

1.6 Classical Statistical Mechanics

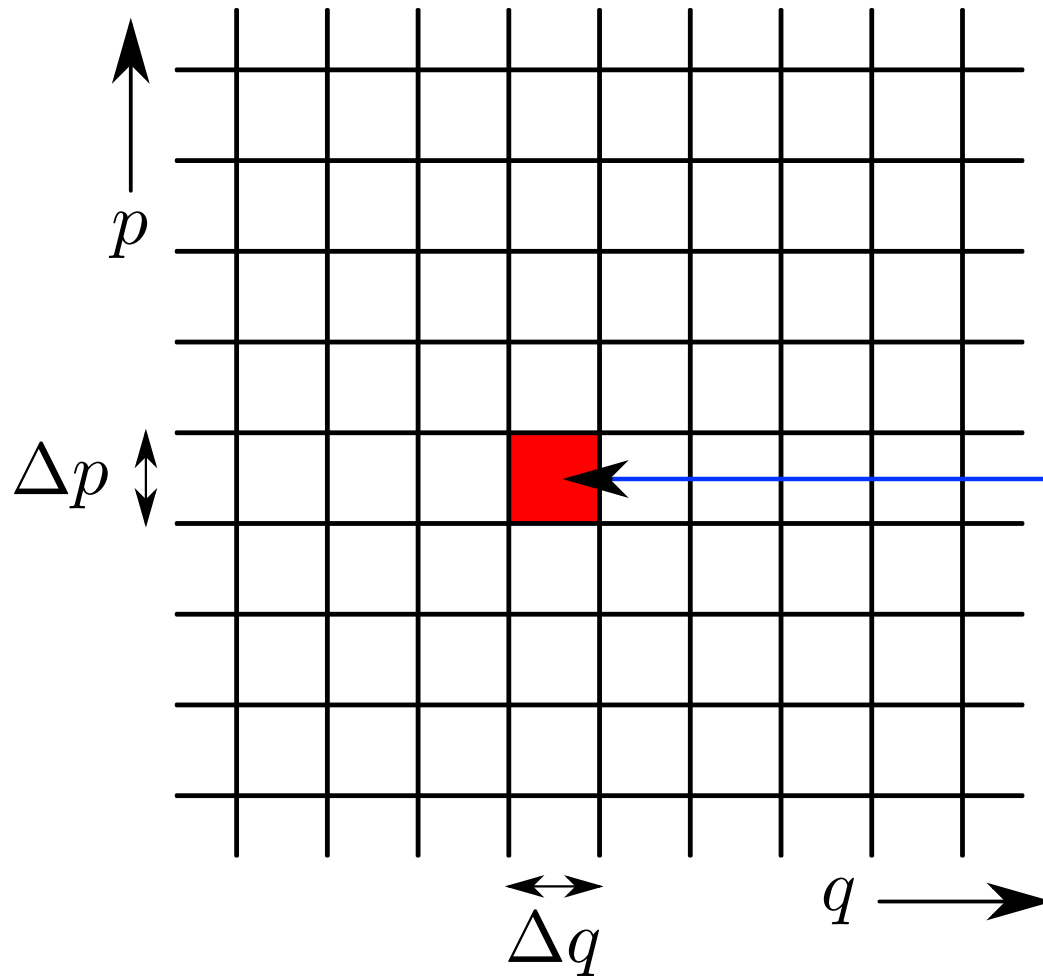
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b.cowan@rhul.ac.uk

Classical Statistical Mechanics

- Classical Mechanics is best formulated in terms of position (q) and momenta (p) coordinates (inc. *generalized* coordinates).
- So we would say a *state* is specified when we know all the position and momenta coordinates.
- The $p - q$ space is called *phase space*.
- So in classical mechanics a *state* is a *point* in phase space.
- Difficulty in *counting* such states since p and q vary continuously; there would be an *infinite* number of states in any region of phase space.
- In Statistical Mechanics it is expedient to erect a *grid* in phase space with cells $\Delta q_x \Delta q_y \Delta q_z \Delta p_x \Delta p_y \Delta p_z$.

Phase space



- In classical statistical mechanics a state corresponds to a cell in phase space.
- I.e. a system is in a given (micro) state if it is in a specified cell in phase space.
- A state in phase space.
- What should be the *size* of the cells?
- Dimension of $p \times q$ is action (like in Planck's constant h).

- We argue that the precise size of the cells should not be important.
- But we note that Quantum Mechanics (Uncertainty principle) tells us we cannot discern a state to finer than a $\Delta p \Delta q$ cell smaller than Planck's constant.

