Termodinâmica estatística: Ensemble e função de partição, Conjunto de microestados discreto.

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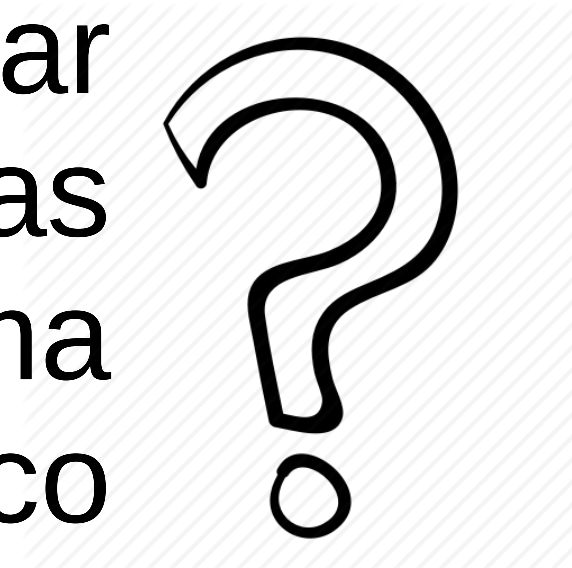
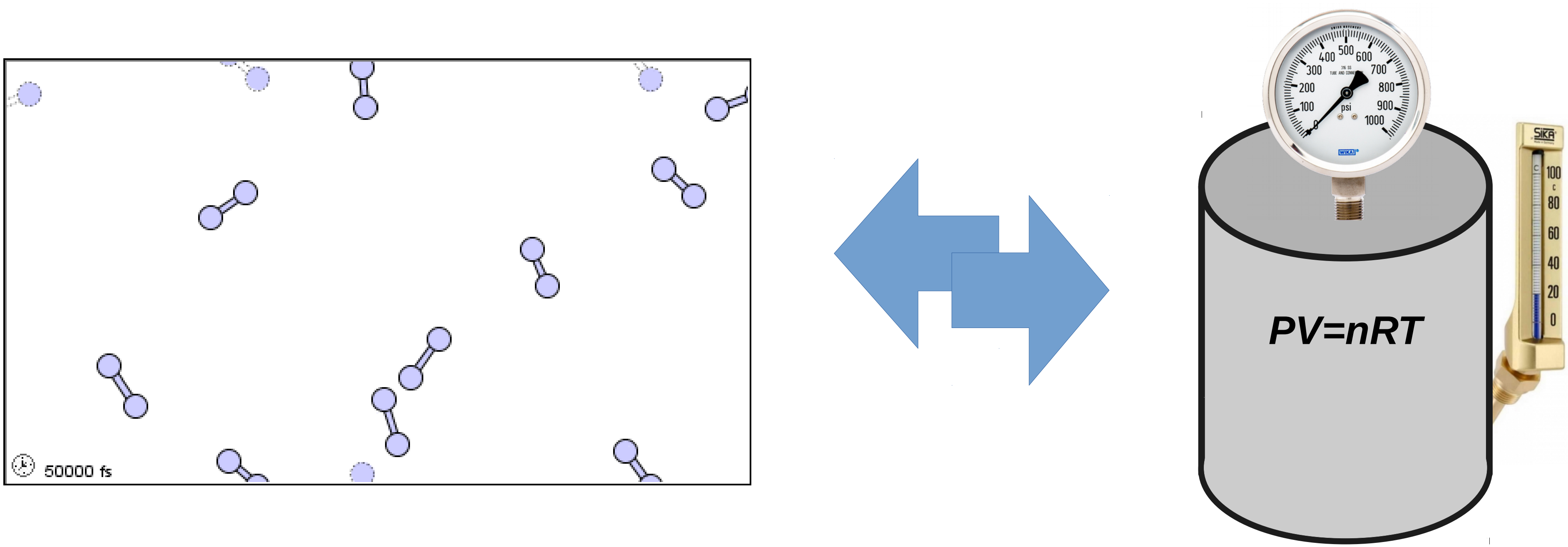
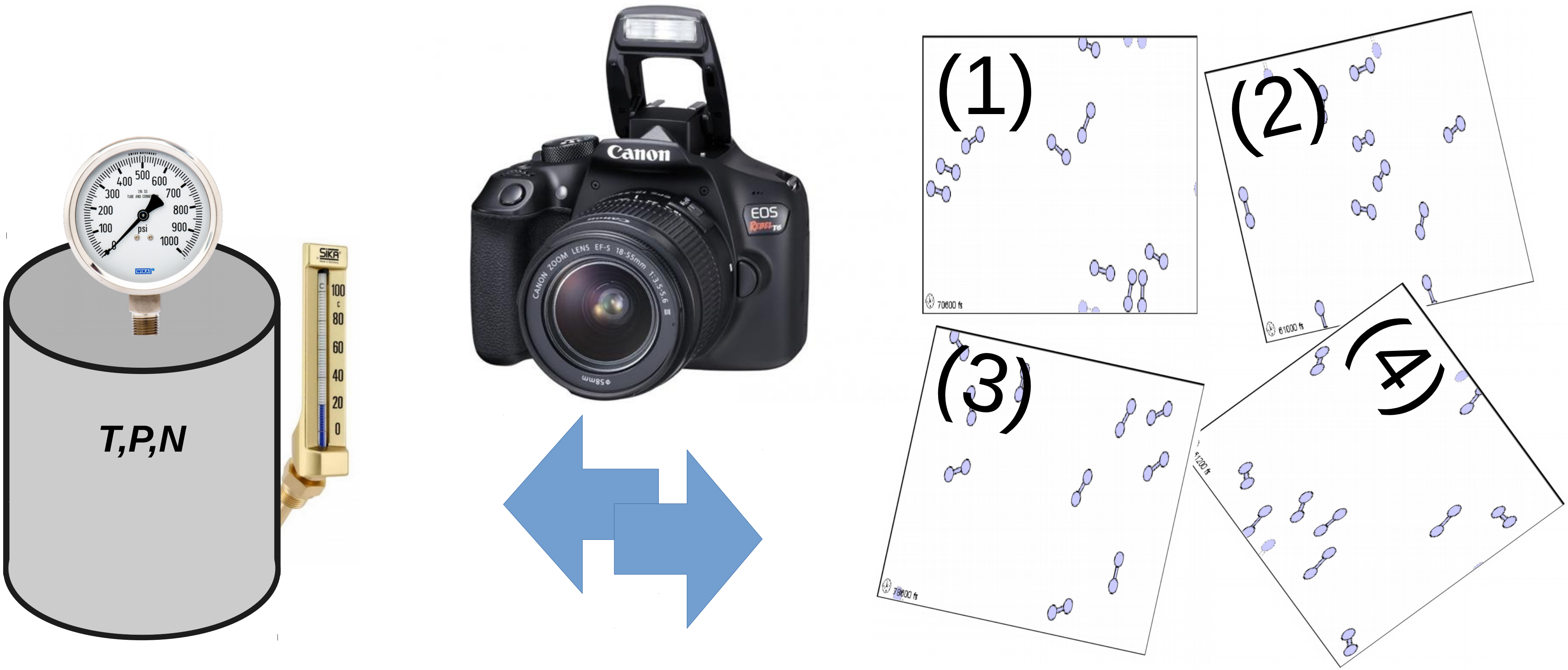
Como relacionar mecânica de partículas com sistema macroscópico





Ensemble

Conjunto de configurações microscópicas compatíveis com uma especificação macroscópica de um sistema.



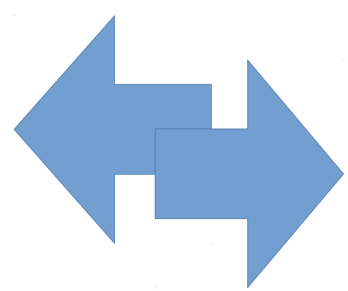
Postulado I

Ensemble de Gibbs

Propriedade termodinâmica no sistema macroscópico

U

dU



Média populacional no *ensemble*

<*E*>

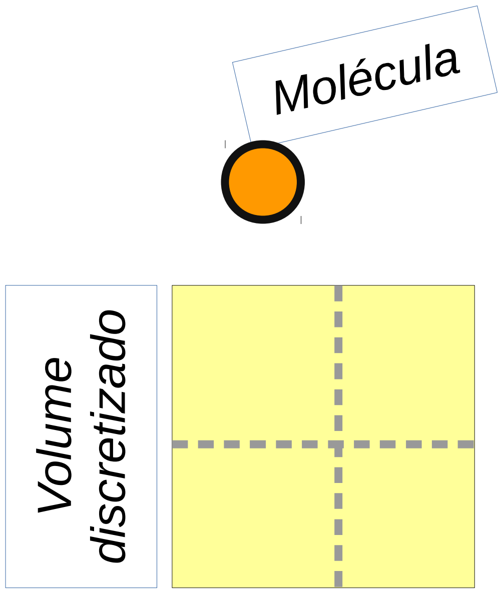
d<*E*>

Especificação macroscópica:

N = 1 partícula

V = 4 células

E = constante



$$i = 1$$

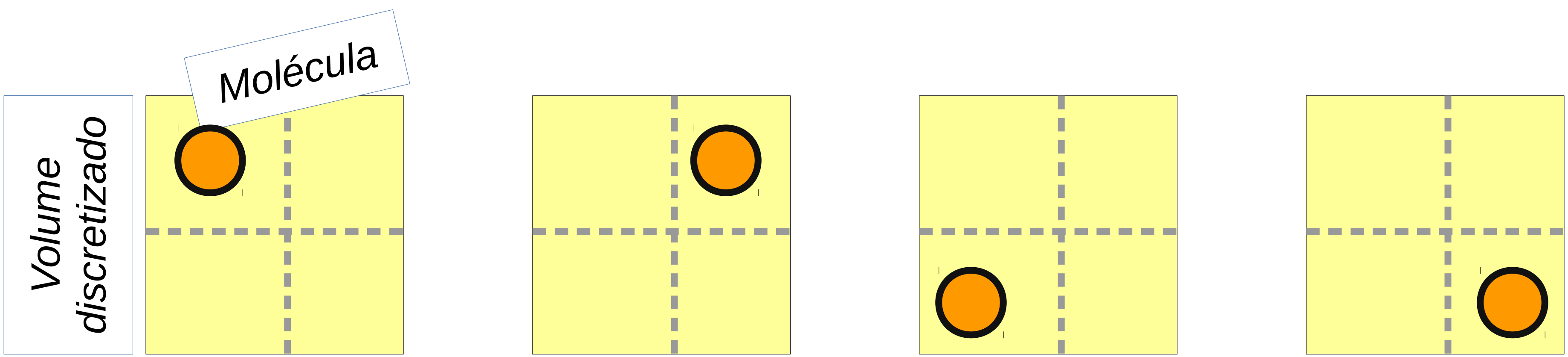
Especificação macroscópica:

N = 1 partícula

V = 4 células

E = constante

Configurações microscópicas diferentes:



$i = 1$ $i = 2$ $i = 3$ $i = 4$

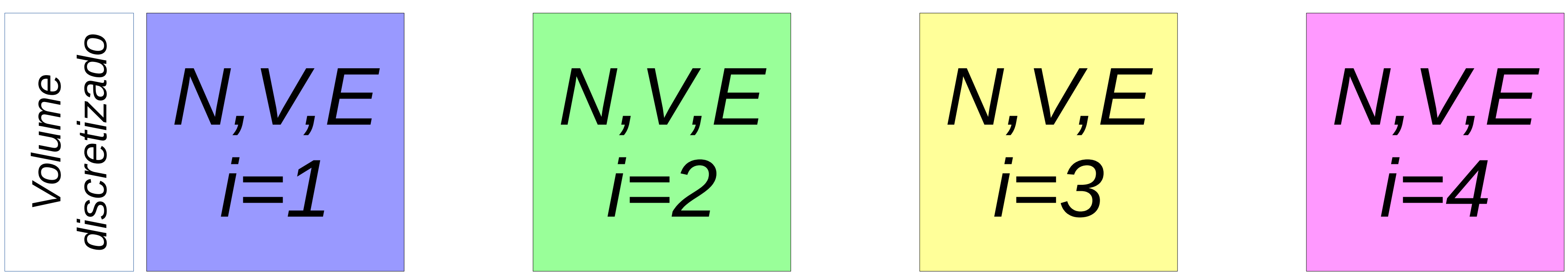
Especificação macroscópica:

