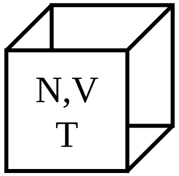
Boltzmanova-Gibbsova formulation of statistical thermodynamics



SYSTEM – particular thermodynamical system *(1 mol of gas in volume V)*

Macroscopic – perfect replica of the system
Microscopic – individual systems are not exactly identical

Defined by N, V
+
interactions

Unambiguously define available energy eigenvalues E_j and corresponding degeneration $\Omega(E_j)$

Principle of equal a priori probabilities

Each of the $\Omega(E_j)$ states must be represented in the ensemble equally

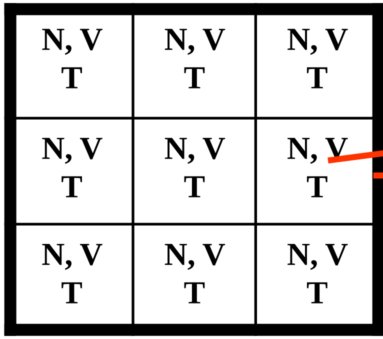
N, V T	**N, V T**	**N, V T**
N, V T	**N, V T**	**N, V T**
N, V T	**N, V T**	**N, V T**

Ensemble characterized by N, V, T
⇒Denoted **CANONICAL ENSEMBLE**
⇒Diatermic walls between systems, ensemble thermally isolated (adiabat. walls)
Total of $\mathbb{A}$ systems is placed in the heatbath (T)

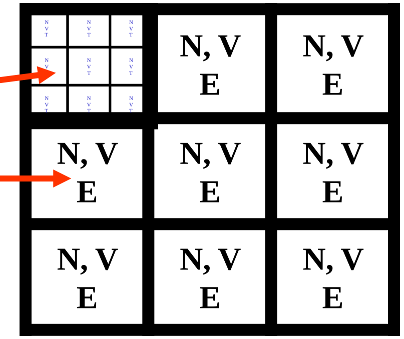
Individual systems have the same temperature T, however they may have different energies E_j.

Canonical ensemble ~ 1 system of **microcanonical enesemble**

(N, V, T)



(Contains $\mathbb{A}$ systems)



($\mathbb{A}$N, $\mathbb{A}$V, $\mathbb{E}$)

Whole **canonical ensemble** thermally isolated from env.
⇒Represents one system of **microcanonical enesemble**

Individual systems of **canonical ensemble** have different energies E_j,
It must hold: $\sum_j a_j E_j = \mathbb{E}$
a_j ... Number of systems having energy E_j
Condition: $\sum_j a_j = \mathbb{A}$
{**a**} … distribuce soustav do energetických hladin

Each **microcanonical enesemble** has energy $\mathbb{E}$.

Principle of equal a priori probabilities

Each distribution{**a**} is equally probable.
Must have the same weight in ensemble average.

- All E_j must be taken into consideration
- Individual systems (E_j) are represented in canonical ensemble proportionally to – $\Omega(E_j)$
- E_j(N,V) ... number of occurrences depends on degeneration

“Population”

{j, E_j, a}

System j

Characterized by E_j

Number of realization of systems (N,V,T)

{**a**} … distribution

Number of realization of distribution **a**

$$W(a) = \frac{\mathbb{A}!}{\prod_k a_k!}$$

Summing over a – all possible distribution over all systems of **microcanonical ensemble.**

Probability that the microcaninical system has distribution (j, a_j, E_j)

$$P_j = \frac{\overline{a_j}}{\mathbb{A}} = \frac{1}{\mathbb{A}} \frac{\sum_a W(a) a_j(a)}{\sum_a W(a)}$$

Number of **canonical systems** in the state *j*.

