The Effective Thermoelectric Properties of Composite Materials

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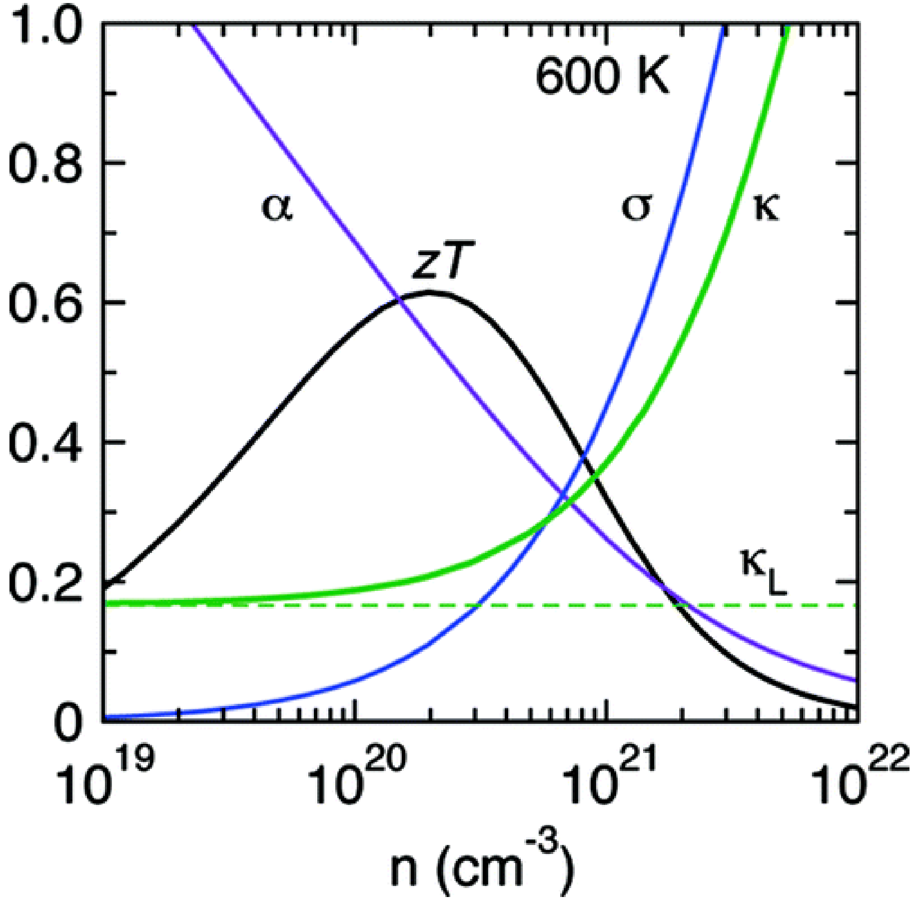
Thermoelectric Figure of Merit

