2.43 ADVANCED THERMODYNAMICS

Spring Term 2024

LECTURE 21

Room 3-442
Tuesday, April 23, 2:30pm - 4:30pm

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Room 3-351d

Systems with chemical reactions

Chemical kinetics

Near-equilibrium linearization

Onsager reciprocity from Ziegler principle of maximum entropy production rate

Relation between rates and affinities: far and near equilibrium

For a single reaction mechanism j, $\sum_i \nu_i^{(j)} A_i = 0$, with rates $\dot\epsilon_j^\pm = k_o^{\pm(j)}(T)\prod_i [N_i]^{\nu_i^{\pm(j)}}$

$$\dot\epsilon_j = \dot\epsilon_j^+ - \dot\epsilon_j^- \qquad \frac{\dot\epsilon_j^+}{\dot\epsilon_j^-} = \exp\left[\frac{Y_j}{R}\right] \quad \Rightarrow \quad \dot\epsilon_j = \dot\epsilon_j^+\left(1-\exp\left[-\frac{Y_j}{R}\right]\right) = \dot\epsilon_j^-\left(\exp\left[\frac{Y_j}{R}\right]-1\right)$$

$$\left.\frac{\partial S}{\partial t}\right|_{\text{chem}} = Y_j\dot\epsilon_j = L_{jj}Y_j^2 = \frac{1}{L_{jj}}\dot\epsilon_j^2 \quad \text{where we define} \quad L_{jj} = \frac{\dot\epsilon_j}{Y_j} = \frac{\dot\epsilon_j^+ - \dot\epsilon_j^-}{R\ln(\dot\epsilon_j^+/\dot\epsilon_j^-)} = \frac{1}{R}(\dot\epsilon_j^\pm)_{\substack{\text{log}\\ \text{mean}}}$$

As the composition approaches chemical equilibrium, $Y_j \to 0$, $\dot\epsilon_j^+ \to \dot\epsilon_{jo}^+$, $\dot\epsilon_j^- \to \dot\epsilon_{jo}^-$, where $\dot\epsilon_{jo}^+ = \dot\epsilon_{jo}^- = (\dot\epsilon_{jo}^\pm)_{\substack{\text{log}\\ \text{mean}}} = R\,L_{jj}^{\text{eq}} = \kappa\,[N_*]_o$, and the expressions linearize to

$$\dot\epsilon_j \to \frac{\dot\epsilon_{jo}^\pm}{R}Y_j = L_{jj}^{\text{eq}}\,Y_j \qquad \dot\epsilon_{jo}^\pm = k_o^{\pm(j)}(T)\prod_i [N_i]_o^{\nu_i^{\pm(j)}} \qquad \left.\frac{\partial S}{\partial t}\right|_{\text{chem}} \to \frac{\dot\epsilon_{jo}^\pm}{R}Y_j^2 = L_{jj}^{\text{eq}}\,Y_j^2 = \frac{1}{L_{jj}^{\text{eq}}}\dot\epsilon_j^2$$

so, near equilibrium, the net reaction rate $\dot\epsilon_j$ becomes linear in the affinity Y_j, and the inverse of coefficient $L_{jj}^{\text{eq}} = \kappa\,[N_*]_o/R$ can be interpreted as the **chemical resistance** to the advancement of the reaction.

$$\text{Recall:} \qquad k_o^\pm(T) = \frac{A^\pm(T)}{[N]^{\nu^\pm}}\exp\left[-\frac{\Delta h_\pm^o(T)}{RT}\right] = \kappa_\pm K_\pm^c(T)$$

Detailed kinetic mechanism for the oxidation of hydrocarbons

$$k_\ell^+(T) \;=\; A_\ell^+ T^{b_\ell^+} \exp\left(-E_\ell^+/RT\right)$$

$$k_\ell^-(T) = k_\ell^+(T)/K_\ell^{co}(T)$$

Hydrogen: K=8 species, I=24 reactions

	Reactions	***A***	***b***	***E***
1	O+O+M=O2+M	1.20E+17	-1	0
2	O+H+M=OH+M	5.00E+17	-1	0
3	H+H+M=H2+M	1.00E+18	-1	0
4	H+H+H2=H2+H2	9.00E+16	-0.6	0
5	H+H+H2O=H2+H2O	6.00E+19	-1.3	0
6	H+OH+M=H2O+M	2.20E+22	-2	0
7	H+O2+M=HO2+M	2.80E+18	-0.9	0
8	H+O2+O2=HO2+O2	2.08E+19	-1.2	0
9	H+O2+H2O=HO2+H2O	1.13E+19	-0.8	0
10	OH+OH+M=H2O2+M	7.40E+13	-0.4	0
11	O+H2=H+OH	3.87E+04	2.7	6260
12	O+HO2=OH+O2	2.00E+13	0	0
13	O+H2O2=OH+HO2	9.63E+06	2	4000
14	H+O2=O+OH	2.65E+16	-0.7	17041
15	H+HO2=O+H2O	3.97E+12	0	671
16	H+HO2=O2+H2	4.48E+13	0	1068
17	H+HO2=OH+OH	8.40E+13	0	635
18	H+H2O2=HO2+H2	1.21E+07	2	5200
19	H+H2O2=OH+H2O	1.00E+13	0	3600
20	OH+H2=H+H2O	2.16E+08	1.5	3430
21	OH+OH=O+H2O	3.57E+04	2.4	-2110
22	OH+HO2=O2+H2O	1.45E+13	0	-500
23	OH+H2O2=HO2+H2O	2.00E+12	0	427
24	HO2+HO2=O2+H2O2	1.30E+11	0	-1630

Not all independent.
E.g., 11-14 = 1-3

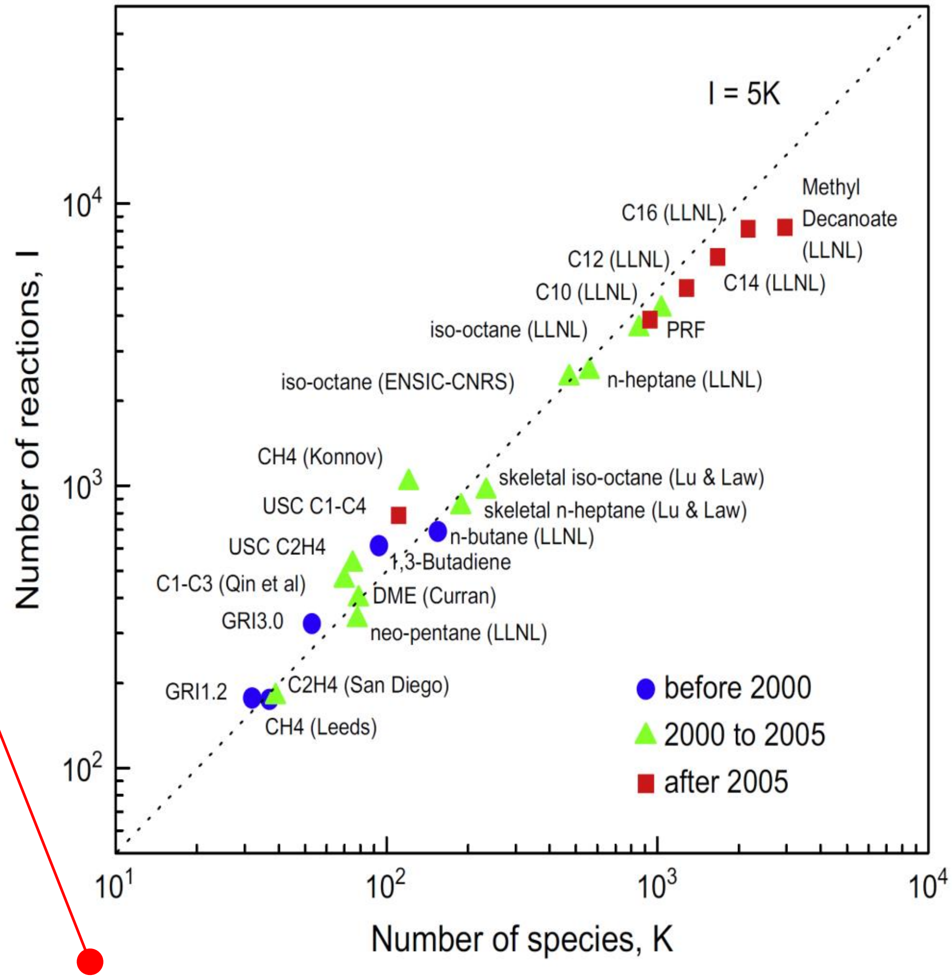

Fig. 10. Size of selected detailed and skeletal mechanisms for hydrocarbon fuels, together with the approximate years when the mechanisms were compiled.

