

Thermodynamics Revisited

①

- * identify the statistical quantities with the thermodynamic quantities
- * consider a system which can exchange work with an external medium and heat with a reservoir \Rightarrow system plus reservoir are thermally isolated from the outside world
- * work depends on external parameters x_i
 - \Rightarrow system Hamiltonian $H(\{x_i\})$
 - \rightarrow give time-dependence of Hamiltonian
 - $H(t) = H(\{x_i(t)\}) \Rightarrow$ quasi-static processes
- * assume wall between system and reservoir is impermeable to molecules
 - \Rightarrow canonical ensemble @ equilibrium

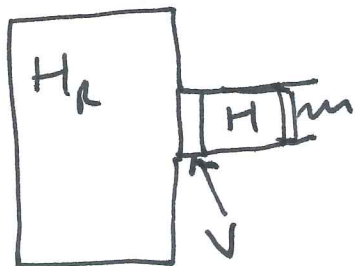
$$H_{TOT} = H + H_R + V$$

H - system Hamiltonian

H_R - Hamiltonian of reservoir

V - interaction

V - surface effect



\Downarrow
contributes negligibly
to energy / entropy

* V is however essential \Rightarrow if $V=0$, system (2) and reservoir are independent

D_{TOT} - density matrix of system plus reservoir

$$i\hbar \frac{dD_{TOT}}{dt} = [H, D_{TOT}] + [H_R, D_{TOT}] + [V, D_{TOT}]$$

D - density matrix of system only

$$D = \text{Tr}_R D_{TOT} \quad (\text{trace out reservoir})$$

$$i\hbar \frac{dD}{dt} = [H, D] + \text{Tr}_R [V, D_{TOT}]$$

show that $\text{Tr}_R [H_R, D_{TOT}] = 0$

$$H_R = I_{SYS} \otimes H_R$$

~~$(H_R)_{\alpha\lambda; \beta\mu} = \delta_{\alpha\beta} H_{\lambda\mu} \Rightarrow$ index α, β - system
index λ, μ - reservoir~~

~~$$\text{Tr}_R [H_R, D_{TOT}] = \sum_{\beta} \sum_{\alpha} (H_R)_{\alpha\lambda; \beta\mu} (D_{TOT})_{\mu\beta; \alpha\lambda}$$~~

$$(H_R)_{\alpha\lambda; \beta\mu} = \delta_{\alpha\beta} (H_R)_{\lambda\mu}$$

$$\text{Tr}_R [H_R, D_{TOT}] = \sum_{\beta} \sum_{\alpha} \delta_{\alpha\beta} (H_R)_{\lambda\mu} (D_{TOT})_{\mu\beta; \alpha\lambda}$$

$$= \sum_{\beta} \sum_{\alpha} (D_{TOT})_{\alpha\lambda; \beta\mu} (H_R)_{\beta\alpha} \delta_{\mu\lambda}$$

$$= \sum_{\alpha\beta} (H_R)_{\alpha\beta} (D_{TOT})_{\alpha\beta; \alpha\alpha} - (D_{TOT})_{\alpha\lambda; \beta\mu} (H_R)_{\beta\alpha} = 0$$

$$i\hbar \frac{dD}{dt} = [H, D] + \text{Tr}_R [V, D_{\text{TOT}}] \quad (3)$$

evolution of this equation is non-Hamiltonian (dD/dt does not depend only on the system Hamiltonian)

- time-evolution of average energies \bar{E}

$$\frac{dE}{dt} = \text{Tr} \left(H \frac{dD}{dt} \right) + \text{Tr} \left(\frac{dH}{dt} D \right)$$

depends on thermal contact with reservoir

$$\begin{aligned} \text{Tr} \left(H \frac{dD}{dt} \right) &= \frac{1}{i\hbar} \text{Tr} \left(H [H, D] \right) + \frac{1}{i\hbar} \text{Tr} \text{Tr}_R [H [V, D_{\text{TOT}}]] \\ &= \frac{1}{i\hbar} \text{Tr}_{\text{TOT}} \left(H [H, D_{\text{TOT}}] \right) + \frac{1}{i\hbar} \text{Tr}_{\text{TOT}} \left(H_* [V, D_{\text{TOT}}] \right) \end{aligned}$$

$$= 0 \quad \text{since } \text{Tr}_{\text{TOT}} H [H, D_{\text{TOT}}] = \text{Tr}_{\text{TOT}} H H D - \text{Tr}_{\text{TOT}} H D H = 0$$

$$= \frac{1}{i\hbar} \text{Tr}_{\text{TOT}} \left(H V D_{\text{TOT}} - H D_{\text{TOT}} V \right) = \frac{1}{i\hbar} \text{Tr}_{\text{TOT}} D_{\text{TOT}} [H, V]$$

