

Statistical physics of Particles

Apr 1st Statistical Mechanics 1st / 2nd law.

Response func. $C_v = \partial Q / \partial T | v$

$$C_p = \partial Q / \partial T | p$$

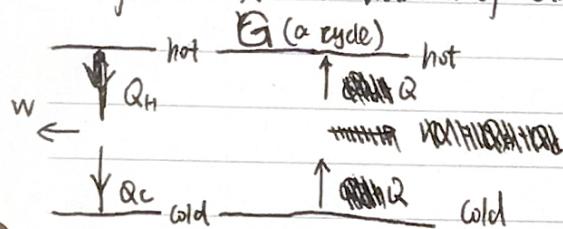
Generalized force	Displacement
tension F	length L
surface tension S	area A
pressure $-P$	volume V
magnetic field H	magnetization M
electric field E	polarization P
chemical potential μ	particle number N

$$\partial W = \sum_i J_i dx_i$$

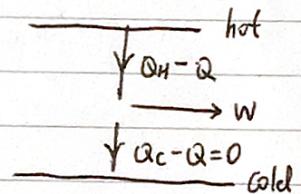
* Kelvin's statement: complete conversion of heat into work (x)

Clausius's statement: transfer heat from a colder to a hotter body (x)

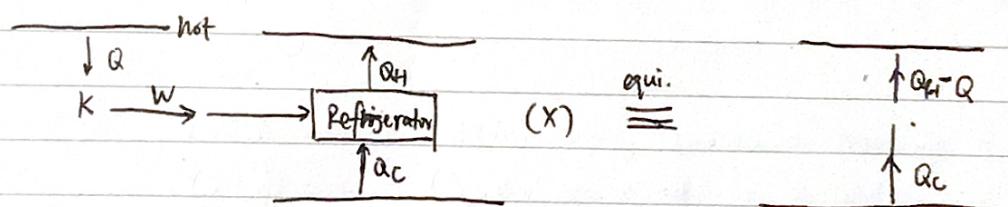
Prof. (a) Assume violation of Clausius's statement.



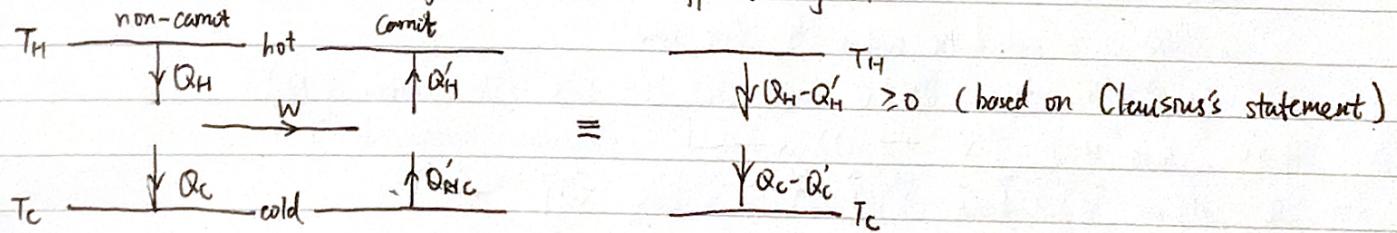
If $Q = Q_C$, low efficiency (x) \equiv



(b) Assume violation of Kelvin's statement.



Carnot's theorem: Carnot engine is the most efficient engine.



$$\frac{W}{Q_H} \leq \frac{W}{Q_C} \Rightarrow \eta_{\text{Carnot}} \geq \eta_{\text{non-Carnot}}$$

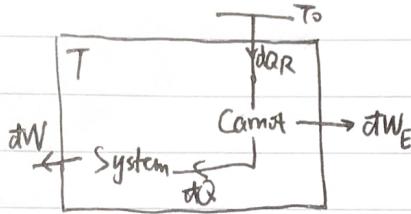
* Set up the Carnot engines running in series,

$$\Rightarrow \eta(T_H, T_C) = \frac{T_H - T_C}{T_H}$$

Entropy: / other thermo potential

Clausius's theorem: $\oint dQ/T \leq 0$

Proof:



$$Q_R = W + W_E \leq 0$$

↓ ↴ Kelvin's statement

external work

Application: 1) State func. $S(B) - S(A) = \int_A^B \frac{dQ_{rev}}{T}$

$$2) \oint \frac{dQ_{rev}}{T} = 0$$

$$3) dE = TdS + \sum_i J_i dx_i$$

4) n methods of doing work, n+1 DOF independent variables (+1 for TdS)

