Thermodynamic Entropy as a Noether Invariant

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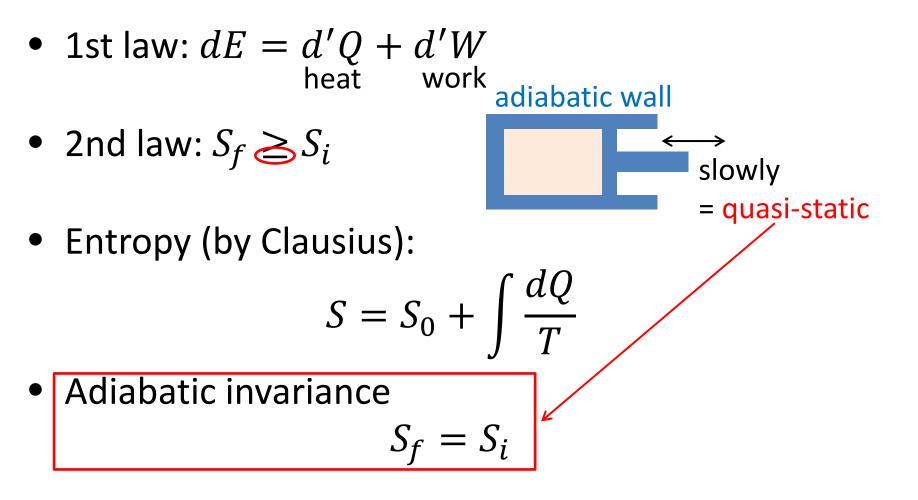
with S. Sasa (Kyoto University) [Phys.Rev.Lett.116,140601 (2016)]

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What is Thermodynamic Entropy? as a Noether Invariant

Thermodynamics

• Oth law: existence of equilibrium state



Thermodynamic Entropy as a Noether Invariant?

Noether theorem in Mechanics

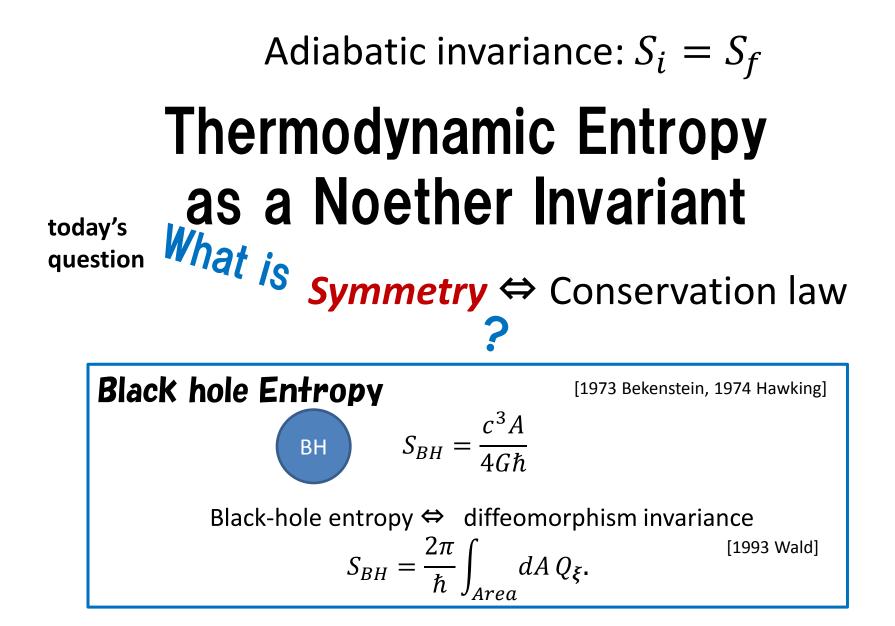
Symmetry ⇔ Conservation law

$$\begin{split} \delta_G I &= 0 \text{ for any } \hat{q} \Leftrightarrow \frac{d}{dt} O_G|_* = 0 \text{ for solutions } \hat{q}_* \\ \text{under } \hat{q} \to \hat{q} + \delta_G \hat{q} & t_f \\ I[\hat{q}] &= \int_{t_i}^{t_f} dt \, L(q(t), \dot{q}(t)) \end{split}$$

> q



Adiabatic invariance: $S_i = S_f$ Thermodynamic Entropy as a Noether Invariant W_{hat} is Symmetry \Leftrightarrow Conservation law



Adiabatic invariance: $S_i = S_f \leftarrow \text{macroscopic}$ Thermodynamic Entropy as a Noether Invariant W_{hat} is Symmetry \Leftrightarrow Conservation law $\wedge \text{microscopic}$?

