

Other Ensembles in Statistical Mechanics

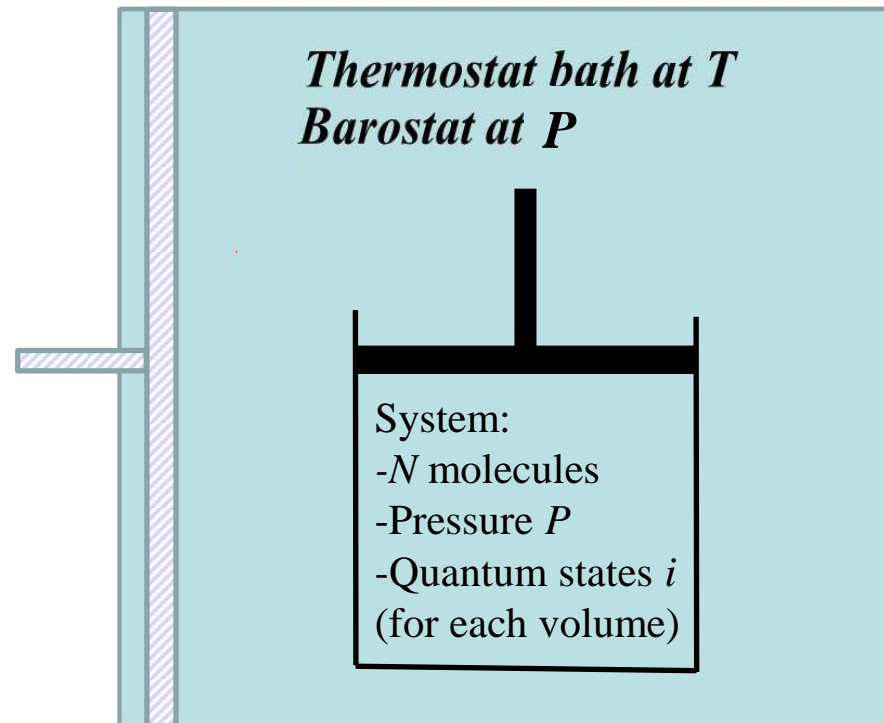
- Other types of external macroscopic constraints can be applied to systems in an ensemble;
- Constraints correspond to external thermodynamics variables;
- Constraints represent conditions under which we experiment on macroscopic systems;
- The procedure of finding the distribution of the system among possible microstates is similar to that of the canonical ensemble;
- Both quantum mechanical and classical forms of the ensemble distributions are given.

Some examples of ensembles

- Constant pressure – constant temperature
- Constant volume – constant temperature – constant chemical potential (Grand canonical ensemble)
- Constant volume – constant energy (Micro-canonical ensemble)
- Constant pressure – constant enthalpy

Statistical mechanics under constant pressure – constant temperature

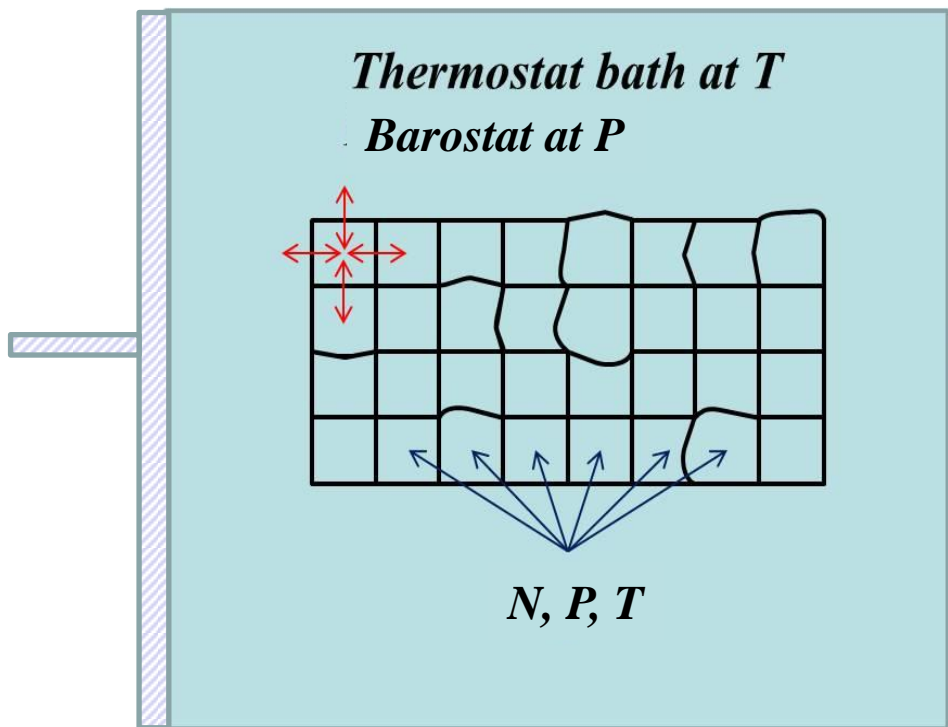
- How do we treat systems at constant pressure and temperature with statistical mechanics?
- The system has constant P , constant T , with N interacting molecules;
- To equilibrate to the desired pressure, the system has flexible walls which allow it to change volume;
- The walls are thermally conducting, allowing exchange of heat energy with the surroundings
- Microscopically, at each volume V_k , the N -molecule **system** is characterized by quantum state $j(V_k)$ with energy $E_i(V_k)$



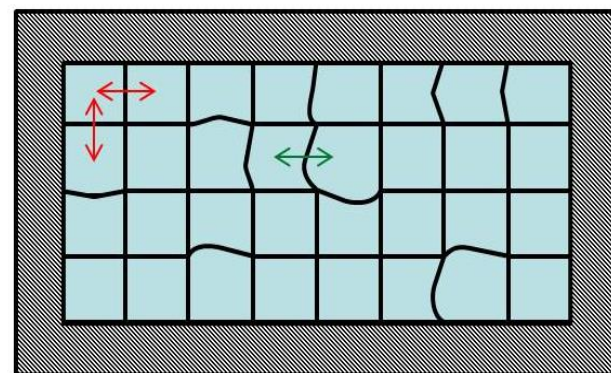
Set-up of the isothermal – isobaric ensemble

- Replicas of the system are placed in contact with each other in a large thermal bath / barostat apparatus;
- The walls of the systems are flexible allowing the volume of each system to change;
- After equilibration, the ensemble is placed in an isolated container with fixed volume. This is called the **isothermal-isobaric ensemble**.

