Ensembles I
Counting microstates

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Schedule

Time	Mon. 20/11/17	Tue. 21/11/17	Wed. 22/11/17	Thur. 23/11/17	Fri. 24/11/17	Mon. 27/11/17	Tue. 28/11/17	Wed. 29/11/17	Thur. 30/11/17	Fri. 01/12/17
9:00	Free Time	Welcome JAG	Free Time	Free Time	Free Time	Free Time	Free Time	Free Time	Free Time	Free Time
9:30		Lecture 1: Overview and Introduction JAG	Lecture 4: Thermodynamics JAG	Lecture 7: Classical Mechanics I JAG	Lecture 10: Ensembles I CO	Lecture 13: Free energies: reaction coordinates JAG	Lecture 16: Calculating properties from simulations JAG	Lecture 19: Electrostatics WvG	Lecture 22: On the ethics of the academic endeavour: where do we go?	Lecture 24: Left-overs/ questions and future perspectives WvG
10:15		Break	Break	Break	Break	Break	Break	Break		Break
10:30		Lecture 2: Molecular Simulations MD/SD/MC CO	Lecture 5: Force-Field Development CO	Lecture 8: Classical Mechanics II JAG	Lecture 11: Ensembles II JAG	Lecture 14: Boundary Conditions I WvG	Lecture 17: Comparison with Experiments WvG	Lecture 20: Polarization WvG	Lecture 25: Students plans I WvG	
11:15		Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break
11:45		Lecture 3: How to simulate using GROMOS CO	Lecture 6: Structure Refinement CO	Lecture 9: Analizing with GROMOS CO	Lecture 12: Free energies: alchemistry CO	Lecture 15: Boundary Conditions II WvG	Lecture 18: Searching & Enhanced Sampling WvG	Lecture 21: Multi -resolution simulations WvG	Lecture 23: QM/MM WvG	Lecture 26: Students plans II
12:30		Break for lunch, self-study, discussion.*	Break for lunch, self-study, discussion.*	Break for lunch, self-study, discussion.*	Break for lunch, self-study, discussion.*	Break for lunch, self-study, discussion.*	Break for lunch, self-study, discussion.*	Break for lunch, self-study, discussion.*	Break for lunch, self-study, discussion.*	Tutorial 10: **
14:00	Registration	Tutorial 2:	Tutorial 3:	Tutorial 4:	Tutorial 5:	Tutorial 6:	Tutorial 7	Tutorial 8:	Tutorial 9:	How to prepare a barbecue
	Tutorial 1 Linux, NLHPC and OS-dongle installation	Running MD GROMOS Tutorial	Running MD Students Plans	Running MD Students Plans	Running MD Students Plans	Statistical Mechanics exercises	Analizing MD: GROMOS Tutorial	Analizing MD: Students Plans	Analizing MD: Students Plans	
16:00	Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break	Coffee Break	
17:30	End of session	End of session	End of session	End of session	End of session	End of session	End of session	End of session	End of session	
20:30	Free time	Free time	Free time	Free time	Beer, Science & Friendship Good Stock Bar	Free time	Free time	Free time	Free time	Farewell

What is statistical mechanics about?

- Provide the link between macroscopic properties and the molecular (nanoscopic) particles.

n, P, T
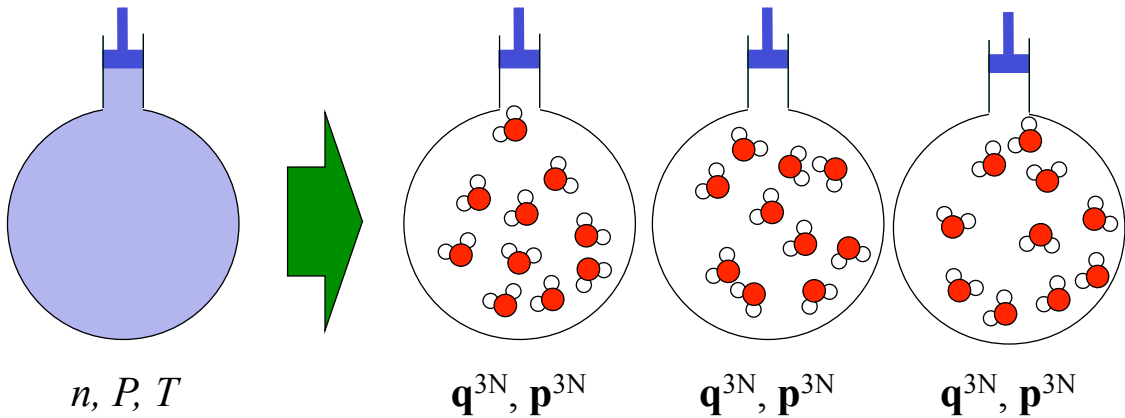
"Macroscopic" view
(e.g. experiment)
Description of a system in terms of measurable (macroscopic) thermodynamic quantities

$\mathbf{q}^{3N}, \mathbf{p}^{3N}$ $\mathbf{q}^{3N}, \mathbf{p}^{3N}$ $\mathbf{q}^{3N}, \mathbf{p}^{3N}$