Fig.10 in T. Lu and C.K. Law, Progress in Energy and Combustion Science 35, 192 (2009).

Relation between rates and affinities: far and near equilibrium

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As the composition approaches chemical equilibrium, $Y_j \to 0$, $\dot\epsilon_j^+ \to \dot\epsilon_{jo}^+$, $\dot\epsilon_j^- \to \dot\epsilon_{jo}^-$, where $\dot\epsilon_{jo}^+ = \dot\epsilon_{jo}^- = (\dot\epsilon_{jo}^\pm)_{\substack{\text{log}\\ \text{mean}}} = R\,L_{jj}^{\text{eq}} = \kappa\,[N_*]_o$, and the expressions linearize to

$$\dot\epsilon_j \to \frac{\dot\epsilon_{jo}^\pm}{R} Y_j = L_{jj}^{\text{eq}}\, Y_j \qquad \dot\epsilon_{jo}^\pm = k_o^{\pm(j)}(T)\prod_i [N_i]_o^{\nu_i^{\pm(j)}} \qquad \left.\frac{\partial S}{\partial t}\right|_{\text{chem}} \to \frac{\dot\epsilon_{jo}^\pm}{R} Y_j^2 = L_{jj}^{\text{eq}}\, Y_j^2 = \frac{1}{L_{jj}^{\text{eq}}}\dot\epsilon_j^2$$

so, near equilibrium, the net reaction rate $\dot\epsilon_j$ becomes linear in the affinity Y_j, and the inverse of coefficient $L_{jj}^{\text{eq}} = \kappa\,[N_*]_o/R$ can be interpreted as the **chemical resistance** to the advancement of the reaction.

In a complex detailed scheme or reaction network, the set of single-step reactions, $j = 1, \ldots, z$, for which we have the rates, may not all be independent of one another, so there is a smaller set of $k = 1, \ldots, \mathrm{z}_{\min}$ **linearly independent** mechanisms $\sum_i \upsilon_i^{(k)} A_i = 0$ such that

$$\nu_i^{(j)} = \sum_{k=1}^{\mathrm{z}_{\min}} x_{jk}\, \upsilon_i^{(k)} \qquad \Rightarrow \qquad Y_j = \sum_{k=1}^{\mathrm{z}_{\min}} x_{jk}\, \Upsilon_k \qquad \left.\frac{\partial S}{\partial t}\right|_{\text{chem}} = \sum_{j=1}^{\mathrm{z}} Y_j\, \dot\epsilon_j = \sum_{k=1}^{\mathrm{z}_{\min}} \Upsilon_k \sum_{j=1}^{\mathrm{z}} x_{jk}\, \dot\epsilon_j = \sum_{k=1}^{\mathrm{z}_{\min}} \Upsilon_k\, \dot\varepsilon_k$$

so the rates $\dot\varepsilon_k = \sum_{j=1}^{\mathrm{z}} x_{jk}\, \dot\epsilon_j$ of the independent reactions turn out to be coupled . . .

Relation between rates and affinities: far and near equilibrium

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$$\nu_i^{(j)} = \sum_{k=1}^{\mathrm{z}_{\min}} x_{jk}\,\upsilon_i^{(k)} \quad\Rightarrow\quad Y_j = \sum_{k=1}^{\mathrm{z}_{\min}} x_{jk}\,\Upsilon_k$$

recall: $$L_{jj} = \frac{\dot\epsilon_j}{Y_j} = \frac{\dot\epsilon_j^+ - \dot\epsilon_j^-}{R\ln(\dot\epsilon_j^+/\dot\epsilon_j^-)} = \frac{1}{R}(\dot\epsilon_j^\pm)_{\substack{\text{log}\\ \text{mean}}}$$

$$\left.\frac{\partial S}{\partial t}\right|_{\text{chem}} = \sum_{j=1}^{\mathrm{z}} Y_j\,\dot\epsilon_j = \sum_{k=1}^{\mathrm{z}_{\min}} \Upsilon_k \underbrace{\sum_{j=1}^{\mathrm{z}} x_{jk}\,\dot\epsilon_j}_{\dot\varepsilon_k} = \sum_{k=1}^{\mathrm{z}_{\min}} \Upsilon_k\,\dot\varepsilon_k = \sum_{j=1}^{\mathrm{z}} L_{jj}\,Y_j^2 = \sum_{k=1}^{\mathrm{z}_{\min}}\sum_{\ell=1}^{\mathrm{z}_{\min}} \Upsilon_k \underbrace{\sum_{j=1}^{\mathrm{z}} x_{jk}\,L_{jj}\,x_{j\ell}}_{\substack{\mathcal{L}_{k\ell} = \mathcal{L}_{\ell k} \ge 0\\ \textbf{symmetric!}}} \Upsilon_\ell$$

$$= \sum_{k=1}^{\mathrm{z}_{\min}}\sum_{\ell=1}^{\mathrm{z}_{\min}} \dot\varepsilon_k\,\mathcal{R}_{k\ell}\,\dot\varepsilon_\ell \ge 0$$

where the **chemical resistance** matrix $\boldsymbol{\mathcal{R}}$ is the inverse of $\boldsymbol{\mathcal{L}}$

so the rates $\dot\varepsilon_k = \sum_{j=1}^{\mathrm{z}} x_{jk}\,\dot\epsilon_j$ of the independent reactions are coupled.

In the **near-equilibrium limit**, $Y_j \to 0\ \forall j$,

$$\dot\varepsilon_k \to \sum_{j=1}^{\mathrm{z}} x_{jk}\,\frac{\dot\epsilon_{jo}^\pm}{R}\,Y_j = \sum_{j=1}^{\mathrm{z}} x_{jk}\,L_{jj}^{\text{eq}}\,Y_j = \sum_{j=1}^{\mathrm{z}} x_{jk}\,L_{jj}^{\text{eq}} \sum_{\ell=1}^{\mathrm{z}_{\min}} x_{j\ell}\,\Upsilon_\ell = \sum_{\ell=1}^{\mathrm{z}_{\min}}\sum_{j=1}^{\mathrm{z}} x_{jk}\,L_{jj}^{\text{eq}}\,x_{j\ell}\,\Upsilon_\ell = \sum_{\ell=1}^{\mathrm{z}_{\min}} \mathcal{L}_{k\ell}^{\text{eq}}\,\Upsilon_\ell$$

$$\left.\frac{\partial S}{\partial t}\right|_{\text{chem}} \to \sum_{k=1}^{\mathrm{z}_{\min}}\sum_{\ell=1}^{\mathrm{z}_{\min}} \Upsilon_k\,\mathcal{L}_{k\ell}^{\text{eq}}\,\Upsilon_\ell = \sum_{k=1}^{\mathrm{z}_{\min}}\sum_{\ell=1}^{\mathrm{z}_{\min}} \dot\varepsilon_k\,\mathcal{R}_{k\ell}^{\text{eq}}\,\dot\varepsilon_\ell \ge 0$$

Nonequilibrium models must satisfy Onsager reciprocal relations near-equilibrium

Linearization of rate-affinity (flux-force) relations

The entropy balance gives: $\dot S_{\rm irr} = \boldsymbol{Y}\cdot\dot{\boldsymbol{\epsilon}}$. Maximum entropy (stable equilibrium) is at: $\boldsymbol{Y}_{\rm eq} = \mathbf{0}$. Suppose your theory assumes: $\dot{\boldsymbol{\epsilon}} = \dot{\boldsymbol{\epsilon}}\left(\boldsymbol{Y}\right)$ with $\dot{\boldsymbol{\epsilon}}\left(\mathbf{0}\right) = \mathbf{0}$, so that $\dot S_{\rm irr} = \boldsymbol{Y}\cdot\dot{\boldsymbol{\epsilon}}\left(\boldsymbol{Y}\right) = \dot S_{\rm irr}\left(\boldsymbol{Y}\right)$. Linearize your rate–affinity relation around $\boldsymbol{Y}_{\rm eq} = \mathbf{0}$:

$$\dot{\boldsymbol{\epsilon}}\left(\boldsymbol{Y}\right) = \underbrace{\dot{\boldsymbol{\epsilon}}\left(0\right)}_{=\mathbf{0}} + \left.\frac{\partial\dot{\boldsymbol{\epsilon}}}{\partial\boldsymbol{Y}}\right|_{\mathbf{0}}\cdot\boldsymbol{Y} + \cdots = \boldsymbol{L}^{\rm eq}\cdot\boldsymbol{Y} + \ldots \quad \text{where } \boldsymbol{L}^{\rm eq} = \left.\frac{\partial\dot{\boldsymbol{\epsilon}}}{\partial\boldsymbol{Y}}\right|_{\mathbf{0}} = \left.\frac{\partial\left(\dot\epsilon_1,\dot\epsilon_2,\ldots,\dot\epsilon_r\right)}{\partial\left(Y_1,Y_2,\ldots,Y_r\right)}\right|_{\mathbf{0}}$$

