New Thermostatistical Principle of Minimum Entropy Production in Linear and Nonlinear Transport Phenomena

Masuo Suzuki

In the recent series of my papers [1, 2, 3] concerning irreversibility and entropy production in transport phenomena, I have derived entropy production from the symmetric part (namely the second-order part, in the linear response) of the density matrix described by the von Neumann equation [1]. Even the heat conduction has been shown [2] to be described by this theory, introducing a thermal field $E_{\mathrm{T}} \propto \mathrm{grad}\, T(\boldsymbol{r})$ for the temperature $T(\boldsymbol{r})$ at the position $\boldsymbol{r}$. A steady state with the current $\boldsymbol{j}$ is maintained by energy supply and heat extraction. This mechanism has been formulated explicitly [2] by extending the von Neumann equation.

The time derivative of the entropy production rate is also expressed [2, 3] by the canonical correlation of the nonlinear (or dressed) current operators. This justifies the Onsager-Prigogine principle of minimum entropy production in the linear response regime [2].

A new variational principle of steady states is found by introducing an integrated type of energy dissipation (or entropy production) instead of instantaneous energy dissipation. This new principle is valid both in linear and nonlinear transport phenomena [3, 4]. Prigogine's dream [5] has now been realized by this new general principle of minimum "integrated" entropy production (or energy dissipation). Applications of this theory to electric conduction, heat conduction, particle diffusion and chemical reactions will be presented in the conference.

[1] M.Suzuki, Physica A **390**(2011)1904. [2] A **391**(2012)1074. [3] Physica A (2012), in preparation.
[4] M.Suzuki, in Prog.Theor.Phys.Supplement (2012). [5] I.Prigogine, *Non-Equilibrium Thermodynamics, Variational Techniques and Stability*, edited by R.J.Donnelly, R.Herman and I.Prigogine (U.C. Press 1966)

Part I

First-Principles Derivation of Entropy Production in Steady States from von Neumann equation

◎ <u>Review of previous theories</u> :

a) <u>energy</u> balance and complex field $Fe^{i\omega t}$ — thermodynamic theory (correct!)

b) by using only linear $\rho_{lr}(t) \rightarrow$ incorrect

$$S(t) \rightarrow -k_B \mathrm{Tr}\, \rho_{lr}(t) \log \rho_{lr}(t)$$

c) $S_Z^{(lr)}(t) = -k_B \mathrm{Tr}\, \rho_{lr} \log \rho_{loc} \rightarrow -\frac{\alpha E^2}{T}$ negative!

d) relative entropy $\rightarrow$ incorrect

e) variational treatment (Onsager, ...) phenomenological theory (correct!)
<u>in linear regime</u>

Purpose : to give first-principles derivation of

Entropy production $\left(\frac{dS}{dt}\right)_{irr} > 0$,

using **von Neumann eq.**

$$i\hbar\frac{\partial\rho(t)}{\partial t} = [\mathcal{H}_0 + \mathcal{H}_1(t), \rho(t)],$$

where $\mathcal{H}_1(t) = -\mathbb{A}\cdot\mathbb{F}(t)$ (external force)

◎ typical case : static electric field

$$\mathbb{A} = e\sum_j \mathbb{r}_j, \quad \mathbb{F}(t) = \mathbb{E}$$

Surprisingly, the correct entropy production is given by the **Second-Order term** $\rho_2(t)$ as

$$\left(\frac{dS}{dt}\right)_{irr} = \frac{1}{T}\mathrm{Tr}\,\mathcal{H}_0\,\rho_2'(t) > 0.$$

$\frac{1}{T}\frac{dU(t)}{dt}$ $\leftarrow$ $U(t) = \mathrm{Tr}\,\mathcal{H}_0\,\rho(t)$

◎ typical case : static electric field $\mathbb{E}$

$$\left(\frac{dS}{dt}\right)_{irr} = \frac{\mathbb{J}\cdot\mathbb{E}}{T} = \frac{\sigma E^2}{T} > 0,$$

where $\mathbb{J} = \sigma\mathbb{E}$ **and** $\dot{j} = \dot{A}$,

$$\sigma = \int_0^\infty dt \int_0^\beta d\lambda\, e^{-\varepsilon t}\langle \dot{j}\,\dot{j}(t+i\hbar\lambda)\rangle_0$$