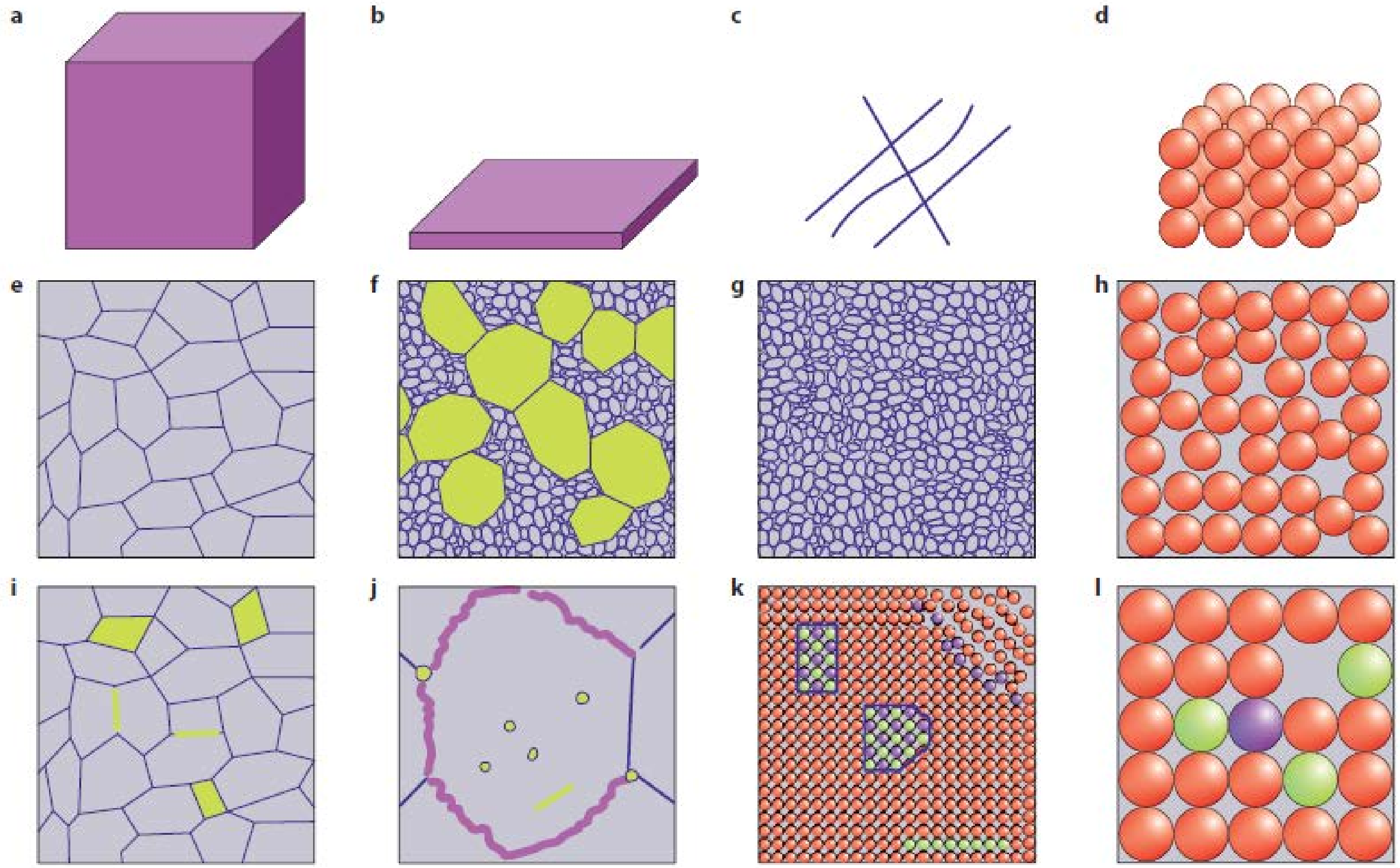


Snyder and Toberer (2008)