Average value of mechanical property in canonical ensemble:

$$\overline{M} = \sum_j M_j P_j$$

Distribution a_j has maximum number of realization when all a_j are equal.
Such distribution is rather narrow for large $\mathbb{A}$.

$$P_j = \frac{a_j^*}{\mathbb{A}} = \frac{1}{\mathbb{A}} \frac{W(a^*) a_j^*}{W(a^*)}$$

Instead of using average – we will use the most probable distribution {**a**}

$$\overline{a_j} = a_j^*$$

Number of possible ways to divide N distinguishable systems into groups:

Distinguishable objects N!

Indistinguishable within groups $\dfrac{N!}{N_1!(N-N_1)!} = \dfrac{N!}{N_1!N_2!}$

Binomial expansion

(Only $N_1+N_2=N$)

$$\left(x+y\right)^N = \sum_{N_1=0}^{N} \frac{N!}{N_1!(N-N_1)!} x^{N-N_1} y^{N_1} = \sum_{N_1,N_2}^{*} \frac{N!}{N_1!N_2!} x^{N_1} y^{N_2}$$

Binomial coefficient

Multinomial expansion

Binomial expansion

$$(x+y)^N = \sum_{N_1=0}^{N} \frac{N!}{N_1!(N-N_1)!} x^{N-N_1} y^{N_1} = \sum\nolimits^{*}_{N_1,N_2} \frac{N!}{N_1!N_2!} x^{N_1} y^{N_2}$$

$$f(N_1) = \frac{N!}{N_1!(N-N_1)!}$$

Searching the maximum of f(N_1)

- N_1 and N are large – f(N_1) considered them as continuous variables
- since ln(x) is monotonic function of x : seraching for maximum of ln f(N_1)

$$\boxed{\frac{d \ln f(N_1)}{dN_1} = 0 \longrightarrow N_1^* = \frac{N}{2}}$$

$$\ln f(N_1) = \ln f(N_1^*) + \frac{1}{2}\left(\frac{d^2 \ln f(N_1)}{dN_1^2}\right)_{N_1=N_1^*} (N_1 - N_1^*)^2 + \cdots$$

=-4/N

Taylor expansion
(1st derivation is zero)

$$\ln f(N_1) = \ln f(N_1^*) - \frac{2}{N} \ln f(N_1) = \ln f(N_1^*) - \frac{2}{N}(N_1 - N_1^*)^2$$

$$\ln f\left(N_1\right)=\ln f\left(N_1^*\right)-\frac{2}{N}\ln f\left(N_1\right)=\ln f\left(N_1^*\right)-\frac{2}{N}\left(N_1-N_1^*\right)^2$$

$$f\left(N_1\right)=f\left(N_1^*\right)\exp\left\{-\frac{2\left(N_1-N_1^*\right)^2}{N}\right\}$$

$$f\left(x\right)=\frac{1}{\left(2\pi\sigma^2\right)^{1/2}}\exp\left\{-\frac{\left(x-x^*\right)^2}{2\sigma^2}\right\}$$

Gaussian distribution

Standard deviation $\sigma\approx\sqrt{N}$

Gaussovsian distribution – delta function in the large N limit

The most probable distribution is a good representation of the average distribution

The same game can be played for multonomial distribution:

sharp maximum for $N_1=N_2=N_3=\cdots=N_s=\dfrac{N}{s}$

Number of realization of distribution **a**

$$W(a)=\frac{\mathbb{A}!}{\prod_k a_k!}$$

Summing over a – all possible distribution over all systems of **microcanonical ensemble.**

Probability that the microcaninical system has distribution (j, a_j, E_j)

$$P_j=\frac{\overline{a_j}}{\mathbb{A}}=\frac{1}{\mathbb{A}}\frac{\sum_a W(a)a_j(a)}{\sum_a W(a)}$$

Number of **canonical systems** in the state *j*.

