling the temperature directly but rather is adding energy at a constant rate.
  - Consider insulated, flexible container of  $H_2O$  at fixed pressure and we slowly add energy to it.
  - When system first reaches liquid-gas transition, a small bubble of gas forms at the top; the bubble grows gradually, inflating and filling the container over a range of energies.
  - The transition from liquid to gas at fixed energy passes through an intermediate **two-phase region**; the temperature of the system stays constant until the last liquid is gone.
- Alternatively, one can see a two-phase region by fixing the temperature and varying (e.g. increasing) the volume.

# Phase Diagram



(Sethna 2020 – All figures in this lecture from Sethna's book)

# Gibbs free energy

- To avoid two-phase mixtures, let us fix (control) the pressure and temperature of the system. Such systems are well described by the Gibbs free energy  $G$ ,

$$G(T, P, N) = E - TS + PV = \mu N,$$

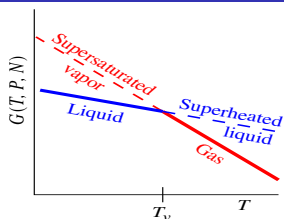
using, for the second equality, Euler relation  $E = TS - PV + \mu N$ , (see exercise 6.9 in Sethna).

- A transition for such a system occurs spontaneously if it decreases the total Gibbs  $G$  free energy.
- System can lower  $G$  by moving material to the phase with the lower chemical potential.  $\Rightarrow$  state with lower chemical potential is favoured, and the phase transition occurs when  $\mu_{\text{liq}} = \mu_{\text{gas}}$ .
- Using thermodynamic shorthand  $dE = TdS - PdV + \mu dN$  gives  $dG = -SdT + VdP + \mu dN$ .
- Varying temperature at fixed pressure and number of particles gives

$$\left. \frac{\partial G}{\partial T} \right|_{P, N} = -S \quad (\star)$$



# Latent heat



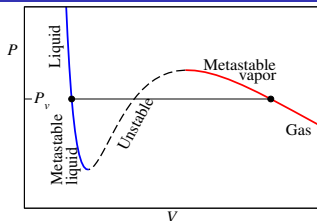
- The difference in the slopes of the 2 lines is given by the difference in entropies between the liquid and the gas (see  $(\star)$ ).
- The thermodynamic definition of entropy says  $\Delta S = \frac{Q}{T}$  that the entropy difference is

$$\Delta S = \frac{LN}{T_v},$$

where  $L$  is the **latent heat** per particle, and  $T_v$  the transition temperature.

- Abrupt phase transitions have jumps in the first derivatives of their free energies.
  - Discuss old terminology: first vs. second order transition. (Footnote 7 in Sethna.)

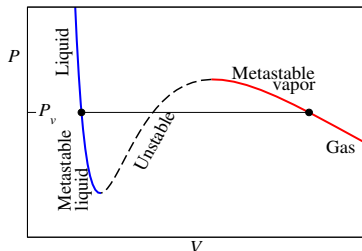
# Maxwell Construction



**Figure:** Pressure vs. volume as we expand/compress material at constant temperature. The dots represent points where pressures and chemical potentials are equal and gas and liquid coexist.

- Liquid (gas) turns metastable as  $V$  increases (decreases) when the pressure reaches the vapour pressure  $P_v$  for that volume.
- Metastable states are well defined only near vapor pressure, where nucleation is slow and lifetime of the state is long (but finite!)
- Dashed line in (a) shows a completely unstable region: a mixture of molecules prepared uniformly in space in this region will spontaneously separate into (a finely inter-tangled network of) the two phases.

# Questions

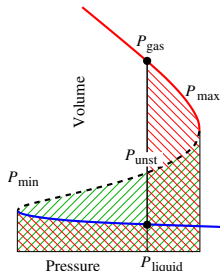


- What is the **vapour pressure**  $P_v$ ?  
(Answer: The pressure at which the liquid and the gas (vapour) phase coexist i.e. are in equilibrium with each other.)
- How can we find the vapour pressure  $P_v$  at which liquid and gas coexist at this temperature?

# Coexistence line

- Coexistence line occurs when Gibbs free energies agree:  $G_{\text{liq}} = G_{\text{gas}}$ ;  $dG = -SdT + VdP + \mu dN$ , so at constant temperature and number of molecules we get

$$\begin{aligned}\Delta G &= \int_C V(P)dP \\ &= \underbrace{\int_{P_{\text{liq}}}^{P_{\text{min}}} V(P)dP}_{<0} + \underbrace{\int_{P_{\text{min}}}^{P_{\text{unst}}} V(P)dP}_{>0} + \underbrace{\int_{P_{\text{unst}}}^{P_{\text{max}}} V(P)dP}_{>0} + \underbrace{\int_{P_{\text{max}}}^{P_{\text{gas}}} V(P)dP}_{<0}\end{aligned}$$



- Note  $P_{\text{liq}} = P_{\text{unst}} = P_{\text{gas}}$  at coexistence, but volumes are different! Hence the path integral is non-zero.
- First 2 terms subtract to give the **lower left hatched area** and last 2 terms subtract to give **minus** the area in the **upper right hatched area**.
- $\implies$  the 2 areas must be equal at the vapor pressure. This is called the **Maxwell equal-area construction**.