$$Z = \frac{\alpha^2 \sigma T}{\kappa_e + \kappa_{ph}}$$

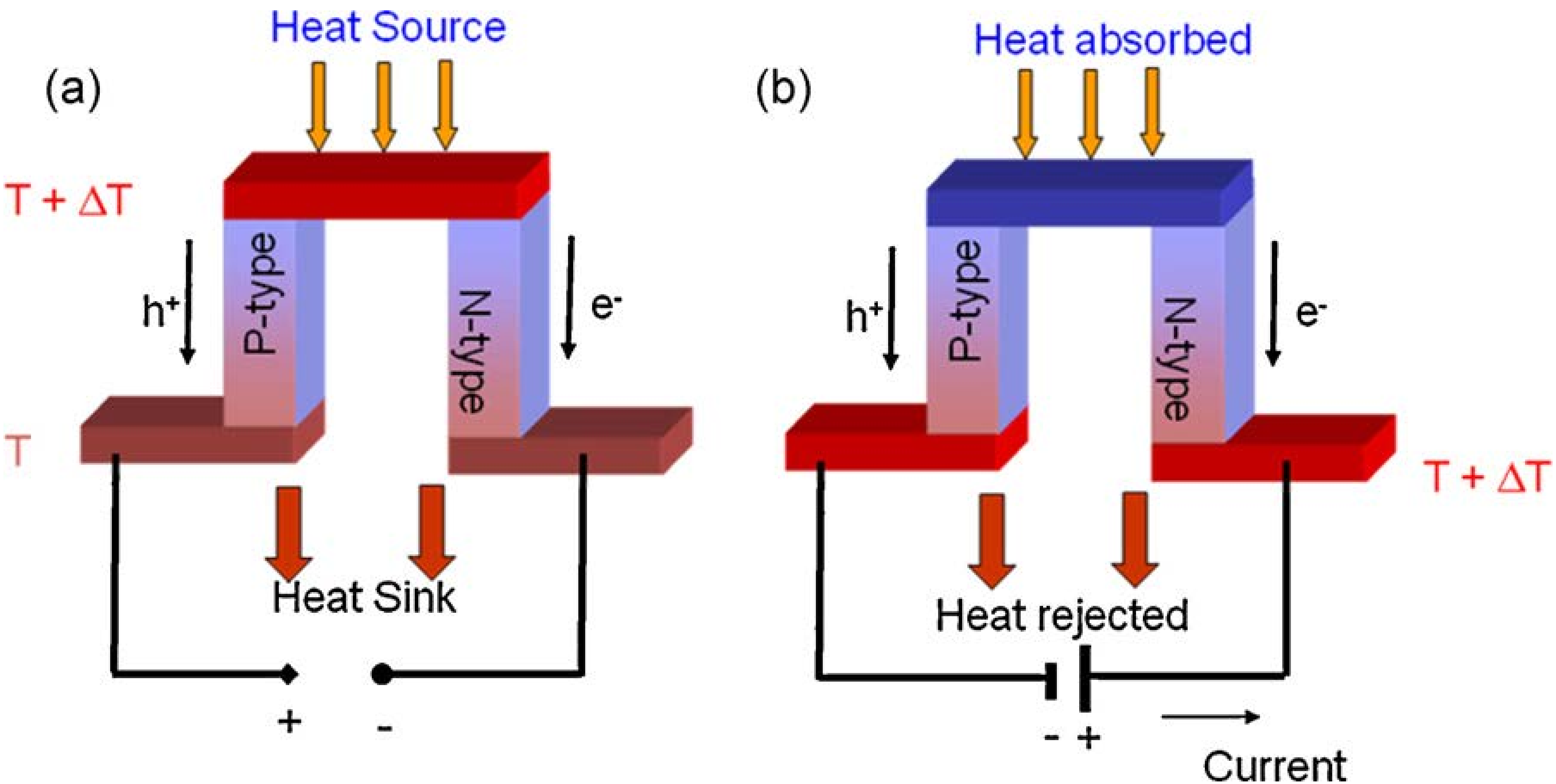
$$\eta_{TE} = \eta_C \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + T_C / T_H}$$

Nanostructured Thermoelectrics



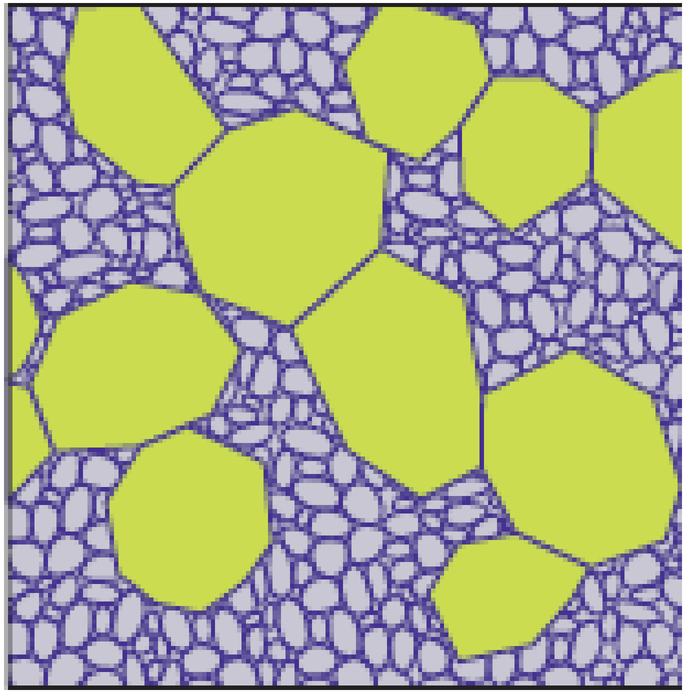
Li et al (2010)

