The Grand Canonical Ensemble

IN THE preceding chapter we developed the formalism of the canonical ensemble and established a scheme of operations for deriving the various thermodynamic properties of a given physical system. The effectiveness of that approach became clear from the examples discussed there; it will become even more vivid in the subsequent studies carried out in this text. However, for a number of problems, both physical and chemical, the usefulness of the canonical ensemble formalism turns out to be rather limited and it appears that a further generalization of the formalism is called for. The motivation that brings about this generalization is physically of the same nature as the one that led us from the microcanonical to the canonical ensemble—it is just the next natural step from there. It comes from the realization that not only the energy of a system but the number of particles as well is hardly ever measured in a "direct" manner; we only estimate it through an indirect probing into the system. Conceptually, therefore, we may regard both N and E as *variables* and identify their expectation values, $\langle N \rangle$ and $\langle E \rangle$, with the corresponding thermodynamic quantities.

Microcanonical Ensemble ⇨ Canonical Ensemble

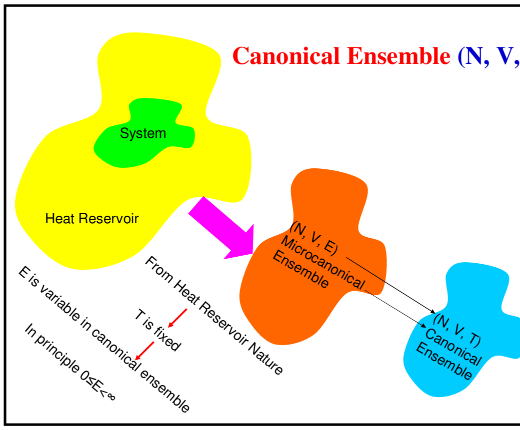
Ω (N, V, E) ⟶ $H = E$

Σ (N, V, E) ⟶ $H \le E$

Γ (N, V, E) ⟶ $(E-1/2\Delta) \le H \le (E+1/2\Delta)$

Microcanonical Ensemble (N, V, E)

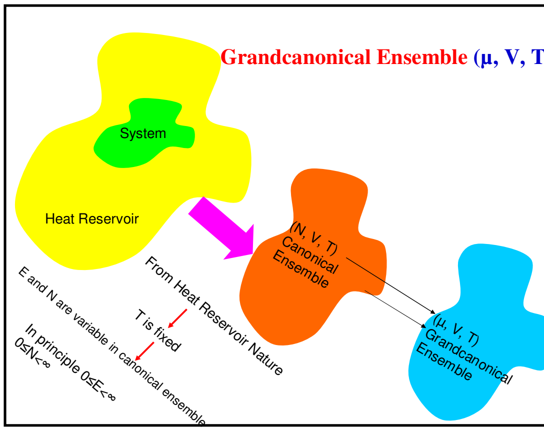
Canonical Ensemble (N, V, T)



Microcanonical Ensemble ⇨ Canonical Ensemble

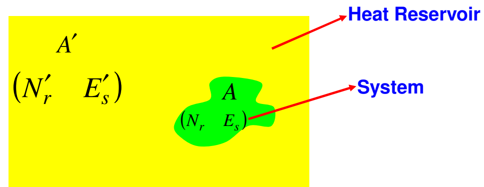
(N, V, E) ⟶ (N, V, T)

Grandcanonical Ensemble (μ, V, T)



The procedure for studying the statistics of the variables N and E is self-evident. We may *either* (i) consider the given system A to be immersed in a large reservoir A' with which it can exchange both energy and particles *or* (ii) regard it as a member of what we may call a *grand canonical ensemble*, which consists of the given system A and a large number of (mental) copies thereof, the members of the ensemble carrying out a mutual exchange of both energy and particles. The end results, in either case, are asymptotically the same.

