

# Thermodynamics & Statistical Physics

## Chapter 5. Thermodynamics of irreversible processes

Yuan-Chuan Zou  
zouyc@hust.edu.cn

School of Physics, Huazhong University of Science and Technology

December 30, 2013

# Table of contents

- ① §5. Thermodynamics of irreversible processes
  - 5.1 Local equilibrium, entropy flux density and production rate
  - 5.2 Linear and nonlinear processes, Onsager relation

## 5.1 Local equilibrium, entropy flux density, entropy local production rate

## 5.1 Local equilibrium, entropy flux density, entropy local production rate

- Irreversible processes.

## 5.1 Local equilibrium, entropy flux density, entropy local production rate

- Irreversible processes.
- 2nd Law:  $dS \geq \frac{\delta Q}{T}$ ,

## 5.1 Local equilibrium, entropy flux density, entropy local production rate

- Irreversible processes.
- 2nd Law:  $dS \geq \frac{\delta Q}{T}$ ,  
= reversible; > irreversible.

## 5.1 Local equilibrium, entropy flux density, entropy local production rate

- Irreversible processes.
- 2nd Law:  $dS \geq \frac{\delta Q}{T}$ ,  
= reversible; > irreversible.
- $dS = d_e S + d_i S$  (e, external; i, internal),

## 5.1 Local equilibrium, entropy flux density, entropy local production rate

- Irreversible processes.
- 2nd Law:  $dS \geq \frac{\delta Q}{T}$ ,  
= reversible; > irreversible.
- $dS = d_e S + d_i S$  (e, external; i, internal),  
 $d_e S$ : exchange of heat and matter;  $d_i S$ : isolated part.



## 5.1 Local equilibrium, entropy flux density, entropy local production rate

- Irreversible processes.
- 2nd Law:  $dS \geq \frac{\delta Q}{T}$ ,  
= reversible; > irreversible.
- $dS = d_e S + d_i S$  (e, external; i, internal),  
 $d_e S$ : exchange of heat and matter;  $d_i S$ : isolated part.
- Rewrite basic equation:  
$$TdS = dU + pdV - \sum_i \mu_i dn_i,$$

## 5.1 Local equilibrium, entropy flux density, entropy local production rate

- Irreversible processes.
- 2nd Law:  $dS \geq \frac{\delta Q}{T}$ ,  
= reversible; > irreversible.
- $dS = d_e S + d_i S$  (e, external; i, internal),  
 $d_e S$ : exchange of heat and matter;  $d_i S$ : isolated part.
- Rewrite basic equation:  
 $TdS = dU + pdV - \sum_i \mu_i dn_i$ , to  
 $TdS = dU + pdV - \sum_i \mu_i dN_i$ , where  $N_i$  is the  
number of molecules of component  $i$ , and  $\mu_i$  is the  
chemical potential of one molecule of component  $i$ .

# Local equilibrium

- No global state parameter (like  $T, p$ ) for non-equilibrium system.

# Local equilibrium

- No global state parameter (like  $T, p$ ) for non-equilibrium system.
- Exists small parts in the system, are approximately in equilibrium, which exist  $(T, p, \mu, \dots)$ .

# Local equilibrium

- No global state parameter (like  $T, p$ ) for non-equilibrium system.
- Exists small parts in the system, are approximately in equilibrium, which exist  $(T, p, \mu, \dots)$ .
- Each small part (in volume) is an open system,  
$$TdS = dU + pdV - \sum_i \mu_i dN_i.$$

# Local equilibrium

- No global state parameter (like  $T, p$ ) for non-equilibrium system.
- Exists small parts in the system, are approximately in equilibrium, which exist  $(T, p, \mu, \dots)$ .
- Each small part (in volume) is an open system,  
$$TdS = dU + pdV - \sum_i \mu_i dN_i.$$
- 1. Neglect volume change  $dV = 0$ ;

# Local equilibrium

- No global state parameter (like  $T, p$ ) for non-equilibrium system.
- Exists small parts in the system, are approximately in equilibrium, which exist  $(T, p, \mu, \dots)$ .
- Each small part (in volume) is an open system,  
$$TdS = dU + pdV - \sum_i \mu_i dN_i.$$
- 1. Neglect volume change  $dV = 0$ ; 2. Divided by  $V$ .

# Local equilibrium

- No global state parameter (like  $T, p$ ) for non-equilibrium system.
- Exists small parts in the system, are approximately in equilibrium, which exist  $(T, p, \mu, \dots)$ .
- Each small part (in volume) is an open system,  
 $TdS = dU + pdV - \sum_i \mu_i dN_i$ .
- 1. Neglect volume change  $dV = 0$ ; 2. Divided by  $V$ .
- $Tds = du - \sum_i \mu_i dn_i$ , where  $n_i$  is the number density of component  $i$ .