"Microscopic" view
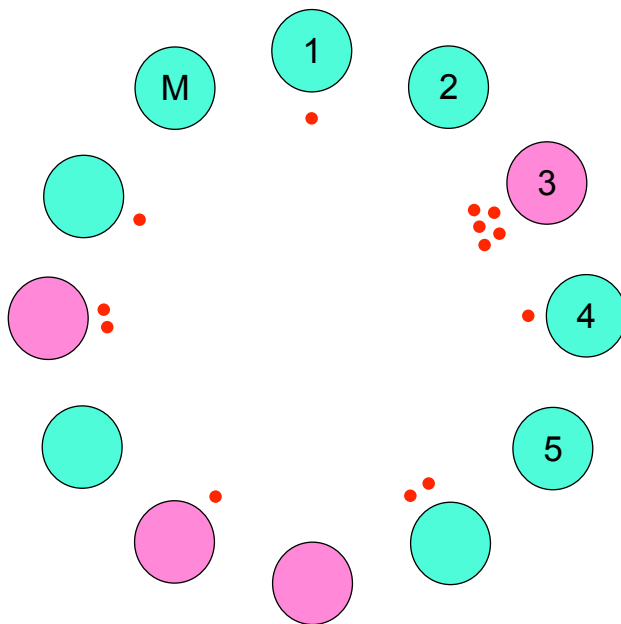(e.g. molecular simulation)
Description of a system in terms of atomic details

Outline

- A game

- States and entropy
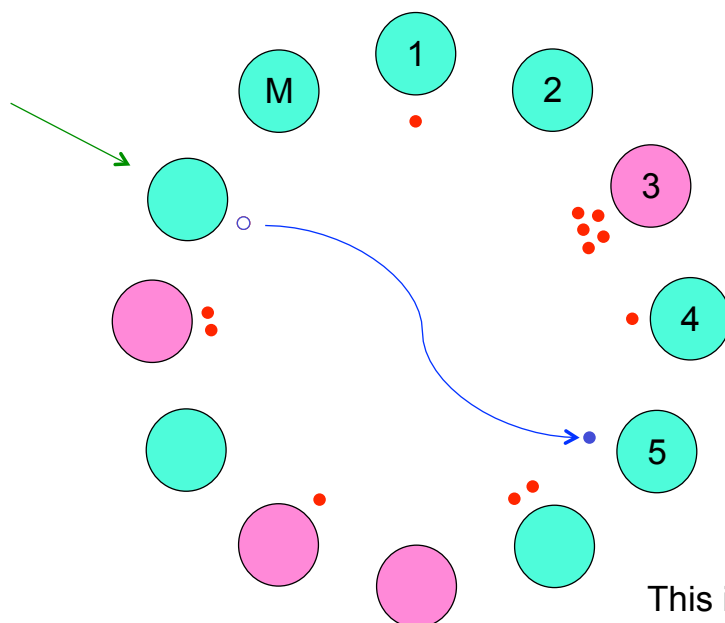
- Microcanonical ensemble

Balls and buckets

- A game with N children sitting in a circle, N_g girls, N_b boys
- Teacher divides M balls at random over them

Balls and buckets

- The teacher picks a random kid
- If it has a ball, it has to give it to another random kid
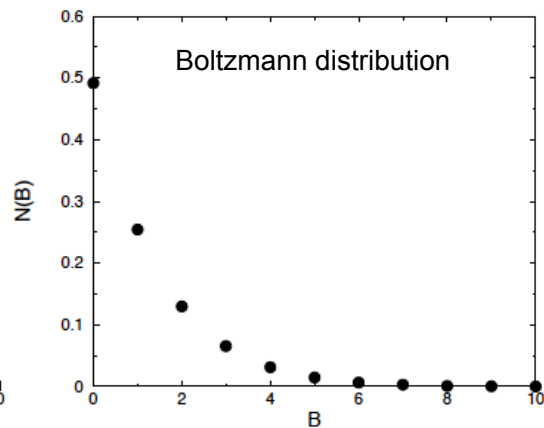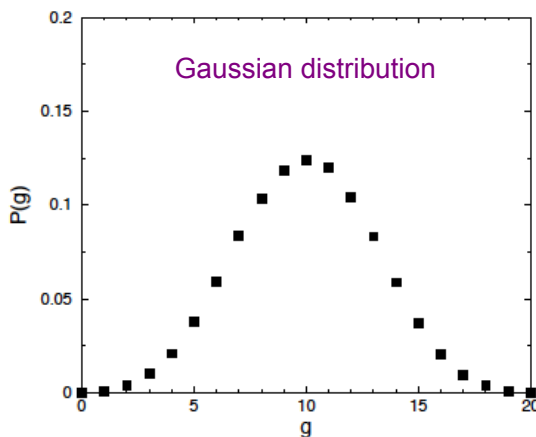

This is repeated until the kids are bored

Balls and buckets

- The average number of balls per kid is <B>=M/N

- The probability that any kid has 0, 1, 2, 3, … balls appears to be

$$P(B) = Ce^{-B/<B>}$$

- What is the average number of balls collected by the girls?

$$\langle g \rangle = f_g M = \frac{N_g}{N} M \quad P(g) = C' e^{-(g-<g>)^2/2\sigma^2}$$

Gaussian distribution

Boltzmann distribution

Balls and buckets

- What if the teacher was not fair initially?
  - The 'correct' distributions will appear after enough steps

- Analogies:
  - The number of balls remains constant (constant energy)
  - No kid can have less than 0 balls (ground-state energy is minimum)

- If M approaches infinity, we reach the thermodynamic limit
  - P(g) becomes very sharply peaked around <g>

- Two approaches to get P(B) (ergodicity)
  - Follow one kid for a long time: time average (MD)
  - Monitor the averages over all kids: ensemble average (MC)