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Distribution a_j has maximum number of realization when all a_j are equal.
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$$P_j=\frac{a_j^*}{\mathbb{A}}=\frac{1}{\mathbb{A}}\frac{W(a^*)a_j^*}{W(a^*)}$$

Instead of using average – we will use the most probable distribution {**a**}

$$\overline{a_j}=a_j^*$$

Searching for distribution **a***, that maximizes W(**a**) under the boundary conditions given:

$$\frac{\partial}{\partial a_j}\left\{\ln W(a) - \alpha\sum_k a_k - \beta\sum_k a_k E_k\right\} = 0$$

$$-\ln a_j^* - \alpha - 1 - \beta E_j = 0$$

$$a_j^* = e^{-\alpha'} e^{-\beta E_j}$$

$$e^{\alpha'} = \frac{1}{\mathbb{A}}\sum_j e^{-\beta E_j}$$

$$P_j = \frac{a_j^*}{\mathbb{A}} = \frac{e^{-\beta E_j(V,N)}}{\sum_j e^{-\beta E_j(V,N)}}$$

$$\beta = \frac{1}{kT}$$

$$Q(N,V,T) = \sum_j e^{-E_j(N,V)/kT}$$

Average value of mechanical property:

$$\overline{E}(N,V,T) = \frac{1}{Q}\sum_j E_j(N,V) e^{-E_j(N,V)/kT}$$

Corresponds to the thermodynamic energy E (postulate)

Average value of mechanical variable in canonical ensemble $\overline{M} = \sum_j M_j P_j$

$$Q(N,V,T) = \sum_j e^{-\beta E_j(N,V)}$$

$$\overline{E}(N,V,T) = \frac{1}{Q}\sum_j E_j(N,V) e^{-\beta E_j(N,V)}$$

Pressure of the system in state *j* p_j

Work done on the system $dE_j = p_j dV$

Change of the energy level due to the volume change $p_j = -\left(\frac{\partial E_j}{\partial V}\right)_N$

$$\overline{p}(N,V,T) = -\frac{1}{Q}\sum_j \left(\frac{\partial E_j(N,V)}{\partial V}\right)_N e^{-\beta E_j(N,V)}$$

finding β

$$\left.\begin{aligned}\left(\frac{\partial \overline{E}}{\partial V}\right)_{N,\beta} &= \ldots = -\overline{p} + \beta\left(\overline{pE}\right) - \beta\,\overline{p}\,\overline{E} \\ \left(\frac{\partial \overline{p}}{\partial \beta}\right)_{N,V} &= \ldots = \overline{E}\,\overline{p} - \left(\overline{pE}\right)\end{aligned}\right\} \quad \left(\frac{\partial \overline{E}}{\partial V}\right)_{N,\beta} + \beta\left(\frac{\partial \overline{p}}{\partial \beta}\right)_{N,V} = -\overline{p}$$

Classical TD: $\left(\frac{\partial \overline{E}}{\partial V}\right)_{N,1/T} + \frac{1}{T}\left(\frac{\partial \overline{p}}{\partial (1/T)}\right)_{N,V} = -p$

$$\beta = \frac{konst.}{T}$$

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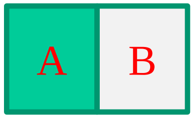
We will show that k is universal constant (Boltzmann constant)



Two systems in thermal contact

A: N_A, V_A, T => available energy levels $\{E_{jA}\}$ with distribution$\{a_j\}$

B: N_B, V_B, T => available energy levels $\{E_{jB}\}$ with distribution$\{b_j\}$

$$W(a,b) = \frac{\mathbb{A}!}{\prod_k a_k!}\frac{\mathbb{B}!}{\prod_j b_j!}$$

Number of states of AB ensemle is a product of number of states for each of the systems.

Setting up canonical and microcanonical ensemles for pair of systems A and B and we search for the most likely distribution

$$\sum_j a_j = A \qquad \sum_j b_j = B = A$$

$$\sum_j \left(a_j E_{jA} + b_j E_{jB}\right) = E$$

Only one relationship must be satisfied for energy !