# Local equilibrium

- No global state parameter (like  $T, p$ ) for non-equilibrium system.
- Exists small parts in the system, are approximately in equilibrium, which exist  $(T, p, \mu, \dots)$ .
- Each small part (in volume) is an open system,  
 $TdS = dU + pdV - \sum_i \mu_i dN_i$ .
- 1. Neglect volume change  $dV = 0$ ; 2. Divided by  $V$ .
- $Tds = du - \sum_i \mu_i dn_i$ , where  $n_i$  is the number density of component  $i$ .
- For the whole component,  $U = \int u d\tau$ ,  $S = \int s d\tau$ ,  
 $N_i = \int n_i d\tau$ ;

# Local equilibrium

- No global state parameter (like  $T, p$ ) for non-equilibrium system.
- Exists small parts in the system, are approximately in equilibrium, which exist  $(T, p, \mu, \dots)$ .
- Each small part (in volume) is an open system,  
 $TdS = dU + pdV - \sum_i \mu_i dN_i$ .
- 1. Neglect volume change  $dV = 0$ ; 2. Divided by  $V$ .
- $Tds = du - \sum_i \mu_i dn_i$ , where  $n_i$  is the number density of component  $i$ .
- For the whole component,  $U = \int u d\tau$ ,  $S = \int s d\tau$ ,  
 $N_i = \int n_i d\tau$ ;  $S$  is a critical variable.

# Entropy flux density and entropy local production rate

## Entropy flux density and entropy local production rate

- Define  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ , where  $\vec{J}_s$  is the entropy flux density (external), and  $\Theta$  is the entropy local production rate (internal).

## Entropy flux density and entropy local production rate

- Define  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ , where  $\vec{J}_s$  is the entropy flux density (external), and  $\Theta$  is the entropy local production rate (internal).
- For the whole system:

# Entropy flux density and entropy local production rate

- Define  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ , where  $\vec{J}_s$  is the entropy flux density (external), and  $\Theta$  is the entropy local production rate (internal).
- For the whole system:
$$\frac{dS}{dt} = \frac{d}{dt} \int s d\tau$$

# Entropy flux density and entropy local production rate

- Define  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ , where  $\vec{J}_s$  is the entropy flux density (external), and  $\Theta$  is the entropy local production rate (internal).
- For the whole system:
$$\frac{dS}{dt} = \frac{d}{dt} \int s d\tau = \int \frac{\partial s}{\partial t} d\tau$$

# Entropy flux density and entropy local production rate

- Define  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ , where  $\vec{J}_s$  is the entropy flux density (external), and  $\Theta$  is the entropy local production rate (internal).
- For the whole system:
$$\frac{dS}{dt} = \frac{d}{dt} \int s d\tau = \int \frac{\partial s}{\partial t} d\tau = \int [-\nabla \cdot \vec{J}_s + \Theta] d\tau$$



# Entropy flux density and entropy local production rate

- Define  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ , where  $\vec{J}_s$  is the entropy flux density (external), and  $\Theta$  is the entropy local production rate (internal).

- For the whole system:

$$\begin{aligned}\frac{dS}{dt} &= \frac{d}{dt} \int s d\tau = \int \frac{\partial s}{\partial t} d\tau = \int [-\nabla \cdot \vec{J}_s + \Theta] d\tau \\ &= -\oint \vec{J}_s \cdot d\vec{\sigma} + \int \Theta d\tau.\end{aligned}$$

# Entropy flux density and entropy local production rate

- Define  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ , where  $\vec{J}_s$  is the entropy flux density (external), and  $\Theta$  is the entropy local production rate (internal).
- For the whole system:
$$\begin{aligned}\frac{dS}{dt} &= \frac{d}{dt} \int s d\tau = \int \frac{\partial s}{\partial t} d\tau = \int [-\nabla \cdot \vec{J}_s + \Theta] d\tau \\ &= -\oint \vec{J}_s \cdot d\vec{\sigma} + \int \Theta d\tau.\end{aligned}$$
- $\frac{d_e S}{dt} = -\oint \vec{J}_s \cdot d\vec{\sigma}$ ,  $\frac{d_i S}{dt} = \int \Theta d\tau$ .

# Entropy flux density and entropy local production rate

- Define  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ , where  $\vec{J}_s$  is the entropy flux density (external), and  $\Theta$  is the entropy local production rate (internal).
- For the whole system:
$$\frac{dS}{dt} = \frac{d}{dt} \int s d\tau = \int \frac{\partial s}{\partial t} d\tau = \int [-\nabla \cdot \vec{J}_s + \Theta] d\tau$$
$$= -\oint \vec{J}_s \cdot d\vec{\sigma} + \int \Theta d\tau.$$
- $\frac{d_e S}{dt} = -\oint \vec{J}_s \cdot d\vec{\sigma}$ ,  $\frac{d_i S}{dt} = \int \Theta d\tau$ .
- Apply to the simplest case: only heat conduction,

# Entropy flux density and entropy local production rate

- Define  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ , where  $\vec{J}_s$  is the entropy flux density (external), and  $\Theta$  is the entropy local production rate (internal).
- For the whole system:
$$\frac{dS}{dt} = \frac{d}{dt} \int s d\tau = \int \frac{\partial s}{\partial t} d\tau = \int [-\nabla \cdot \vec{J}_s + \Theta] d\tau$$
$$= -\oint \vec{J}_s \cdot d\vec{\sigma} + \int \Theta d\tau.$$
- $\frac{d_e S}{dt} = -\oint \vec{J}_s \cdot d\vec{\sigma}$ ,  $\frac{d_i S}{dt} = \int \Theta d\tau$ .
- Apply to the simplest case: only heat conduction,
- internal energy density:  $\frac{\partial u}{\partial t} = -\nabla \cdot \vec{J}_q$ , where  $\vec{J}_q$  is the heat flux density.