Equilibrium between a system and a heat reservoir



T is fixed but E_s , E'_s and N_r, N'_r are variables

$$E_s + E'_s = E^{(0)} = const \qquad N_r + N'_r = N^{(0)} = const$$

$$\Omega^o(N_r, N_r^{'}, E_s, E_s^{'}) = \Omega'(N_r^{'}, E_S^{'})\Omega(N_r, E_S)$$
$$= \Omega(N_r, E_S)\Omega'(N^{(o)} - N_r, E^{(o)} - E_s)$$
$$= \Omega(N_r, E_s)\Omega'(N_r, E_s) = \Omega^{(o)}(N_r, E_s)$$

$$P(N_r, E_s) = P_{r,s} = \frac{\Omega^{(o)}(N_r, E_s)}{\Omega^{(o)}{}_{tot}} = cte$$

$$\Omega^{(o)}(N_r, E_s) = \Omega(N_r, E_s)\Omega'(N_{r'}, E_{s'}) \propto \Omega'(N'_r, E'_s)$$

$$P_{r,s} \propto \Omega'(N_{r'}, E_{s'}) \Rightarrow P_{r.s} \propto \Omega'(N^{(o)} - N_r, E^{(o)} - E_S)$$

$$\ln\Omega'(N_{r'}, E_{s'}) = \ln\Omega'(N^{(o)} - N_r, E^{(o)} - E_s)$$
$$= \ln\Omega'(N^{(o)}, E^{(o)}) + \left(\frac{\partial \ln\Omega'}{\partial N'}\right)(-N_r) + \left(\frac{\partial \ln\Omega'}{\partial E'}\right)(-E_s) + \ldots$$
$$\approx \ln\ \Omega'(N^{(o)}, E^{(o)}) + \frac{\mu'}{KT'}N_r - \frac{1}{KT}E_s$$

$$\left(\frac{\partial \ln\Omega'}{\partial N'}\right) = -\frac{\mu'}{KT'} \quad , \quad \left(\frac{\partial \ln\Omega'}{\partial E'}\right) = \frac{1}{KT}$$

$$\ln\ P_{r,s} \propto \ln\Omega'(N^{(o)} - N_r, E^{(o)} - E_s) = \frac{\mu' N_r}{KT'} - \frac{1}{KT'}ES$$

$$\ln\ P_{r,s} \propto \frac{\mu' N_r}{KT'} - \frac{1}{KT'}ES$$

$$P_{r,s} \propto \exp\left(\frac{\mu' N_r}{KT'} - \frac{1}{KT'}ES\right)$$

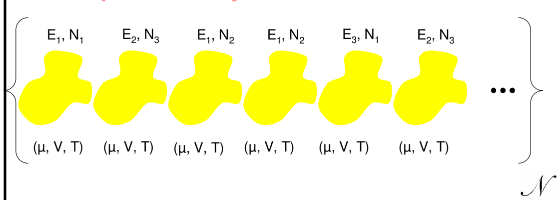
$$P_{r,s} \propto \exp\left(-\alpha N_r - \beta E_s\right)$$

$$\alpha = \frac{-\mu}{KT} \qquad \& \qquad \beta = \frac{1}{KT}$$

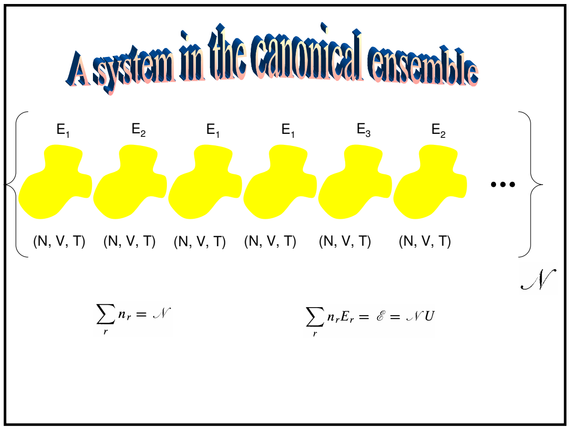
$$P_{r,s} = \frac{\exp(-\alpha N_r - \beta E_S)}{\sum_{r,s}\exp(-\alpha N_r - \beta E_S)}$$