$$(E, \{x_i\}) \quad \frac{\partial S}{\partial E}|_x = \frac{1}{T}, \quad \frac{\partial S}{\partial x_i}|_{E, x_j \neq i} = -\frac{J_i}{T}$$

$$5) \int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ_{rev}}{T} \leq 0 \Rightarrow \int_A^B \frac{dQ}{T} \leq S(B) - S(A) = \Delta S$$

$$\Rightarrow dS \geq \frac{dQ}{T}$$

(system)

for net $dQ=0$ (adiabatic process), $\Delta S \geq 0$ * (Adiabatic attains maximum S in equilibrium)

① Entropy (maximum) in equilibrium in adiabatic process (NVE) (no heat $dQ=0$)

② Enthalpy (minimum) in equilibrium in adiabatic process (NpE) (no heat $dQ=0$)

mechanical equilibrium with a constant external force.

$dW \leq J \delta x$ (loss of external work to dissipation) * work input into the system dW

& $dQ=0$ ↓ adiabatic system. & first law

$\delta E \leq J \delta x \rightarrow \delta H \leq 0$ and $\delta H = \delta E - J \delta x$ (the definition of H)

$\Rightarrow \delta H \leq 0$; where $H = E - \vec{J} \cdot \vec{x} \rightarrow (1) \leftarrow$ (Legendre transformation)

$$dH = dE - d(J \cdot x) = TdS + \vec{J} \cdot d\vec{x} - \vec{x} \cdot d\vec{J} - \vec{J} \cdot d\vec{x} = TdS - \vec{x} \cdot d\vec{J} \rightarrow (2)$$

{ Notes: eqn. (1): variations of H when approaching equilibrium (some parameters that is not a func of state)
is varied (e.g. some kinds of \vec{x}_i) use δ (non-equilibrium)
eqn. (2): in the equilibrium coordinates use d (equilibrium) }

Therefore, at equilibrium $H(S, \vec{J})$ and from eqn.(2) $x_i = -\frac{\partial H}{\partial J_i}|_{S, J_{j \neq i}}$

$$\text{Examples: } C_p = \frac{\partial Q}{\partial T}|_p = \frac{\partial E + PV}{\partial T}|_p = \frac{d(E+PV)}{dT}|_p = \frac{dH}{dT}|_p$$

Thermo potential

- ③ **Helmholtz free energy** ($\delta w = 0$)
 From Clausius's theorem, $\oint dQ/T \leq 0 \Rightarrow \delta Q \leq T\delta S \Rightarrow \delta E \leq T\delta S$
 $\Rightarrow \delta F \leq 0$, where $F = E - TS$ (Legendre transform)

$$dF = d(E-TS) = -SdT + \vec{J} \cdot d\vec{x} \Rightarrow F(T, \vec{x}) \text{ at equilibrium}$$

$$J_i = \frac{\partial F}{\partial x_i} \Big|_{T, X_j \neq i}, \quad S = -\frac{\partial F}{\partial T} \Big|_X$$

* internal energy $\Rightarrow H$ Free energy: $E = F + TS = F - T \frac{\partial F}{\partial T} \Big|_X = -T^2 \frac{\partial F}{\partial T} \Big|_X$

Summary for Inequalities in thermo potentials

$\delta Q = 0$	$\text{constant } T$
$\delta w = 0$	$\delta S \geq 0 \quad \delta F \leq 0$
constant J	$\delta H \leq 0 \quad \delta G \leq 0$
e.g.	$\delta E - J\delta x \leq 0 \xrightarrow{\text{constant } J} \delta E - \delta(Jx) \leq 0 \Rightarrow \frac{\delta H = \delta E - \delta(Jx)}{\delta H \leq 0}$

- ④ **Gibbs free energy** (isothermal transformation with constant J_{ext})

$$\begin{aligned} \text{I} \quad & \frac{\delta w}{\delta Q} \leq J \cdot \delta x \Rightarrow \delta E \leq T\delta S + \vec{J} \cdot \vec{\delta x} \Rightarrow \delta G \leq 0 \\ & \text{where } G = E - TS - \vec{J} \cdot \vec{x} \quad (\text{Legendre transform}) \\ \text{II} \quad & \delta G = -SdT - \vec{x} \cdot d\vec{J} \quad \& \quad G(T, \vec{J}) \end{aligned}$$

