

Thermodynamics from Statistical Mechanics

The Microcanonical Distribution

An isolated system is a system which does not interact with its surrounding; no energy, constituents (molecules or particles) or volume are exchanged.

The microcanonical ensemble is an ensemble of isolated systems with a fixed energy E_0
number of constituents N
and volume V

All systems in the ensemble obey energy conservation $E(p, q) = E_0$

So what is the microcanonical distribution $p(p, q)$?

From postulate of a priori equal probabilities, any microstate with energy $E = E_0$ has equal probability.

We can say $p(p, q)$:

- vanishes for $E \neq E_0$
- is constant for $E = E_0$
- Respects normalisation condition

These lead to the function being the Dirac- δ function:

$$p(p, q) = C \delta(E(p, q) - E_0)$$

The normalisation condition can give us a value for C :

$$C \int \delta(E(p, q) - E_0) dp dq = 1$$

phase space

→ This integral is to volume of accessible phase space $\Delta \Gamma$

$$\therefore C \Delta \Gamma = 1$$

$$\Rightarrow C = \frac{1}{\Delta \Gamma}$$

So the microcanonical distribution is:

$$p(p, q) = \frac{\delta(E(p, q) - E_0)}{\Delta \Gamma}$$

which gives us the total number of microstates:

$$W = \frac{\Delta \Gamma}{h^{Ndf}}$$

Entropy in Statistical Mechanics: Discrete Systems

For a discrete system, given a certain macrostate with a statistical weight W_i , we define a statistical entropy:

$$\sigma_i = k W_i$$

$$\text{for } W = \sum_i W_i :$$

$$\sigma = k W$$

Statistical entropy is an extensive quantity so therefore respects additivity:

Consider a system A with N_A particles and a system B with N_B particles. If the systems are combined, total number of particles is $N_{A+B} = N_A + N_B$. The total number of microstates of the combined system is the product of the num microstates of the individual parts: $W_{A+B} = W_A W_B$.

$$\therefore \sigma_{A+B} = k(W_{A+B}) = k(W_A W_B) = k W_A + W_B = \underline{\underline{\sigma_A + \sigma_B}} \quad \text{so } \sigma_i \text{ is additive!}$$

Entropy of an Ideal Paramagnet

Let's consider an ideal paramagnet composed of N independent particles each with dipole magnetic moments \underline{m} of equal length m .

We apply an external \underline{B} field and observe each particle has an orientation parallel (with +ve magnetic moment and $E = -mB$) or antiparallel (with -ve magnetic moment and $E = +mB$).

With $B = 0$, each magnetic moment has equal probability to be positive or negative.

In this case, the system is considered isolated and we apply postulate of equal a priori probability, to say that since each particle has 2 possibilities, and there are N particles, there are 2^N possible configurations, each with probability $\frac{1}{2^N} = \left(\frac{1}{2}\right)^N$.

Each macrostate corresponds to a fixed number of positive magnetic moments $N\uparrow$, so $N\downarrow = N - N\uparrow$.

Statistical weight of each macrostate is given by binomial distribution:

$$W(N, N\uparrow) = \binom{N}{N\uparrow} = \frac{N!}{N\uparrow(N - N\uparrow)!}$$

The statistical entropy is:

$$S(N, N\uparrow) = k(W(N, N\uparrow))$$

If we introduce magnetisation $M = \Delta N m$ with $\Delta N = (N\uparrow - N\downarrow)$, probability of finding system with magnetisation M is:

$$P(M) = P(N, \Delta N) = \frac{1}{2^N} \frac{N!}{\left[\frac{1}{2}(N + \Delta N)\right]! \left[\frac{1}{2}(N - \Delta N)\right]!}$$

For very large N , this becomes:

$$P(M) \xrightarrow{N \rightarrow \infty} \frac{1}{\sqrt{\pi N}} e^{-(\Delta N)^2/2N}$$

a gaussian distribution
centred on most probable macrostate, $M=0$

Let's now calculate the entropy for the macrostate in
thermal equilibrium, i.e. $M=0$ where $\uparrow\uparrow = \downarrow\downarrow$

$$W(N, \uparrow\uparrow = \frac{N}{2}) = \frac{N!}{\left[\left(\frac{N}{2}\right)!\right]^2}$$

using Stirling's approximation for $\left(\frac{N}{2}\right)!$ and $(N)!$

$$\ln(N!) \approx N \ln N - N + \frac{1}{2} \ln(2\pi N) \quad \text{and similar for } \left(\frac{N}{2}\right)!$$

$$\text{so } \sigma(N, \uparrow\uparrow = \frac{N}{2}) = \ln[W(N, \uparrow\uparrow = \frac{N}{2})]$$