=> Probabilities are proportional to the same constant for systems in thermal contact !

$$P_{ij} = \frac{e^{-\beta E_{iA}}}{Q_A}\frac{e^{-\beta E_{jB}}}{Q_B} = P_{iA}P_{jB}$$

Connecting classical and statistical TD:

$$d\bar{E} = \sum_j E_j dP_j + \sum_j P_j dE_j$$

$$= \delta q_{rev} - \delta w_{rev}$$

Entropy:

$$Q(N,V,T) = \sum_j e^{-\beta E_j(N,V)}$$

$$f(\beta, E_1, E_2, E_3, \ldots) = \ln\left\{\sum_j e^{-\beta E_j}\right\}$$

$$df =$$

Connecting classical and statistical TD:

$$d\bar{E} = \sum_j E_j dP_j + \sum_j P_j dE_j$$

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$$df = \left(\frac{\partial f}{\partial \beta}\right)_{E_j'} d\beta + \sum_k \left(\frac{\partial f}{\partial E_k}\right)_{\beta, E_j'} dE_k$$

Total derivative

$$\frac{-\sum_k E_k e^{-\beta E_k}}{Q} = \bar{E}$$

$$\frac{-\beta e^{-\beta E_k}}{Q} = -\beta P_k$$

$$df = -\bar{E} d\beta - \beta \sum_j P_j dE_j$$

$$d(f + \beta\bar{E}) = \beta\left(d\bar{E} - \sum_j P_j dE_j\right)$$

$$d(\ln Q + \beta\bar{E}) = \beta\delta q_{rev}$$

Internal energy change

Reversible heat

Work done on the system
Change of volume dV ~ change of energy levels E_j
For original distribution a_j : $a_j\ dE_j$ is the work done
Corresponding sum – reversible work performed on the ensemble

Derivative of the state function
⇒β is an integration factor q_{rev}

2nd law of TD

Connecting classical and statistical TD:

$$d\bar{E} = \sum_j E_j dP_j + \sum_j P_j dE_j$$

$$= \delta q_{rev} - \delta w_{rev}$$

Entropy:

$$d\ \ f + \beta\bar{E}\ = \beta\left(d\bar{E} - \sum_j P_j dE_j\right)$$

Internal energy change

Volume work done on the system

Reversible heat

$$d\ \ \ln Q + \beta\bar{E}\ = \beta\delta q_{rev}$$

$$d\left(\ln Q + \frac{\bar{E}}{kT}\right) = \frac{\delta q_{rev}}{kT}$$

$$d\left(k\ln Q + \frac{\bar{E}}{T}\right) = \frac{\delta q_{rev}}{T}$$

$$\oint \frac{dQ}{T} = 0$$

2nd law of theormodynamics
➔ (dQ/T) is a total differencial of state function ➔ definition of etnropy S

$$S = \frac{\bar{E}}{T} + k\ln Q + const.$$

Constant independent of N, V, T
It set to zero

Connecting classical and statistical TD:

$$Q(N,V,T)=\sum_j e^{-E_j(N,V)/kT}$$

Canonical partition function

$$\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}= \longrightarrow$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}= \longrightarrow$$

$$S=\frac{\overline{E}}{T}+k\ln Q+const. \longrightarrow$$

$$A=E-TS \longrightarrow$$

Connecting classical and statistical TD:

$$Q(N,V,T)=\sum_j e^{-E_j(N,V)/kT}$$

Canonical partition function

$$\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}=\frac{\sum_j E_j e^{-E_j/kT}}{kT^2 Q}=\frac{\overline{E}}{kT^2} \longrightarrow \overline{E}=kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}=-\frac{\sum_j \left(\frac{\partial E_j}{\partial V}\right) e^{-E_j/kT}}{kTQ}=\frac{\overline{p}}{kT} \longrightarrow \overline{p}=kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$$

$$S=\frac{\overline{E}}{T}+k\ln Q+const. \longrightarrow S=kT\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}+k\ln Q$$

$$A=E-TS \longrightarrow A(N,V,T)=-kT\ln Q$$

Obtained from quantum mechanics (E_j) ⟷ Calculation of theormodynamical properties from the molecular properties