Intrisic Heterogeneity



Pichanusakorn and Prabhakar Bandaru (2010)

Thermoelectric Composites



Can the effective thermoelectric figure of merit of a composite material be higher than all its constituents, excluding the effects of size and interface? and how can we take advantages of the size and interfacial effects of composite materials to further enhance their thermoelectric figure of merit?

Effective Figure of Merit

Bergman et al (1991, 1999): The effective figure of merit of a composite can never exceed the largest value of figure of merit in any of its component, in the absence of size and interface effects.

$$J = \hat{Q} \nabla \psi,$$

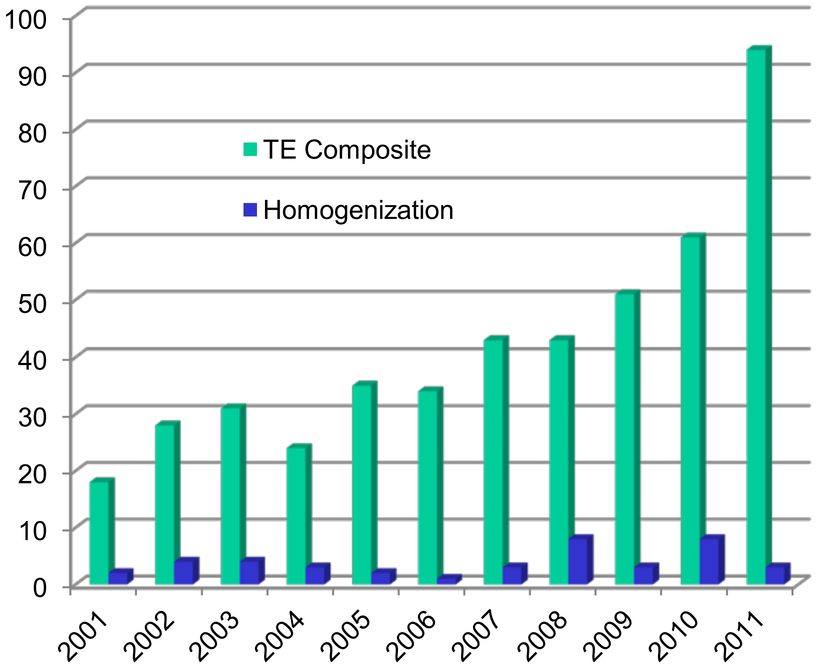
where

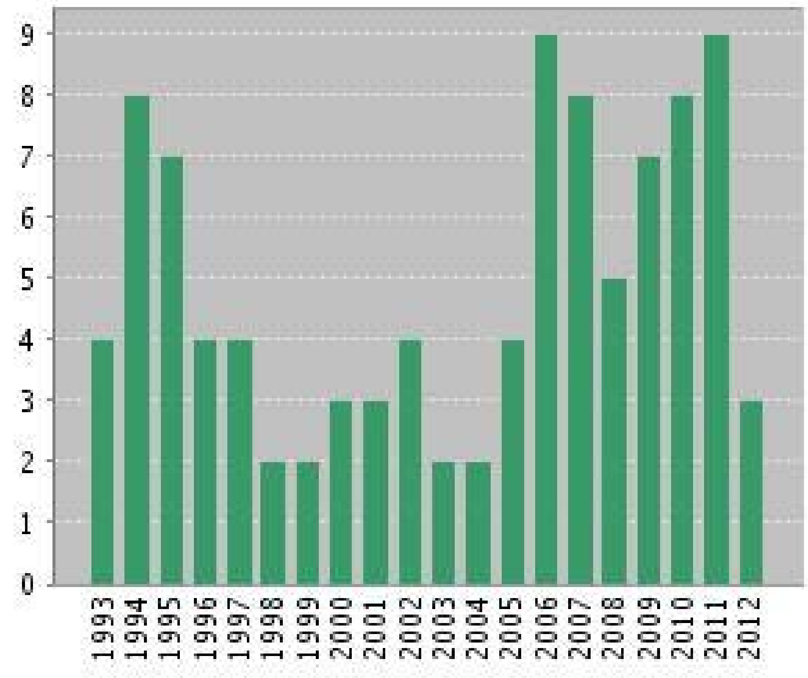
$$J \equiv \begin{pmatrix} \mathbf{J}_1 \\ \mathbf{J}_2 \end{pmatrix} \equiv \begin{pmatrix} -\mathbf{J}_E/e \\ -\mathbf{J}_S/k \end{pmatrix},$$