N = 1 partícula

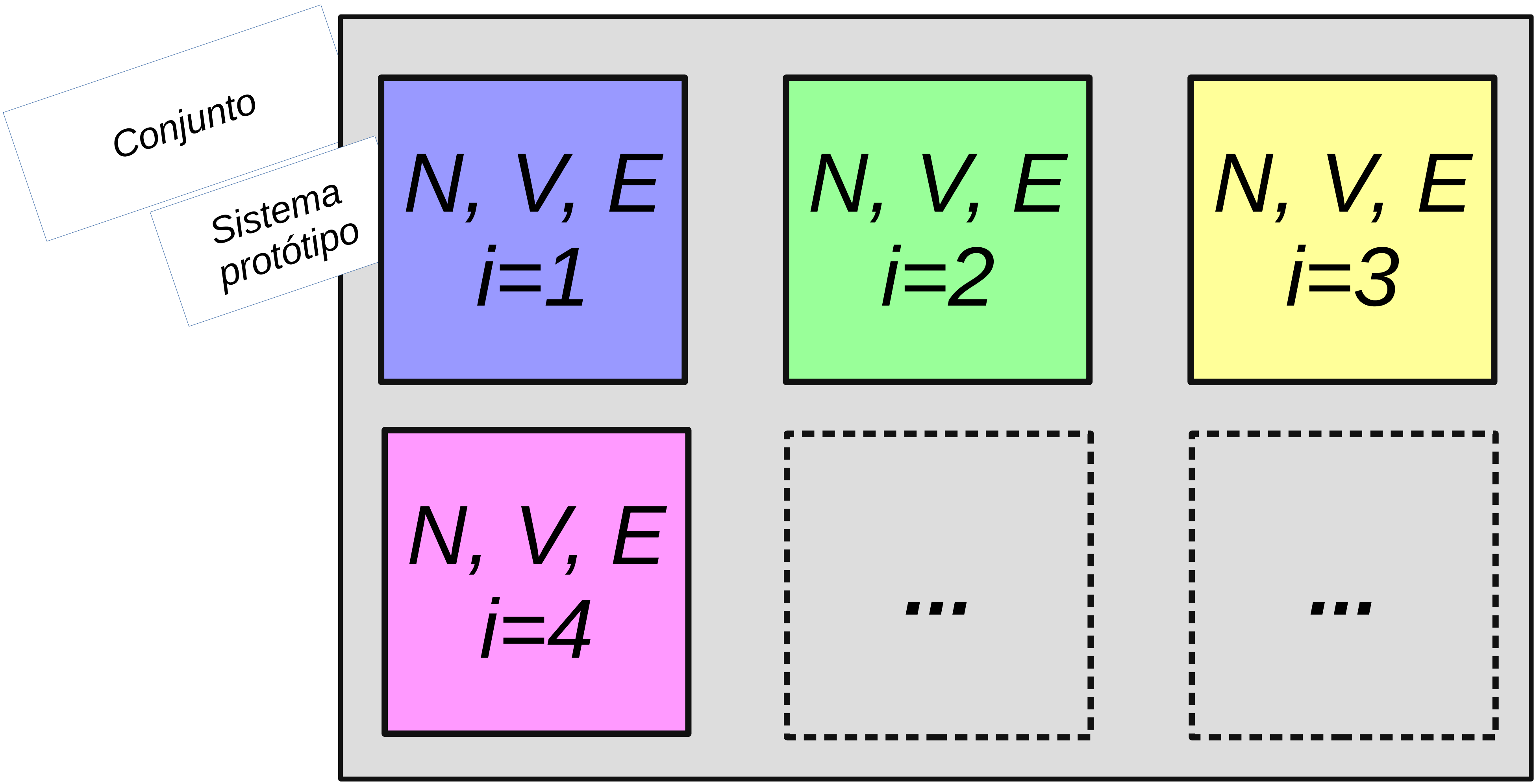
V = 4 células

E = constante

Configurações microscópicas diferentes:

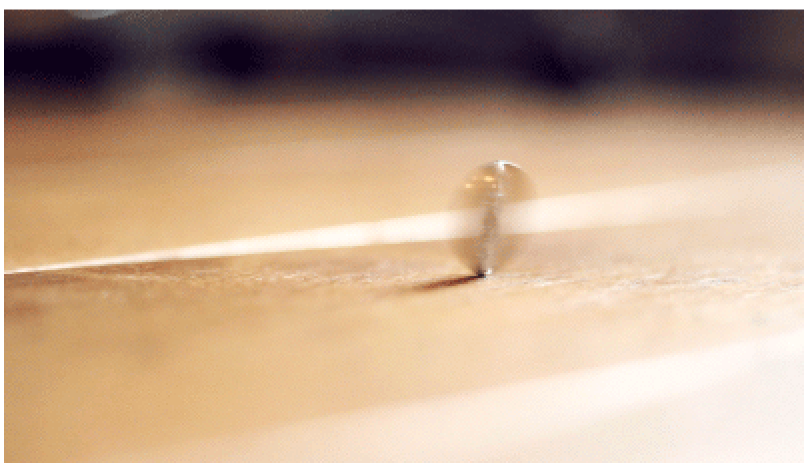


Ensemble microcanônico (N, V, E)



Postulado II

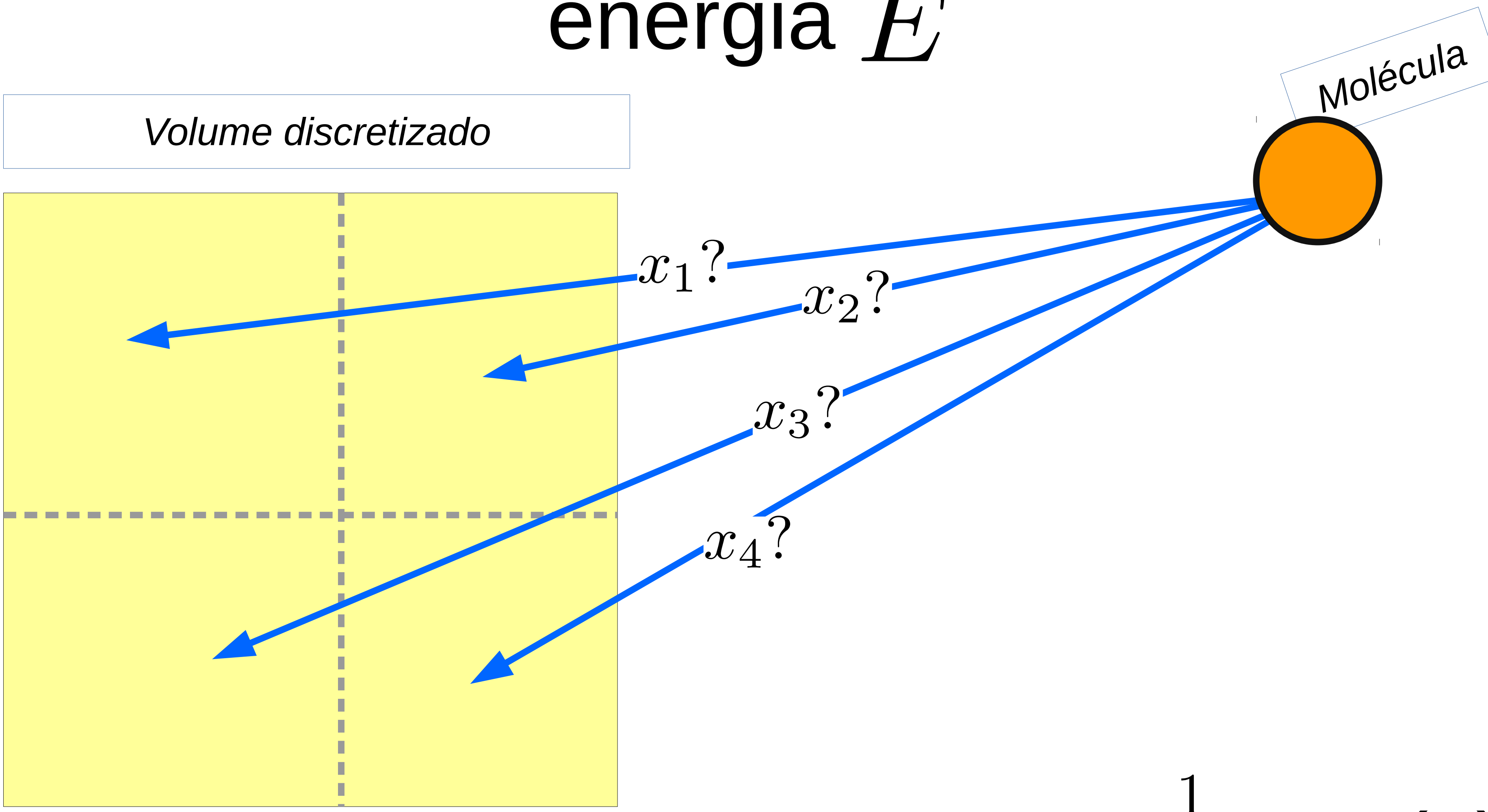
Probabilidades iguais *a priori*



$p_1 = 50\%$

$p_2 = 50\%$

Espaço de fases discretizado em um número Ω de estados com a mesma energia E

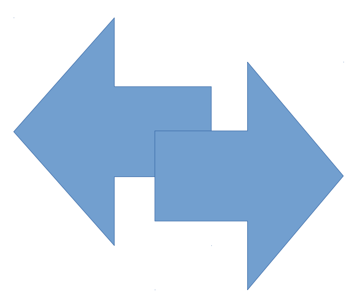


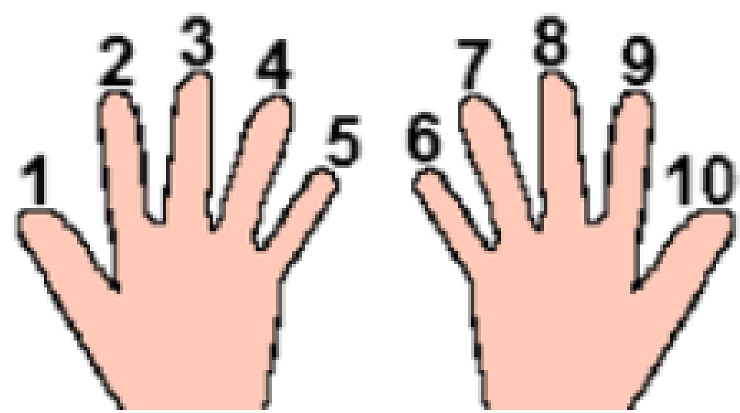
$$p_i = \frac{1}{\Omega\left(N, V, E\right)} \quad (1)$$

Função de partição microcanônica

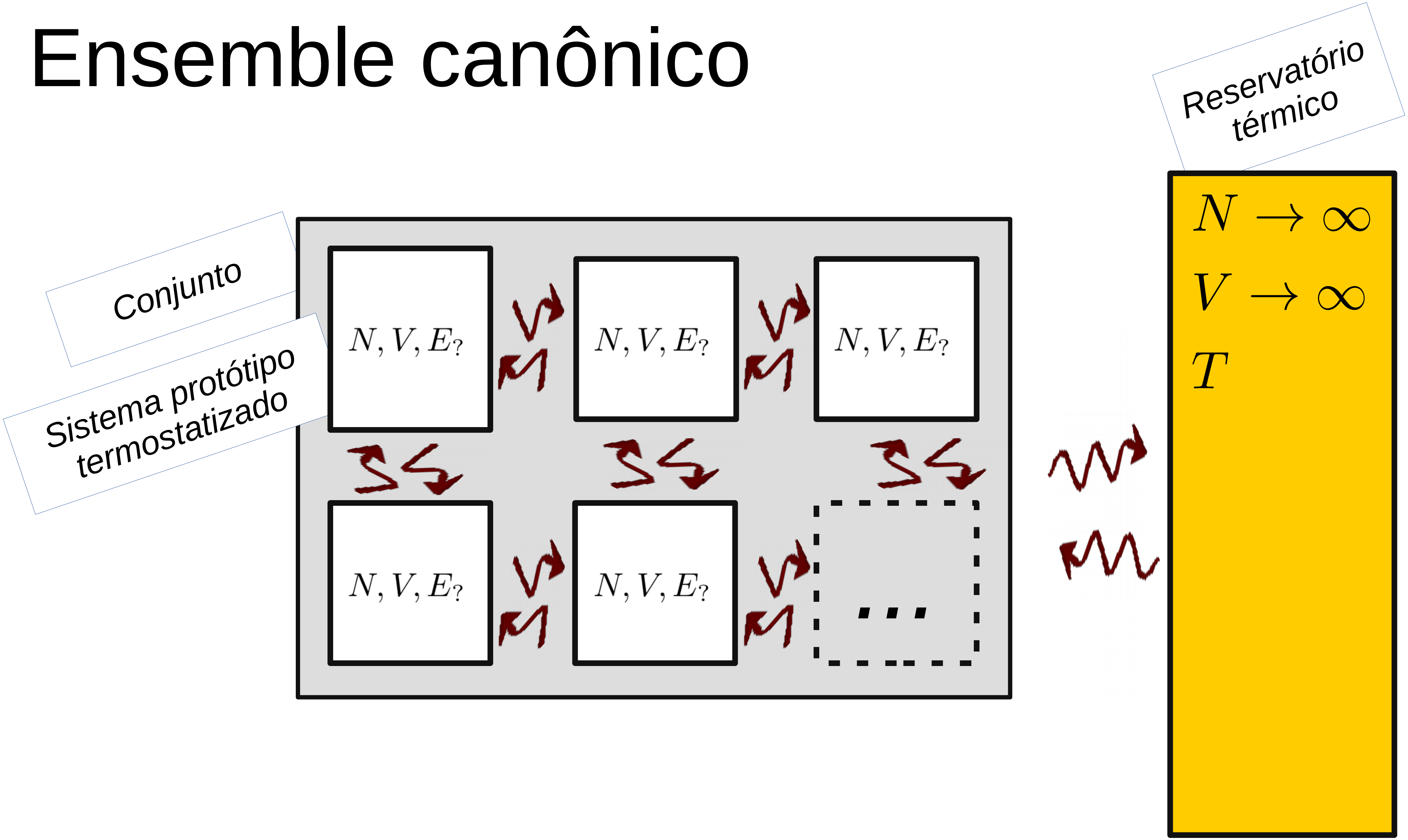
- A contagem do número de configurações microscópicas compatíveis com a especificação macroscópica do nível de energia *E.*