Isolated systems

- No heat transfer, no work (mechanical or chemical):
  - Constant number of particles, volume and energy: NVE
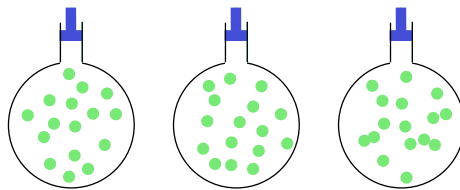
- At constant E, any individual particle can still have an energy E_k
- If N_k particles have energy E_k we can write that

$$E = \sum_k N_k E_k \qquad N = \sum_k N_k$$

- For the game, this was the total number of kids N and the total number of balls M. With N_k kids having k balls:

$$M = \sum_k N_k k \qquad N = \sum_k N_k$$

Isolated systems

- The individual particles have an energy E_k
- They may exchange energy through collisions
  - (passing the balls around)

- The distribution of positions and velocities does not depend on the kind of collisions

- Rather we make a fundamental assumption:

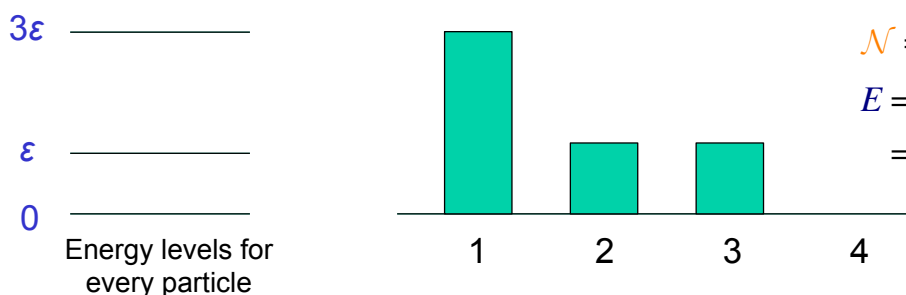 - All possible configurations of the system with the same overall energy are equally likely

Let's look at an example

- Individual particles have three energy levels:
  - $E_0 = 0$ $\qquad E_1 = \varepsilon$ $\qquad E_2 = 3\varepsilon$
- For N particles we can define the system state S
  - $\mathcal{S} = (k_1, k_2, ..., k_N)$ $\qquad$ (specify energy level for all particles)
- And we can write the system distribution
  - $\mathcal{N} = (N_0, N_1, N_2)$ $\quad$ (specify number of particles at every level)

$$E = \sum_k N_k E_k \qquad N = \sum_k N_k$$

- Example for $N = 4$

Possible state of the system

$$\mathcal{S} = (2,1,1,0)$$

$$\mathcal{N} = (1,2,1)$$

$$E = 1 \cdot 3\varepsilon + 2 \cdot \varepsilon + 1 \cdot 0$$
$$= 5\varepsilon$$

3ε

ε

0

Energy levels for every particle

1　2　3　4

Enforce total energy

- If the total energy is forced to be 3ε list all possible states

|	$\mathcal{S} = (k_1, k_2, k_3, k_4)$				$\mathcal{N} = (N_0, N_1, N_2)$		
#	k_1	k_2	k_3	k_4	N_0	N_1	N_2
1	0	0	0	2	3	0	1
2	0	0	2	0	3	0	1
3	0	2	0	0	3	0	1
4	2	0	0	0	3	0	1
5	1	1	1	0	1	3	0
6	1	1	0	1	1	3	0
7	1	0	1	1	1	3	0
8	0	1	1	1	1	3	0

- Eight states are possible, with two distinct distributions
- The fundamental assumption says that all eight are equally likely

Larger values of N

- Let's increase the number of particles, but keep the energy at 3ε
- For $N = 5$ we have:
  - 5 possibilities to get $\mathcal{N}_1 = (4,0,1)$
  - 10 possibilities to get $\mathcal{N}_2 = (2,3,0)$

> Every individual configuration is equally likely

- For large N, the number of possibilities for $\mathcal{N}_1 = (N-1,0,1)$ is much smaller than for $\mathcal{N}_2 = (N-3,3,0)$
- For large N, a single distribution becomes dominant: $\mathcal{N}^*$