Ensemble equilibrated with thermal bath and barostat



Isolated ensemble at fixed total energy \mathcal{E}

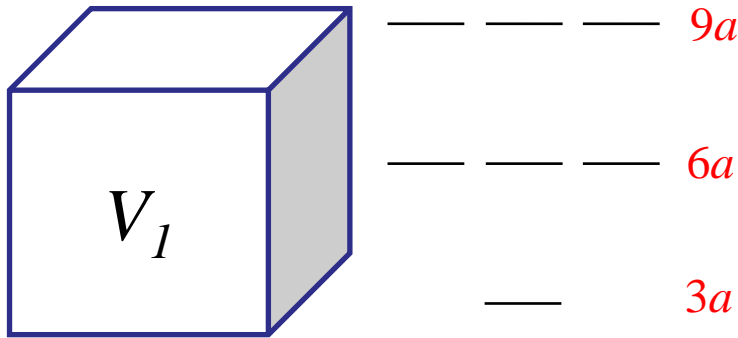


Systems are enclosed in a rigid container of total volume \mathcal{V}

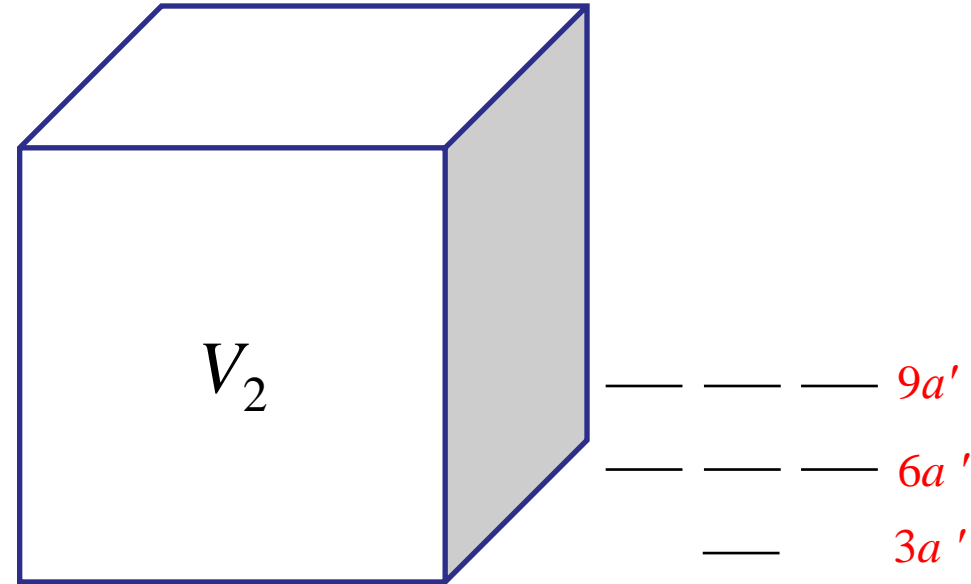
How does the system volume effect the quantum states?

Example: Particle in a cube (box) quantum states depend on the volume of the box, V

$$E_{\mathbf{n}}(V_k) = \frac{h^2}{8mV_k^{2/3}} (n_x^2 + n_y^2 + n_z^2)$$



$$E_{\mathbf{n}}(V_1) = \frac{h^2}{8mV_1^{2/3}} (n_x^2 + n_y^2 + n_z^2)$$



$$E_{\mathbf{n}}(V_2) = \frac{h^2}{8mV_2^{2/3}} (n_x^2 + n_y^2 + n_z^2)$$

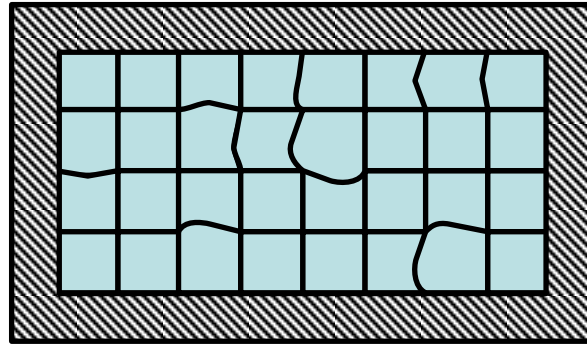
Pressure for a particle in a box state \mathbf{n} :

$$P_{\mathbf{n}}(V_{\ell}) = \left(\frac{\partial E_{\mathbf{n}}(V_{\ell})}{\partial V} \right) = \frac{h^2}{12mV_{\ell}^{5/3}} (n_x^2 + n_y^2 + n_z^2)$$

Distribution of systems in isothermal-isobaric ensemble among energy levels

The systems in the ensemble are characterized by first binning them according to volume, and according to energy levels for that volume

\mathcal{A} systems
 \mathcal{E} total energy
 \mathcal{V} total volume



- Separate systems according to volume
- For each volume bin for energy level

Energy bins for V_1

Energy bins for V_2

Energy bins for V_3

...