$$\Omega\,(N,V,E)$$

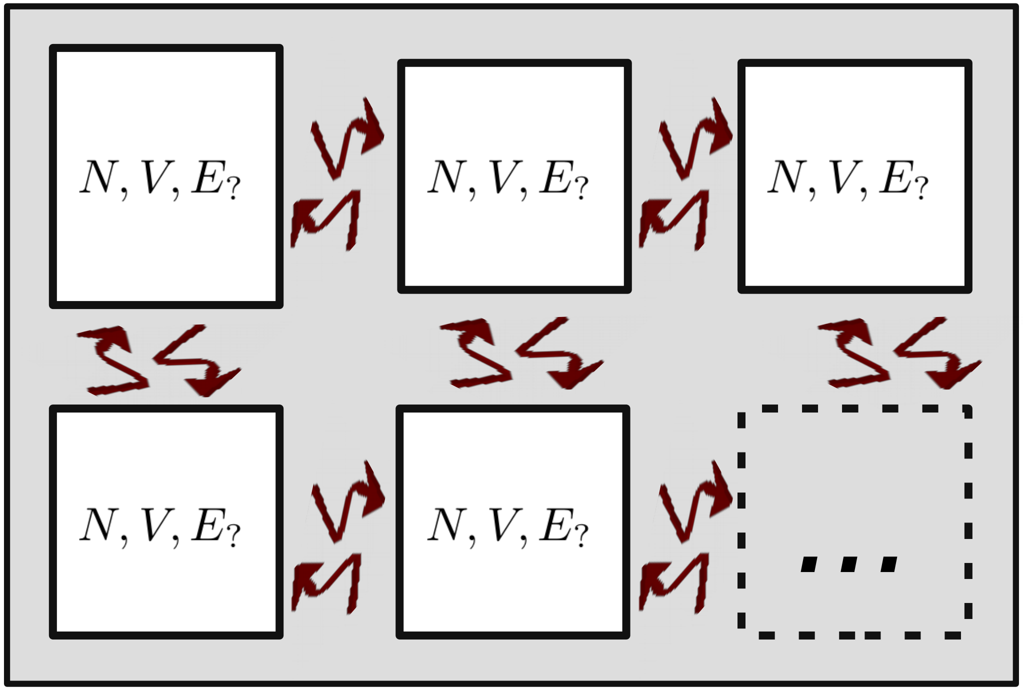




Ensemble canônico

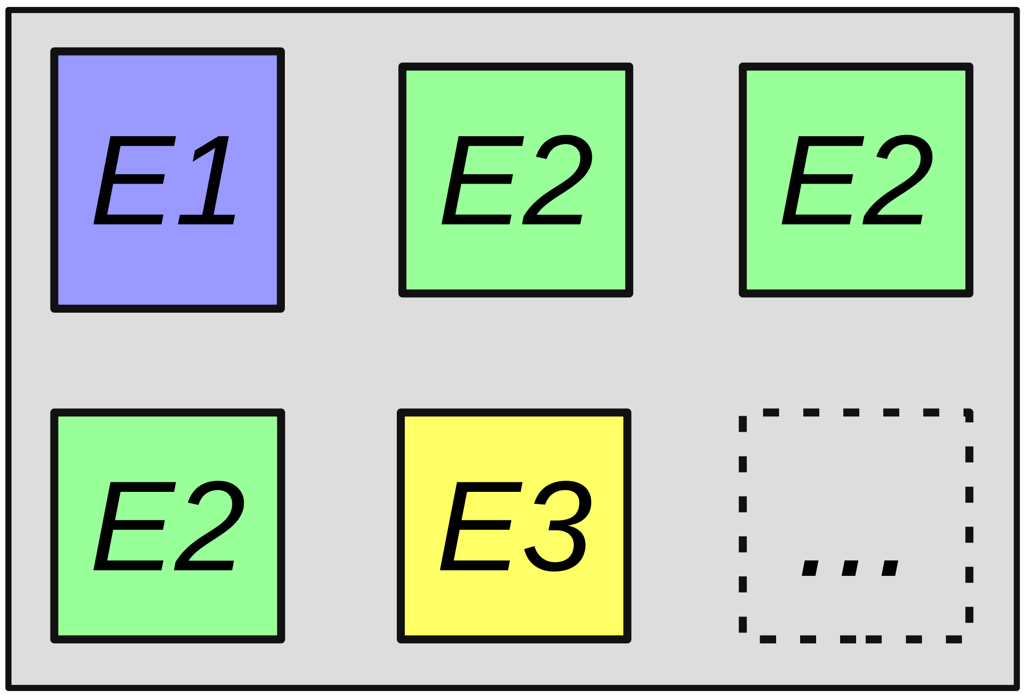


Ensemble canônico (N, V, T)



$$\mathcal{A}$$

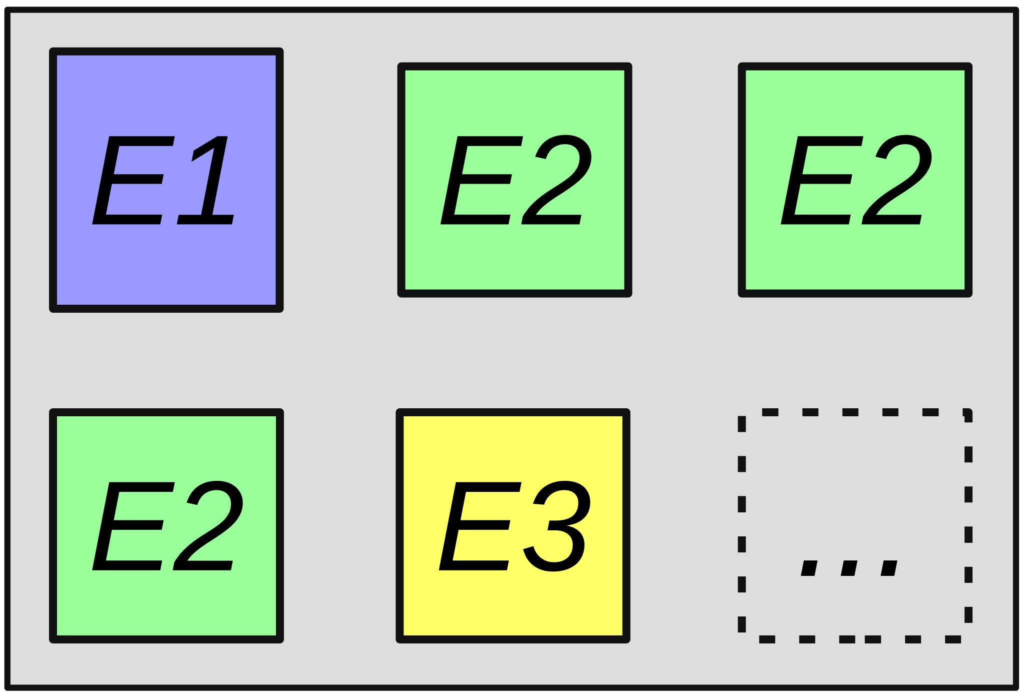
Número total de sistemas propótipo termostatizados



$$\sum_{\mathcal{A}}(E_i) = \mathcal{E}$$

Energia total constante

Caracterização da distribuição de estados no conjunto construído



 # Energia

> *E1, E2, E3...*

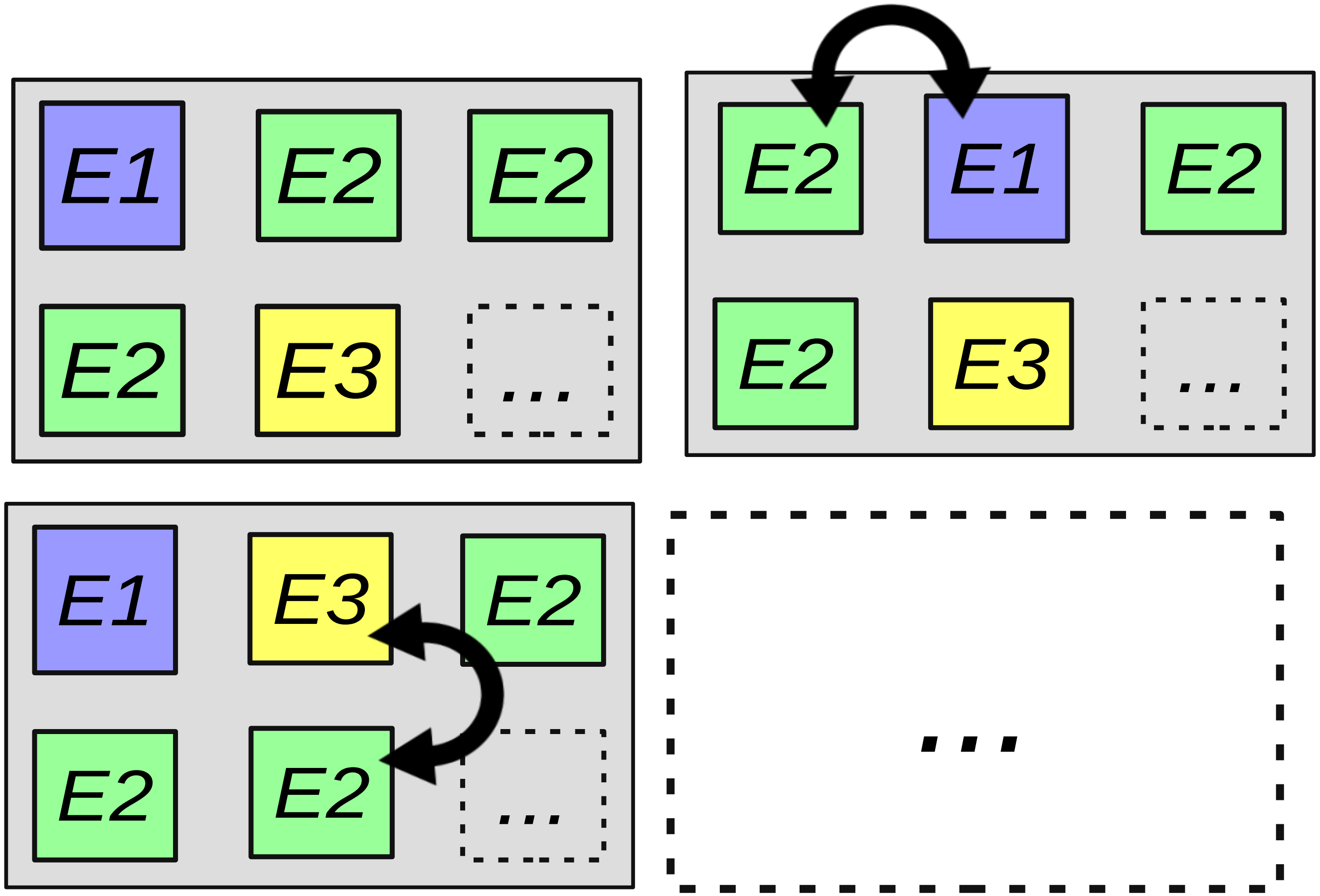
 # Frequência

> *a1, a2, a3…*

 # Distribuição

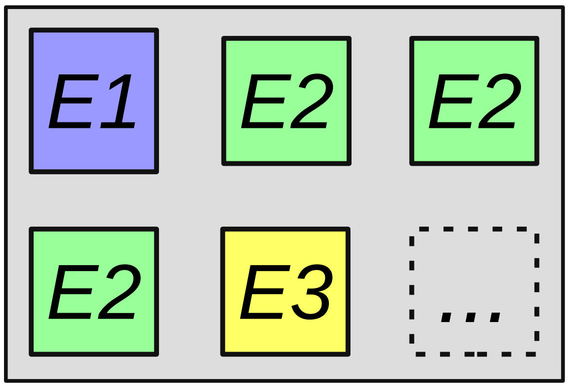
> *{a}1*

Possíveis formas de realizar uma distribuição $\{a\}_1$



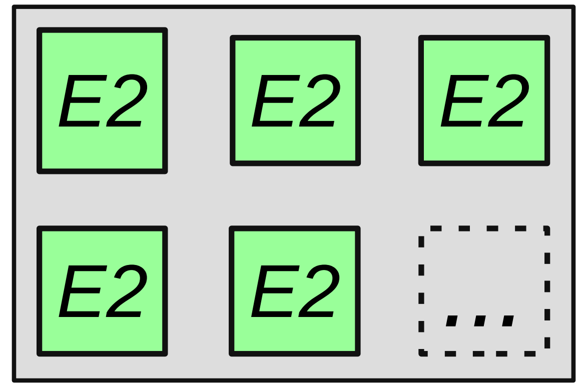
$$W(\{a\}) = \frac{(a_1 + a_2 + a_3 + \ldots)!}{a_1!\, a_2!\, a_3!\, \ldots} = \frac{\left(\sum_i (a_i)\right)!}{\prod_i (a_i!)} \qquad (2)$$