$$\nabla \psi \equiv \begin{pmatrix} \nabla \psi_1 \\ \nabla \psi_2 \end{pmatrix} \equiv \begin{pmatrix} \nabla (e\phi) \\ \boxed{\nabla (kT)} \end{pmatrix},$$

$$\hat{Q} \equiv \begin{pmatrix} Q_{11} & Q_{12} \\ Q_{12} & Q_{22} \end{pmatrix} \equiv \begin{pmatrix} \sigma/e^2 & \sigma\alpha/ek \\ \sigma\alpha/ek & \boxed{\gamma/k^2 T} \end{pmatrix}$$

Current State of Art





Graeme Milton (2002): There is a lot of confusion, particularly in the composite materials community, as to appropriate form of the thermoelectric equations.

Governing Equations

Transport Equations

$$-\mathbf{J} = \sigma \nabla \phi + \sigma \alpha \nabla T$$

$$\mathbf{J}_Q = \boxed{-T\sigma\alpha} \nabla \phi - (\boxed{T\sigma\alpha^2} + \kappa) \nabla T = T\alpha \mathbf{J} - \kappa \nabla T$$

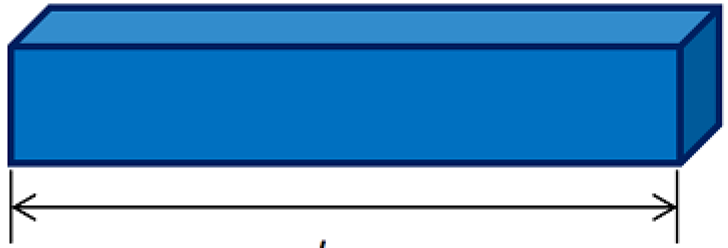
$$\mathbf{J}_U = \mathbf{J}_Q + \phi \mathbf{J}$$