!!

Our Philosophy

- We shall write the size of a $\Delta p \Delta q$ cell as h . At this stage its size will be undetermined. Later, by comparing results with those calculated by *quantum* statistical mechanics, we will identify this h as Planck's constant.

Connection between classical/quantum statistical mechanics

- The general rule is that sums over states in the quantum case correspond to integrals over phase space in the classical case.

$$\sum_{\text{single particle states}} \rightarrow \frac{1}{h^3} \int d^3p d^3q$$

Note the appearance of the h factors ensures dimensionality.

1.6.2 Boltzmann and Gibbs Phase Spaces

(Transatlantic communication in latter half of 19th Century)

Boltzmann:

Phase space has 6 dimensions: 3 position coordinates q_x, q_y, q_z .

3 momentum coordinates p_x, p_y, p_z .

State of a system comprising N particles represented by N points in this 6 dimensional phase space.

Gibbs:

Phase space has $6N$ dimensions: 3 q 's and 3 p 's for each particle.

State of this system represented by 1 point in this $6N$ dimensional space.

1.6.3 The Fundamental Postulate in the Classical Case

The classical version of the Fundamental Postulate states that **for an isolated system all available regions of phase space on the constant energy hypersurface are equally likely.**

1.6.4 The classical partition function

The classical analogue of the quantum partition function is given by

$$Z = \frac{1}{h^{3N}} \int e^{-H(p_i, q_i)/kT} d^{3N}p d^{3N}q$$

The function $H(p_i, q_i)$ is the energy of the system expressed as a function of the position and momentum coordinates $\{q_i\}$ and $\{p_i\}$. This is the *Hamiltonian*.

1.6.5 The equipartition theorem

Energy of i^{th} degree of freedom (from p_i)

$$\langle E_i \rangle = \frac{1}{Z} \int \mathbf{E}_i e^{-E(q_1 \dots q_i \dots q_N, p_1 \dots p_i \dots p_N)/kT} d^{3N} q d^{3N} p$$

-- no p_i --

↓ ↓

$$\langle E_i \rangle = \frac{\int E_i e^{-E_i/kT} dp_i \int e^{-E(q_1 \dots q_i \dots q_N, p_1 \dots p_N)/kT} d^{3N} q d^{3N-1} p}{\int e^{-E_i/kT} dp_i \int [\text{same integral as above - no } p_i]}$$

$$\langle E_i \rangle = \frac{\int E_i e^{-E_i/kT} dp_i}{\int e^{-E_i/kT} dp_i}$$

Use the beta trick: $\beta = 1/kT \dots$

The beta trick

Quantities like

$$Ee^{-E/kT}$$

we might wish to sum or integrate.

Put $1/kT$ to β , so we have

$$Ee^{-\beta E}.$$

We can “bring down” the E by differentiating $e^{-\beta E}$ with respect to β :

$$Ee^{-\beta E} = -\frac{\partial}{\partial \beta} e^{-\beta E}.$$

This is the **beta trick**.

The beta trick gives

$$\langle E_i \rangle = \frac{\int E_i e^{-\beta E_i} dp_i}{\int e^{-\beta E_i} dp_i} = - \frac{\int \frac{\partial}{\partial \beta} e^{-\beta E_i} dp_i}{\int e^{-\beta E_i} dp_i}.$$

Interchange derivative and integral

$$\langle E_i \rangle = - \frac{\frac{\partial}{\partial \beta} \int e^{-\beta E_i} dp_i}{\int e^{-\beta E_i} dp_i}.$$

This is the derivative of the logarithm

$$\langle E_i \rangle = - \frac{\partial}{\partial \beta} \ln \left[\int e^{-\beta E_i} dp_i \right]. \quad \text{-----}$$

note this

Next trick — you don't need to do the integral; just change variables:

Let's just put $E_i = bp_i^2$ and substitute $\beta p_i^2 = y^2$, so that

$$\int e^{-\beta E_i} dp_i = \beta^{-1/2} \int e^{-by^2} dy .$$

The logarithm of this is

$$\ln \left[\int e^{-\beta E_i} dp_i \right] = -\frac{1}{2} \ln \beta + \ln \left[\int e^{-by^2} dy \right] .$$

We have to differentiate with respect to β — so the integral drops out:

$$\frac{\partial}{\partial \beta} \ln \left[\int e^{-\beta E_i} dp_i \right] = -\frac{1}{2\beta} .$$

We just found
$$\frac{\partial}{\partial \beta} \ln \left[\int e^{-\beta E_i} dp_i \right] = -\frac{1}{2\beta}.$$

And since we require

$$\langle E_i \rangle = -\frac{\partial}{\partial \beta} \ln \left[\int e^{-\beta E_i} dp_i \right]$$

Our result is that

$$\langle E_i \rangle = \frac{1}{2\beta}.$$

So finally change back to $kT = 1/\beta$, giving

$$\langle E_i \rangle = \frac{kT}{2}.$$

(If $E_i \propto p_i^n$ or q_i^n then corresponding $\langle E_i \rangle = kT/n$ — even n .)

