TOPICS IN CONDENSED MATTER PHYSICS - LECTURE 1

ELEMENTS OF STATISTICAL QUANTUM MECHANICS

GENERAL CONSIDERATIONS

- LIMITED KNOWLEDGE OF A QUANTUM SYSTEM → QUANTUM THERMODYNAMICS
  DIFFERENCE BETWEEN TWO TYPES OF PROBABILITY: THE "STRANGE, FUNDAMENTAL" PROBABILITY OF QM (WHICH APPEAR FOR ONE SINGLE PARTICLE ALREADY) AND THE "STATISTICAL PROBABILITY" DUE TO LIMITED KNOWLEDGE OF A SYSTEM WITH TYPICALLY MANY PARTICLES

- QUANTITIES OF INTEREST ARE:
  - → PARTITION FUNCTION Z
  - → STATISTICAL OPERATOR $\hat{\varrho}$
  - → ENTROPY S

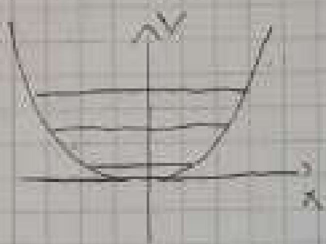
  OUT OF WHICH WE CALCULATE ENERGY, PRESSURE, THERM. POTEN

- IN DEPENDENCE OF THE SYSTEM AND THE ENVIRONMENT, ONE SPEAKS OF MICROCANONICAL, CANONICAL OR GRANDCANONICAL ENSEMBLES (GENERALIZATIONS ARE POSSIBLE).

- APPLICATIONS IN ALL REALMS OF PHYSICS
  - → GAS OF FERMIONS OR BOSONS (BOTH IN PARTICLE AND SOLID STATE PHYSICS)
    - GAS OF ELECTRONS IN A CRYSTAL
    - NUCLEI AND NEUTRON STARS
    - GAS OF PHOTONS
    - GAS OF PHONONS
  - → LINK TO THEORY OF INFORMATION

1 EXAMPLE - SINGLE PARTICLE IN A ONE-DIMENSIONAL HARMONIC OSCILLATOR AT A GIVEN TEMPERATURE T

$V(x) = \frac{1}{2} m\omega^2 x^2$



THE ON BASIS OF EIGENVALUES OF THE HAMILTONIAN $H = T + V$ IS GIVEN BY

$\{|m\rangle\}$ with $H|m\rangle = E_m|m\rangle$

$$E_m = \omega\left(m + \frac{1}{2}\right) \qquad [\hbar = 1]$$

recall $H = T + V = \omega(a^\dagger a + 1/2)$

with $[a, a^\dagger] = 1$, $|m\rangle = N(a^\dagger)^m|0\rangle$.

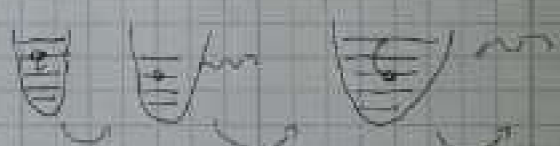
SUPPOSE NOW THAT THIS SYSTEM IS COMPLETELY ISOLATED AND WE MEASURE THE ENERGY. THEN IN THIS CASE IF YOU KNOW THE ENERGY YOU KNOW THE STATE

$\rightsquigarrow E_m = \omega(m + 1/2)$ fixes unambiguously $|s\rangle \equiv |m\rangle$.

THIS IS INDEED THE "MICROCANONICAL" SYSTEM FOR THIS SIMPLE EXAMPLE $E = E_m$ ie NO ENERGY FLUCTUATION!!

SUPPOSE NOW THAT WE PLACE OUR OSCILLATOR IN A THERMAL BATH WITH TEMPERATURE T. THE ENERGY OF THE SYSTEM IS NOT FIXED BUT JUMPS UP AND DOWN.

