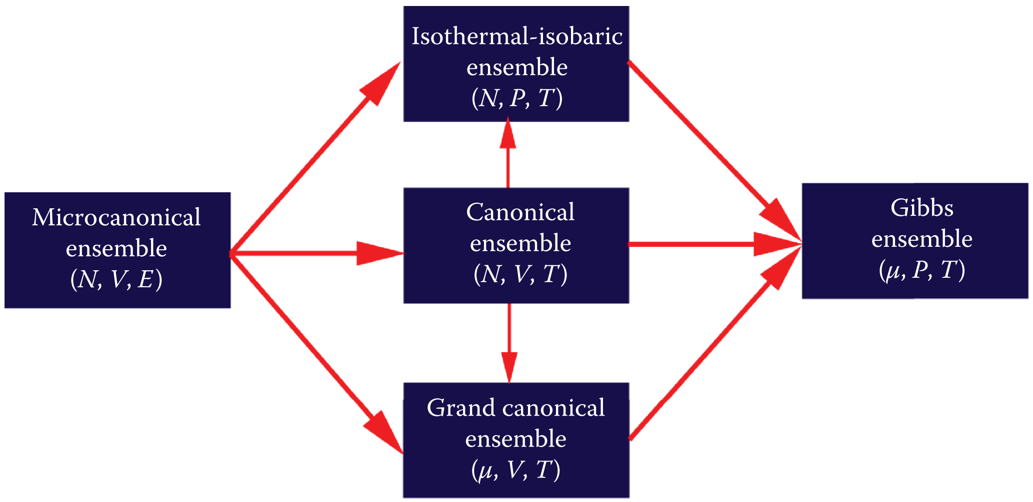
Ensemble

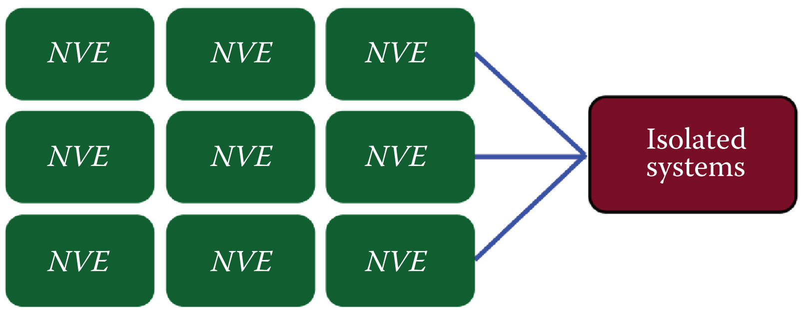
The concept of an ensemble is a brilliant mental construct

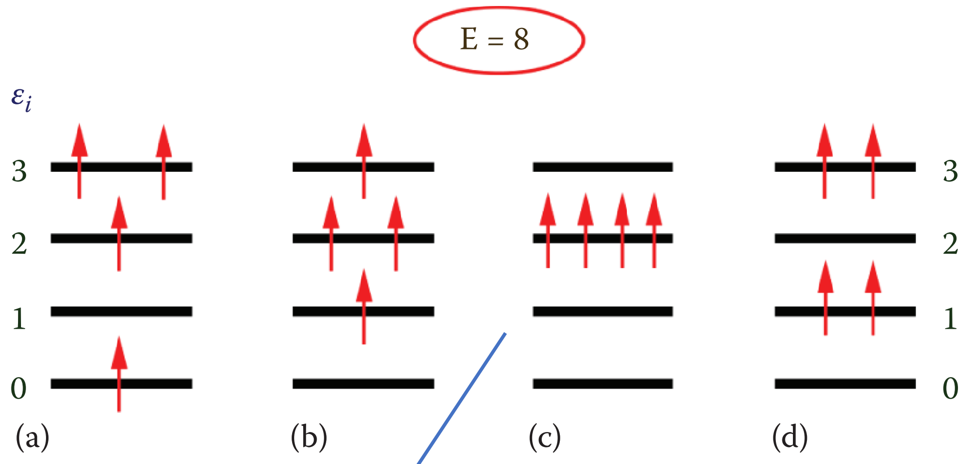
System must have a large number of microscopic states (positions and momenta), and natural motion of system at non-zero temperature takes the system through a finite fraction of these states in a time comparable to time of measurement of the macroscopic properties.

