C5.3 Statistical Mechanics

ANDREAS MÜNCH
Lecturer
Mathematical Institute
University of Oxford

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UNIVERSITY OF OXFORD
Mathematical Institute

Oxford Mathematics

List of Lectures

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;
  - or of all individuals in a large social network
- 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!

Random walks

- Paths that take successive steps in random directions
- Arise as:
  - **Partial sums of fluctuating quantities**
  - Trajectories of particles undergoing repeated collisions
  - Shapes of long, linked systems (polymer chains)

Partial sums of fluctuating quantities

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

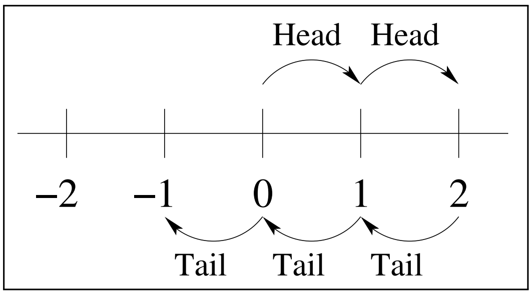
$$S_N = \sum_{i=1}^{N} l_i$$

- Sequence S_1, S_2, S_3, gives 1D random walk

Example: Coin Flip

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

- Interpretation as random walk:



- Average value for an unbiased coin:

$$\langle l_i \rangle = \frac{1}{2}(+1) + \frac{1}{2}(-1) = 0 \quad \Longrightarrow \quad \langle S_N \rangle = \sum_{i=1}^{N} \langle l_i \rangle = 0$$

- Unfortunately, the average is not very interesting.

Root Mean Square (RMS) of S_N

- RMS of partial sums defined as $\sigma_s \equiv \sqrt{\langle S_N^2 \rangle}$
  - $\langle S_1^2 \rangle = \frac{1}{2}(+1)^2 + \frac{1}{2}(-1)^2 = 1$
  - $\langle S_{N+1}^2 \rangle = \langle (S_N + l_{N+1})^2 \rangle = \langle S_N^2 \rangle + 2\langle S_N l_{N+1} \rangle + \langle l_{N+1}^2 \rangle$
  - $\langle l_{N+1}^2 \rangle = 1$
  - $\langle S_N l_{N+1} \rangle = \langle S_N \rangle \langle l_{N+1} \rangle = 0 \cdot 0 = 0.$
  - $\Longrightarrow \quad \langle S_{N+1}^2 \rangle = \langle S_N^2 \rangle + 1$

  Thus, by induction, $\boldsymbol{\sigma_s = \sqrt{N}}$.
- **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)

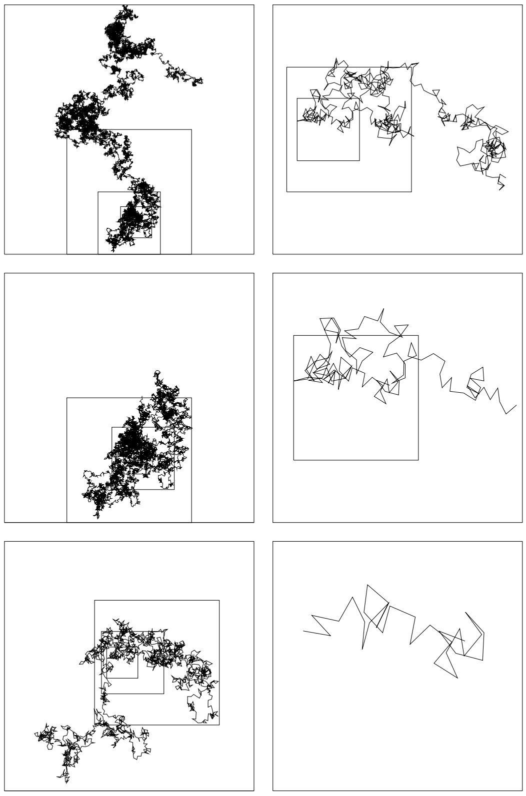
- Characteristic jagged appearance.
- Example of **Scale Invariance**: Looks the same at any zoom level (larger than the step size)!
- Example of **Universality:** Two-coin flip, drunkard's walk etc. produce same same RMS:

$$\sigma_s = N^{1/2}.$$

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

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

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



Sethna, 2012

Collective behaviour for random walks

- What happens on when we have many particles, on long length and time scales?
  - E.G. the spreading of perfume molecules colliding with the air molecules?
- We want to describe this by the density $\rho(x, t)$ of perfume molecules at a point x and time t.
- Alternative: For an individual particle random walking particle, we could ask for the probability density $\rho(x, t)$ that it is at position x at time t (at long times & large scales.)
- If the random walk is non-interacting, these view points are the same: The probability distribution of one particle describes the density of all particles. of one particle describes the density of all particles.
- The second view point is more convenient for us.

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.
- At each time step, particle position changes by a step $l(t)$,

$$x(t + \Delta t) = x(t) + l(t)$$

- Assume probability distribution is $\chi(l)$.
  - E.G. coin flips: $\chi(l) = (1/2)\delta(l+1) + (1/2)\delta(l-1))$
- Assume χ is normalised to 1, mean 0 and standard derivation a, i.e.

$$\int \chi(l)\,\mathrm{d}l = 1, \quad \int l\chi(l)\,\mathrm{d}l = 0, \quad \int l^2\chi(l)\,\mathrm{d}l = a^2.$$

Question:

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

Continuum limit of random walks in 1D (2)

- Particle goes from (x', t) to $(x, t + \Delta t)$ if $l(t) = x - x'$
  This has probability: $\chi(l) = \chi(x - x')$
- Particle ends up at $(x, t + \Delta t)$ going through (x', t) with probability: $\rho(x', t)\chi(x - x')$.
- Integrate over all intermediate positions x':

$$\rho(x, t + \Delta t) = \int_{-\infty}^{\infty} \rho(x', t)\chi(x - x')\,\mathrm{d}x' = \int_{-\infty}^{\infty} \rho(x - z, t)\chi(z)\,\mathrm{d}z.$$

- Choose step size $\Delta x \ll$ length scale over which ρ varies.

$$\begin{aligned}
\rho(x, t + \Delta t) &= \int_{-\infty}^{\infty} \left(\rho - z\rho_x + \frac{1}{2}z^2\rho_{xx} + \cdots\right)\chi(z)\,\mathrm{d}z \\
&\approx \rho\int \chi(z)\,\mathrm{d}z - \rho_x\int z\chi(z)\,\mathrm{d}z + \frac{1}{2}\rho_{xx}\int z^2\chi(z)\,\mathrm{d}z \\
&= \rho(x,t) + \frac{1}{2}a^2\rho_{xx}.
\end{aligned}$$

Continuum limit of random walks in 1D (3)

$$\rho(x, t + \Delta t) = \rho(x, t) + \frac{1}{2} a^2 \rho_{xx}$$

- Choose $\Delta t \ll$ time scale on which ρ changes

$$\rho(x, t + \Delta t) \approx \rho(x, t) + \rho_t \Delta t.$$

- Combining gives the diffusion equation

$$\boxed{\rho_t = \frac{a^2}{2\Delta t} \rho_{xx}} \qquad (*)$$

Extensions and Remarks

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

Key concepts

1. **Entropy:** Fundamental measure of disorder or information in system.
2. **Phases:** SM explains existence of phases:
   - solid-liquid-gas phases
   - superfluids or liquid crystals, others ...
3. **Phase Transitions**
   - **Abrupt:** E.G. Melting of a cube
   - **Continuous:** Criticality, universality, scaling invariance [if time permits]
4. **The Boltzmann equation:** The kinetic theory of gases.
5. **Fluctuations and Correlations:** SM describes entire distribution beyond averages [briefly touched upon as part of other topics]
6. **Further Applications** [as time permits]

***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.

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.)

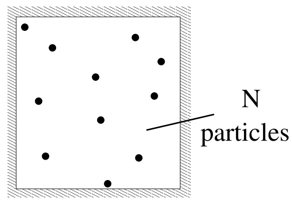
Lecture 2: Temperature and Equilibrium (I)

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.



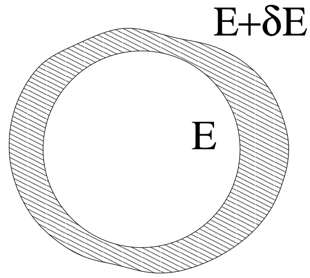
- **Configuration space:** $3N$-dimensional space of positions
$$\mathbf{q} = (x_1, y_1, z_1, \ldots, x_N, y_N, z_N) = (\mathbf{q}_1, \ldots, \mathbf{q}_N)$$
- **Momentum space:** $3N$-dimensional space of momenta
$$\mathbf{p} = (\mathbf{p}_1, \ldots, \mathbf{p}_N)$$
- **Phase space:** $6N$-dimensional space of positions & momenta
$$(\mathbf{q}, \mathbf{p}) = (\mathbf{q}_1, \ldots, \mathbf{q}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N).$$
- $(\mathbf{q}(t), \mathbf{p}(t))$ 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
  $\Longrightarrow$ 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 $\delta E \to 0$.



