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# A continuum theory of thermoelectric materials and proposed large-scale applications

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# Bottom-up vs. Top-down

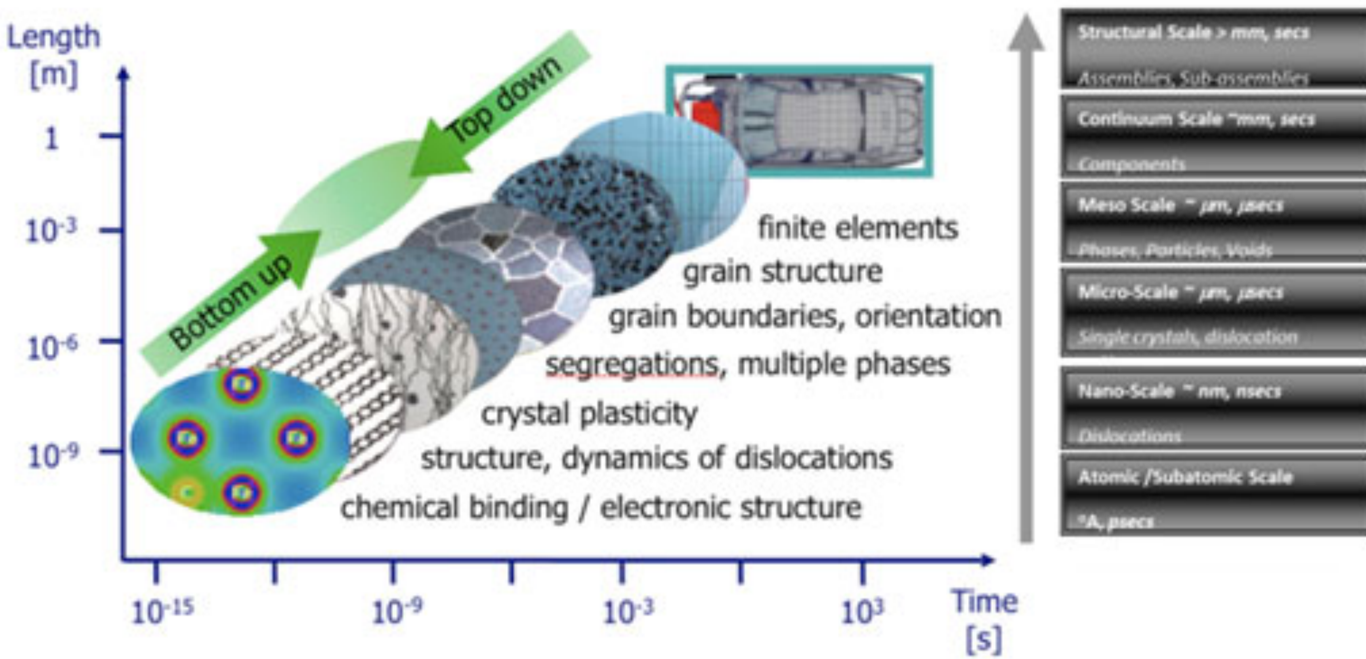
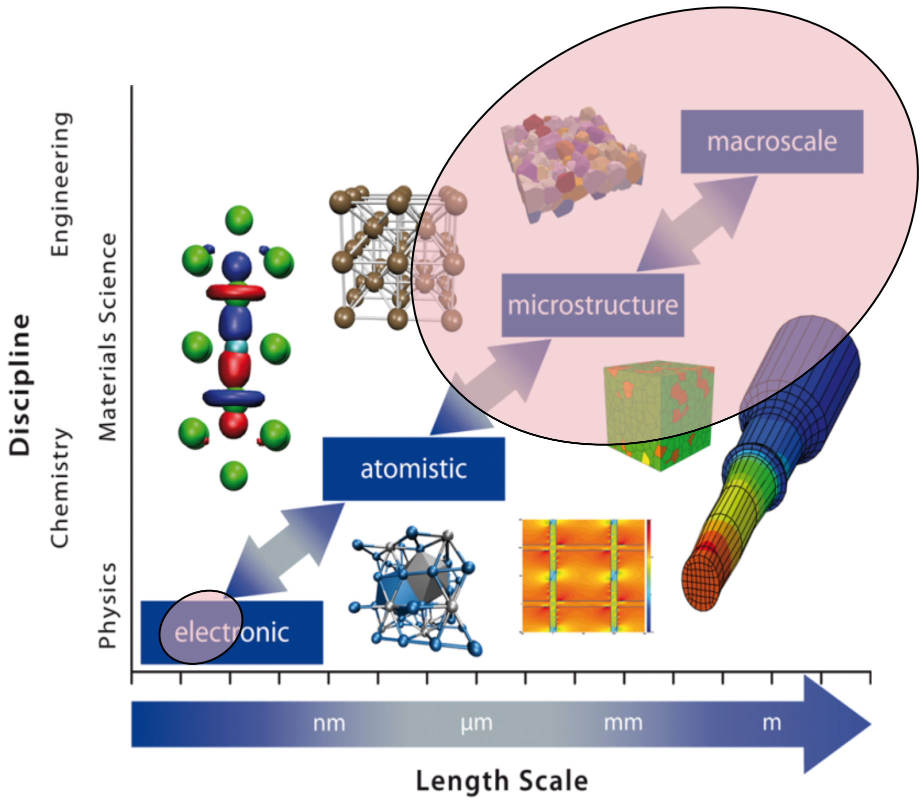
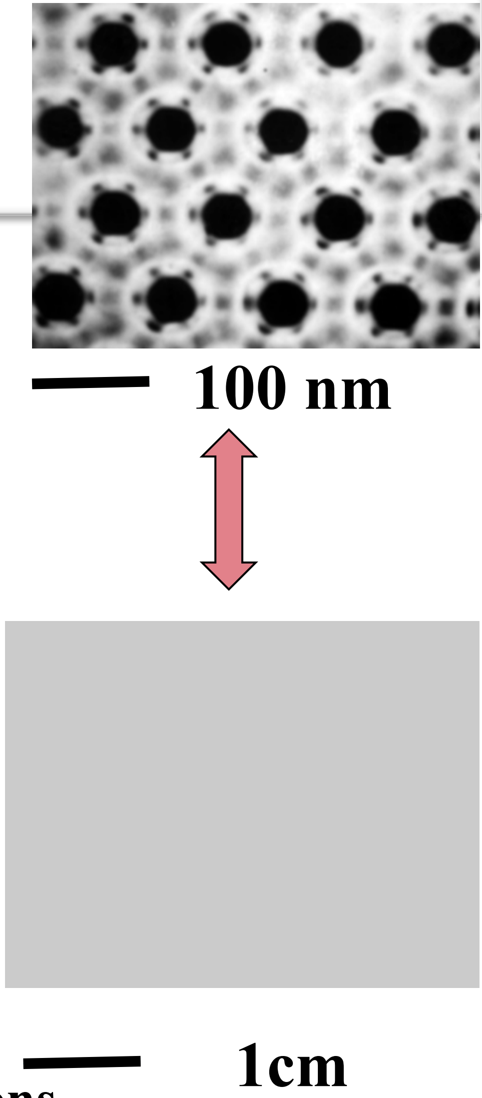



Figure fromhttp://eng.jhu.edu/wse/civil/page/mechanics-of-materials

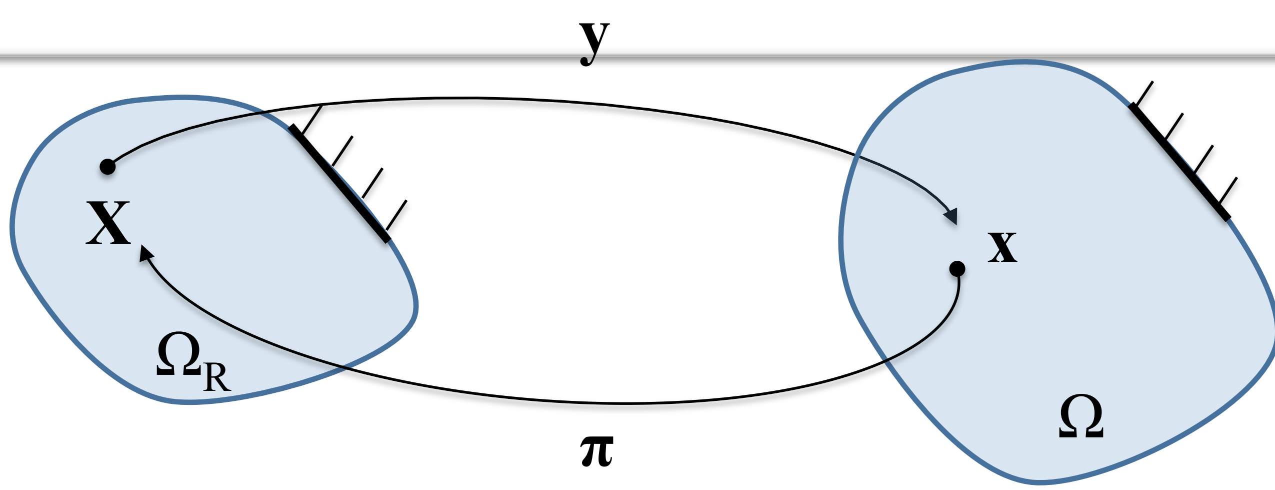
# Main problem




- Effective/macroscopic properties – Microstructure relations
- Designing optimal microstructures for applications
- etc

# Continuum Mechanics



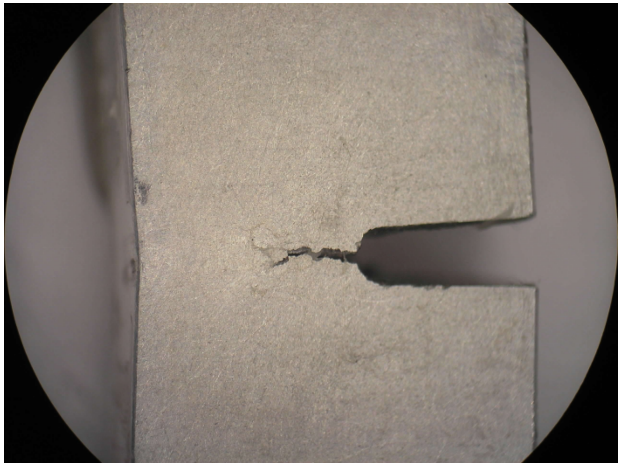

**(a)** Ref. config. **(b)** Current config.

- Kinematics: thermodynamic variables to describe the system (μ, T)
- Balance / conservation Laws: $\mathrm{Div}(\tilde{\Sigma} + \tilde{\Sigma}_M) = 0$, $\mathrm{Div}\tilde{\mathbf{D}} = 0$, etc
- Constitutive Relations: $\mathcal{C}(\tilde{\Sigma}, \mathbf{F}, \tilde{\mathbf{D}}, \tilde{\mathbf{E}}, \tilde{\mathbf{P}}) = 0$
  - Frame indifference
  - Material symmetries
  - Laws of thermodynamics