$$\approx N \ln N - N - 2 \left(\frac{N}{2} \ln \left(\frac{N}{2}\right) - \frac{N}{2} \right) + \frac{1}{2} \ln(2\pi N) - \ln(\pi N)$$

we can expand
these last two:

$$\frac{1}{2} \ln(2\pi N) - \ln(\pi N)$$

$$= \frac{1}{2} \ln(2) + \frac{1}{2} \ln(\pi N) - \ln(\pi N)$$

$$= \frac{1}{2} \ln(2) - \frac{1}{2} \ln(\pi N) = \frac{1}{2} \ln\left(\frac{2}{\pi N}\right) = -\frac{1}{2} \ln\left(\frac{\pi N}{2}\right)$$

$$\therefore \sigma(N, \uparrow\uparrow = \frac{N}{2}) = N \ln N - N \ln\left(\frac{N}{2}\right) - \frac{1}{2} \ln\left(\frac{\pi N}{2}\right)$$

$$\sigma(N, \uparrow\uparrow = \frac{N}{2}) = \frac{N \ln 2 - \frac{1}{2} \ln\left(\frac{\pi N}{2}\right)}{}$$

negligible compared to $N \ln 2$

so entropy of all the macrostates (i.e. total number of microstates) is

$$\ln(2^N) = N \ln 2$$

This exercise shows that the entropy of the whole accessible set
of microstates is basically equal to the entropy of the most
probable condition.

Entropy of Classical Systems

Let's extend the definition of statistical entropy for discrete systems to continuous systems as well.

For a set of macroscopic observables x_i , with macrostates corresponding to intervals $[x_i, x_i + \Delta x_i]$, the statistical weights denoted $\Delta W_i = W(x_i, x_i + \Delta x_i)$. The entropy of the macrostate is:

$$\sigma_i = k \Delta W_i$$

The entropy of the total system is:

$$\sigma = k W$$

$$\text{where } W = \sum_i \Delta W_i$$

Law of Increasing Entropy

Statistically, it is overwhelmingly likely entropy will increase in an isolated system. A gas allowed to expand into a larger volume $V_f > V_i$ will fill the volume V_f , thus having more microstates (more coordinates). It is very unlikely (but not impossible) that the gas stays in volume V_i or stays in a smaller volume.

For a reversible process: $TdS = dQ_R$

if $dQ_R = 0$ (isolated system) then $dS = 0$ and so number of microstates remains constant.

For irreversible process: $TdS > dQ$

if $dQ = 0$ (isolated system) then $dS > 0$ and the number of microstates increases.

Thermal Equilibrium and Statistical Definition of Temperature

We will now introduce the definition of temperature and pressure in statistical mechanics.

Consider two isolated systems A and B not in contact with each other. Equilibrium has been reached in each system.

Now we place these two systems in contact.

Consider the case where only energy (not volume) is allowed to be exchanged.

After a while this combined system will find a new state with constant temperature, it will be in equilibrium.

If system A has energy E_A and system B has E_B , then $E = E_A + E_B$ is conserved during the whole thermalisation process (the process to get to equilibrium).

After a time longer than the relaxation time, the two systems will be in equilibrium and the entropy of the combined system is:

$$\sigma = \sigma_A + \sigma_B$$

Let's consider the entropy σ during thermalisation as a function of just E_A . When equilibrium is reached σ has reached a maximum value so:

$$\frac{d\sigma}{dE_A} = 0 \quad \text{but since } \sigma = \sigma_A + \sigma_B:$$

$$\frac{d\sigma_A}{dE_A} + \frac{d\sigma_B}{dE_A} = 0$$

$$\text{but } \frac{d\sigma_B}{dE_A} = \frac{d\sigma_B}{dE_B} \frac{dE_B}{dE_A} \xrightarrow{\text{constant}} = \frac{d\sigma_B}{dE_B} \frac{d}{dE_A} \{E - E_A\} = - \frac{d\sigma_B}{dE_B}$$

$$\therefore \frac{d\sigma_A}{dE_A} - \frac{d\sigma_B}{dE_B} = 0 \quad \frac{d\sigma_A}{dE_A} = \frac{d\sigma_B}{dE_B}$$

If we define statistical temperature τ as:

$$\boxed{\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial E} \right)_{V, N}}$$

then $\tau_A = \tau_B$ the condition for thermal equilibrium.

This temperature is a statistical quantity with same units as E and is only meaningful for macroscopic systems.

"So in thermal equilibrium, any macroscopic subsystem of an isolated system is at the same temperature."