Microcanonical Ensemble (3)

- Phase space volume of energy shell
$$\mathcal{V}(E,\delta E) = \int_{H(\mathbf{p},\mathbf{q})\in(E,E+\delta E)} \mathrm{d}\mathbf{q}\,\mathrm{d}\mathbf{p}$$
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
$$\Omega(E) \equiv \frac{\mathcal{V}(E,\delta E)}{\delta E} = \frac{1}{\delta E}\int_{H(\mathbf{p},\mathbf{q})\in(E,E+\delta E)} \mathrm{d}\mathbf{q}\,\mathrm{d}\mathbf{p}$$
in the limit $\delta E \to 0$ (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:
$$\langle O\rangle_E = \frac{1}{\Omega(E)}\left[\frac{1}{\delta E}\int_{H(\mathbf{p},\mathbf{q})\in(E,E+\delta E)} O(\mathbf{q},\mathbf{p})\,\mathrm{d}\mathbf{q}\,\mathrm{d}\mathbf{p}\right], \quad \delta E \to 0.$$

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, $U = 0$
  $\Longrightarrow$ Energy independent of $\mathbf{q}$,
  $\Longrightarrow$ Position and momenta can be considered separately when calculating Ω.

  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 $\mathbf{q}$ $\Longrightarrow$ 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?

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

- 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

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

- Stirling's formula

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

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

(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 $1 = \sum_m P_m \approx \int_{-\infty}^{\infty} P_0 \exp\left(-\frac{m^2}{N}\right) \, \mathrm{d}m = P_0\sqrt{\pi N}$
- 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

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

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

- Thus the $\sum P_m$ over $m \leqslant$ 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 $\delta E \to 0$)

Obtaining $\tilde{\Omega}$

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

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

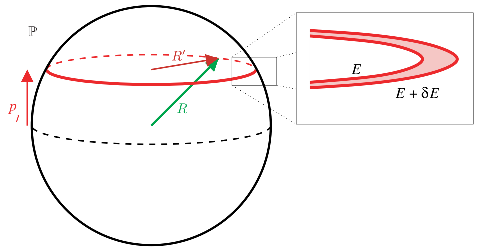
- Hence

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

Exercise

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

Determining $\rho(p_1)$



(Sethna 2020)

- $\rho(p_1) = \lim_{\delta E \to 0} \dfrac{\text{Annular area}}{\text{Shell volume}}$
- $\dfrac{\text{Annular area}}{\delta E} = \dfrac{\mathrm{d}}{\mathrm{d}E}\mu\left(S_{R_1}^{3N-2}\right),$

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

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

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

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

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 $\int_{-\infty}^{+\infty} \rho(p_1)\,\mathrm{d}p_1 = 1$ gives
$$\boxed{\rho(p_1) = \frac{1}{\sqrt{2\pi m(2E/3N)}} \exp\left(\frac{3N}{2E}\frac{(-p_1^2)}{2m}\right)}$$
- 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.

- 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.

Remarks

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

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

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 $\exp(-E/k_B T)$.

Remarks (continued)

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

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

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

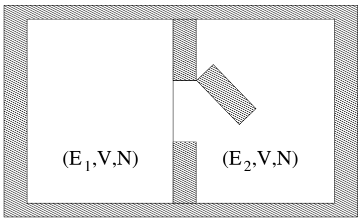
This is an example of the **Equipartition Theorem**:
"Each harmonic degree of freedom in a classical equilibrium system has average energy $k_B T/2$."

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)



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

- **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)!

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 $E = E_1 + E_2$.
- 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.
- Then the probability density $\rho(E_1)$ of sys 1 having *any state* with energy E_1 must be

$$\rho(E_1) \propto \Omega_1(E_1)\Omega_2(E - E_1),$$

- Normalisation:

$$\rho(E_1) = \Omega_1(E_1)\Omega_2(E - E_1) \Big/ \boxed{\int \Omega_1(E_1)\Omega_2(E - E_2)\,\mathrm{d}E_1}$$

- **Intuition (and homework):** $\boxed{\int \cdots \mathrm{d}E_1} = \int \Omega(E)\,\mathrm{d}E.$

First Step: Result

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

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).

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

- Equality of $(1/\Omega)(\mathrm{d}\Omega/\mathrm{d}E)$ 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

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

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

$$\left.\frac{\mathrm{d}S_1}{\mathrm{d}E_1}\right|_{E_1=E_1^*} - \left.\frac{\mathrm{d}S_2}{\mathrm{d}E_2}\right|_{E_2=E-E_1^*} = 0$$

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

Remarks

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 δE (heat) energy from the heat bath (= external world) at temperature T.

Equilibria between systems with other types of interactions

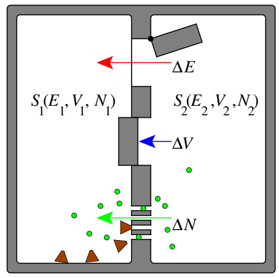
What happens if we allow the system to exchange volume or particles?

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 ΔT, ΔV or ΔN move from subsystem 1 to subsystem 2?



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

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
$$\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_{V,N}$$
- $② = 0$: Maximising entropy with respect to volume exchange sets $\partial S/\partial V|_{E,N}$ equal. Hence define pressure via
$$\frac{P}{T} = \frac{\partial S}{\partial V}\bigg|_{E,N}.$$
- $③ = 0$: Maximising entropy with respect to particle exchange sets $\partial S/\partial N|_{E,V}$ equal. Hence define chemical potential via
$$-\frac{\mu}{T} = \frac{\partial S}{\partial N}\bigg|_{E,V}.$$
- These definitions are often summarized as
$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}E + \frac{P}{T}\,\mathrm{d}V - \frac{\mu}{T}\,\mathrm{d}N.$$

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

A lot of information can be obtained/recovered from

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}E + \frac{P}{T}\,\mathrm{d}V - \frac{\mu}{T}\,\mathrm{d}N. \qquad (*)$$

- 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)

$$\mathrm{d}S = \left.\frac{\partial S}{\partial E}\right|_{V,N} \mathrm{d}E + \left.\frac{\partial S}{\partial V}\right|_{E,N} \mathrm{d}V + \left.\frac{\partial S}{\partial N}\right|_{E,V} \mathrm{d}N$$

  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)**.

derivatives of thermodynamic potentials with respect to their arguments.

The (inner) energy E as a thermodynamic potential

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

$$\mathrm{d}E = T\,\mathrm{d}S - P\,\mathrm{d}V + \mu\,\mathrm{d}N.$$

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

$$\mathrm{d}E = \left.\frac{\partial E}{\partial S}\right|_{V,N} \mathrm{d}S + \left.\frac{\partial E}{\partial V}\right|_{S,N} \mathrm{d}V + \left.\frac{\partial E}{\partial N}\right|_{S,V} \mathrm{d}N$$

- Thus

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

  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 $f = f(x,y)$
  - $\left.\frac{\partial f}{\partial x}\right|_y = \frac{1}{\left.\frac{\partial x}{\partial f}\right|_y}$
  - $\left.\frac{\partial f}{\partial x}\right|_y \left.\frac{\partial x}{\partial y}\right|_f \left.\frac{\partial y}{\partial f}\right|_x = -1$ **NOT $= +1$!**
- Find $\partial E/\partial V|_{S,N}$:

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

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

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

Thus $\boxed{\left.\frac{\partial E}{\partial V}\right|_{S,N} = -P.}$ "Force" associated with volume increase.

Other ways to find derivatives (2)

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

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

$$= -\frac{\mu}{T} \frac{1}{\partial E/\partial N|_{S,V}} T \quad \text{(First identity \& see above)}$$

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":
  - $E = (3/2)Nk_BT$
  - $PV = Nk_BT$ 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

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

Refinements

Refinement #1

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

This removes dimensions from Ω 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

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

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

  This is the standard formula for the entropy of an ideal gas.
- Introduce $\rho = N/V$ particle density
  $\lambda = \hbar/\sqrt{4\pi mE/3N}$ thermal de Broglie wavelength.

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

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, adabiatic 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 $\Longrightarrow$ 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

$$\dot{q_\alpha} \equiv \frac{\mathrm{d}q_\alpha}{\mathrm{d}t} = \frac{\partial \mathcal{H}}{\partial p_\alpha}$$
$$\dot{p_\alpha} \equiv \frac{\mathrm{d}p_\alpha}{\mathrm{d}t} = -\frac{\partial \mathcal{H}}{\partial q_\alpha}, \qquad \alpha = 1, \ldots, 3N,$$

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

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

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

This gives

$$\dot{q_\alpha} = \frac{p_\alpha}{m_\alpha},$$
$$\dot{p_\alpha} = -\frac{\partial U}{\partial q_\alpha} \equiv f_\alpha(q_1, \ldots, q_{3N}), \qquad f_\alpha\text{: force on coordinate } \alpha,$$

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

Local conservation of probability density

- Consider the probability density ρ in phase space,

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

Vaguely, think of the integral of ρ 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 $\mathbf{p}(0) = \mathbf{p}_0$, $\mathbf{q}(0) = \mathbf{q}_0$,
- ρ is *locally conserved*, that is, the integral of ρ over a region $D(t)$ that is convected with the flow, $D(t) = \phi(D(0), t)$, remains constant:

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{D(t)} \rho(\mathbf{p}, \mathbf{q}, t) \, \mathrm{d}q_1 \ldots \mathrm{d}q_{3N} \, \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = 0$$

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

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

Local conservation of probability density (2)

- ... carrying over from the previous slide

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

- The divergence theorem implies

$$\int_D [\rho_t + \operatorname{div}(\rho \dot{\mathbf{q}}, \rho \dot{\mathbf{p}})] \prod_\alpha \mathrm{d}q_\alpha \, \mathrm{d}p_\alpha = 0 \qquad \forall D$$

- 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^{nd} and 4^{th} terms (blue) in cancel.