In general, Symmetry of $\rho(t)$ is important:

$$\rho(t) = \rho_{\text{odd (antisym)}}(t) + \rho_{\text{even (symmetric)}}(t) ;$$

$$\rho_{\text{odd (antisym)}}(t) = \rho_1(t) + \rho_3(t) + \cdots$$

contributes to current.

$$\rho_{\text{even (sym)}}(t) = \rho_0 + \rho_2(t) + \cdots$$

to entropy.

Thus, the **current** is described by the **odd fluctuating part**; **entropy production or irreversibility is** described by the **even part of fluctuation**

$$\left(\rho_2(t) + \rho_4(t) + \cdots\cdots ! \right).$$

$$\mathbb{J}_E = \mathrm{Tr}\, \mathbf{j}\, \rho_{odd}(t) = \sigma_E \mathbb{E}, \quad \boxed{\text{general nonlinear case}}$$

$$\sigma_E = \sigma_0 + \sigma_2 E^2 + \cdots + \sigma_{2n} E^{2n} + \cdots; \sigma_0 = \sigma$$

$$\left(\frac{dS}{dt}\right)_{irr}(E) = \frac{\mathbb{J}_E \cdot \mathbb{E}}{T(t)} = \frac{(\sigma_0 + \sigma_2 E^2 + \cdots) E^2}{T(t)} > 0$$

even in the nonlinear regime.

◎ Scheme of Steady State with Entropy Production

energy supply $\left(\frac{\partial \rho_{\mathrm{a}}(t)}{\partial t}\right)_{\mathrm{es}} = \eta_{\mathrm{es}}(t)$ → heat generation $\langle \mathcal{H}_1 \rangle_t \to \langle \mathcal{H}_0 \rangle_t$ → heat extraction $\left(\frac{\partial \rho_{\mathrm{s}}(t)}{\partial t}\right)_{\mathrm{he}} = -\epsilon_{\mathrm{r}}(\rho_{\mathrm{s}}(t) - \rho_0)$

$\downarrow$

$$\boxed{\left(\frac{dS}{dt}\right)_{\mathrm{irr}} = \frac{1}{T}\mathrm{Tr}\mathcal{H}_0 \rho_{\mathrm{s}}'(t) = \frac{\boldsymbol{J}_F \cdot \boldsymbol{F}}{T} > 0}$$

$$\left(\frac{d}{dt}\rho(t) = -\mathcal{L}\rho(t) + \mathcal{L}_{\mathrm{s}}(t)\rho_0 \quad \to \quad \rho^{(\mathrm{st})}(t) = \rho(0) + t\rho'(0)\right)$$

• Entropy operator:

$$\mathcal{S} \equiv -k_B \log \rho_{eq} = \frac{\mathcal{H}_0 - \mathcal{F}_0}{T}$$

$$\therefore \; S(t) = \mathrm{Tr}\,\mathcal{S}\rho(t) \quad \therefore \; \underline{\left(\frac{dS}{dt}\right)_{irr} = \frac{1}{T}\mathrm{Tr}\mathcal{H}_0 \rho'_{sym}(t)}$$

Part II
General Formulas of Nonlinear Responses and Time-derivative of Entropy Production

◎ General nonlinear response:

$$\mathbb{J}_F = \mathrm{Tr}\, \mathbf{j}\, \rho(t) = \int_{t_0}^{t} dt' \int_0^{\beta} d\lambda \left\langle \mathbf{j}(-i\hbar\lambda)\, \mathcal{U}^{-1}(t,t')\, \mathbf{j}\, \mathcal{U}(t,t') \right\rangle_0 \cdot \mathbb{F}(t')$$

for $\mathcal{H}(t) = \mathcal{H}_0 - A\cdot\mathbb{F}(t)$ and

$$\mathcal{U}(t,t') = \exp_+\left(\frac{1}{i\hbar}\int_{t'}^{t} \mathcal{H}(s)\,ds\right)$$

$$= 1 + \frac{1}{i\hbar}\int_{t'}^{t}\mathcal{H}(t_1)\,dt_1 + \cdots + \left(\frac{1}{i\hbar}\right)^n \int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2 \cdots \int_{t'}^{t_{n-1}} dt_n\, \mathcal{H}(t_1)\cdots\mathcal{H}(t_n) + \cdots$$