Field Equations

$$\nabla \cdot \mathbf{J} = 0 \qquad \nabla \cdot \mathbf{J}_U = 0$$

$$\nabla \cdot \mathbf{J}_Q = \boxed{-\nabla \phi \cdot \mathbf{J}}$$

Homogeneous Thermoelectric



$$\frac{d^2T}{dx^2}=-\frac{J^2}{\sigma\kappa}$$

$$\frac{d^2\phi}{dx^2}=\alpha\frac{J^2}{\sigma\kappa}$$

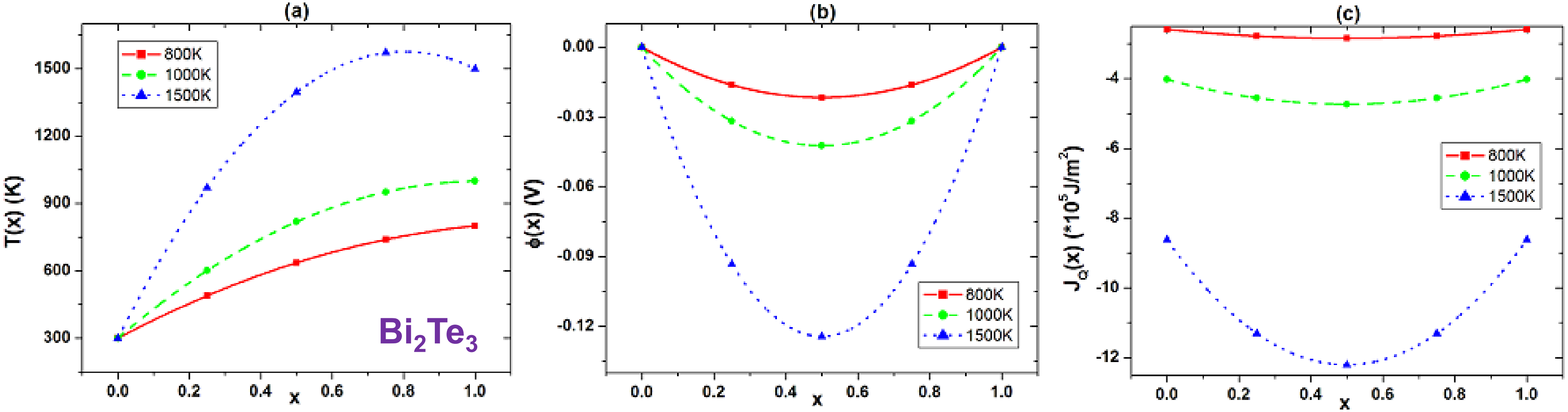
$$T=-\frac{J^2}{2\sigma\kappa}x^2+c_1x+c_2$$

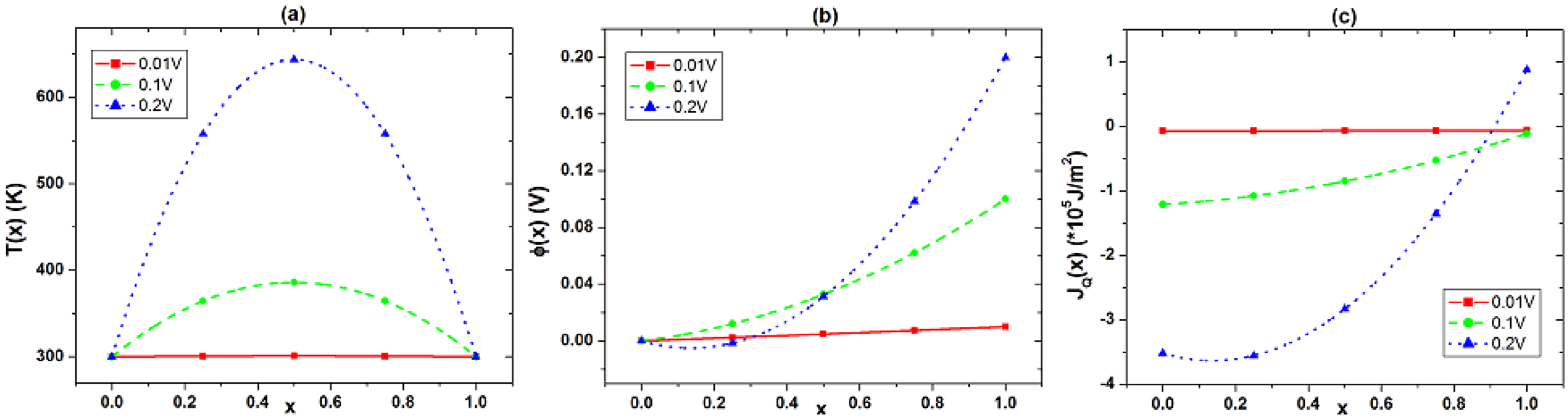
$$\phi=\frac{\alpha J^2}{2\sigma\kappa}x^2-[\frac{\alpha J^2}{2\sigma\kappa}+\frac{J}{\sigma}+(T_1-T_0)\alpha]x+c_3$$