Therefore, the entropy production is a quadratic form of the affinities and the matrix $\boldsymbol{L}$ of coefficients must be **non-negative** (positive semi-definite)

$$\dot S_{\rm irr} = \boldsymbol{Y}\cdot\boldsymbol{L}^{\rm eq}\cdot\boldsymbol{Y} + \cdots \geq 0 \quad \Rightarrow \quad \boldsymbol{L}^{\rm eq} \geq 0$$

We may also expand $\dot S_{\rm irr}(\boldsymbol{Y}) = \boldsymbol{Y}\cdot\dot{\boldsymbol{\epsilon}}\left(\boldsymbol{Y}\right)$ in Tayor series around $\boldsymbol{Y}_{\rm eq} = \mathbf{0}$

$$\dot S_{\rm irr} = \underbrace{\dot S_{\rm irr}\left(0\right)}_{=\,0} + \underbrace{\left.\frac{\partial\dot S_{\rm irr}}{\partial\boldsymbol{Y}}\right|_{\mathbf{0}}\cdot\boldsymbol{Y}}_{=^{*}\,0} + \frac{1}{2}\boldsymbol{Y}\cdot\underbrace{\frac{\partial^2\dot S_{\rm irr}}{\partial\boldsymbol{Y}\partial\boldsymbol{Y}}}_{=^{**}\,\boldsymbol{L}^{\rm eq}+\boldsymbol{L}^{\rm eq\,T}}\Bigg|_{\mathbf{0}}\cdot\boldsymbol{Y} + \ldots \underbrace{=}_{**} \frac{1}{2}\boldsymbol{Y}\cdot\left(\boldsymbol{L}^{\rm eq}+\boldsymbol{L}^{\rm eq\,T}\right)\cdot\boldsymbol{Y} + \cdots = \boldsymbol{Y}\cdot\boldsymbol{L}^{\rm eq}\cdot\boldsymbol{Y} + \ldots$$

$$*\!:\ \frac{\partial\dot S_{\rm irr}}{\partial Y_j} = \dot\epsilon_j + \sum_i Y_i\frac{\partial\dot\epsilon_i}{\partial Y_j} \qquad **\!:\ \frac{\partial^2\dot S_{\rm irr}}{\partial Y_k\partial Y_j} = \frac{\partial\dot\epsilon_j}{\partial Y_k} + \frac{\partial\dot\epsilon_k}{\partial Y_j} + \sum_i Y_i\frac{\partial^2\dot\epsilon_i}{\partial Y_k\partial Y_j}$$

But **Onsager** (1931; Nobel, 1968) proved on statistical grounds that the matrix of **generalized conductivities** (and hence also its inverse, **generalized resistances**) should also be symmetric:

$$\boldsymbol{L}^{\rm eq} = \boldsymbol{L}^{\rm eq\,T}$$

Nonequilibrium models must satisfy Onsager reciprocal relations near-equilibrium

Explicit relations for the case of two rates and two affinities

$$\dot{\boldsymbol{\epsilon}} = \boldsymbol{L}\cdot\boldsymbol{Y} \quad :$$

$$\begin{cases} \dot\epsilon_1 = L_{11}\,Y_1 + L_{12}\,Y_2 \\ \\ \dot\epsilon_2 = L_{21}\,Y_1 + L_{22}\,Y_2 \end{cases} \leftrightarrow \begin{cases} \dot\epsilon_1 = \dfrac{\det\boldsymbol{L}}{L_{22}}\,Y_1 + \dfrac{L_{12}}{L_{22}}\,\dot\epsilon_2 \\ \\ \dot\epsilon_2 = \dfrac{L_{21}}{L_{11}}\,\dot\epsilon_1 + \dfrac{\det\boldsymbol{L}}{L_{11}}\,Y_2 \end{cases} \leftrightarrow \begin{cases} (\det\boldsymbol{L})\,Y_1 = L_{22}\,\dot\epsilon_1 - L_{12}\,\dot\epsilon_2 \\ \\ (\det\boldsymbol{L})\,Y_2 = -L_{21}\,\dot\epsilon_1 + L_{11}\,\dot\epsilon_2 \end{cases}$$

$$\boldsymbol{L} = \boldsymbol{L}^{\mathrm{T}} \quad : \quad L_{12} = L_{21} \qquad\qquad \boldsymbol{L} \geq 0 \quad : \quad \begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} \geq 0$$

$$\det\boldsymbol{L} = a_1 a_2 = \det\begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} = L_{11}L_{22} - L_{12}L_{21} \geq 0$$

$$\operatorname{Tr}\boldsymbol{L} = a_1 + a_2 = \operatorname{Tr}\begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix} = L_{11} + L_{22} \geq 0 \qquad L_{11} \geq 0 \qquad L_{22} \geq 0$$

$$\dot S_{\mathrm{irr}} = \boldsymbol{Y}\cdot\boldsymbol{L}\cdot\boldsymbol{Y} = \begin{pmatrix} Y_1 & Y_2 \end{pmatrix}\begin{pmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{pmatrix}\begin{pmatrix} Y_1 \\ Y_2 \end{pmatrix} = L_{11}\,Y_1^2 + 2L_{12}\,Y_1 Y_2 + L_{22}\,Y_2^2$$

$$= L_{11}\left(Y_1 + \frac{L_{12}}{L_{11}}Y_2\right)^2 + \frac{\det\boldsymbol{L}}{L_{11}}\,Y_2^2 = \frac{\det\boldsymbol{L}}{L_{22}}\,Y_1^2 + L_{22}\left(Y_2 + \frac{L_{12}}{L_{22}}Y_1\right)^2$$

$$= \frac{1}{L_{11}}\,\dot\epsilon_1^2 + \frac{\det\boldsymbol{L}}{L_{11}}\,Y_2^2 = \frac{\det\boldsymbol{L}}{L_{22}}\,Y_1^2 + \frac{1}{L_{22}}\,\dot\epsilon_2^2$$

Onsager relations in the linear regime as a consequence of the principle of maximum entropy production rate (Ziegler, 1958)

Given the **constraint** $\dot{S}_{\rm irr}=\sum_i Y_i\,\dot\epsilon_i$, which is required by the balance equations, assume linear relations between rates and affinities, $\dot\epsilon_i=\sum_j L_{ij}Y_j$, so that

$$\dot{S}_{\rm irr}=\sum_i\sum_j Y_iL_{ij}Y_j \qquad \text{and} \qquad \frac{\partial\dot{S}_{\rm irr}}{\partial Y_i}=\sum_j(L_{ij}+L_{ji})\,Y_j$$

Assume $\dot{S}_{\rm irr}$ is maximal subject to the constraint. Using the method of Lagrange multipliers,

maximize $\dot{S}_{\rm irr}$ subject to $\dot{S}_{\rm irr}-\sum_i\dot\epsilon_iY_i=0$, i.e., maximize $\mathcal{L}=\dot{S}_{\rm irr}-\lambda\left(\dot{S}_{\rm irr}-\sum_i\dot\epsilon_iY_i\right)$

$$0=\left(\frac{\partial\mathcal{L}}{\partial Y_i}\right)_{\dot{\boldsymbol\epsilon}}=(1-\lambda)\,\frac{\partial\dot{S}_{\rm irr}}{\partial Y_i}+\lambda\,\dot\epsilon_i \quad\Rightarrow\quad \dot\epsilon_i=\frac{\lambda-1}{\lambda}\frac{\partial\dot{S}_{\rm irr}}{\partial Y_i}\quad(1)$$

Ziegler orthogonality

Substitute this back into the constraint, to determine the Lagrange multiplier:

$$\dot{S}_{\rm irr}=\frac{\lambda-1}{\lambda}\sum_i\frac{\partial\dot{S}_{\rm irr}}{\partial Y_i}Y_i=\frac{\lambda-1}{\lambda}\sum_i\sum_j(L_{ij}+L_{ji})Y_jY_i=\frac{\lambda-1}{\lambda}2\sum_i\sum_j L_{ij}Y_jY_i=\frac{\lambda-1}{\lambda}2\dot{S}_{\rm irr}$$

Therefore we must have $2(\lambda-1)/\lambda=1$ implies $\lambda=2$ and we may rewrite Eq.(1) as follows

$$\dot\epsilon_i=\frac{1}{2}\frac{\partial\dot{S}_{\rm irr}}{\partial Y_i} \qquad \text{or} \qquad \sum_j L_{ij}Y_j=\frac{1}{2}\sum_j(L_{ij}+L_{ji})Y_j$$

that is, $2\sum_j L_{ij}Y_j-\sum_j L_{ij}Y_j-\sum_j L_{ji}Y_j=0$ or $\sum_j(L_{ij}-L_{ji})Y_j=0$

This holds for all possible combinations of values of the Y_j's only if $L_{ij}=L_{ji}$, i.e., if the matrix is symmetric.