In particular, if $\mathbb{F}(t) = \mathbb{F}$ (constant), then we have

$$\mathbb{J}_F = \sigma_F \cdot \mathbb{F} \;;\; \sigma_F = \int_0^{\infty} dt \int_0^{\beta} d\lambda \left\langle \mathbf{j}(-i\hbar\lambda)\, \mathbf{j}(t;\mathbb{F}) \right\rangle_0$$

In the linear case, we obtain Kubo formula

$$\sigma_{\mathrm{Kubo}} = \int_0^{\infty} dt \int_0^{\beta} d\lambda\, \underset{\substack{\uparrow \\ \text{(adiabatic factor)}}}{e^{-\varepsilon t}} \left\langle \mathbf{j}\,\mathbf{j}(t+i\hbar\lambda) \right\rangle_0$$

⊙ New Formula of the Time-Derivative of Entropy Production

⊙
$$\frac{d\sigma_S(t)}{dt} = \frac{F^2}{T}\int_0^\beta d\lambda \left\langle \dot{j}(-i\hbar\lambda)\dot{j}(t;F)\right\rangle_0$$

where

$$\dot{j}(-i\hbar\lambda) = e^{\lambda\mathcal{H}_0}\dot{j}e^{-\lambda\mathcal{H}_0} \quad \text{and} \quad \dot{j}(t;F) = e^{-\frac{t\mathcal{H}}{i\hbar}}\dot{j}e^{\frac{t\mathcal{H}}{i\hbar}}$$

(dressed current operator)

$$\mathcal{H} = \mathcal{H}_0 - A\cdot F$$

This formula can be obtained after long calculations from the formula of the entropy production:

$$\sigma_S(t) \equiv \left(\frac{dS}{dt}\right)_{irr} = \frac{d}{dt}\mathrm{Tr}\,S\rho(t) = \frac{1}{T}\frac{d}{dt}\mathrm{Tr}\,\mathcal{H}_0\rho(t) = \frac{1}{T}\mathrm{Tr}\,\mathcal{H}\rho_{sym}(t)$$

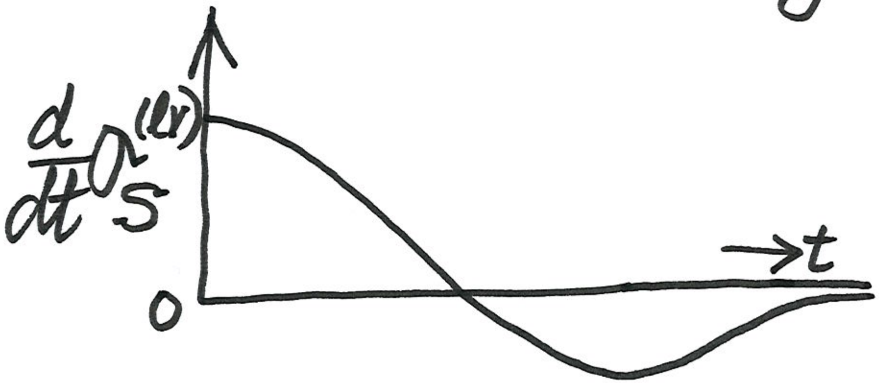
⊙ Note that this formula is related to the nonlinear transport coefficient σ_F as

$$\underline{\underline{\sigma_F}} = \int_0^\infty dt\int_0^\beta d\lambda\left\langle \dot{j}(-i\hbar\lambda)\dot{j}(t;F)\right\rangle_0 = \int_0^\infty dt\,\frac{d\sigma_S(t)}{dt}\cdot\frac{T}{F^2} = \underline{\underline{\frac{T}{F^2}\sigma_S(\infty)}}$$