# Why multiscale modeling?

- Constitutive laws: $\sigma = \mathbf{C}\mathbf{E}$ $\quad \mathbf{D} = \epsilon \mathbf{E}$ $\quad \mathbf{B} = \frac{1}{\mu}\mathbf{H}$
  - Multifunctional: $\mathcal{C}(\tilde{\Sigma}, \mathbf{F}, \tilde{\mathbf{D}}, \tilde{\mathbf{E}}, \tilde{\mathbf{P}}) = 0$

- Cross-scale interactions: cracks, turbulence, etc



- http://www.youtube.com/embed/iBuuVd0JlIM

From NY Times (12Jun07) Wake Turbulence

# Multiscale analysis

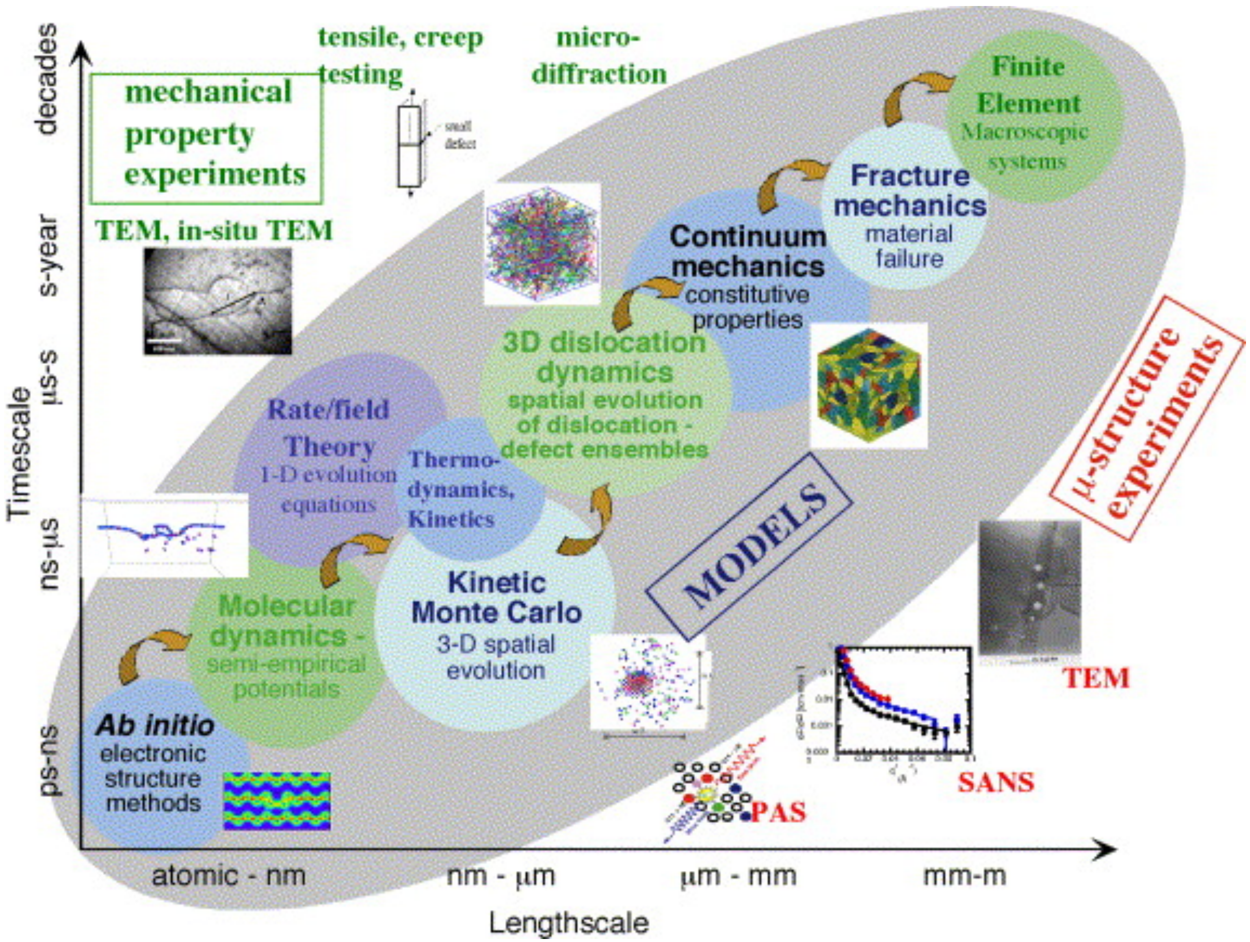
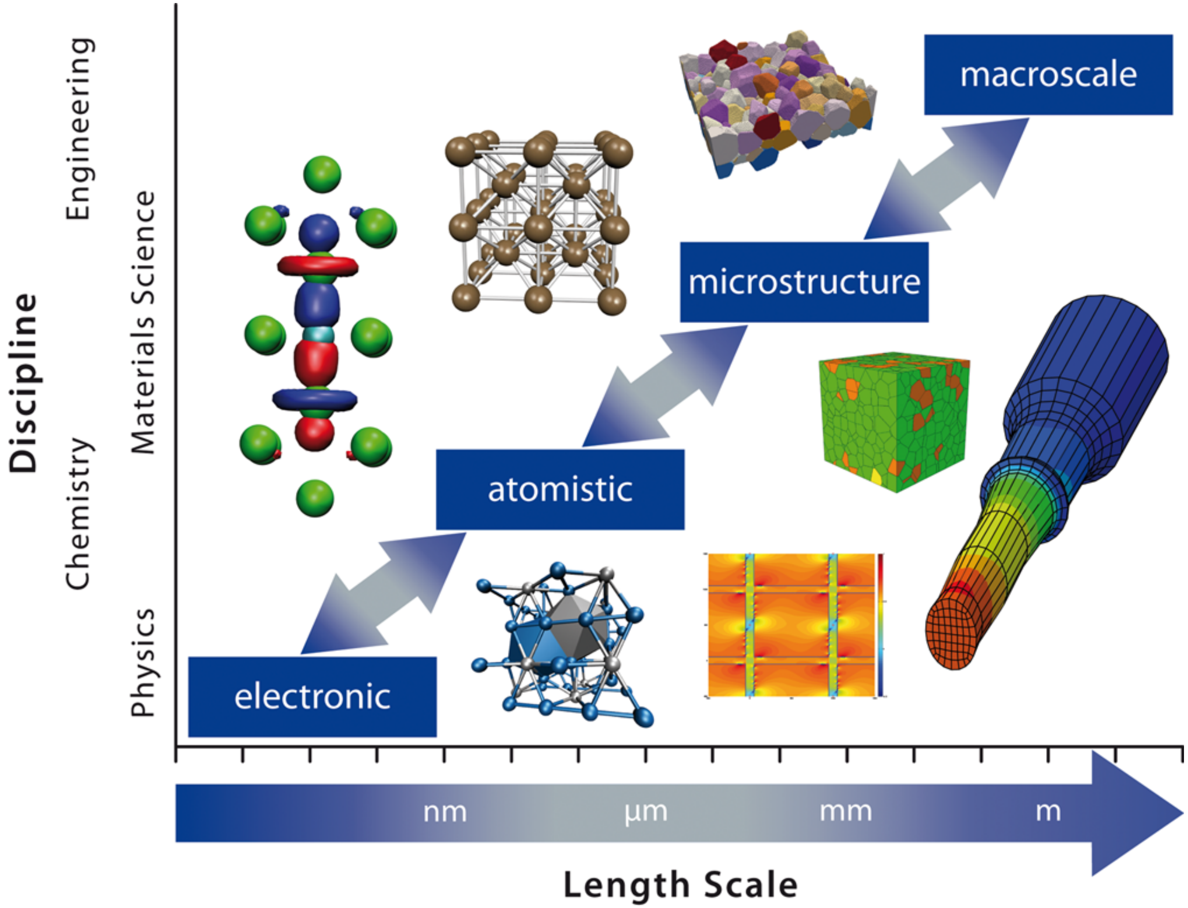



Figure from JNM, 329–333, Part A by Wirth et al. 2004

# Multidisciplinary




Mathematics

Figure from http://www.icams.de/content/research-at-icams/research-index.html

# Bridging scales and disciplines: materials genome initiative

the WHITE HOUSE PRESIDENT BARACK OBAMA

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## Materials Genome Initiative: A Renaissance of American Manufacturing

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Posted by Tom Kalil and Cyrus Wadia on June 24, 2011 at 09:03 AM EDT

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From the synthetic fibers in Kevlar vests to the lithium-based compounds that power your laptop, advanced materials are so much a part of our everyday lives it's not surprising that many people don't appreciate how difficult it is to develop them. It can take 20 or more years to transition a material from discovery to a commercial product on store shelves. Those lithium ion batteries, for example, which are ubiquitous today not only in laptops but in all kinds portable electronic devices, were first proposed in the mid-1970s but only achieved broad market adoption and use in the late 1990s.