$$Q(N,V,T)=\sum_E \Omega\ N,V,E\ e^{-E(N,V)/kT}$$

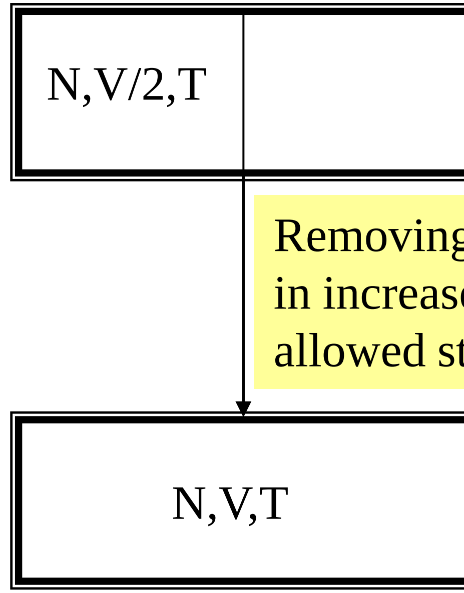
Instead of sum over states we can sum over energy level and take into consideration the degeneration

2nd law of thermodynamics

$$A(N,V,T) = -kT \ln Q$$

$$Q(N,V,T) = \sum_E \Omega(N,V,E)\, e^{-E(N,V)/kT}$$

Number of states with energy E Ω(N,V,E) cannot become lower due to barrier removal – original states are still available



Ω_1(N,V,E)

Removing the wall results in increased number of allowed states E_j (~ V^N)

Ω_2(N,V,E)

<u>Considering izothermic process:</u>

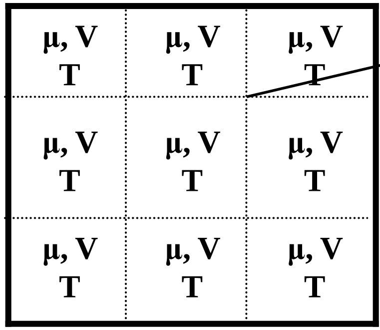
$$\Omega_2(N,V,E) \geq \Omega_1(N,V,E)$$

$$Q_2 - Q_1 = \sum_E \left(\Omega_2(N,V,E) - \Omega_1(N,V,E)\right) e^{-E/kT} > 0$$

$$\Delta A = A_2 - A_1 = -kT \ln \frac{Q_2}{Q_1} < 0$$

In general: lifting up certain restrictions leads to an increased number of available quantum states; Population of new states => ***spontaneous process***

Grand Canonical Ensemble



Diathermic permeable walls allowing heat exchange and molecular transport

Adiabatic walls – thermal isolation

a_{Nj} ... Number of systems in ensemble having N molecules and energy E_j

$$\sum_N \sum_j a_{Nj} = \mathbb{A}$$ Number of systems in ensemble

$$\sum_N \sum_j a_{Nj} E_{Nj} = \mathbb{E}$$ Total energy of GCE ensemble - constant

$$\sum_N \sum_j a_{Nj} N = \mathbb{N}$$ Number of molecules in the ensemble

Grand Canonical Ensemble represents one system of microcalorimetric systému (N,V,E).

$\Rightarrow$ Principle of equal a priori probabilities

Boundary conditions

GCE – similarly to CE – searching for the most probable distribution.

$$W(a_{Nj}) = \frac{\mathbb{A}!}{\prod_N \prod_j a_{Nj}!}$$

$$a^*_{Nj} = e^{-\alpha} e^{-\beta E_{Nj}\ V}\ e^{-\gamma N}$$

α

$$P_{Nj}\ \ V,\beta,\gamma\ \ = \frac{a^*_{Nj}}{\mathbb{A}} = \frac{e^{-\beta E_{Nj}\ V}\ e^{-\gamma N}}{\sum_N \sum_j e^{-\beta E_{Nj}\ V}\ e^{-\gamma N}}$$

$$\beta = \frac{1}{kT}$$

Averaged values of mechanical variables in GCE:

$$\Xi\ \ V,\beta,\gamma\ \ = \sum_N \sum_j e^{-\beta E_{Nj}\ V}\ e^{-\gamma N}$$

"ksi"

$$\overline{E}\ \ V,\beta,\gamma\ \ = \frac{1}{\Xi} \sum_N \sum_j E_{Nj}\ \ V\ \ e^{-\beta E_{Nj}\ V}\ e^{-\gamma N} = -\left(\frac{\partial \ln \Xi}{\partial \beta}\right)_{V,\gamma}$$

$$\overline{p}\ \ V,\beta,\gamma\ \ = \frac{1}{\Xi} \sum_N \sum_j \left(-\frac{\partial E_{Nj}}{\partial V}\right) e^{-\beta E_{Nj}\ V}\ e^{-\gamma N} = \frac{1}{\beta}\left(\frac{\partial \ln \Xi}{\partial V}\right)_{\beta,\gamma}$$

$$\overline{N}\ \ V,\beta,\gamma\ \ = \frac{1}{\Xi} \sum_N \sum_j N e^{-\beta E_{Nj}\ V}\ e^{-\gamma N} = -\left(\frac{\partial \ln \Xi}{\partial \gamma}\right)_{V,\beta}$$

γ

$$f \quad \beta, \gamma, \quad E_{Nj} \quad V \qquad = \ln \Xi = \ln \sum_N \sum_j e^{-\beta E_{Nj} \quad V} e^{-\gamma N}$$

$$df =$$

γ

$$f\;\;\beta,\gamma,\;\;E_{Nj}\;\;V\;\;\;\;=\ln\varXi=\ln\sum_{N}\sum_{j}e^{-\beta E_{Nj}\;\;V}\;e^{-\gamma N}$$

$$df=\left(\frac{\partial f}{\partial\beta}\right)_{\gamma,\;E_{Nj}}d\beta+\left(\frac{\partial f}{\partial\gamma}\right)_{\beta,\;E_{Nj}}d\gamma+\sum_{N}\sum_{j}\left(\frac{\partial f}{\partial E_{Nj}}\right)_{\beta,\gamma,E_{Nj}'}dE_{Nj}$$

Using equations for E, N, p

$$df=-\overline{E}d\beta-\overline{N}d\gamma-\beta\sum_{N}\sum_{j}P_{Nj}dE_{Nj}$$

Considering the volume work only

$$df=-\overline{E}d\beta-\overline{N}d\gamma+\beta\overline{p}dV$$

$$+d\;\;\beta\overline{E}\;\;+d\;\;\gamma\overline{N}$$

$$d\;\;\;f+\beta\overline{E}+\gamma\overline{N}\;\;=\beta d\overline{E}+\beta\overline{p}dV+\gamma d\overline{N}$$