During the thermalisation process (while the system is not at equilibrium), the total entropy increases $\frac{d\sigma}{dt} > 0$ since the thermal contact increases accessible phase space $\Delta \Gamma$

$$\frac{d\sigma}{dt} = \frac{d\sigma_A}{dt} + \frac{d\sigma_B}{dt} = \frac{d\sigma_A}{dE_A} \frac{dE_A}{dt} + \frac{d\sigma_B}{dE_B} \frac{dE_B}{dt} > 0$$

during thermalisation, total energy is conserved so

$$\frac{dE_A}{dt} = - \frac{dE_B}{dt}$$

$$\therefore \frac{d\sigma}{dt} = \frac{dE_A}{dt} \left(\frac{1}{\tau_A} - \frac{1}{\tau_B} \right) > 0$$

Mechanic Equilibrium and Statistical Definition of Pressure

Now consider the same setup but this time suppose the wall between system A and B can also move.

Hence, the volumes V_A and V_B can change, though $V_A + V_B = V$ is constant.

Entropy now depends on two variables, E_A and V_A .

In equilibrium, one has:

$$d\sigma = \left. \frac{\partial \sigma}{\partial V_A} \right|_{E_A} dV_A + \left. \frac{\partial \sigma}{\partial E_A} \right|_{V_A} dE_A = 0 \quad \text{but } \sigma = \sigma_A + \sigma_B$$

$$d\sigma = \left[\left. \frac{\partial \sigma_A}{\partial V_A} \right|_{E_A} + \left. \frac{\partial \sigma_B}{\partial V_A} \right|_{E_A} \right] dV_A + \left[\left. \frac{\partial \sigma_A}{\partial E_A} \right|_{V_A} + \left. \frac{\partial \sigma_B}{\partial E_A} \right|_{V_A} \right] dE_A = 0$$

$$\text{but } \left. \frac{\partial \sigma_A}{\partial E_A} \right|_{V_A} = - \left. \frac{\partial \sigma_B}{\partial E_B} \right|_{V_B} \quad \text{and} \quad \left. \frac{\partial \sigma_A}{\partial V_A} \right|_{E_A} = - \left. \frac{\partial \sigma_B}{\partial V_B} \right|_{E_B} \quad \text{so:}$$

$$d\sigma = \left[\left. \frac{\partial \sigma_A}{\partial V_A} \right|_{E_A} - \left. \frac{\partial \sigma_B}{\partial V_B} \right|_{E_B} \right] dV_A + \left[\left. \frac{\partial \sigma_A}{\partial E_A} \right|_{V_A} + \left. \frac{\partial \sigma_B}{\partial E_B} \right|_{V_B} \right] dE_A = 0$$

Total equilibrium implies $T_A = T_B$ so the second term vanishes.

We also require mechanical equilibrium:

$\Pi_A = \Pi_B$ where Π is statistical pressure defined as

$$\boxed{\frac{\Pi}{T} = \left. \frac{\partial \sigma}{\partial V} \right|_{E, N}}$$

"In Mechanical equilibrium, any macroscopic subsystem of an isolated system has the same pressure"

$$\frac{d\sigma}{dt} = \frac{1}{T} \frac{dV_A}{dt} (\Pi_A - \Pi_B) > 0 \quad \text{once thermal equilibrium has been reached}$$

so this implies subsystem with higher pressure expands in volume.

Connection between Statistical and Thermodynamic Quantities

$$d\sigma = \left. \frac{\partial \sigma}{\partial E} \right|_V dE + \left. \frac{\partial \sigma}{\partial V} \right|_E dV$$

$$d\sigma = \frac{1}{T} dE + \frac{\Pi}{T} dV$$

$$\Rightarrow dE = T d\sigma - \Pi dV$$

This is analogous to Fundamental Relation!

$$T d\sigma = dQ$$

$$- \Pi dV = dW$$

$$\Rightarrow dW = -p dV \text{ so:}$$

$$\underline{\underline{\Pi = p}} \quad \underline{\underline{T d\sigma = T ds}}$$

This is possible only if $T = CT$ and $\sigma = \frac{S}{C}$ for some constant C .

Consider $PV = Nk_B T$

From $\sigma = \ln W$, we know that if energy is constant $W \propto V^N$
so $\sigma \propto N \ln V$

From definition of pressure:

[from $\frac{\Pi}{T} = \left. \frac{\partial \sigma}{\partial V} \right|_E$ and differentiating $N \ln V$]

$$\frac{P}{T} = \left. \frac{\partial \sigma}{\partial V} \right|_E = \frac{N}{V}$$

Therefore:

$$\underline{\underline{PV = NT}}$$

This is analogous to $PV = Nk_B T$

so we find $C = k_B$ since we previously stated $T = CT$

$$\therefore \underline{\underline{T = k_B T}}$$

$$\underline{\underline{\sigma = \frac{S}{k_B}}}$$

$$\underline{\underline{\Pi = p}}$$

Statistical
and TD
quantities relations
are shown left.