Outras possíveis distribuições de estados no conjunto canônico



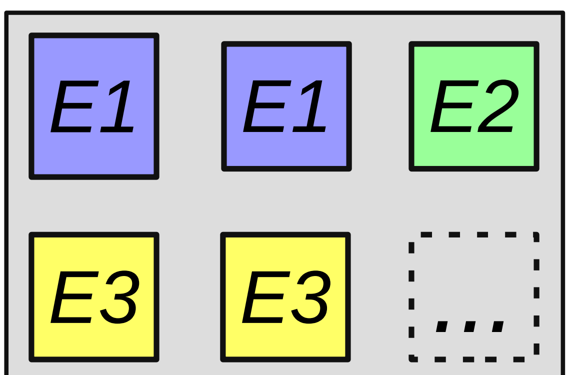
$$\sum_{\{a\}_1} (E_i) = \mathcal{E}$$

$$W\left(\{a\}_1\right)$$



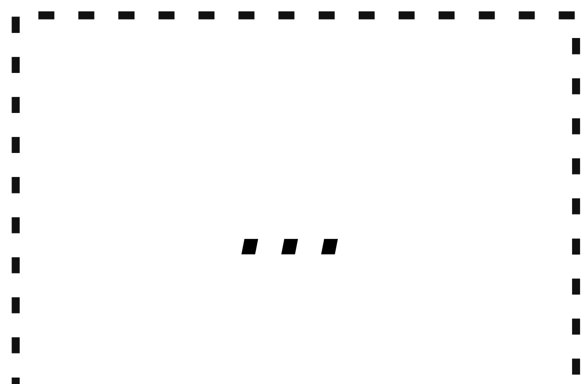
$$\sum_{\{a\}_2} (E_i) = \mathcal{E}$$

$$W\left(\{a\}_2\right)$$



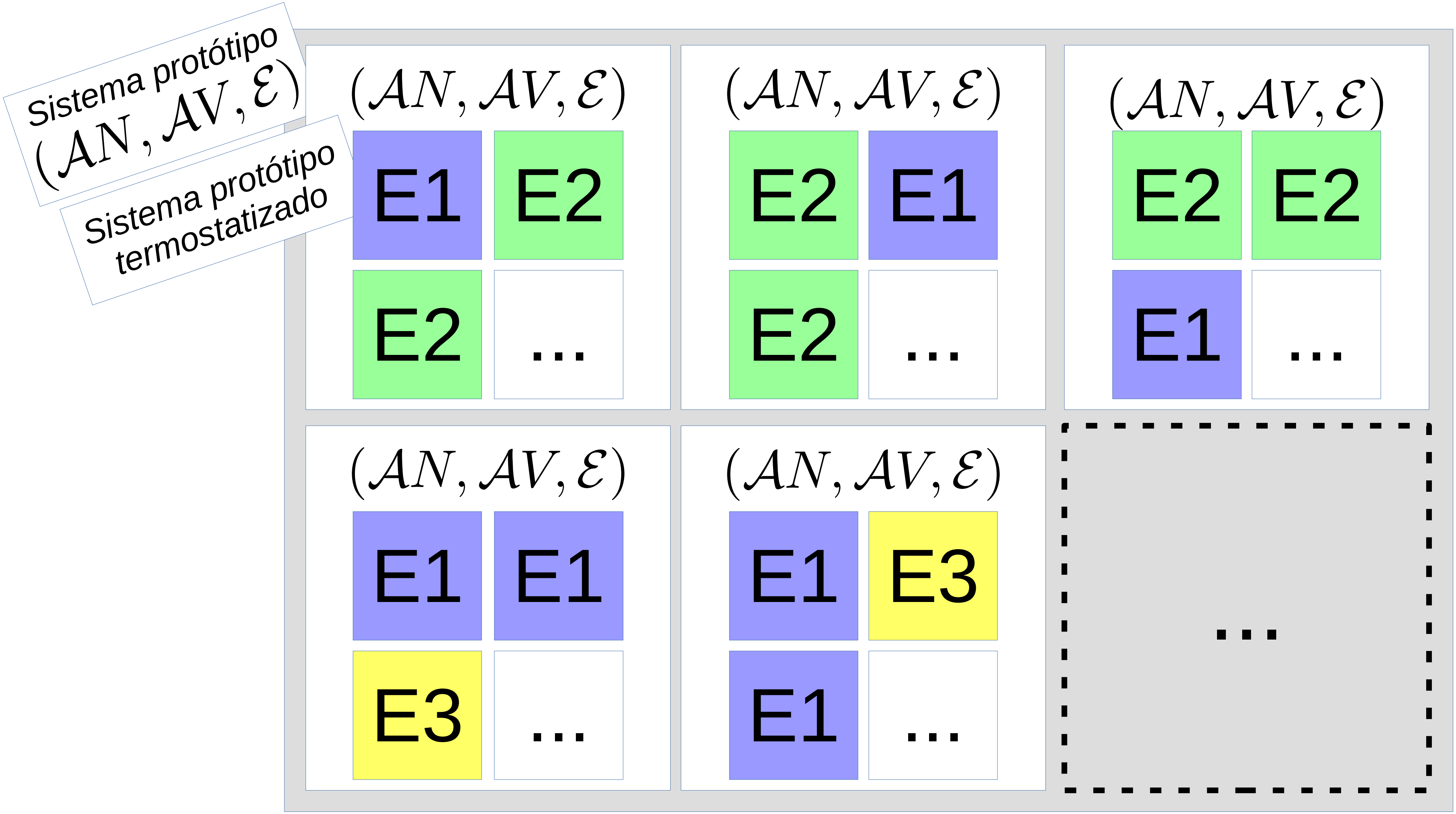
$$\sum_{\{a\}_3} (E_i) = \mathcal{E}$$

$$W\left(\{a\}_3\right)$$

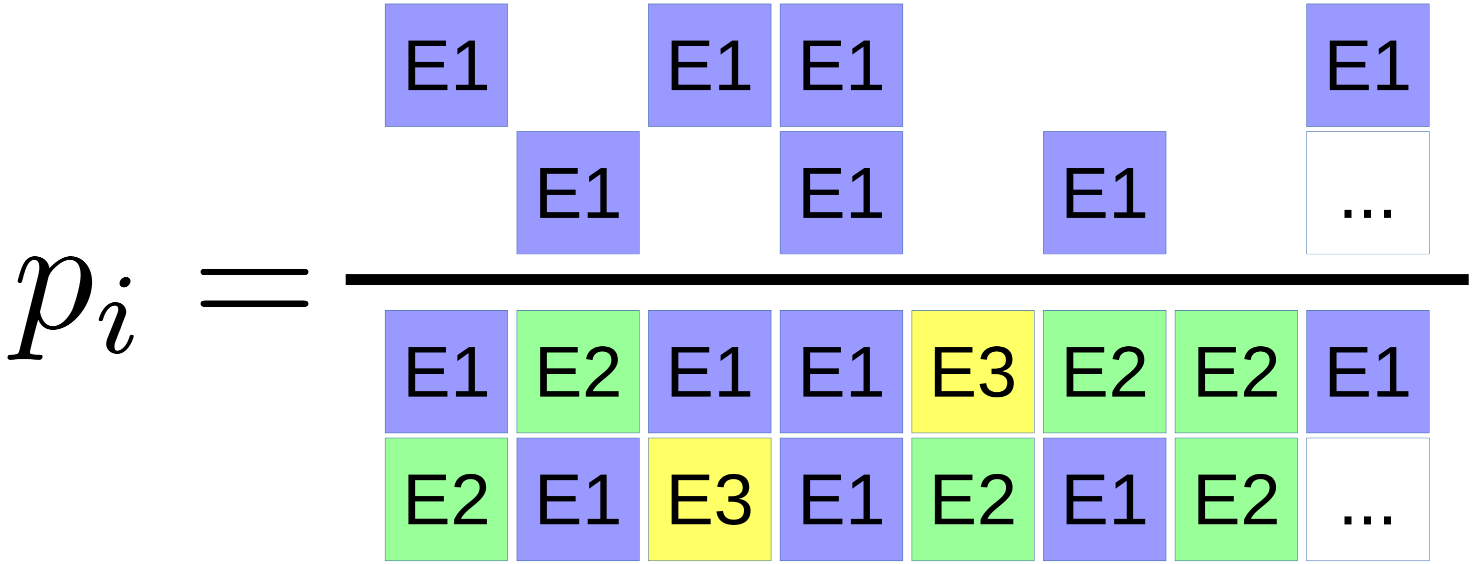


$$\sum_{\{a\}_{\ldots}} (E_i) = \mathcal{E}$$

$$W\left(\{a\}_{\ldots}\right)$$



Qual a probabilidade p_i de ocorrência de um estado i, com energia E_i, no ensemble canônico?


$p_i =$
E1 E1 E1 E1
E1 E1 E1 ...
E1 E2 E1 E1 E3 E2 E2 E1
E2 E1 E3 E1 E2 E1 E2 ...

$$p_i = \frac{\begin{array}{cccccccc} E1 & & E1 & E1 & & & & E1 \\ & E1 & & E1 & & E1 & & \ldots \end{array}}{\begin{array}{cccccccc} E1 & E2 & E1 & E1 & E3 & E2 & E2 & E1 \\ E2 & E1 & E3 & E1 & E2 & E1 & E2 & \ldots \end{array}}$$

Probabilidade de ocorer um estado i no ensemble canônico

$$p_i = \frac{n_i}{N_\mathrm{T}}$$

Número de ocorrências de um estado i em algum sistema termostatizado de algum sistema protótipo $(\mathcal{A}N, \mathcal{A}V, \mathcal{E})$

Número total de sistemas termotatizados dentre todos os sistemas protótipo $(\mathcal{A}N, \mathcal{A}V, \mathcal{E})$ no conjunto microcanônico

$$p_i = \frac{n_i}{\sum_{\{a\}} \left(W\left(\{a\}\right)\mathcal{A}\right)}$$

Número de sistemas termotatizados em um sistema protótipo $(\mathcal{A}N, \mathcal{A}V, \mathcal{E})$

Número de realizações para uma distribuição $\{a\}$

Soma ao longo de todas as distribuições $\{a\}$

Soma ao longo de todas as distribuições $\{a\}$

Número de realizações para uma distribuição $\{a\}$

Número de ocorrências do estado i
em uma dada distribuição $\{a\}$

$$p_i = \frac{\sum\limits_{\{a\}} \left(W\left(\{a\}\right)\; a_i \right)}{\sum\limits_{\{a\}} \left(W\left(\{a\}\right)\; \mathcal{A} \right)} \qquad (3)$$

$$p_i = \frac{W(\{a\}_1)\ a_i + W(\{a\}_2)\ a_i + W(\{a\}_3)\ a_i + W(\{a\}_4)\ a_i + W(\{a\}_5)\ a_i + \ldots}{W(\{a\}_1)\ \mathcal{A} + W(\{a\}_2)\ \mathcal{A} + W(\{a\}_3)\ \mathcal{A} + W(\{a\}_4)\ \mathcal{A} + W(\{a\}_5)\ \mathcal{A} + \ldots}$$

$\ldots$

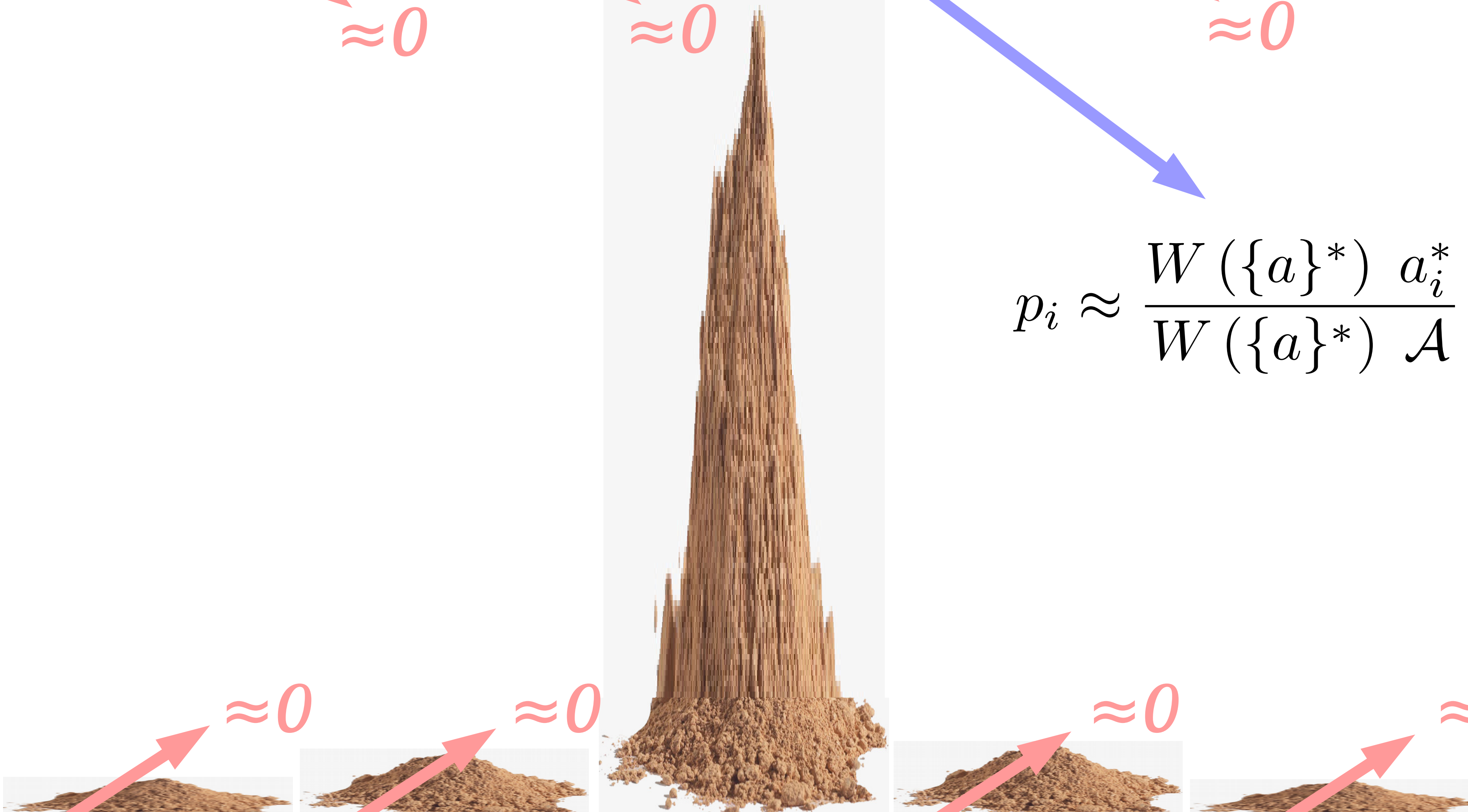
$W(\{a\}_1)$ $W(\{a\}_2)$ $W(\{a\}_3)$ $W(\{a\}_4)$ $W(\{a\}_5)$

$$p_i = \frac{W\left(\{a\}_1\right)\ a_i + W\left(\{a\}_2\right)\ a_i + W\left(\{a\}_3\right)\ a_i + W\left(\{a\}_4\right)\ a_i + W\left(\{a\}_5\right)\ a_i + \ldots}{W\left(\{a\}_1\right)\ \mathcal{A} + W\left(\{a\}_2\right)\ \mathcal{A} + W\left(\{a\}_3\right)\ \mathcal{A} + W\left(\{a\}_4\right)\ \mathcal{A} + W\left(\{a\}_5\right)\ \mathcal{A} + \ldots}$$