- term describes exchange of energy in the form of heat \Rightarrow depends on coupling between system/reservoir

second term $\text{Tr}(D \frac{dH}{dt}) = \underbrace{\left\{ \text{Tr}(D \frac{\partial H}{\partial x_i}) \right\}}_{\text{depends on change in external parameters}} \frac{\partial x_i}{\partial t}$ (4)

$$dE = \underbrace{\text{Tr}(HdD)}_{dQ} + \underbrace{\text{Tr}(DdH)}_{dW}$$

energy exchange in the form of heat
 \rightarrow changes the density matrix / probabilities of energy level occupations

$dQ = \text{Tr}(HdD) \rightarrow$ valid for both quasi-static processes and for processes for which H is constant

$$\Delta Q = \text{Tr}(H \Delta D)$$

$dW = \text{Tr}(DdH)$ valid only for quasi-static processes

Entropy and Temperature: Second law (5)

* physical interpretation of β

→ in canonical ensemble $1/\beta \rightarrow$ temperature scale

* consider two independent systems: α, α

system (a) E_a, β_a

system (b) E_b, β_b

if two systems placed in thermal contact

$$E_{\text{tot}} = E_a + E_b \quad \text{and} \quad \beta_a = \beta_b$$

↓
only constraint is now on total energy → only one Lagrange multiplier instead of two

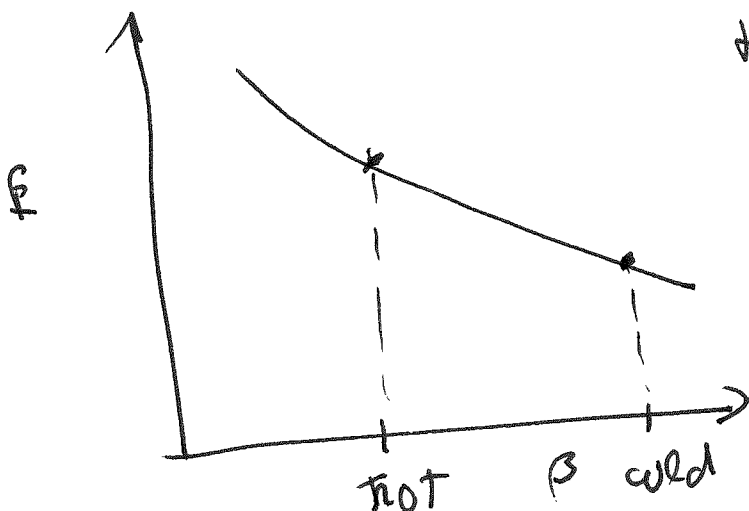
$$E = - \frac{\partial \ln Z}{\partial \beta} \quad Z - \text{convex function of } \beta$$

↓
energy is a decreasing function of β

to reach equilibrium

hot β increases (cools) and gives energy to the cold system

whose β decreases



energy flows from hot to cold

* let's show that β is proportional to $1/T$ (6)

consider entropy variations

$$dS_B = -k \text{Tr} d\hat{D}_B (\ln \hat{D}_B + 1) = -k \text{Tr} d\hat{D}_B \ln \hat{D}_B$$

$$= -k \text{Tr} d\hat{D}_B [-\beta \hat{H} - \ln Z]$$

using $\text{Tr} d\hat{D}_B = 0$ ($\text{Tr} \hat{D}_B = 1$)

$$dS_B = \beta k \text{Tr} d\hat{D}_B \hat{H}$$

$$\Rightarrow dS_B = \beta k dQ$$

since $dS = \frac{dQ}{T}$

(from Carnot engine analysis \Rightarrow so this is a thermodynamic relation)

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$$dS_B = \beta k T dS$$

what is $\beta k T$?

$$\frac{\partial S_B}{\partial \beta} = \beta k T \frac{\partial S}{\partial \beta}$$

$$\frac{\partial S_B}{\partial x_i} = \beta k T \frac{\partial S}{\partial x_i}$$

second derivatives (mixed)

$$\frac{\partial^2 S_B}{\partial \beta \partial x_i} = \beta k T \frac{\partial^2 S}{\partial \beta \partial x_i}$$