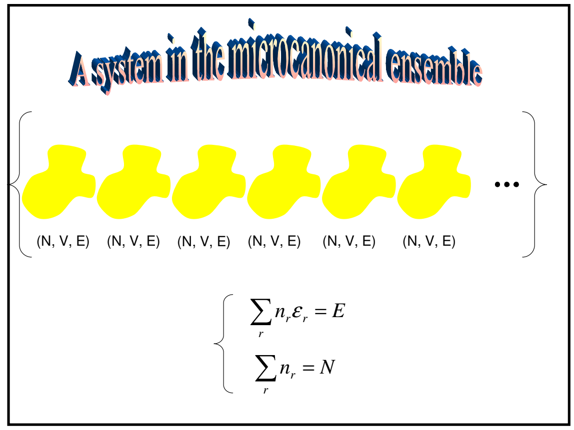
Partition Function

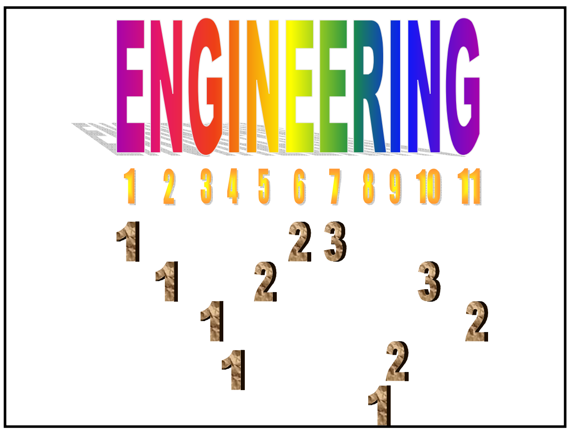
A system in the grandcanonical ensemble

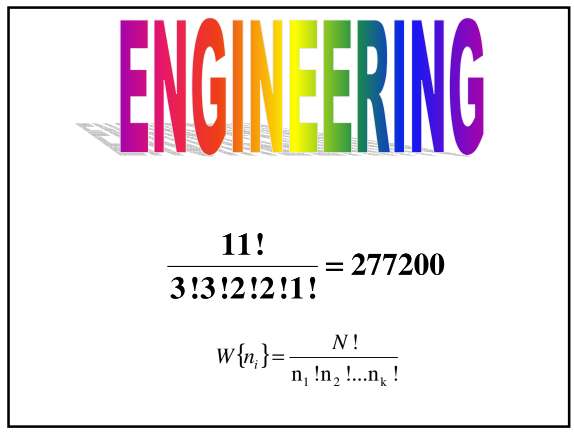


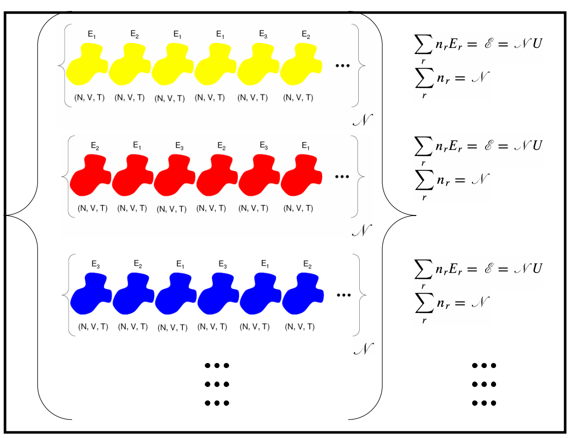
$$\sum_{r.s} n_{r,s} = \mathcal{N} \qquad \sum_{r,s} n_{r,s}E_s = \mathcal{N}\overline{E} \qquad \sum_{r,s} n_{r,s}N_r = \mathcal{N}\overline{N}$$