$P(\mathcal{N})$

$$\mathcal{N}^* = \mathcal{N}_2 = (N-3,3,0)$$

$$P(\mathcal{N}_2) > P(\mathcal{N}_1)$$

$$\mathcal{N}_1 = (N-1,0,1)$$

N
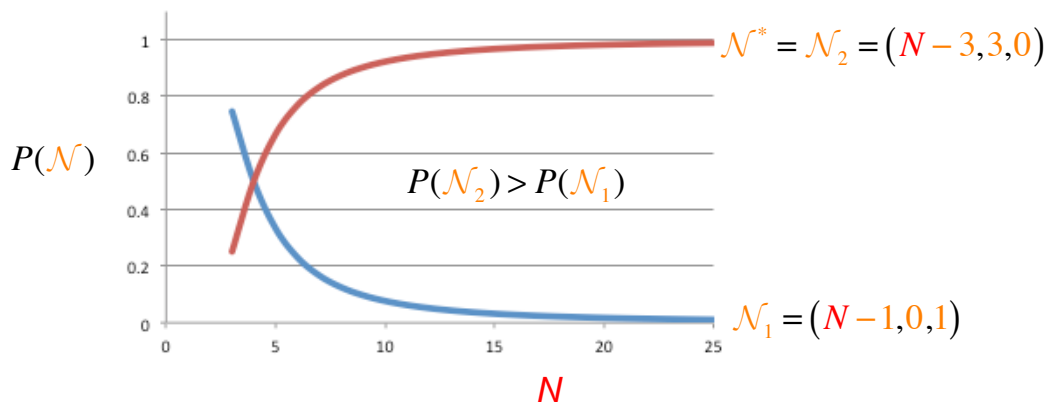
The possibilities of distributing

- We need to calculate the number of possibilities to get a given distribution

- If I have N objects, 1, 2, 3, … N, I can list them in $N!$ ways
  - N=3: (1 2 3) / (1 3 2) / (2 1 3) / (2 3 1) / (3 1 2) / (3 2 1)
  - First pick one (N possibilities), pick the next (N-1 possibilities), etc. until I have to pick the last one (1 possibility)
  - $N(N$-1)(N-2)…1 = $N!$

- If I have N objects and I want to distribute them in 2 groups
  - N=3, M=1: (1 | 2 3) / (2 | 1 3) / (3 | 1 2)
  - We don't want to count (1 | 3 2) / (2 | 3 1) / (3 | 2 1) separately
  - Total number of possibilities is 3! / (1! 2!) = 6/(1*2) = 3
  - In general, dividing N objects in two classes with M and N-M

$$W = \begin{pmatrix} N \\ M \end{pmatrix} = \frac{N!}{M!(N-M)!}$$

Number of possibilities

- Generalizing

$$W = \begin{pmatrix} N \\ M \end{pmatrix} = \frac{N!}{M!(N-M)!}$$

- from two states to an infinite amount of states, we get

$$W(\mathcal{N}) = \frac{N!}{\prod\limits_{k}^{\infty} N_k!}$$

- This will be a big number, so we write

$$\ln W(\mathcal{N}) = \ln N! - \ln \prod\limits_{k}^{\infty} N_k! = \ln N! - \sum\limits_{k}^{\infty} \ln N_k!$$

- and now remember Sterlings rule for big N:

$$\ln N! \approx N \ln N - N$$

- and as N_k is also big

$$\ln N_k! \approx N_k \ln N_k - N_k$$

Number of possibilities

- So, then we can write

$$\ln W(\mathcal{N}) = \ln N! - \sum\limits_{k}^{\infty} \ln N_k!$$

$$= N \ln N - N - \sum\limits_{k}^{\infty} N_k \ln N_k + \sum\limits_{k}^{\infty} N_k$$

$$= N \ln N - \sum\limits_{k}^{\infty} N_k \ln N_k$$

$$= -\sum\limits_{k}^{\infty} N_k \left(\ln N_k - \ln N \right)$$

$$= -N \sum\limits_{k}^{\infty} \frac{N_k}{N} \left(\ln \frac{N_k}{N} \right)$$

$$= -N \sum\limits_{k}^{\infty} P(k \mid \mathcal{N}) \ln P(k \mid \mathcal{N})$$

Redistribution of particles over the states at constant NVE is a spontaneous process, for which Entropy increases

Entropy is proportional to N (extensive variable)

Boltzmann's suggestion

- Boltzmann postulates that the statistical entropy is

$$S(\mathcal{N}) = k_B \ln W(\mathcal{N})$$

- In the thermodynamic limit $N \to \infty$

  - The statistical entropy becomes the thermodynamic entropy

  $$S(U,V,N) = k_B \ln W(\mathcal{N}^*) = -Nk_B \sum_k P(k) \ln P(k)$$

  - Similarly, the thermodynamic energy is approached by the total energy of the particles

  $$U = E = \sum_k^\infty N_k E_k$$

Boltzmann

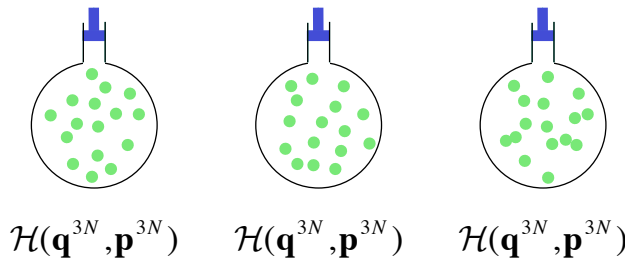- You can visit him at Zentralfriedhof in Vienna

$$S(\mathcal{N}) = k_B \ln W(\mathcal{N})$$

- As we did during a workshop on Entropy in May 2014

Ensembles

- By now, we have implicitly defined the microcanonical ensemble
- At constant N, V, E, all configurations have the same probability

- If we have a system of N particles, it is completely defined by the positions $\mathbf{q}$ and momenta $\mathbf{p}$ of the individual particles
- We can calculate their energy through the Hamiltonian $\mathcal{H}(\mathbf{q}^{3N}, \mathbf{p}^{3N})$

$$\mathcal{H}(\mathbf{q}^{3N}, \mathbf{p}^{3N}) \qquad \mathcal{H}(\mathbf{q}^{3N}, \mathbf{p}^{3N}) \qquad \mathcal{H}(\mathbf{q}^{3N}, \mathbf{p}^{3N})$$

… infinite number of microstates

$$P_{NVE}(\mathbf{q}, \mathbf{p}) = \begin{cases} 1/W(E,V,N) & \text{if} \quad E \leq \mathcal{H}(\mathbf{q}, \mathbf{p}) \leq E + \Delta \\ 0 & \text{otherwise} \end{cases}$$