$$J=\alpha\sigma(T_0-T_1)+\sigma(\phi_0-\phi_1)$$

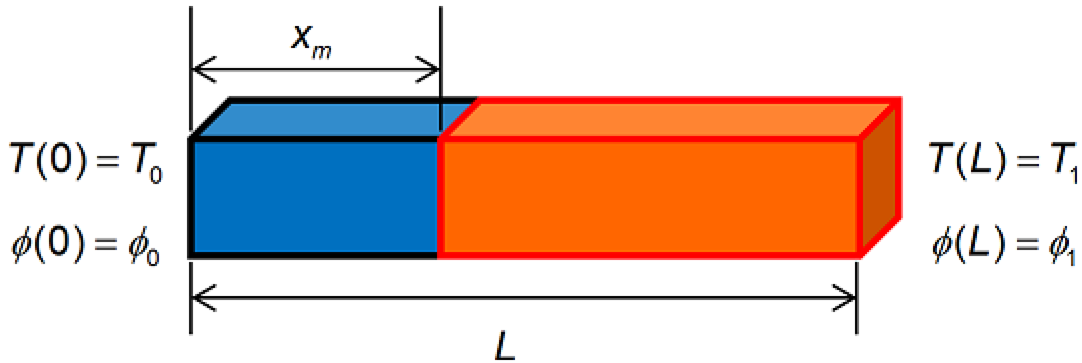
All the coefficients are assumed to be temperature independent