≈0 ≈0 ≈0 ≈0

≈0 ≈0 ≈0 ≈0

$$p_i \approx \frac{W\left(\{a\}^*\right)\ a_i^*}{W\left(\{a\}^*\right)\ \mathcal{A}}$$



$W\left(\{a\}_1\right)$ $W\left(\{a\}_2\right)$ $W\left(\{a\}_3\right)$ $W\left(\{a\}_4\right)$ $W\left(\{a\}_5\right)$

$$p_i = \frac{\underbrace{W(\{a\}_1)}_{\approx 0}\ a_i + \underbrace{W(\{a\}_2)}_{\approx 0}\ a_i + W(\{a\}_3)\ a_i + \underbrace{W(\{a\}_4)}_{\approx 0}\ a_i + \underbrace{W(\{a\}_5)}_{\approx 0}\ a_i + \dots}{\underbrace{W(\{a\}_1)}_{\approx 0}\ \mathcal{A} + \underbrace{W(\{a\}_2)}_{\approx 0}\ \mathcal{A} + W(\{a\}_3)\ \mathcal{A} + \underbrace{W(\{a\}_4)}_{\approx 0}\ \mathcal{A} + \underbrace{W(\{a\}_5)}_{\approx 0}\ \mathcal{A} + \dots}$$

$$p_i \approx \frac{\cancel{W(\{a\}^*)}\ a_i^*}{\cancel{W(\{a\}^*)}\ \mathcal{A}}$$

=1

$$p_i \approx \frac{a_i^*}{\mathcal{A}} \qquad (4)$$

≈0 ≈0 ≈0 ≈0




...

$W(\{a\}_1)$ $W(\{a\}_2)$ $W(\{a\}_3)$ $W(\{a\}_4)$ $W(\{a\}_5)$

Distribuição *mais provável*

Otimização de $W(\{a\})$
em relação a cada a_i

Restrito a:

$$\sum_i (a_i) = \mathcal{A} \qquad (5)$$

$$\sum_i (a_i\ E_i) = \mathcal{E} \qquad (6)$$

Distribuição *mais provável*

Otimização de $W(\{a\})$
em relação a cada a_i

Restrito a:

$$\sum_i (a_i) = \mathcal{A} \qquad (5)$$

$$\sum_i (a_i \; E_i) = \mathcal{E} \qquad (6)$$

$$\left(\frac{\partial}{\partial a_i} \left(\ln \left(W(\{a\}) \right) - \alpha \sum_i (a_i) - \beta \sum_i (a_i \; E_i) \right) \right)_{a_{j \neq i}} = 0 \qquad (7)$$

(2):

$$W\left(\{a\}\right) = \frac{\left(\sum_i (a_i)\right)!}{\prod_i (a_i!)}$$

(2):

$$W\left(\{a\}\right) = \frac{\left(\sum_i \left(a_i\right)\right)!}{\prod_i \left(a_i!\right)}$$

ln x = ln y

$$\ln\left(W\left(\{a\}\right)\right) = \ln\left(\sum_i \left(a_i\right)!\right) - \ln\left(\prod_i \left(a_i!\right)\right)$$

(2):

$$W\left(\{a\}\right) = \frac{\left(\sum_i \left(a_i\right)\right)!}{\prod_i \left(a_i!\right)}$$

ln x = ln y

$$\ln\left(W\left(\{a\}\right)\right) = \ln\left(\sum_i \left(a_i\right)!\right) - \ln\left(\prod_i \left(a_i!\right)\right)$$

$$= \ln\left(\sum_i \left(a_i\right)!\right) - \sum_i \left(\ln\left(a_i!\right)\right)$$

ln Π... = Σ ln...

(2):

$$W(\{a\}) = \frac{\left(\sum_i (a_i)\right)!}{\prod_i (a_i!)}$$

ln x = ln y

$$\ln(W(\{a\})) = \ln\left(\sum_i (a_i)!\right) - \ln\left(\prod_i (a_i!)\right)$$

ln Π... = Σ ln...

$$= \ln\left(\sum_i (a_i)!\right) - \sum_i (\ln(a_i!))$$

aproximação de Stirling:

ln x! = x ln x - x

$$= \sum_i (a_i) \ln\left(\sum_i (a_i)\right) - \sum_i (a_i) - \sum_i (a_i \ln(a_i) - a_i)$$

$$\mathrm{d}\ln\left(W\left(\{a\}\right)\right) = \mathrm{d}\left(\sum_i \left(a_i\right)\ln\left(\sum_i \left(a_i\right)\right) - \sum_i \left(a_i\right)\right) - \mathrm{d}\left(\sum_i \left(a_i \ln\left(a_i\right) - a_i\right)\right)$$

$$\mathrm{d}\ln\left(W(\{a\})\right) = \mathrm{d}\left(\sum_i (a_i)\ln\left(\sum_i (a_i)\right) - \sum_i (a_i)\right) - \mathrm{d}\left(\sum_i (a_i \ln(a_i) - a_i)\right)$$

*d*Σ *x* = Σ *dx*

$$= \sum_i (\mathrm{d}a_i)\ln\left(\sum_i (a_i)\right) + \sum_i (a_i)\frac{1}{\sum_i (a_i)}\sum_i (\mathrm{d}a_i) - \sum_i (\mathrm{d}a_i)$$

$$\mathrm{d}\ln\left(W(\{a\})\right) = \mathrm{d}\left(\sum_i (a_i)\ln\left(\sum_i (a_i)\right) - \sum_i (a_i)\right) - \mathrm{d}\left(\sum_i \left(a_i \ln(a_i) - a_i\right)\right)$$

$d\Sigma\ x = \Sigma\ dx$

$$= \sum_i (\mathrm{d}a_i)\ln\left(\sum_i (a_i)\right) + \sum_i (a_i)\frac{1}{\sum_i (a_i)}\sum_i (\mathrm{d}a_i) - \sum_i (\mathrm{d}a_i)$$

$=1$

$$- \left(\sum_i \left(\mathrm{d}a_i \ln(a_i) + a_i \frac{1}{a_i}\mathrm{d}a_i - \mathrm{d}a_i\right)\right)$$

$$\mathrm{d}\ln\left(W\left(\{a\}\right)\right) = \mathrm{d}\left(\sum_i (a_i)\ln\left(\sum_i (a_i)\right) - \sum_i (a_i)\right) - \mathrm{d}\left(\sum_i \left(a_i \ln(a_i) - a_i\right)\right)$$

$d\Sigma\, x = \Sigma\, dx$

$$= \sum_i (\mathrm{d}a_i)\ln\left(\sum_i (a_i)\right) + \underbrace{\sum_i (a_i)\frac{1}{\sum_i (a_i)}}_{=1}\sum_i (\mathrm{d}a_i) - \sum_i (\mathrm{d}a_i)$$

$$- \left(\sum_i \left(\mathrm{d}a_i \ln(a_i) + \underbrace{a_i \frac{1}{a_i}}_{=1}\mathrm{d}a_i - \mathrm{d}a_i\right)\right)$$

$(1-1)\, dx = 0$

$$= \sum_i \left(\ln\left(\sum_i (a_i)\right)\mathrm{d}a_i\right) - \sum_i \left(\ln(a_i)\,\mathrm{d}a_i\right)$$

$$\mathrm{d}\ln\left(W(\{a\})\right) = \mathrm{d}\left(\sum_i (a_i)\ln\left(\sum_i (a_i)\right) - \sum_i (a_i)\right) - \mathrm{d}\left(\sum_i \left(a_i \ln(a_i) - a_i\right)\right)$$

dΣ x = Σ dx

$$= \sum_i (\mathrm{d}a_i)\ln\left(\sum_i (a_i)\right) + \underbrace{\sum_i (a_i)\frac{1}{\sum_i (a_i)}}_{=1}\sum_i (\mathrm{d}a_i) - \sum_i (\mathrm{d}a_i)$$

$$-\left(\sum_i\left(\mathrm{d}a_i \ln(a_i) + \underbrace{a_i\frac{1}{a_i}}_{=1}\mathrm{d}a_i - \mathrm{d}a_i\right)\right)$$

(1-1) dx = 0

$$= \sum_i\left(\ln\left(\sum_i (a_i)\right)\mathrm{d}a_i\right) - \sum_i\left(\ln(a_i)\,\mathrm{d}a_i\right)$$

dx/dx =1

dy/dx=0

$$\left(\frac{\partial \ln\left(W(\{a\})\right)}{\partial a_i}\right)_{a_{j\neq i}} = \ln\left(\sum_i (a_i)\right) - \ln(a_i) \qquad (8)$$

$$\left(\frac{\partial \alpha \sum_i (a_i)}{\partial a_i} \right)_{a_{j \neq i}} = \alpha \tag{9}$$

$$\left(\frac{\partial \beta \sum_i (a_i \; E_i)}{\partial a_i} \right)_{a_{j \neq i}} = \beta \; E_i \tag{10}$$

(7): $$\left(\frac{\partial}{\partial a_i}\left(\ln\left(W(\{a\})\right) - \alpha\sum_i (a_i) - \beta\sum_i (a_i\ E_i)\right)\right)_{a_{j\neq i}} = 0$$

(7): $$\left(\frac{\partial}{\partial a_i}\left(\ln\left(W\left(\{a\}\right)\right)-\alpha\sum_i\left(a_i\right)-\beta\sum_i\left(a_i\ E_i\right)\right)\right)_{a_{j\neq i}}=0$$

(8): $$\left(\frac{\partial\ln\left(W\left(\{a\}\right)\right)}{\partial a_i}\right)_{a_{j\neq i}}=\ln\left(\sum_i\left(a_i\right)\right)-\ln\left(a_i\right)$$

(9): $$\left(\frac{\partial\alpha\sum_i\left(a_i\right)}{\partial a_i}\right)_{a_{j\neq i}}=\alpha$$

(10): $$\left(\frac{\partial\beta\sum_i\left(a_i\ E_i\right)}{\partial a_i}\right)_{a_{j\neq i}}=\beta\ E_i$$

(7): $$\left(\frac{\partial}{\partial a_i}\left(\ln\left(W(\{a\})\right)-\alpha\sum_i (a_i)-\beta\sum_i (a_i\ E_i)\right)\right)_{a_{j\neq i}}=0$$

(8): $$\left(\frac{\partial \ln\left(W(\{a\})\right)}{\partial a_i}\right)_{a_{j\neq i}}=\ln\left(\sum_i (a_i)\right)-\ln(a_i)$$

(9): $$\left(\frac{\partial \alpha\sum_i (a_i)}{\partial a_i}\right)_{a_{j\neq i}}=\alpha$$

(10): $$\left(\frac{\partial \beta\sum_i (a_i\ E_i)}{\partial a_i}\right)_{a_{j\neq i}}=\beta\ E_i$$

Substituição

$$\ln\left(\sum_i (a_i)\right)-\ln(a_i)-\alpha-\beta\ E_i=0 \tag{11}$$

O multiplicador α

(11):

$$\ln\left(\sum_i (a_i)\right) - \ln(a_i) - \alpha - \beta\, E_i = 0$$

O multiplicador α

(11):

$$\ln\left(\sum_i (a_i)\right) - \ln(a_i) - \alpha - \beta\ E_i = 0$$

$e^x = e^y$

$$\frac{a_i}{\sum_i (a_i)} = e^{-\beta E_i}/e^{\alpha}$$ (12)