Microcanonical ensemble

- Transform from a discrete enumeration to continuous variables
- The number of possible configurations is called the density of states or the partition function

$$W(E,V,N) = \Omega(E,V,N) = \frac{1}{N!} \frac{1}{h^{3N}} \iint d\mathbf{q}\, d\mathbf{p}$$

- h is the quantum mechanical volume of a microstate in phase space (has unit of mass·length^2/time)
- The factor N! comes from the indistinguishability of the particles
- The normalization holds

$$\frac{1}{N!} \frac{1}{h^{3N}} \iint P(\mathbf{p}, \mathbf{q})\, d\mathbf{q}\, d\mathbf{p} = 1$$

- and we can calculate the expectation value (average) of any quantity A

$$\langle A \rangle_{NVE} = \frac{1}{N!} \frac{1}{h^{3N}} \iint P(\mathbf{p}, \mathbf{q}) A(\mathbf{p}, \mathbf{q})\, d\mathbf{q}\, d\mathbf{p}$$

Let's go back to a discrete example

- A system of N molecules
- Every molecule can be in one of three energy states
  - $E_0 = 0$ $E_1 = \varepsilon$ $E_2 = 2\varepsilon$
  - N_k denotes the numbers in state k

$$N_0 + N_1 + N_2 = N$$

$$N_1 \varepsilon + 2 N_2 \varepsilon = U$$

- From this, we can write

$$N_2 = \frac{U - N_1 \varepsilon}{2\varepsilon} \qquad N_0 + N_1 + \frac{U - N_1 \varepsilon}{2\varepsilon} = N$$

$$\left(1 - \frac{1}{2}\right) N_1 = N - N_0 - \frac{U}{2\varepsilon} \quad \Rightarrow \quad N_1 = 2N - 2N_0 - \frac{U}{\varepsilon}$$

$$N_1 = \frac{U - 2 N_2 \varepsilon}{\varepsilon} \qquad N_0 + \frac{U - 2 N_2 \varepsilon}{\varepsilon} + N_2 = N$$

$$(-2 + 1) N_2 = N - N_0 - \frac{U}{\varepsilon} \quad \Rightarrow \quad N_2 = N_0 - N + \frac{U}{\varepsilon}$$

By applying the constraints of constant N and U, we can write N_1 and N_2 as function of N_0, N and U

Another example

- The distribution is then

$$\mathcal{N} = (N_0, N_1, N_2)$$
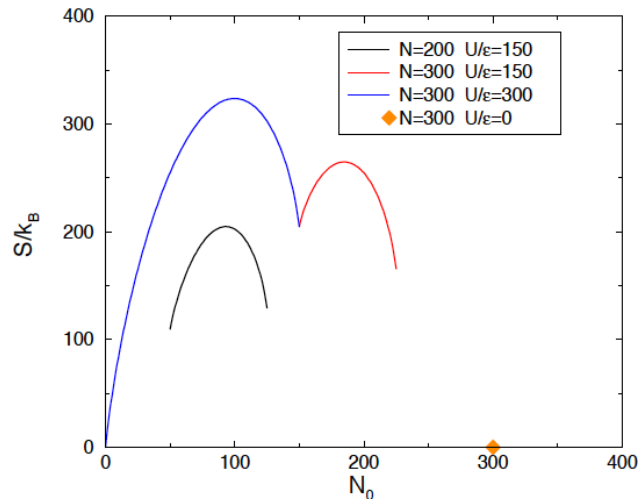$$= (N_0, 2N - 2N_0 - U/\varepsilon, N_0 - N + U/\varepsilon)$$

- And we can also write

$$W(\mathcal{N}) = \frac{N!}{N_0! N_1! N_2!}$$

$$S = k_B \ln W(\mathcal{N}) = k_B \ln \left[\frac{N!}{N_0!(2N - 2N_0 - U/\varepsilon)!(N_0 - N + U/\varepsilon)!} \right]$$

- this is something we can even calculate in Excel (for $N = 50$)

Another example

- For $N = 300$ and $U = 0$, there is only one point, because there is only one possible distribution: $\mathcal{N} = (300,0,0)$ and $S = 0$
- For $N = 300$ and $U/\varepsilon = 300$, maximum entropy for $\mathcal{N}^* = (100,100,100)$
- For $N = 300$ and $U/\varepsilon = 150$, max S at $N_0 = 180$; $P(0) = 180/300 = 0.6$
- For $N = 200$ and $U/\varepsilon = 150$, max S at $N_0 = 80$; $P(0) = 80/200 = 0.4$
  - More particles, same energy: more have to be in the ground state

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Determine the most likely distribution

- We want to find the distribution that maximizes

$$\ln W(\mathcal{N}) = -\sum_k^\infty N_k \ln \frac{N_k}{N}$$

- Under the conditions that N and E are constant

$$N = \sum_k^\infty N_k \qquad E = \sum_k^\infty N_k E_k$$

- Formulate the constraints as Lagrange multipliers

$$N - \sum_k^\infty N_k = 0 \qquad E - \sum_k^\infty N_k E_k = 0$$

- And define an alternative function to maximize

Determine the most likely distribution

- We want to maximize the function

$$\Phi(\mathcal{N}) = \ln W(\mathcal{N}) - \alpha\left(N - \sum_k^\infty N_k\right) + \beta\left(E - \sum_k^\infty N_k E_k\right)$$

$$= -\sum_k^\infty N_k \ln\frac{N_k}{N} - \alpha\left(N - \sum_k^\infty N_k\right) + \beta\left(E - \sum_k^\infty N_k E_k\right)$$

- The derivative with respect to any N_k gives

$$\frac{\partial\Phi(\mathcal{N})}{\partial N_k} = -\ln\frac{N_k}{N} - N_k\frac{N}{N_k}\frac{1}{N} + \alpha - \beta E_k = 0$$

- and from that we derive

$$\ln\frac{N_k}{N} = -1 + \alpha - \beta E_k$$

$$P(k) = e^{\alpha-1}e^{-\beta E_k} = Q^{-1}e^{-\beta E_k}$$

- So the probability of a state k is proportional to $\exp(-\beta E_k)$

What is Q?