In the linear case, we have

$$\frac{d}{dt}\sigma_s^{(lr)}(t) = \int_0^\beta \langle \dot{j}\dot{j}(t+i\hbar\lambda)\rangle_0 \, d\lambda \cdot \frac{F^2}{T} \quad \therefore \quad \sigma_s^{(l)} = \frac{F^2}{T}\sigma_{Kubo}$$

⊙ This has a negative long-time tail:



Thus, we have

$$\frac{d}{dt}\sigma_s^{(lr)}(t) < 0$$

for large t.

This yields a microscopic proof of Prigogine's stability criterion in the linear case.

⊙ The present formula reveals the essence of the principle of minimum entropy production in the steady state near equilibrium (in the linear case).

This does not hold in a general nonlinear case.

◎ We have to find a new general principle!

Part III : New Principle of Minimum Entropy Production beyond Onsager–Prigogine Variational Theory

⊙ Onsager's reciprocity relation and least energy dissipation theorem

Def. Entropy production (due to thermodynamics 1st law)

$$\sigma = \sum_{i=1}^{n} J_i X_i = \sum_{i=1}^{n}\sum_{j=1}^{n} L_{ij} X_i X_j \geq 0$$

where the current J_i is given by

$$J_i = \sum_{j=1}^{n} L_{ij} X_j \quad \text{(linear response)}$$

X_j : conjugate force

⊙ Reciprocity relation

$L_{ij} = L_{ji}$ due to the time reversal sym. of fluctuation in equil.

→ least energy dissipation theorem $\frac{\partial \sigma}{\partial X_i} = 0$ $(i = k+1, \cdots, n)$

with $\frac{\partial \sigma}{\partial X_i} = 2J_i$ $(i = 1, 2, \cdots, k)$

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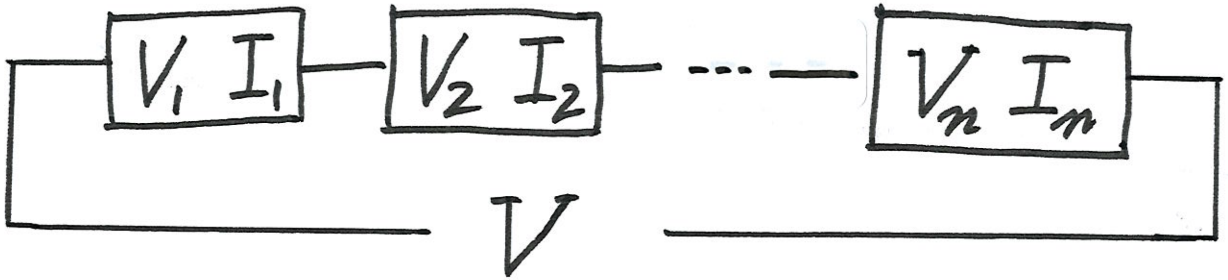
◎ Feynman's demonstration of least dissipation theorem in a linear electric circuit

(The Feynman Lectures on Physics, Vol. II, 1964)



$\Rightarrow I_1 = I_2 = \cdots = I_n$, as it should be.

∘ entropy production for the fixed total voltage V

$$\sigma \equiv \frac{dS}{dt} = \frac{1}{T}(V_1 I_1 + V_2 I_2 + \cdots + V_n I_n)$$

$$= \frac{1}{T}\left(L_{11} V_1^2 + L_{22} V_2^2 + \cdots + L_{(n-1)(n-1)} V_{n-1}^2 + L_{nn}\left(V - \sum_{k=1}^{n-1} V_k\right)^2\right)$$

◎ minimization of σ yields

$$I_1 = I_2 = \cdots = I_n,$$ as it should be.

◎ Physics is very attractive, but this does not hold in nonlinear cases: $L_{jj} = L_{jj}(V_j)$ problem.