OVEN AT TEMPERATURE T



WE REALIZE THAT $\langle E\rangle$ IS CONSTANT BUT E FLUCTUATES BECAUSE OF ENERGY EXCHANGE WITH THE ENVIRONMENT

THE PARTITION FUNCTION Z IS:

$$Z = \sum_{m=0}^{\infty} e^{-\beta E_m}$$

$\beta = \frac{1}{k_B T} = \frac{1}{T}$, E_m "eigenvalues", $\sum_m$ sum over all the energy eigenvalues

- THE IDEA IS THAT THE STATE "$|m\rangle$" IS REALIZED WITH A PROBABILITY PROPORTIONAL TO $e^{-\beta E_m} = e^{-E_m/T}$
- FOR A CERTAIN T THE STATES WITH $E_m \lesssim T$ GIVE A SIZABLE CONTRIBUTION TO Z. CONVERSELY, THE LEVELS WITH $E_m \gg T \to$ ARE ININFLUENTE SINCE $e^{-E_m/T} \ll 1$ FOR THOSE CASES.
- THE PROBABILITY THAT THE SYSTEM IS IS DESCRIBED BY $|m\rangle$ IS GIVEN BY

$$P_m = \frac{e^{-\beta E_m}}{Z}$$

OBVIOUSLY, BY CONSTRUCTION:

$$\sum_{m=0}^{\infty} P_m = \frac{\sum_m e^{-\beta E_m}}{Z} = \frac{Z}{Z} = 1$$

as it must!

- THE ENERGY IS NOT FIXED, BUT WE CAN EASILY CALCULATE THE MEAN ENERGY

$$\langle E \rangle = \sum_{m=0}^{\infty} P_m E_m \qquad \text{(weighted sum)}$$

ONE CAN ALSO CALCULATE THE FLUCTUATION AS:

$$\Delta E = \sqrt{\langle E^2 \rangle - \langle E \rangle^2}$$

no short example

- THE ENERGY $\langle E \rangle$ CAN BE ALSO BE CALCULATED AS:

$$\boxed{\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z}$$

(THIS IS INDEED "GENERAL" ALTHOUGH WE PRESENT IT IN A SIMPLIFIED FRAMEWORK)

NAMELY

$$Z = Z(\beta) = \sum_n e^{-\beta E_n}$$

$$\frac{\partial}{\partial \beta} \ln Z = \frac{\frac{\partial Z}{\partial \beta}}{Z} = \frac{\sum_n (-E_n) e^{-\beta E_n}}{Z} = -\sum_n E_n P_n = -\langle E \rangle$$

APPLYING THE SAME TRICKS ONE CAN EASILY SHOW THAT:

$$\boxed{(\Delta E)^2 = \frac{\partial^2}{\partial \beta^2} \ln Z}$$

SUBTLE BUT IMPORTANT POINT: IN A CERTAIN SYSTEM, WITH A CERTAIN TEMPERATURE T, T IS "FIXED" (T = 100 MeV, e.g.) HOW CAN YOU DERIVE W.R.T. A FIXED ONE?

WHAT IT IS MEANT IS THE FOLLOWING:

LET T_0 BE THE TEMPERATURE OF THE SYSTEM

THEN: $Z(\beta = 1/T)$ WITH β AS A VARIABLE

$$\langle E \rangle = -\left(\frac{\partial}{\partial \beta} \ln Z\right)_{\beta = \beta_0 = 1/T_0}$$

FIRST DERIVE, THEN SET THE NUMBER

LIMITS:

$\beta = 0$ $(T = \infty)$ $\mapsto$ ALL STATES $|n\rangle$ ARE EQUIPROBABLES!

$\beta = \infty$ $(T = 0)$ $\mapsto$ $P_{|0\rangle} = 1$ $\to$ ONLY THE GROUND STATE IS REALIZED

$P_{|n \neq 0\rangle} = 0$

THIS IS INDEED A GENERAL PROPERTY.

2 EXAMPLE : 3D HARMONIC OSCILLATOR

$V(x,y,z) = \frac{1}{2} m \omega^2 (x^2+y^2+z^2)$

(NOTE: the same ω in all 3 directions!)

$$H = T + V = -\frac{\hbar^2}{2m}\Delta + V = \hbar\omega\left(a_x^\dagger a_x + a_y^\dagger a_y + a_z^\dagger a_z + \underbrace{\frac{3}{2}}_{\frac{1}{2}+\frac{1}{2}+\frac{1}{2}}\right)$$

A certain state which is an eigenstate of H is then defined by 3 natural numbers

$$|m_1, m_2, m_3\rangle \qquad \text{with } m_k = 0,1,2,\ldots$$

$$E = \hbar\omega(m_1+m_2+m_3+3/2) = \hbar\omega(N+3/2) = E_N$$

where N is the "principal quantum nr" for this system.

THE GROUND STATE IS GIVEN BY $m_1 = m_2 = m_3 = 0 \rightarrow N = 0$. THERE IS ONLY ONE STATE WITH THIS ENERGY: $|0,0,0\rangle$.