- The normalization constant Q is readily determined

$$N = \sum_k^\infty N_k$$

- so that means that

$$\sum_k^\infty P(k) = \sum_k^\infty \frac{N_k}{N} = \frac{N}{N} = 1$$

- and thus

$$\sum_k^\infty P(k) = \sum_k^\infty Q^{-1}e^{-\beta E_k} = 1$$

$$= \frac{1}{Q}\sum_k^\infty e^{-\beta E_k} = 1$$

$$Q = \sum_k^\infty e^{-\beta E_k}$$

Q is the partition function of the canonical ensemble. We will see it come back often

and what is β?

- That is not so straightforward. We start from the characteristic equation for the total energy

$$dU = -PdV + \sum_{i=1}^{N} \mu_i dn_i + TdS$$

- and we look at the temperature

$$T = \left(\frac{\partial U}{\partial S} \right)_{N,V}$$

- Using a chain rule towards β

$$T = \left(\frac{\partial U}{\partial \beta} \right)_{N,V} \left(\frac{\partial \beta}{\partial S} \right)_{N,V} = \left(\frac{\partial U}{\partial \beta} \right)_{N,V} \bigg/ \left(\frac{\partial S}{\partial \beta} \right)_{N,V}$$

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towards β

- The thermodynamic energy U, is the expectation value $<E>$

$$U = \langle E \rangle = \sum_{k}^{\infty} N_k E_k = N \sum_{k}^{\infty} P(k) E_k$$

- which gives

$$\left(\frac{\partial U}{\partial \beta} \right)_{N,V} = N \sum_{k}^{\infty} E_k \frac{\partial P(k)}{\partial \beta}$$

- and for the entropy we had

$$S(U,V,N) = -Nk_B \sum_{k} P(k) \ln P(k)$$

$$\left(\frac{\partial S}{\partial \beta} \right)_{N,V} = -Nk_B \sum_{k}^{\infty} \left(\ln P(k) + 1 \right) \frac{\partial P(k)}{\partial \beta}$$

- Because $\sum P(k) = 1$ $\sum \frac{\partial P(k)}{\partial \beta} = 0$

$$\left(\frac{\partial S}{\partial \beta} \right)_{N,V} = -Nk_B \sum_{k}^{\infty} \ln P(k) \frac{\partial P(k)}{\partial \beta}$$

towards β

- We use $P(k) = Q^{-1}e^{-\beta E_k}$ for the first $P(k)$

$$\left(\frac{\partial S}{\partial \beta}\right)_{N,V} = -Nk_B \sum_k^\infty \ln \frac{e^{-\beta E_k}}{Q} \frac{\partial P(k)}{\partial \beta}$$

$$= -Nk_B \sum_k^\infty (-\beta E_k - \ln Q) \frac{\partial P(k)}{\partial \beta}$$

$$\sum \frac{\partial P(k)}{\partial \beta} = 0$$

$$= N\beta k_B \sum_k^\infty E_k \frac{\partial P(k)}{\partial \beta}$$

- Coming back to the temperature, we get

$$T = \left(\frac{\partial U}{\partial \beta}\right)_{N,V} \bigg/ \left(\frac{\partial S}{\partial \beta}\right)_{N,V}$$

$$= N\sum_k^\infty E_k \frac{\partial P(k)}{\partial \beta} \bigg/ N\beta k_B \sum_k^\infty E_k \frac{\partial P(k)}{\partial \beta}$$

$$= \frac{1}{\beta k_B} \qquad \boxed{\beta = \frac{1}{k_B T}}$$

Summary

- For a system of N particles and a constant energy E:
    - There are many different configurations possible
    - Every configuration has the same probability
    - Various configurations lead to the same distribution
    - The system will adopt the most likely distribution
    - The most likely distribution corresponds to the highest entropy, S

    - Maximize the number of possibilities to get a certain distribution, under the condition that N and E are constant

    - Leads to Boltzmann distribution, with the probability for any particle to be in state k: $P(k) = Q^{-1}e^{-\beta E_k}$

    - Q is the partition function
    - $\beta = 1/k_B T$

Summary

- Any microstate with constant N, V, E has equal probability
- Boltzmann linked the statistical entropy to
  - the number of different states
  - the number of microstates
  - the phase space integral

- From the microcanonical ensemble (NVE) we can derive all other ensembles:

  - Canonical ensemble   (NVT)
  - Isothermal-isobaric ensemble   (NPT)
  - Grand-Canonical ensemble   (μVT)
  - …