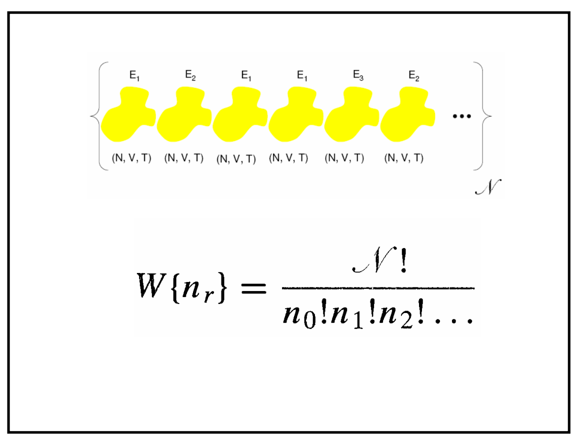

A system in the canonical ensemble
E_1 E_2 E_1 E_1 E_3 E_2
(N, V, T) (N, V, T) (N, V, T) (N, V, T) (N, V, T) (N, V, T)
$\mathcal{N}$
$\sum_r n_r = \mathcal{N}$
$\sum_r n_r E_r = \mathcal{E} = \mathcal{N} U$

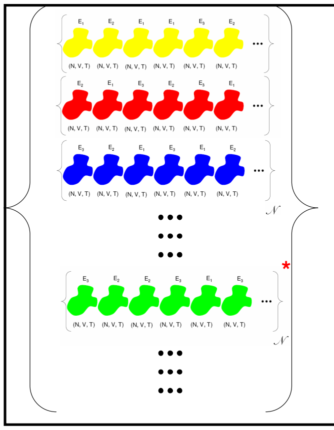

A system in the microcanonical ensemble
(N, V, E) (N, V, E) (N, V, E) (N, V, E) (N, V, E) (N, V, E)
$\sum_r n_r \varepsilon_r = E$
$\sum_r n_r = N$


ENGINEERING
1 2 3 4 5 6 7 8 9 10 11


ENGINEERING
$\frac{11!}{3!3!2!2!1!} = 277200$
$W\{n_i\} = \frac{N!}{n_1!n_2!\ldots n_k!}$


$\sum_r n_r E_r = \mathcal{E} = \mathcal{N} U$
$\sum_r n_r = \mathcal{N}$


E_1 E_2 E_1 E_1 E_3 E_2
(N, V, T) (N, V, T) (N, V, T) (N, V, T) (N, V, T) (N, V, T)
$\mathcal{N}$
$W\{n_r\} = \frac{\mathcal{N}!}{n_0!n_1!n_2!\ldots}$

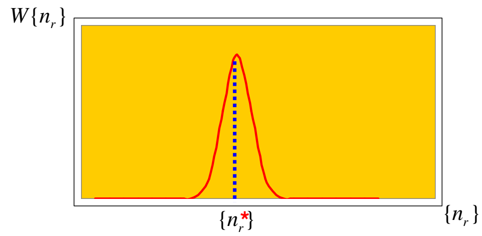


$$\sum_r n_r E_r = \mathscr{E} = \mathscr{N}U$$
$$\sum_r n_r = \mathscr{N}$$
$$\sum_r n_r E_r = \mathscr{E} = \mathscr{N}U$$
$$\sum_r n_r = \mathscr{N}$$
$$\sum_r n_r E_r = \mathscr{E} = \mathscr{N}U$$
$$\sum_r n_r = \mathscr{N}$$

$\vdots$

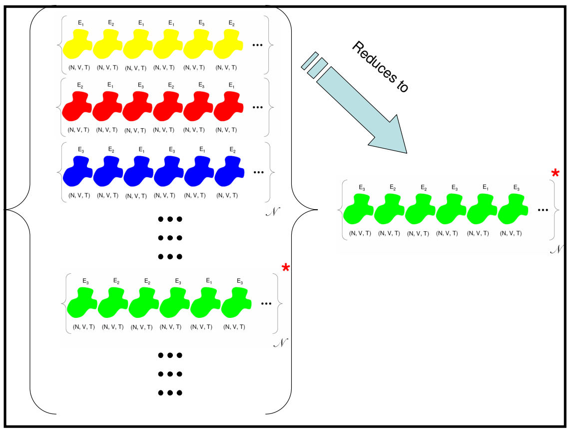
$$\sum_r n_r^* E_r = \mathscr{E} = \mathscr{N}U$$
$$\sum_r n_r^* = \mathscr{N}$$