This current "time-to-market" from discovery to deployment for new classes of materials is far too slow, given the range of urgent problems that advanced materials can help us solve. New materials, for example, can enable

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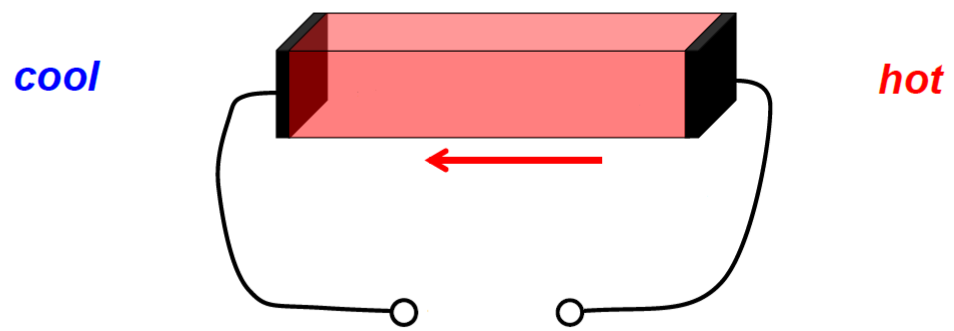
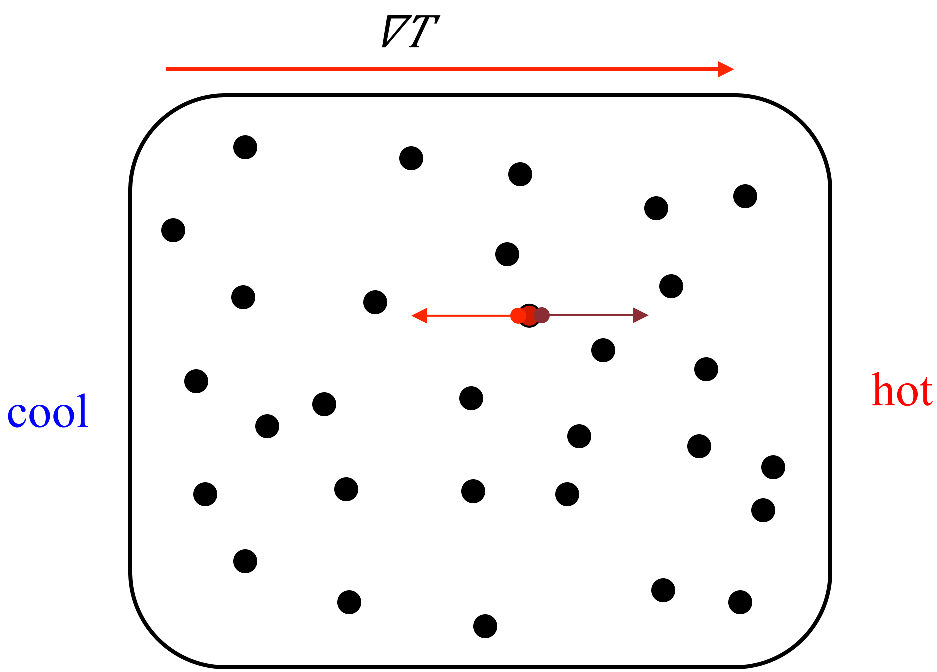
# Introduction

- Thermoelectric effects: coupling of electric field and temperature gradient




- Seebeck coefficient: $e = s \nabla T, \quad j_e = 0$
- Peltier coefficient: $q = \beta j_e, \quad \nabla T = 0$
- Electric conductivity: $j_e = \sigma e, \quad \nabla T = 0$
- Thermoconductivity: $q = -\kappa \nabla T, \quad j_e = 0$

# Microscopic theory




- Ideal gas (MB statistics):

$$s = -\frac{k_b}{2e} = -0.43e - 4\,V/K$$

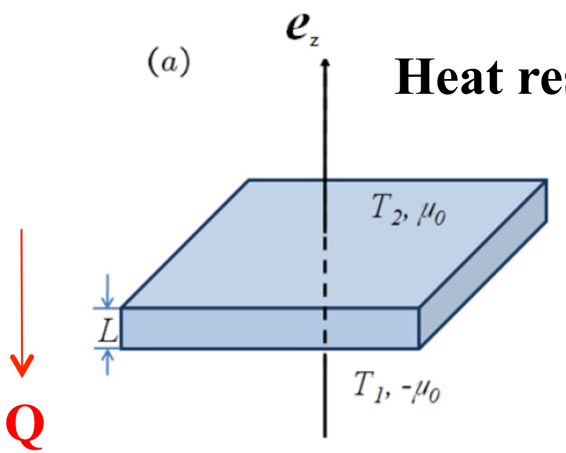
- Free electron gas (FD statistics) :

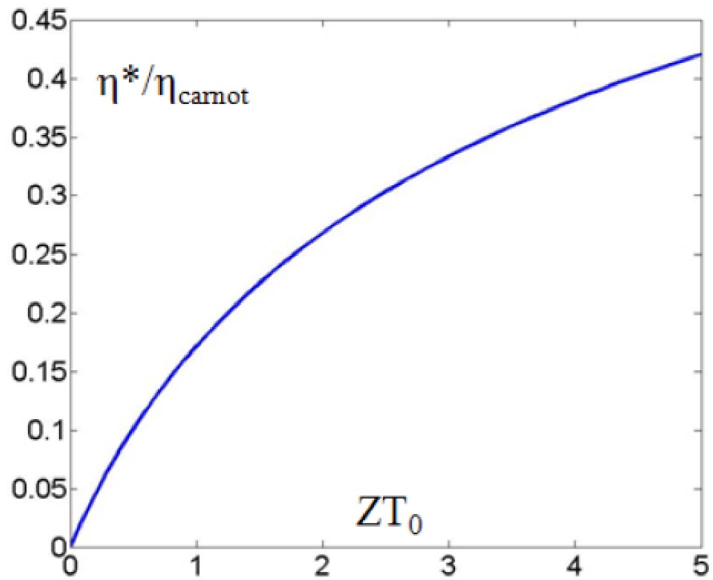
$$s = -\frac{k_b}{2e}\frac{\pi^2 k_b T}{3\varepsilon_F} = -0.43e - 6\,V/K$$

- Band theory for semi-conductor (MB statistics) :

$$s = \frac{k_b}{q^*}(\frac{E_c - \varepsilon_F}{k_b T} + \delta_n) \sim -0.43e - 4\,V/K$$

# Figure of merits and power factor




❖ Power factor: $$\dot{W}_{\max} = \frac{\alpha_z^2 \delta T^2}{4\sigma_z L^2} = \frac{P_f}{4}\left(\frac{\delta T}{L}\right)^2$$ $$P_f = s^2\sigma$$

❖ Figure of merit: $$\frac{\eta^*}{\eta_{\text{carnot}}} = \frac{\sqrt{1+ZT_0}-1}{\sqrt{1+ZT_0}+1}$$ $$ZT_0 = T_0 s^2 \sigma / \kappa$$

# Advantage/Disadvantage of TE devices

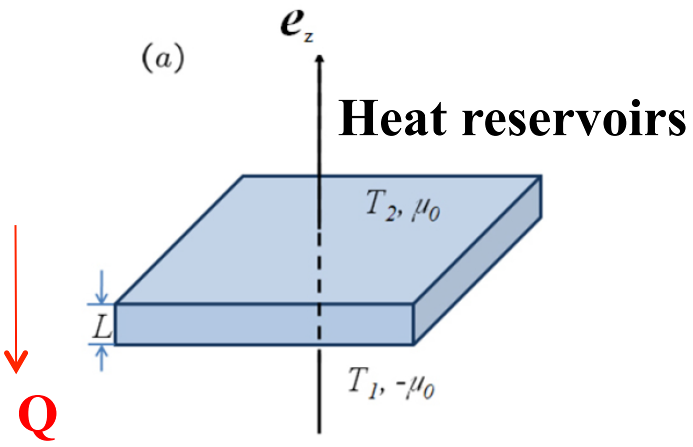
❖ Advantage:

- Portability
- Silence
- Reliability
- Capable of converting heat resources of low temperature difference!

❖ Disadvantage:

- Low efficiency: Figure of merit
- Low capacity (Power output/ weight): Power factor

# Cost of generated electricity




- Cost of materials:

$$\sim 1/P_f$$

- Cost of fuels:

$$\sim 1/ZT_0$$

- Power factor: $$\dot{W}_{\max} = \frac{\alpha_z^2 \delta T^2}{4\sigma_z L^2} = \frac{P_f}{4}\left(\frac{\delta T}{L}\right)^2$$ $$P_f = s^2\sigma$$

- Figure of merit: $$\frac{\eta^*}{\eta_{\text{carnot}}} = \frac{\sqrt{1+ZT_0}-1}{\sqrt{1+ZT_0}+1}$$ $$ZT_0 = T_0 s^2 \sigma/\kappa$$

# Usable energy content in ocean

❖ Second Law of thermodynamics:

$$\eta_{\text{carnot}} = \frac{T_h - T_c}{T_h}$$

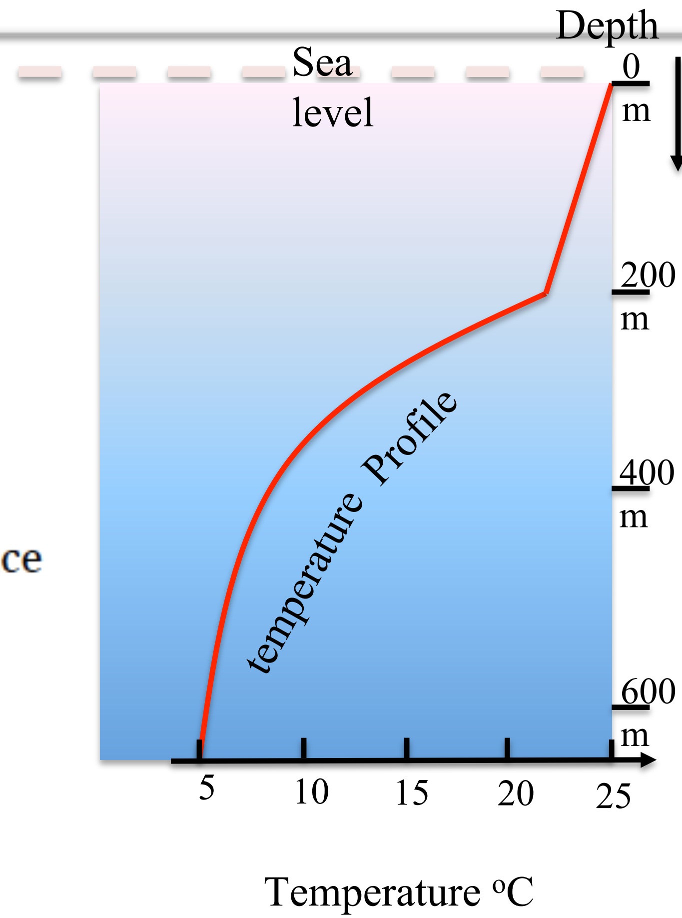
❖ Usable energy per ton water:

$W = C_p \eta_{carnot} (T_h - T_c) = 1.6$ kWh for 20K difference

$\propto (T_h - T_c)^2$

1 Megawatt ~ 180 $l/s$ ~ 1-2 Million USD

Kitchen faucet ~ 0.1 $l/s$

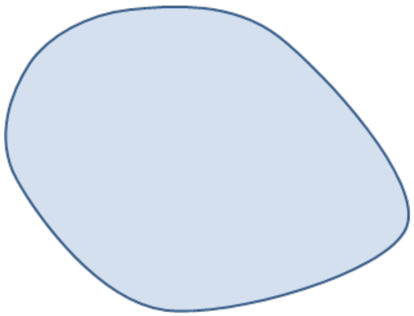



❖ Critical material property to improve for large-scale applications:

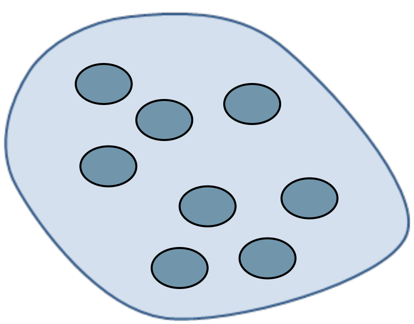
Power factor!