\therefore

$$\boxed{S = k_B \ln W}$$

The Boltzmann
definition of
entropy.

Ideal Gas in Microcanonical Ensemble

Let's try and derive the entropy of an ideal gas with the machinery of the microcanonical ensemble.

Let's start with $S = k_B \ln W$ where here, $W = \frac{\Delta \Gamma}{h^{3N}}$ where $\Delta \Gamma$ is volume of accessible region of phase space. For an ideal gas:

$$\Delta \Gamma = \int_{E(p,q)} dp dq \quad \text{where} \quad E_0 - \frac{\Delta E}{2} \leq E(p,q) \leq E_0 + \frac{\Delta E}{2}$$

ΔE is some measurement error
 E_0 is a constant

$$= \int_{E(p,q)} \prod_{i=1}^{3N} dq_i \prod_{i=1}^{3N} dp_i$$

$$= V^N \int_{E(p,q)} \prod_{i=1}^{3N} dp_i$$

The energy $E(p,q)$ is given by the sum of all kinetic energies

$$E(p,q) = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

It can be shown after some funky maths that for huge N :

$$\Delta \Gamma \approx V^N \Omega_{3N} \quad \text{where} \quad \Omega_{3N} = \int \prod_{i=1}^{3N} dp_i = \frac{\pi^{3N/2}}{(3N/2)!} R^{3N} \quad R = \sqrt{2mE}$$

You don't need to remember this, just $\Delta \Gamma = V^N \Omega_{3N}$

$$\sigma = \frac{S}{k_B} = \ln W$$

$$= \ln \left[\frac{\Delta \Gamma}{h^{3N}} \right] = N \ln \left[V \pi^{3/2} \left(\frac{2mE}{h^2} \right)^{3/2} \right] - \ln \left[\left(\frac{3N}{2} \right)! \right]$$

Using Stirling's approximation: $\ln \left[\left(\frac{3N}{2} \right)! \right] = \frac{3N}{2} \ln \left(\frac{3N}{2} \right) - \frac{3N}{2}$

$$\text{so } \sigma = \frac{S}{k_B} = N \ln \left[\frac{V}{h^3} \left(\frac{4\pi m}{3} \right)^{3/2} \left(\frac{U}{N} \right)^{3/2} \right] + \frac{3N}{2}$$

after writing $E = U$ and replacing R with $\sqrt{2mE}$

This is currently not additive so not extensive. So it's not done yet! Let's split the system into 2 parts $\frac{V}{2}$ and $\frac{V}{2}$

$$N_1 = \frac{N}{2}, V_1 = \frac{V}{2}, U_1 = \frac{U}{2} \text{ and same for } N_2, V_2 \text{ and } U_2$$

$$\sigma_1 + \sigma_2 = \frac{N}{2} \ln\left(\frac{1}{2}(\text{term})\right) + \frac{3N}{4} + \frac{N}{2} \ln\left(\frac{1}{2}(\text{term})\right) + \frac{3N}{4}$$

$$\text{where term} = \frac{V}{N} \left(\frac{4\pi m}{3}\right)^{3/2} \left(\frac{U}{N}\right)^{3/2}$$

We expect $\sigma_{1+2} = \sigma_1 + \sigma_2$ but we don't get this!

$$= N \ln\left(\frac{1}{2}(\text{term})\right) + \frac{3N}{2}$$

so what do we do? We consider identical particles as being indistinguishable.

If a particle is volume element of phase space $[q_i, q_i + dq_i], [p_i, p_i + dp_i]$ and a particle b is $[q_j, q_j + dq_j], [p_j, p_j + dp_j]$. If these particles are identical, if we swap the particles, we still have the same microstate.

So we need to divide our total number of microstates by $N!$

$$W = \frac{\Delta\Gamma}{h^{3N} N!} \text{ which now gives us:}$$

$$\sigma = N \ln \left[\frac{V}{N h^3} e \left(\frac{4\pi m}{3} \right)^{3/2} \left(\frac{U}{N} \right)^{3/2} \right] + \frac{3N}{2} \quad \text{after using Stirling's approximation again}$$

This is now additive. From this, we can find

$$\frac{1}{T} = \frac{\partial \sigma}{\partial E} = \frac{3}{2} \frac{N}{E} \quad \text{so} \quad \underline{\underline{E = \frac{3}{2} N k_B T}} \quad \text{another well known formula}$$