# Entropy flux density and entropy local production rate

- Define  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ , where  $\vec{J}_s$  is the entropy flux density (external), and  $\Theta$  is the entropy local production rate (internal).
- For the whole system:  

$$\frac{dS}{dt} = \frac{d}{dt} \int s d\tau = \int \frac{\partial s}{\partial t} d\tau = \int [-\nabla \cdot \vec{J}_s + \Theta] d\tau$$

$$= -\oint \vec{J}_s \cdot d\vec{\sigma} + \int \Theta d\tau.$$
- $\frac{d_e S}{dt} = -\oint \vec{J}_s \cdot d\vec{\sigma}$ ,  $\frac{d_i S}{dt} = \int \Theta d\tau$ .
- Apply to the simplest case: only heat conduction,
- internal energy density:  $\frac{\partial u}{\partial t} = -\nabla \cdot \vec{J}_q$ , where  $\vec{J}_q$  is the heat flux density.
- No volume change, no matter flow, the basic equation:  $T ds = du$

# Entropy flux density and entropy local production rate

- Define  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ , where  $\vec{J}_s$  is the entropy flux density (external), and  $\Theta$  is the entropy local production rate (internal).
- For the whole system:  

$$\frac{dS}{dt} = \frac{d}{dt} \int s d\tau = \int \frac{\partial s}{\partial t} d\tau = \int [-\nabla \cdot \vec{J}_s + \Theta] d\tau$$

$$= -\oint \vec{J}_s \cdot d\vec{\sigma} + \int \Theta d\tau.$$
- $\frac{d_e S}{dt} = -\oint \vec{J}_s \cdot d\vec{\sigma}$ ,  $\frac{d_i S}{dt} = \int \Theta d\tau$ .
- Apply to the simplest case: only heat conduction,
- internal energy density:  $\frac{\partial u}{\partial t} = -\nabla \cdot \vec{J}_q$ , where  $\vec{J}_q$  is the heat flux density.
- No volume change, no matter flow, the basic equation:  $T ds = du \Rightarrow \frac{\partial s}{\partial t} = \frac{1}{T} \frac{\partial u}{\partial t}$

# Entropy flux density and entropy local production rate

- Define  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ , where  $\vec{J}_s$  is the entropy flux density (external), and  $\Theta$  is the entropy local production rate (internal).
- For the whole system:
$$\frac{dS}{dt} = \frac{d}{dt} \int s d\tau = \int \frac{\partial s}{\partial t} d\tau = \int [-\nabla \cdot \vec{J}_s + \Theta] d\tau$$
$$= -\oint \vec{J}_s \cdot d\vec{\sigma} + \int \Theta d\tau.$$
- $\frac{d_e S}{dt} = -\oint \vec{J}_s \cdot d\vec{\sigma}$ ,  $\frac{d_i S}{dt} = \int \Theta d\tau$ .
- Apply to the simplest case: only heat conduction,
- internal energy density:  $\frac{\partial u}{\partial t} = -\nabla \cdot \vec{J}_q$ , where  $\vec{J}_q$  is the heat flux density.
- No volume change, no matter flow, the basic equation:  $T ds = du \Rightarrow \frac{\partial s}{\partial t} = \frac{1}{T} \frac{\partial u}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_q$ .

# Entropy flux density and entropy local production rate

- $$\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_q$$



# Entropy flux density and entropy local production rate

- $$\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_q = -\left[ \nabla \cdot \frac{\vec{J}_q}{T} - \vec{J}_q \cdot \nabla \frac{1}{T} \right]$$

# Entropy flux density and entropy local production rate

- $$\begin{aligned}\frac{\partial s}{\partial t} &= -\frac{1}{T} \nabla \cdot \vec{J}_q = -\left[\nabla \cdot \frac{\vec{J}_q}{T} - \vec{J}_q \cdot \nabla \frac{1}{T}\right] \\ &= -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T}.\end{aligned}$$

# Entropy flux density and entropy local production rate

- $\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_q = -[\nabla \cdot \frac{\vec{J}_q}{T} - \vec{J}_q \cdot \nabla \frac{1}{T}]$   
 $= -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T}.$
- Compare with  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta,$

# Entropy flux density and entropy local production rate

- $$\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_q = -\left[\nabla \cdot \frac{\vec{J}_q}{T} - \vec{J}_q \cdot \nabla \frac{1}{T}\right]$$
$$= -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T}.$$
- Compare with  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta,$   
 $\vec{J}_s = \frac{\vec{J}_q}{T}, \Theta = \vec{J}_q \cdot \nabla \frac{1}{T}.$

# Entropy flux density and entropy local production rate

- $\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_q = -[\nabla \cdot \frac{\vec{J}_q}{T} - \vec{J}_q \cdot \nabla \frac{1}{T}]$   
 $= -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T}.$
- Compare with  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta,$   
 $\vec{J}_s = \frac{\vec{J}_q}{T}, \Theta = \vec{J}_q \cdot \nabla \frac{1}{T}.$
- Define  $\vec{X}_q \equiv \nabla \frac{1}{T},$  as heat flow force,

# Entropy flux density and entropy local production rate

- $\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_q = -[\nabla \cdot \frac{\vec{J}_q}{T} - \vec{J}_q \cdot \nabla \frac{1}{T}]$   
 $= -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T}.$
- Compare with  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta,$   
 $\vec{J}_s = \frac{\vec{J}_q}{T}, \Theta = \vec{J}_q \cdot \nabla \frac{1}{T}.$
- Define  $\vec{X}_q \equiv \nabla \frac{1}{T},$  as heat flow force, then  
 $\Theta = \vec{J}_q \cdot \vec{X}_q.$