Equipartition theorem:

For a classical (non-quantum) system, each degree of freedom with a quadratic dependence on coordinate or momentum gives a contribution to the internal energy of $kT/2$.

1.6.6 Consequences of equipartition

- Each “quadratic” degree of freedom gives internal energy $kT/2$

Differentiate E with respect to T to obtain C_V :

- Lattice vibrations (both p and q contributions): $C_V = 3R$ per mol
- Gas of particles (only p contribution): $C_V = \frac{3}{2}R$ per mol

(R is the gas constant $R = N_A k$).

Constant heat capacity!!

Equipartition breaks down when quantum effects become important – at low temperatures.

Liouville's Theorem and Boltzmann's H theorem

Can we understand the law of entropy increase from microscopic first principles?

1.6.7 Liouville's theorem

Entropy – classical analogue of

$$S = -k \sum_j P_j \ln P_j = -k \langle \ln P \rangle$$

is

$$S = -k \int \rho \ln \rho \, d^n p \, d^n q = -k \langle \ln \rho \rangle$$

where $\rho(p_i, q_i, t)$ = density of points in phase space.

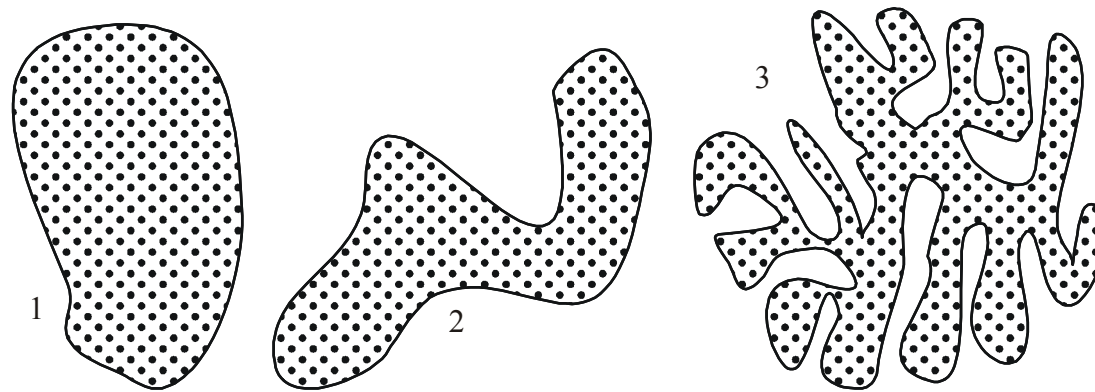
Evolution of S (or ρ) with time? Should be consistent with Second Law.

But... Liouville's theorem \rightarrow

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

- S appears to remain constant !!!!!!!!!