(from 1st eqn.)

$$\frac{\partial^2 S_B}{\partial \beta \partial x_i} = \underbrace{\frac{\partial}{\partial \beta}(\beta k T)}_{\text{}} \frac{\partial S}{\partial x_i} + \beta k T \frac{\partial^2 S}{\partial \beta \partial x_i}$$

two equations only hold simultaneously if $\beta k T = \text{constant}$

- we can then set $\beta h T = 1$

(7)

- implies that $S - S_B = \text{constant}$

$$\left(\frac{\partial S}{\partial \beta} = \frac{\partial S_B}{\partial \beta}, \quad \frac{\partial S}{\partial x_i} = \frac{\partial S_B}{\partial x_i} \right)$$

- S goes to zero at small T ($T \rightarrow 0$)

reason: 3rd law of thermodynamics

- S_B goes to zero at small T ($T \rightarrow 0$)

reason: system becomes a pure state

$$\Rightarrow \boxed{S = S_B}$$

Boltzmann entropy is identical to thermodynamic entropy

note: $\beta \geq 0$ $T \geq 0$ for a Hamiltonian

bounded only from below

if Hamiltonian is also bounded from above

β can be negative (or T can be negative)

Entropy of mixing

(8)

* entropy change can occur also in a way unrelated to heat \Rightarrow mixing

* consider classical mono-atomic ideal gas

$$H = \sum_i \frac{p_i^2}{2m}$$

\rightarrow partition function Z is a product of partition functions of single atoms

$$Z = \text{Tr} e^{-\beta H} = \text{Tr} e^{-\beta \sum_i \frac{p_i^2}{2m}} = \text{Tr} \prod_{i=1}^N e^{-\frac{\beta p_i^2}{2m}}$$

$$= \left[\text{Tr} e^{-\frac{\beta p^2}{2m}} \right]^N = Z_1^N$$

$$Z_1 = \text{Tr} \left[e^{-\frac{\beta p^2}{2m}} \right] = \frac{V}{h^3} \int d\vec{p} e^{-\frac{\beta p^2}{2m}} = \frac{V}{h^3} \left(\frac{2mT}{\beta} \right)^{3/2}$$

$$Z = \frac{V^N}{h^{3N}} \left(\frac{2mT}{\beta} \right)^{3N/2} = V^N \left(\frac{2Tm}{\beta h^2} \right)^{3N/2}$$

taking account of indistinguishability

$$Z = \frac{V^N}{N!} \left(\frac{2Tm}{\beta h^2} \right)^{3N/2}$$

$N!$ factor cannot be justified rigorously in classical mechanics, its origin is quantum

- can derive it by starting with independent fermions or bosons and taking the large T limit \rightarrow in this case effects of indistinguishability are reduced

- however - if we do not use it for the classical partition function \Rightarrow entropy is not extensive

(9)

$$S = +k \ln Z + k \beta \bar{E}$$

if $Z = V^N \left(\frac{2\pi m}{\beta h^2} \right)^{3N/2}$

$$S = \underbrace{Nk \ln V}_{\downarrow} + \frac{3Nk}{2} \ln \left(\frac{2\pi m}{\beta h^2} \right) + \frac{3Nk}{2}$$

this term is not extensive

but if $Z = \frac{V^N}{N!} \left(\frac{2\pi m}{\beta h^2} \right)^{3N/2}$

$$S = Nk \ln V + \frac{3N}{2} k \ln \left(\frac{2\pi m}{\beta h^2} \right) - \frac{3Nk}{2} - Nk \ln N + Nk$$

$$S = Nk \ln \frac{V}{N} + \frac{3N}{2} k \ln \left(\frac{2\pi m}{\beta h^2} \right) + \frac{5Nk}{2}$$

THUS: $Z = \frac{V^N}{N!} \left(\frac{2\pi m}{\beta h^2} \right)^{3N/2}$

classical calculation

$$\Sigma_{\text{class}} = C \int d\vec{r}_i d\vec{p}_i e^{-\frac{p_i^2}{2m}}$$

$$= C V^N \left(\frac{2\pi T}{P} \right)^{3N/2}$$

$$C = \frac{1}{N! h^{3N}}$$

$h \rightarrow$ element of phase space volume