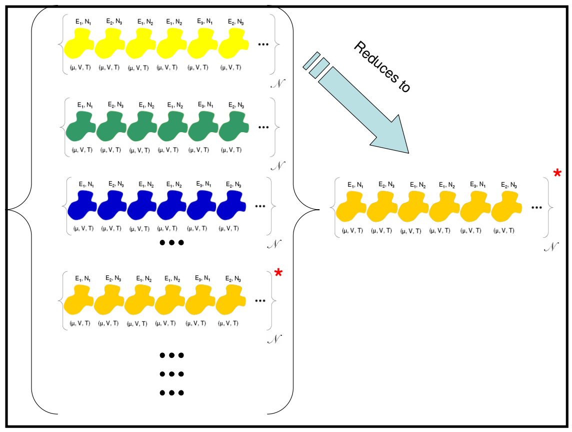
$\vdots$



$$P_r = \langle n_r \rangle = \frac{\sum'_{\{n_r\}} n_r W\{n_r\}}{\sum'_{\{n_r\}} W\{n_r\}} \approx \frac{n_r^*}{\sum_r n_r^*} = \frac{n_r^*}{\mathscr{N}}$$

$W\{n_r^*\}$ >> All the other $W\{n_r\}$'s





The method of most probable values

$$W\{n_r\} = \frac{\mathscr{N}!}{\prod_{r,s} n_{r,s}!}$$

$$\ln W\{n_{r,s}\} = \ln(\mathscr{N}!) - \ln(\prod_{r,s} n_{r,s}!) = \ln(\mathscr{N}!) - \sum_{r,s} \ln(n_{r,s}!)$$

$$\ln W\{n_r\} \approx \mathscr{N}\ln\mathscr{N} - \mathscr{N} - \sum_{r,s}(n_{r,s}\ln n_{r,s} - n_{r,s})$$
$$= \mathscr{N}\ln\mathscr{N} - \mathscr{N} - \sum_{r,s} n_{r,s}\ln n_{r,s} + \sum_{r,s} n_{r,s}$$
$$= \mathscr{N}\ln\mathscr{N} - \mathscr{N} - \sum_{r,s} n_{r,s}\ln n_{r,s} + \mathscr{N}$$
$$= \mathscr{N}\ln\mathscr{N} - \sum_{r,s} n_{r,s}\ln n_{r,s}$$

$$W\{n_{r,s}\} = \mathscr{N}\ln\mathscr{N} - \sum_{r,s} n_{r,s}\ln n_{r,s}$$

$$\sum_{r,s} n_{r,s} = \mathscr{N} \qquad \sum_{r,s} n_{r,s}E_s = \mathscr{N}\bar{E} \qquad \sum_{r,s} n_{r,s}N_r = \mathscr{N}\bar{N}$$

$$\delta(\ln W\{n_{r,s}\}) = 0 - \sum_{r,s}(\ln n_{r,s} + n_{r,s}\frac{1}{n_{r,s}})\delta n_{r,s}$$
$$\delta(\ln W\{n_{r,s}\}) = -\sum_{r,s}(\ln n_{r,s} + 1)\delta n_{r,s}$$

$$\delta\left[\ln W\{n_{r,s}\} - \gamma\sum_{r,s} n_{r,s} - \beta\sum_{r,s} n_{r,s}E_s - \alpha\sum_{r,s} n_{r,s}N_r\right] = 0$$

$$\left\{\begin{array}{l} \sum_{r,s} n_{r,s} = \mathscr{N} \\ \sum_{r,s} n_{r,s}E_s = \mathscr{N}\bar{E} \\ \sum_{r,s} n_{r,s}N_r = \mathscr{N}\bar{N} \end{array}\right. \Longrightarrow \left\{\begin{array}{l} \sum_{r,s} \delta n_{r,s} = 0 \\ \sum_{r,s} E_s\delta n_{r,s} = 0 \\ \sum_{r,s} N_r\delta n_{r,s} = 0 \end{array}\right.$$

$$\delta\left[\ln W\{n_{r,s}\} - \gamma\sum_{r,s} n_{r,s} - \beta\sum_{r,s} n_{r,s}E_s - \alpha\sum_{r,s} n_{r,s}N_r\right] = 0$$

