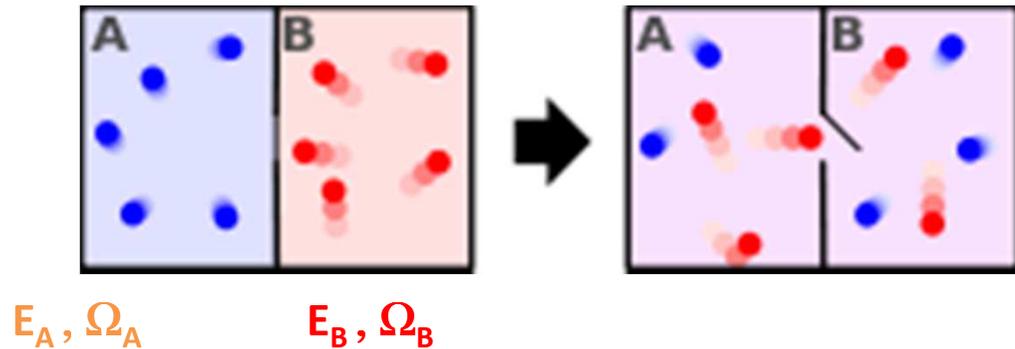


Basic Statistical Mechanics: Temperature and entropy



- Consider a system with total energy E consisting of 2 weakly interacting subsystems A and B.
Weakly interacting = subsystems can exchange energy and $E = E_A + E_B$
- The degeneracy Ω of E is astronomically large (10^{23}). These are the number of eigenstates $\Omega(E, V, N)$ of a system with energy E and N particles in a volume V .
- For a given choice of E_A , the number of degenerated states Ω of the total system is $\Omega_A(E_A) \cdot \Omega_B(E_B)$.
- It is convenient to have a measure of the degeneracy of the subsystems that is additive.

- It is convenient to have a measure of the degeneracy of the subsystems that is additive (**log !**).

$$\ln \Omega (E_A, E_B) = \ln \Omega (E_A, E - E_A) = \ln \Omega_A (E_A) + \ln \Omega_B (E - E_A) \quad (1)$$

- Subsystems A and B can exchange energy. Every energy state of the total system is equally likely.
- The number of eigenstates Ω_A depends strongly on the value of E_A . The most likely value for E_A is the one which maximizes $\ln \Omega(E_A, E - E_A)$, i.e. one has :

$$\frac{\partial \ln \Omega(E_A, E - E_A)}{\partial E_A} = 0$$

or, using (1):

$$\frac{\partial \ln \Omega_A(E_A)}{\partial E_A} + \frac{\partial \ln \Omega_B(E - E_A)}{\partial E_A} = \frac{\partial \ln \Omega_A(E_A)}{\partial E_A} - \frac{\partial \ln \Omega_B(E_B)}{\partial E_B} = 0$$

because one remembers that $E_A + E_B = E = \text{constant}$ so that $dE_A + dE_B = 0$.

$$\left(\frac{\partial \ln \Omega_A(E_A)}{\partial E_A} \right)_{N_A, V_A} = \left(\frac{\partial \ln \Omega_B(E_B)}{\partial E_B} \right)_{N_B, V_B}$$

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With a short-hand notation : $\beta_A = \left(\frac{\partial \ln \Omega_A(E_A)}{\partial E_A} \right)_{N_A, V_A}$

one has: $\beta_A(E_A, V_A, N_A) = \beta_B(E_B, V_B, N_B)$

for the most probable value of each subsystem (maximum of Ω with respect to E_A or E_B). Assume all the energy is in A, one will have energy transfer until equ. (2) is satisfied.

Or : when the equilibrium of the system is reached, $\ln \Omega$ is at its maximum : $S = k_B \ln \Omega$

Second law of Thermodynamics: **Entropy S** of a system (N,V,E) is at its maximum when the system is in thermal equilibrium.