⇒Let's first find the microscopic description of the adiabatic invariance of entropy.

Setup

 Consider N classical particles with short-range interaction in a box of volume V. <u>adiabatic wall</u>

• The action

$$I[\hat{q}] = \int_{t_i}^{t_f} dt \, L(q(t), \dot{q}(t), V(t))$$

 $q(t) \in \mathbb{R}^{3N}$: a collection of coordinates of N particles V(t): time-dependent volume \Rightarrow A protocol (functional form of V(t)) is fixed.

Example:
$$L = \sum_{i=1}^{N} \frac{1}{2} m \dot{r}_i - \sum_{i < j} U_{int} (|r_i - r_j|) - \sum_{i=1}^{N} U_{Wall}(r_i; V(t))$$

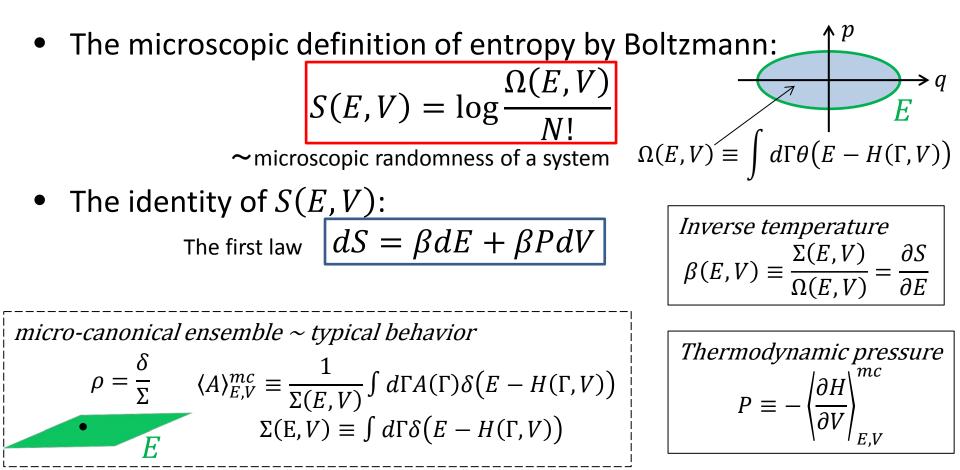
• The energy

$$E(q, \dot{q}, V) = \dot{q} \frac{\partial L}{\partial \dot{q}} - L$$

Boltzmann Entropy

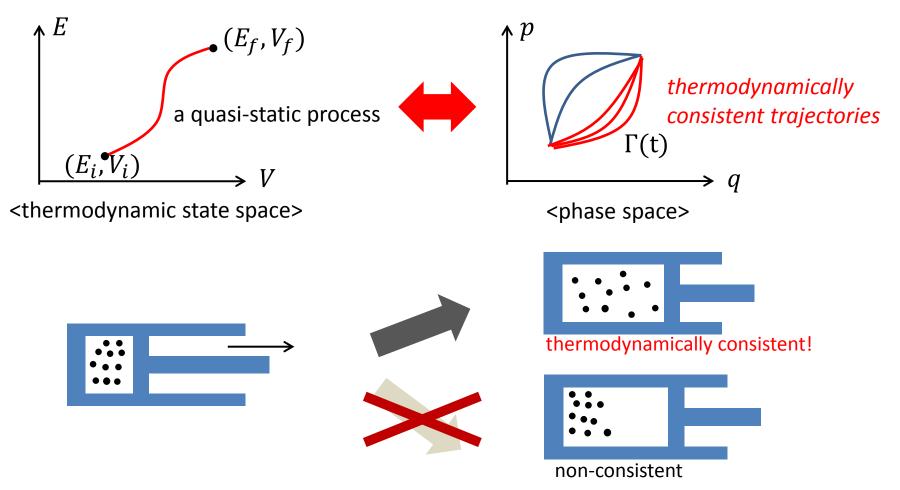
• Consider the Hamiltonian formulation:

a phase space coordinate $\Gamma = (q, p)$ with $p \equiv \frac{\partial L}{\partial \dot{q}}$ Hamiltonian $H(\Gamma, V) = E(q, \dot{q}(q, p, V), V)$

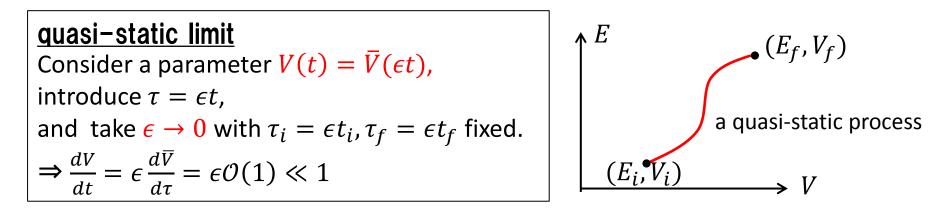


Bridge between micro and macro

- We are interested in quasi-static time evolution of the macroscopic system.
- ⇒Consider a class of phase-space trajectories consistent with quasi-static processes in thermodynamics.