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

Liouville's theorem

Liouville's theorem (2)

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

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = 0.$$

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

Liouville's theorem: Summary

1. $\mathrm{d}\rho/\mathrm{d}t = 0$, 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 ρ 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!

Ergodicity

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.

Ergodicity (alternative Definition)

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 $(\mathbf{p}(0), \mathbf{q}(0))$

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

Definition of the microcanonical ensemble average

Let S denote the energy surface.

$$\langle O \rangle_S = \int_S \rho(\mathbf{p}, \mathbf{q}, t) O(\mathbf{p}, \mathbf{q})\, \mathrm{d}q_1 \ldots \mathrm{d}q_{3N}\, \mathrm{d}p_1 \ldots \mathrm{d}p_{3N}.$$

(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 ρ 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

$$\begin{aligned}
\overline{O(\mathbf{p}(0), \mathbf{q}(0))} &= \lim_{T\to\infty} \frac{1}{T} \int_0^T O(\mathbf{q}(\tau), \mathbf{p}(\tau))\, \mathrm{d}\tau, \\
\overline{O(\mathbf{p}(t), \mathbf{q}(t))} &= \lim_{T\to\infty} \frac{1}{T} \int_0^T O(\mathbf{q}(t+\tau), \mathbf{p}(t+\tau))\, \mathrm{d}\tau \\
&= \lim_{T\to\infty} \frac{1}{T+t} \int_t^{T+t} O(\mathbf{q}(\tau), \mathbf{p}(\tau))\, \mathrm{d}\tau \\
&= \lim_{\tilde{T}\to\infty} \frac{1}{\tilde{T}} \int_t^{\tilde{T}} O(\mathbf{q}(\tau), \mathbf{p}(\tau))\, \mathrm{d}\tau.
\end{aligned}$$

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

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.

$\Longrightarrow$ R_a is an ergodic component
$\Longrightarrow$ 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 ρ is stationary and uniform on the energy surface.

Sketch of a proof:
For stationary solutions, the ensemble average is time independent,

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle O \rangle_S = \int_S \rho_t(\mathbf{p}, \mathbf{q}, t) O(\mathbf{p}, \mathbf{q}) \, \mathrm{d}q_1 \ldots \mathrm{d}q_{3N} \, \mathrm{d}p_1 \ldots \mathrm{d}p_{3N} = 0.$$

Thus

$$\langle O \rangle_S = \lim_{T \to \infty} \frac{1}{T} \int_0^T \langle O \rangle_s \, \mathrm{d}t$$

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

$$\langle O\rangle_S = \lim_{T\to\infty}\frac{1}{T}\int_0^T\int_S \rho(\mathbf{p},\mathbf{q},t)O(\mathbf{p},\mathbf{q})\,\mathrm{d}q_1\ldots\mathrm{d}q_{3N}\,\mathrm{d}p_1\ldots\mathrm{d}p_{3N}\,\mathrm{d}t,$$

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

$$= \lim_{T\to\infty}\frac{1}{T}\int_0^T\int_{\phi(S,t)} \rho(\mathbf{p},\mathbf{q},t)O(\mathbf{p},\mathbf{q})\,\mathrm{d}q_1\ldots\mathrm{d}q_{3N}\,\mathrm{d}p_1\ldots\mathrm{d}p_{3N}\,\mathrm{d}t$$

$$= \lim_{T\to\infty}\frac{1}{T}\int_0^T\int_S \rho(\phi(\mathbf{p}(0),\mathbf{q}(0),t),t)O(\phi(\mathbf{p}(0),\mathbf{q}(0),t))\,\mathrm{d}q_1(0)\ldots[\ldots]\,\mathrm{d}t$$

and since ρ is constant along trajectories,

$$= \int_S \rho(\mathbf{p}(0),\mathbf{q}(0),0)\lim_{T\to\infty}\frac{1}{T}\int_0^T O(\phi(\mathbf{p}(0),\mathbf{q}(0),t))\,\mathrm{d}t\,\mathrm{d}q_1(0)\ldots[\ldots]$$

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

$$= a^*,$$

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

Remarks

- 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)

Overview

- 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

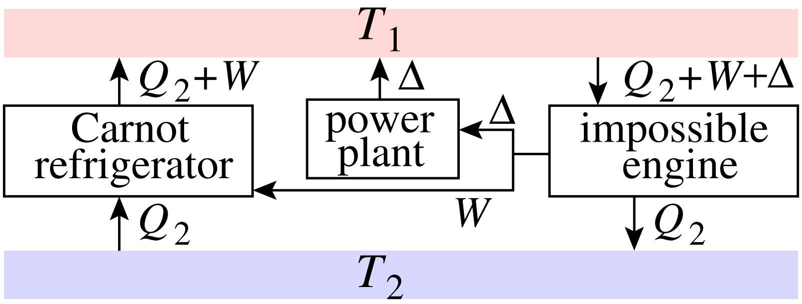
Irreversibility

- 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)

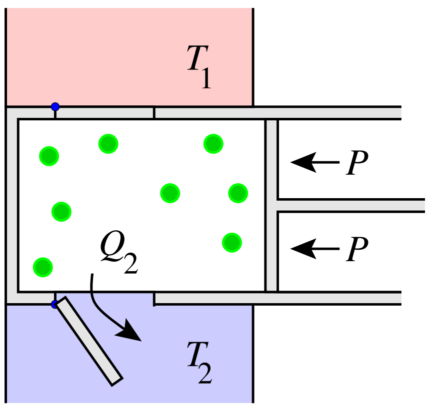
- All reversible engines (for the same T_1, T_2) have the same efficiency.

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 $W = Q_1 - Q_2$



(Sethna 2020)

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

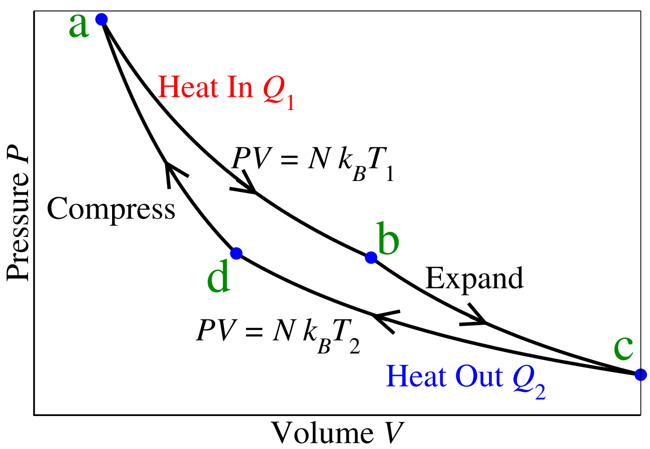
The Carnot Cycle

Step 1: $(a \to b)$**.** 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: $(b \to c)$**.** The cylinder is disconnected from baths. The piston expands further, cooling gas down to temperature T_2.

Step 3: $(c \to d)$**.** 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: $(d \to a)$**.** The cylinder is disconnected again, the gas compressed further, until the temperature is at T_1, returning the cylinder to its original state.



(Sethna 2020)

Energy balance for the Carnot Cycle

- Work W done on outside world is:

$$W = \oint F\,\mathrm{d}x = \int \frac{F}{A} A\,\mathrm{d}x = \oint P dV$$
$$= \text{ area inside } PV\text{-loop}.$$

- 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!).
  $\Longrightarrow$ use simplest material as work medium: a mono-atomic ideal gas.
- Reminder regarding mono-atomic ideal gasses:
  - Equation of state: $PV = Nk_BT$
  - Equipartition theorem: $E =$ kinetic energy $= (3/2)Nk_BT$.