{ Notes: Legendre transform used to change variables to the most natural set of coordinates for describing a particular situation. }

- ⑤ In chemical reactions (equilibrium within states)

$$\rightarrow \text{chemical work: } \delta w = \mu dN \quad \mu = \{\mu_i\} \quad N = \{N_i\}$$

$$\rightarrow \text{equilibrium without mechanical work: } \boxed{\text{Grand Potential } G}$$

$$(1) \quad G = E - TS - \mu N = G(T, \mu, x)$$

$$(2) \quad \delta G \leq 0 \quad \text{in } \checkmark \text{ chemical equilibrium}$$

$$(3) \quad dG = -SdT + \vec{J} \cdot d\vec{x} - \vec{\mu} d\vec{N} \quad \text{in chemical equilibrium}$$

Example:

V, N	Fix coordinates are N, V, T $\rightarrow F(N, V, T)$
$N_s = N - N_w$	$dF = -SdT - PdV + \mu dN$
N_w	Assume all processes are very slow,

out-of-equilibrium value $F(V, T, N/N_w) = F_w(T, N_w) + F_s(V, T, N - N_w)$

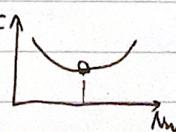
equilibrium point is obtained by minimizing F

$$\delta F = \frac{\partial F}{\partial N_w} \Big|_{T, V} \delta N_w - \frac{\partial F}{\partial N_s} \Big|_{T, V} \delta N_w$$

$$\text{II} \quad \text{II}$$

$$\rightarrow \mu_w(V, T) = \mu_s(V, T)$$

equilibrium



1.8 Mathematical Results (Most importantly, the basic principle is $dE = Tds + \sum_i J_i dx_i$ (quasi-reversible))

n ways of mechanical works $\Rightarrow n+1$ DOF in equilibrium state ($J_i dx_i$ & Tds)

(1) Extensivity: $E(x_s, x_x, x_N) = \lambda E(s, x, N)$

$$\frac{\partial}{\partial \lambda} E(x_s, x_x, x_N) \Big|_{\lambda=1} = E(s, x, N) \Rightarrow \left[\frac{\partial E}{\partial s} \Big|_{x, N} \frac{\partial s}{\partial \lambda} + \sum_i \frac{\partial E}{\partial x_i} \Big|_{s, v_j, N} \frac{\partial x_i}{\partial \lambda} + \sum_i \frac{\partial E}{\partial N_i} \Big|_{s, v, N_j} \frac{\partial N_i}{\partial \lambda} \right]_s = E$$

Therefore, $E = \underbrace{\frac{\partial E}{\partial s} \Big|_{x, N} s}_{\text{from 1st/2nd law}} + \sum_i \underbrace{\frac{\partial E}{\partial x_i} \Big|_{s, v_j, N} x_i}_{dE = T ds + \sum_i J_i dx_i} + \sum_i \underbrace{\frac{\partial E}{\partial N_i} \Big|_{s, v, N_j} N_i}_{dN_i} \Rightarrow E = TS + \sum_i J_i x_i + \sum_i \mu_i N_i$

\hookrightarrow Gibbs-Duhem Eqn. $SdT + \vec{x} \cdot d\vec{J} + \vec{N} \cdot d\vec{\mu} = 0$

* Notes: extensivity is an additional assumption, relying on short-range interactions between constituents of the system. Gravity may break it. But $dE = Tds + \vec{J} \cdot d\vec{x} + \vec{\mu} \cdot d\vec{N}$ always valid

* E.g. isothermal $dT=0$ $-Vdp + Ndm = 0$ & ideal gas law, $PV = Nk_B T$

$$\frac{d\mu}{N} = \frac{V}{N} \frac{dp}{P} = k_B T \frac{dp}{P}$$

$$\Rightarrow \mu = \mu_0 + k_B T \ln \frac{P}{P_0} = \mu_0 - k_B T \ln \frac{V}{V_0} \quad \text{where } (P_0, V_0, \mu_0) \text{ is reference point}$$