BUT IF WE CONSIDER $N=1$ WE ALREADY HAVE A DEGENERACY OF "3":

$|1,0,0\rangle, |0,1,0\rangle, |0,0,1\rangle$ have an energy of $E_1 = \hbar\omega(1+\ldots$

DEGENERACY FACTOR D_N FOR A CERTAIN "N" IS GIVEN BY THE FOLLOWING REASONING:

$N = m_1 + m_2 + m_3$

FOR A FIXED m_1, m_2 CAN VARY FROM "0" UP TO "$N - m_1 + 1$". THEN, SUM OVER m_1

$$D_N = \sum_{m_1=0}^{N} (N - m_1 + 1) = (N+1)(N+1) - \frac{N(N+1)}{2} = \frac{1}{2}(N+1)(N+\ldots$$

FOR INSTANCE:

$N=5,\ m_1=2 \mapsto m_2 = 0,1,2,3$

$$m_1 \mapsto \underbrace{m_2 = 0, 1, \ldots, N-m_1}_{N-m_1+1 \text{ values}}$$

NOW, ASSUME THAT THE OSCILLATOR IS COMPLETELY ISOLATED AND HAS A CERTAIN ENERGY E_N. IN THIS CASE, BECAUSE OF THE DEGENERACY, EVEN IF WE KNOW THE ENERGY EXACTLY, WE DO NOT KNOW THE STATE.

EACH ONE OF THE $\frac{1}{2}(N+1)(N+2)$ STATES WITH

$|m_1, m_2, m_3 \,/\, m_1+m_2+m_3 = N\rangle$ IS EQUIPROBABLE.

NOW, WE ASSIGN IN THIS CASE THE PROBABILITY

$P = \frac{1}{D_N}$ TO EACH ONE OF THE STATES.

FOR INSTANCE, FOR $N=1,\ E_1 = \omega(1+1/2)$, ALL THE 3 STATES

$|1,0,0\rangle, |0,1,0\rangle, |0,0,1\rangle$

ARE EQUIPROBABLE AND EACH OF THOSE HAS A PROB. OF 1/3.

IN THIS CASE THE PARTITION FUNCTION IS INDEED GIVEN BY

$$Z = \sum_{k=1}^{D_N} 1 = D_N \quad (Z_N) \rightarrow \text{(it depends only on } N\text{, no temperature here)}$$

THE PROB. OF A STATE IS THEN GIVEN BY $P = 1/Z$

THIS IS THE MICROCANONICAL ENSEMBLE!

3. EXAMPLE: H-atom

AN ELECTRON IN THE COULOMB POTENTIAL $V(r) = -\frac{e^2}{r}$

WITH $r = \sqrt{x^2+y^2+z^2}$ HAS THE FOLLOWING ENERGY EIGENSTAT...

$$|\underbrace{n}_{\substack{\text{PRINCIPAL}\\ \text{QUANTUM}\\ \text{NUMBER}}}, \underbrace{\ell}_{\substack{\text{ANGULAR}\\ \text{MOMENTUM}\\ \vec{L}^2}}, \underbrace{m}_{\substack{\text{3rd comp.}\\ L_z}}, \underbrace{m_s}_{\substack{\text{spin}\\ S_z}} \rangle$$

(→ remember that $\vec{S}^2$ is fixed for e... electrons)

$$H|n,\ell,m,m_s\rangle = E_n|n,\ell,m,m_s\rangle \quad \text{with} \begin{cases} E_n = -\frac{e^2}{2a_0}\frac{1}{n^2} \\ a_0 = \frac{\hbar^2}{me^2} \end{cases}$$

$$\begin{cases} \vec{L}^2|n,\ell,m,m_s\rangle = \hbar^2\ell(\ell+1)|n,\ell,m,m_s\rangle \\ L_z|n,\ell,m,m_s\rangle = \hbar m|n,\ell,m,m_s\rangle \end{cases}$$

with $\ell = 0,1,\dots,n-1 \qquad m = -\ell,\dots,\ell$

$$S_z|n,\ell,m,m_s\rangle = \hbar m_s|n,\ell,m,m_s\rangle$$

with $m_s = \pm 1/2$ (↑ up ↓ down)

$$\left(\vec{S}^2|n,\ell,m,m_s\rangle = \hbar^2\frac{1}{2}\left(\frac{1}{2}+1\right)|n,\ell,m,m_s\rangle\right)$$

ALSO IN THIS CASE WE HAVE A DEGENERACY OF THE ENE...