# Entropy flux density and entropy local production rate

- $$\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_q = -[\nabla \cdot \frac{\vec{J}_q}{T} - \vec{J}_q \cdot \nabla \frac{1}{T}]$$
$$= -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T}.$$
- Compare with  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ ,  
 $\vec{J}_s = \frac{\vec{J}_q}{T}$ ,  $\Theta = \vec{J}_q \cdot \nabla \frac{1}{T}$ .
- Define  $\vec{X}_q \equiv \nabla \frac{1}{T}$ , as heat flow force, then  
 $\Theta = \vec{J}_q \cdot \vec{X}_q$ .
- If heat conduction obeys the Fourier's law,  
 $\vec{J}_q = -\kappa \nabla T$ , then

# Entropy flux density and entropy local production rate

- $\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_q = -[\nabla \cdot \frac{\vec{J}_q}{T} - \vec{J}_q \cdot \nabla \frac{1}{T}]$   
 $= -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T}.$
- Compare with  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta,$   
 $\vec{J}_s = \frac{\vec{J}_q}{T}, \Theta = \vec{J}_q \cdot \nabla \frac{1}{T}.$
- Define  $\vec{X}_q \equiv \nabla \frac{1}{T},$  as heat flow force, then  
 $\Theta = \vec{J}_q \cdot \vec{X}_q.$
- If heat conduction obeys the Fourier's law,  
 $\vec{J}_q = -\kappa \nabla T,$  then  $\Theta = \vec{J}_q \cdot \nabla \frac{1}{T}$



# Entropy flux density and entropy local production rate

- $\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_q = -[\nabla \cdot \frac{\vec{J}_q}{T} - \vec{J}_q \cdot \nabla \frac{1}{T}]$   
 $= -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T}.$
- Compare with  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta,$   
 $\vec{J}_s = \frac{\vec{J}_q}{T}, \Theta = \vec{J}_q \cdot \nabla \frac{1}{T}.$
- Define  $\vec{X}_q \equiv \nabla \frac{1}{T},$  as heat flow force, then  
 $\Theta = \vec{J}_q \cdot \vec{X}_q.$
- If heat conduction obeys the Fourier's law,  
 $\vec{J}_q = -\kappa \nabla T,$  then  $\Theta = \vec{J}_q \cdot \nabla \frac{1}{T} = -\vec{J}_q \cdot \frac{\nabla T}{T^2}$

# Entropy flux density and entropy local production rate

- $$\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_q = -[\nabla \cdot \frac{\vec{J}_q}{T} - \vec{J}_q \cdot \nabla \frac{1}{T}]$$
$$= -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T}.$$
- Compare with  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ ,  
$$\vec{J}_s = \frac{\vec{J}_q}{T}, \Theta = \vec{J}_q \cdot \nabla \frac{1}{T}.$$
- Define  $\vec{X}_q \equiv \nabla \frac{1}{T}$ , as heat flow force, then  
$$\Theta = \vec{J}_q \cdot \vec{X}_q.$$
- If heat conduction obeys the Fourier's law,  
$$\vec{J}_q = -\kappa \nabla T, \text{ then } \Theta = \vec{J}_q \cdot \nabla \frac{1}{T} = -\vec{J}_q \cdot \frac{\nabla T}{T^2}$$
$$= \kappa \frac{(\nabla T)^2}{T^2}.$$

# Entropy flux density and entropy local production rate

- $$\frac{\partial s}{\partial t} = -\frac{1}{T} \nabla \cdot \vec{J}_q = -[\nabla \cdot \frac{\vec{J}_q}{T} - \vec{J}_q \cdot \nabla \frac{1}{T}]$$
$$= -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T}.$$
- Compare with  $\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta$ ,  
$$\vec{J}_s = \frac{\vec{J}_q}{T}, \Theta = \vec{J}_q \cdot \nabla \frac{1}{T}.$$
- Define  $\vec{X}_q \equiv \nabla \frac{1}{T}$ , as heat flow force, then  
$$\Theta = \vec{J}_q \cdot \vec{X}_q.$$
- If heat conduction obeys the Fourier's law,  
$$\vec{J}_q = -\kappa \nabla T, \text{ then } \Theta = \vec{J}_q \cdot \nabla \frac{1}{T} = -\vec{J}_q \cdot \frac{\nabla T}{T^2}$$
$$= \kappa \frac{(\nabla T)^2}{T^2}.$$
- $\Theta \geq 0.$

# Entropy flux density and entropy local production rate

- Apply to a more realistic case: temperature and chemical potential, non-uniform

# Entropy flux density and entropy local production rate

- Apply to a more realistic case: temperature and chemical potential, non-uniform  
— heat conduction and matter flow.

# Entropy flux density and entropy local production rate

- Apply to a more realistic case: temperature and chemical potential, non-uniform  
— heat conduction and matter flow.
- Energy conservation:  $\frac{\partial u}{\partial t} + \nabla \cdot \vec{J}_u = 0$ ,

# Entropy flux density and entropy local production rate

- Apply to a more realistic case: temperature and chemical potential, non-uniform  
— heat conduction and matter flow.
- Energy conservation:  $\frac{\partial u}{\partial t} + \nabla \cdot \vec{J}_u = 0$ ,  
matter conservation:  $\frac{\partial n}{\partial t} + \nabla \cdot \vec{J}_n = 0$ .