$$TdS=dE+pdV-\mu dN$$

$$\beta=\frac{1}{kT}$$

$$\gamma=\frac{-\mu}{kT}$$

$$S=\frac{\overline{E}}{T}-\frac{\overline{N}\mu}{T}+k\ln\varXi$$

Grand Canonical Ensemble

$$\Xi\left(V,T,\mu\right)=\sum_{N}\sum_{j}e^{-E_{Nj}(V)/kT}e^{\mu N/kT}$$

Partition function GCE => Describes open isothermal systems

$$Q(N,V,T)=\sum_{j}e^{-E_j(N,V)/kT}$$

$$\Xi\left(V,T,\mu\right)=\sum_{N}Q(N,V,T)e^{\mu N/kT}$$

$$\lambda=e^{\mu/kT}\Leftrightarrow\mu=kT\ln\lambda$$

λ ... Absolute activity

$$\Xi\left(V,T,\mu\right)=\sum_{0}^{\infty}Q(N,V,T)\lambda^{N}$$

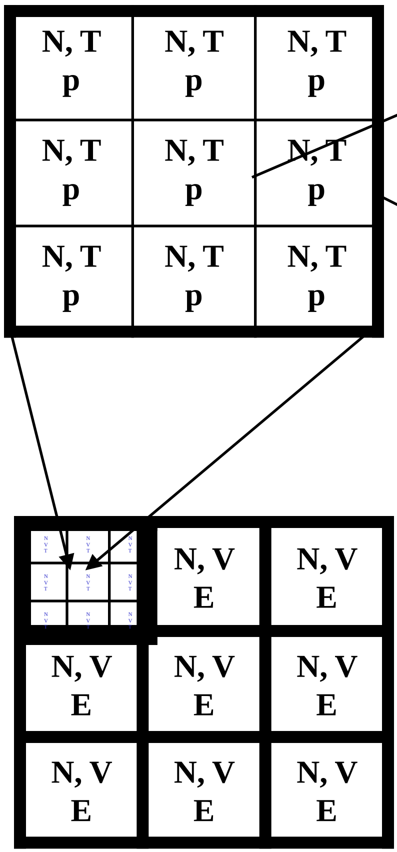
Partition function GCE – for certain cases it is more suitable than canonical one.

$$\left.\begin{aligned}&G=\mu N=E+pV-TS\\&S=\frac{\overline{E}}{T}-\frac{\overline{N}\mu}{T}+k\ln\Xi\end{aligned}\right\}$$

$$pV=kT\ln\Xi\left(V,T,\mu\right)$$

pV is characteristic function of GCE

Isothermal-isobaric Ensemble



Flexibal diathermic walls
Heat transfer and flexible volume

Neprospustné adiabatické stěný – teplená izolace

Partition function

$$\Delta(N,T,p) = \sum_E \sum_V \Omega \;\; N,V,E \;\; e^{-E/kT} e^{-pV/kT}$$

$$G = -kT \ln \Delta(N,T,p)$$

Gibbs energy is characteristic function of IIE

Any other set of independent variables can be used for the definition of ensemble and corresponding partition function can be derived

All the ensembles are equivalent in the limit for large systems in the equilibrium :

$$Q(N,V,T) = \sum_E \Omega\ \ N,V,E\ \ e^{-E(N,V)/kT}$$

Probability of „observation“ of particular energy value … P(E)

$$P(E) = C\Omega\ \ E\ \ e^{-E/kT}$$

Extremely narrow Gaussian distribution for large N (C is normalization factor)

=> $E = E^* = \overline{E}$

$$Q(N,V,T) = \Omega\ \ N,V,\overline{E}\ \ e^{-\overline{E}(N,V)/kT}$$

Energy is in ensemble uniformly distributed into individual systems – small fluctuations

<u>=> Canonical ensemble changes to microcanonical ensemble!</u>

We can select an ensemble based on the “mathematical convenience”, regardless TD variables describing the system.

Microcanonical ensemble

$$\boxed{\Omega(N,V,E)}$$

$$S\ \ N,V,E\ \ = k\ln\Omega$$

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

Canonical ensemble

$$Q(N,V,T) = \sum_E \Omega\ \ N,V,E\ \ e^{-E(N,V)/kT}$$

$$A(N,V,T) = -kT\ln Q$$

$$dA = -SdT - pdV + \mu dN$$

$$S = kT\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k\ln Q$$

Charakteristické funkce souboru

Grand canonical ensemble

$$\Xi\ \ V,T,\mu\ \ = \sum_N \sum_E \Omega(N,V,E)e^{-E\ \ N,V\ \ /kT}e^{\mu N/kT}$$