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

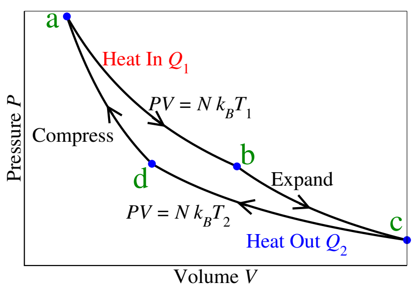
- $(a \to b)$: From energy conservation,

$$\begin{aligned} Q_1 &= E_b - E_a + W_{ab} \\ &= \frac{3}{2}Nk_BT_1 - \frac{3}{2}Nk_BT_1 + \int_a^b P\,\mathrm{d}V \\ &= \int_a^b \frac{3}{2}Nk_BT\frac{1}{V}\,\mathrm{d}V, \end{aligned}$$

  Thus we have:

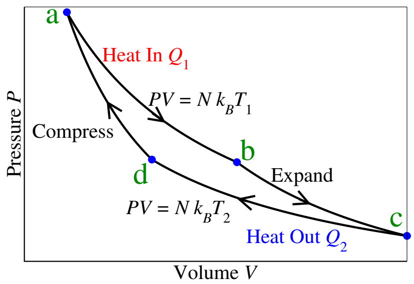
$$Q_1 = Nk_BT_1 \log\left(\frac{V_b}{V_a}\right).$$

- $(c \to d)$: Similarly, $Q_2 = Nk_BT_2 \log\left(\frac{V_c}{V_d}\right).$



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

- $(b \to c)$: We need to determine the ideal gas behaviour under expansion/compression without any heat in- or outflow ("adiabatic" expansion or compression).
  - Energy conservation $\mathrm{d}E = -P\,\mathrm{d}V$
  - Using $E = (3/2)Nk_bT$ and $P = Nk_BT/V$ gives
$$\frac{3}{2}\frac{\mathrm{d}T}{T} = -\frac{\mathrm{d}V}{V}.$$
  - Integrating from b to c gives $\frac{V_c}{V_b} = \left(\frac{T_1}{T_2}\right)^{3/2}$
- $(d \to a)$: 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

- $\frac{Q_1}{T_1} \underset{\textbf{Step 1}}{=} Nk_B \log\left(\frac{V_b}{V_a}\right) \underset{\textbf{Step 2\&4}}{=} Nk_b \log\left(\frac{V_c}{V_d}\right) \underset{\textbf{Step 3}}{=} \frac{Q_2}{T_2}.$
- 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
$$\varepsilon \leqslant \varepsilon_R.$$
- 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 $\varepsilon = (Q_1 - Q_2)/Q_1$
$$\Delta S_{\text{tot}} = \frac{Q_2}{T_2} - \frac{Q_1}{T_1} = \frac{Q_1}{T_2}\left(1 - \frac{T_2}{T_1} - \frac{Q_1 - Q_2}{Q_1}\right) = \frac{Q_1}{T_2}(\varepsilon_R - \varepsilon) \geqslant 0.$$
- **For real engines: $\Delta S_{\text{tot}} > 0$.**
- Macroscopic behaviour provides "arrow of time", while microscopic laws are time-invariant!

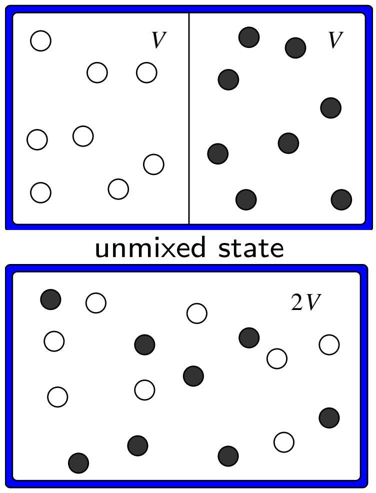
Definition 2: Entropy as disorder

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.**



mixed state
(Sethna 2020)

- The entropy of the mixed state is:

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

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

$$\Delta S = S_m - S_u = N k_B \log 2.$$

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:

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

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

Maxwell's demon and osmotic pressure

- **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^{nd} 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

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

- For the micro-canonical ensemble, where

$$\rho_{\mathsf{eq}} = \frac{1}{\text{shell volume}} = \frac{1}{\Omega(E)\delta E}$$
$$\implies \qquad S_{\mathsf{micro}} = k_B \log(\Omega(E)\delta E)$$

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

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

  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)

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

- 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 $S_i(p_1, \ldots, p_M)$: Axiomatic definition

Axioms

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

- The entropy is maximal for equal probabilities

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

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

- The entropy is unaffected by states of zero probability

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

- 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,
  $A = \{A_k\}$ with $|A| = M$, $\quad B = \{B_l\}$ with $|B| = N$,
  let $S_I(A) \equiv S_I(p_1, \ldots, p_M)$, $\quad S_I(B) \equiv S_I(q_1, \ldots, q_N)$.
- 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

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

$$S_I(A|B_l) \equiv S_I(c_l, \ldots, c_{Ml}).$$

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

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

Information entropy: Additivity and Shannon entropy

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

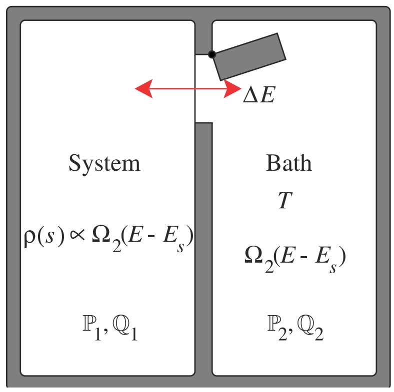
Lecture 7: Free Energies (I)

Introduction

- 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.



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- 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 $E - E_s$:

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

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,

$$\Longrightarrow \quad \frac{1}{T_2} = \frac{\partial S_2}{\partial E_2} \approx \text{const.} \quad \text{in } (E - E_A, E - E_B)$$

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

- 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

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

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

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

- 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

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

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

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

$$\Longrightarrow \qquad N c_v = -\frac{1}{k_B T^2}\frac{\partial^2 \log Z}{\partial\beta^2}$$

- On the other hand

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

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.

Consequences

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:

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

  - 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

Entropy and the Helmholtz free energy

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

- 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

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

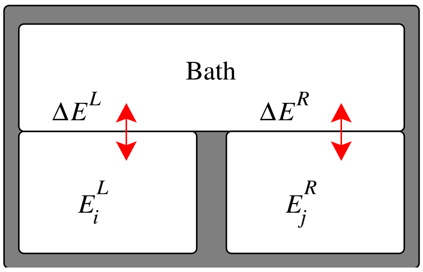
- Notice that it follows (directly from our definition of A) that

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

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 $\beta = 1/k_B T$.

$$Z = \sum_{i,j} \mathrm{e}^{-\beta\left(E_i^L + E_j^R\right)}$$
$$= \left(\sum_i \mathrm{e}^{-\beta E_i^L}\right)\left(\sum_j \mathrm{e}^{-\beta E_j^R}\right) = Z^L Z^R$$
$$\Rightarrow A = -k_B T \log Z = -k_B T \log(Z^L Z^R)$$
$$= A^L + A^R.$$



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- 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

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

where λ 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 undistinguishable particles

- For **undistinguishable** particles: $Z_{\text{ideal}}^{\text{undist}} = \dfrac{(l/\lambda)^{3N}}{N!}$.
- $\langle E\rangle$ doesn't change, but A does

$$
\begin{aligned}
A_{\text{ideal}}^{\text{undist}} &= -k_B T \log\left(\frac{(l/\lambda)^{3N}}{N!}\right) = -Nk_BT\log\left(\frac{V}{\lambda^3}\right) + k_BT\log(N!) \\
&\sim -Nk_BT\log\left(\frac{V}{\lambda^3}\right) + k_BT(N\log(N) - N) \quad \text{(Stirling)} \\
&= -Nk_BT\left[\log\left(\frac{V}{N\lambda^3}\right) + 1\right] \\
&= Nk_BT\left(\log(\rho\lambda^3) - 1\right), \qquad (\rho = N/V).
\end{aligned}
$$

$$
\begin{aligned}
\Rightarrow\ S^{\text{undist}} &= -\frac{\partial A_{\text{ideal}}^{\text{undist}}}{\partial T} = -Nk_B\left(\log(\rho\lambda^3) - 1\right) - Nk_BT\frac{\partial \log(T^{-3/2})}{\partial T} \\
&= Nk_B\left(\frac{5}{2} - \log(\rho\lambda^3)\right).
\end{aligned}
$$

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

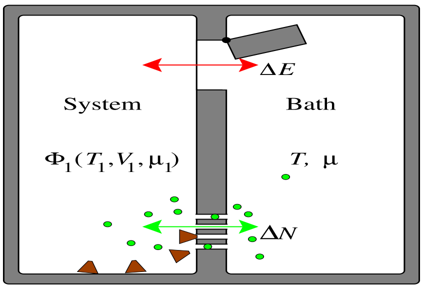
Further examples

- **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

$$\rho(s) \propto \Omega_2(E - E_1, N - N_1) = \mathrm{e}^{\frac{S_2(E-E_1, N-N_1)}{k_B}} \qquad [E_1 \ll E,\, N_1 \ll N]$$

$$\propto e^{\frac{-E_1 \frac{\partial S_2}{\partial E} - N_1 \frac{\partial S_2}{\partial N}}{k_B}} = e^{\frac{-E_1}{k_B T} + \frac{N_1 \mu}{k_B T}} = e^{\frac{-(E_1 - \mu N_1)}{k_B T}},$$

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 $\mu = \frac{\partial E}{\partial N}|_{S,V}$ 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 μ, and it then exhibits thermal number fluctuations about that filling.
- Analogously to canonical ensemble, there is a normalization factor called the grand partition function:
$$\Xi(T,V,\mu) = \sum_n e^{-\frac{(E_n-\mu N_n)}{k_B T}} \qquad (2)$$
It normalizes the prob. dens. & is a generating function.
- Prob. density of state s_i is $\rho(s_i) = e^{-\frac{E_i-\mu N_i}{k_B T}} \Big/ \Xi$
- 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; ℓ_M - internal label of a state within subset
s_{M,ℓ_M} - Corresponding label in $\{s\}$; $E_{M,\ell_M} = E_{s_{M,\ell_M}}$ - its energy.

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

- 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

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

$$= -\frac{1}{\Xi^2}\frac{(\sum_m N_m e^{-\frac{1}{k_B T}(E_m - \mu N_m)})^2}{k_B T} + \frac{1}{\Xi}\frac{\big(\sum_m N_m^2 e^{-\frac{1}{k_B T}(E_m - \mu N_m)}\big)}{k_B T}$$

$$= \frac{\langle N^2 \rangle - \langle N \rangle^2}{k_B T} = \frac{\langle (N - \langle N \rangle)^2 \rangle}{k_B T} = [\text{rms of fluctuations of } N]^2$$

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 ($N \to \infty$)
  - 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.