O multiplicador α

(11):

$$\ln\left(\sum_i (a_i)\right) - \ln(a_i) - \alpha - \beta\ E_i = 0$$

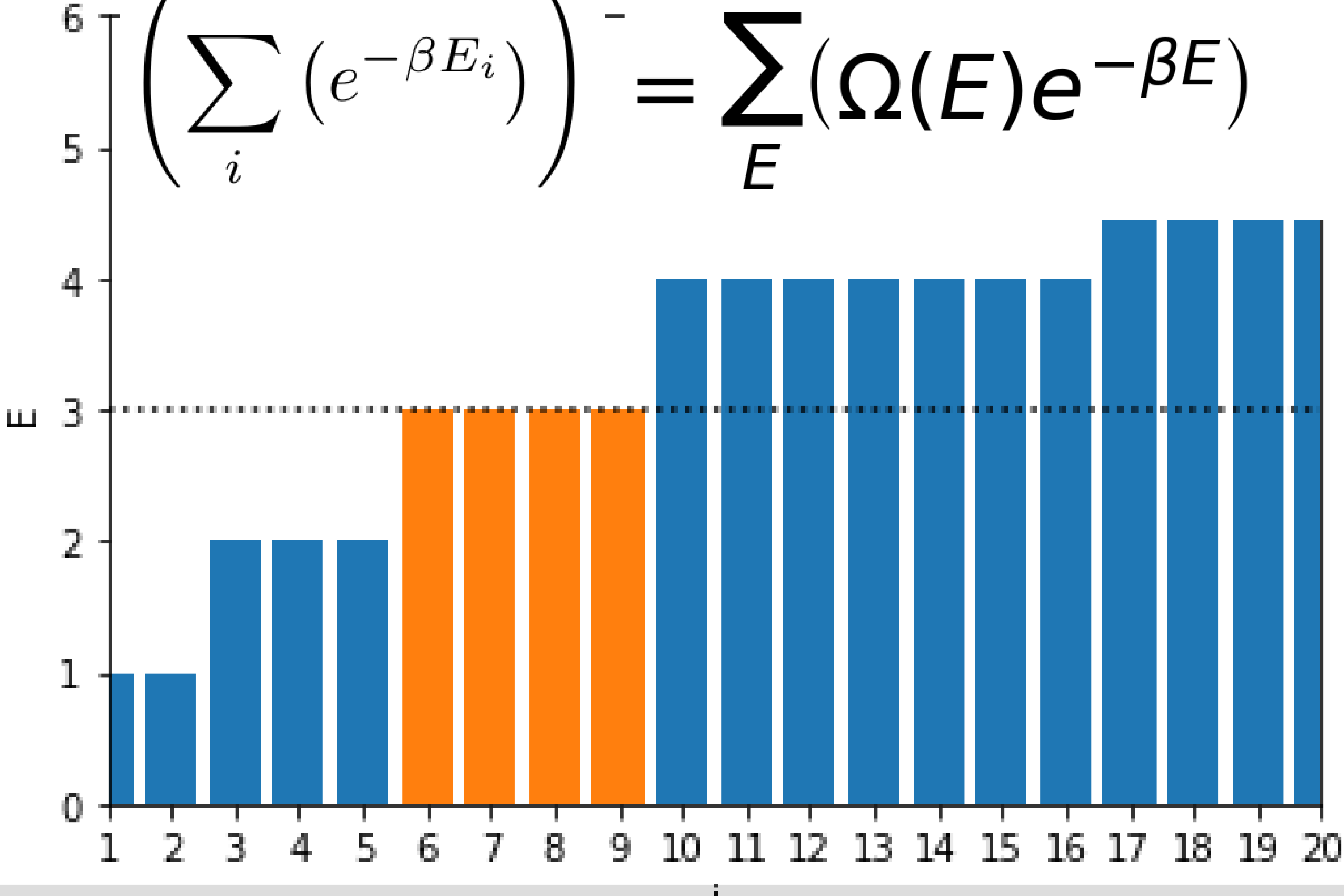
$e^x = e^y$

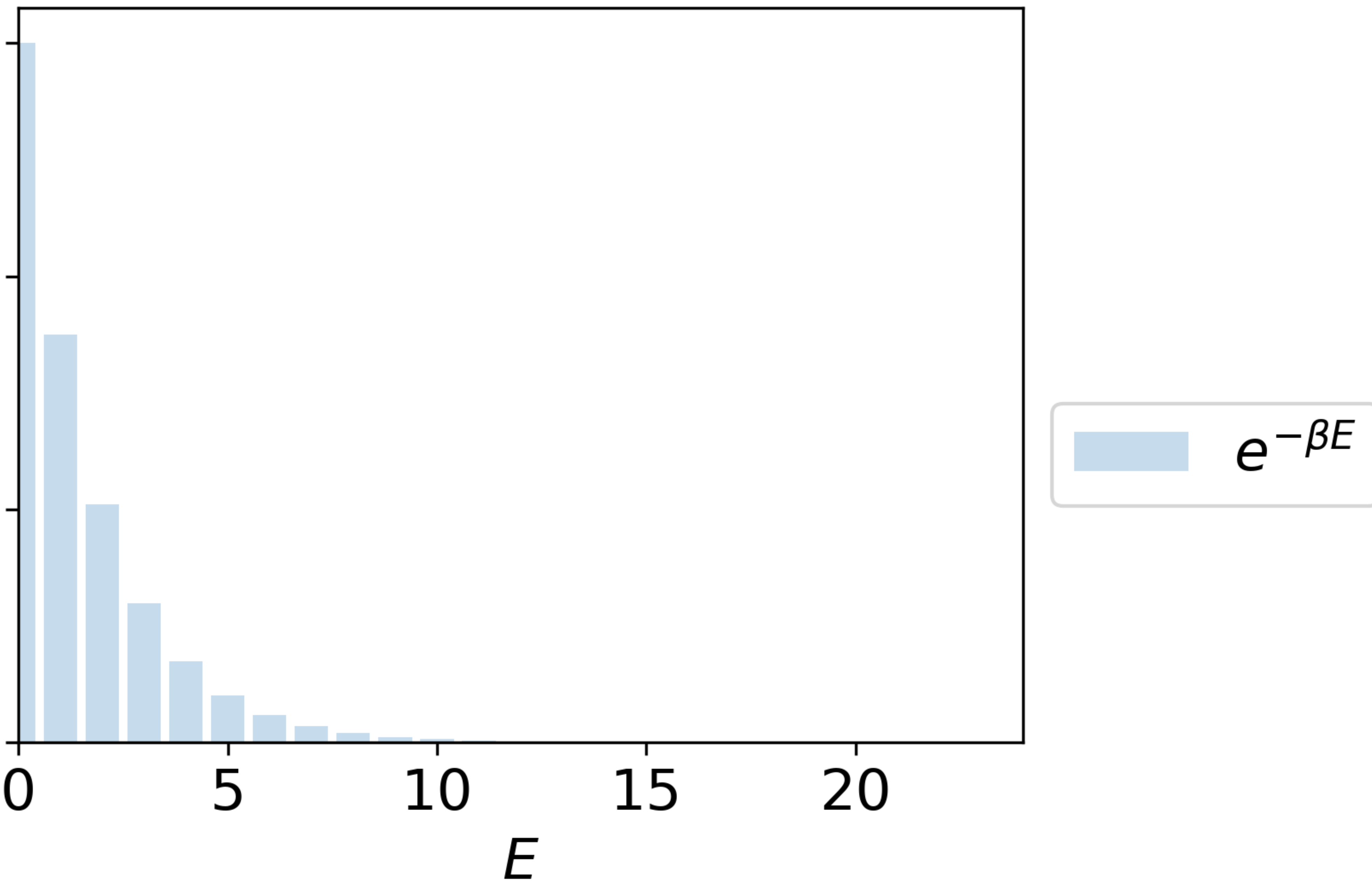
$$\frac{a_i}{\sum_i (a_i)} = e^{-\beta E_i}/e^{\alpha} \quad (12)$$

Isolando α

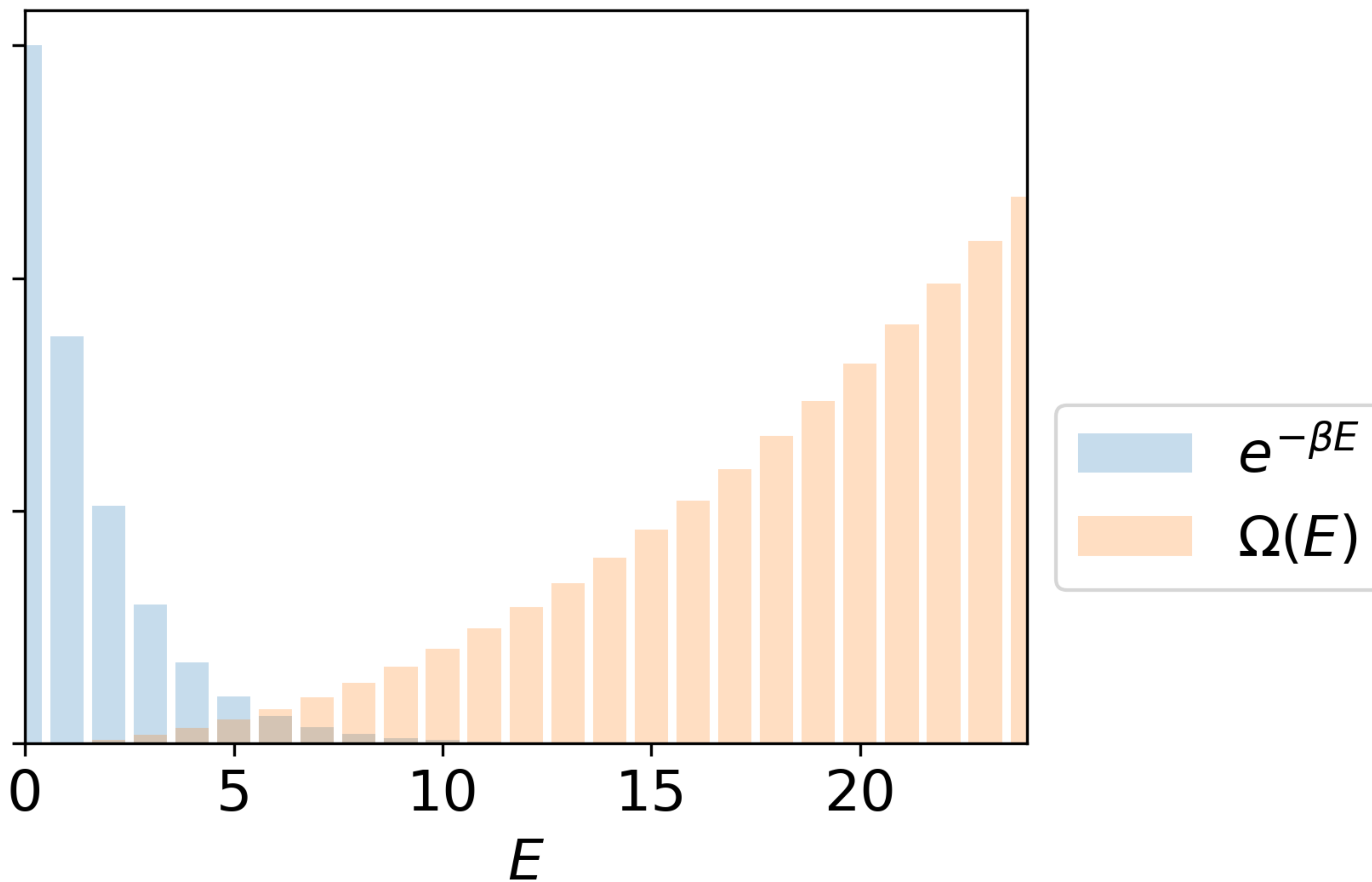
$$\alpha = \ln\left(\sum_i \left(e^{-\beta E_i}\right)\right) \quad (13)$$

$$\left(\sum_i \left(e^{-\beta E_i}\right)\right)^{-} = \sum_E \left(\Omega(E)e^{-\beta E}\right)$$