E_{1A_1}	E_2	E_3	E_4	E_5
E_6				

$E'_1 A'_1$	E'_2	E'_3	E'_4	E'_5
E'_6				

$E''_1 A''_1$	E''_2	E''_3	E''_4	E''_5

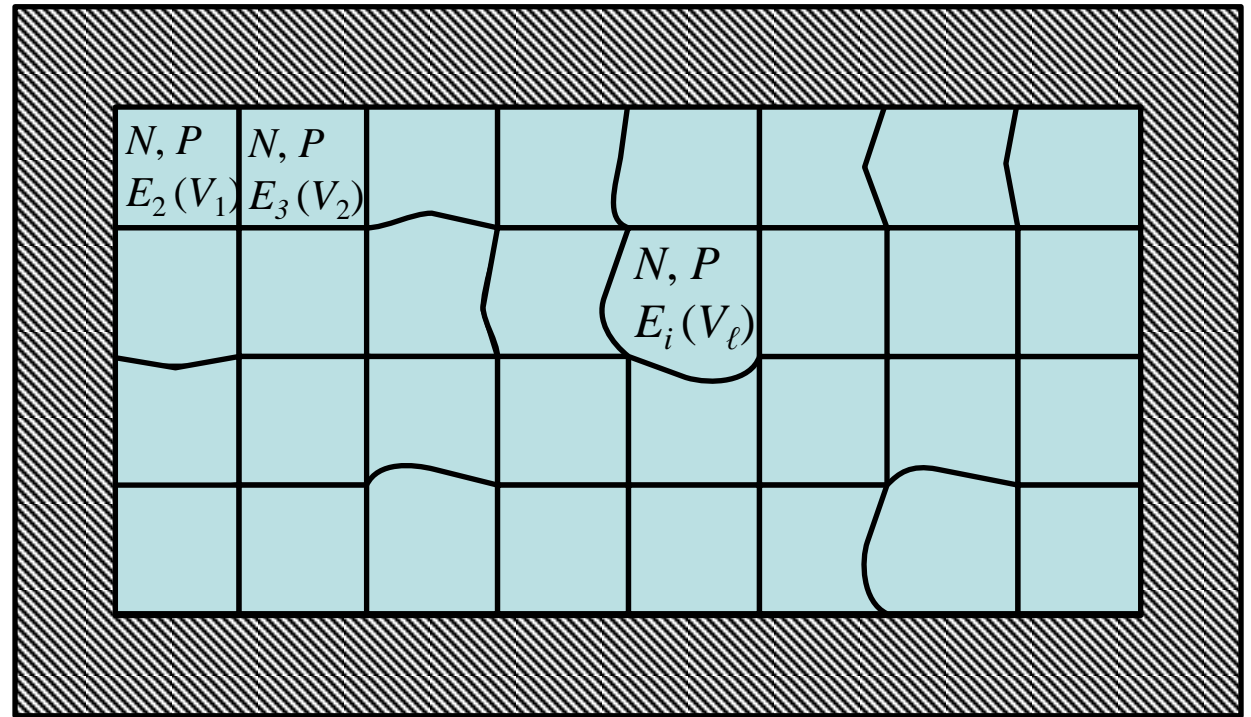
The isothermal-isobaric ensemble

- In the isothermal-isochoric ensemble different system volumes may be encountered.
- Each volume V_k has its corresponding states i of energy $E_i(V_k)$

$$\left\{ \begin{array}{l} V_1 \leftrightarrow E_i(V_1) \\ V_2 \leftrightarrow E_i(V_2) \\ \dots \\ V_\ell \leftrightarrow E_i(V_\ell) \end{array} \right.$$

Constraints on the ensemble distribution

$$\left\{ \begin{array}{l} \sum_{V_k} \left[\sum_j A_j(V_k) \right] = \mathcal{A} \\ \sum_{V_k} \left[\sum_j A_j(V_k) E_j(V_k) \right] = \mathcal{E} \\ \sum_{V_k} \left[\sum_j A_j(V_k) V_k \right] = \mathcal{V} \end{array} \right.$$



→ The continuous volume variation is represented by the summation to simplify notation

The \mathcal{E} , \mathcal{A} and \mathcal{V} are mathematical constructs

Most probable distribution in the isothermal-isobaric ensemble

The ways the members of the ensemble can be distributed among systems of volume V_k and states j

$$W(\{\mathbf{A}\}) = \frac{\mathcal{A}!}{\prod_{V_k} \left[\prod_j A_j(V_k)! \right]}$$

Constraints on the distribution

$$\begin{cases} \sum_{V_k} \left[\sum_j A_j(V_k) \right] = \mathcal{A} \\ \sum_{V_k} \left[\sum_j A_j(V_k) E_j(V_k) \right] = \mathcal{E} \\ \sum_{V_k} \left[\sum_j A_j(V_k) V_k \right] = \mathcal{V} \end{cases}$$

Each V_k has a set of associated energy levels $E_j(V_k)$

Find the most probable distribution, subject to constraints of the system: Lagrange method of undetermined multipliers

Derivative with respect to the occupancy of state i associated with the volume V_ℓ

$$\frac{\partial}{\partial A_i(V_\ell)} \left\{ \ln W(\{\mathbf{A}\}) - \alpha \left(\sum_{V_k} \sum_j A_j(V_k) - \mathcal{A} \right) - \beta \left(\sum_{V_k} \sum_j A_j(V_k) E_j(V_k) - \mathcal{E} \right) - \delta \left(\sum_{V_k} \sum_j A_j(V_k) V_k - \mathcal{V} \right) \right\} = 0$$