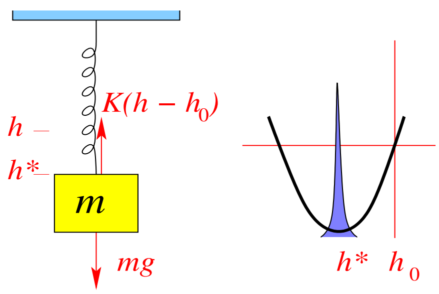
What is Thermodynamics? (2)

- **Axioms 'laws' of thermodynamics**
  1. Transitivity of equilibria: if 2 systems are in equilib. w/ a 3^{rd} 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. $S \to 0$ as temp $\to 0K$ 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



(Sethna 2020)

- Mass on a spring; at $h^\star$ 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., $\frac{1}{2}K(h-h^\star)^2 = \frac{1}{2}k_B T$.
- If $K = 10\frac{N}{m}$ at room temp. $(k_B T \approx 4 \times 10^{-21} J)$, then the fluctuations have size

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

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

Mechanics: Friction and Fluctuations (3)

- 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.):

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

  where γ represents friction (or dissipation), and $\xi(t)$ is a random noise force coming from internal vibrational DOF of the system.
- The strength of noise ξ 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.:

$$3\mathrm{H}_2 + \mathrm{N}_2 \rightleftharpoons 2\mathrm{NH}_3 \qquad (\star)$$

- 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 ν_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: $\prod_i [X_i]^{\nu_i} = K_{\text{eq}}(T) \qquad (\star\star)$
- For $(\star)$, this gives $\frac{[NH_3]^2}{[N_2][H_2]^3} = K_{\text{eq}}(T)$.
- 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 μ_X is the chemical potential of molecule X.
- Reaction proceeds until A is at a min, so
$$-3\mu_{H_2} - \mu_{N_2} + 2\mu_{NH_3} = 0 \qquad (\star\star\star) \qquad \text{in equilib.}$$

Chemical Equilibria and Reaction Rates (3)

- To derive the law of mass action, we assume that the molecules are uncorrelated in space
$\Rightarrow$ each molecular species is a separate ideal gas.
$\Rightarrow$ for each gas,
$$A(N, V, T) = Nk_BT\left[\log\left(\frac{N}{V}\lambda^3\right) - 1\right] + NF_0,$$
where
$$\begin{cases} \lambda = \frac{h}{\sqrt{2\pi m k_B T}} & \text{is the thermal de Broglie wavelength} \\ NF_0 & \text{comes from internal free energy of the molecules,} \\ & \text{see footnote 31 on (Sethna, pg. 119)} \end{cases}$$

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

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:

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

  where

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

  and

$$\Delta F_{\text{net}} = -3F_0^{\text{H}_2} - F_0^{\text{N}_2} + 2F_0^{\text{NH}_3},$$
$$K_0 = \frac{\lambda_{\text{H}_2}^9 \lambda_{\text{N}_2}^3}{\lambda_{\text{NH}_3}^6} = \frac{h^6 m_{\text{NH}_3}^3}{8\pi^3 k_B^3 T^3 m_{\text{H}_2}^{3/2} m_{\text{N}_2}^{3/2}} \propto T^{-3}$$

  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**

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

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

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

Free Energy Density for the Ideal Gas (2)

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

$$P\{\rho\} = \frac{e^{-\beta\int\mathcal{F}^{\text{ideal}}(\rho(\vec{x}))\,\mathrm{d}\vec{x}}}{Z} \qquad (\beta{=}1/k_BT)$$

- As usual, free energy $F\{\rho\} = \int\mathcal{F}^{\text{ideal}}(\rho(\vec{x}))\,\mathrm{d}\vec{x}$ 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 ΔV, 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^{st} Variation of $\mathcal{F}$ w.r.t ρ

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

- For the ideal-gas free energy, which has no gradient term of ρ, 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 $\gamma =$ const. $=$ "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

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

- Combine this with conservation of ρ,

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

- 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 describtion 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 we bridge the entire spectrum of length scales from the particle physics to the continuum description.

Plan for today

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,
$$f(\mathbf{r}, \mathbf{v}, t)\, d\mathbf{v}\, d\mathbf{r} \tag{3}$$
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 $\Delta t \to 0$, 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 $\mathrm{d}f/\mathrm{d}t$.
- 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 ρ describes the density of an ensemble of trajectories in the $6N$-dimensional phase space Γ.
- Then the **s-particle probability density** is defined as

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

  where $\mathbf{p}_k = m\mathbf{v}_k$, $\mathbf{q}_k = \mathbf{r}_k$.
- Define the **s-particle distribution function** $f_s(\gamma_1, \ldots, \gamma_s)$ as the expectation value of finding *any* s (of the total of N) particles at positions $(\gamma_1, \ldots, \gamma_s)$.

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

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:

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

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 $\mathbf{a}_{ij} = -\frac{1}{m}\boldsymbol{\nabla}_{\mathbf{r}_i} W_{ij}$ (not summed) as the force per unit mass on particle i due to particle j. ($\boldsymbol{\nabla}_{\mathbf{r}_i}$ 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

$$\frac{\partial f_s}{\partial t} + \sum_{i=1}^{s}\left[\mathbf{v}_i.\boldsymbol{\nabla}_{\mathbf{r}_i} f_s + \left\{\mathbf{g} + \sum_{j=1}^{s}\mathbf{a}_{ij}\right\}.\boldsymbol{\nabla}_{\mathbf{v}_i} f_s\right] \tag{7}$$

$$= -\sum_{i=1}^{s}\int_P \mathbf{a}_{i,s+1}.\boldsymbol{\nabla}_{\mathbf{v}_i} f_{s+1}\, d\gamma_{s+1}. \tag{8}$$

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

$$\frac{\partial f}{\partial t} + \mathbf{v}.\boldsymbol{\nabla}_{\mathbf{r}} f + \mathbf{g}.\boldsymbol{\nabla}_{\mathbf{v}} f = -\int_P \mathbf{a}_{12}.\boldsymbol{\nabla}_{\mathbf{v}} f_2\, d\gamma_2. \tag{9}$$

- 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

$$Q = -\int_P \mathbf{a}(\mathbf{r}-\mathbf{s}).\boldsymbol{\nabla}_{\mathbf{v}} f(\mathbf{r},\mathbf{v},t) f(\mathbf{s},\mathbf{w},t)\, d\mathbf{s}\, d\mathbf{w}. \tag{10}$$

- You will show that for short range forces,

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

Plan for today

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.

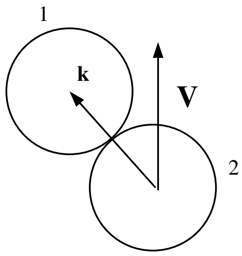
The collision integral

- 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,

$$Q = Q_+ - Q_-, \tag{12}$$

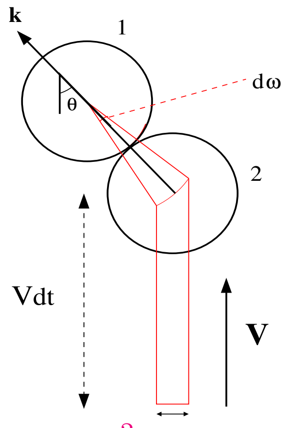
where Q_+ and Q_- are the gain and loss from collisions, respectively.

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:
$$-\mathbf{V} \cdot \mathbf{k} = \mathbf{V}' \cdot \mathbf{k}, \quad \mathbf{V} - (\mathbf{V} \cdot \mathbf{k})\mathbf{k} = \mathbf{V}' - (\mathbf{V}' \cdot \mathbf{k})\mathbf{k}. \qquad (**)$$
- Combining $(*)$ and $(**)$ gives
$$\mathbf{v}' = \mathbf{v} + (\mathbf{V} \cdot \mathbf{k})\mathbf{k}, \quad \mathbf{w}' = \mathbf{w} - (\mathbf{V} \cdot \mathbf{k})\mathbf{k}. \qquad (13)$$

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_{cyl} is the volume of the cylinder,
$$dV_{\text{cyl}} = \mathbf{d}^2 \mathbf{k} \cdot \mathbf{V}\, d\omega(\mathbf{k})\, dt. \qquad (14)$$
- $(-\mathbf{d}\mathbf{k})$ 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

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

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

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

  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

$$d\mathbf{v}'\, d\mathbf{w}' = J\, d\mathbf{v}\, d\mathbf{w}, \tag{17}$$

where J is the Jacobian of the transformation,

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

- Evaluating the coefficients, we find

$$J = \begin{vmatrix} I - K & K \\ K & I - K \end{vmatrix}, \tag{19}$$

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

$$K_{ij} = k_i k_j. \tag{20}$$

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:

$$\begin{pmatrix} \mathbf{m} \\ \mathbf{0} \end{pmatrix}, \begin{pmatrix} \mathbf{n} \\ \mathbf{0} \end{pmatrix}, \begin{pmatrix} \mathbf{0} \\ \mathbf{m} \end{pmatrix}, \begin{pmatrix} \mathbf{0} \\ \mathbf{n} \end{pmatrix}, \begin{pmatrix} \mathbf{k} \\ \mathbf{k} \end{pmatrix}, \begin{pmatrix} \mathbf{k} \\ -\mathbf{k} \end{pmatrix}, \tag{21}$$

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

$$d\mathbf{v}'\, d\mathbf{w}' = d\mathbf{v}\, d\mathbf{w} \tag{22}$$

in (16).