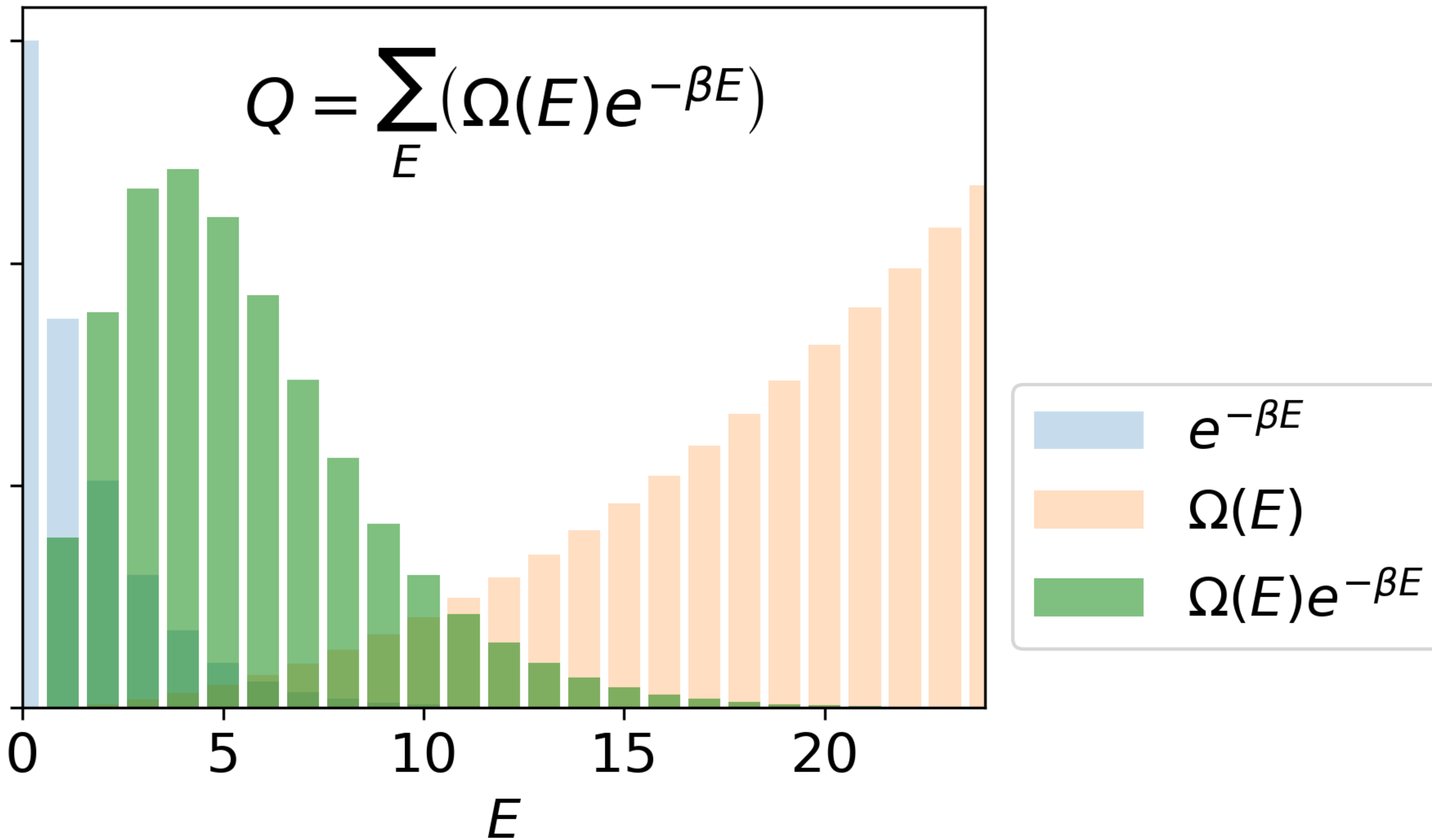


0
5
10
15
20
E
$e^{-\beta E}$



0
5
10
15
20
E
$e^{-\beta E}$
$\Omega(E)$

A função de partição canônica.



Probabilidade no ensemble canônico

(12): $$p_i = \frac{a_i}{\sum_i (a_i)} = e^{-\beta E_i}/e^{\alpha}$$

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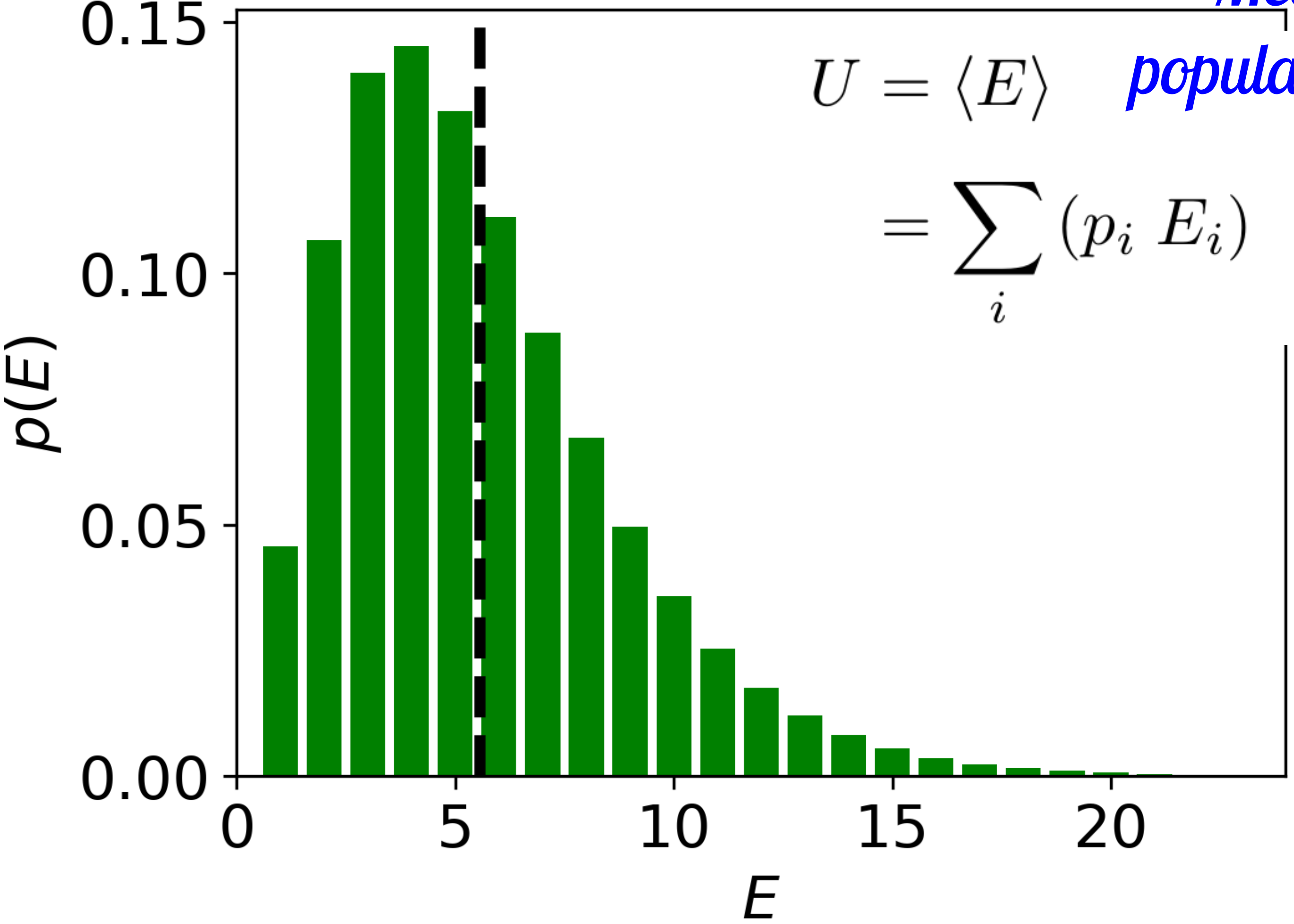
Isolando p

$$p_i = \frac{e^{-\beta\ E_i}}{\sum_i \left(e^{-\beta\ E_i}\right)} \qquad (14)$$

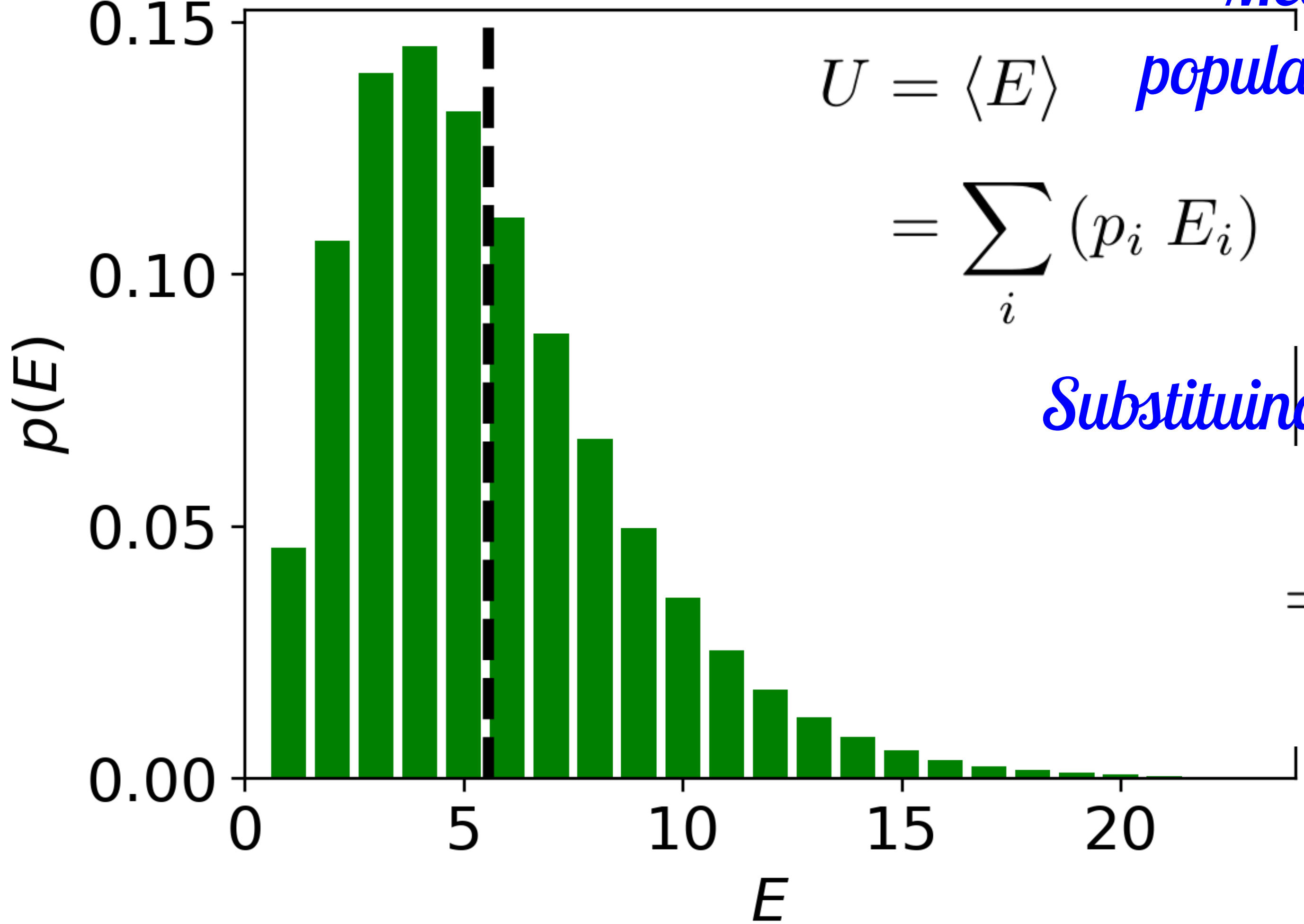
Energia interna



$$U = \langle E \rangle = \sum_i (p_i \, E_i)$$

Média populacional

Energia interna



Média populacional

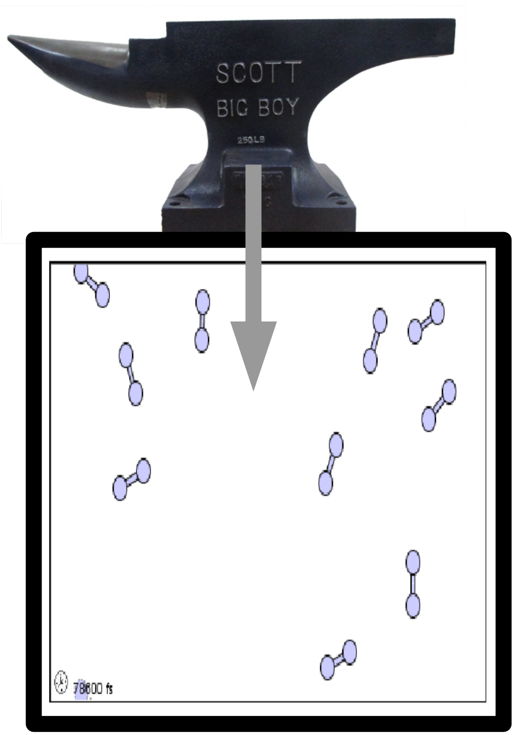
$$U = \langle E \rangle$$

$$= \sum_i (p_i \; E_i)$$

Substituindo p

$$= \frac{\sum_i \left(e^{(-\beta E_i)} E_i\right)}{\sum_i \left(e^{(-\beta E_i)}\right)}$$