Different types of Ensembles



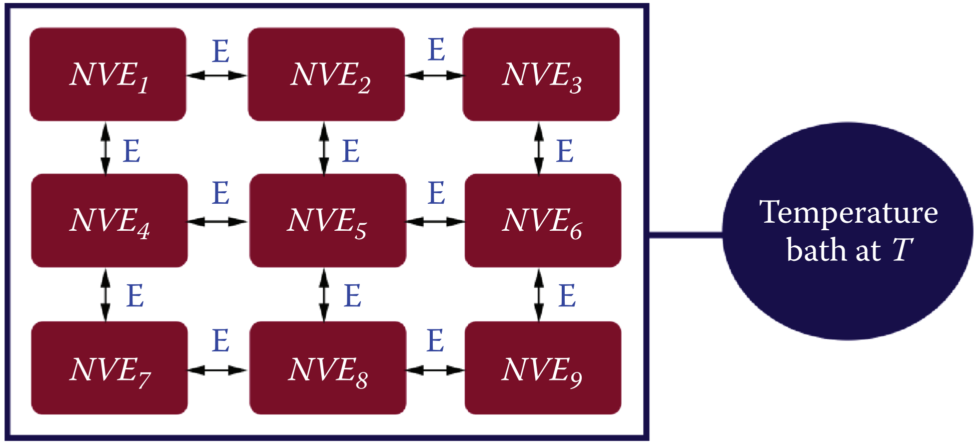
A microcanonical ensemble consists of mental replicas of the original (NVE) system (Isolated System)

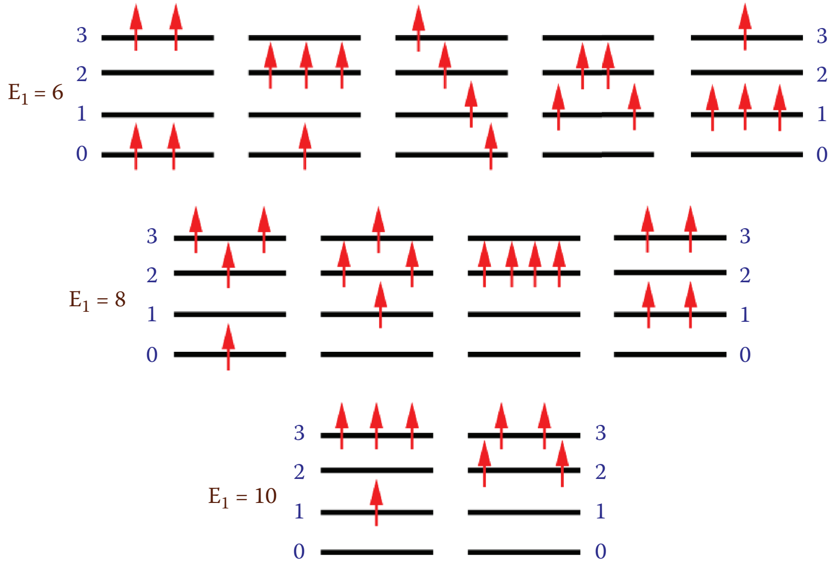




Four arrangements giving rise to same total energy (these are microstates)

Canonical ensemble





Canonical ensemble, where energy of each system can fluctuate. The systems are kept at temperature T by putting the super-system in a bath and establishing thermal contacts between the individual systems

$N_s \rightarrow$ Total no. of systems

$N \rightarrow$ No. of particles in each system

<u>Super-System</u>

(Isolated)

$N_t = N_s N$

$\hookrightarrow$ total no. of particles

$V_t = N_s V$

$\hookrightarrow$ total volume

E_t = Total energy

$(N_t, V_t, E_t) \rightarrow$ then we can construct a microcanonical ensemble starting here

$\boxed{\sum_j n_j = N_s \qquad \sum_j n_j E_j = E_t}$ $\rightarrow$ constraints

If the particles are distinguishable

$$\Omega(\{n_j\}) = \frac{N_s!}{n_1!\, n_2!\, n_3! \cdots\cdots}$$ (elaborate this later) . . . . (1)

* Biman Bagchi
* Mc.Quarrie

No. of ways . . . .