# Entropy flux density and entropy local production rate

- Apply to a more realistic case: temperature and chemical potential, non-uniform  
— heat conduction and matter flow.
- Energy conservation:  $\frac{\partial u}{\partial t} + \nabla \cdot \vec{J}_u = 0$ ,  
matter conservation:  $\frac{\partial n}{\partial t} + \nabla \cdot \vec{J}_n = 0$ .
- $\vec{J}_u = \vec{J}_q + \mu \vec{J}_n$ .



# Entropy flux density and entropy local production rate

- Apply to a more realistic case: temperature and chemical potential, non-uniform  
— heat conduction and matter flow.
- Energy conservation:  $\frac{\partial u}{\partial t} + \nabla \cdot \vec{J}_u = 0$ ,  
matter conservation:  $\frac{\partial n}{\partial t} + \nabla \cdot \vec{J}_n = 0$ .
- $\vec{J}_u = \vec{J}_q + \mu \vec{J}_n$ .
- $\therefore \frac{\partial u}{\partial t} = -\nabla \cdot \vec{J}_q - \nabla \cdot (\mu \vec{J}_n)$ .

# Entropy flux density and entropy local production rate

- Apply to a more realistic case: temperature and chemical potential, non-uniform  
— heat conduction and matter flow.
- Energy conservation:  $\frac{\partial u}{\partial t} + \nabla \cdot \vec{J}_u = 0$ ,  
matter conservation:  $\frac{\partial n}{\partial t} + \nabla \cdot \vec{J}_n = 0$ .
- $\vec{J}_u = \vec{J}_q + \mu \vec{J}_n$ .
- $\therefore \frac{\partial u}{\partial t} = -\nabla \cdot \vec{J}_q - \nabla \cdot (\mu \vec{J}_n)$ .
- $ds = \frac{1}{T}(du - \mu dn)$ ,

# Entropy flux density and entropy local production rate

- Apply to a more realistic case: temperature and chemical potential, non-uniform  
— heat conduction and matter flow.
- Energy conservation:  $\frac{\partial u}{\partial t} + \nabla \cdot \vec{J}_u = 0$ ,  
matter conservation:  $\frac{\partial n}{\partial t} + \nabla \cdot \vec{J}_n = 0$ .
- $\vec{J}_u = \vec{J}_q + \mu \vec{J}_n$ .
- $\therefore \frac{\partial u}{\partial t} = -\nabla \cdot \vec{J}_q - \nabla \cdot (\mu \vec{J}_n)$ .
- $ds = \frac{1}{T}(du - \mu dn)$ ,  
 $\Rightarrow \frac{\partial s}{\partial t} = \frac{1}{T} \frac{\partial u}{\partial t} - \frac{\mu}{T} \frac{\partial n}{\partial t}$

# Entropy flux density and entropy local production rate

- Apply to a more realistic case: temperature and chemical potential, non-uniform  
— heat conduction and matter flow.
- Energy conservation:  $\frac{\partial u}{\partial t} + \nabla \cdot \vec{J}_u = 0$ ,  
matter conservation:  $\frac{\partial n}{\partial t} + \nabla \cdot \vec{J}_n = 0$ .
- $\vec{J}_u = \vec{J}_q + \mu \vec{J}_n$ .
- $\therefore \frac{\partial u}{\partial t} = -\nabla \cdot \vec{J}_q - \nabla \cdot (\mu \vec{J}_n)$ .
- $ds = \frac{1}{T}(du - \mu dn)$ ,  

$$\Rightarrow \frac{\partial s}{\partial t} = \frac{1}{T} \frac{\partial u}{\partial t} - \frac{\mu}{T} \frac{\partial n}{\partial t}$$

$$= -\frac{1}{T} \nabla \cdot \vec{J}_q - \frac{1}{T} \nabla \cdot (\mu \vec{J}_n) + \frac{\mu}{T} \nabla \cdot \vec{J}_n$$

# Entropy flux density and entropy local production rate

- Apply to a more realistic case: temperature and chemical potential, non-uniform  
— heat conduction and matter flow.
- Energy conservation:  $\frac{\partial u}{\partial t} + \nabla \cdot \vec{J}_u = 0$ ,  
matter conservation:  $\frac{\partial n}{\partial t} + \nabla \cdot \vec{J}_n = 0$ .
- $\vec{J}_u = \vec{J}_q + \mu \vec{J}_n$ .
- $\therefore \frac{\partial u}{\partial t} = -\nabla \cdot \vec{J}_q - \nabla \cdot (\mu \vec{J}_n)$ .
- $ds = \frac{1}{T}(du - \mu dn)$ ,  

$$\Rightarrow \frac{\partial s}{\partial t} = \frac{1}{T} \frac{\partial u}{\partial t} - \frac{\mu}{T} \frac{\partial n}{\partial t}$$

$$= -\frac{1}{T} \nabla \cdot \vec{J}_q - \frac{1}{T} \nabla \cdot (\mu \vec{J}_n) + \frac{\mu}{T} \nabla \cdot \vec{J}_n$$

$$= -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T} - \frac{\vec{J}_n}{T} \cdot \nabla \mu.$$