In particular, Prigogine emphasized the importance to solve this

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◎ My demonstration of minimum entropy production in electric circuits dual to Feynman's example (1994,『Statistical mechanics』(M.S., Iwanami, in Japanese)

→ for the fixed total current I

p. 254 → これは定常状態では σ が最小になることを意味する．これをエントロピー生成速度最小の原理という．ただし，以上の議論は，線形応答の範囲で，Onsager の相反定理が成り立つ場合に正当化される．

簡単な応用例としては，Kirchhoff の法則をエントロピー生成速度最小の原理，すなわち，Joule 熱発生最小の条件より導くことができる．図 4-6 のような電気回路を例にとると，Joule 熱 W は，Joule heat W

$$\boxed{W = I_1{}^2R_1+(I-I_1)^2R_2+(I_1-I_5)^2R_3+(I-I_1+I_5)^2R_4+I_5{}^2R_5} \tag{4.318}$$

と与えられ，変分条件 minimization of W

$$\frac{\partial W}{\partial I_1}=0, \qquad \frac{\partial W}{\partial I_5}=0 \tag{4.319}$$

から，容易に Kirchhoff の法則，すなわち，$I_1R_1+I_3R_3=I_2R_2+I_4R_4$ などが導かれる*．電荷保存は最初から仮定した．

Kirchhoff law

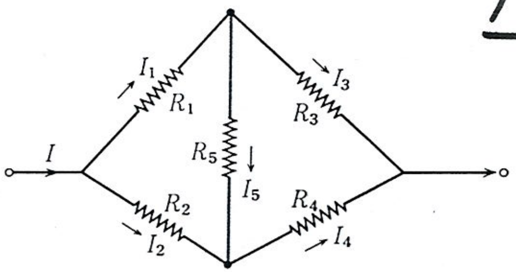

図 4-6　Kirchhoff の法則とエントロピー生成速度(すなわち Joule 熱発生)最小の原理．

* エントロピー生成速度を一定，すなわち Joule 熱発生速度を一定にする条件の下では，電流が最大原理によって Kirchhoff の法則が導かれる．すなわち，(4.318)で W=一定 とおいて，I を I_1 の関数とみなし，偏微分すると，$\partial I/\partial I_1=(I_2R_2+I_4R_4-I_1R_1-I_3R_3)/(I_2R_2+I_4R_4)$ となり，$\partial I/\partial I_1=0$ より Kirchhoff の法則が得られる．(岩波「統計力学」(鈴木増雄)より.)

◎ Unfortunately, this does not work when $\{R_j\}$ depend on current $\{I_j\}$: $R_j=R_j(I_j)$

nonlinear responses.

This has been a long-term basic difficult problem!

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◎ **New theory**: General theorem of minimum entropy production including nonlinear responses (to be in Physica A (2012) Paper III)

Before giving my general theory, it will be interesting to explain my many trials to extend this theorem to nonlinear responses. (From a half century experience.)

— Stay hungry. Stay foolish. (S. Jobs) (愚直であれ)

⊙ A simple example of nonlinear resistance : $R_j = R_j(I_j) = a_j I_j^m$ $(m>0)$

Minim. of $\tilde{Q} = \sum I_j^2 R_j(I_j)$ gives a correct result!

However, if we add another term (ex. $R_j = \underset{(\text{constant})}{a_{0j}} + a_j I_j^m$), then we fail!

⊙ Answer!

These many trials suggest to consider a new type of the integral form

$$◎\quad \tilde{Q}^I = \sum_j \int_0^{I_j} R_j(I)\, I\, dI \Leftarrow \sum_j \int_0^t I_j(t) R_j(I_j(t)) \dot{I}_j(t)\, dt \quad \text{with } I_j(t) = I_j$$

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New Principle: Principle of **M**inimum **I**ntegrated **E**nergy **D**issipation (MIED)

in Nonlinear Electric Circuits whose resistances depend on the current I: $R_j = R_j(I)$