(2) Maxwell relations: follow from the commutative property $\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$

$$\frac{\partial E}{\partial s \partial x_i} \Big|_{x, N} = T \quad \text{and} \quad \frac{\partial E}{\partial x_i} \Big|_{s, x_j, N} = J_i$$

$$\frac{\partial^2 E}{\partial s \partial x_i} = \frac{\partial^2 E}{\partial x_i \partial s} = \frac{\partial T}{\partial x_i} \Big|_s = \frac{\partial J_i}{\partial s} \Big|_{x_i} \quad \xrightarrow{(\partial y / \partial x) = (\partial x / \partial y)^{-1}} \quad \frac{\partial s}{\partial J_i} \Big|_{x_i} = \frac{\partial x_i}{\partial T} \Big|_s$$

E.g. $\frac{\partial \mu}{\partial p} \Big|_{N, T} = \frac{\partial V}{\partial N} \Big|_{P, T} = \frac{k_B T}{P} \quad \leftarrow \quad dG(P, N, T) = Vdp - SdT + \mu dN$

ideal gas: $pV = nRT$

$$\frac{\partial s}{\partial V} \Big|_{E, N} = \frac{P}{T} = - \frac{(\partial E / \partial V)_{S, N}}{(\partial E / \partial S)_{V, N}} \quad \leftarrow \quad dE = Tds - pdV + \mu dN$$

$$\hookrightarrow \boxed{\frac{\partial s}{\partial V} \Big|_{E, N} \frac{\partial E}{\partial S} \Big|_{V, N} \frac{\partial V}{\partial E} \Big|_{S, N} = -1} \quad \text{chain rule of differentiation}$$

(3) The Gibbs phase rule:

n ways of performing way $\left\{ \begin{array}{l} \text{1) } n+c+1 \text{ (DDF)} \\ \text{c chemical constituents} \end{array} \right.$ involves $\rightarrow dE = Tds + \vec{J} \cdot d\vec{x} + \vec{\mu} \cdot d\vec{N}$

② intensive variables \rightarrow constrained by $SdT + \vec{x} \cdot d\vec{J} + \vec{N} \cdot d\vec{\mu} = 0$

③ at least one extensive variables

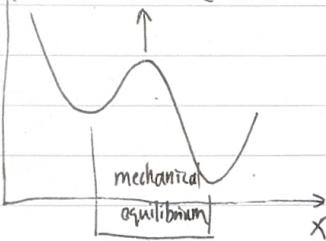
E.g. ~~steam~~ steam - water - ice system

1 component ; 1 means to do no work \Rightarrow 2 intensive variables & 1 extensive variables
(water) (hydrostatic) (P, T) or (U, T)

→ Generally, $f(DOF) = n + c + 1 - p$ (phase number)

1.9 Stability conditions

Concave (unaccessible)



Condition: 1) $J_i = -\frac{dU}{dx} = 0$ (force)

2) $\frac{d^2U}{dx^2} > 0$

In the presence of external force J , minimize $H = U - Jx$.

In $X_{eq}(J)$, require $\frac{d^2H}{dx^2} = \frac{d^2U}{dx^2} > 0$

Convex (with finite force J)

A particle moving freely in an external potential $U(x)$ dissipates energy and settles to equilibrium at minimum value of U . ($\frac{d^2U}{dx^2} > 0$)

Minimize enthalpy: $H = U - Jx$ $\frac{d^2H}{dx^2} = \frac{d^2U}{dx^2} > 0 \Rightarrow$ new equilibrium point $x_{eq}(J) \rightarrow$ convex of $U(x)$ is accessible

More than one mechanical coordinates \rightarrow any δx_i results in an increase of energy

\Rightarrow more symmetric
|||

Equivalent eqn.

\hookrightarrow generalized in chemistry

uniformity of an extended thermodynamic body

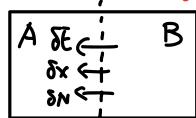
$$\sum_{i,j} \frac{\partial^2 U}{\partial x_i \partial x_j} \delta x_i \delta x_j > 0 \quad \text{or} \quad \sum_{i,j} \frac{\partial^2 H}{\partial x_i \partial x_j} \delta x_i \delta x_j > 0$$

$$\delta J_i = \delta \left(\frac{\partial U}{\partial x_i} \right) = \sum_j \frac{\partial^2 U}{\partial x_i \partial x_j} \delta x_j \quad (\delta: \text{change in non-equilibrium})$$

$$\sum_i \delta J_i \delta x_i > 0$$

$$\delta T \delta S + \sum_i \delta J_i \delta x_i + \sum_\alpha \delta \mu_\alpha \delta N_\alpha > 0 \quad (\text{thermal \& chemical inputs})$$