## Part 2

# Nucleation: Critical Droplet Theory

# Nucleation: Critical Droplet Theory

- On a humid night, as temperature drops, the air can become supersaturated with water vapour. **How does this metastable vapour turn into drops of dew or tiny water droplets to make up fog or clouds?**
- The Gibbs free energy (hence chemical potential) difference between gas and liquid grows as temperature decreases below  $T_v$ . Estimate:

$$\left. \frac{\partial G}{\partial T} \right|_{P,N} = -S \quad \text{and} \quad \Delta S = \frac{LN}{T_v}$$
$$\Rightarrow \Delta\mu = \frac{(G_{\text{gas}} - G_{\text{liq}})}{N} = \frac{1}{N} \left( \left. \frac{\partial(G_{\text{gas}} - G_{\text{liq}})}{\partial T} \right|_{P,N} \Delta T \right)$$
$$= \frac{\Delta S \Delta T}{N} = \left( \frac{LN}{T_v} \right) \left( \frac{\Delta T}{N} \right) = \frac{L\Delta T}{T_v}$$

- Supersaturation means  $\Delta\mu > 0$ , so why doesn't vapour just condense to liquid (releasing heat) beforehand?
- The obstacle impeding the formation of droplets is the **surface tension**.

- Surface tension is given by

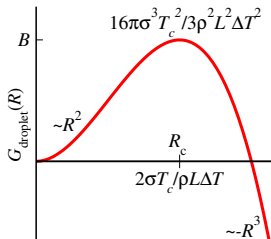
$$\begin{aligned} \sigma &= \text{Gibbs free energy per unit area of interface between liquid and gas} \\ &\left[ = \frac{G_{\ell g} - \frac{1}{2}(G_{\ell\ell} + G_{g g})}{A} \quad (\text{See footnote 12 in Sethna section 11.3}) \right] \end{aligned}$$

- Gibbs free energy grows as the area  $A$  and bulk free energy gain grows as volume  $V$ , so tiny droplets cost the system more than they gain.

# Energy barrier & Critical droplet radius

- Consider spherical droplet of radius  $R$ ; the surface Gibbs free energy is  $\sigma A$ ; if the liquid has  $\rho_{\text{liq}}$  particles per unit volume and each particle provides a free energy gain of  $\Delta\mu = \frac{L\Delta T}{T_v}$  then the bulk free energy gain is  $V\rho_{\text{liq}}$ .

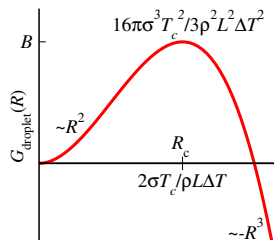
$$\therefore G_{\text{droplet}}(R) = \sigma A - V\rho_{\text{liq}}\Delta\mu = 4\pi R^2\sigma - \left(\frac{4}{3}\pi R^3\right)\rho_{\text{liq}}\frac{L\Delta T}{T_v}$$



- The gas remains a gas until a rare thermal fluctuation pays the critical energy cost to reach the top of the barrier, making a **critical droplet**.



## Energy barrier & Critical droplet radius (2)



- One finds the critical droplet radius  $R_c$  and the height of free energy barrier  $B$  by maximizing  $G(R)$ :

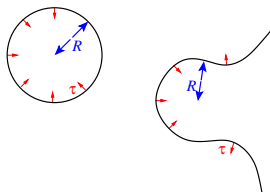
$$\begin{aligned} \frac{\partial G_{\text{droplet}}}{\partial R} \Big|_{R_c} &= 8\pi\sigma R_c - 4\pi\rho_{\text{liq}} \left( \frac{L\Delta T}{T_v} \right) r_c^2 = 0 \\ \Rightarrow R_c &= \frac{2\sigma T_v}{\rho_{\text{liq}} L \Delta T}, \quad B = \frac{16\pi\sigma^3 T_v^2}{3\rho_{\text{liq}}^2 L^2} \frac{1}{(\Delta T)^2} \end{aligned}$$

# Nucleation rates

- The net droplet nucleation rate per volume is  $\Gamma = (\text{const.}) \times \exp\left(\frac{-B}{k_B T}\right)$ .
- Note the following:
  - Critical droplet radius  $R_c \propto \frac{1}{\Delta T}$ ; if you undercool the gas by a tiny amount, you need a large droplet to overcome the surface tension.
  - $B \propto \frac{1}{(\Delta T)^2}$ : The energy barrier for nucleation diverges at  $T_v$ .
- Critical droplet theory calculates the rare fluctuations that take us over the energy barrier (Read note 14 in Sethna, section 11.3)
- The rates we have calculated are for **homogenous nucleation**, the rate of forming a new phase in a clean system w/o boundaries.
- Since nucleation is suppressed very strongly by surface tension, the system tries to bypass at least part of the free energy barrier; this is why droplets usually form on grass or your windows rather than forming in the air and dropping down.

# Coarsening

- Tiny objects merging into bigger ones (e.g., salad dressing after one stops shaking, and numerous examples in materials science and geophysics).
- This can also be seen in abstract situation like the Ising model



**Figure:** Snapshot of a coarsening system; most features here have a characteristic length scale of radius  $R \sim L(t)$ ,  $L(t)$  =time dependent length scale of the smallest features.

- Coarsening involves the smaller features shrinking to zero, leaving only the larger scales behind.
- Coarsening is driven by surface tension: the system can lower its free energy by lowering the interfacial area between different domains.