We introduce the Integrated Energy Dissipation by

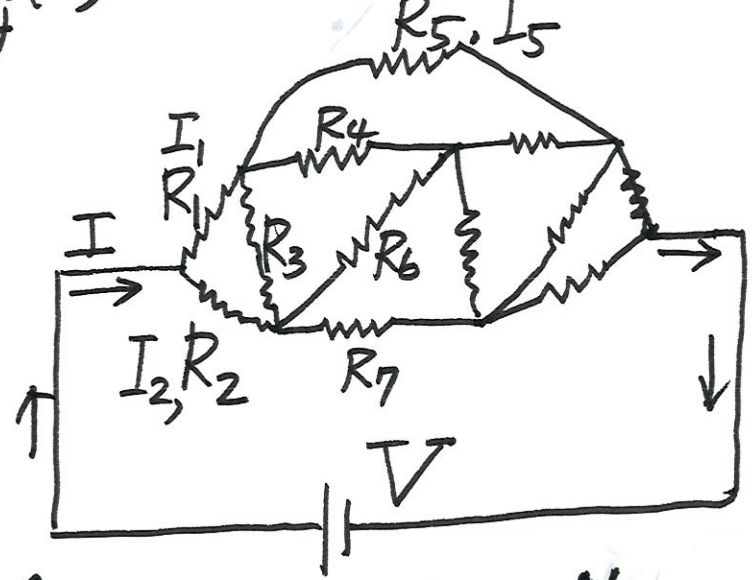
$$\sigma_j(I_j) \equiv \int_0^{I_j} R_j(I)\,dI^2 = 2\int_0^{I_j} R_j(I)\,I\,dI$$

Principle: $\boxed{\sum_j^{\text{all}} \sigma_j(I_j) = \min}$

(This is an extension of Prigogine's minimum entropy production)
(M. Suzuki, Physica A (2011)...)

$\Downarrow$

Kirchhoff's second law for any circuit with the current conservation.



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This *integrated energy dissipation* does give finally a desired correct law! In Feynman's case, we consider

$$Q^{I} = \sum_j \int_0^{V_j} I_j(V)\,dV = \sum_j \int_0^{t} I_j(V_j(t))\dot{V}(t)\,dt$$

with $V_j(t) = V_j$

4-c) General formulation

$$\sigma^{I} = \int d\mathbf{r} \int_0^{X(\mathbf{r})} J(X(\mathbf{r}))\,dX(\mathbf{r}) = \int d\mathbf{r} \int_0^{t} J(X(\mathbf{r},t))\dot{X}(\mathbf{r},t)\,dt$$

with $X(\mathbf{r},t) = X(\mathbf{r})$

where $\int d\mathbf{r}$ denotes the volume integral in continuous systems such as thermal conduction and chemical reaction.