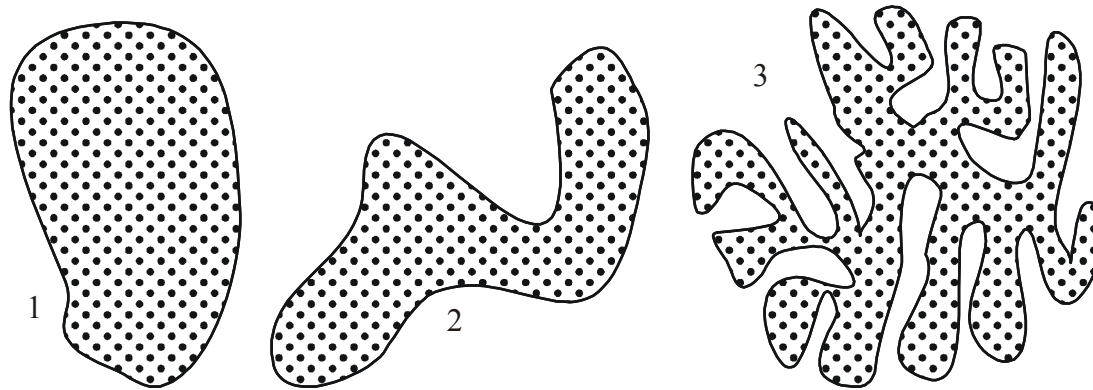
1.6.8 Boltzmann's H theorem



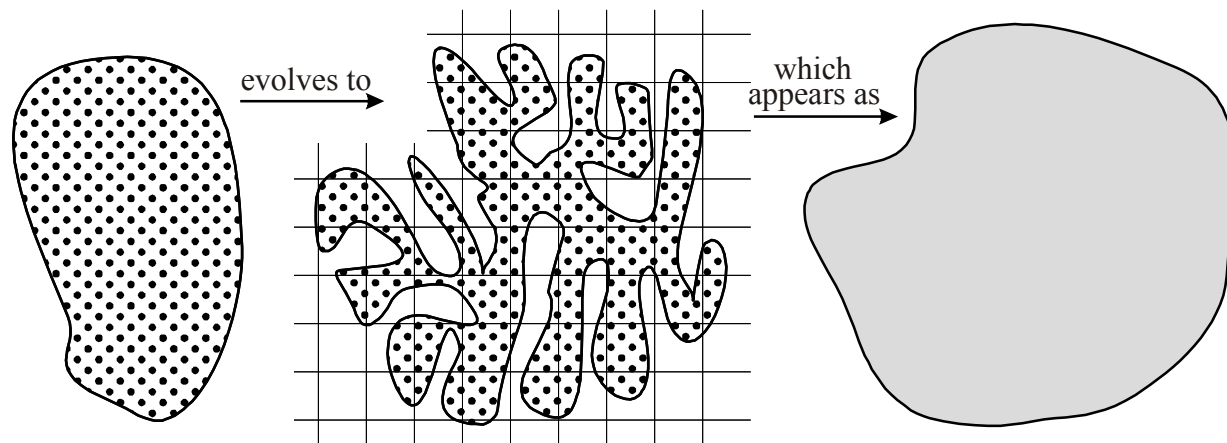
Evolution of a region of phase space



1.6.8 Boltzmann's H theorem



Evolution of a region of phase space



Apparent reduction in density in phase space

Chapter 2

Practical Calculations with Ideal Systems

2.2 Identical Particles

2.2.1 Indistinguishability

If we had an assembly of N identical but *distinguishable* particles the resultant partition function would be the product of the (same) partition functions of a single particle, z

$$Z = z^N .$$

Partition function of a composite system

Proof of

$$Z = z^N.$$

Start with **two** systems: A and B with partition functions z_a, z_b — and then generalise

$$z_a = \sum_i e^{-\epsilon_i^a/kT}, \quad z_b = \sum_j e^{-\epsilon_j^b/kT}.$$

Denote the energy of microstates of system A as ϵ_i^a and those of system B as ϵ_j^b .

In particular, note that i is the summation index for the A system states and j is the summation index for the B system states.

A general microstate of the composite system has energy

$$\epsilon_{ij} = \epsilon_i^a + \epsilon_j^b.$$

Note we need *two* indices since we must specify the state of the A system and the state of the B system in order to specify the state of the composite system.

The partition function of the composite system is then

$$Z = \sum_{ij} e^{-\epsilon_{ij}/kT} = \sum_{ij} e^{-(\epsilon_i^a + \epsilon_j^b)/kT}$$

which can be factorised:

$$= \sum_{ij} e^{-\epsilon_i^a/kT} e^{-\epsilon_j^b/kT}.$$

The first exponential depends on i and the second exponential depends on j . This means that the sum over i operates only on the first exponential and the sum over j operates only on the second exponential. In other words

$$Z = \sum_i e^{-\epsilon_i^a/kT} \sum_j e^{-\epsilon_j^b/kT}.$$

But this is simply the product $z_a z_b$. Thus we have shown that

$$Z = z_a z_b.$$

By extension, for N similar systems

$$Z = z^N$$

2.2.1 Indistinguishability continued

If we had an assembly of N identical but *distinguishable* particles the resultant partition function would be the product of the (same) partition functions of a single particle, z

$$Z = z^N .$$

The key question is that of *indistinguishability* of the atoms or molecules of a many-body system. When two identical molecules are interchanged the system is still in the same microstate, so the distinguishable particle result *overcounts* the states in this case.

