

Gibbs distribution

How does one find probability distributions for arbitrary systems?

Consider a big system consisting of very many particles. Split it into subsystems which also have lots of particles.

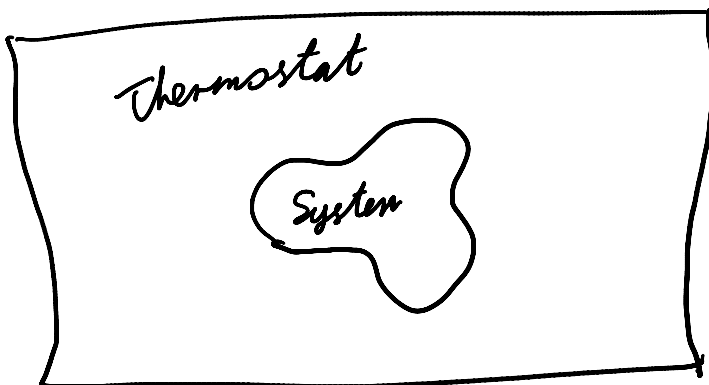
Energy of a subsystem $E \propto R^3 \propto N$,
 N is the number of particles in each subsystem

Interaction energy $E_{\text{surf}} \propto R^2$

$$\frac{E_{\text{surf}}}{E} \propto \frac{R^2}{R^3} \propto \frac{1}{R} \propto N^{-\frac{1}{3}}$$

The interaction becomes negligible when the number of particles is large. Then the subsystems are quasi-independent.

$$E \approx \sum_i \epsilon_i$$



Pick one subsystem there. While it is in equilibrium,
L + f. l H.

Pick one subsystem there. While it is in equilibrium, its energy fluctuates. We want to find the probability of states of this subsystem

Now Subsystem \rightarrow System

Rest of the system \rightarrow Thermostat

$$\hat{H} = \hat{H}_{\text{Syst}} + \hat{H}_{\text{env}} + \hat{V}_{\text{Syst-env}}$$

The system is quantum

$\Omega(\epsilon) \delta \epsilon$ - the number of states of the system in the energy interval $(\epsilon, \epsilon + \delta \epsilon)$

$\Omega(\epsilon)$ - density of states

Because of the coupling \hat{V} , the system will gradually go through all of its states

$w_i = \lim_{T \rightarrow 0} \frac{t_i}{T}$ - prob-ty for the i -th state

States with the same energy are equiprobable

Let's consider a system who has been staying in a narrow interval $\delta \epsilon$ of energies during the interval when we observe the system

Introduce the concept of the density of states

$\Omega(\epsilon) d\epsilon$ - the number of states in a given energy interval $(\epsilon, \epsilon + d\epsilon)$

energy interval $(\epsilon, \epsilon + d\epsilon)$

$$\Omega(\epsilon) = \frac{1}{(2\pi\hbar)^f} \frac{d\Gamma}{dE}$$

What if the system was closed = did not exchange energy with the environment — this is always true for sufficiently short intervals of time, when the interaction with the environment may be neglected

Let's assume the system's energy has been located in a very interval $d\epsilon$

Then $w_i \propto \Omega(\epsilon_i)$

If the interval becomes infinitely narrow,

$$w_i = \text{const} \cdot \delta(E - \epsilon_i) d\Gamma$$

— microcanonical distribution

(By definition, the microcanonical distribution is the distribution in which $P = \frac{1}{N}$, where N is the number of states available

Now let's assume that we observe the system for a very long time. The energy E of system + environment is conserved.

