Reconciling Statistical Physics and Thermodynamics

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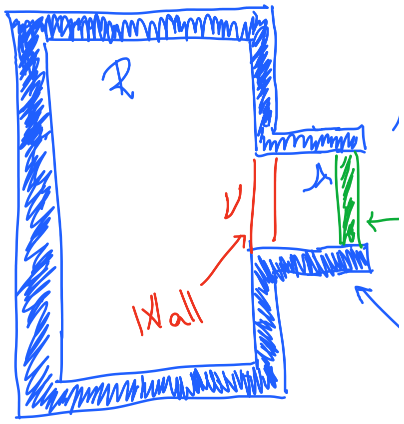
Let's now reconcile our statistical mechanics description with our (thermodynamics)

Reservoir ≡



$N_R \gg N_A$

$E_R \gg N_A$

Let's define

Density operator

In the Heisenbe

$i\hbar \frac{dD_{Tot}}{dt} = [$

A note

$A^{(\alpha)}_{\alpha k;c\gamma} =$

Taking only t

$Tr_\alpha[\hat{A}^{(\alpha)} D] =$

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Returning

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

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$$Tr_R\left[i\hbar \frac{dD_{TOT}}{dt}\right] = Tr_R[H_{TOT}, D_{TOT}]$$

$$= Tr_R[H_R + H_A + V$$

$H_R = H_R^{(R)} \otimes I^{(A)}$

$H_A = I^{(R)} \otimes H_A^{(A)}$

$$= \cancel{Tr_R[H_R, D_{TOT}]} \to 0 \; +$$

$$+ Tr_R[V, D_{TOT}]$$

(I) $$i\hbar \frac{dD_A}{dt} = \underbrace{[H_A, D_A]}_{\text{because}} + Tr_R[V$$

$$Tr_R[H_A, D_{TOT}] = Tr_R[H_A I$$

$$Tr_R[D_{T}$$

$$= H_A\, Tr_R[$$

$= ② H_A D_A -$

$$= \sum_{\alpha} \sum_{\gamma c} \hat{A}^{(\alpha)}_{a\alpha;c\gamma} D_{c\gamma;b\alpha}$$

$$= \sum_{\alpha} \sum_{c\gamma} A^{(\alpha)}_{a\gamma} \delta_{ac} D_{c\gamma;b\alpha}$$

$$= \sum_{\alpha} \sum_{\gamma} A^{(\alpha)}_{a\gamma} D_{a\gamma;b\alpha}$$

$$= \sum_{\gamma} \sum_{\alpha} \underbrace{D_{a\gamma;b\alpha} A^{(\alpha)}_{\alpha\gamma}}_{\sum_c D_{a\gamma;c\alpha} A^{(\alpha)}_{\alpha\gamma}\delta_{cb}}$$

$$= \sum_{\gamma} \sum_{c\alpha} D_{a\gamma;c\alpha} \hat{A}^{(\alpha)}_{c\alpha;b\gamma}$$

$$= \sum_{\gamma} \left[D\hat{A}^{(\alpha)} \right]_{a\gamma;b\gamma} = Tr_{\alpha}\, D\hat{A}^{(\alpha)}$$

$$\gamma \in \{\alpha\}$$

$\Rightarrow$ The partial trace is also cyclic provided

$$\hat{A} = \hat{A}^{(\alpha)} \otimes \mathbb{I}^{(a)}$$

$$\Rightarrow \quad Tr_{\alpha}\left[\left[\hat{A}^{(\alpha)}, D\right]\right] = Tr_{\alpha}\left[A^{(\alpha)} D\right] - Tr_{\alpha}\left[D A^{(\alpha)}\right]$$

$$= 0$$

Returning

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

interaction term: does not include any new variables or states

$$Tr_R\left[i\hbar \frac{dD_{TOT}}{dt}\right] = Tr_R\left[H_{TOT}, D_{TOT}\right]$$

$$= Tr_R\left[H_R + H_A + V, D_{TOT}\right]$$

$H_R = H_R^{(R)} \otimes \mathbb{I}^{(A)}$

$H_A = \mathbb{I}^{(R)} \otimes H_A^{(A)}$

$$= \cancel{Tr_R\left[H_R, D_{TOT}\right]} \rightarrow 0 + Tr_R\left[H_A, D_{TOT}\right]$$