# Why continuum theory?

- Geometric effects?
- Boundary conditions?



- Predictive model for TE composites



- Onsager's relations

$$\boldsymbol{L}_1 = \begin{pmatrix} T\sigma & T\sigma s \\ \beta\sigma & \kappa + \beta\sigma s \end{pmatrix}$$

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^T, \boldsymbol{\beta} = T\boldsymbol{s}^T, \boldsymbol{\kappa} = \boldsymbol{\kappa}^T$$

- Positive-definite of the material coefficient tensor

$$\boldsymbol{L}_1 > \boldsymbol{0}$$

# Empirical constitutive relations

$$\boldsymbol{j_1} = \boldsymbol{L_1} \boldsymbol{f_1}$$

$\boldsymbol{j_1} = \begin{pmatrix} \boldsymbol{j_e} \\ \boldsymbol{j_s} \end{pmatrix}$: flux

$\boldsymbol{f_1} = \frac{1}{T}\begin{pmatrix} \boldsymbol{e} \\ \boldsymbol{g} \end{pmatrix}$: driving forces

$$\boldsymbol{L_1} = \begin{pmatrix} T\sigma & T\sigma \mathbf{s} \\ \boldsymbol{\beta}\sigma & \boldsymbol{\kappa} + \boldsymbol{\beta}\sigma\mathbf{s} \end{pmatrix}$$

- Seebeck coefficient: $\boldsymbol{e} = \mathbf{s}\, \nabla T,\quad \boldsymbol{j_e} = 0$
- Peltier coefficient: $\boldsymbol{q} = \boldsymbol{\beta}\, \boldsymbol{j_e},\quad \nabla T = 0$
- Electric conductivity: $\boldsymbol{j_e} = \sigma \boldsymbol{e},\quad \nabla T = 0$
- Thermoconductivity: $\boldsymbol{q} = -\boldsymbol{\kappa}\, \nabla T,\quad \boldsymbol{j_e} = 0$

$\boldsymbol{e} = -\nabla\mu, \mathbf{g} = -\nabla T,\ \boldsymbol{j_e},\ \boldsymbol{j_s} = \frac{\boldsymbol{q}}{T}$: entropy flux, $\boldsymbol{j_u} = \boldsymbol{q} + \mu\boldsymbol{e}$: energy flux

# Constitutive model

- Choices of "driving-forces":

$$\boldsymbol{e} = -\nabla\mu, \mathbf{g} = -\nabla T, \qquad \boldsymbol{f_1} = \frac{1}{T}\begin{pmatrix}\boldsymbol{e}\\ \boldsymbol{g}\end{pmatrix} \longrightarrow \boldsymbol{f} = \boldsymbol{\Lambda f_1}$$

- Choices of "fluxes":

$$\boldsymbol{q},\ \boldsymbol{j}_e,\ \boldsymbol{j}_s = \frac{\boldsymbol{q}}{T}\text{: entropy flux},\ \boldsymbol{j}_u = \boldsymbol{q} + \mu\boldsymbol{e}\text{: energy flux}$$

$$\boldsymbol{j_1} = \begin{pmatrix}\boldsymbol{j_e}\\ \boldsymbol{j_s}\end{pmatrix} \longrightarrow \boldsymbol{j} = \boldsymbol{\Gamma j_1}$$

$$\boldsymbol{L_1} \longrightarrow \boxed{\boldsymbol{L} = \boldsymbol{\Gamma L_1 \Lambda^{-1}}}$$

# An alternative viewpoint

- Near-equilibrium thermodynamics:

State variables: $\nabla \boldsymbol{u}=(\nabla u_1, \cdots, \nabla u_{\mathrm{m}}) =: \boldsymbol{F}$

Rate of entropy generation: $\gamma = \gamma(\boldsymbol{u}, \boldsymbol{F})$

$$= \gamma(\boldsymbol{u}, 0) + \boldsymbol{F} \cdot \boldsymbol{B}(\boldsymbol{u}, 0) + \boldsymbol{F} \cdot \boldsymbol{C}(\boldsymbol{u}, 0)\boldsymbol{F} + \cdots$$

$\gamma(\boldsymbol{u}, \boldsymbol{F}) \geq 0$ ⟹

$\gamma(\boldsymbol{u}, 0) = 0,\quad \boldsymbol{B}(\boldsymbol{u}, 0) = 0,\quad \boldsymbol{C}(\boldsymbol{u}, 0) > 0$

"Conjugate variables":

$$\mathbf{S} = \frac{\partial}{2\partial \boldsymbol{F}} \gamma(\boldsymbol{u}, \boldsymbol{F})$$

$$\boldsymbol{j}_1 = \begin{pmatrix} \boldsymbol{j}_e \\ \boldsymbol{j}_s \end{pmatrix}$$

**Indeed, by the first law we have** $\gamma = \boldsymbol{j}_1 \cdot \boldsymbol{f}_1$

$$\boldsymbol{f}_1 = \frac{1}{T}\begin{pmatrix} \boldsymbol{e} \\ \boldsymbol{g} \end{pmatrix}$$

# Implication of Gauge symmetry

- Invariance of entropy generation rate:

$$\gamma = \gamma(\mu, T; \boldsymbol{F}) = \gamma(\mu + c, T; \boldsymbol{F}) \quad \Longrightarrow$$

$$\boldsymbol{L}_1 = \begin{pmatrix} T\boldsymbol{\sigma} & T\boldsymbol{\sigma}\mathbf{s} \\ T\boldsymbol{s}^T\boldsymbol{\sigma} & \boldsymbol{\kappa} + T\boldsymbol{s}^T\boldsymbol{\sigma}\mathbf{s} \end{pmatrix}$$

independent of $\mu$

# Conservation laws

- Steady states:

$$\operatorname{div} \boldsymbol{j_e} = 0$$
$$\operatorname{div} \boldsymbol{j_u} = 0$$

$$\boldsymbol{j} = \begin{pmatrix} \boldsymbol{j_e} \\ \boldsymbol{j_u} \end{pmatrix} = \boldsymbol{\Lambda j_1}, \qquad \boldsymbol{\Lambda} = \begin{pmatrix} \boldsymbol{I} & \boldsymbol{0} \\ \mu \boldsymbol{I} & T\boldsymbol{I} \end{pmatrix}$$

To keep the invariance of entropy generation, the corresponding "driving-forces" or "state variables" has to be chosen as

$$\boldsymbol{f} = \boldsymbol{\Lambda}^{-T} \boldsymbol{f_1} \Longrightarrow \boldsymbol{L} = \boldsymbol{\Lambda L_1 \Lambda}^T$$

$$\boldsymbol{L} = \begin{pmatrix} T\boldsymbol{\sigma} & \mu T\boldsymbol{\sigma} + T^2\boldsymbol{\sigma s} \\ \mu T\boldsymbol{\sigma} + T^2\boldsymbol{\sigma s} & \mu^2 T\boldsymbol{\sigma} + \mu T^2(\boldsymbol{s}^T\boldsymbol{\sigma} + \boldsymbol{\sigma s}) + T^2(\boldsymbol{\kappa} + T\boldsymbol{s}^T\boldsymbol{\sigma s}) \end{pmatrix}$$

$$\boldsymbol{j_1} = \begin{pmatrix} \boldsymbol{j_e} \\ \boldsymbol{j_s} \end{pmatrix}$$

$$\boldsymbol{f_1} = \frac{1}{T}\begin{pmatrix} \boldsymbol{e} \\ \boldsymbol{g} \end{pmatrix}$$

# Field equations

- Steady states:
  - ❖ $\operatorname{div} \boldsymbol{L}\boldsymbol{f} = 0$

$$\boldsymbol{f} = \begin{pmatrix} -\nabla \frac{\mu}{T} \\ \nabla \frac{1}{T} \end{pmatrix}$$

$$\boldsymbol{L}(\mu, T) = \begin{pmatrix} T\boldsymbol{\sigma} & \mu T\boldsymbol{\sigma} + T^2\boldsymbol{\sigma s} \\ \mu T\boldsymbol{\sigma} + T^2\boldsymbol{\sigma s} & \mu^2 T\boldsymbol{\sigma} + \mu T^2(\boldsymbol{s}^T\boldsymbol{\sigma} + \boldsymbol{\sigma s}) + T^2(\boldsymbol{\kappa} + T\boldsymbol{s}^T\boldsymbol{\sigma s}) \end{pmatrix}$$

❖ The above system of equations are intrinsically nonlinear since it is not possible to eliminate the $\mu$-dependence of $\boldsymbol{L}$

# Linearization

- Small temperature difference and $\mu$ variations:

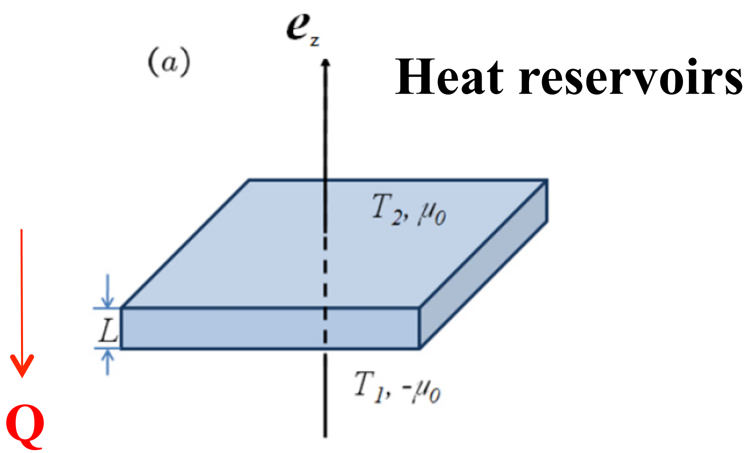
$$(\mu, T) = (0, T_0)$$

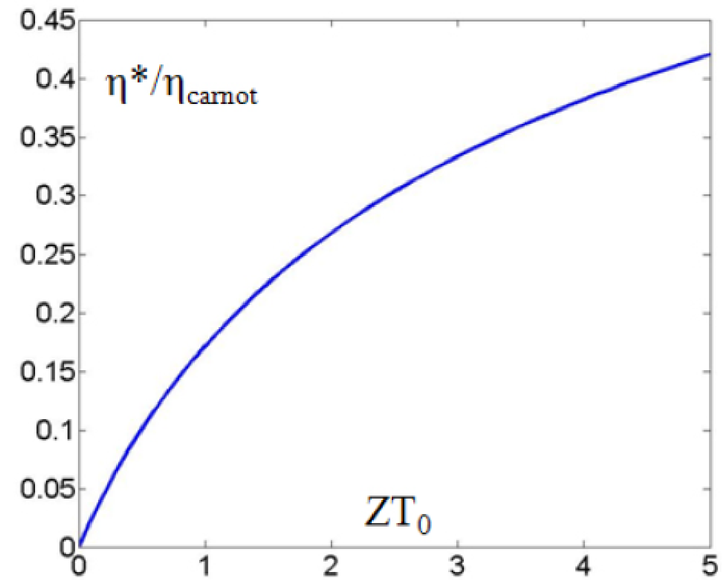
$$\boldsymbol{L}(0, T_0) = \begin{pmatrix} T_0\boldsymbol{\sigma} & T^2\boldsymbol{\sigma}\mathbf{s} \\ T_0^2\,\boldsymbol{\sigma}\mathbf{s} & T_0^2\,(\boldsymbol{\kappa} + T_0\boldsymbol{s}^T\boldsymbol{\sigma}\mathbf{s}) \end{pmatrix}$$

$$\boldsymbol{f} = \begin{pmatrix} -\nabla\dfrac{\mu}{T} \\ \nabla\dfrac{1}{T} \end{pmatrix}$$

❖ $\text{div}\,\boldsymbol{L}\boldsymbol{f} = 0$

# Figure of merits and power factor

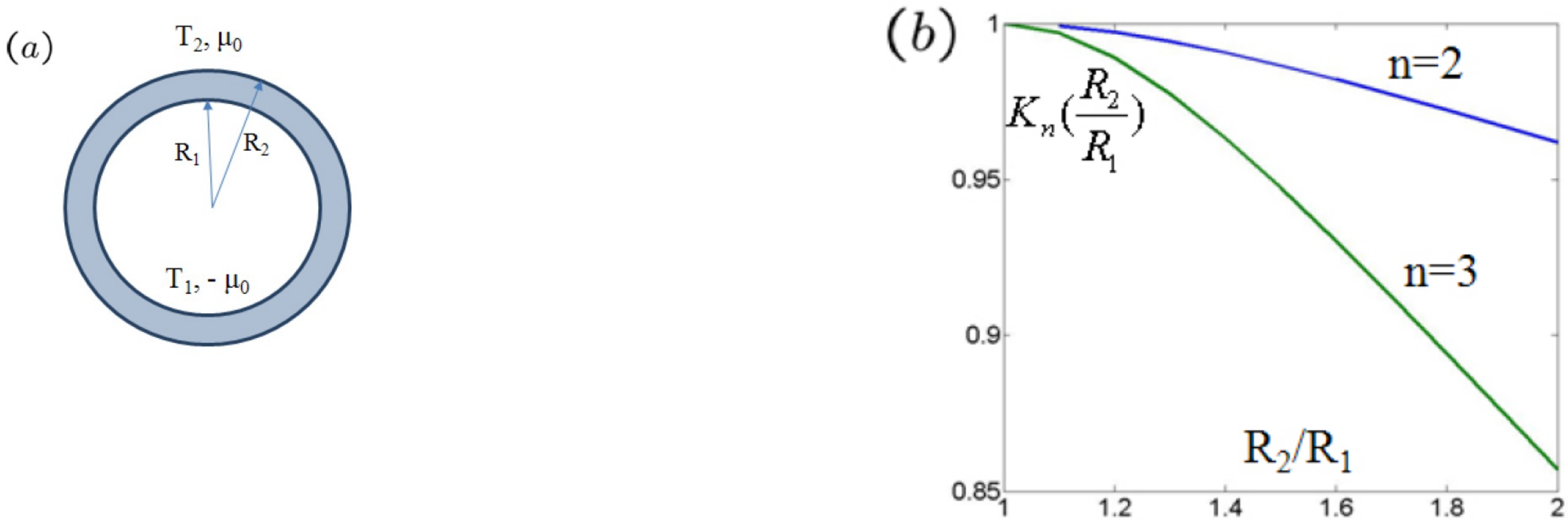



- Power factor: $$\dot{W}_{\max} = \frac{\alpha_z^2 \delta T^2}{4\sigma_z L^2} = \frac{P_f}{4}\left(\frac{\delta T}{L}\right)^2$$ $$P_f = s^2\sigma$$

- Figure of merit: $$\frac{\eta^*}{\eta_{\text{carnot}}} = \frac{\sqrt{1+ZT_0}-1}{\sqrt{1+ZT_0}+1}$$ $$ZT_0 = T_0 s^2 \sigma / \kappa$$

# Geometric effects

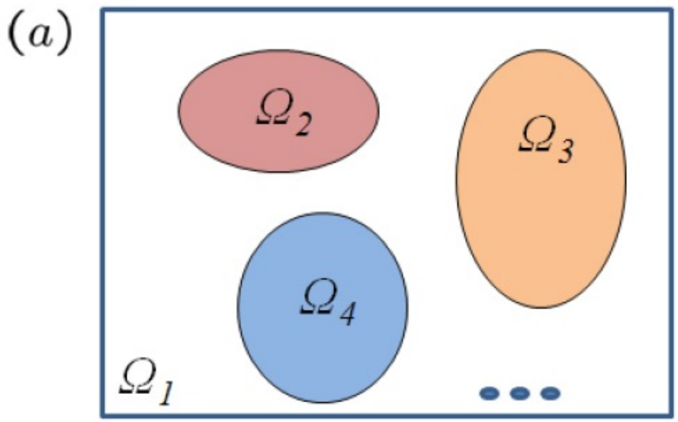



❖ Power factor: $$\dot{W}_{\max} = \frac{P_f K_n(\frac{R_2}{R_1})}{4}\left(\frac{\delta T}{R_2 - R_1}\right)^2$$

❖ Figure of merit remains the same.

❖ More general geometries and boundary conditions?

# Homogenization




❖ $\operatorname{div} \boldsymbol{Lf} = 0$

$$\boldsymbol{f} = \begin{pmatrix} -\nabla \frac{\mu}{T} \\ \nabla \frac{1}{T} \end{pmatrix}$$

$$\boldsymbol{L}(0, T_0; \boldsymbol{x}) = \begin{pmatrix} T_0 \boldsymbol{\sigma} & T^2 \boldsymbol{\sigma} \mathbf{s} \\ T_0^2 \, \boldsymbol{\sigma} \mathbf{s} & T_0^2 \, (\boldsymbol{\kappa} + T_0 \mathbf{s}^T \boldsymbol{\sigma} \mathbf{s}) \end{pmatrix}$$

❖ Unit cell problem:

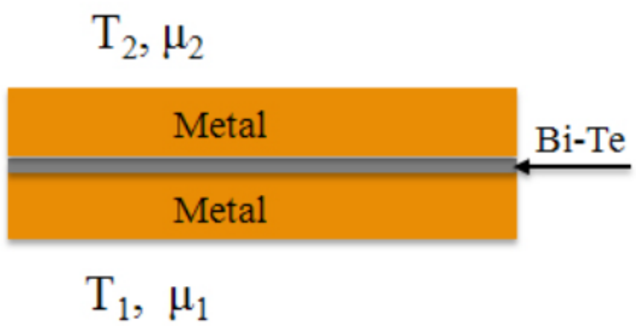
$$\begin{cases} \operatorname{div}[\mathbf{C}(\mathbf{x})(\nabla \mathbf{v} + \mathbf{F})] = 0 & \text{on } Y, \\ \mathbf{v} \text{ is periodic} & \text{on } \partial Y. \end{cases}$$

❖ Variational formulation:

$$\mathbf{F} \cdot \mathbf{C}^e \mathbf{F} = \min_{\mathbf{v} \in \mathbb{W}} \left\{ \int_Y (\nabla \mathbf{v} + \mathbf{F}) \cdot \mathbf{C}(\mathbf{x}) (\nabla \mathbf{v} + \mathbf{F}) \right\}$$

# Closed-form solutions: laminates

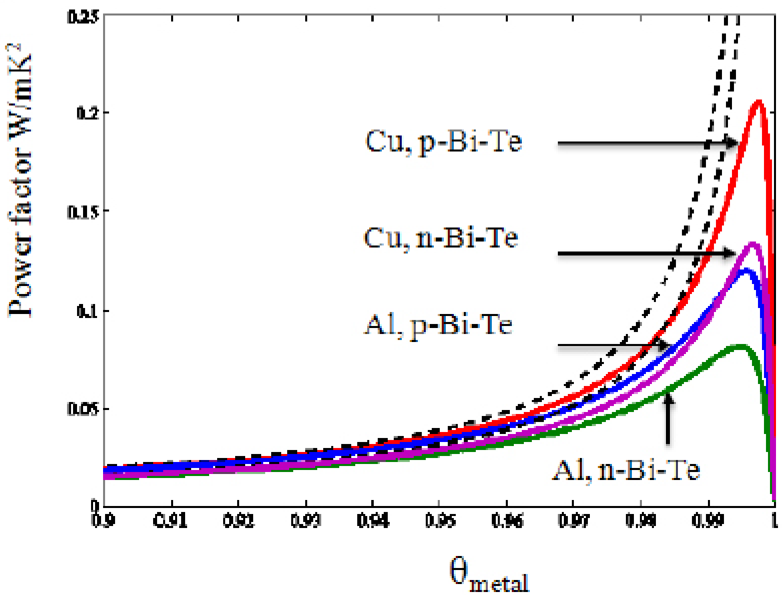
(a)




$$\mathbf{A}^e := \begin{bmatrix} T_0\sigma_z & T_0^2\alpha_z \\ T_0^2\alpha_z & T_0^2\kappa_z' \end{bmatrix}$$