Then

$$w_i \propto \Omega_{\text{env}}(E - \varepsilon_i)$$

Naively, one may try to expand

$$\Omega_{\text{env}}(E - \varepsilon_i) \approx \Omega_{\text{env}}(E) - \varepsilon_i \frac{\partial \Omega_{\text{env}}}{\partial E}$$

However, one may not expand Ω_{env} like this, because energy is an additive function, and Ω_{env} isn't

If we considered 2 systems, 1 and 2, with energies $E_1 - \varepsilon_1$ and $E_2 - \varepsilon_2$, their density of states would be $\Omega_{\text{env}}(E_1 - \varepsilon_1) \Omega_{\text{env}}(E_2 - \varepsilon_2)$, and energy $E_1 + E_2 - \varepsilon_1 - \varepsilon_2$.

$$\Omega_{\text{env}}(E - \varepsilon_i) = e^{S(E - \varepsilon_i)}$$

where S is some function. Now S may be expanded

$$S(E - \varepsilon_i) = \ln \Omega_{\text{env}}(E - \varepsilon_i)$$

$$S(E - \varepsilon_i) \approx S(E) - \frac{\partial S}{\partial E} \varepsilon_i \equiv S(E) = \sigma - \frac{\varepsilon_i}{\theta}$$

$$\text{where } \frac{1}{\theta} = \frac{\partial S}{\partial E}$$

$$\text{Then } \Omega(E - \varepsilon_i) = e^{\sigma(E)} e^{-\frac{\varepsilon_i}{\theta}}$$

$$w_n = A e^{-\frac{E_n}{\theta}}$$

E_n

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With normalisation,

$$w_n = \frac{e^{-\frac{E_n}{\theta}}}{\sum_i e^{-\frac{E_i}{\theta}}}$$

$$Z = \sum_i e^{-\frac{E_i}{\theta}} \text{ - partition function}$$

Different equilibrium distributions are different by their parameters θ .

Let's consider two systems with parameters θ_1 and θ_2 which are in equilibrium with each other.

The probability of a state of a compound system

$$w = w_1 w_2 = A_1 A_2 e^{-\frac{E_1}{\theta_1}} e^{-\frac{E_2}{\theta_2}}$$

$$\text{On the other hand, } w = A e^{-\frac{E_1 + E_2}{\theta}}$$

$$\text{Then } \theta = \theta_1 = \theta_2$$

$$\theta = T \text{ - statistical temperature}$$

$$w_n = \frac{1}{Z} e^{-\frac{E_n}{T}}, \quad Z = \sum_i e^{-\frac{E_i}{T}}$$

Transition to classical statistics

$H(\vec{p}, \vec{Q})$ - the classical limit of the quantum Hamiltonian

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To transition to classical mechanics, the level spacing $\Delta \varepsilon_i = \varepsilon_{i+1} - \varepsilon_i$ has to be small compared to the temperature T . Then $e^{-\frac{\varepsilon_i}{T}}$ may be replaced by $e^{-\frac{E}{T}}$.

Now we will characterise the state of the system by classical \vec{P}, \vec{Q} . That "classical state" has the energy $E(\vec{P}, \vec{Q})$.

The number of states in the energy interval is

$$\Omega(E) d = \frac{\partial \Gamma}{\partial E} \frac{dE}{(2\pi\hbar)^f}$$

$$dw = \frac{e^{-\frac{E}{T}}}{Z} \frac{\partial \Gamma}{\partial E} \frac{dE}{(2\pi\hbar)^f}$$

$$Z = \frac{1}{(2\pi\hbar)^f} \int e^{-\frac{E}{T}} \frac{\partial \Gamma}{\partial E} dE = \frac{1}{(2\pi\hbar)^f} \int e^{-\frac{E(\vec{P}, \vec{Q})}{T}} d\vec{P} d\vec{Q}$$

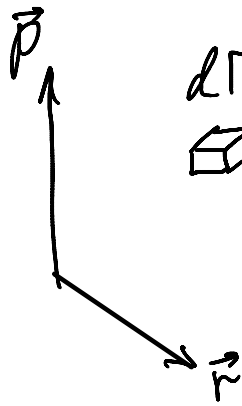
- classical Gibbs distribution

In terms of the statistical distribution function

$$\rho(\vec{P}, \vec{Q}) = \text{const} \cdot e^{-\frac{E(\vec{P}, \vec{Q})}{T}}$$

$$\left(\text{const} = \frac{1}{(2\pi\hbar)^f Z} \right)$$

One may apply that to a classical ideal gas
 One may derive Maxwell distribution from here:

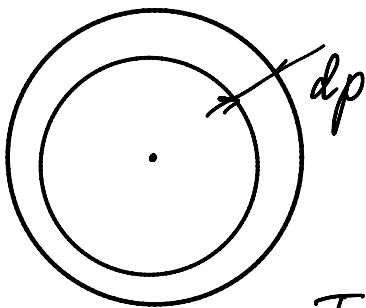


$$d\Gamma = dp_x dp_y dp_z dx dy dz$$



$$d\Gamma = p^2 dp \sin\theta d\theta d\varphi dV$$

Let's find the density of states
 The states with energies between ϵ and $\epsilon + d\epsilon$



$$\frac{p dp}{m} = d\epsilon$$

$$dp = \frac{m}{p} d\epsilon = \frac{m}{\sqrt{2m\epsilon}} d\epsilon = \sqrt{\frac{m}{2}} \frac{d\epsilon}{\sqrt{\epsilon}}$$

The number of states with momenta
 between p and $p + dp$

$$\frac{4\pi p^2 dp \cdot V}{(2\pi\hbar)^3} = \frac{1}{2\pi^2\hbar^3} 2m\epsilon \sqrt{\frac{m}{2}} \frac{d\epsilon}{\sqrt{\epsilon}} = \Omega(\epsilon) d\epsilon$$

$$\Omega(\epsilon) = \frac{m^{\frac{3}{2}}}{\sqrt{2}\pi^2\hbar^3} \sqrt{\epsilon}$$

$$dw = \text{const.} \cdot e^{-\frac{\epsilon}{T}} \sqrt{\epsilon} d\epsilon$$

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We could have worked in momentum representation

$$dw = \text{const.} \cdot e^{-\frac{p^2}{2mT}} p^2 dp$$

Another example: a 2-level system

$$\hat{H} = -\frac{1}{2} \vec{B} \hat{\sigma} \quad (\text{in units of } \mu_B)$$

$$\text{Energies of states: } E_{\uparrow} = -\frac{B}{2}, \quad E_{\downarrow} = \frac{B}{2}$$

$$Z = e^{-\frac{B}{2T}} + e^{\frac{B}{2T}} = 2 \cosh\left(\frac{B}{2T}\right)$$

$$w_{\uparrow} = \frac{e^{\frac{B}{2T}}}{2 \cosh\left(\frac{B}{2T}\right)}, \quad w_{\downarrow} = \frac{e^{-\frac{B}{2T}}}{2 \cosh\left(\frac{B}{2T}\right)}$$

The average spin along the direction of magnetic field is given by

$$\langle \sigma_z \rangle = \frac{1}{2} \frac{e^{\frac{B}{2T}} - e^{-\frac{B}{2T}}}{2 \cosh\left(\frac{B}{2T}\right)} = \frac{1}{2} \tanh\left(\frac{B}{2T}\right)$$

Let's assume there is some potential energy $U(\vec{r})$
Coordinate \vec{r} and momentum \vec{p} are good quantum numbers.

$$dn(\vec{r}, \vec{p}) = \text{const.} \cdot e^{-\frac{\epsilon(\vec{p}) + U(\vec{r})}{T}} d\vec{p} d\vec{r}$$

Integrating out momenta,
 $U(\vec{r})$

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$$dn(\vec{r}) = \text{const.} \cdot e^{-\frac{U(\vec{r})}{T}} d\vec{r}$$

→ $n(\vec{r}) = n_0 e^{-\frac{U(\vec{r})}{T}}$ — Boltzmann distribution

When $U = mgz$

$$n(z) = n_0 e^{-\frac{mgz}{T}}$$