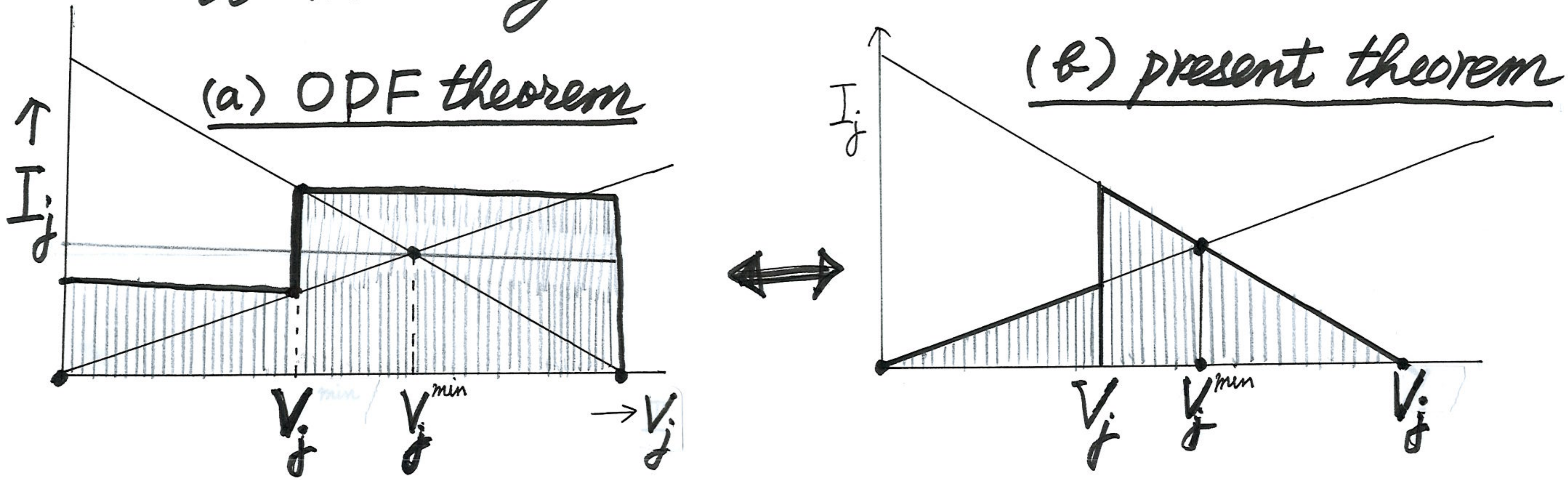
We have also

$$\tilde{\sigma}^{I} = \int d\mathbf{r} \int_0^{J(\mathbf{r})} \underbrace{J(\mathbf{r},t)R(J(\mathbf{r},t))}_{= X(J(\mathbf{r},t))}\,dJ(\mathbf{r},t) = \int d\mathbf{r} \int_0^{t} \underbrace{J(\mathbf{r},t)R(J(\mathbf{r},t))}_{= X(J(\mathbf{r},t))}\dot{J}(\mathbf{r},t)\,dt$$

with $J(\mathbf{r},t) = J(\mathbf{r})$

◎ Why valid is OPF theorem in the linear regime?

We explain the reason in an electric circuit.
to minimize both areas.



They differ only by the factor 2.
This does not affect the rational treatment.
Thus, the <u>instantaneous min. dissipation</u> <u>happens</u> to be valid.

⓪ Variational Principle in Nonlinear Diffusion

- particle density $n(\mathbf{r})$ at position $\mathbf{r}$,
- particle current $\mathbf{j}(\mathbf{r}) = D(F(\mathbf{r}))\mathbf{F}(\mathbf{r})$; $\mathbf{F}(\mathbf{r}) = -\nabla n(\mathbf{r})$
- $D(F)$: <u>nonlinear</u> diffusion constant (force)

According to our new general theory, we introduce the variational function

$$I = \int_V d\mathbf{r} \int_0^{F(\mathbf{r})} \mathbf{j}(\mathbf{r}) \cdot d\mathbf{F}(\mathbf{r}) = \int_V d\mathbf{r} \int_0^{\mathbf{F}(\mathbf{r})} D(F(\mathbf{r}))\left(\mathbf{F}(\mathbf{r})\right) d\mathbf{F}(\mathbf{r})$$

Euler's equation yields the steady state

$$\nabla \left(D(F(\mathbf{r})) \nabla n(\mathbf{r}) \right) = 0.$$

This is our desired result!

If $D(F(\mathbf{r})) = D$ (constant), then we have $\nabla^2 n(\mathbf{r}) = 0$!

Variational Theory of Thermal Diffusion in the linear case : $\lambda = \lambda(T(x))$ for temperature $(T = T(x))$

This is a very difficult problem which has been tried by many people (Prigogine et al).

Now I have found the following vari. func.

$$I = \int dx \, \overset{\text{(weight!)}}{\underline{\lambda(T(x))}} \int_0^{F(x)} \lambda(T(x)) F(x) \, dF(x) \qquad F(x) = -\frac{dT(x)}{dx}$$

$$= \frac{1}{2} \int dx \, \lambda^2(T(x)) F^2(x) = \frac{1}{2} \int dx \, (j(x))^2$$

Now, a new aspect appears!

we need the weight $\lambda(T(x))$ in the variational integral!

$\Rightarrow$ steady state:

$$\frac{d}{dx}\left(\lambda(T(x)) \frac{dT(x)}{dx}\right) = 0 \quad \therefore \quad \lambda(T(x)) \frac{dT(x)}{dx} = C$$