Calculation of the collision integral (4)

Dividing by the hypervolume element and noting that

$$\mathbf{k}' \cdot \mathbf{V}' = \mathbf{k} \cdot \mathbf{V}, \tag{23}$$

we obtain the source term Q_+ in the form

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

and the collision term takes the final form

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

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

Discussion

- Result from 1^{st} principles calculation (**Boltzmann collision integral**):

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

- Result from BBGKY hierarchy:

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

  and after combination with the hard-sphere approximation:

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

- 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

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

  where ρ 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 (μ 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)!

Outline

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 ψ and show that if
$$I = \int_U \psi(\mathbf{v}) Q \, d\mathbf{v} = 0. \tag{29}$$
is satisfied, then $\bar{\psi}$ (to be defined) satisfies the conservation law
$$\frac{\partial(\rho\bar{\psi})}{\partial t} + \boldsymbol{\nabla} \cdot (\rho\bar{\psi}\mathbf{u}) + \boldsymbol{\nabla} \cdot \mathbf{J}_\psi = \rho\overline{\mathbf{g} \cdot \boldsymbol{\nabla}_\mathbf{v}\psi}. \tag{30}$$
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
$$n = \int_U f \, d\mathbf{v}, \tag{31}$$
where we suppose $f \to 0$ as $|\mathbf{v}| \to \infty$.
- If the molecules have mass m, then the density is defined as
$$\rho = mn. \tag{32}$$
- We also define the mean velocity by
$$n\mathbf{u} = \int_U f\mathbf{v} \, d\mathbf{v}, \tag{33}$$
- More generally, the mean $\bar{\psi}$ of a quantity ψ is defined by
$$n\bar{\psi} = \int_U f\psi \, d\mathbf{v}. \tag{34}$$

Step 1

Evolution of the averages (1)

- We have the following identity:

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

- 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 $f \to 0$ as $|\mathbf{v}| \to \infty$.
- 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)

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

where

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

is the molecular flux of ψ, 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 ψ depends only on $\mathbf{v}$, since then $\psi_t = \nabla\psi = 0$.
- This has the proper form for a conservation law for ψ, 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 ψ 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
  $$I_+ \equiv \int_U \psi(\mathbf{v}) Q_+ \, d\mathbf{v} = \int_\Sigma \psi(\mathbf{v}) f(\mathbf{v}'(\mathbf{v},\mathbf{w})) f(\mathbf{w}'(\mathbf{v},\mathbf{w})) \, d\Sigma, \qquad (40)$$
  where
  $$f(\mathbf{v}) \equiv f(\mathbf{r},\mathbf{v},t), \quad \Sigma = U^2 \times \Omega_+, \quad \Omega_+ = \{\mathbf{k} \,|\, \mathbf{V}\cdot\mathbf{k} > 0\},$$
  $$d\Sigma = d\Omega \, d\mathbf{w} \, d\mathbf{v}, \quad d\Omega = d^2\mathbf{k}\cdot\mathbf{V} \, d\omega(\mathbf{k}),$$
  $$\mathbf{v}' = \mathbf{v} + (\mathbf{V}\cdot\mathbf{k})\mathbf{k}, \quad \mathbf{w}' = \mathbf{w} - (\mathbf{V}\cdot\mathbf{k})\mathbf{k}, \quad \mathbf{V} = \mathbf{w} - \mathbf{v}.$$
- 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
  $$I_+ = \int_\Sigma \psi(\mathbf{v}') f(\mathbf{v}) f(\mathbf{w}) \, d\Sigma. \qquad (41)$$

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
$$I = I_+ - I_- = \int_\Sigma [\psi(\mathbf{v}') - \psi(\mathbf{v})] f(\mathbf{v}) f(\mathbf{w})\, d\Sigma. \tag{42}$$
- 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
$$I = \int_{U^2} \int_{\mathbf{V}.\mathbf{k}'>0} [\psi(\mathbf{w}') - \psi(\mathbf{w})] f(\mathbf{v}) f(\mathbf{w})\, d^2\mathbf{k}'.\mathbf{V}\, d\omega\, d\mathbf{w}\, d\mathbf{v}. \tag{43}$$
- Adding the two expressions (noting that $\mathbf{k}'$ is a dummy variable),
$$2I = \int_\Sigma [\psi(\mathbf{v}') + \psi(\mathbf{w}') - \psi(\mathbf{v}) - \psi(\mathbf{w})] f(\mathbf{v}) f(\mathbf{w})\, d\Sigma. \tag{44}$$
- It follows from this that (29), that is, $I = 0$, is satisfied identically if
$$\psi(\mathbf{v}') + \psi(\mathbf{w}') = \psi(\mathbf{v}) + \psi(\mathbf{w}), \tag{45}$$
Such ψ 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 ψ 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. δ-functions, we see that $[\psi(\mathbf{v}') + \ldots]$ must be pointwise zero, and equation (45) follows.

Step 3

Conservation laws for mass, momentum and energy.

It is straightforward to see that

$$\psi = 1, \ \mathbf{v}, \ \tfrac{1}{2}v^2. \tag{46}$$

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
$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \mathbf{u}) = 0. \tag{47}$$
- For $\psi = \mathbf{v}$, we obtain **conservation of momentum** in the form
$$\frac{\partial \rho \mathbf{u}}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \mathbf{u}\mathbf{u}) = \boldsymbol{\nabla} \cdot \boldsymbol{\sigma} + \rho \mathbf{g}, \tag{48}$$
where the stress tensor is defined by $\quad \boldsymbol{\sigma} = -\rho \overline{\mathbf{u}'\mathbf{u}'}, \qquad (49)$
- For $\psi = \frac{1}{2}v^2$, we obtain **energy conservation:**
$$\frac{\partial}{\partial t}(\tfrac{1}{2}\rho u^2 + \rho e) + \boldsymbol{\nabla} \cdot [(\tfrac{1}{2}\rho u^2 + \rho e)\mathbf{u}] = -\boldsymbol{\nabla} \cdot \mathbf{q} + \boldsymbol{\nabla} \cdot (\boldsymbol{\sigma}.\mathbf{u}) + \rho \mathbf{g}.\mathbf{u}, \tag{50}$$
where the internal energy/unit mass is defined by $\quad e = \frac{1}{2}\overline{u'^2}, \qquad (51)$

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

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
$$\tfrac{1}{2}m\overline{u'^2} = \tfrac{3}{2}kT, \tag{53}$$
where $k = 1.38 \times 10^{-23}$ J K^{-1} is Boltzmann's constant.
- In addition, we define the pressure in the usual way as
$$p = -\tfrac{1}{3}\sigma_{kk} = \tfrac{1}{3}\rho\overline{u'^2}, \tag{54}$$
- From this, we can derive the ideal gas law
$$p = nkT = \frac{\rho R T}{M}, \tag{55}$$
where the ideal gas constant & the molecular weight are defined by, resp.,
$$R = kA, \quad M = Am, \tag{56}$$
($A = 6 \times 10^{23}$Avogadro's number.)

Lecture 10, Part 2
The H-theorem

Purpose

- 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.

$$\text{Define} \qquad H = \int_U f \ln f \, d\mathbf{v}. \tag{57}$$

- 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

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

- Thus

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

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

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

where

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

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

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

Adding the two results, we obtain

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

Derivation of Boltzmann's H–theorem (3)

- Applying (63) gives

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

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

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

  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.,

$$f = A\exp[\mathbf{B}\cdot\mathbf{v} - \tfrac{1}{2}Cv^2], \qquad (66)$$

  or equivalently, completing the square,

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

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

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

- Carrying out the calculations, we find

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

Maxwellian distribution (2)

Thus

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

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

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

where

$$c = \sqrt{\frac{kT}{m}} = \sqrt{\frac{RT}{M}} = \sqrt{\frac{p}{\rho}} \tag{72}$$

is the isothermal sound speed.

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

Goal

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

The task

- 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

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

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

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

  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 tan the typical macroscopic size L of the system (e.g. the "box").