Graphical illustration of the

Ziegler orthogonality relation

$$\dot{\boldsymbol{\epsilon}} = \boldsymbol{L} \cdot \boldsymbol{Y} \quad \text{or} \quad \boldsymbol{Y} = \boldsymbol{R} \cdot \dot{\boldsymbol{\epsilon}} \qquad \dot{S}_{\text{irr}} = \boldsymbol{Y} \cdot \boldsymbol{L} \cdot \boldsymbol{Y} = \dot{\boldsymbol{\epsilon}} \cdot \boldsymbol{R} \cdot \dot{\boldsymbol{\epsilon}}$$

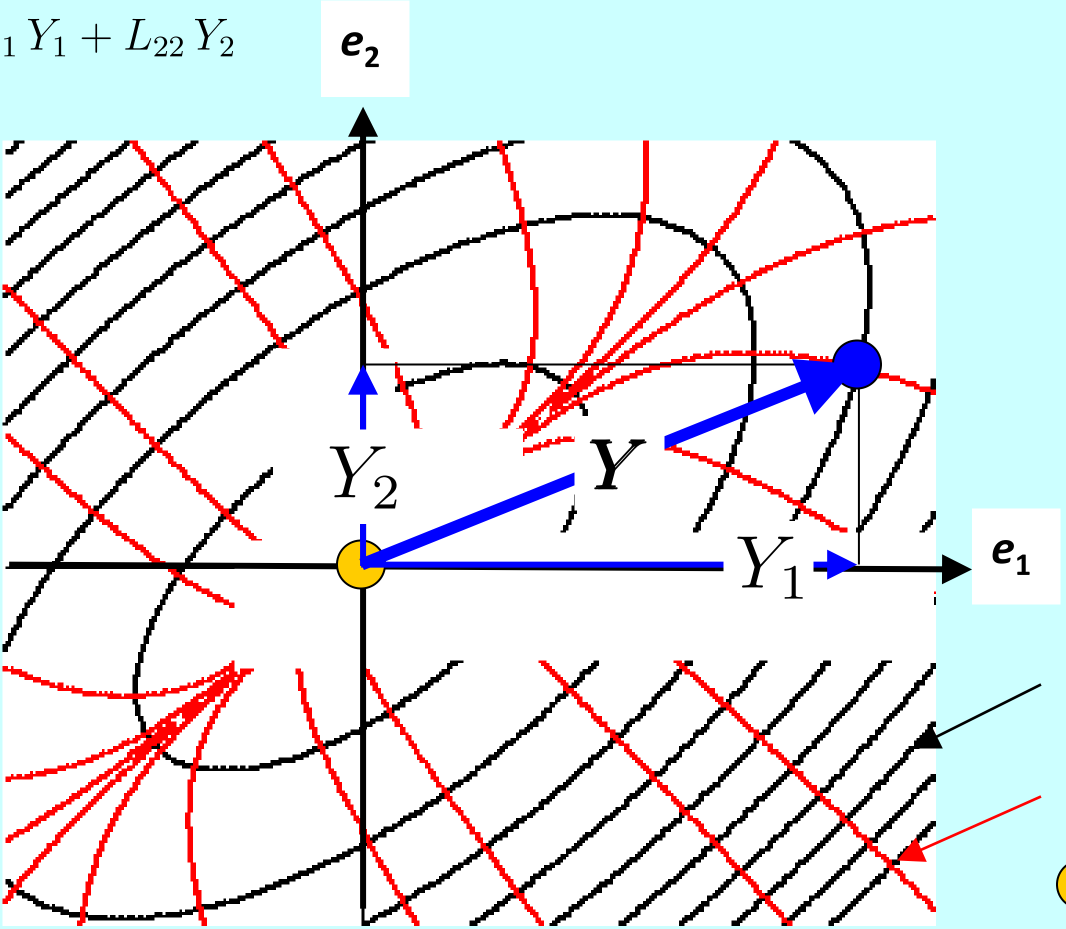
$$\dot{\epsilon}_1 = L_{11}\,Y_1 + L_{12}\,Y_2$$

$$\dot{\epsilon}_2 = L_{21}\,Y_1 + L_{22}\,Y_2$$

$$\dot{\boldsymbol{\epsilon}} = \frac{1}{2}\frac{\partial \dot{S}_{\text{irr}}}{\partial \boldsymbol{Y}}$$

$$\boldsymbol{Y} = Y_1\,\boldsymbol{e}_1 + Y_2\,\boldsymbol{e}_2$$

$$\dot{\boldsymbol{\epsilon}} = \dot{\epsilon}_1\,\boldsymbol{e}_1 + \dot{\epsilon}_2\,\boldsymbol{e}_2$$



constant–$\dot{S}_{\text{irr}}$ contours

orthogonal curves

● equilibrium state

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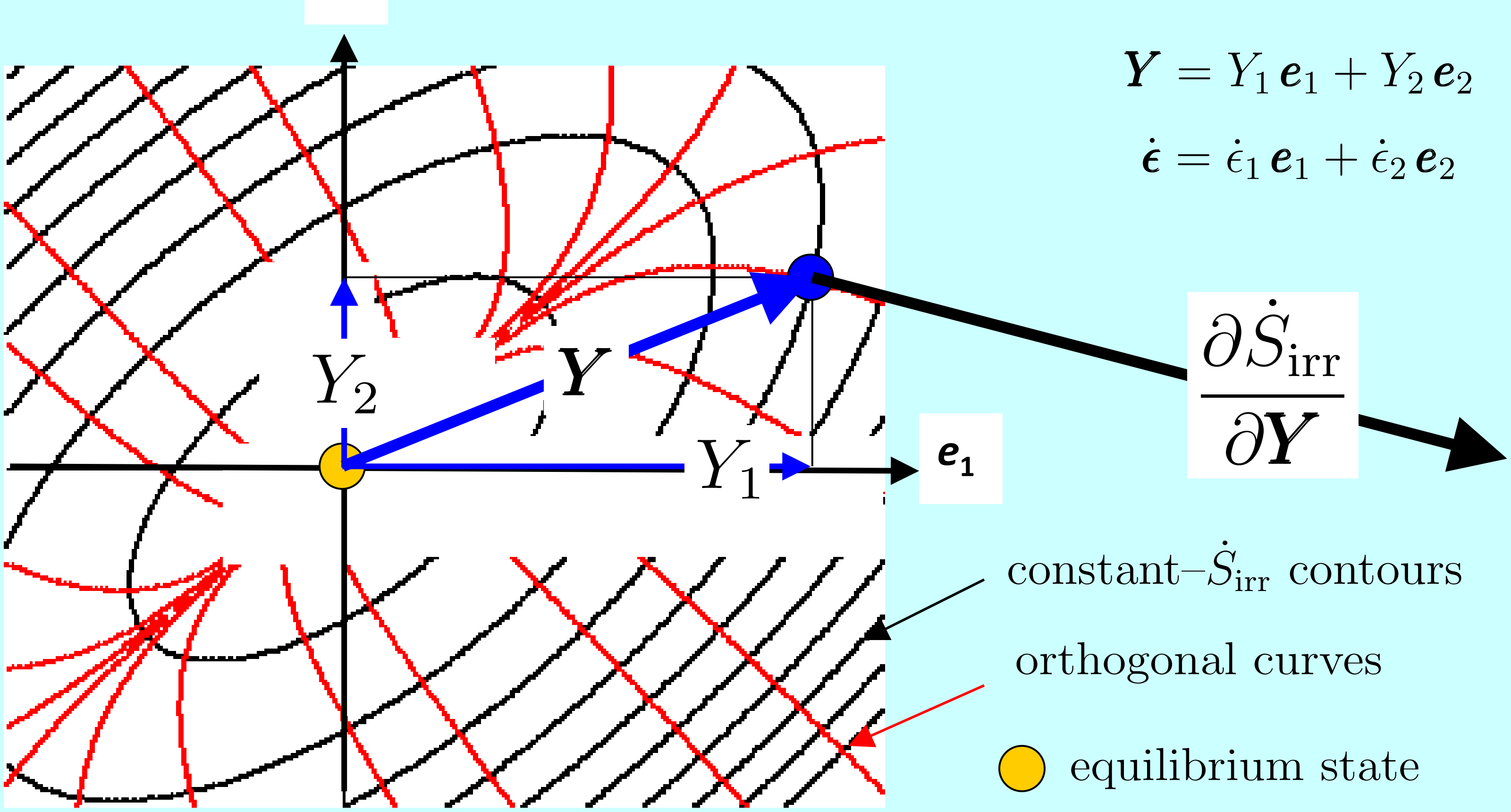