Equation (2) then has a natural implication, the statistical **definition of temperature**:

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$$\frac{1}{T} = k_B \beta = \left(\frac{\partial S}{\partial E} \right)_{V,N}$$

so that at thermal equilibrium, one has: $T_A = T_B$

Heat bath : Assume that a system A is in thermal equilibrium with a large heat bath (system B).

If the system A has an energy E_i , then the bath has $E_B = E - E_i$ and a degeneracy of $\Omega_B(E - E_i)$. The probability P_i to find the system A at energy i is given by :

$$P_i = \frac{\Omega_B(E - E_i)}{\sum_j \Omega_B(E - E_j)}$$

And expanding (Taylor) around $E_i = 0$, one obtains for $\Omega_B(E - E_i)$

$$\ln \Omega_B(E - E_i) = \ln \Omega_B(E) - E_i \left(\frac{\partial \ln \Omega_B(E)}{\partial E} \right) + \mathcal{O}\left(\frac{E_i^2}{E^2}\right)$$

$$\ln \Omega_B(E - E_i) = \ln \Omega_B(E) - E_i \left(\frac{\Omega_B(E)}{\partial E} \right) + \mathcal{O}\left(\frac{1}{E}\right)$$

Or :

$$\ln \Omega_B(E - E_i) = \ln \Omega_B(E) - \frac{E_i}{k_B T} + \mathcal{O}\left(\frac{1}{E}\right)$$

And inserted into :

$$P_i = \frac{\Omega_B(E - E_i)}{\sum_j \Omega_B(E - E_j)}$$

leads to the well-known Boltzmann distribution:

$$P_i = \frac{\exp(-E_i/k_B T)}{\sum_j \exp(-E_j/k_B T)}$$

Average energy of the system:

$$\langle E \rangle = \frac{\sum_i E_i \exp(-E_i/k_B T)}{\sum_j \exp(-E_j/k_B T)} = - \frac{\partial \ln \sum_j \exp\left(-\frac{E_j}{k_B T}\right)}{\partial \left(\frac{1}{k_B T}\right)} = - \frac{\partial \ln Q}{\partial \left(\frac{1}{k_B T}\right)} = - \frac{\partial \ln Q}{\partial \beta}$$

Where one has introduced the **Partition function**

$$Q = \sum_j \exp\left(-\frac{E_j}{k_B T}\right)$$

From the partition function,

$$Q = \sum_j \exp\left(-\frac{E_j}{k_B T}\right)$$

one can now compute the free energy $F=U-TS$ of the system via using the Maxwell thermodynamic relation:

$$E = -\frac{\partial\left(\frac{F}{T}\right)}{\partial\left(\frac{1}{T}\right)}$$

which is equal to :

$$F = -k_B T \ln Q = -k_B T \ln \sum_j \exp\left(-\frac{E_j}{k_B T}\right)$$

- **F is the workhorse for equilibrium statistical mechanics**, as one can write :

$$S = -\frac{\partial F}{\partial T}$$

$$C_p = T \frac{\partial S}{\partial T}$$

etc.

Back to the phase space

- ❑ Consider again, an isolated system (microcanonical Ensemble) having
 $E=\text{cst}$, $N=\text{cst}$, $V=\text{cst}$
Natural setting for microscopic evolution per Newton's equations of motion.
- ❑ Consider starting an isolated system in a particular microstate. As the system evolves and approaches equilibrium, the total energy E remains constant, at the same value that it had for the initial microstate.
- ❑ The **principle of equal a priori probabilities** then states that the system will ultimately visit all of the microstates with that value of E with the same frequency.
- ❑ The function $\Omega(E, V, N)$ counts the number of microstates for atoms in volume V that have energy E , and is called the **density of states** or **microcanonical partition function**. It is given by:

$$\begin{aligned}\Omega(E, V, N) &= \frac{1}{h^{3N} N!} \int \int \dots \int \delta[H(\mathbf{p}^N, \mathbf{r}^N) - E] d\mathbf{p}_1 d\mathbf{p}_2 \dots d\mathbf{p}_N d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \\ &= \frac{1}{h^{3N} N!} \int \delta[H(\mathbf{p}^N, \mathbf{r}^N) - E] d\mathbf{p}^N d\mathbf{r}^N\end{aligned}$$

where H is the Hamiltonian of the system and δ is the Dirac functions

Defining Ensembles

Canonical Ensemble: system characterized by two thermodynamics variables
Temperature T and total number of particles N.