Number of systems in ensemble with volume V_ℓ in state i in most probable distribution

$$A_i^*(V_\ell) = e^{-\alpha} e^{-\beta E_i(V_\ell)} e^{-\delta V_\ell}$$

Most probable distribution in the isothermal-isobaric ensemble

Number of systems in ensemble with volume V_ℓ in state i in most probable distribution

$$A_i^*(V_\ell) = e^{-\alpha} e^{-\beta E_i(V_\ell)} e^{-\delta V_\ell}$$

The undetermined multiplier α can be eliminated as before

The probability of finding a system in the ensemble with volume V_ℓ and state i :

$$P_i(V_\ell) = \frac{A_i^*(V_\ell)}{\mathcal{A}} = \frac{e^{-\beta E_i(V_\ell)} e^{-\delta V_\ell}}{\sum_{V_k} \sum_j e^{-\beta E_j(V_k)} e^{-\delta V_k}} = \frac{e^{-\beta E_i(V_\ell)} e^{-\delta V_\ell}}{\Delta(N, \beta, \delta)}$$

↑
Isothermal – isobaric partition function

The probability includes an **energy** factor and a **volume** factor!

$$\Delta(N, \beta, \delta) = \sum_{V_k} \sum_j e^{-\beta E_j(V_k)} e^{-\delta V_k}$$

Isothermal-isobaric partition function

Other undetermined multipliers can be found by using the thermodynamic equation of state

$$\left(\frac{\partial H}{\partial P}\right)_{T,N} = V + \frac{1}{T} \left(\frac{\partial V}{\partial 1/T}\right)_{N,P}$$

We construct the statistical mechanical equivalent. Comparing the two allows us to identify the Lagrangian multipliers β and δ (see canonical ensemble derivation)

$$\beta = \frac{1}{kT} ; \quad \delta = \frac{P}{kT} \quad \Delta(N, T, P) = \sum_{V_\ell} \sum_j e^{-E_j/kT} e^{-PV_\ell/kT}$$

$$\ln \Delta(N, P, T) = \ln \left[\sum_{V_k} \sum_j e^{-E_j(N, V_k)/kT} e^{-PV_k/kT} \right]$$

$$\left[\frac{\partial \ln \Delta(N, P, T)}{\partial T} \right]_{N,P} = \frac{1}{kT^2} \frac{\sum_{V_\ell} \sum_j (E_j + PV_\ell) e^{-E_i(N, V_\ell)/kT} e^{-PV_\ell/kT}}{\sum_{V_k} \sum_i e^{-E_i(N, V_k)/kT} e^{-PV_k/kT}}$$

Average enthalpy: $\langle H(N, P, T) \rangle = kT^2 \left[\frac{\partial \ln \Delta(N, P, T)}{\partial T} \right]_{N,P}$

Formulas for the isothermal-isobaric partition function

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

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

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

Characteristic thermodynamics function for the isothermal-isobaric ensemble:

$$G = H - TS = -kT \ln \Delta(N, T, P)$$

Alternative expressions for the isothermal-isobaric ensemble:

$$\begin{aligned} \Delta(N, T, P) &= \sum_{V_\ell} \sum_E \Omega(N, V_\ell, E) e^{-E/kT} e^{-PV_\ell/kT} \\ &= \sum_{V_\ell} Q(N, V_\ell, E) e^{-PV_\ell/kT} \end{aligned}$$

Sum over energy levels

Fluctuations in the enthalpy and volume distribution

The temperature derivative of the enthalpy is the heat capacity:

$$\frac{d\langle H \rangle}{dT} = \frac{1}{kT^2} \left(\langle H^2 \rangle - \langle H \rangle^2 \right) = \frac{1}{kT^2} \sigma_H^2 = C_p$$

The distribution is very narrow for many molecule systems

$$\frac{\sigma_H}{\langle H \rangle} \propto \frac{1}{\sqrt{N}}$$

Variance of the pressure distribution?

$$\sigma_V^2 = \langle V^2 \rangle - \langle V \rangle^2 = -kT \left(\frac{\partial \langle V \rangle}{\partial P} \right)_{N,T}$$

Does this relate to a thermodynamic quantity?

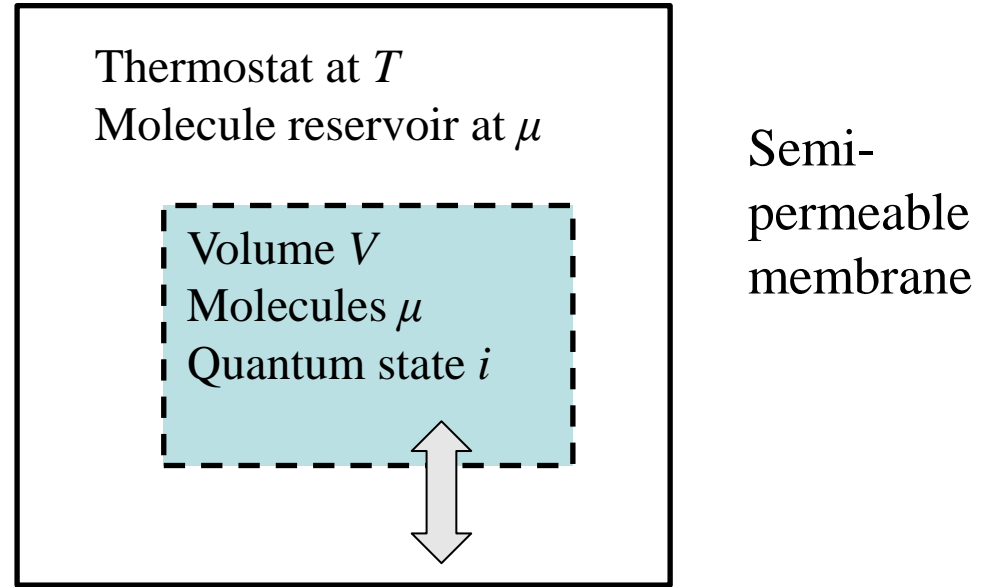
We can show:

$$\frac{\sigma_V}{\langle V \rangle} \propto \frac{1}{\sqrt{N}}$$

Statistical mechanics of open systems: Grand canonical ensemble

The system set-up:

- Constant volume
- Molecule exchange with environment
- Heat exchange with the environment



- A system of constant volume which can exchange heat and molecules with the surroundings;
- For each number of molecules, the system is characterized by a quantum state $E_i(N)$:

For 1 molecule: $E_1(1), E_2(1), E_3(1), \dots, E_i(1), \dots$

For 2 molecules: $E'_1(2), E'_2(2), E'_3(2), \dots, E'_i(2), \dots$

For 3 molecules: $E''_1(3), E''_2(3), E''_3(3), \dots, E''_i(3), \dots$

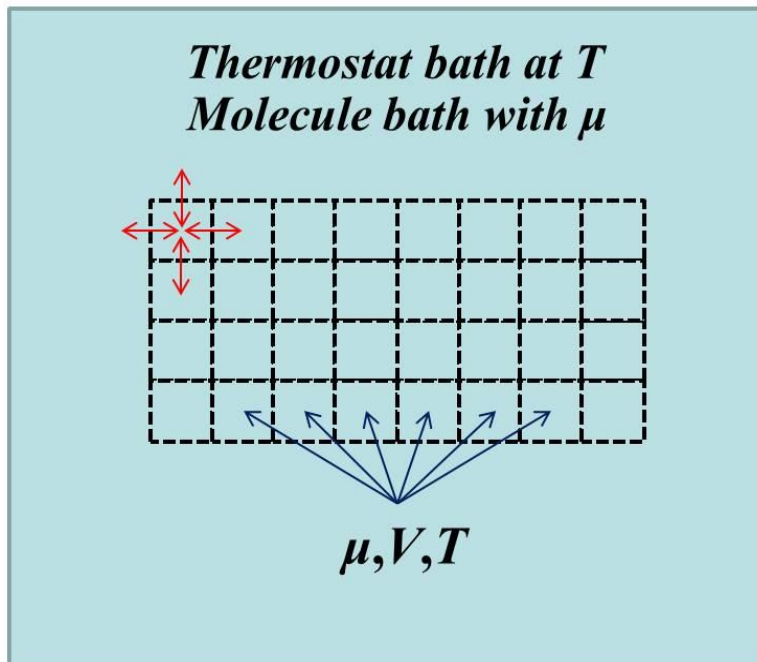
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For N molecules: $E_1(N), E_2(N), E_3(N), \dots, E_i(N), \dots$

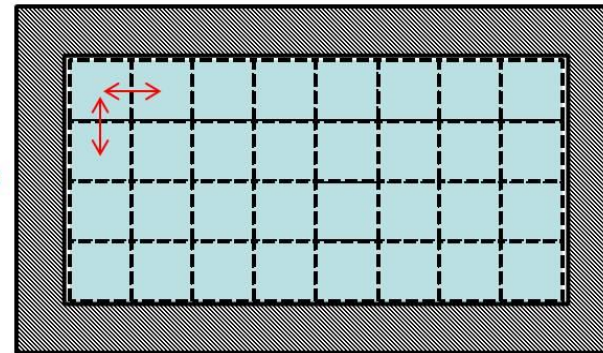
Grand canonical ensemble – Open systems

- The N -molecule **system as a whole** is characterized by a quantum state E_i
- Replicas of the system are placed in contact with each other in a large thermal bath / molecule bath
- After equilibration, the replicas which now have the same μ , T , and V are placed in an isolated container

Ensemble equilibrated with thermal and molecule bath



Isolated ensemble at T and μ

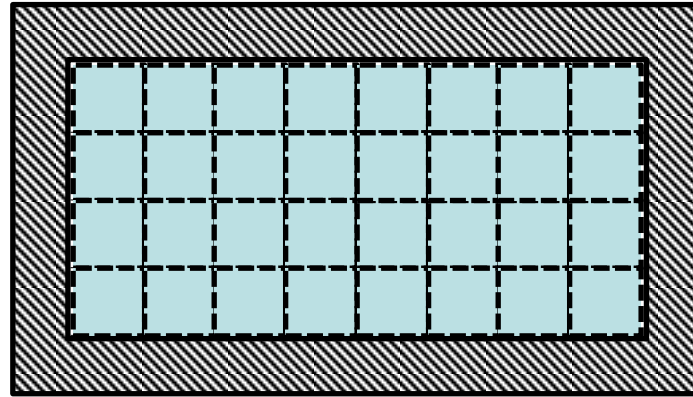


Total energy in the ensemble \mathcal{E} ,
Total number of systems in the ensemble \mathcal{A} ,
Total number of molecules in the ensemble \mathcal{N}

Distribution of systems in grand canonical ensemble among energy levels

The ensemble of systems are characterized by placing each system into a bin corresponding to first a particular number of molecules, then to energy levels for that number of particles

\mathcal{A} systems
 \mathcal{E} total energy
 \mathcal{N} total molecules



First bin for no. of molecules
 Second bin for energy level

Energy bins for N_1

E_{1A_1}	E_2	E_3	E_4	E_5
E_6				

Energy bins for N_2

$E'_{1A'_1}$	E'_2	E'_3	E'_4	E'_5
E'_6				

Energy bins for N_3

$E''_{1A''_1}$	E''_2	E''_3	E''_4	E''_5

...