# Entropy flux density and entropy local production rate

- $$\begin{aligned}\frac{\partial s}{\partial t} &= -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T} - \frac{\vec{J}_n}{T} \cdot \nabla \mu, \\ \frac{\partial s}{\partial t} &= -\nabla \cdot \vec{J}_s + \Theta.\end{aligned}$$

# Entropy flux density and entropy local production rate

- $$\begin{aligned}\frac{\partial s}{\partial t} &= -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T} - \frac{\vec{J}_n}{T} \cdot \nabla \mu, \\ \frac{\partial s}{\partial t} &= -\nabla \cdot \vec{J}_s + \Theta. \\ \Rightarrow \vec{J}_s &= \frac{\vec{J}_q}{T}, \quad \Theta = \vec{J}_q \cdot \nabla \frac{1}{T} - \vec{J}_n \cdot \frac{\nabla \mu}{T}.\end{aligned}$$

# Entropy flux density and entropy local production rate

- $$\frac{\partial s}{\partial t} = -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T} - \frac{\vec{J}_n}{T} \cdot \nabla \mu,$$
$$\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta.$$
$$\Rightarrow \vec{J}_s = \frac{\vec{J}_q}{T}, \quad \Theta = \vec{J}_q \cdot \nabla \frac{1}{T} - \vec{J}_n \cdot \frac{\nabla \mu}{T}.$$
- Define matter flow “force”  $\vec{X}_n = -\frac{1}{T} \nabla \mu$ , and heat flow “force”  $\vec{X}_q = \nabla \frac{1}{T}$ ,



# Entropy flux density and entropy local production rate

- $$\frac{\partial s}{\partial t} = -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T} - \frac{\vec{J}_n}{T} \cdot \nabla \mu,$$
$$\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta.$$

$$\Rightarrow \vec{J}_s = \frac{\vec{J}_q}{T}, \quad \Theta = \vec{J}_q \cdot \nabla \frac{1}{T} - \vec{J}_n \cdot \frac{\nabla \mu}{T}.$$

- Define matter flow “force”  $\vec{X}_n = -\frac{1}{T} \nabla \mu$ , and heat flow “force”  $\vec{X}_q = \nabla \frac{1}{T}$ ,  
 $\therefore \Theta = \vec{J}_q \cdot \vec{X}_q + \vec{J}_n \cdot \vec{X}_n.$

# Entropy flux density and entropy local production rate

- $$\frac{\partial s}{\partial t} = -\nabla \cdot \frac{\vec{J}_q}{T} + \vec{J}_q \cdot \nabla \frac{1}{T} - \frac{\vec{J}_n}{T} \cdot \nabla \mu,$$
$$\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \Theta.$$
$$\Rightarrow \vec{J}_s = \frac{\vec{J}_q}{T}, \quad \Theta = \vec{J}_q \cdot \nabla \frac{1}{T} - \vec{J}_n \cdot \frac{\nabla \mu}{T}.$$
- Define matter flow “force”  $\vec{X}_n = -\frac{1}{T} \nabla \mu$ , and heat flow “force”  $\vec{X}_q = \nabla \frac{1}{T}$ ,  
 $\therefore \Theta = \vec{J}_q \cdot \vec{X}_q + \vec{J}_n \cdot \vec{X}_n.$
- Generally,  $\Theta = \sum_k \vec{J}_k \cdot \vec{X}_k.$

# Table of contents

- ① §5. Thermodynamics of irreversible processes
  - 5.1 Local equilibrium, entropy flux density and production rate
  - 5.2 Linear and nonlinear processes, Onsager relation

## 5.2 Linear and nonlinear processes, Onsager relation

## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:

## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:
  1. Temperature

## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:
  1. Temperature  $\rightarrow$  heat flow,

## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:
  1. Temperature  $\rightarrow$  heat flow,  
 $\vec{J}_q = -\kappa \nabla T$ , Fourier's law.



## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:
  1. Temperature  $\rightarrow$  heat flow,  
 $\vec{J}_q = -\kappa \nabla T$ , Fourier's law.
  2. Density

## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:
  1. Temperature  $\rightarrow$  heat flow,  
 $\vec{J}_q = -\kappa \nabla T$ , Fourier's law.
  2. Density  $\rightarrow$  diffusion (matter flow),

## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:

1. Temperature  $\rightarrow$  heat flow,

$$\vec{J}_q = -\kappa \nabla T, \text{ Fourier's law.}$$

2. Density  $\rightarrow$  diffusion (matter flow),

$$\vec{J}_n = -D \nabla n, \text{ Fick's law.}$$

## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:

1. Temperature  $\rightarrow$  heat flow,

$$\vec{J}_q = -\kappa \nabla T, \text{ Fourier's law.}$$

2. Density  $\rightarrow$  diffusion (matter flow),

$$\vec{J}_n = -D \nabla n, \text{ Fick's law.}$$

3. Electric potential

## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:
  1. Temperature  $\rightarrow$  heat flow,  
 $\vec{J}_q = -\kappa \nabla T$ , Fourier's law.
  2. Density  $\rightarrow$  diffusion (matter flow),  
 $\vec{J}_n = -D \nabla n$ , Fick's law.
  3. Electric potential  $\rightarrow$  charge transport,

## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:

1. Temperature  $\rightarrow$  heat flow,

$$\vec{J}_q = -\kappa \nabla T, \text{ Fourier's law.}$$

2. Density  $\rightarrow$  diffusion (matter flow),

$$\vec{J}_n = -D \nabla n, \text{ Fick's law.}$$

3. Electric potential  $\rightarrow$  charge transport,

$$\vec{J}_e = \sigma \vec{E} = -\sigma \nabla V.$$

## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:

1. Temperature  $\rightarrow$  heat flow,

$$\vec{J}_q = -\kappa \nabla T, \text{ Fourier's law.}$$

2. Density  $\rightarrow$  diffusion (matter flow),

$$\vec{J}_n = -D \nabla n, \text{ Fick's law.}$$

3. Electric potential  $\rightarrow$  charge transport,

$$\vec{J}_e = \sigma \vec{E} = -\sigma \nabla V.$$

4. Velocity

## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:

1. Temperature  $\rightarrow$  heat flow,

$$\vec{J}_q = -\kappa \nabla T, \text{ Fourier's law.}$$

2. Density  $\rightarrow$  diffusion (matter flow),

$$\vec{J}_n = -D \nabla n, \text{ Fick's law.}$$

3. Electric potential  $\rightarrow$  charge transport,

$$\vec{J}_e = \sigma \vec{E} = -\sigma \nabla V.$$

4. Velocity  $\rightarrow$  viscosity (momentum transport),



## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:

1. Temperature  $\rightarrow$  heat flow,

$$\vec{J}_q = -\kappa \nabla T, \text{ Fourier's law.}$$

2. Density  $\rightarrow$  diffusion (matter flow),

$$\vec{J}_n = -D \nabla n, \text{ Fick's law.}$$

3. Electric potential  $\rightarrow$  charge transport,

$$\vec{J}_e = \sigma \vec{E} = -\sigma \nabla V.$$

4. Velocity  $\rightarrow$  viscosity (momentum transport),

$$P_{xy} = \eta \frac{dv}{dx}.$$

## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:

1. Temperature  $\rightarrow$  heat flow,

$$\vec{J}_q = -\kappa \nabla T, \text{ Fourier's law.}$$

2. Density  $\rightarrow$  diffusion (matter flow),

$$\vec{J}_n = -D \nabla n, \text{ Fick's law.}$$

3. Electric potential  $\rightarrow$  charge transport,

$$\vec{J}_e = \sigma \vec{E} = -\sigma \nabla V.$$

4. Velocity  $\rightarrow$  viscosity (momentum transport),

$$P_{xy} = \eta \frac{dv}{dx}.$$

- Summation:

## 5.2 Linear and nonlinear processes, Onsager relation

- Non-uniform  $\rightarrow$  transport:

1. Temperature  $\rightarrow$  heat flow,

$$\vec{J}_q = -\kappa \nabla T, \text{ Fourier's law.}$$

2. Density  $\rightarrow$  diffusion (matter flow),

$$\vec{J}_n = -D \nabla n, \text{ Fick's law.}$$

3. Electric potential  $\rightarrow$  charge transport,

$$\vec{J}_e = \sigma \vec{E} = -\sigma \nabla V.$$

4. Velocity  $\rightarrow$  viscosity (momentum transport),

$$P_{xy} = \eta \frac{dv}{dx}.$$

- Summation:

$$\vec{J} = L \vec{X}, \text{ where } \vec{J} \text{ is the flux density, } \vec{X} \text{ is the "force".}$$

# Linear processes, Onsager relation

- For coexistence of multi-factors: (like  $T, \rho$ )

# Linear processes, Onsager relation

- For coexistence of multi-factors: (like  $T, \rho$ )

$$J_k = \sum_l L_{kl} X_l.$$

# Linear processes, Onsager relation

- For coexistence of multi-factors: (like  $T, \rho$ )  
$$J_k = \sum_l L_{kl} X_l.$$
- Onsager relation:  $L_{kl} = L_{lk}.$

# Linear processes, Onsager relation

- For coexistence of multi-factors: (like  $T, \rho$ )  
$$J_k = \sum_l L_{kl} X_l.$$
- Onsager relation:  $L_{kl} = L_{lk}.$
- Entropy production  $\Theta = \sum_k J_k X_k$

# Linear processes, Onsager relation

- For coexistence of multi-factors: (like  $T, \rho$ )  
$$J_k = \sum_l L_{kl} X_l.$$
- Onsager relation:  $L_{kl} = L_{lk}.$
- Entropy production  $\Theta = \sum_k J_k X_k = \sum_{kl} L_{kl} X_k X_l.$



# Linear processes, Onsager relation

- For coexistence of multi-factors: (like  $T, \rho$ )  
$$J_k = \sum_l L_{kl} X_l.$$
- Onsager relation:  $L_{kl} = L_{lk}.$
- Entropy production  $\Theta = \sum_k J_k X_k = \sum_{kl} L_{kl} X_k X_l.$
- Consider two “forces”,  
$$\Theta = L_{11} X_1^2 + (L_{12} + L_{21}) X_1 X_2 + L_{22} X_2^2$$