[In general, there are many distributions that are consistent with $\sum_j n_j = N_s$]

Probability of observing a given state n_j with energy E_j:

$$p_j = \frac{\bar{n}_j}{N_s} = \frac{1}{N_s} \boxed{\frac{\sum_j n_j \Omega(\{n_j\})}{\sum_j \Omega(\{n_j\})}} \rightarrow \bar{n}_j \quad \cdots \quad (2)$$

$$\simeq \frac{1}{N_s} \frac{n_j^* \Omega(\{n_j^*\})}{\Omega(\{n_j^*\})} = \frac{n_j^*}{N_s}$$

Most probable value

$n_j^* \rightarrow$ is the value of n_j that maximises $\Omega(\{n_j\})$

In any particular distribution, $\frac{n_j}{N_s}$ is the fraction of systems of the canonical ensemble in the j-th energy state. The overall probability p_j that a system is in the j-th energy state is obtained by averaging $\frac{n_j}{N_s}$ over all the allowed distributions, giving equal weight to the each one

principle of equal a priori probabilities

$$\frac{\partial}{\partial n_j}\left(\underbrace{\ln\Omega(\{n_j\})} - \alpha\sum_j n_j - \beta\sum n_j E_j\right) = 0$$

LUM

$$\left(0 - \cancel{n_j}\frac{1}{\cancel{n_j}} - \ln n_j^* - \alpha - \beta E_j\right) = 0$$

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

or, $\ln n_j^* = -(1+\alpha) - \beta E_j \qquad \alpha' = 1+\alpha$

$$= -\alpha' - \beta E_j$$

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

$$\sum n_j^* = N_s = e^{-\alpha'}\sum_j e^{-\beta E_j}$$

or, $e^{+\alpha'} = \dfrac{\sum_j e^{-\beta E_j}}{N_s} \Rightarrow$

$N_s = \sum n_j$

$\sum n_j E_j = E_t$

$\ln N! \simeq N\ln N - N$

(Stirling Approximation)

$$\ln\Omega(\{n_j\}) = \ln N_s! - \ln\prod_j n_j!$$

$$= N_s\ln N_s - N_s - \sum_j \ln n_j! \qquad \left[\, n_1!\, n_2! \cdots = \prod_j n_j! \,\right]$$

$$= N_s\ln N_s - \cancel{N_s} - \sum_j n_j\ln n_j \underbrace{+\sum_j n_j}_{N_s}$$

$$\ln\Omega = N_s\ln N_s - \sum_j n_j\ln n_j$$

$$P_j = \frac{n_j^*}{N_s} = \frac{\cancel{N_s}}{\sum_j e^{-\beta E_j}}\cdot\frac{e^{-\beta E_j}}{\cancel{N_s}}$$

$$P_j = e^{-\beta E_j}\Big/\sum_j e^{-\beta E_j}$$ Boltzmann distribution

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

canonical partition function

What about β? $\rightarrow$ LATER and show $\beta = \frac{1}{k_B T}$

$$\bar{E} = \sum_j P_j E_j = \frac{\sum_j E_j e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

$$d\bar{E} = \sum_j \left(E_j \, dP_j + P_j \, dE_j \right)$$

$$P_j = \frac{e^{-\beta E_j}}{Q} \; ; \quad \ln P_j = -\beta E_j - \ln Q$$

or,

$$E_j = -\frac{1}{\beta} \left(\ln P_j + \ln Q \right)$$

$$d\bar{E} = \sum_j \left(-\frac{1}{\beta}\right)\left(\ln P_j + \ln Q\right) dP_j + \sum_j P_j \left(\frac{\partial E_j}{\partial V}\right) dV$$