$$pV = kT\ln\Xi\ \ V,T,\mu$$

$$d\ \ pV\ \ = SdT + Nd\mu + pdV$$

$$S = kT\left(\frac{\partial \ln \Xi}{\partial T}\right)_{\mu,V} + k\ln\Xi$$

Isothermal-isobaric ensemble

$$\Delta(N,T,p) = \sum_E \sum_V \Omega\ \ N,V,E\ \ e^{-E/kT}e^{-pV/kT}$$

$$G = -kT\ln\Delta(N,T,p)$$

$$dG = -SdT + Vdp + \mu dN$$

$$S = kT\left(\frac{\partial \ln \Delta}{\partial T}\right)_{N,p} + k\ln\Delta$$

Microcanonical ensemble

$$\boxed{\Omega(N,V,E)}$$

$$\boxed{S\;\;N,V,E\;\;=k\ln\Omega}$$

$$dS=\frac{1}{T}dE+\frac{p}{T}dV-\frac{\mu}{T}dN$$

$$\frac{1}{kT}=\left(\frac{\partial\ln\Omega}{\partial E}\right)_{N,V}$$

$$\frac{p}{kT}=\left(\frac{\partial\ln\Omega}{\partial V}\right)_{N,E}$$

$$\frac{\mu}{kT}=\left(\frac{\partial\ln\Omega}{\partial N}\right)_{V,E}$$

Canonical ensemble

$$\boxed{Q(N,V,T)=\sum_{E}\Omega\;\;N,V,E\;\;e^{-E(N,V)/kT}}$$

$$A(N,V,T)=-kT\ln Q$$

$$dA=-SdT-pdV+\mu dN$$

$$\boxed{S=kT\left(\frac{\partial\ln Q}{\partial T}\right)_{N,V}+k\ln Q}$$

$$\overline{E}=kT^{2}\left(\frac{\partial\ln Q}{\partial T}\right)_{N,V}$$

$$\overline{p}=kT\left(\frac{\partial\ln Q}{\partial V}\right)_{N,T}$$

$$\overline{\mu}=-kT\left(\frac{\partial\ln Q}{\partial N}\right)_{V,T}$$

Grand canonical ensemble

$$\boxed{\Xi\;\;V,T,\mu\;\;=\sum_{N}\sum_{E}\Omega(N,V,E)e^{-E\;\;N,V\;\;/kT}e^{\mu N/kT}}$$

$$pV=kT\ln\Xi\;\;V,T,\mu$$

$$d\;\;pV\;\;=SdT+Nd\mu+pdV$$

$$\boxed{S=kT\left(\frac{\partial\ln\Xi}{\partial T}\right)_{\mu,V}+k\ln\Xi}$$

$$N=kT\left(\frac{\partial\ln\Xi}{\partial\mu}\right)_{V,T}$$

$$p=kT\left(\frac{\partial\ln\Xi}{\partial V}\right)_{\mu,T}$$

Isothermal-isobaric ensemble

$$\boxed{\Delta(N,T,p)=\sum_{E}\sum_{V}\Omega\;\;N,V,E\;\;e^{-E/kT}e^{-pV/kT}}$$

$$G=-kT\ln\Delta(N,T,p)$$

$$dG=-SdT+Vdp+\mu dN$$

$$\boxed{S=kT\left(\frac{\partial\ln\Delta}{\partial T}\right)_{N,p}+k\ln\Delta}$$

$$\mu=-kT\left(\frac{\partial\ln\Delta}{\partial N}\right)_{T,p}$$

$$V=-kT\left(\frac{\partial\ln\Delta}{\partial p}\right)_{N,T}$$

POSTULATE ①. Ensemble average corresponds to TD average.

> Mean value of arbitrary mechanical property *M* (in a real system it would be obtained by time averaging aver the sufficiently long period of time) is equal to the mean value obtained for the ensemble; systems of this ensemble must reproduce TD state of real system. (Strictly speaking it holds only for $N \to \infty$)

POSTULATE ②. Principle of equal a priori probabilities.

> For the ensemble representing isolated TD system (microcanonicle ensemble) all the ensemble elements are distributed with the equal probability among all quantum states available for N, V, E.

Mechanical properties of molecules → **Thermodynamical propertis of ensemble**

Partition function

GCE partition function of two-component system

a) derive the partition function

b) find the expression for TD properties

GCE partition function of ideal mono-atomic gas is

$$\boxed{\Xi = e^{q\lambda}} \qquad \boxed{q = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V}$$

Find the TD properties of such gas (internal energy, pressure, etc.)