H being the Hamiltonian of the system, the partition function reads :

$$Q(V, \beta, N) = \sum_{\alpha} \exp(-\beta \mathcal{H}(\alpha)) \quad \text{or} \quad Q(V, \beta, N) = \frac{1}{\Lambda^{3N} N!} \int_0^V dr^N e^{-\beta H(r^N)}$$

where $\beta=1/k_B T$ and Λ volume of the phase space. The sum runs over all configurations α of the system. The free energy $F(V, N, \beta)$ of the system is equal to :

$$\beta F(V, \beta, N) = -\ln(Q(V, \beta, N)).$$

and the probability of having a configuration α as : $P(V, \beta, N; \alpha) = \frac{\exp(-\beta \mathcal{H}(\alpha))}{Q(V, \beta, N)}$.

Example: Consider a two state model with energies E1 and E2. The partition function and the probability of finding are given by :

$$Q = e^{-E1/k_B T} + e^{-E2/k_B T} \quad P(i) = e^{-\frac{E_i}{k_B T}} / (e^{-\frac{E1}{k_B T}} + e^{-\frac{E2}{k_B T}})$$

Other thermodynamic quantities can be derived from the moments of the probability distribution :

Mean energy:

$$\begin{aligned} U(V, \beta, N) &= \frac{\partial(\beta F(V, \beta, N))}{\partial \beta} \\ &= \sum_{\alpha} \mathcal{H}(\alpha) P(V, \beta, N; \alpha) \end{aligned}$$

Heat capacity :

$= \langle \mathcal{H}(\alpha) \rangle$ First moment (mean) of the Hamiltonian

$$\begin{aligned} C_v(V, \beta, N) &= -k_B \beta^2 \frac{\partial U(V, \beta, N)}{\partial \beta} \\ &= k_B \beta^2 \left(\sum_{\alpha} \mathcal{H}^2(\alpha) P(V, \beta, N; \alpha) - \left(\sum_{\alpha} \mathcal{H}(\alpha) P(V, \beta, N; \alpha) \right)^2 \right) \\ &= k_B \beta^2 (\langle \mathcal{H}(\alpha)^2 \rangle - \langle \mathcal{H}(\alpha) \rangle^2) \end{aligned}$$

variance of the Hamiltonian, involving the second moment

Grand Canonical Ensemble: system characterized by two thermodynamics variables Temperature T and chemical potential μ . It also implies that the total number of particles N can change (remember link between m and Gibbs energy).

The partition function reads :
$$\Xi(V, \beta, \mu) = \sum_{N=0}^{\infty} \sum_{\alpha_N} \exp(-\beta(\mathcal{H}_N(\alpha_N) - \mu N))$$

where the sum runs over over N particles and over all configurations for systems having a number of particles going from 0 to ∞ .

By definition, the **Grand Potential $\Omega(V, \beta, \mu)$** is given by :

$$\beta\Omega(V, \beta, \mu) = -\ln(\Xi(V, \beta, \mu))$$

And similarly the probability distribution:
$$P(V, \beta, \mu; \alpha_N) = \frac{\exp(-\beta(\mathcal{H}_N(\alpha_N) - \mu N))}{\Xi(V, \beta, \mu)}$$

Or the mean number of particles:

$$\begin{aligned} \langle N(V, \beta, \mu) \rangle &= - \frac{\partial(\beta\Omega(V, \beta, \mu))}{\partial(\beta\mu)} \\ &= \sum_N \sum_{\alpha_N} N P(V, \beta, \mu; \alpha_N) \end{aligned}$$

Isothermal-isobaric (NPT) Ensemble: system characterized by three thermodynamics variables : Temperature T , Pressure P and number of particles N.