A and B are equal (stable to unstable)



$E(T), x(J), \mu(N) \parallel$ at fixed E, x, N

\rightarrow first-order relation:

$$\delta T_A = -\delta T_B = \delta T, \quad \delta J_A = -\delta J_B = \delta J; \quad \delta \mu_A = -\delta \mu_B = \delta \mu$$

$$S = S_A + S_B = \left(\frac{E_A}{T_A} - \frac{J_A}{T_A} x_A - \frac{\mu_A}{T_A} N_A \right) + \left(\frac{E_B}{T_B} - \frac{J_B}{T_B} x_B - \frac{\mu_B}{T_B} N_B \right)$$

first order change $\frac{1}{T_A} \delta E_A$ & $\frac{1}{T_B} \delta E_B$ $E_A \delta(\frac{1}{T_A})$ & $E_B \delta(\frac{1}{T_B})$...
are all eliminated

second order are the same

\downarrow intensive \downarrow intensive

$$\delta S = \delta S_A + \delta S_B = 2 \left[\delta E_A \delta \left(\frac{1}{T_A} \right) - \delta \left(\frac{J_A}{T_A} \right) \delta x_A - \delta \left(\frac{\mu_A}{T_A} \right) \delta N_A \right]$$

$$= 2 \left[-\frac{\delta E_A \delta T_A}{T_A^2} - \frac{T_A \delta J_A - J_A}{T_A^2} \delta x_A - \frac{T_A \delta \mu_A - \mu_A}{T_A^2} \delta N_A \right]$$

$$= -\frac{2}{T_A} \left[\delta T_A \left(\frac{\delta E_A - J_A \delta x_A - \mu_A \delta N_A}{T_A} \right) + \delta J_A \delta x_A + \delta \mu_A \delta N_A \right]$$

$$= -\frac{2}{T_A} \left[\delta T_A \delta S_A + \delta J_A \delta x_A + \delta \mu_A \delta N_A \right]$$

stable equilibrium: any change leads to a decrease of entropy

$$\delta T \delta S + \delta J \delta x + \delta \mu \delta N \geq 0$$

Example: δT and δx with $\delta N = 0$
same result for any constraint

$$\left\{ \begin{array}{l} \delta S = \frac{\partial S}{\partial T} \Big|_x \delta T + \frac{\partial S}{\partial x_i} \Big|_T \delta x_i \\ \delta J_i = \frac{\partial J_i}{\partial T} \Big|_x \delta T + \frac{\partial J_i}{\partial x_j} \Big|_T \delta x_j \end{array} \right. \quad \& \quad \delta T \delta S + \delta J_i \delta x_i + \delta \mu \delta N \geq 0$$

$$\frac{\partial S}{\partial T} \Big|_x (\delta T)^2 + \frac{\partial J_i}{\partial x_j} \Big|_T \delta x_j \delta x_i + \frac{\partial S}{\partial x_i} \Big|_T \delta x_i \delta T + \frac{\partial J_i}{\partial T} \Big|_x \delta T \delta x_i \geq 0$$

↓

as $dF = d(E - TS) = -SdT + Jdx$

Maxwell Relation: $-\left(\frac{\partial S}{\partial x}\right)_T = \left(\frac{\partial J}{\partial T}\right)_x$

\Rightarrow quadratic form, so it is positive for any δT or δx_i

Example: δT with δx , $\delta N = 0$

$$C_x = \frac{\partial Q}{\partial T} \Big|_x = T \left(\frac{\partial S}{\partial T} \right)_x \geq 0$$

δx_i with δT , $\delta x_{i \neq j}$, $\delta N = 0$

Matrix of coefficients $\frac{\partial J_i}{\partial x_j} \Big|_T$ must be positive definite
positive definite matrix: all eigenvalues are positive
so trace and determinant are positive as well.

pressure (mechanical)
& Chemical work for gas

$$\begin{bmatrix} -\frac{\partial P}{\partial V} \Big|_{T,N} & -\frac{\partial P}{\partial N} \Big|_{T,V} \\ \frac{\partial U}{\partial V} \Big|_{T,N} & \frac{\partial U}{\partial N} \Big|_{T,V} \end{bmatrix} \quad \begin{array}{l} \text{diagonals are all inverse response funcs.} \\ K_{T,N} = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_{T,N} \quad \& \quad \frac{\partial U}{\partial N} \Big|_{T,V} \\ \text{diagonals are positive.} \end{array}$$