Applied Statistical Thermodynamics

BOKU

Applied Statistical Thermodynamics

Backup slides

MATHEMATICAL BACKGROUND

BOKU

Some maths – Stirlings approximation

- We will often need $N!$ for very large N

- Consider N as a continuous variable and $N!$ as a continuous function of N that can be differentiated with respect to N

$$\ln N! = \ln[N(N-1)(N-2)...\cdot 1]$$

$$= \ln \prod_{k=1}^{N} k = \sum_{k=1}^{N} \ln k \approx \int_{1}^{N} \ln x \, dx$$

use: $\ln(ab) = \ln a + \ln b$

replace sum by integral

$$= \left[x \ln x - x \right]_{1}^{N}$$
$$= N \ln N - N + 1$$
$$\approx N \ln N - N$$

for large N, we can neglect 1

Some maths – Lagrange multipliers

- We need to minimize or maximize a function $f(x_1, x_2, ..., x_n)$: solve

$$df = \frac{\partial f}{\partial x_1} dx_1 + \frac{\partial f}{\partial x_2} dx_2 + ... + \frac{\partial f}{\partial x_n} dx_n = 0$$

change df in f should be zero

- If we want to find the solution, under specific conditions, we can formulate a constraint in the form $g(x_1, x_2, ..., x_n) = 0$

- Then the easy solution to df = 0 by setting all $\partial f / \partial x = 0$ does not work, because $g(x_1, x_2, ..., x_n)$ makes that the dx_i are dependent:

$$dg = \frac{\partial g}{\partial x_1} dx_1 + \frac{\partial g}{\partial x_2} dx_2 + ... + \frac{\partial g}{\partial x_n} dx_n = 0$$

is zero because g is constant

- Instead, we solve this equation

$$\left(\frac{\partial f}{\partial x_1} + \lambda \frac{\partial g}{\partial x_1} \right) dx_1 + \left(\frac{\partial f}{\partial x_n} + \lambda \frac{\partial g}{\partial x_n} \right) dx_2 + ... + \left(\frac{\partial f}{\partial x_n} + \lambda \frac{\partial g}{\partial x_n} \right) dx_n = 0$$

- Now, the dx_i are independent: set the terms in () to zero and solve for the Lagrange multiplier λ

Some maths – Lagrange multipliers

- Example
- Find the stationary points of the function $f(x,y)=4x^2 + 3x + 2y^2 + 6y$ under the constraint $g(x,y) = y - 4x - 2 = 0$

$$\frac{\partial f}{\partial x} = 8x + 3 \qquad \frac{\partial f}{\partial y} = 4y + 6$$

$$\frac{\partial g}{\partial x} = -4 \qquad \frac{\partial g}{\partial y} = 1$$

$$\left(\frac{\partial f}{\partial x} + \lambda \frac{\partial g}{\partial x} \right) dx + \left(\frac{\partial f}{\partial y} + \lambda \frac{\partial g}{\partial y} \right) dy = 0$$

$$\left(8x + 3 + \lambda(-4) \right) dx + \left(4y + 6 + \lambda \right) dy = 0$$
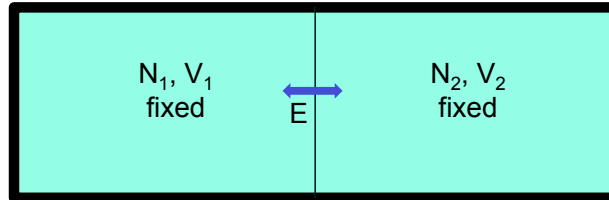
- Gives a set of three equations with three unknowns:

$$\left. \begin{array}{l} 8x - 3 - 4\lambda = 0 \\ 4y + 6 + \lambda = 0 \\ y - 4x - 2 = 0 \end{array} \right\} \Rightarrow \begin{array}{l} x = {}^{-59}\!/_{72} \\ y = {}^{-23}\!/_{18} \\ (\lambda = {}^{8}\!/_{9}) \end{array}$$

Backup slides

LINK TO THERMODYNAMICS

Link to thermodynamics

- Let's consider two systems at constant N and V that can exchange heat.
- Together they form a closed and isolated system

- System 1: N_1, V_1 fixed; E_1 variable
- System 2: N_2, V_2 fixed; E_2 variable
- Two systems together $E = E_1 + E_2$ is constant

- what are the most probable value of E_1 and E_2 in the systems
- write these optimal values as E_1^* and $E_2^* = E - E_1^*$

Link to thermodynamics

- Solution is very similar to the individual particles earlier
- The probability that we have E_1 for system 1 (and also E_2 for system 2) is proportional to the number of possibilities

$$P(E_1) \propto \Omega_1(E_1)\Omega_2(E_2) = \Omega_1(E_1)\Omega_2(E - E_1)$$

- The maximum of this is

$$\frac{\partial}{\partial E_1}\Omega_1(E_1)\Omega_2(E - E_1) = \frac{\partial \Omega_1(E_1)}{\partial E_1}\Omega_2(E - E_1) + \Omega_1(E_1)\frac{\partial \Omega_2(E - E_1)}{\partial E_2}\cdot -1 = 0$$

$$\frac{\partial \Omega_1(E_1)}{\partial E_1}\Omega_2(E - E_1) = \Omega_1(E_1)\frac{\partial \Omega_2(E - E_1)}{\partial E_2}$$

$$\frac{1}{\Omega_1(E_1^*)}\frac{\partial \Omega_1(E_1)}{\partial E_1}\bigg|_{E_1=E_1^*} = \frac{1}{\Omega_2(E - E_1^*)}\frac{\partial \Omega_2(E - E_1)}{\partial E_2}\bigg|_{E_1=E_1^*}$$

$$\frac{\partial}{\partial E_1}\ln\Omega_1(E_1^*) = \frac{\partial}{\partial E_2}\ln\Omega_2(E - E_1^*)$$