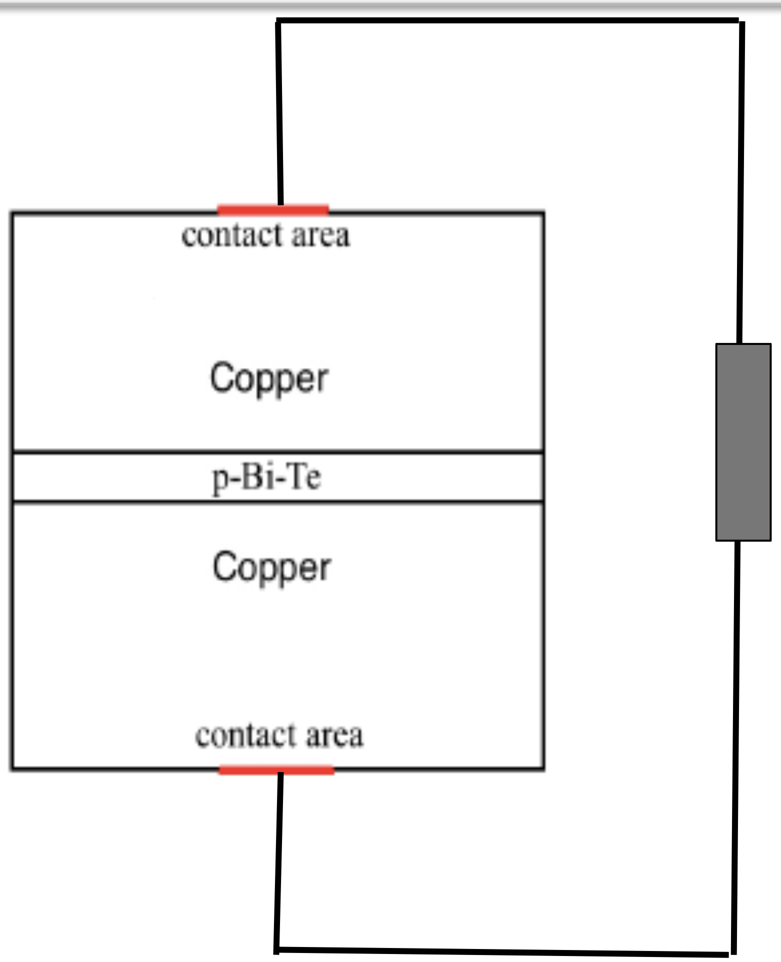
$$= (\theta_1 \mathbf{A}_1^{-1} + \theta_2 \mathbf{A}_2^{-1})^{-1}.$$

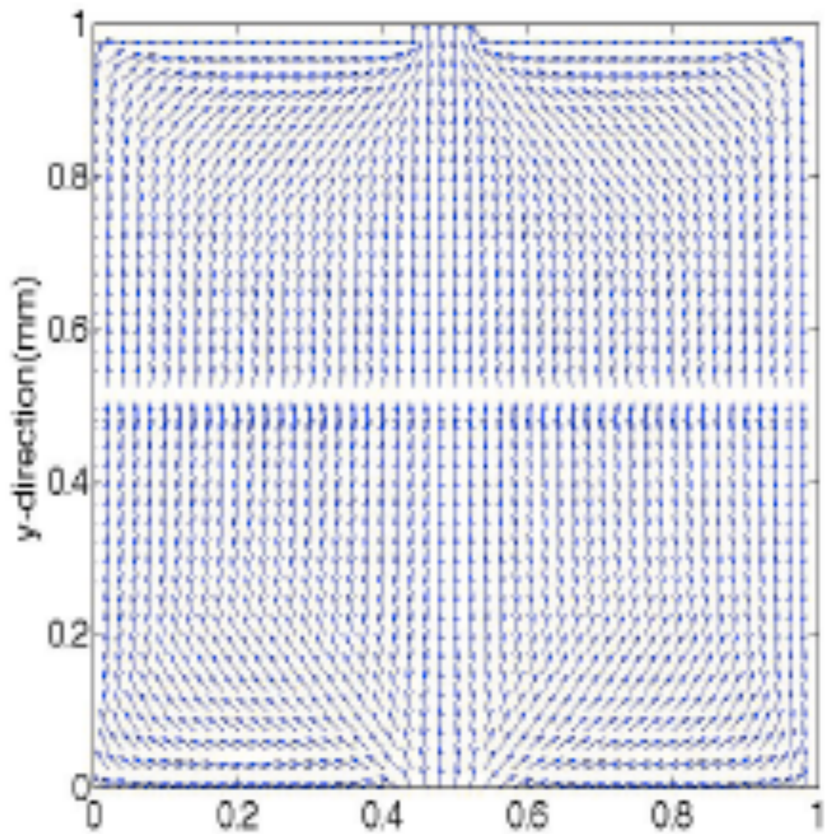
(b)



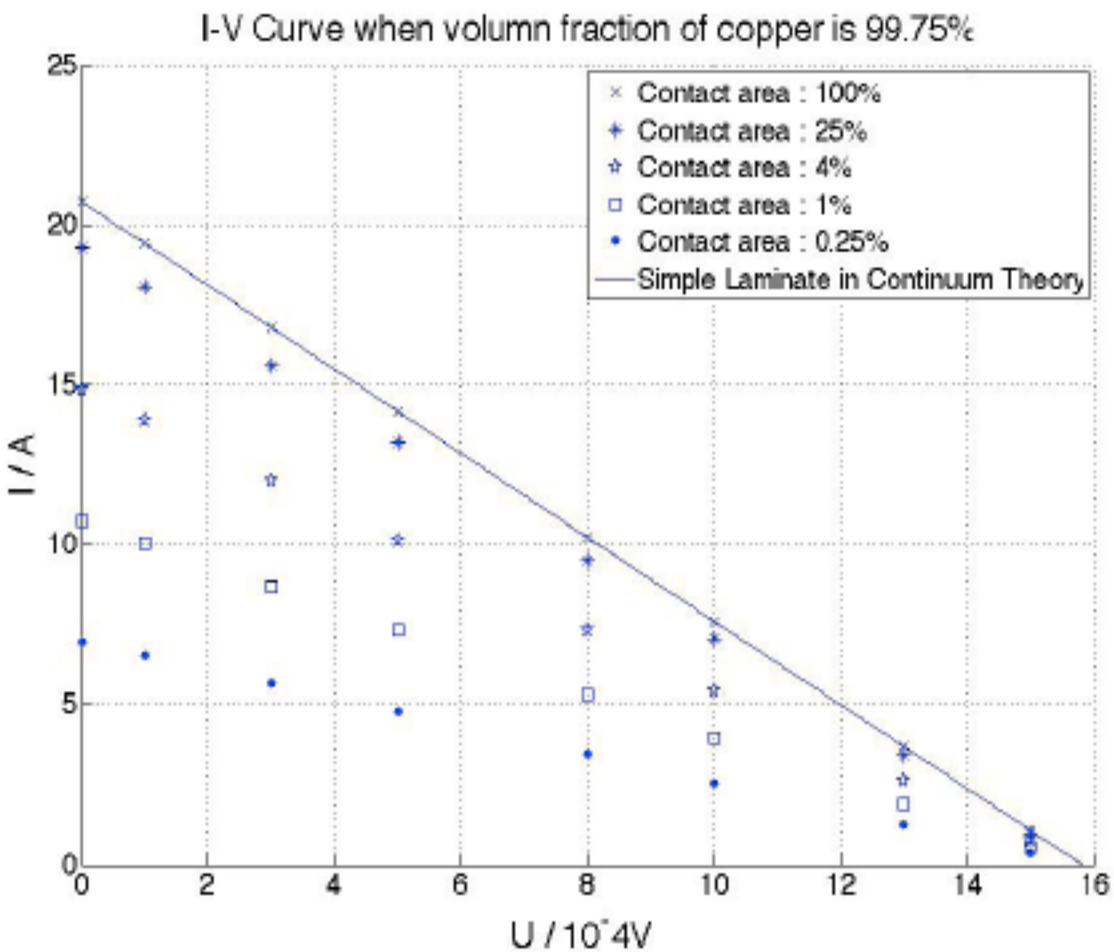

❖ Power factors can be improved by orders of magnitudes by simply laminating a good conductors, e.g., Copper, and a moderate good TE semiconductors, e.g., Bi-Te !

# Effect of electric contact area (1)

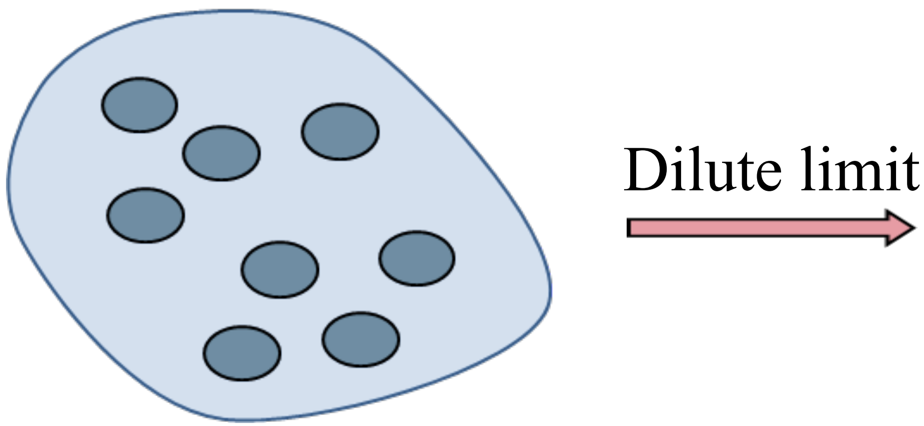


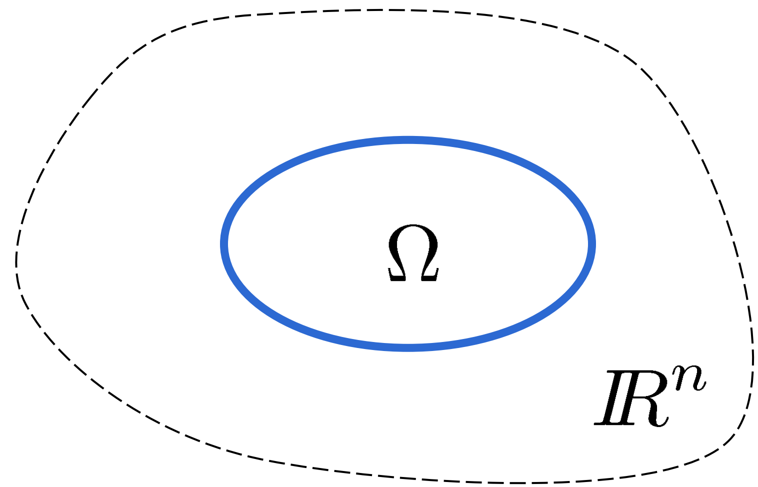



# Effect of electric contact area (2)



# Modeling of particulate composites




- Dilute limit: Eshelby's solutions

$$\begin{cases} \Delta u = \chi_\Omega & \text{on} \quad I\!R^n \\ \text{boundary conditions} & \text{at} \quad \infty \end{cases}$$