Thermodynamically consistent trajectory



The conditions of thermodynamically consistent trajectory $\Gamma(t)$: (1) $E(t) = \overline{E}(\tau)$ $E(t) = H(\Gamma(t), V(t))$ (2) $\int_{\tau_i}^{\tau_f} d\tau \frac{d\overline{V}}{d\tau} \left[\frac{\partial H}{\partial V} - \left\langle \frac{\partial H}{\partial V} \right\rangle_{\overline{E}(\tau), \overline{V}(\tau)}^m \right] = 0$ mechanical work = thermodynamic work

in the quasi-static limit.

Microscopic description of adiabatic invariance of entropy

Let's consider time evolution of $S(t) = S\left(E(\Gamma(t), V(t)), V(t)\right)$ in the quasi-static limit $\epsilon \to 0$.

$$S(t_f) - S(t_i) = \int_{t_i}^{t_f} dt \frac{dS(t)}{dt}$$

 $\frac{dS = \beta dE - \beta \left\langle \frac{\partial H}{\partial V} \right\rangle_{E,V}^{mc} dV}{\text{``heat'' ``work''}} = \int_{t_i}^{t_f} dt \beta \left[\frac{dE}{dt} - \dot{V} \left\langle \frac{\partial H}{\partial V} \right\rangle_{E(t),V(t)}^{mc} \right]$ $\frac{dE(t)}{dt} = \frac{\partial H}{\partial \Gamma} \dot{\Gamma} + \frac{\partial H}{\partial V} \dot{V} = \frac{\partial H}{\partial V} \dot{V}$ $= \int_{-\infty}^{\tau_f} d\tau \,\beta \, \frac{d\overline{V}}{d\tau} \left[\frac{\partial H}{\partial V} - \left(\frac{\partial H}{\partial V} \right)_{\overline{F}(\tau) \, \overline{V}(\tau)}^{mc} \right]$ Adiabatic 0 $dE = \delta Q + \delta W$ condition 0 *Thermodynamically consistent trajectory* $\int d\tau \frac{d\overline{V}}{d\tau} \left| \frac{\partial H}{\partial V} - \left(\frac{\partial H}{\partial V} \right)_{=\langle \cdot \rangle = \overline{v} \langle \cdot \rangle} \right| = 0$ \Rightarrow We will find the symmetry

corresponding to this conservation law in the Noether theorem.

A generalized Noether theorem

• The Noether theorem in text books

$$\delta_G I = 0$$
 for any $\hat{q} \Leftrightarrow \frac{d}{dt} O_G|_* = 0$ for solutions \hat{q}_*
under $\hat{q} \to \hat{q} + \delta_G \hat{q}$



• A generalized Noether theorem

A non–uniform time translation

• Consider a non-uniform time translation

$$t \to t' = t + \eta \xi(q, \dot{q}, t)$$

$$q(t) \to q'(t') = q(t)$$

$$V(t) \to V'(t') = V(t')$$

$$\delta_{G}I = \eta \int_{t_{i}}^{t_{f}} dt \left[-\mathcal{E}\dot{q} + \frac{d}{dt}(\xi E) \right]$$

 η : infinitesimal parameter

(←just relabeling)

(\leftarrow The protocol is fixed.)

$$\varepsilon \equiv \frac{\partial L}{\partial q} - \frac{d}{dt} \frac{\partial L}{\partial \dot{q}}$$

• Suppose that there exist $\xi(q, \dot{q}, t)$ and $\psi(q, \dot{q}, t)$ s.t.

$$\delta_{G}I = \eta \int_{t_{i}}^{t_{f}} dt \frac{d\psi}{dt}$$
$$\Rightarrow -\int_{t_{i}}^{t_{f}} dt \, \xi = \left[\psi + \xi E\right]_{t_{i}}^{t_{f}}$$

 $\Rightarrow \psi + \xi E$ is conserved on $q_*(t)$!