The energy states of ideal gas systems with different numbers of molecules

one-particle
quantum states

$$E_{\mathbf{n}}(1) = \frac{h^2}{8mV^{2/3}} (n_x^2 + n_y^2 + n_z^2)$$

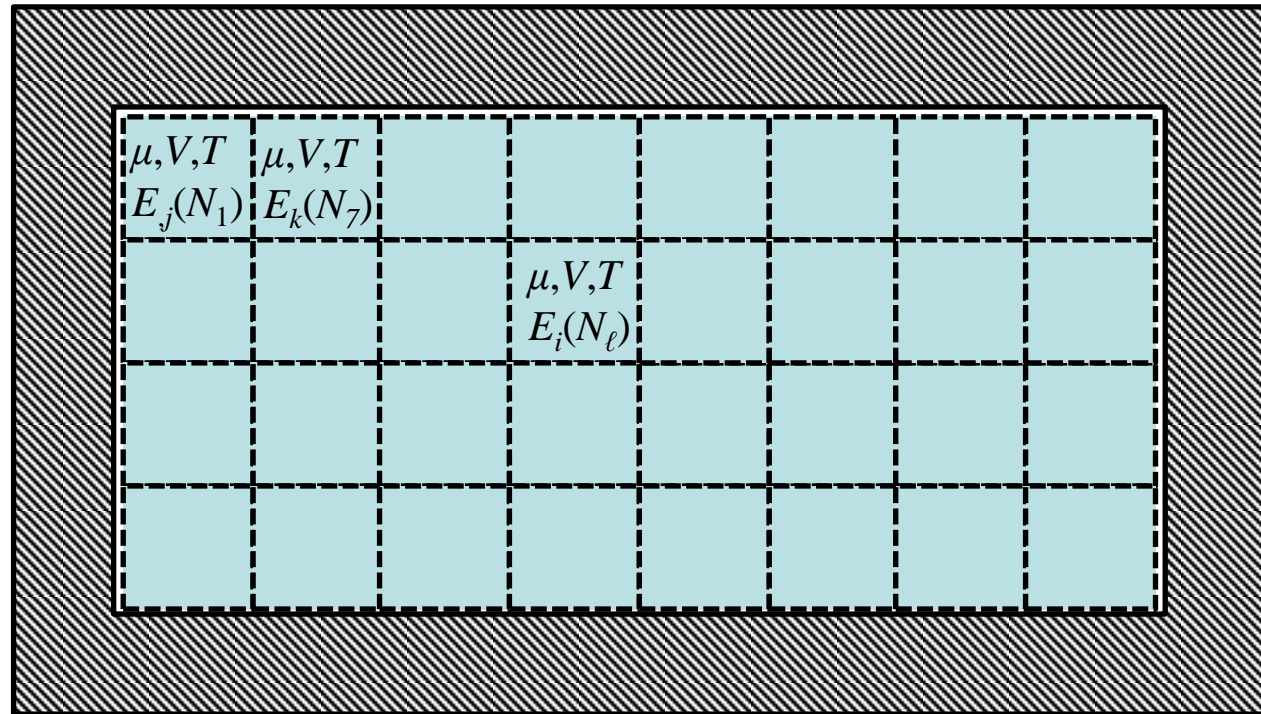
two-particle
quantum states

$$E_{\mathbf{n}}(2) = \frac{h^2}{8mV^{2/3}} (n_{x1}^2 + n_{y1}^2 + n_{z1}^2 + n_{x2}^2 + n_{y2}^2 + n_{z2}^2)$$

Find the most probable distribution for the states in the grand-canonical ensemble, subject to constraints of the system,

Constraints on the system:

$$\left\{ \begin{array}{l} \sum_{N_k} \left[\sum_j A_j(N_k) \right] = \mathcal{A} \\ \sum_{N_k} \left[\sum_j A_j(N_k) E_j(N_k) \right] = \mathcal{E} \\ \sum_{N_k} \left[\sum_j A_j(N_k) N_k \right] = \mathcal{N} \end{array} \right.$$



Most probable distribution for the Grand Canonical Ensemble

The ways the ensemble can be distributed among systems with N molecule and state i

$$W(\{\mathbf{A}\}) = \frac{\mathcal{A}!}{\prod_{N_k} \prod_j A_j(N_k)!}$$

Constraints on the distribution

$$\left\{ \begin{array}{l} \sum_{N_k} \left[\sum_j A_j(N_k) \right] = \mathcal{A} \\ \sum_{N_k} \left[\sum_j A_j(N_k) E_j(N_k) \right] = \mathcal{E} \\ \sum_{N_k} \left[\sum_j A_j(N_k) N_k \right] = \mathcal{N} \end{array} \right.$$

Find the most probable distribution, subject to constraints of the system,

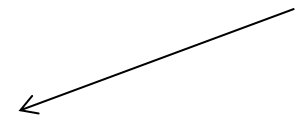
$$\frac{\partial}{\partial A_i(N_\ell)} \left\{ \ln W(\{\mathbf{A}\}) - \alpha \left(\sum_{N_k} \sum_j A_j(N_k) - \mathcal{A} \right) - \beta \left(\sum_{N_k} \sum_j A_j(N_k) E_j(N_k) - \mathcal{E} \right) - \gamma \left(\sum_{N_k} \sum_j A_j(N_k) N_k - \mathcal{N} \right) \right\} = 0$$

Number of systems in ensemble with N molecules in state j in most probable distribution

$$A_i^*(N_\ell) = e^{-(1+\alpha)} e^{-\beta E_i(N_\ell)} e^{-\gamma N_\ell}$$

Grand canonical partition function
Greek letter xi

$$P_i(N_\ell) = \frac{A_i^*(N_\ell)}{\mathcal{A}} = \frac{e^{-\beta E_i(N_\ell)} e^{-\gamma N_\ell}}{\sum_{N_k} \sum_j e^{-\beta E_j(N_k)} e^{-\gamma N_k}} = \frac{e^{-\beta E_i(N_\ell)} e^{-\gamma N_\ell}}{\Xi(V, \beta, \gamma)}$$



Probability includes **energy** (Boltzmann) factor and **molecule number** factor.