Important Ensemble given that most of experimental work is performed at constant pressure (chemical reaction, measurement,...).

The partition function can be written as a weighted sum of the $Q(V,\beta,N)$ of the canonical ensemble, i.e.

$$\Delta(P, \beta, N) = \int Q(V, \beta, N) e^{-\beta PV} C dV$$

In order to have a non-dimensional quantity for $\Delta(P,\beta,N)$, one can choose :

$$C = \beta P \quad \text{or} \quad C = N/V$$

leading to :

$$Q(P, \beta, N) = \frac{\beta P}{\Lambda^{3N} N!} \int_0^\infty dV \exp(-\beta PV) \int_0^V d\mathbf{r}^N \exp(-\beta U(\mathbf{r}^N))$$

out of which can be computed the Gibbs energy $G(P,\beta,N)$ and the probability Π

$$\beta G(P, \beta, N) = -\ln(Q(P, \beta, N)). \quad \Pi(P, \beta, \mu; \alpha_V) = \frac{\exp(-\beta V) \exp(-\beta(U(\mathbf{r}^N)))}{Q(P, \beta, N)}.$$

Example of Ensemble calculation:

Ideal gas consisting of N monoatomic molecules

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

$$Q = \frac{1}{h^{3N} N!} \int e^{-\beta H} d\Gamma = \frac{1}{h^{3N} N!} \int e^{-\beta H} \prod_{i=1}^{3N} dq_i dp_i$$

Integration over the position is immediate. The Hamiltonian being the sum of individual degrees of freedom, the integral is equal to the 3N-th power of the integral with respect to one degree of freedom.

$$\int_{-\infty}^{+\infty} e^{-\beta p^2/2m} dp = \sqrt{\frac{2m}{\beta}} \int_{-\infty}^{+\infty} e^{-x^2} dx = \sqrt{\frac{2\pi m}{\beta}}$$

And:

$$Q(V, \beta, N) = \frac{V^N}{h^{3N} N!} \left[\sqrt{\frac{2\pi m}{\beta}} \right]^{3N}$$

The free energy is : $F = -kT \ln Q = -NkT \left[\frac{3}{2} \ln T + \ln \frac{V}{N} + \ln \frac{e(2\pi mk)^{\frac{3}{2}}}{h^3} \right]$

using Stirling formula: $\ln N! = N \ln N - N$

From the free energy :

$$F = -NkT \left[\frac{3}{2} \ln T + \ln \frac{V}{N} + \ln \frac{e(2\pi mk)^{\frac{3}{2}}}{h^3} \right]$$

one can compute the pressure via : $p = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = \frac{NkT}{V}$ F = - pdV - SdT

Remember that the partition function in isobaric-isothermal (NPT) Ensemble is :

$$\Delta(P, \beta, N) = \int Q(V, \beta, N) e^{-\beta PV} dV = \frac{1}{h^{3N} N!} \left[\sqrt{\frac{2\pi m}{\beta}} \right]^{3N} \int_0^{+\infty} e^{-\beta PV} V^N dV$$

$$= \frac{1}{h^{3N}} \left[\sqrt{\frac{2\pi m}{\beta}} \right]^{3N} \left(\frac{kT}{p} \right)^{N+1}$$

The Gibbs energy is : $G = -kT \ln \Delta(P, \beta, N) = -NkT \left[\frac{5}{2} \ln T - \ln P + \ln \frac{k^{5/2} (2\pi m)^{\frac{3}{2}}}{h^3} \right]$

One recovers the volume via : $V = - \left(\frac{\partial G}{\partial P} \right)_{T,N} = \frac{NkT}{P}$ G = - VdP - SdT