- Let's derive the symmetry for adiabatic invariance of entropy.
- The condition of symmetry is non-trivial:

$$-\int_{t_i}^{t_f} dt \, \mathcal{E}\dot{q}\xi = \int_{t_i}^{t_f} dt \frac{d}{dt}(\psi + \xi E)$$

• Consider now

$$\xi = \Xi(E(q, \dot{q}, V), V), \qquad \psi = \Psi(E(q, \dot{q}, V), V)$$

and restrict trajectories to thermodynamically consistent ones.

 \Rightarrow The condition becomes

$$\Xi \left[dE - dV \left\langle \frac{\partial H}{\partial V} \right\rangle_{E,V}^{mc} \right] = d(\Psi + E\Xi)$$

 \Rightarrow The solution is

$$\Xi = \mathcal{F}(S)\beta$$

←Symmetry emerges for thermodynamically consistent trajectories!

• The Noether invariant is

$$\Psi + E\Xi = \int^{S} dS' \,\mathcal{F}(S')$$

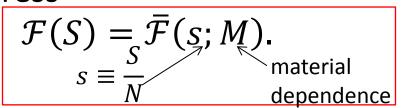
Assume that this is extensive.



$$= \begin{cases} \Psi + E\Xi \rightarrow \lambda(\Psi + E\Xi) \\ E \rightarrow \lambda E \end{cases}$$

$$= \begin{cases} \Psi \rightarrow \lambda \Psi \\ \Xi \rightarrow \Xi \\ \text{intensive} \end{cases} \quad \beta \rightarrow \beta \end{cases} \quad \Xi \beta^{-1} = \mathcal{F}(S) \text{ is intensive} \\ \text{and independent of } V. \end{cases}$$

• Here we can express



• Consider a composite system.

$$\beta_{A} = \beta_{B}$$

$$\Xi_{A} = \Xi_{B}$$

$$\widehat{F}(s_{A}; M_{A}) = \overline{F}(s_{B}; M_{B})$$

$$\widehat{F}(M_{A} - M_{A} - M_{A})$$
matter M_{A}
matter M_{B}

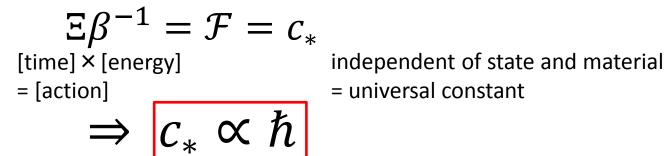
• If
$$M_A = M_B = M$$

 $\Rightarrow \overline{\mathcal{F}}(s_A; M) = \overline{\mathcal{F}}(s_B; M)$ for any s_A, s_B
 $\Rightarrow \overline{\mathcal{F}}(s; M) = c(M)$

• If
$$M_A \neq M_B$$

 $\Rightarrow c(M_A) = c(M_B)$ for any M_A, M_B
 $\Rightarrow c(M) = c_*$

• Thus, we obtain



⇒Our framework based on classical theory has led to the existence of the Planck constant.

• Therefore, we have

$$\Xi = a\hbar\beta$$

$$\Psi + E\Xi = \int^{S} dS' \mathcal{F}(S') = a\hbar(S + bN)$$

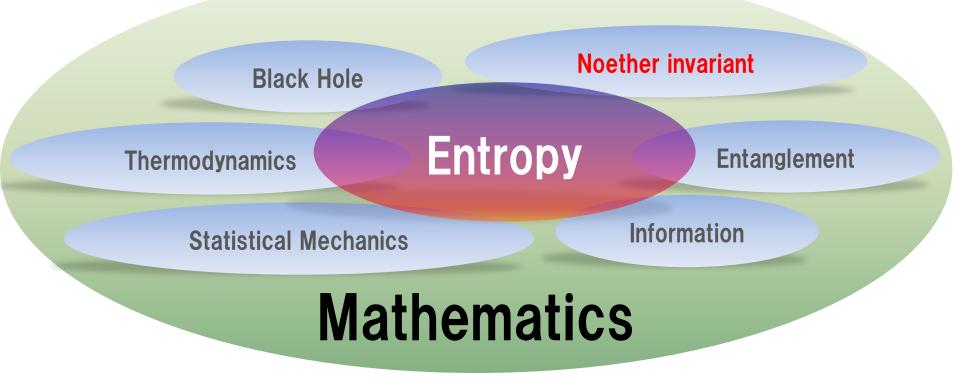
Main result

• In the macroscopic system, the symmetry $t \rightarrow t + \eta \hbar \beta (E(t), V(t))$

emerges for "thermodynamically consistent trajectories".

- Then, the Noether invariant is $\Psi + E\Xi = \hbar(S + bN).$
- This provides a new and unique characterization of entropy.

Various aspects of entropy on mathematics



Math connects different physics and makes new ideas.

Thank you very much!