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

Outline

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

$$v_0 = \sqrt{\frac{kT_0}{m}}. \tag{75}$$

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

$$l = \frac{1}{n_0^{1/3}}. \tag{76}$$

- 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

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

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

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

$$t_f = \frac{l_f}{v_0}, \tag{78}$$

and a mean collision time

$$t_c = \frac{d}{v_0}. \tag{79}$$

Non-dimensionalisation – The resulting scalings

- We non-dimensionalise the variables as

$$n \sim n_0, \quad f \sim \frac{n_0}{v_0^3}, \quad Q \sim \frac{n_0^2 d^2}{v_0^2}, \quad \mathbf{r} \sim L,$$

$$\mathbf{v} \sim v_0, \quad \mathbf{g} \sim g, \quad t \sim \frac{L}{v_0}, \quad T \sim T_0, \tag{80}$$

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

$$\varepsilon \left[\frac{\partial f}{\partial t} + \boldsymbol{\nabla}_{\mathbf{r}}.(f\mathbf{v}) + \frac{1}{F^2} \boldsymbol{\nabla}_{\mathbf{v}}.(f\mathbf{g}) \right] = Q,$$

$$Q = \int_U \int_{\Omega_+} [f(\mathbf{r}, \mathbf{v}', t) f(\mathbf{r}, \mathbf{w}', t) - f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{w}, t)] \, d\Omega \, d\mathbf{w}. \tag{81}$$

- 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*.
    $\Longrightarrow$ 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

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

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

$$Q(f, g)(\mathbf{v}) =$$

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

- By putting

$$f = e^{\Phi}, \tag{85}$$

(83) can be written in the form

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

A multi-scale expansion – The leading order solution

- We expand the solution as

$$\Phi = \Phi_0 + \varepsilon\phi + \dots . \tag{87}$$

- To leading order

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

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

- 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

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

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

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

By putting

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

(83) can be written in the form

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

We expand the solution as

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

Formulation of the next order correction problem

- To next order, we have the linear equation

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

  where we define the linear integral operator

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

  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),

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

Overview (of solution steps)

We want to solve

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

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 $\mathcal{N} = \mathrm{span}\{1, \mathbf{v}, \frac{1}{2}v^2\}$.
3. Therefore the integral equation (89) only has solutions if

$$\langle \dot{\Phi}_0, \eta \rangle = 0 \tag{92}$$

   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) ϕ of (89).

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

- Consider the integral

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

  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

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

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

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

$$\text{i.e.} \qquad \langle \psi, \mathcal{L}\phi \rangle = \langle \mathcal{L}\psi, \phi \rangle \tag{96}$$

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

Overview (of solution steps)

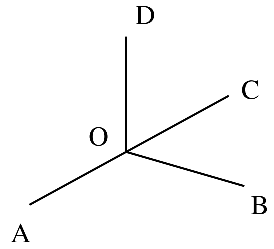
We want to solve
$$\mathcal{L}\phi = \dot{\Phi}_0. \qquad \text{[see (89)]}$$

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 $\mathcal{N} = \mathrm{span}\{1, \mathbf{v}, \frac{1}{2}v^2\}$.**
3. Therefore the integral equation (89) only has solutions if
$$\langle \dot{\Phi}_0, \eta \rangle = 0 \qquad (*)$$
for all $\eta \in \mathcal{N}$ of $\mathcal{L}$ (Fredholm Alternative). Applying $(*)$ recovers the conservation laws.
4. We can now find the solution(s) ϕ of (89).

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

- We now show that $\mathcal{N} \equiv \{\eta : \mathcal{L}\eta = 0\} = \mathrm{span}\{1, \mathbf{v}, \frac{1}{2}v^2\} \equiv \mathcal{S}$.
- 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
$$\langle \phi, \mathcal{L}\phi \rangle \leqslant 0, \qquad (97)$$
- Equality holds in (97) if and only if $\Delta\phi = 0$, i.e. if ϕ is a summational invariant.
- Implication: If $\phi \in \mathcal{N}$, then ϕ is a summational invariant. Therefore, all we need to show is that $\mathcal{S}$ contains all summational invariants i.e. any ϕ 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 $\mathrm{span}\{1, \mathbf{v}, \frac{1}{2}v^2\}$.

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

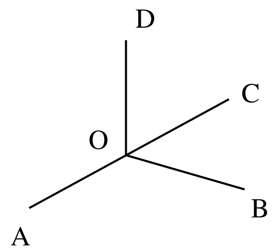


- Suppose ϕ is a summational invariant with $\phi = 0$ on the five points O: $(0,0,0)$, A: $(0,-1,0)$, B: $(1,0,0)$, C: $(0,1,0)$ and D: $(0,0,1)$
- Since $\phi = 0$ on three points of the square spanned by OBC, then $\phi = 0$ on the fourth, that is at $(1,1)$ (say $\equiv E$). Suppressing the third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

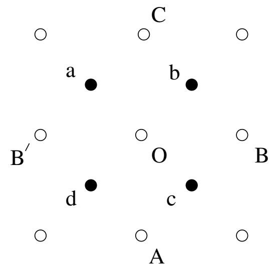


- Let $\mathbf{v} = A = (0,-1)$, $\mathbf{w} = C = (0,1)$, and $\mathbf{k} = (-1,-1)/\sqrt{2}$. Then

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

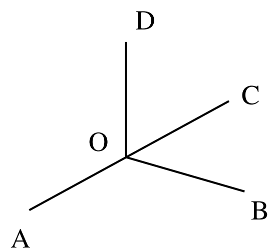
  Thus, if $B' \equiv -B$, we have $\phi(B') = \phi(A) + \phi(C) - \phi(B) = 0$.
- Using the argument of the previous slide, we can now conclude $\phi = 0$ on the reflected cuboid spanned by $OAB'CD$.
- Repeating reflections shows that $\phi = 0$ on $\mathbb{Z}\times\mathbb{Z}\times\mathbb{Z}$.

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 ϕ is continuous, then it is identically zero.

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



- Finally, suppose that ϕ is summational and continuous.
- We can uniquely choose (five) coefficients a, $\mathbf{b}$ and c so that the function
$$\psi = a + \mathbf{b}.\mathbf{v} + \tfrac{1}{2}cv^2 \in \mathcal{S} \qquad (98)$$
is equal to ϕ 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

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

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

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

   and show that $\mathcal{L}$ is self adjoint with respect to $\langle \cdot, \cdot \rangle$
2. The null space of $\mathcal{L}$ is $\mathcal{N} = \mathrm{span}\{1, \mathbf{v}, \frac{1}{2}v^2\}$.
3. **Therefore the integral equation (89) only has solutions if**

$$\langle \dot{\Phi}_0, \eta \rangle = 0 \tag{$*$}$$

   for all $\eta \in \mathcal{N}$ of $\mathcal{L}$ (Fredholm Alternative). Applying $(*)$ recovers the conservation laws.
4. We can now find the solution(s) ϕ 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

$$\Phi_0 = A - \tfrac{1}{2}Cu'^2, \qquad \mathbf{u}' = \mathbf{v} - \mathbf{u}, \tag{100}$$

where

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

are functions of $\mathbf{r}$ and t but not of $\mathbf{v}$.
- The calculation then yields

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

where

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

and

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

- Note that

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

Applying the solvability condition (2)

Reminder: The previous equations are

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

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

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

- 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

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

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 $\mathcal{N} = \mathrm{span}\{1, \mathbf{v}, \frac{1}{2}v^2\}$.
3. Therefore the integral equation (89) only has solutions if

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

   for all $\eta\in\mathcal{N}$ of $\mathcal{L}$ (Fredholm Alternative). Applying $(*)$ recovers the conservation laws.
4. **We can now find the solution(s) ϕ of (89).**

Solution for ϕ

- A particular solution we seek of
$$\mathcal{L}\phi = -\mathbf{W}\cdot\boldsymbol{\nabla} C + CU_{ij}\frac{\partial u_i}{\partial x_j}. \qquad (89)$$
can be written as
$$\phi = -\boldsymbol{\xi}\cdot\boldsymbol{\nabla} C + C\boldsymbol{\eta}:\boldsymbol{\nabla}\mathbf{u}, \qquad (104)$$
where
$$\mathcal{L}\boldsymbol{\xi} = \mathbf{W}, \quad \mathcal{L}\boldsymbol{\eta} = \mathbf{U}. \qquad (105)$$
- The solutions of (105) have the form
$$\boldsymbol{\xi} = -F(u')\mathbf{u}', \quad \boldsymbol{\eta} = -G(u')\mathbf{U}. \qquad (106)$$
- 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 ϕ can always be moved to Φ_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 $\boldsymbol{\xi}$ and $\boldsymbol{\eta}$

For the problem (see (105), (105))
$$\mathcal{L}\boldsymbol{\xi} = \mathbf{W} = \left(\tfrac{1}{2}u'^2 - \tfrac{5}{2}T^*\right)\mathbf{u}'$$
we will now discuss our claim that the solution has the form
$$\boldsymbol{\xi} = -F(u')\mathbf{u}'. \qquad \text{(cf. 106)}$$

- 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
$$\mathcal{L}\boldsymbol{\phi} = \int_U f_0(w)\left[\int_{\Omega_+}\Delta\boldsymbol{\phi}(\mathbf{v},\mathbf{w},\boldsymbol{\Omega})\,d\Omega\right]d\mathbf{w}, \qquad (107)$$
which recognises that the Maxwellian is a function of the magnitude of $\mathbf{w}$, and that $\Delta\boldsymbol{\phi}$ is a function of both $\mathbf{v}$ and $\mathbf{w}$, which together define the sphere spanned by $\boldsymbol{\Omega}$, as well as the direction element $\boldsymbol{\Omega}$.
- Now suppose that
$$\boldsymbol{\phi} = g(v)\mathbf{v}; \qquad (108)$$
thus $\mathcal{L}\boldsymbol{\phi}$ is a vector.