Now the number of ways of redistributing N particles when there are n_1 particles in the first state, n_2 particles in the second state etc. is

$$\frac{N!}{n_1! n_2! n_3! \dots}$$

so that for a given distribution $\{n_i\}$ the partition function for identical indistinguishable particles is

$$Z = \frac{n_1! n_2! n_3! \dots}{N!} z^N .$$

2.2.2 Classical approximation

In the classical case we have then

$$Z = \frac{1}{N!} z^N.$$

The Helmholtz free energy

$$F = -kT \ln Z$$

is thus

$$F = -NkT \ln z + kT \ln N!.$$

This is N times the Helmholtz free energy for a single particle plus an extra term depending on T and N . So the second term can be ignored so long as we differentiate with respect to something other than T or N . Thus when differentiating with respect to volume to find the pressure, the result is N times that for a single particle.

2.3 Ideal Classical Gas

2.3.2 Classical approach

The classical partition function is given by the integral

$$z = \frac{1}{h^3} \int e^{-\varepsilon/kT} d^3 p d^3 q$$

where for the ideal gas $\varepsilon = p^2/2m$. Thus the q integrals are trivial, giving a factor V , and we have

$$z = \frac{V}{h^3} \left[\int_{-\infty}^{\infty} e^{-p^2/2mkT} dp \right]^3.$$

The integral is transformed to a pure number by changing variables:

$p = x\sqrt{2mkT}$ so that

$$z = \frac{V}{h^3} (2mkT)^{3/2} \left[\int_{-\infty}^{\infty} e^{-x^2} dx \right]^3.$$

As in the quantum calculation, the physics is all outside the integral and the integral is just a pure number. The value of the integral is $\sqrt{\pi}$ so that

$$z = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

just as in the “quantum” calculation. *This* justifies the use of h in the normalization factor for the classical state element of phase space.

(But physical consequences?)

Write

$$z = \frac{V}{\Lambda^3}, \quad \text{where} \quad \Lambda = \frac{h}{(2\pi mkT)^{1/2}}.$$

Here Λ is known as the **thermal de Broglie wavelength**. It has a very important meaning.

2.3.3 Thermodynamic properties

We start from the Helmholtz free energy:

$$F = -kT \ln Z = \overset{\text{typo}}{\downarrow} NkT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{Ve}{N} \right],$$

giving

$$p = kT \left. \frac{\partial \ln Z}{\partial V} \right|_{T,N} = NkT \left. \frac{\partial \ln z}{\partial V} \right|_T = \frac{NkT}{V}.$$

This is the ideal gas equation, **and from this** we identify k as Boltzmann's constant.

The internal energy is

$$E = kT^2 \left. \frac{\partial \ln Z}{\partial T} \right|_{V,N} = NkT^2 \frac{d \ln T^{3/2}}{dT} = \frac{3}{2} NkT.$$

This is the result we obtained previously from equipartition. This gives another important property of an ideal gas: the internal energy depends *only* on temperature (not pressure or density). This is known as Joule's law. From the energy expression we obtain the thermal capacity

$$C_V = \left. \frac{\partial E}{\partial T} \right|_{V,N} = \frac{3}{2} Nk.$$

This is a constant, independent of temperature, in violation of the Third Law. This is because of the classical approximation – ignoring multiple state occupancy etc. We also find the entropy and chemical potential:

$$S = Nk \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{kT e^{5/2}}{p} \right],$$

$$\mu = -kT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{kT}{p} \right].$$

Sackur-Tetrode equation

$$S = Nk \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{kT e^{5/2}}{p} \right]$$

\Rightarrow

$$S = \frac{5}{2} Nk \ln T - Nk \ln p + Nks_0$$

- Latter equation can be derived by thermodynamics alone.
- Constant s_0 known as the Sakur-Tetrode constant

Naïve interpretation of this equation is **wrong**.

2.3.4 The $1/N!$ term in the partition function

The Gibbs paradox

Gibbs didn't know about indistinguishable particles. So he wrote

$$Z = z^N.$$

We found

$$z = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V.$$

So (according to Gibbs)

$$F = -kT \ln Z = -NkT \ln z = -NkT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \right].$$

The right hand expression is NOT extensive.

$$F = -NkT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \right] !?!?$$

The square bracket must be intensive - so you must divide V by a *dimensionless extensive* quantity — like N . Gibbs chose N and so he wrote

$$F = -NkT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{V}{N} \right].$$

We had a divisor of $N!$ in the partition function. Since by Stirling's approximation, $\ln N! = N \ln(N/e)$, we found

$$F = -NkT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{Ve}{N} \right].$$