$$D_n = 2\sum_{\ell=0}^{n-1}(2\ell+1) = 4\cdot\frac{(n-1)(n)}{2} + 2n = 2n^2 - \cancel{2n} + \cancel{2n}\dots$$

$$= 2n^2$$

spin

MICROCANONICAL ENSAMBLE: THE ENERGY IS FIXED. BUT THEN,

ALL STATES $|n, \ell, m, m_r\rangle$ WITH FIXED "n" ARE EQUIPROBABLE

$$P_{|n,\ell,m,m_r\rangle} = \frac{1}{2n^2}$$

$$\left(Z = 2n^2 \right)$$

CANONICAL ENSAMBLE:

THE SYSTEM IS AT A GIVEN TEMPERATURE T.

THEN:

$$Z = \sum_{n,\ell,m,m_r} e^{-\beta E_n}$$

IS THE PARTITION FUNCTION. DUE TO THE DEGENERACY:

$$Z = \sum_{n=1}^{\infty} 2n^2 e^{-\beta E_n} \qquad \langle E \rangle = -\partial_\beta \ln Z.$$

ALL STATES WITH A GIVEN "n" ARE EQUIPROBABLE.

POSSIBLE CONSTRAINTS ON THE SYSTEM:

SOMETIMES THERE ARE FURTHER CONSTRAINTS ON THE SYS
WHICH "DE FACTO" REDUCE THE ELEMENTS OF THE HILBERT SPACE.

LET US DO A CONCRETE EXAMPLE WITH OUR H-ATOM

SUPPOSE THAT ONLY STATE WITH $L_z = 0$ (i.e. $m = 0$) AR ALLOWED. (FOR INSTANCE if $m \neq 0 \to$ they are "kicked out")

THEN, ONE SHOULD PERFORM A REDUCED SUM

$$Z = \sum_{n, \ell, m_s} e^{-\beta E_n} = \sum_{n=1}^{\infty} 2(n-1) e^{-\beta E_n}$$

THIS IS OBVIOUSLY A DIFFERENT "Z" FROM THE PREVIOUS ONE !!!

HERE WE SUM OVER A REDUCED HILBERT SPACE

$\{ |n, \ell, \underline{m = 0}, m_s \rangle \}$

ADD. CONSTRAINS ON THE SYSTEM

THE CORRECT SUM DEPENDS ON THE SYSTEM THAT YOU STUDY....

FURTHER EXCHANGE WITH THE ENVIRONMENT

NOT ONLY ENERGY CAN BE EXCHANGED BETWEEN THE SYSTEM AND THE ENVIRONMENT, BUT IN PRINCIPLE EVERY OTHER QUANTITY. THIS LEADS TO THE DEFINITION OF VARIOUS "GRAND-CANONICAL ENSEMBLES"

(A TYPICAL EXAMPLE IS WHEN THE NUMBER OF PARTICLES IS <u>NOT</u> FIXED. THIS IS THE USUAL GRAND-CANONICAL EXAMPLE STUDIED IN TEXTBOOKS).

STILL, FOR THE MOMENT, WE DO ANOTHER EXAMPLE BY USING THE H-ATOM.

SUPPOSE THAT EACH $m = -\ell, \dots, \ell$ IS ALLOWED BUT THAT THEY ARE NOT ALL EQUIPROBABLE: SOME ARE MORE PROBABLE THAN OTHERS.

(THEN, THE SYSTEM EXCHANGES L_z WITH THE ENVIRONMENT. L_z IS NOT FIXED BUT FLUCTUATES AND SOME VALUES ARE FAVOURED)

$$\mathcal{Z} = \sum_{n,\ell,m,m_s} e^{-\beta E_n - \gamma m_s}$$

analogue to β, but along the "direction of L_z"

$$\mathcal{Z} = \mathcal{Z}(\beta, \gamma)$$

For $\gamma > 0$, ONE HAS THAT NEGATIVE "m" ARE FAVOURED.

$$P_{|n,\ell,m,m_s\rangle} = \frac{e^{-\beta E_n - \gamma m_s}}{\mathcal{Z}}$$

IS THE PROB THAT THE STATE $|n,\ell,m,m_s\rangle$ IS REALIZED.