$$\delta\ln W\{n_{r,s}\} - \gamma\sum_{r,s}\delta n_{r,s} - \beta\sum_{r,s} n_{r,s}\delta E_s - \alpha\sum_{r,s} n_{r,s}\delta N_r = 0$$

$$\delta(\ln W\{n_{r,s}\}) = -\sum_{r,s}(\ln n_{r,s}+1)\delta n_{r,s}$$

$$-\sum_{r,s}(\ln n_{r,s}+1)\delta n_{r,s} - \gamma\sum_{r,s}\delta n_{r,s} - \beta\sum_{r,s} E_s\delta n_{r,s} - \alpha\sum_{r,s} N_r\delta n_{r,s} = 0$$

$$\sum_{r,s}(\ln n_{r,s} + 1 + \gamma + \beta E_s + \alpha N_r)\delta n_{r,s} = 0$$

$$\ln n^*_{r,s} + 1 + \gamma + \beta E_s + \alpha N_r = 0$$

$$\ln n^*_{r,s} = -(1+\gamma) - \beta E_s - \alpha N_r$$

$$\ln n^*_{r,s} = \ln C - \beta E_s - \alpha N_r$$

$$\ln n^*_{r,s} = \ln C - \beta E_s - \alpha N_r$$

$$\ln n^*_{r,s} - \ln C = -\beta E_s - \alpha N_r$$

$$\ln\frac{n^*_{r,s}}{C} = -\beta E_s - \alpha N_r$$

$$n^*_{r,s} = C\exp(-\beta E_s - \alpha N_r)$$

$$\sum_{r,s} n^*_{r,s} = \mathcal{N} = \sum_{r,s} Ce^{-\beta E_s - \alpha N_r} = C\sum_{r,s} e^{-\beta E_s - \alpha N_r}$$

$$C = \frac{\mathcal{N}}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}}$$

$$n^*_{r,s} = \frac{\mathcal{N}}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}} e^{-\beta E_s - \alpha N_r}$$

$$\frac{n^*_{r,s}}{\mathcal{N}} = \frac{e^{-\beta E_s - \alpha N_r}}{\sum_{r} e^{-\beta E_s - \alpha N_r}}$$

$$\sum_{r,s} n^*_{r,s}E_s = \mathcal{N}\,\overline{E}$$

$$\sum_{r,s}\mathcal{N}\frac{e^{-\beta E_s - \alpha N_r}}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}}E_s = \mathcal{N}\,\overline{\mathrm{E}}$$

$$\mathcal{N} = cte \quad \rightarrow \mathcal{N}\sum_{r,s}\frac{e^{-\beta E_s - \alpha N_s}}{\sum_{r,s} e^{-\beta E_r}}E_s = \mathcal{N}\,\overline{\mathrm{E}}$$

$$\sum_{r,s}\frac{e^{-\beta E_s - \alpha N_r}}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}}E_s = \overline{E}$$

$$\frac{\sum_{r,s} E_s e^{-\beta E_s - \alpha N_r}}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}} = \overline{E}$$

$$\frac{n^*_{r,s}}{\mathcal{N}} = \frac{e^{-\beta E_s - \alpha N_r}}{\sum_{r} e^{-\beta E_s - \alpha N_r}}$$

$$\sum_{r,s} n^*_{r,s}N_r = \mathcal{N}\,\overline{N}$$

$$\sum_{r,s}\mathcal{N}\frac{e^{-\beta E_s - \alpha N_r}}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}}N_r = \mathcal{N}\,\overline{\mathrm{N}}$$

$$\mathcal{N} = cte \rightarrow \mathcal{N}\sum_{r,s}\frac{e^{-\beta E_s - \alpha N_s}}{\sum_{r,s} e^{-\beta E_r}}N_r = \mathcal{N}\overline{\mathrm{N}}$$

$$\sum_{r,s}\frac{e^{-\beta E_s - \alpha N_r}}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}}N_r = \overline{N}$$

$$\frac{\sum_{r,s} N_r e^{-\beta E_s - \alpha N_r}}{\sum_{r,s} e^{-\beta E_s - \alpha N_r}} = \overline{N}$$