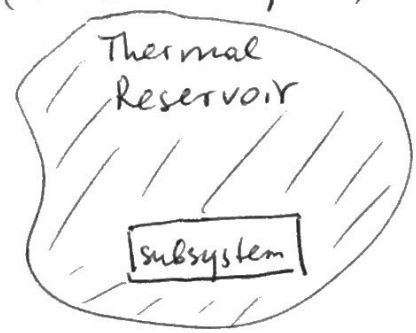
Gibbs distribution

(isolated system)



Consider an isolated system in statistical equilibrium:

$$\rho(p,q) = \text{const.}\ \delta(E - E_0)$$ microcanonical ensemble prob. density

Here $E = H(p,q)$ is the Hamiltonian

$E_0 = \text{const}$ is the conserved energy value.

Consider a small subsystem with $E_s = H_s(p_s, q_s)$, $E_s \ll E_0$.

The rest will play the role of a thermal reservoir

with $E_R = H_R(p_R, q_R)$, $p = (p_R, p_s)$, $q = (q_R, q_s)$

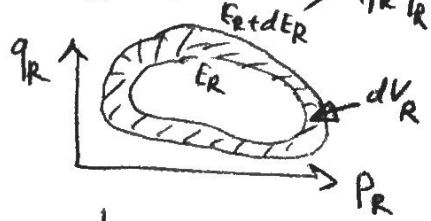
and $$H(p,q) \approx H_R(p_R, q_R) + H_s(p_s, q_s)$$

(neglecting small interaction at the boundary)

Probability density of the subsystem is

$$\rho_s(p_s, q_s) \overset{\text{Def}}{=\!=} \int \rho\, dp_R\, dq_R = \text{const} \int \delta(E_R + E_s - E_0)\, dp_R\, dq_R$$

We can change integration variable:



$$dp_R\, dq_R = \frac{dV_R}{dE_R}\, dE_R,$$ where dV_R is the phase-space volume corresponding to $H(p,q) \in [E_R, E_R + dE_R]$

After integration of the Dirac delta-function,

$$\rho_s(p_s, q_s) = \text{const} \left(\frac{dV_R}{dE_R}\right)_{E_R = E_0 - E_s}$$

Recall that, in equilibrium, the energy E_R has small fluctuations (variance $\delta E_R \ll E_R$), and it occupies $\frac{\delta V_R}{h^n} \approx e^{S_R/k_B}$ microstates (see Def. of the entropy). Hence,

$$\frac{dV_R}{dE_R} \approx \frac{\delta V_R}{\delta E_R} \approx \underbrace{\frac{h^n}{\delta E_R}}_{\substack{\text{approximately} \\ \text{const for} \\ E_R = E_0 - E_s \approx E_0}} \underbrace{e^{S_R/k_B}}_{\substack{\text{changes strongly} \\ \text{because of the} \\ \text{exponential dependence}}}$$

We obtain,

$$\rho_s(p_s, q_s) \approx \text{const} \cdot \left(e^{S_R/k_B}\right)_{E_R = E_0 - E_s}.$$

Since $E_s \ll E_0$ (small subsystem), we can use the Taylor expansion:

$$S_R(E_R) \underset{E_R = E_0 - E_s}{\approx} S_R(E_0) - \underbrace{\frac{dS_R}{dE_R}}_{\substack{\left(\text{Def: } T = \frac{dU}{dS}\right) \\ U \approx E_R}} E_s = \text{const} - \frac{E_s}{T}$$

This yields: $\rho_s(p_s, q_s) = \text{const} \cdot e^{-\frac{E_s}{k_B T}}$

Thus, for any small subsystem, the probability density has the form

$$\rho(p,q) = A \exp\left(-\frac{E}{k_B T}\right), \quad \text{dropping index } s.$$

Here $E = H(p,q)$ is the energy of this subsystem, ~~and~~ T is its temperature, and A is a constant factor.

Let us compute the entropy:

$$S \overset{\text{def}}{=} k_B \overline{\log \frac{1}{h^n \rho}} = -k_B \overline{\log\left(h^n A \exp\left(-\frac{E}{k_B T}\right)\right)}$$

$$= -k_B \log h^n A + \frac{\mathcal{U}}{T}, \quad \text{where } \mathcal{U} = \overline{E} \text{ is the internal energy.}$$

$$\Rightarrow k_B T \log h^n A = \mathcal{U} - ST = F \quad (\text{free energy})$$

We obtained $A = \frac{1}{h^n} \exp \frac{F}{k_B T}$.

The final result is the <u>Gibbs probability distribution</u>

$$\boxed{\rho(p,q) = \frac{1}{h^n} \exp\left(\frac{F-E}{k_B T}\right)}$$

where $E = H(p,q)$ is the energy (Hamiltonian), F is the free energy and T is the temperature of the subsystem.