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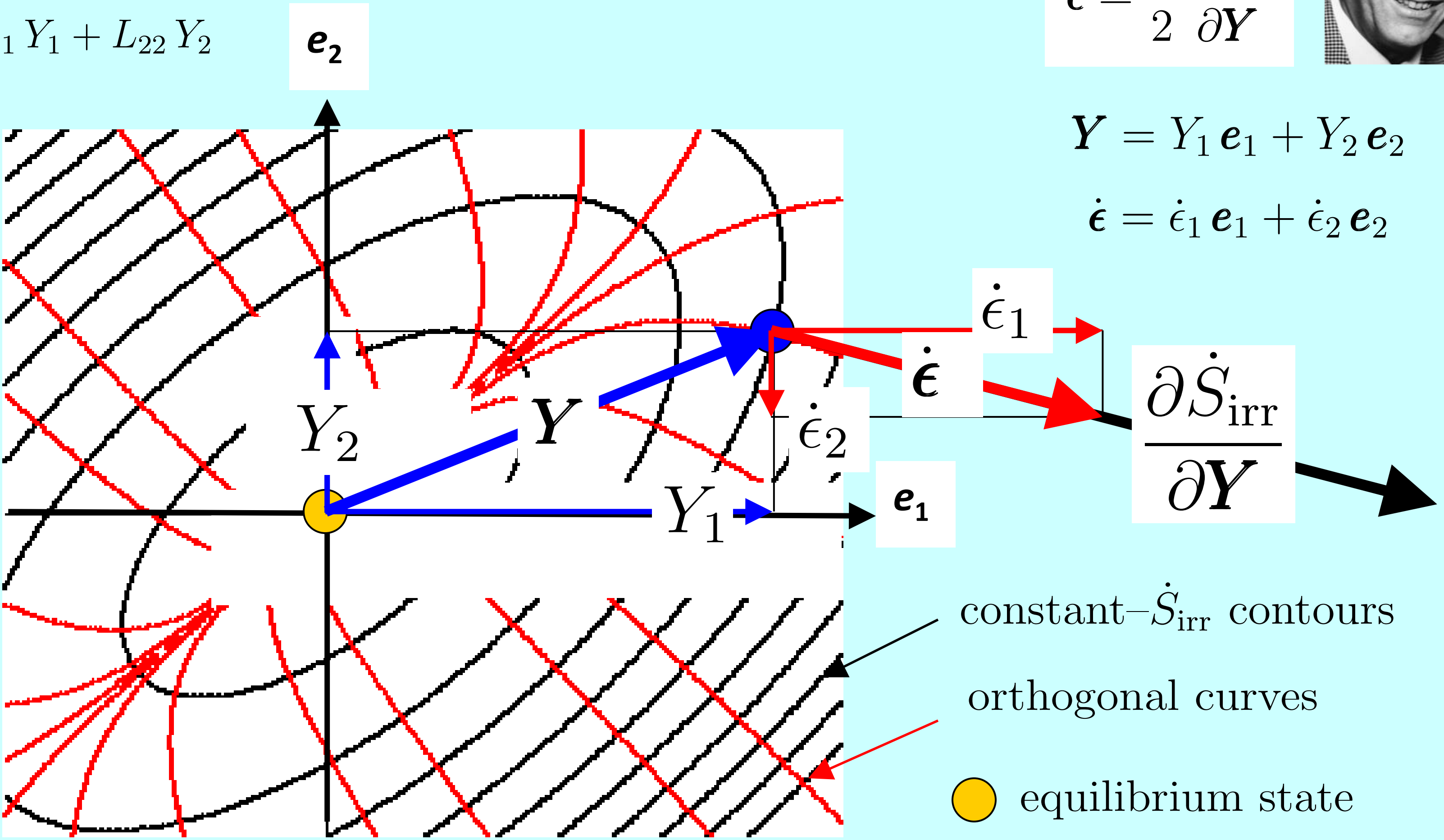
$$\boldsymbol{Y} = Y_1\,\boldsymbol{e}_1 + Y_2\,\boldsymbol{e}_2$$

$$\dot{\boldsymbol{\epsilon}} = \dot{\epsilon}_1\,\boldsymbol{e}_1 + \dot{\epsilon}_2\,\boldsymbol{e}_2$$



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Ziegler orthogonality relation

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$$\dot\epsilon_1 = L_{11}\,Y_1 + L_{12}\,Y_2$$

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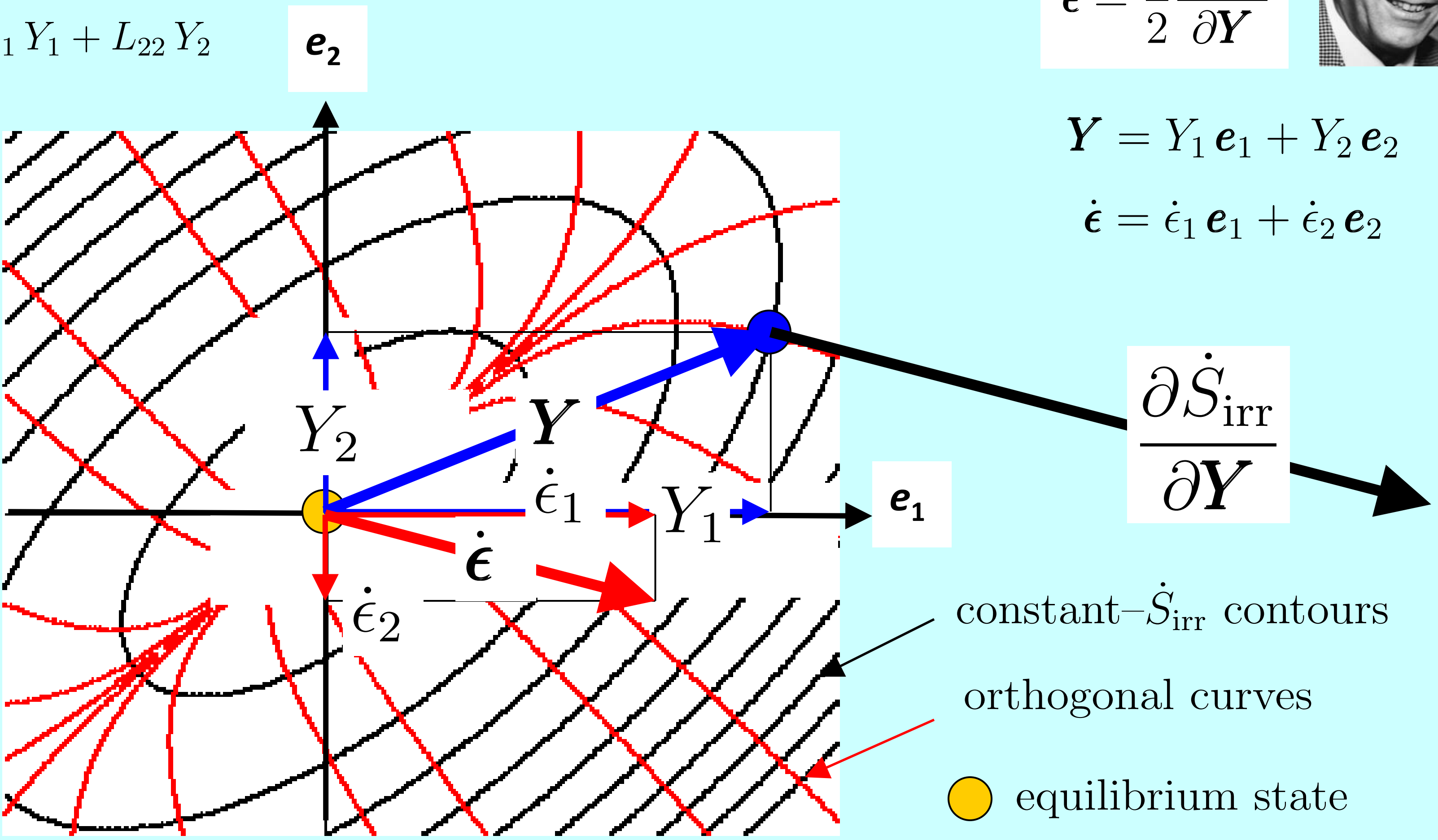
$$\boldsymbol{\dot\epsilon} = \frac{1}{2}\frac{\partial \dot S_{\rm irr}}{\partial \boldsymbol{Y}}$$