  - Maxwell-Eshelby's solution

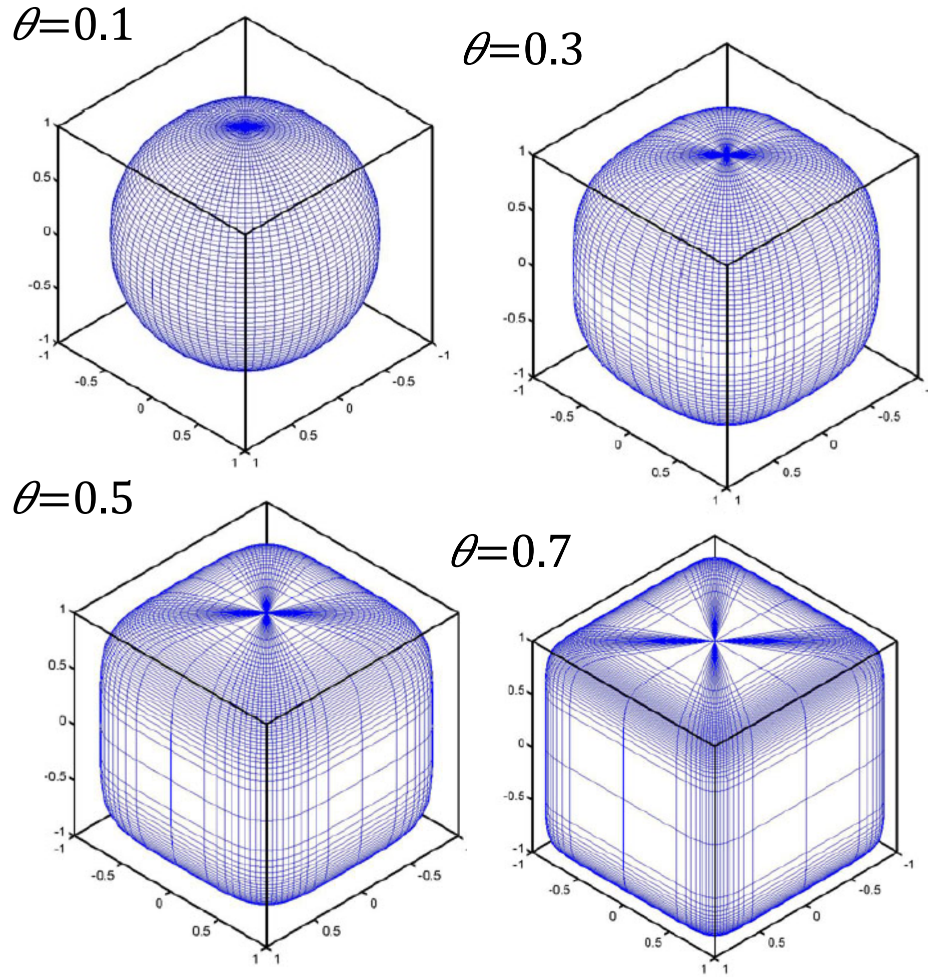
$$\boxed{\nabla\nabla u = \mathbf{Q} \qquad \text{on} \quad \Omega}$$

# Closed-form solutions: E-inclusions

❖ Definition:

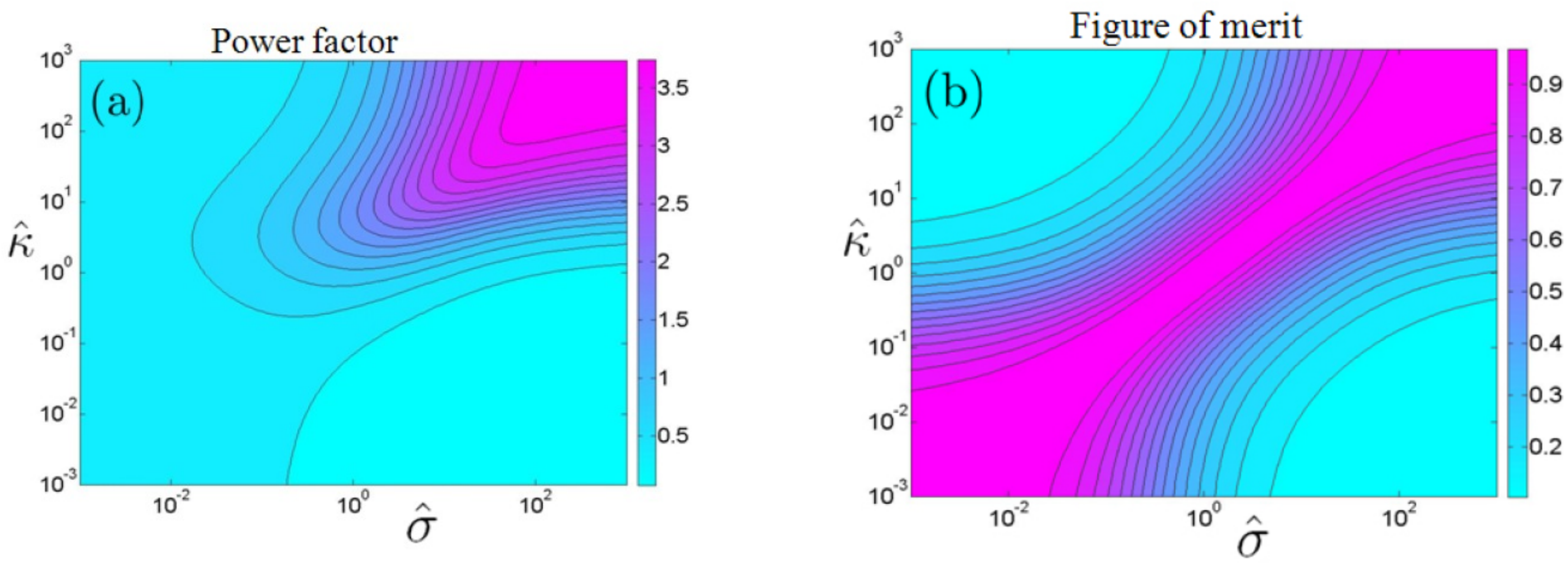
$$\begin{cases} \nabla^2 \phi = \theta - \chi \Omega_2 & \text{on } Y, \\ \nabla\nabla\phi = -(1-\theta)\mathbf{Q} & \text{on } \Omega_2, \\ \text{periodic boundary conditions} & \text{on } \partial Y, \end{cases}$$

❖ Closed-form solution can be obtained for TE composites with microstructures of periodic E-inclusions.



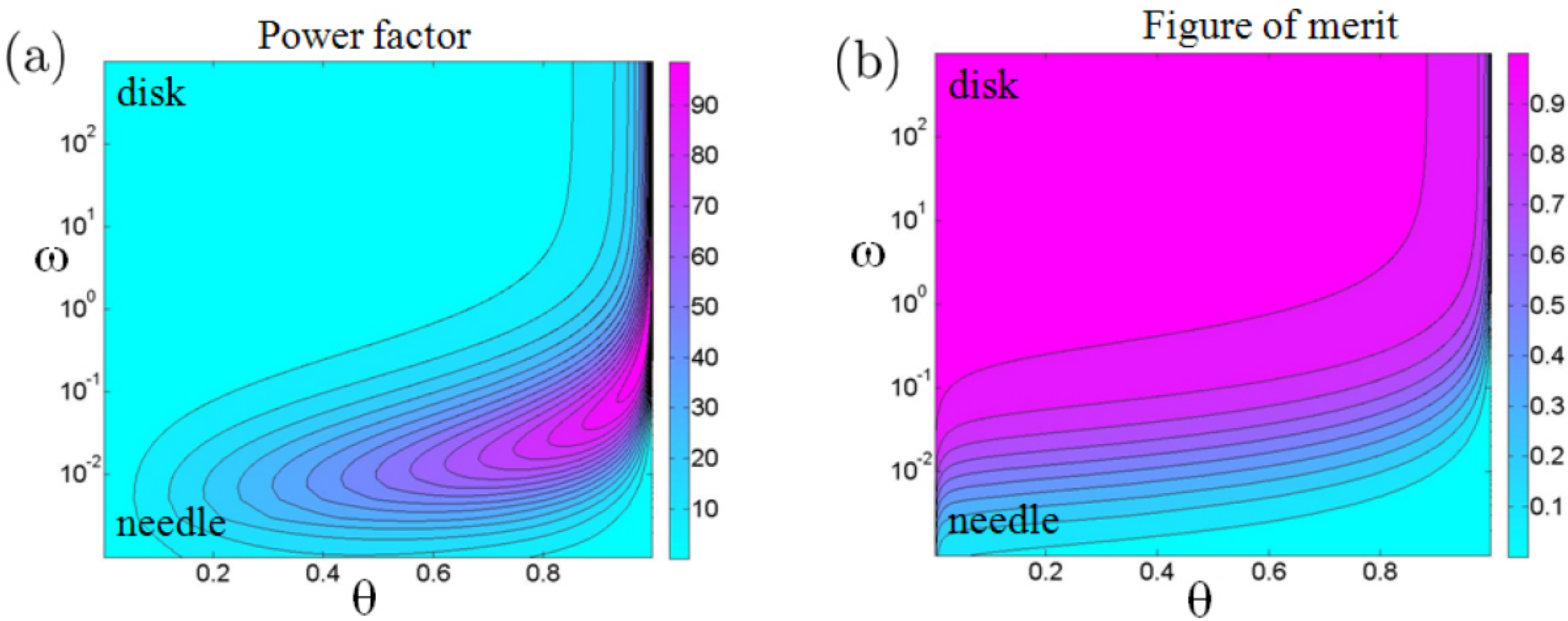
# Designing TE composites (1)

$$\mathbf{C}^e = \mathbf{C}_1 + \theta[(1-\theta)\triangle\mathbf{C}\mathbf{R} - \mathbb{I}]^{-1}\triangle\mathbf{C}$$