Partition function

Normalization condition: $\int \rho \, dp\, dq = 1.$

$$\frac{1}{h^n} e^{\frac{F}{k_B T}} \underbrace{\int e^{-\frac{H(p,q)}{k_B T}} dp\, dq}_{Z} = 1$$

$$\boxed{F = -k_B T \log Z,}$$

where $\boxed{Z := \int \frac{dp\, dq}{h^n} \exp\left(-\frac{H(p,q)}{k_B T}\right)}$ is called the partition function.

These formulas provide the <u>analytic</u> expression for the free energy (thermodynamics) in terms of the Hamiltonian of microscopic motion!

Z (and F) are functions of T and parameters of the system (Volume, number of particles, etc.)

<u>Obs</u> At microscale, dynamics of particles is described by quantum mechanics. Thus, quantum mechanical formulation must be used in general

$$Z = \sum_{\substack{\text{all energy} \\ \text{states } E_i}} \exp\left(-\frac{E_i}{k_B T}\right).$$

Some properties allow classical description.

Ideal gas

N particles with weak interaction, which can be neglected: $H(p,q) = \sum_{a=1}^{N} \frac{p_a^2}{2m}$ (kinetic energy only)

Phase space : $(p,q) \in \mathbb{R}^{2n}$, $n = 3N$ is the number of degrees of freedom.

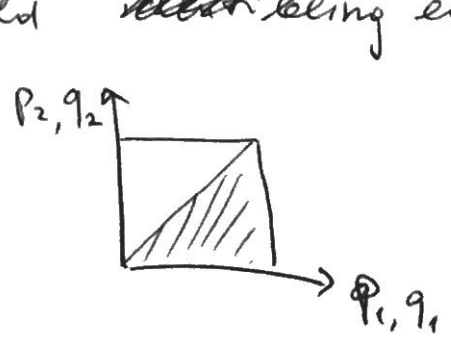
BUT Any permutation of particles is the identical configuration an SHOULD NOT BE COUNTED!

Obs This is a fundamental property of particles in quantum mechanics

In classical mechanics, phase space is

$(p,q) \in \mathbb{R}^{2n} \mid S_N$ (space with all permuted states ~~identi~~ being equivalent)

Implementation :



consider $(p,q) \in \mathbb{R}^{2n}$

but with $dp\,dq \to \frac{dp\,dq}{N!}$

(divide by a number of equivalent states).

Obs In Def of chemical potential, we add a particle, without telling which particle (index) we add.

Partition function: $Z = \int \exp\left(-\frac{\sum_{a=1}^{N} p_a^2/2m}{k_B T}\right) \frac{dp\,dq}{h^{3N} N!}$.

Free energy: $F = -k_B T \log Z =$

$$= -k_B T \log\left[\frac{1}{h^{3N} N!} \int dq \int dp \exp\left(-\frac{\sum_{a=1}^{N} p_a^2/2m}{k_B T}\right)\right]$$

$\int dq = \int dq_1 \cdots \int dq_N = V^N$, V is the system volume

$$\int dp \exp(\cdots) = \underbrace{\left[\int dp_1 \exp\left(-\frac{p_1^2/2m}{k_B T}\right)\right]}_{\text{all integrals for } a=1,\dots,N \text{ are the same}}^N = \left[f(T)\right]^N$$

some function of T.

$$\log N! \simeq N \log \frac{N}{e}, \quad \log h^{3N} = 3N \log h$$

Substituting all, we have

$$F = -k_B T \left(-N \log \frac{N}{e} + N \underbrace{\tilde{f}(T)}_{(f - 3\log h)} + N \log V\right)$$

or

$$\boxed{F = -k_B N T \log \frac{eV}{N} + N \underbrace{\tilde{\tilde{f}}(T)}_{-k_B T \tilde{f}(T)}}$$

Obs: Recall that $F = F(T, V, N)$.

Pressure: $P = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{\partial}{\partial V}\left(-k_B N T \log V\right) = \frac{k_B N T}{V}$

$$PV = k_B N T$$

Molar density $\rho = \frac{N}{N_A V}$, $N_A = 6 \cdot 10^{23}$ Avogadro number (1 mole)

$$\boxed{P = \rho R T}$$ ideal gas state equation.

where $R = N_A k_B \approx 8.3 \frac{J}{K \cdot mol}$ is the ideal gas constant

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Mixture of gases A, B, C:

Partition function: $Z = Z_A \cdot Z_B \cdot Z_C \Rightarrow F = F_A + F_B + F_C$

$\Rightarrow P = \frac{\partial F}{\partial V} = P_A + P_B + P_C$, where

$$\underbrace{P_A = \rho_A R T, \quad P_B = \rho_B R T, \quad P_C = \rho_C R T}_{\text{partial pressure of gas components}}.$$

or $P_A = s_A P$, $P_B = s_B P$, $P_C = s_C P$, where

$s_A = \frac{\rho_A}{\rho_A + \rho_B + \rho_C}$, etc. are (molar) saturations

with $s_A + s_B + s_C = 1$.