Derivation of the form (106) for $\boldsymbol{\xi}$ and $\boldsymbol{\eta}$ (continued)

- Let us consider the effect of a rotation about the $\mathbf{v}$ axis on $\mathcal{L}\boldsymbol{\phi}$, that is, we multiply $\mathcal{L}\boldsymbol{\phi}$ 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
$$\mathbf{w} = R^T\mathbf{w}^*, \quad \mathbf{k} = R^T\mathbf{k}^*, \tag{109}$$
then
$$\mathbf{v}' = R^T\mathbf{v}^{*\prime}, \quad \mathbf{w}' = R^T\mathbf{w}^{*\prime}, \tag{110}$$
and thus
$$\Delta\boldsymbol{\phi}(\mathbf{v},\mathbf{w},\boldsymbol{\Omega}) = \Delta\boldsymbol{\phi}(\mathbf{v},R^T\mathbf{w}^*,R^T\boldsymbol{\Omega}^*) = R^T\Delta\boldsymbol{\phi}(\mathbf{v},\mathbf{w}^*,\boldsymbol{\Omega}^*), \tag{111}$$
where $\boldsymbol{\Omega}^*$ is the direction element associated with $\mathbf{k}^*$.
- The direction sphere Ω_+ 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),
$$R\mathcal{L}\boldsymbol{\phi} = \mathcal{L}\boldsymbol{\phi}, \tag{112}$$

Derivation of the form (106) for $\boldsymbol{\xi}$ and $\boldsymbol{\eta}$ (end)

- Letting $\mathbf{u} = \mathcal{L}\boldsymbol{\phi}$, 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
$$\mathcal{L}[g(v)\mathbf{v}] = h(v)\mathbf{v}, \tag{113}$$
where h must be a function only of $v = |\mathbf{v}|$.
- We see that if $\boldsymbol{\xi} = -F(u')\mathbf{u}'$, then $\mathcal{L}\boldsymbol{\xi}$ 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 $\boldsymbol{\eta}$ in (106).

Lecture 12: A continuum limit: The Chapman-Enskog Method (II) – The constitutive relations for stress and heat flux

Outline

- Derive the constitutive law for the stresses including an expression for the viscosity μ
- Derive the constitutive law for the heat flux including an expression for the thermal conductivity k.
- Establish positivity of μ and k
- Calculate numerical values for μ 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

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

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 β_{ijkl}

(Case $i \neq j$)

- We have

$$\tau_{ij} = 2\mu\dot{\varepsilon}_{ij}, \quad (117)$$

where

$$\dot{\varepsilon}_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) \quad (118)$$

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 μ is independent of the particular choice of i and j; in fact, we have also

$$\mu^* = \frac{1}{T^{*3/2}}\langle GU_{ij}, U_{ij} \rangle = \frac{1}{T^{*3/2}}\left.\langle Gu_i'^2, u_j'^2 \rangle\right|_{i\neq j}. \quad (120)$$

Calculating β_{ijkl}
(Case $i = j$)

- We have
$$\tau_{ii} = \frac{\sqrt{mkT}}{d^2} \sum_k \frac{1}{T^{*3/2}} \langle GU_{kk}, u_i'^2 \rangle \frac{\partial u_k}{\partial x_k}, \tag{121}$$
and for each value of k, we find
$$\langle GU_{kk}, u_i'^2 \rangle = \langle Gu_k'^2, u_i'^2 \rangle - (\tfrac{1}{3}G_1 + \tfrac{2}{3}G_2), \tag{122}$$
where
$$G_1 = \langle Gu_i'^2, u_i'^2 \rangle, \quad G_2 = \langle Gu_i'^2, u_j'^2 \rangle \Big|_{i \neq j} \tag{123}$$
- As in the previous case, these are independent of i, j.
- By direct calculation, we have, putting $\mathbf{u}' = \sqrt{T^*}(x, y, z) = \sqrt{T^*}\mathbf{r}$,

$$\begin{aligned} G_1 &= \frac{n^* T^{*2}}{(2\pi)^{3/2}} \int_U G(r) e^{-\frac{1}{2}r^2} x^4 \, dV = \frac{n^* T^{*2}}{4} \sqrt{\frac{2}{\pi}} \int_0^\infty G(r) r^6 e^{-\frac{1}{2}r^2} \, dr, \\ G_2 &= \frac{n^* T^{*2}}{(2\pi)^{3/2}} \int_U G(r) e^{-\frac{1}{2}r^2} x^2 y^2 \, dV = \frac{1}{3} G_1. \end{aligned} \tag{124}$$

Final form for μ^*

- It follows from (121) that [sum over k only]
$$\tau_{ii} = 2\mu \left[\frac{\partial u_i}{\partial x_i} - \tfrac{1}{3}\dot{\varepsilon}_{kk} \right] \tag{125}$$
- Together with (117), this yields the general formula
$$\tau_{ij} = 2\mu(\dot{\varepsilon}_{ij} - \tfrac{1}{3}\dot{\varepsilon}_{kk}\delta_{ij}). \tag{126}$$
- From (120) and (124), we have
$$\mu = \frac{\sqrt{mkT}}{d^2} \mu^*,$$
$$\mu^* = \frac{G_2}{T^{*3/2}} = \frac{1}{12} \sqrt{\frac{2}{\pi}} \int_0^\infty G^*(r) r^6 e^{-\frac{1}{2}r^2} \, dr, \tag{127}$$
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

$$q_i = \frac{1}{d^2 L}\sqrt{\frac{k^3 T_0^3}{m}}\langle \phi, \tfrac{1}{2}u'^2 u_i' \rangle. \tag{128}$$

To calculate the inner product, note that since $\phi \perp \mathcal{N}$,

$$\langle \phi, \tfrac{1}{2}u'^2 u_i' \rangle = \langle \phi, W_i \rangle, \tag{129}$$

and in view of (104) and the fact that $\mathbf{U} \perp \mathbf{W}$, we have

$$\langle \phi, \tfrac{1}{2}u'^2 u_i' \rangle = -\langle \xi_j, W_i \rangle \frac{\partial C}{\partial x_j}, \tag{130}$$

summed over j. Since both $\boldsymbol{\xi}$ and $\mathbf{W}$ are proportional to $\mathbf{u}'$, it follows that $\langle \xi_j, W_i \rangle = 0$ if $i \neq j$, and thus

$$\langle \phi, \tfrac{1}{2}u'^2 u_i' \rangle = -\frac{1}{T^{*2}}\langle \xi_i, W_i \rangle \frac{\partial T^*}{\partial x_i} \tag{131}$$

(not summed).

Heat flux and thermal conductivity (2)

Converting the temperature gradient to dimensional units, we find

$$\mathbf{q} = -k_T \boldsymbol{\nabla} T, \tag{132}$$

where the thermal conductivity is

$$k_T = \frac{k^*}{d^2}\left(\frac{k^3 T}{m}\right)^{1/2}, \tag{133}$$

and

$$\left.\begin{aligned} k^* = \frac{1}{T^{*5/2}}\langle \xi_i, W_i \rangle &= \frac{1}{T^{*5/2}}\langle F u_i', (\tfrac{1}{2}u'^2 - \tfrac{5}{2}T^*) u_i' \rangle \\ &= \frac{1}{3T^{*5/2}}\langle F, (\tfrac{1}{2}u'^2 - \tfrac{5}{2}T^*) u'^2 \rangle. \end{aligned}\right\} \tag{134}$$

Making the substitution $u' = r\sqrt{T^*}$ and writing

$$F = \frac{T^{*1/2} F^*(r)}{n^*}, \tag{135}$$

this last integral can be explicitly written as

$$k^* = \frac{4\pi}{3}\int_0^\infty e^{-\frac{1}{2}r^2} F^*(r) \left(\tfrac{1}{2}r^2 - \tfrac{5}{2}\right) r^4 \, dr. \tag{136}$$

Viscosity and thermal conductivity are positive

- Remaining task: Show that μ 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

$$\langle \psi, \mathcal{L}\psi \rangle = -\tfrac{1}{4} \int_\Sigma f_0(\mathbf{v}) f_0(\mathbf{w}) (\Delta\psi)^2 \, d\Sigma < 0. \tag{137}$$

- It follows that (137) applies for $\psi = \boldsymbol{\xi}, \boldsymbol{\eta}$, and thus from (105)

$$\langle \boldsymbol{\xi}, \mathbf{W} \rangle > 0, \quad \langle G(u')\mathbf{U}, \mathbf{U} \rangle > 0, \tag{138}$$

  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 μ^* and k^* are given in (127) and online notes. Chapman and Cowling (1970, page 168) evaluate after solving for F and G,

$$\mu^* = \frac{5}{16\sqrt{\pi}} \approx 0.176, \quad k^* = \frac{75}{64\sqrt{\pi}} \approx 0.661. \tag{139}$$

- It is of interest to compare the corresponding dimensional values

$$\mu \sim \frac{0.18\sqrt{mkT}}{d^2}, \quad k_T \sim \frac{0.66}{d^2} \left(\frac{k^3 T}{m} \right)^{1/2}, \tag{140}$$

  with actual measured values. We take as **representative values for air**:

$$m \sim 5 \times 10^{-26} \text{ kg}, \quad k = 1.38 \times 10^{-23} \text{ J K}^{-1},$$
$$d \sim 3.6 \times 10^{-10} \text{ m}, \quad T \sim 300 \text{ K} \tag{141}$$

- These give $\mu \sim 1.8 \times 10^{-5}$ Pa s and $k_T \sim 0.08$ W m^{-1} K^{-1}.
- The first is about right, whereas the actual value of k_T is about 3× 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.