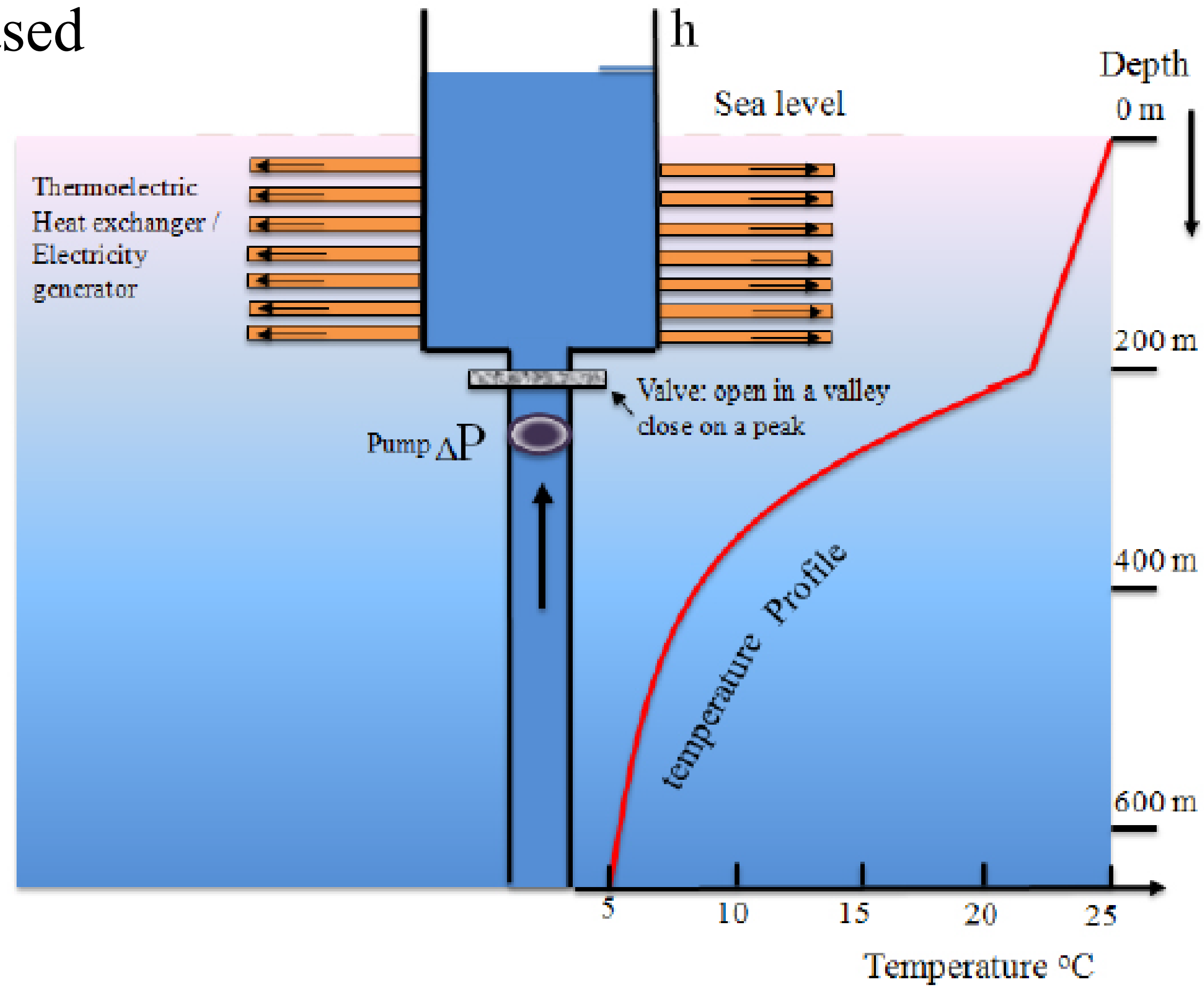
# Designing TE composites (2)

$$\mathbf{C}^e = \mathbf{C}_1 + \theta[(1-\theta)\triangle\mathbf{C}\mathbf{R} - \mathbb{I}]^{-1}\triangle\mathbf{C}$$



# Large-scale power plants by TE effects

❖ Ocean-based



# Advantage of TE power plant

- Advantage:
  - Renewability
  - Green
  - Scalability
  - Reliability
  - Unlimited
- Ocean naturally absorb, store and concentrate solar energy

Economic?

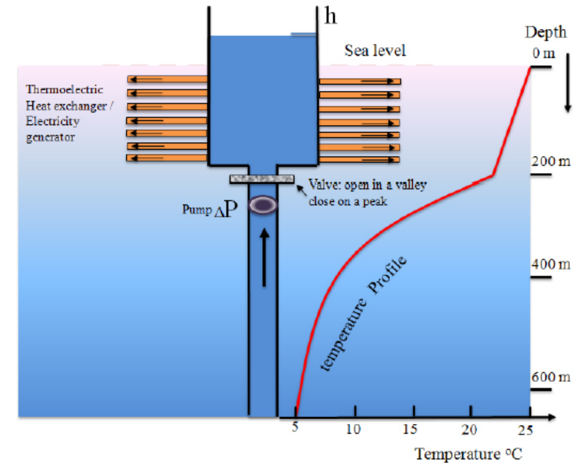
- Critical material property to improve for large-scale applications:

Power factor!

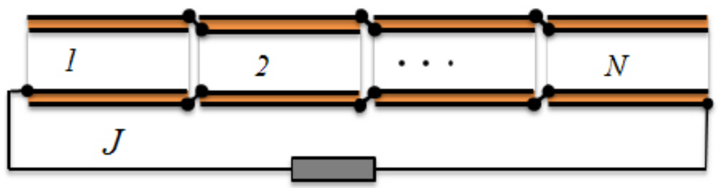
# Design of large-scale ocean-based power plants

❖ Designs for 1Megawatt power gain (10K-difference)

| $t_{tb}$ | $R_{tb}$ | $L_{tb}$ | $f_{max}$ | h | $P_{gain}$ | $N_{tb}$ |
|---|---|---|---|---|---|---|
| mm | cm | m | | m | kW | |
| 0.1 | 1 | 1 | 0.43 | 1.11 | 1.39 | 719 |
| 0.2 | 1 | 1 | 0.52 | 0.75 | 0.841 | 1189 |
| 0.5 | 1 | 1 | 0.63 | 0.43 | 0.408 | 2453 |
| 1 | 1 | 1 | 0.70 | 0.28 | 0.227 | 4415 |




(a) Electric connection of the TE tube of the same type



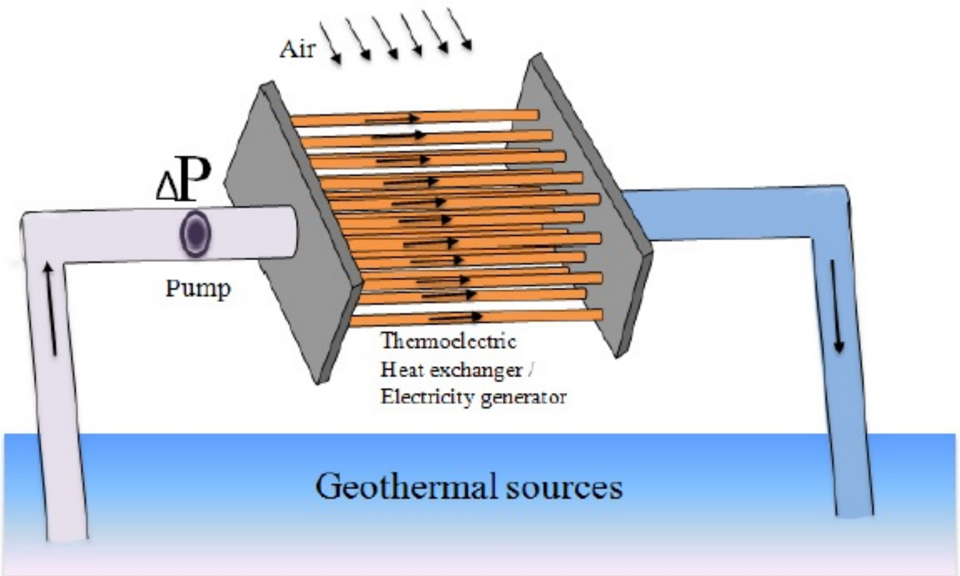

❖ Power factor: $\dot{W}_{max} = \frac{\alpha_z^2 \delta T^2}{4\sigma_z L^2} = \frac{P_f}{4}(\frac{\delta T}{L})^2$

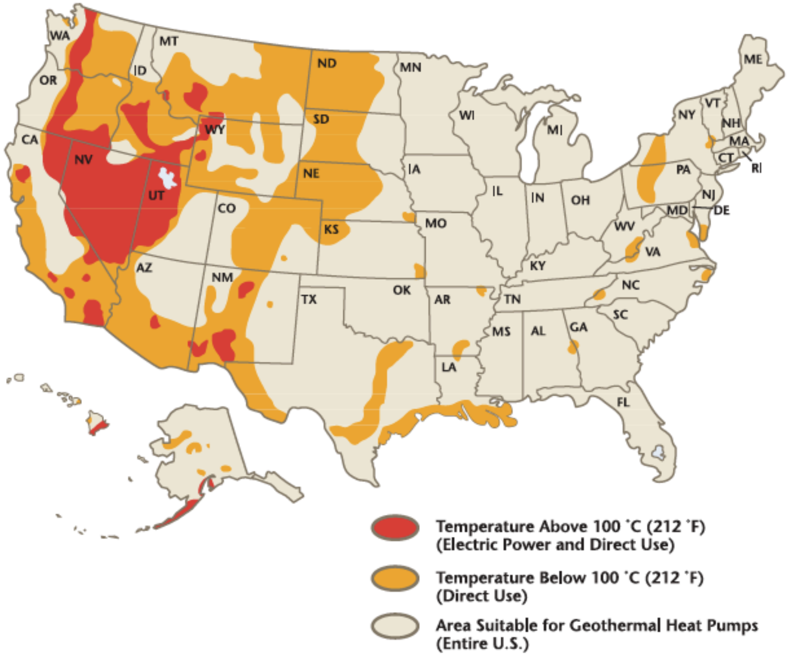
$$P_f = s^2\sigma$$

Annual cost: 2 Million $

# Large-scale power plants by TE effects

❖ Geothermal sources




❖ Number of TE tubes:

$$\sim 1/\delta T^2$$