$$\boldsymbol{Y} = Y_1\,\boldsymbol{e}_1 + Y_2\,\boldsymbol{e}_2$$

$$\boldsymbol{\dot\epsilon} = \dot\epsilon_1\,\boldsymbol{e}_1 + \dot\epsilon_2\,\boldsymbol{e}_2$$



constant–$\dot S_{\rm irr}$ contours

orthogonal curves

● equilibrium state

Nonequilibrium in heat transfer

Fourier law of thermal conduction

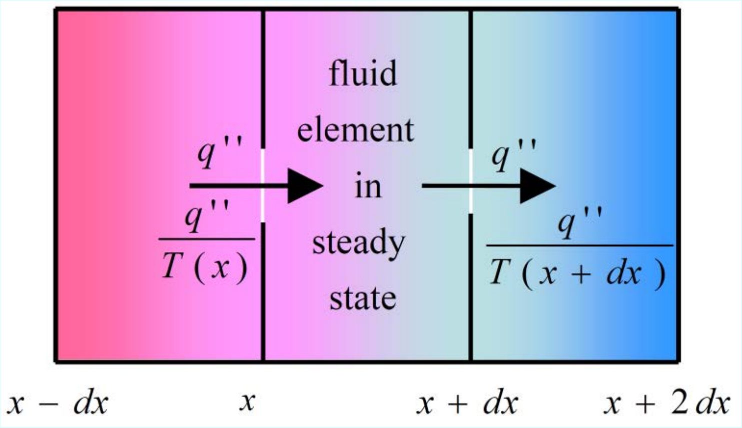
Onsager relations and symmetry of the thermal conductivity tensor

Cattaneo law of damped thermal wave

Familiar near-equilibrium, nonequilibrium states

steady-state heat flux

$$q''(x) = q''(x+dx) = q''$$



Energy balance:

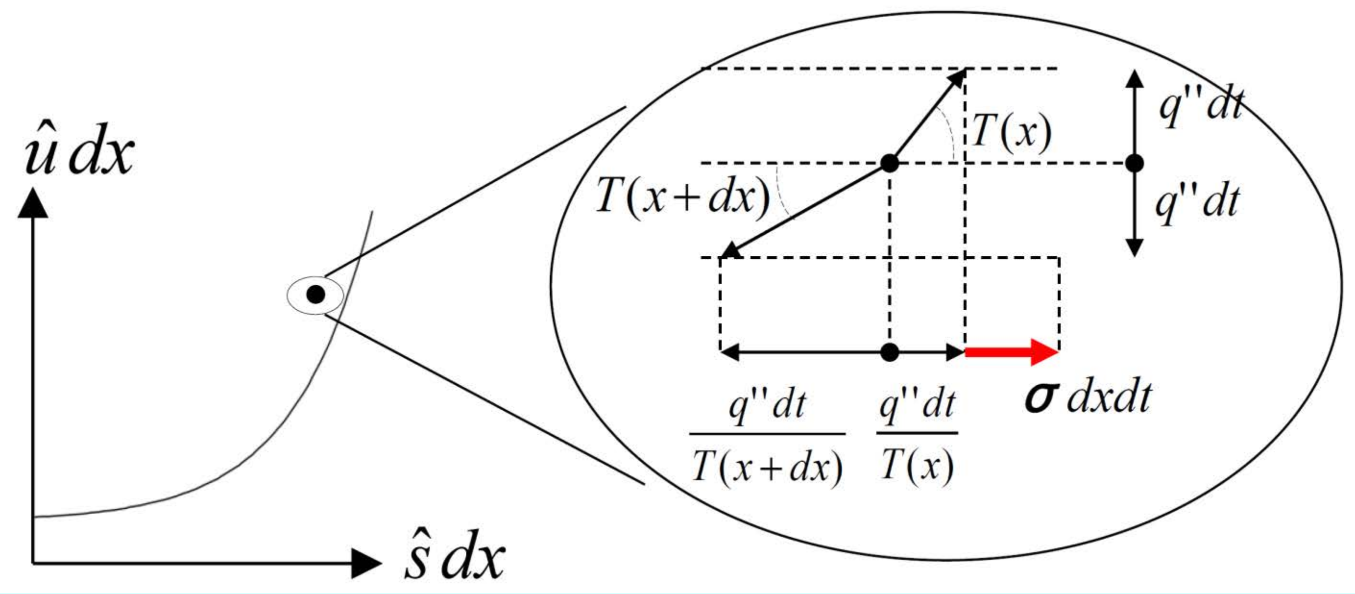
$$0 = q''(x) - q''(x+dx) = -(\partial q''/\partial x)\,dx = 0$$

Entropy balance:

$$0 = \left[\frac{q''}{T(x)} - \frac{q''}{T(x+dx)}\right] A + \dot{s}'''_{\mathrm{irr}}\, A\, dx$$

$$\sigma = \dot{s}'''_{\mathrm{irr}} = \frac{q''}{dx}\,\frac{T(x) - T(x+dx)}{T(x)T(x+dx)} \approx -\frac{q''}{T^2}\frac{dT}{dx} = q''\frac{d}{dx}\frac{1}{T}$$

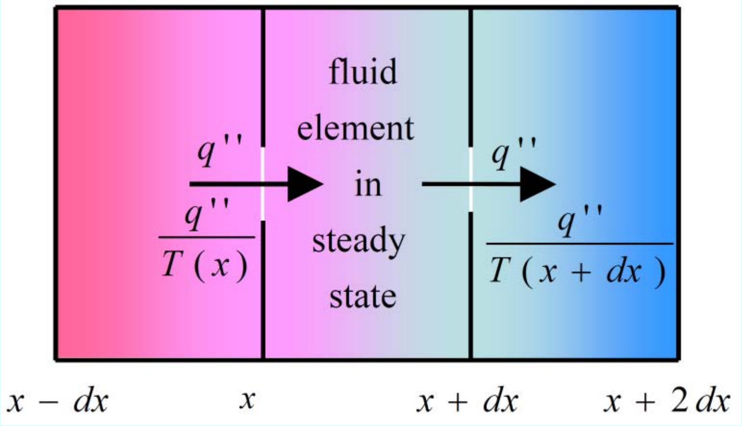
The entropy needed to sustain the steady state is generated by irreversibility.



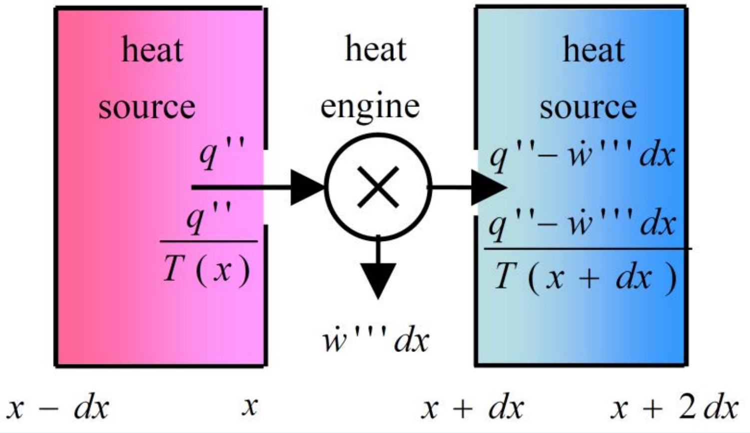
Familiar near-equilibrium, nonequilibrium states

steady-state heat flux

$$q''(x) = q''(x+dx) = q''$$



$$q''(x+dx) = q''(x) - \dot{w}'''_{\text{rev}}\,dx$$



Steady-state spontaneous heat flux in 1D (energy balance requires $\partial q''/\partial x = 0$). The entropy balance yields

$$\sigma = \dot{s}'''_{\text{irr}} = \frac{q''}{dx}\,\frac{T(x)-T(x+dx)}{T(x)T(x+dx)} \approx -\frac{q''}{T^2}\frac{dT}{dx} = q''\frac{d}{dx}\frac{1}{T}$$