$$+ Tr_R\left[V\, D_{TOT}\right]$$

I $$i\hbar \frac{dD_A}{dt} = \underbrace{\left[H_A, D_A\right]} + Tr_R\left[V, D_{TOT}\right]$$

because

$$Tr_R\left[H_A, D_{TOT}\right] = Tr_R\left[H_A D_{TOT}\right] - Tr_R\left[D_{TOT} H_A\right]$$

$$= H_A\, Tr_R\left[D_{TOT}\right] - Tr_R\left[D_{TOT}\right] H_A$$

$$= H_A D_A - D_A H_A$$

With that in mind let's calculate the time evolution of the average energy in region Δ

$$E_\Delta = Tr_\Delta D_\Delta H_\Delta$$

$$\frac{dE_\Delta}{dt} = \frac{d}{dt}\left(Tr_\Delta\left[D_\Delta H_\Delta\right]\right) = \underbrace{Tr_\Delta\left(H_\Delta \frac{dD_\Delta}{dt}\right)}_{1} + \underbrace{Tr_\Delta\left(D_\Delta \frac{dH_\Delta}{dt}\right)}_{2}$$

from (I)

1 $$Tr_\Delta\left(H_\Delta \frac{dD_\Delta}{dt}\right) = Tr_\Delta\left[H_\Delta\left\{[H_\Delta, D_\Delta]\frac{1}{i\hbar} + \frac{1}{i\hbar}Tr_R[V, D_{TOT}]\right\}\right]$$

$$= \frac{1}{i\hbar} Tr_\Delta\left[H_\Delta[H_\Delta, D_\Delta]\right] + \frac{1}{i\hbar} Tr_\Delta Tr_R\left(H_\Delta[V, D_{TOT}]\right)$$

$$Tr_\Delta Tr_R(\hat{B}) = Tr_{TOT}(\hat{B})$$

$$Tr_\Delta\left[H_\Delta[H_\Delta, D_\Delta]\right] = Tr_\Delta\left[H_\Delta H_\Delta D - H_\Delta D_\Delta H_\Delta\right]$$

$$= \underbrace{Tr_\Delta\left[H_\Delta H_\Delta D\right]}_{\text{cyclic}} - Tr_\Delta\left[H_\Delta D_\Delta H_\Delta\right]$$

$$= 0$$

(I) $$i\hbar \frac{dD_A}{dt} = \underbrace{[H_A, D_A]}_{\text{because}} + Tr_R [V, D_{TOT}]$$

because

$$Tr_R [H_A, D_{TOT}] = Tr_R (H_A D_{TOT}] - Tr_R [D_{TOT} H_A]$$

$$= H_A Tr_R [D_{TOT}] - Tr_R [D_{TOT}] H_A$$

$$= H_A D_A - D_A H_A$$

(1) $$Tr_A \left(H_A \frac{dD_A}{dt} \right) = \frac{1}{i\hbar} Tr_{TOT} \underbrace{\left[H_A V D_{TOT} - H_A D_{TOT} V \right]}_{\text{cyclical}}$$

$$= \frac{1}{i\hbar} Tr_{TOT} \left[D_{TOT} [H_A, V] \right]$$

Notes: (1) average of a quantity

$$= \frac{1}{i\hbar} \langle [H_A, V] \rangle_{TOT}$$

(2) involves the coupling to the reservoir $\Rightarrow$ heat

(2) $$Tr_A \left(D_A \frac{dH_A}{dt} \right) \equiv \text{Work}$$

Notes: (1) average of a quantity $\left\langle \frac{dH_A}{dt} \right\rangle$

(2) changes to the system from external factors

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In differential form

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$$dE = \underbrace{\mathrm{Tr}(H\, d D)}_{đQ} + \underbrace{\mathrm{Tr}(D\, dH)}_{đW}$$

1st law

Now let's remember

$$\langle \hat{A}_j \rangle = \frac{\partial \ln Z[\lambda]}{\partial \lambda_j}$$

For the canonical ensemble (we know average energy)

$\lambda_1 = -\beta$ $\quad \hat{A}_1 \equiv \hat{H}$

$\beta \geq 0$ (the minus sign will be clear shortly)

$$D_\beta = \frac{1}{Z} \exp -\beta \hat{H}$$

and $\quad \langle \hat{H} \rangle = E = -\dfrac{\partial \ln Z}{\partial \beta}$