# Linear processes, Onsager relation

- For coexistence of multi-factors: (like  $T, \rho$ )  
$$J_k = \sum_l L_{kl} X_l.$$
- Onsager relation:  $L_{kl} = L_{lk}.$
- Entropy production  $\Theta = \sum_k J_k X_k = \sum_{kl} L_{kl} X_k X_l.$
- Consider two “forces”,  
$$\begin{aligned}\Theta &= L_{11}X_1^2 + (L_{12} + L_{21})X_1X_2 + L_{22}X_2^2 \\ &= L_{11}X_1^2 + 2L_{12}X_1X_2 + L_{22}X_2^2.\end{aligned}$$

# Linear processes, Onsager relation

- For coexistence of multi-factors: (like  $T, \rho$ )  
$$J_k = \sum_l L_{kl} X_l.$$
- Onsager relation:  $L_{kl} = L_{lk}.$
- Entropy production  $\Theta = \sum_k J_k X_k = \sum_{kl} L_{kl} X_k X_l.$
- Consider two “forces”,  
$$\begin{aligned}\Theta &= L_{11} X_1^2 + (L_{12} + L_{21}) X_1 X_2 + L_{22} X_2^2 \\ &= L_{11} X_1^2 + 2L_{12} X_1 X_2 + L_{22} X_2^2.\end{aligned}$$
- $\Theta \geq 0$ , requires,  $L_{11} > 0$ ,  $L_{11} L_{22} > L_{12}^2.$   
(Properties of the coefficients  $L$ .)

# Non-linear processes

# Non-linear processes

- Linear processes can only describe the system near to the equilibrium state.

# Non-linear processes

- Linear processes can only describe the system near to the equilibrium state.
- For the general case,  $J_k = \sum_l L_{kl} X_l$  does not hold.

# Non-linear processes

- Linear processes can only describe the system near to the equilibrium state.
- For the general case,  $J_k = \sum_l L_{kl} X_l$  does not hold.
- $J_k(\{X_l\}) \equiv J_k(X_1, \dots, X_l, \dots)$ , expand:

# Non-linear processes

- Linear processes can only describe the system near to the equilibrium state.
- For the general case,  $J_k = \sum_l L_{kl} X_l$  does not hold.
- $J_k(\{X_l\}) \equiv J_k(X_1, \dots, X_l, \dots)$ , expand:  
$$J_k(\{X_l\}) = J_k(0) + \sum_l \left( \frac{\partial J_k}{\partial X_l} \right)_0 X_l + \frac{1}{2} \sum_{l,n} \left( \frac{\partial^2 J_k}{\partial X_l \partial X_n} \right)_0 X_l X_n + \dots$$



# Non-linear processes

- Linear processes can only describe the system near to the equilibrium state.
- For the general case,  $J_k = \sum_l L_{kl} X_l$  does not hold.
- $J_k(\{X_l\}) \equiv J_k(X_1, \dots, X_l, \dots)$ , expand:  

$$J_k(\{X_l\}) = J_k(0) + \sum_l \left( \frac{\partial J_k}{\partial X_l} \right)_0 X_l + \frac{1}{2} \sum_{l,n} \left( \frac{\partial^2 J_k}{\partial X_l \partial X_n} \right)_0 X_l X_n + \dots$$
- $J_k(0)$  corresponds to  $\{X_l\} = 0$ ,  $J_k(0) = 0$ .

# Non-linear processes

- Linear processes can only describe the system near to the equilibrium state.
- For the general case,  $J_k = \sum_l L_{kl} X_l$  does not hold.
- $J_k(\{X_l\}) \equiv J_k(X_1, \dots, X_l, \dots)$ , expand:  

$$J_k(\{X_l\}) = J_k(0) + \sum_l \left( \frac{\partial J_k}{\partial X_l} \right)_0 X_l + \frac{1}{2} \sum_{l,n} \left( \frac{\partial^2 J_k}{\partial X_l \partial X_n} \right)_0 X_l X_n + \dots$$
- $J_k(0)$  corresponds to  $\{X_l\} = 0$ ,  $J_k(0) = 0$ .  
 Define  $L_{kl} \equiv \left( \frac{\partial J_k}{\partial X_l} \right)_0$ ,  $L_{kln} \equiv \left( \frac{\partial^2 J_k}{\partial X_l \partial X_n} \right)_0$ ,

# Non-linear processes

- Linear processes can only describe the system near to the equilibrium state.
- For the general case,  $J_k = \sum_l L_{kl} X_l$  does not hold.
- $J_k(\{X_l\}) \equiv J_k(X_1, \dots, X_l, \dots)$ , expand:  

$$J_k(\{X_l\}) = J_k(0) + \sum_l \left( \frac{\partial J_k}{\partial X_l} \right)_0 X_l + \frac{1}{2} \sum_{l,n} \left( \frac{\partial^2 J_k}{\partial X_l \partial X_n} \right)_0 X_l X_n + \dots$$
- $J_k(0)$  corresponds to  $\{X_l\} = 0$ ,  $J_k(0) = 0$ .  
 Define  $L_{kl} \equiv \left( \frac{\partial J_k}{\partial X_l} \right)_0$ ,  $L_{kln} \equiv \left( \frac{\partial^2 J_k}{\partial X_l \partial X_n} \right)_0$ ,  

$$J_k = \sum_l L_{kl} X_l + \frac{1}{2} \sum_{l,n} L_{kln} X_l X_n + \dots$$

# Table of contents

- ① §5. Thermodynamics of irreversible processes
  - 5.1 Local equilibrium, entropy flux density and production rate
  - 5.2 Linear and nonlinear processes, Onsager relation