The entropy generated by irreversibility is related to the maximum work extraction lost opportunity

If the fluid element is replaced by a reversible heat engine (entropy balance requires $\partial(q''/T)/\partial x = 0$), the energy balance yields

$$\dot{w}'''_{\text{rev}} = \frac{q''}{dx}\left[1-\frac{T(x+dx)}{T(x)}\right] \approx -\frac{q''}{T}\frac{dT}{dx} = Tq''\frac{d}{dx}\frac{1}{T}$$

$$w'''_{\text{rev}}\Big|_{\partial(q''/T)/\partial x=0} = T\sigma\Big|_{\partial q''/\partial x=0}$$

In the 3D general case:

$$\sigma = \underline{q}''\cdot\underline{\nabla}\frac{1}{T} \qquad \text{when} \quad \underline{\nabla}\cdot\underline{q}''=0$$

$$\frac{\dot{w}'''_{\text{rev}}}{T} = \underline{q}''\cdot\underline{\nabla}\frac{1}{T} \qquad \text{when} \quad \underline{\nabla}\cdot\frac{\underline{q}''}{T}=0$$

Fourier law of thermal conduction

Proceed by analogy with the near-equilibrium chemical kinetic model

$$\dot{s}'''_{\rm irr} = \underline{q}'' \cdot \underline{\nabla}(1/T)$$

$$\text{assume } \underline{q}'' = \underline{q}''\left[\underline{\nabla}(1/T)\right] \text{ with } \underline{q}''[0] = \underline{0}$$

$$\text{linearize: } \underline{q}'' = \underbrace{\left.\frac{\partial \underline{q}''}{\partial \underline{\nabla}(1/T)}\right|_{\mathbf{0}}}_{=\underline{\underline{L}}} \cdot \underline{\nabla}(1/T) + \ldots$$

$$\dot{S}_{\rm irr} = \dot{\boldsymbol{\epsilon}} \cdot \boldsymbol{Y}$$

$$\text{assume } \dot{\boldsymbol{\epsilon}} = \dot{\boldsymbol{\epsilon}}(\boldsymbol{Y}) \text{ with } \dot{\boldsymbol{\epsilon}}[0] = \mathbf{0}$$

$$\text{linearize: } \dot{\boldsymbol{\epsilon}} = \underbrace{\left.\frac{\partial \dot{\boldsymbol{\epsilon}}}{\partial \boldsymbol{Y}}\right|_{\mathbf{0}}}_{=\boldsymbol{L}} \cdot \boldsymbol{Y} + \ldots$$

Define the **thermal conductivity tensor** $\underline{\underline{k}} = \underline{\underline{L}}/T^2$

and obtain the **Fourier law of thermal conduction**

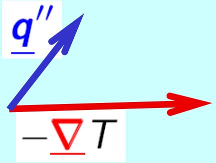
$$\underline{q}'' = -\underline{\underline{k}} \cdot \underline{\nabla} T$$

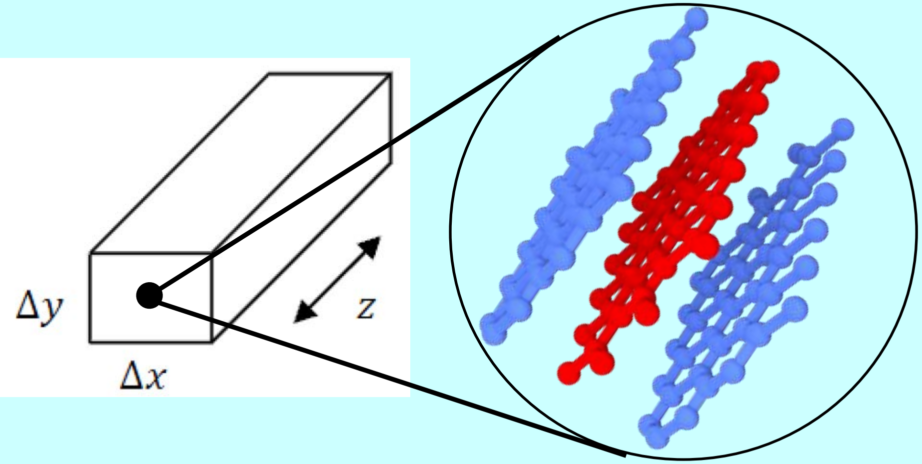
For example, consider an **anisotropic material**, and assume a 2D temperature field ($T = T(x,y,z)$ with $\partial T/\partial z = 0$) with boundary conditions such that $q''_z = 0$:

$$\begin{pmatrix} q''_x \\ q''_y \end{pmatrix} = -\begin{pmatrix} k_{xx} & k_{xy} \\ k_{xy} & k_{yy} \end{pmatrix} \cdot \begin{pmatrix} \partial T/\partial x \\ \partial T/\partial y \end{pmatrix}$$

$$q''_x = -k_{xx}\frac{\partial T}{\partial x} - k_{xy}\frac{\partial T}{\partial y}$$

$$q''_y = -k_{xy}\frac{\partial T}{\partial x} - k_{yy}\frac{\partial T}{\partial y}$$

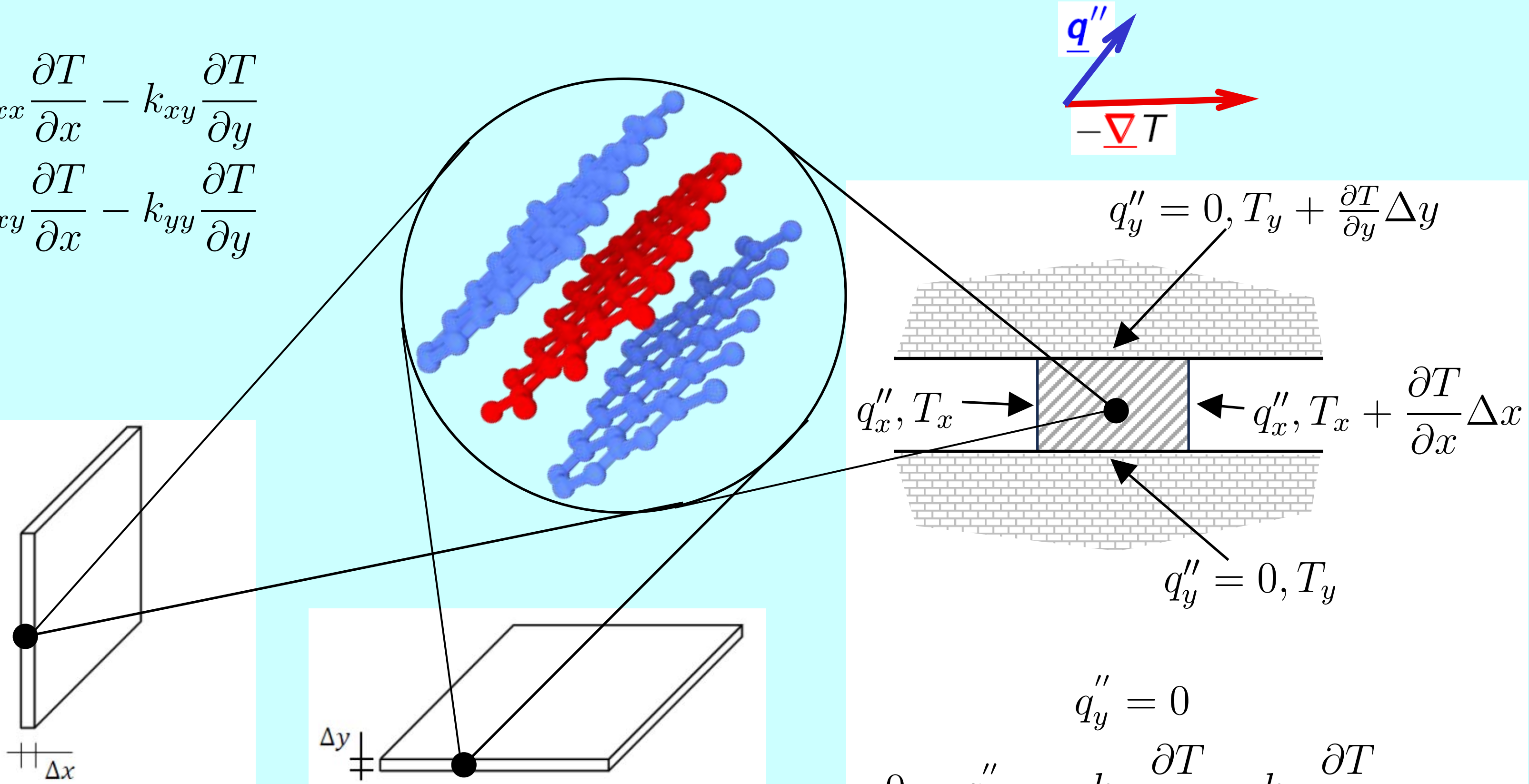




Fourier law of thermal conduction

$$q''_x = -k_{xx}\frac{\partial T}{\partial x} - k_{xy}\frac{\partial T}{\partial y}$$