Thermodynamic relations for the grand canonical ensemble

$$\Xi(V, \beta, \gamma) = \sum_{N_k} \sum_j e^{-\beta E_{j(N_k)}} e^{-\gamma N_k}$$

We use the grand canonical partition function to find expressions for mechanical variables and then substitute them into a suitable thermodynamic relation:

$$\langle E \rangle = \frac{\sum_{N_\ell} \sum_i E_i(N_\ell) e^{-\beta E_i(N_\ell)} e^{-\gamma N_\ell}}{\sum_{N_k} \sum_j e^{-\beta E_{j(N_k)}} e^{-\gamma N_k}} = - \left(\frac{\partial \ln \Xi}{\partial \beta} \right)_{V, \gamma}$$

$$\langle P \rangle = \frac{\sum_{N_\ell} \sum_i \left(- \frac{\partial E_i(N_\ell)}{\partial V} \right) e^{-\beta E_i(N_\ell)} e^{-\gamma N_\ell}}{\sum_{N_k} \sum_j e^{-\beta E_{j(N_k)}} e^{-\gamma N_k}} = \frac{1}{\beta} \left(\frac{\partial \ln \Xi}{\partial V} \right)_{\beta, \gamma}$$

$$\langle N \rangle = \frac{\sum_{N_\ell} \sum_i N_\ell e^{-\beta E_i(N_\ell)} e^{-\gamma N_\ell}}{\sum_{N_k} \sum_j e^{-\beta E_{j(N_k)}} e^{-\gamma N_k}} = - \left(\frac{\partial \ln \Xi}{\partial \gamma} \right)_{\beta, V}$$

We construct the statistical mechanical equivalent of a thermodynamic relation and compare the two to identify the Lagrange multipliers β and γ

$$d [\ln \Xi(V, \beta, \gamma)] = - \langle E \rangle d\beta - \langle N \rangle d\gamma + \langle P \rangle \beta dV$$

Grand canonical partition function

Adding $d[\langle E \rangle \beta + \langle N \rangle \gamma]$ to both sides of the last equation gives:

$$d[\ln \Xi(V, \beta, \gamma) + \langle E \rangle \beta + \langle N \rangle \gamma] = \beta d\langle E \rangle + \gamma d\langle N \rangle + \langle P \rangle \beta dV$$

Compare this to the thermodynamic relation: $TdS = dE + PdV - \mu dN$

Gives: $\beta = \frac{1}{kT} \quad \gamma = \frac{-\mu}{kT}$

- The grand canonical ensemble can be called the **isopotential-isothermal-isochoric** ensemble

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

PV is the characteristic function of the grand canonical ensemble

$$G = N\mu = E + PV - TS \quad \Longrightarrow \quad PV = kT \ln \Xi(\mu, V, T)$$

Write the grand canonical partition function in terms of energy levels

$$\begin{aligned} \Xi(\mu, V, T) &= \sum_{N_k} \sum_E \Omega(E, N_k, V) e^{-E(N_k, V)/kT} e^{\mu N_k/kT} \\ &= \sum_{N_k} Q(N_k, V, T) e^{\mu N_k/kT} \end{aligned}$$

Fluctuations in the number of molecules in the grand canonical distribution

The variance of the number of molecule in the systems:

$$\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = kT^2 \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{N,T} = \left(\frac{\langle N \rangle^2 kT \kappa}{V} \right)_{N,T}$$

The distribution is very narrow for many molecule systems

$$\left(\frac{\partial \mu}{\partial \langle N \rangle} \right)_{V,T} = \frac{V^2}{N^2} \left(\frac{\partial P}{\partial V} \right)_{N,T}$$

The distribution is very narrow for many molecule systems

$$\frac{\sigma_N}{\langle N \rangle} = \left(\frac{kT \kappa}{V} \right)^{1/2} \propto \frac{1}{\sqrt{N}}$$

The distribution of the number of particles is narrow Gaussian function for many molecule systems

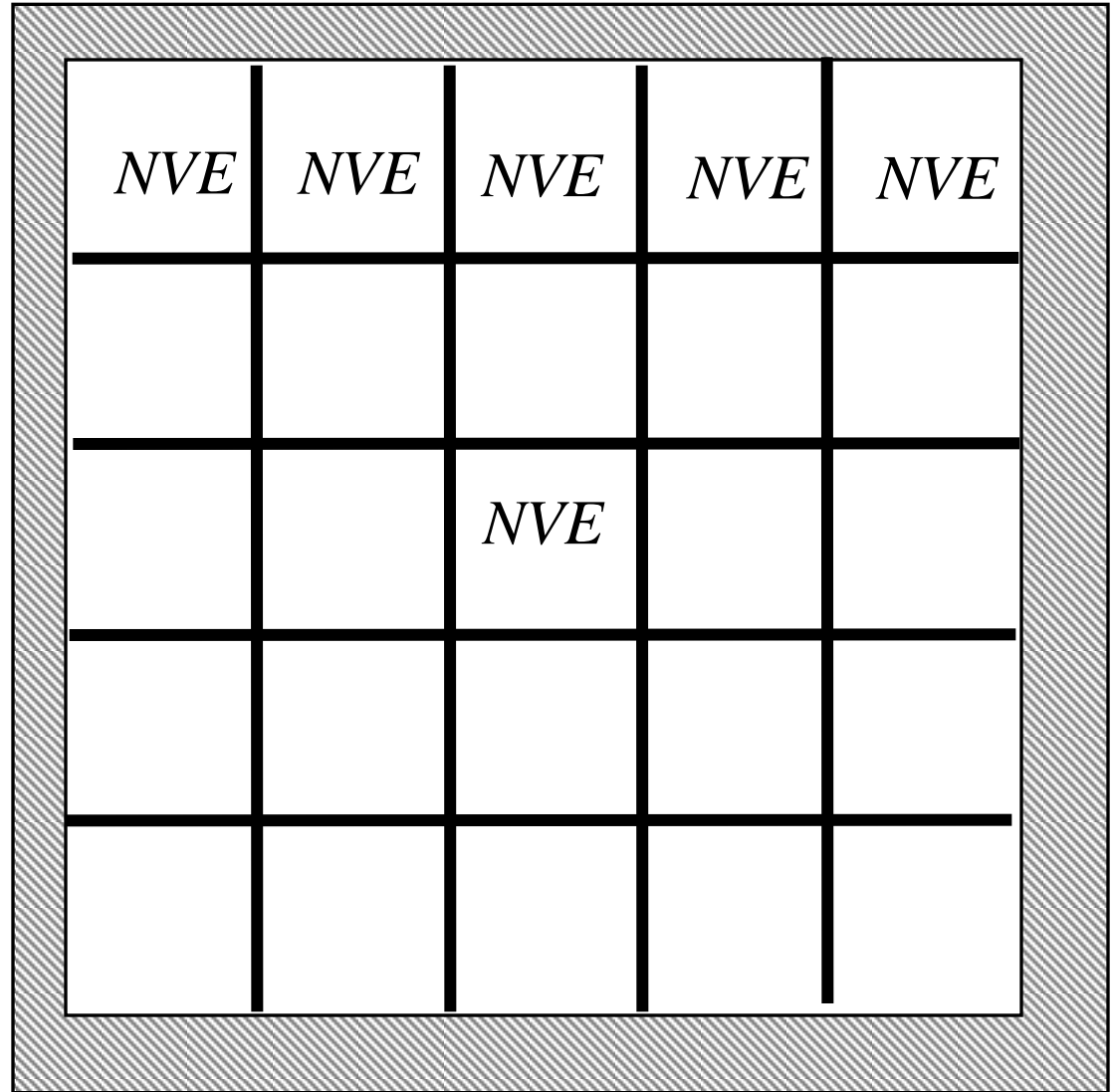
$$P(N) = P(\langle N \rangle) \exp \left[- \frac{(N - \langle N \rangle)^2}{2kT \left(\partial \langle N \rangle / \partial \mu \right)_{V,T}} \right]$$