Link to thermodynamics

- We already had that

$$S(U,V,N) = k_B \ln W(\mathcal{N}^*)$$

$$S_1(U,V,N) = k_B \ln \Omega_1(E_1^*)$$

- which means that the last line from the previous slide becomes

$$\frac{\partial}{\partial E_1} \ln \Omega_1(E_1^*) = \frac{\partial}{\partial E_2} \ln \Omega_2(E - E_1^*)$$

$$\frac{1}{k_B} \frac{\partial S_1(E_1^*)}{\partial E_1} = \frac{1}{k_B} \frac{\partial S_2(E - E_1^*)}{\partial E_2}$$

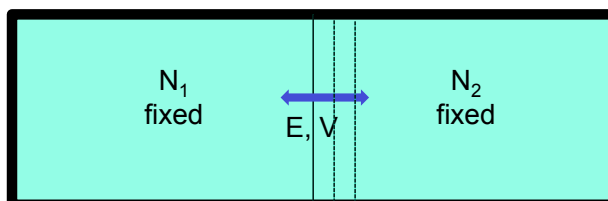- And because $\quad T = \left(\dfrac{\partial U}{\partial S} \right)_{N,V}$

> This will be an important finding when we introduce the canonical NVT ensemble

- we get $\quad \dfrac{1}{k_B T_1} = \dfrac{1}{k_B T_2} \Rightarrow T_1 = T_2$

- So the two systems will be in thermal equilibrium

And mechanical equilibrium

- Let's consider two systems at constant N that can exchange heat and mechanical volume
- Together they form a closed and isolated system

- System 1: N_1 fixed; E_1, V_1 variable
- System 2: N_2 fixed; E_2, V_2 variable
- Two systems together $E = E_1 + E_2$ and $V = V_1 + V_2$ are constant

- what are the most probable values of E_1 and E_2 and of V_1 and V_2 in the systems?
- write these optimal values as
  E_1^* and $E_2^* = E - E_1^*$ $\qquad$ V_1^* and $V_2^* = V - V_1^*$

Changing E and V

- Solution is very similar to the previous case
- The probability that we have E_1, V_1 for system 1 (and also E_2,V_2 for system 2) is proportional to the number of possibilities

$$P(E_1,V_1) \propto \Omega_1(E_1,V_1)\Omega_2(E_2,V_2) = \Omega_1(E_1,V_1)\Omega_2(E-E_1,V-V_1)$$

- Setting

$$\frac{\partial}{\partial E_1}P(E_1^*,V_1) = 0$$

- leads to

$$\frac{1}{k_B}\frac{\partial S_1(E_1^*,V_1)}{\partial E_1} = \frac{1}{k_B}\frac{\partial S_2(E-E_1^*,V-V_1)}{\partial E_2}$$

$$T_1 = T_2$$

- Next step, also set

$$\frac{\partial}{\partial V_1}P(E_1,V_1^*) = 0$$

The volume derivatives

- So

$$\frac{\partial}{\partial V_1}\Omega_1(E_1,V_1)\Omega_2(E-E_1,V-V_1) =$$

$$\frac{\partial\Omega_1(E_1,V_1)}{\partial V_1}\Omega_2(E-E_1,V-V_1) + \Omega_1(E_1,V_1)\frac{\partial\Omega_2(E-E_1,V-V_1)}{\partial V_2}\cdot -1 = 0$$

- which we reshuffle to

$$\frac{\partial\Omega_1(E_1,V_1)}{\partial V_1}\Omega_2(E-E_1,V-V_1) = \Omega_1(E_1,V_1)\frac{\partial\Omega_2(E-E_1,V-V_1)}{\partial V_2}$$

$$\frac{1}{\Omega_1(E_1,V_1^*)}\frac{\partial\Omega_1(E_1,V_1)}{\partial V_1}\bigg|_{V_1=V_1^*} = \frac{1}{\Omega_2(E-E_1,V-V_1^*)}\frac{\partial\Omega_2(E-E_1,V-V_1)}{\partial V_2}\bigg|_{V_1=V_1^*}$$

$$\frac{\partial}{\partial V_1}\ln\Omega_1(E_1,V_1^*) = \frac{\partial}{\partial V_2}\ln\Omega_2(E-E_1,V-V_1^*)$$

Mechanical equilibrium

- Putting in the entropy definition

$$S_1(U,V,N) = k_B \ln \Omega_1(E_1^*)$$

- gives

$$\frac{\partial}{\partial V_1} \ln \Omega_1(E_1, V_1^*) = \frac{\partial}{\partial V_2} \ln \Omega_2(E - E_1, V - V_1^*)$$

$$\frac{1}{k_B} \frac{\partial S_1(E_1, V_1^*)}{\partial V_1} = \frac{1}{k_B} \frac{\partial S_2(E - E_1, V - V_1^*)}{\partial V_2}$$

- And because

$$T = \left(\frac{\partial U}{\partial S}\right)_N \qquad P = \left(\frac{\partial U}{\partial V}\right)_N \qquad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_N$$

- we get

$$\frac{P_1}{k_B T_1} = \frac{P_2}{k_B T_2} \Rightarrow P_1 = P_1$$

This will be an important finding when we introduce the isothermal isobaric NPT ensemble

- So the systems will be in thermal and mechanical equilibrium

BOKU