$$q''_y = -k_{xy}\frac{\partial T}{\partial x} - k_{yy}\frac{\partial T}{\partial y}$$



$$\frac{\partial T}{\partial y} = 0$$

$$q''_x = -k_{xx}\frac{\partial T}{\partial x}$$

$$k_{xx} = -\left.\frac{q''_x}{\partial T/\partial x}\right|_{\partial T/\partial y=0}$$

$$\frac{\partial T}{\partial x} = 0$$

$$q''_y = -k_{yy}\frac{\partial T}{\partial y}$$

$$k_{yy} = -\left.\frac{q''_y}{\partial T/\partial y}\right|_{\partial T/\partial x=0}$$

$$q''_y = 0$$

$$0 = q''_y = -k_{xy}\frac{\partial T}{\partial x} - k_{yy}\frac{\partial T}{\partial y}$$

$$\frac{k_{xy}}{k_{yy}} = -\left.\frac{\partial T/\partial y}{\partial T/\partial x}\right|_{q''_y=0}$$

$$q''_x = -\left(k_{xx} - \frac{k_{xy}^2}{k_{yy}}\right)\frac{\partial T}{\partial x}$$

Righi-Leduc effect

Anisotropic Fourier conduction in 2D - special change of coordinates

Energy balance: $\rho c_v \partial_t T = -\underline{\nabla} \cdot \underline{q}''$ with Fourier law: $\underline{q}'' = -\underline{\underline{k}} \cdot \underline{\nabla} T$

At steady state ($\partial_t T = 0$) with $\underline{\underline{k}}$ uniform and indep of T, it reduces to

$0 = \underline{\underline{k}} : \underline{\underline{\nabla\nabla}} T$ where the tensor $\underline{\underline{\nabla\nabla}} T$ is the Hessian of T

For a 2D symmetric problem: $$0 = k_{xx}\frac{\partial^2 T}{\partial x^2} + 2k_{xy}\frac{\partial^2 T}{\partial x \partial y} + k_{yy}\frac{\partial^2 T}{\partial y^2}$$

Letting $k = \sqrt{k_{xx}k_{yy} - k_{xy}^2}$ and changing to non-orthogonal coordinates:

$$\begin{bmatrix} X \\ Y \end{bmatrix} = \frac{1}{k_{yy}} \begin{bmatrix} k_{yy} & -k_{xy} \\ 0 & k \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$ rewrites as: $$0 = k\left(\frac{\partial^2 T}{\partial X^2} + \frac{\partial^2 T}{\partial Y^2}\right)$$

The heat flux vector in the original coordinates is

$$\begin{bmatrix} q_x \\ q_y \end{bmatrix} = \frac{1}{k_{yy}} \begin{bmatrix} k & k_{xy} \\ 0 & 1 \end{bmatrix} \begin{bmatrix} q_X \\ q_Y \end{bmatrix}$$ where : $$q_X = -k\frac{\partial T}{\partial X} \quad q_Y = -k\frac{\partial T}{\partial Y}$$

Cattaneo-Vernotte heat conduction equation

(eliminates the paradox of instantaneous propagation implied by Fourier heat equation)

Assume $S < S_{\rm SES} = S(U,V,\underline{n})$. In terms of a constant and uniform parameter $b > 0$,

$$\boxed{\rho s = \rho s_{\rm SES} - \frac{b}{2}\,\underline{q}''\cdot\underline{q}''} \quad \text{so that} \quad {\rm d}(\rho s) = {\rm d}(\rho s_{\rm SES}) - b\,\underline{q}''\cdot{\rm d}\underline{q}''$$

The energy and entropy balance equations, and the Gibbs equation may be written as

$$\partial_t(\rho u) = -\underline{\nabla}\cdot\underline{q}'' \qquad \partial_t(\rho s) = -\underline{\nabla}\cdot(\underline{q}''/T) + \sigma \qquad {\rm d}(\rho s_{\rm SES}) = (1/T){\rm d}(\rho u)$$

Combining them yields $\boxed{\sigma = \underline{q}''\cdot\left[\underline{\nabla}(1/T) - b\,\partial_t\underline{q}''\right]}$ so that assuming $\boxed{\underline{q}'' = L\,\left[\underline{\nabla}(1/T) - b\,\partial_t\underline{q}''\right]}$

with L a positive constant, assures that $\sigma \geq 0$ and substitution into the energy balance yields

$$\partial_t(\rho u) = -\underline{\nabla}\cdot\underline{q}'' = -L\nabla^2(1/T) - bL\,\partial_t(\underline{\nabla}\cdot\underline{q}'') = -L\nabla^2(1/T) + bL\,\partial_t(\partial_t(\rho u))$$

Assuming constant c_v and ρ so that $\partial_t(\rho u) = \rho c_v \partial_t T$, and defining γ, α and C as noted below, yields the Cattaneo heat equation (1948), which is a damped wave equation

$$\frac{\partial^2 T}{\partial t^2} + \gamma\frac{\partial T}{\partial t} = C^2\nabla^2 T \quad \text{where} \quad \begin{array}{ll} C = \sqrt{\alpha/bL} & \text{wave celerity} \\ \gamma = 1/bL & \text{damping coefficient} \\ \alpha = k/\rho c_v & \text{thermal diffusivity} \end{array}$$

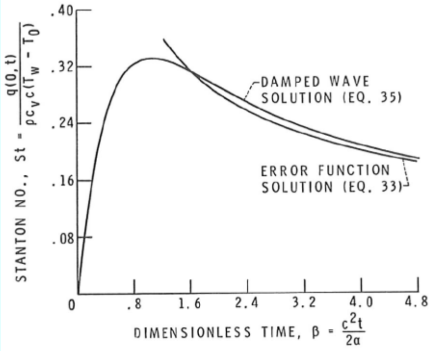
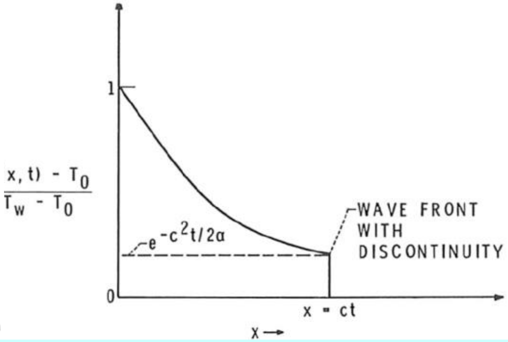
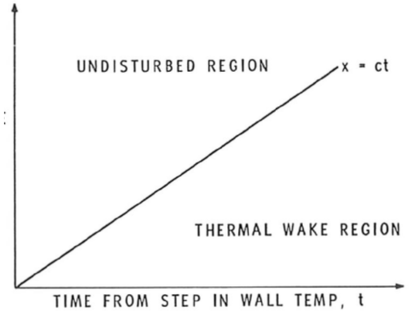
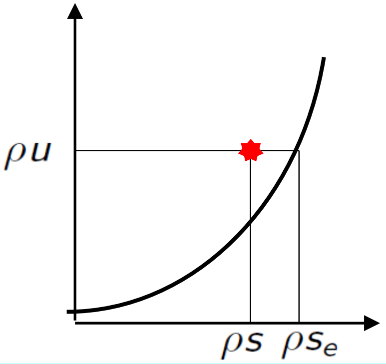


Fig. 3 Heat flux at wall as a function of time-short time solution







Baumeister, Hamill, Hyperbolic Heat-Conduction Equation—A Solution for the Semi-Infinite Body Problem, J.Heat Transfer, 91, 543 (1969)

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Slide 20:

Figure showing heat flux at wall as a function of time-short time solution, typical temperature profile showing discontinuity at wave front, and map of undisturbed and thermal wake regions © The American Society of Mechanical Engineers. All rights reserved. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use.

2.43 Advanced Thermodynamics
Spring 2024