(if $\gamma = 0$ all the states with the same E_n are equiprobable)

THE MEAN VALUE OF $\langle L_z \rangle$ IS GIVEN BY:

$$\langle L_z \rangle = \sum_{n,\ell,m,m_s} P_{n,\ell,m,m_s} \cdot m = -\frac{\partial Z}{\partial \gamma}$$

[OF COURSE, AGAIN THE ACTUAL VALUE IS OBTAINED BY SETTING $\gamma = \gamma_0$ WHERE γ_0 IS THE NUMBER CORRESPONDING TO A "PHYSICAL REALIZATION.]

NOTICE THAT EVEN IN THE CASE IN WHICH $\gamma_0 = 0$ (AND THUS ALL "m" ARE EQUIPROBABLE, I STILL CAN CONSIDER Z AS

$Z = Z(\beta, \gamma)$

AND THEN GET $\langle L_z \rangle$ AS $\langle L_z \rangle = -\frac{\partial}{\partial \gamma} Z(\beta,\gamma)\Big|_{\gamma=\gamma_0=0}$.

IN THIS SENSE, THE CANONICAL POTENTIAL (THE ONE WITH CAN BE OBTAINED AS

Z $Z_c(\beta) = Z(\beta, \gamma = \gamma_0 = 0)$.

• OF COURSE, IF YOU SET $\gamma = 0$ FROM THE VERY ONSET YOU CANNOT USE THE FORMULA $-\partial_\gamma \ln Z$ AS THIS IS VALID ONLY FOR $Z = Z(\beta, \gamma)$!

STILL, ONE CAN STILL CALCULATE THE MEAN VALUE AS

$$\langle L_z \rangle = \sum_{n,\ell,m,m_s} P_{n,\ell,m,m_s} \cdot m = \sum_{n,\ell,m,m_s} \frac{e^{-\beta E_n}}{Z_c(\beta)} \cdot m$$

$$\left(\sum_{n,m,m_s} \frac{e^{-\beta E_n}}{Z_c(\beta)} \right) \sum_{m=-\ell}^{\ell} m = 0$$

(this is due to the symmetry of this particular case)

PARTITION FUNCTION: GENERAL FORMULATION

ALL WHAT SAID BEFORE FOR L_2 IS INDEED PRETTY GENERAL...

CONSIDER A CERTAIN SYSTEM. DETERMINE THE HILBERT-SPACE OF THIS SYSTEM.
(IF THERE ARE SOME CONSTRAINTS, THE PHYSICAL HILBERT SPACE IS THEN "REDUCED")

H IS THE HAMILTONIAN, Q_i $i=1,\dots,N$ MUTUAL OPERATORS WHICH COMMUTE WITH THE HAMILTONIAN AND WITHIN THEMSELVES:

$$[H, Q_i] = 0 \quad , \quad [Q_i, Q_j] = 0$$

THE HILBERT SPACE IS $\{|n, k_1, \dots, k_N\rangle\}$
WITH

$$\begin{cases} H|m, k_1, \dots, k_N\rangle = E_m |m, k_1, \dots, k_m\rangle \\ Q_i|m, k_1, \dots, k_m\rangle = q_{i,k_i} |m, k_1, \dots, k_m\rangle \end{cases}$$

THEN, THE MOST GENERAL PARTITION FUNCTION IS DEFINED AS:

$$Z = \sum_{m, k_1, \dots, k_N} \langle m, k_1, \dots, k_m| e^{-\beta H - \gamma_1 Q_1 - \dots - \gamma_N Q_N} |m, k_1, \dots, k_m\rangle$$

$$= Z(\beta, \gamma_1, \dots, \gamma_N)$$

$$\boxed{\langle Q_i \rangle = -\frac{\partial}{\partial \gamma_i} \ln Z} \qquad \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$$

All of them must be then evaluated at particular value of β and γ_i.

NOTE: THE FULL MATHEMATICAL HILBERT SPACE MIGHT CONTAIN FURTHER Q_i, $i = N+1, \dots, NM$
BUT WE ASSUME THAT THESE ARE FIXED FROM THE VERY BEGINNING.