Microcanonical (isoenergy, isochoric) ensemble

Each system is confined with

- Rigid walls (constant volume)
- Non-heat conducting walls (constant energy)

In this ensemble, each system does not have contact with the external world and so mechanics alone would suffice to describe the system!



Statistical mechanics of the microcanonical ensemble

Each system is confined to

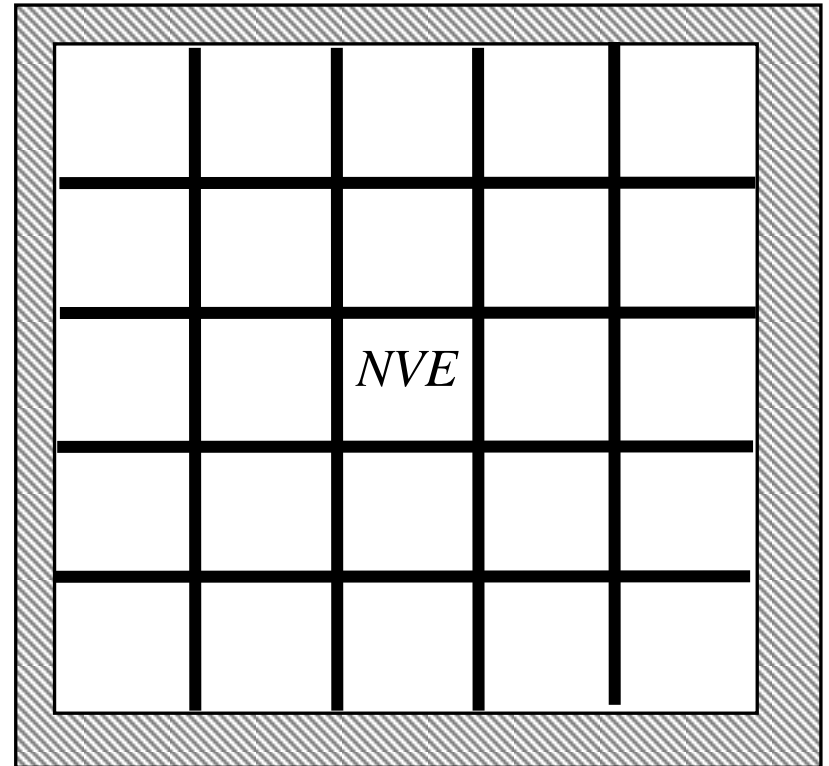
- Constant volume
- Constant energy, E
- The energy level may be degenerate, with individual states E_j all having energy E
- Degeneracy is $\Omega(E)$
- A_j is the occupancy of state j

Number of ways the systems in the ensemble can be distributed + constraint

$$W(\{\mathbf{A}\}) = \frac{\mathcal{A}!}{\prod_j A_j!} \quad \sum_j A_j = \mathcal{A}$$

$$\frac{\partial}{\partial A_i} \left\{ \ln W(\{\mathbf{A}\}) - \alpha \left(\sum_j A_j - \mathcal{A} \right) \right\} = 0 \Rightarrow A_j^* = e^{-(1+\alpha)} \Rightarrow \sum_{j=1}^{\Omega} A_j^* = \mathcal{A} = \sum_{j=1}^{\Omega} e^{-(1+\alpha)} = e^{-(1+\alpha)} \Omega$$

$$P_i = \frac{A_i^*}{\mathcal{A}} = \frac{1}{\Omega(N, V, E)} \quad \longrightarrow \quad S = k \ln \Omega(N, V, E)$$



Classical versions of the ensembles

Classical versions are available for the partition functions of other ensembles

- These expressions, along with the ergodic hypothesis form the basis of molecular dynamics and Monte Carlo simulation methods
- *See text for explicit classical forms for all partition functions*