The entropy

$$S_B = -k_B \mathrm{Tr}\left[D_B \ln D_B\right]$$

$$d(x\ln x) = dx \ln x + x\frac{dx}{x} = \ln x + 1$$

In differential form

$$dS_B = -k_B \mathrm{Tr}\left[\ln D_B \, dD_B + dD_B\right]$$

$$= -k_B \mathrm{Tr}\left[\underbrace{\ln D_B}_{-\ln Z - \beta H} dD_B\right] - k_B \mathrm{Tr}\left[dD_B\right]$$

$$\mathrm{Tr}\, D_B = 1$$

$$\Rightarrow \mathrm{Tr}\left[dD_B\right] = 0$$

$$= +k_B \mathrm{Tr}\left[\underbrace{\ln Z}_{\text{scalar}} dD_B\right] + k_B \beta \underbrace{\mathrm{Tr}\left[H dD_B\right]}_{đQ = \mathrm{Tr}[H dD_B]}$$

$$\ln Z \, \mathrm{Tr}\left[\cancel{dD_B}\right] \to 0$$

$$\Rightarrow dS_B = k\beta\, đQ$$

From thermodynamics definition of entropy in quasi-static processes

$$dS = \frac{đQ}{T}$$

$$\Rightarrow dS_B = k\beta T dS$$

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

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

where x_i is some external parameter used by experimentalists to alter the Hamiltonian

From (2)

$$\frac{\partial^2 S_B}{\partial \beta \partial x_i} = \frac{\partial}{\partial \beta}\left(k\beta T \frac{\partial S}{\partial x_i}\right) = \frac{\partial^2 S}{\partial \beta \partial x_i} k_B \beta T + \frac{\partial (k_B \beta T)}{\partial \beta}\frac{\partial S}{\partial x_i}$$

From (1)

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

The minimal model that makes (1) and (2) consistent is

$$k_B \beta T = \text{constant}$$

$$\frac{\partial (k\beta T)}{\partial \beta} = \frac{\partial (k_B \beta T)}{\partial x_i} = 0$$

We have freedom to choose k_B provided it is positive $S[D] \geq 0$

$$\Rightarrow \quad dS_B = dS$$

$$\boxed{\beta = \frac{1}{kT}}$$

for equilibrium quasi-static process

Integrating to obtain the entropy

$$\int_0^T dS_B = \int_0^T dS$$

$$S_B(T) - S_B(0) = S(T) - S(0)$$

From the third law $\lim_{T\to 0} \lim_{V\to\infty} \frac{1}{V} S = 0$

From QM as $T \to 0$ the system tends to be in the ground state

$$S_B \to 0$$

$$\Rightarrow \quad S_B = S$$

The microscopically obtained Boltzmann entropy is equal to the thermodynamics entropy

Assuming now that all we know about the number of particles in the system is

$$\langle N \rangle = \mathrm{Tr}\, D_B \hat{N} \leftarrow \text{Number operator}$$

$$\Rightarrow D_B = \frac{1}{Z} \exp\left[-\beta \hat{H} + \alpha \hat{N}\right]$$

Lagrange multiplier

In differential form

$$dS_B = -k_B \mathrm{Tr}\left[dD_B (\ln D_B + 1)\right]$$

$$= -k_B \mathrm{Tr}\left[dD_B \ln D_B\right] + \cancelto{0}{\mathrm{Tr}\left[dD_B\right]}$$

$$= -k_B \mathrm{Tr}\left[-\ln Z \, dD_B - \beta H dD_B + \alpha \hat{N} dD_B\right]$$

$$= k_B \beta \underbrace{\mathrm{Tr}\left(H dD_B\right)} - k_B \alpha \overbrace{\mathrm{Tr}\left(\hat{N} dD_B\right)}^{dN}$$

considering no external parameter is changed $\Rightarrow dE$

$$\Rightarrow dS_B = k_B \beta \, dE - k_B \alpha \, dN$$

From Thermodynamics

$$dS = T dE - \frac{\mu}{T} dN$$

At the same time

$S_B = S \rightarrow$ Thermodynamic entropy

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