- THE CANONICAL ENSEMBLE IS THE ONE OBTAINED BY SETTING ALL THE $\gamma_i = 0$ (FROM THE VERY BEGINNING)

$$Z_c(\beta) = Z(\beta, 0, \dots, 0)$$

(FLUCTUATION OF ENERGY, ALL OTHER QUANTUM NUMBERS ARE EQUIPROBABLE)

- THE MICROCANONICAL ENSEMBLE IS OBTAINED BY FIRST ASSUMING THAT THE ENERGY IS FIXED. THE HILBERT SPACE IS GIVEN BY

$$\{ |\underset{\substack{\downarrow \\ \text{FIXED}}}{m_0}, k_1, \dots, k_N \rangle \equiv |k_1, \dots k_N\rangle \}$$

$$Z(\gamma_1, \dots, \gamma_N) = \sum_{k_1 \dots k_N} \langle k_1, \dots, k_N | e^{-\gamma_1 Q_1 \dots - \gamma_N Q_N} | k_1 \dots k_N \rangle$$

THEN, THE MICROCANONICAL POTENTIAL IS OBTAINED BY ASSUMING ALL THE STATES EQUIPROBABLE:

$$Z_M = Z(0, \dots, 0) = \sum_{k_1 \dots k_m} \langle k_1 \dots k_N | k_1 \dots k_N \rangle = D_{m_0}$$

THE GRAND CANONICAL ENSEMBLE IS OBTAINED WHEN $Q_1 \equiv N$ (nr of particles) AND WHEN ALL THE OTHER LAGRANGE MULTIPLIERS ARE SET TO ZERO

$$Z_{GC}(\beta, \gamma_1) = Z(\beta, \gamma_1, 0, \ldots, 0)$$

$$= \sum_{m, k_1, \ldots, k_N} \langle m, k_1, \ldots, k_N | e^{-\beta H - \gamma_1 N} | m, k_1, \ldots, k_N \rangle$$

IT IS THEN CONVENTION TO DEFINE: $\gamma_1 = -\beta\mu$

$$Z_{GC}(\beta, \mu) = \sum_{m, k_1, \ldots, k_N} \langle m, k_1, \ldots, k_N | e^{-\beta(H - \mu N)} | m, k_1, \ldots, k_N \rangle$$

(GENERALIZATIONS: DIFFERENT KINDS OF PARTICLES $\mapsto \mu_i \quad i = 1, \ldots K$)

BUT, AGAIN, THE CHOICE OF N IS USUALLY DONE BECAUSE IT IS USEFUL, BUT THE SAME TYPE OF REASONING APPLIES TO EACH CONSERVED CHARGE.

ENTROPY.

PHYS. HILBERT SPACE $\{|m, l_1, \ldots, l_N\rangle\}$.

↳ A CERTAIN STATE IS REALIZED WITH PROBABILITY

$$P_{|m,l_1 \ldots l_N\rangle} = \frac{e^{-\beta E_m - \delta_1 q_{1,l_1}}}{Z(\beta, \delta_1, \ldots, \delta_N)}$$

(most general expression for the generalized grand canonical ensemble)

THE ENTROPY OF THE SYSTEM IS DEFINED AS:

$$S = -k_B \sum_{m, l_1 \ldots l_m} P_{|m,l_1 \ldots l_N\rangle} \ln P_{|m,l_1 \ldots l_N\rangle}$$

• ENTROPY IN THE MICROCANONICAL ENSEMBLE: $m = m_0$ "fixed"

$|l_1, \ldots, l_N\rangle$ ↦ all of them with prob. $1/D_{m_0}$

THEN:

$$S = -k_B \sum_{l_1 \ldots l_m} \frac{1}{D_{m_0}} \ln \frac{1}{D_{m_0}} = k_B \ln D_{m_0}$$

$$\boxed{S = k_B \ln D_{m_0}} = k_B \ln \mathcal{N}$$

↳ log of the NR OF STATES.

THE LARGER $\mathcal{N}$, THE LARGER THE ENTROPY

- ENTROPY IN THE CANONICAL ENSEMBLE:

$$P_{|m, l_1, \dots l_N\rangle} = \frac{e^{-\beta E_m}}{Z}$$

$$Z = \sum_{n, l_1, \dots l_N} e^{-\beta E_m}$$

$$\frac{S}{k_B} = \ln Z_c(\beta) + \beta \langle E \rangle$$

- ENTROPY IN THE MOST GENERAL CASE:

$$\boxed{\frac{S}{k_B} = \ln Z + \beta \langle E \rangle + \gamma_1 \langle Q_1 \rangle + \dots + \gamma_N \langle Q_N \rangle}$$

$$S = k_B \ln Z + k_B \beta \langle E \rangle + k_B \gamma_1 \langle Q_1 \rangle + \dots + k_B \gamma_N \langle Q_N \rangle$$

⇝ $F = -k_B T \ln Z$ is also called the "free energy".

⇝ Specific heat: $C_V = \frac{\partial \langle E \rangle}{\partial T}$ (important in solid state physics