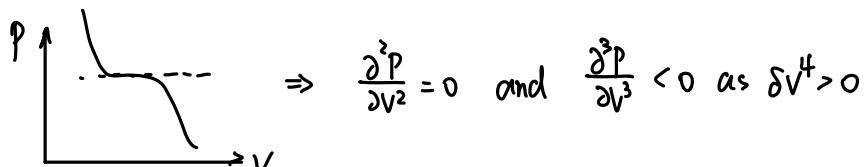
$$-\frac{\partial P}{\partial V} \Big|_{T,N} \frac{\partial U}{\partial N} \Big|_{T,V} + \frac{\partial P}{\partial N} \Big|_{T,V} \frac{\partial U}{\partial V} \Big|_{T,N} \geq 0$$

critical point of gas

$$\frac{\partial P}{\partial V} \Big|_{T,N} = 0 \quad (\text{Not justified but works for Taylor expansion})$$

$$\delta P(T=T_c) = \frac{\partial P}{\partial V} \Big|_{T,N} \delta V + \frac{1}{2} \frac{\partial^2 P}{\partial V^2} \Big|_{T,N} \delta V^2 + \frac{1}{3!} \frac{\partial^3 P}{\partial V^3} \Big|_{T,N} \delta V^3$$

$$\text{as } -\delta P \delta V \geq 0 \Rightarrow \delta P \delta V \leq 0 \Rightarrow \frac{1}{2} \frac{\partial^2 P}{\partial V^2} \Big|_{T,N} \delta V^2 + \frac{1}{3!} \frac{\partial^3 P}{\partial V^3} \Big|_{T,N} \delta V^4 \leq 0$$



The entropy of all system at zero absolute temperature is a universal constant that can be taken to be zero. $\lim_{T \rightarrow 0} S(X, T) = 0$

Consequence:

1. $S(T=0, X) = 0$ for all coordinates X

$$\lim_{T \rightarrow 0} \frac{\partial S}{\partial X} \Big|_T = 0$$

2. Heat capacity must vanish as $T \rightarrow 0$

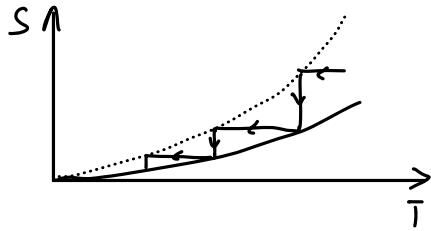
since $S(T, X) - S(0, X) = \int_0^T dT' \frac{C_X(T')}{T'}$ and the integral diverges

as $T \rightarrow 0$ unless $\lim_{T \rightarrow 0} C_X(T) = 0$

3. Thermal expansivities also vanish as $T \rightarrow 0$ since

$$\alpha_J = \frac{1}{X} \frac{\partial X}{\partial T} \Big|_J \xrightarrow{\text{Maxwell relation}} \frac{1}{X} \frac{\partial S}{\partial J} \Big|_T \stackrel{?}{=} 0$$

Weaker statement for 3rd law 4. impossible to cool any system to absolute zero in a finite number of steps.



Justify the laws of thermodynamics from a macroscopic point of view.

1st law:

0th and 2nd law:

conservation of energy in both macroscope and microscope

Macroscopic: an irreversible approach to equilibrium

Microscopic: collective tendency of large numbers of degrees of freedom

$$S/N = k_B \ln(g_N)/N . \quad g_N: \text{degeneracy of states}$$

Macroscopic: $\lim_{T \rightarrow 0} S = 0$

Microscopic: $\lim_{N \rightarrow \infty} \ln(g_N)/N = 0 \text{ at } T=0$

limiting possible number of ground states for a many-body system.

↳ equivalent to a restriction on degeneracy of ground states of a quantum mechanical system

Limitations of classical statistical mechanics

1. Low temperature and energy (quantum effect)

2. inapplicability to glassy phases

- freezing of supercooled liquids into configurations with extremely slow dynamics (not truly equilibrium phase but subject to all laws of thermodynamics) → see Problems HU