$$d\bar{E} = -\frac{1}{\beta} \sum_j \ln P_j \, dP_j - \frac{1}{\beta} \ln Q \underbrace{\cancel{\sum_j dP_j}}_{0} + \sum_j P_j \left(\frac{\partial E_j}{\partial V}\right) dV$$

$$d\bar{E} = -\frac{1}{\beta} \sum_j \ln P_j \, dP_j + \sum_j P_j \left(\frac{\partial E_j}{\partial V}\right) dV$$

$$S = -k_B \sum_j P_j \ln P_j$$

$$dS = -k_B \, d \sum_j P_j \ln P_j = -k_B \left(\underbrace{\sum_j P_j \cancel{/P_j} \, dP_j}_{0} + \sum_j \ln P_j \, dP_j \right)$$

$$dS = -k_B \sum_j \ln P_j \, dP_j$$

$$d\bar{E} = \left(-\frac{1}{\beta}\right)\left(-\frac{dS}{k_B}\right) + \sum_j P_j \left(\partial E_j / \partial V\right) dV$$

$$d\bar{E} = \frac{1}{\beta k_B} dS + \sum_j P_j \left(\partial E_j / \partial V\right) dV \quad \text{.. (A)}$$

Thermodynamics

$$p = -\sum_j P_j \left(\frac{\partial E_j}{\partial V}\right)$$

$$dE = T\,dS - p\,dV \quad \text{.. (B)}$$

$$\Rightarrow \quad T = \frac{1}{\beta k_B} \Rightarrow \beta = \frac{1}{k_B T}$$

$$Q = \sum_j e^{-\beta E_j}$$

$$\ln Q = \ln\left(\sum_j e^{-\beta E_j}\right)$$

$$\frac{\partial \ln Q}{\partial \beta} = \frac{1}{\sum_j e^{-\beta E_j}} \sum_j (-E_j) e^{-\beta E_j} = -\sum_j E_j e^{-\beta E_j} \Big/ \sum_j e^{-\beta E_j}$$

$$\bar{E} = \sum_j P_j E_j \qquad P_j = \frac{e^{-\beta E_j}}{Q}$$

$$= -\bar{E}$$

$$\beta = \frac{1}{k_B T}$$

$$d\beta = -\frac{1}{k_B T^2} dT$$

$$\text{or } \frac{\partial}{\partial \beta} = -k_B T^2 \frac{\partial}{\partial T}$$

$$\bar{E} = -\frac{\partial \ln Q}{\partial \beta}$$

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

Internal energy

$$\frac{\partial \ln Q}{\partial V} = \frac{1}{\sum_j e^{-\beta E_j}} (-\beta) \sum_j e^{-\beta E_j} \left(\frac{\partial E_j}{\partial V}\right)$$

$$= \beta\left(-\frac{\sum_j e^{-\beta E_j} \left(\partial E_j / \partial V\right)}{Q}\right) = \beta p$$

Pressure

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

$$S = -k_B \sum_j P_j \ln P_j$$

$$= -k_B \sum_j \frac{e^{-\beta E_j}}{Q} \ln\left(\frac{e^{-\beta E_j}}{Q}\right) = -k_B \sum_j \frac{e^{-\beta E_j}}{Q}\left(-\beta E_j - \ln Q\right)$$

$$= k_B \beta \left(\frac{\sum e^{-\beta E_j} E_j}{Q}\right) + k_B \ln Q$$

$$S = \frac{1}{T}\bar{E} + k_B \ln Q = k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} + k_B \ln Q$$

$$A = E - TS$$

$\downarrow$

Helmholtz free energy

$$A = \cancel{k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}} - \cancel{k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}} - k_B T \ln Q$$

$$A = -k_B T \ln Q$$

$\rightarrow$ Thermodynamic potential in canonical ensemble

$$S = k_B \ln \Omega$$

$\hookrightarrow$ T.P. in mic-rocanonical ensemble

Grand-canonical ensemble