Pressão



$$\Delta E_i = P \Delta V$$

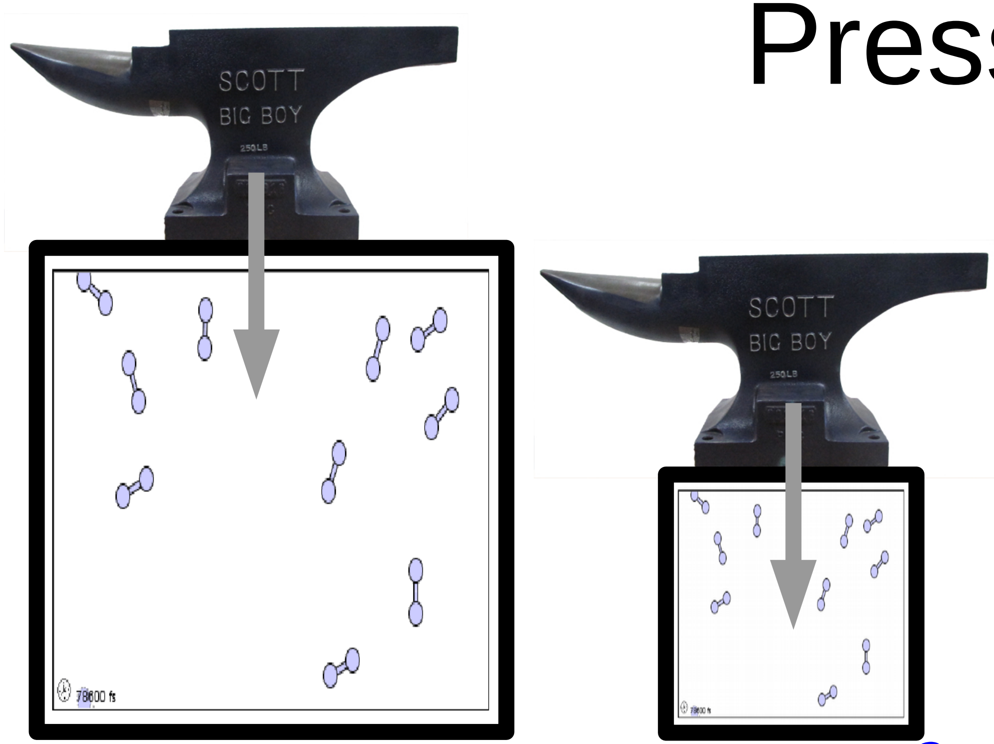
$$P = \frac{\partial E_i}{\partial V}$$

Média populacional

$$P = \left\langle -\left(\frac{\partial E_i}{\partial V}\right)_N \right\rangle$$

$$= \sum_i \left(-\left(\frac{\partial E_i}{\partial V}\right)_N p_i \right)$$

Pressão



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Média populacional

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$$= \sum_i \left(-\left(\frac{\partial E_i}{\partial V}\right)_N p_i \right)$$

Substituindo p

$$= \frac{\sum_i \left(-\left(\frac{\partial E_i}{\partial V}\right)_N \right) e^{(-\beta E)}}{\sum_i \left(e^{(-\beta E_i)} \right)} \quad (17)$$

Variação da energia interna

(16): $$U = \sum_i (p_i \; E_i)$$

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Invertendo p(ℰ)

$$E_i = -\frac{1}{\beta}\left(\ln(pi) + \ln\left(\sum_i \left(e^{-\beta \; E_i}\right)\right)\right) \qquad (15)$$

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Substituindo ℰ

$$\mathrm{d}U = \sum_i \left(\left(-\frac{1}{\beta}\ln\left(\sum_i \left(e^{-\beta E_i}\right)\right) + \ln(p_i)\right)\mathrm{d}p_i\right) + \sum_i (p_i \mathrm{d}E_i)$$

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ℰ depende apenas de V (a N constante)

$$\mathrm{d}U = \sum_i \left(\left(-\frac{1}{\beta}\ln\left(\sum_i \left(e^{-\beta E_i}\right)\right) + \ln(p_i)\right)\mathrm{d}p_i\right) + \sum_i \left(\left(\frac{\partial E_i}{\partial V}\right)_N p_i \mathrm{d}V\right)$$

$$\mathrm{d}U = \sum_i \left(\left(-\frac{1}{\beta} \ln \left(\sum_i \left(e^{-\beta E_i} \right) \right) + \ln \left(p_i \right) \right) \mathrm{d}p_i \right) + \sum_i \left(\left(\frac{\partial E_i}{\partial V} \right)_N p_i \mathrm{d}V \right)$$

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Substituindo P

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$$\mathrm{d}U = \sum_i \left(\left(-\frac{1}{\beta} \ln \left(\sum_i \left(e^{-\beta E_i} \right) \right) + \ln \left(p_i \right) \right) \mathrm{d}p_i \right) + \sum_i \left(\left(\frac{\partial E_i}{\partial V} \right)_N p_i \mathrm{d}V \right)$$

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Probabilidades normalizadas

$$\sum \left(p_i \right) = 1 \qquad (19)$$

$$\sum_i \left(\mathrm{d}p_i \right) = 0 \qquad (20)$$

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Separando os termos em dp

$$\mathrm{d}U = \sum_i \left(-\frac{1}{\beta} \ln \left(\sum_i \left(e^{-\beta E_i} \right) \right) \mathrm{d}p_i \right) + \sum_i \left(\ln\left(p_i\right) \mathrm{d}p_i \right) - P\mathrm{d}V$$

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Substituindo Σdp

$$\mathrm{d}U = -\frac{1}{\beta} \sum_i \left(\ln \left(p_i \right) \mathrm{d}p_i \right) - P\mathrm{d}V$$

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Comparando $\Sigma \ln p \, dp$ com $d\,\Sigma p \ln p$

$$\mathrm{d}\sum_i \left(p_i \ln\left(p_i\right)\right) = \sum_i \left(p_i \frac{1}{p_i}\mathrm{d}p_i\right) + \sum_i \left(\ln\left(p_i\right)\mathrm{d}p_i\right)$$

(21)

$$\mathrm{d}U = -\frac{1}{\beta}\sum_i \left(\ln\left(p_i\right)\mathrm{d}p_i\right) - P\mathrm{d}V$$

Comparando $\Sigma \ln p \, dp$ com $d \, \Sigma p \ln p$

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$$\mathrm{d}U = -\frac{1}{\beta}\sum_i \left(\ln\left(p_i\right)\mathrm{d}p_i\right) - P\mathrm{d}V$$

Comparando Σln p dp com d Σp ln p

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Substituindo d Σp ln p

$$\mathrm{d}U = -\frac{1}{\beta}\mathrm{d}\sum_i \left(p_i \ln\left(p_i\right)\right) - P\mathrm{d}V \qquad (22)$$

Entropia e Temperatura

(22): $$\mathrm{d}U = -\frac{1}{\beta}\mathrm{d}\sum_i \left(p_i \ln\left(p_i\right)\right) - P\mathrm{d}V$$

Entropia e Temperatura

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$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \qquad (23)$$

Entropia e Temperatura

(22): $$\mathrm{d}U = -\frac{1}{\beta}\mathrm{d}\sum_i \left(p_i \ln\left(p_i\right)\right) - P\mathrm{d}V$$

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \qquad (23)$$

$$\beta = \frac{1}{k_\mathrm{B}T} \qquad (24)$$

$$S = -k_\mathrm{B}\sum_i \left(p_i \ln\left(p_i\right)\right) \qquad (25)$$

$$k_{\mathrm{B}} = 1.380650 \times 10^{-23}\ \mathrm{J\ K^{-1}}$$

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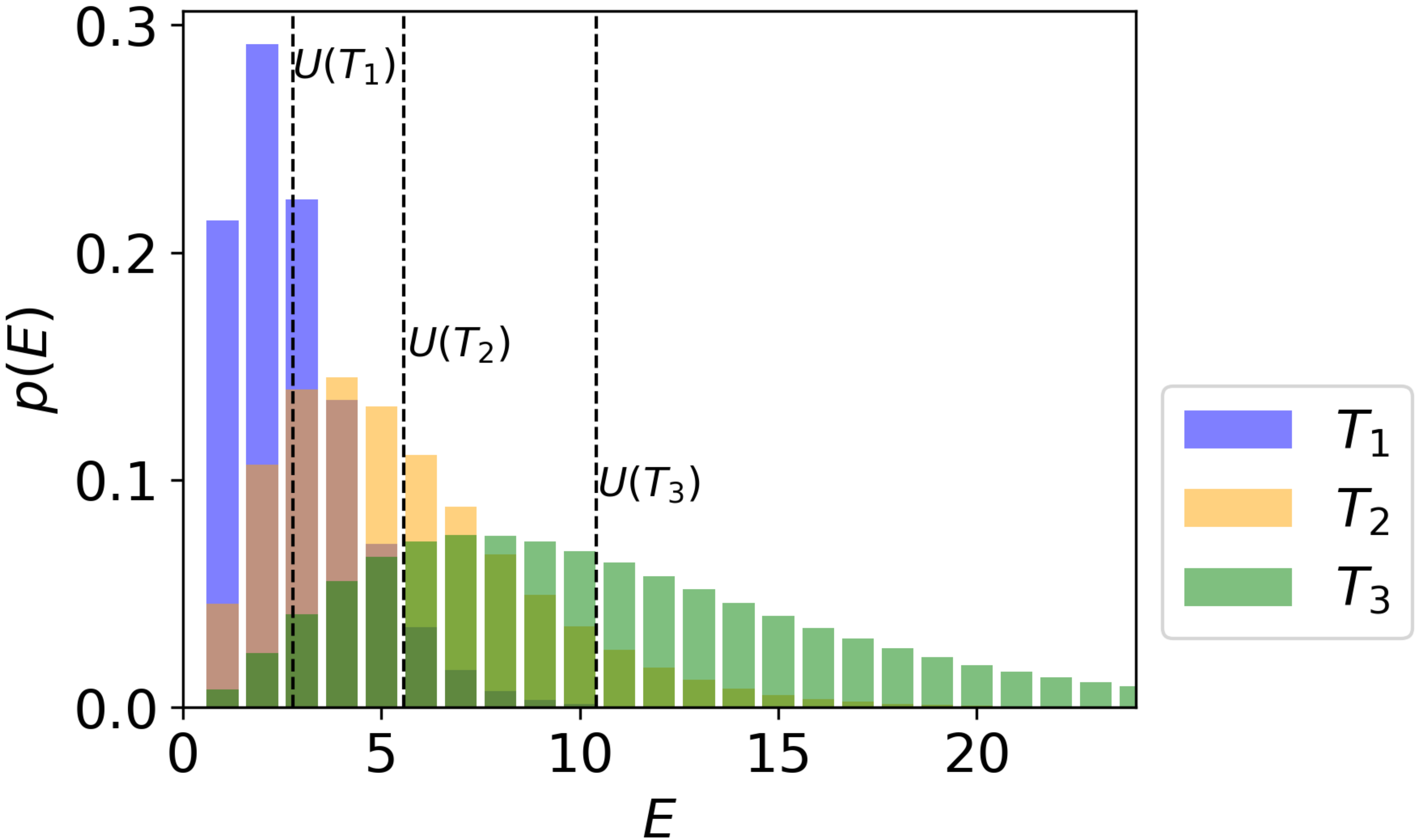
$$R = k_\mathrm{B}\ N_\mathrm{A}$$

$$R = 8.314468640294\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

Quanto maior a temperatura, maior a energia média e maior a probabilidade de observar estados de alta energia.



Energia de Helmholtz

(25): $$S = -k_\mathrm{B}\sum_i \left(p_i \ln\left(p_i\right)\right)$$

$$A = U - TS$$

$$A = U + Tk_\mathrm{B}\sum_i \left(p_i \ln\left(p_i\right)\right)$$

Substituindo β

$$= U + \sum_i \left(p_i \ln\left(p_i\right)\right)/\beta$$

Substituindo U

$$= \sum_i \left(p_i E_i\right) + \sum_i \left(p_i \ln\left(p_i\right)\right)/\beta$$

Agrupando termos em p

$$= \sum_i \left(p_i \left(\ln\left(p_i\right) + \beta E_i\right)\right)/\beta \qquad (26)$$

$$A = \sum_i \left(p_i \left(\ln\left(p_i\right) + \beta E_i\right)\right)/\beta$$

Substituindo p

$$= \sum_i \left(p_i \left(\ln\left(\frac{e^{-\beta E_i}}{\sum_i \left(e^{-\beta E_i}\right)}\right) + \beta E_i\right)\right)/\beta$$

ln a/b = ln a - ln b

ln e^x = x

$$= \sum_i \left(p_i \left(-\beta E_i - \ln\left(\sum_i \left(e^{-\beta E_i}\right)\right) + \beta E_i\right)\right)/\beta$$

+x-x=0

$$= \sum_i \left(p_i \left(-\ln\left(\sum_i \left(e^{-\beta E_i}\right)\right)\right)\right)/\beta$$

Σcx = cΣx

$$= \sum_i \left(p_i\right) \left(-\ln\left(\sum_i \left(e^{-\beta E_i}\right)\right)\right)/\beta$$

Σp=1

$$= -\ln\left(\sum_i \left(e^{-\beta E_i}\right)\right)/\beta$$

Substituindo β

$$= -k_{\mathrm{B}} T \ln\left(\sum_i \left(e^{-\beta E_i}\right)\right)$$

Energia de Helmholtz e a função de partição canônica

$$A = -k_{\mathrm{B}} T \ln(Q) \qquad (28)$$

Entropia no ensemble microcanônico

$$S = -k_{\mathrm{B}} \sum_i \left(p_i \ln\left(p_i\right)\right)$$

Substituindo p

$$= -k_{\mathrm{B}} \sum_i \left(\frac{e^{-\beta E_i}}{\sum_i \left(e^{-\beta E_i}\right)} \ln\left(\frac{e^{-\beta E_i}}{\sum_i \left(e^{-\beta E_i}\right)} \right)\right)$$

$\Sigma_1^{\Omega} c = \Omega\, c$

$$= -k_{\mathrm{B}} \Omega(E_i) \frac{e^{-\beta E_i}}{\Omega(E_i) e^{-\beta E_i}} \ln\left(\frac{e^{-\beta E_i}}{\Omega(E_i) e^{-\beta E_i}} \right)$$

=1 =1

$x/x=1$

$$= -k_{\mathrm{B}} \Omega(E_i) \frac{1}{\Omega(E_i)} \ln\left(\frac{1}{\Omega(E_i)} \right)$$

$$S = k_{\mathrm{B}} \ln \Omega(E)$$

$$S = k_{\mathrm{B}} \ln \Omega$$