One-dimensional Analysis





Heterogeneous Thermoelectric

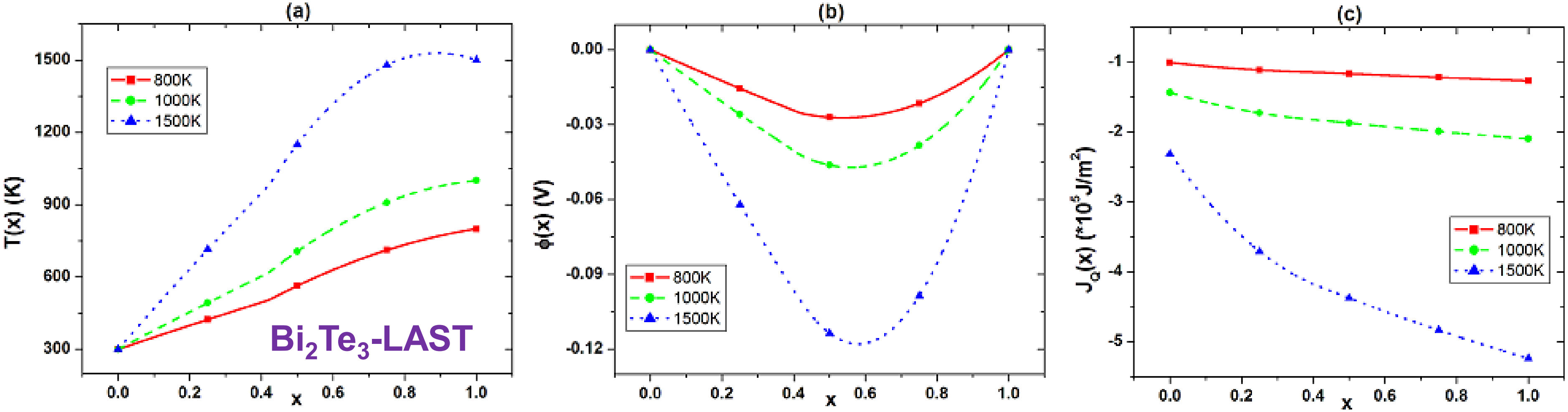


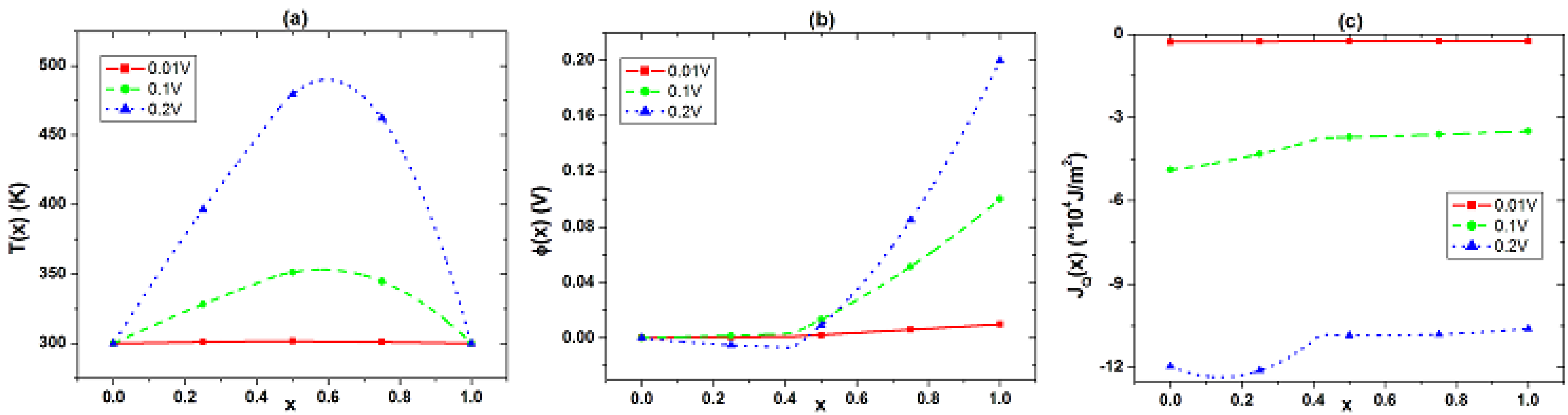
$$T = \begin{cases} -\dfrac{J^2}{2\sigma_A \kappa_A} x^2 + a_A x + b_A, 0 \le x < f \\ -\dfrac{J^2}{2\sigma_B \kappa_B} x^2 + a_B x + b_B, f < x \le 1 \end{cases}$$

$$\phi = \begin{cases} \dfrac{\alpha_A J^2}{2\sigma_A \kappa_A} x^2 - (\dfrac{J}{\sigma_A} + \alpha_A a_A) x + c_A, 0 \le x < f \\ \dfrac{\alpha_B J^2}{2\sigma_B \kappa_B} x^2 - (\dfrac{J}{\sigma_B} + \alpha_B a_B) x + c_B, f < x \le 1 \end{cases}$$

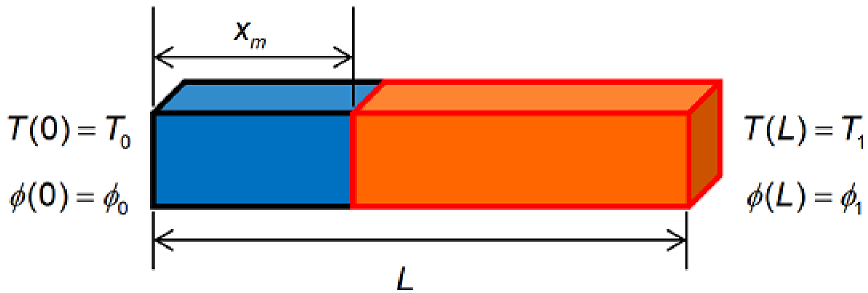
All the coefficients are assumed to be temperature independent

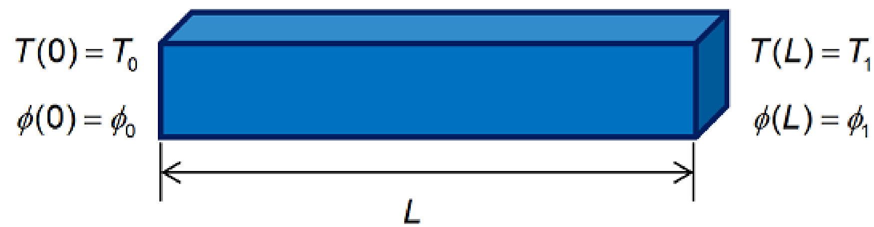
One-dimensional Analysis





Equivalency Principle

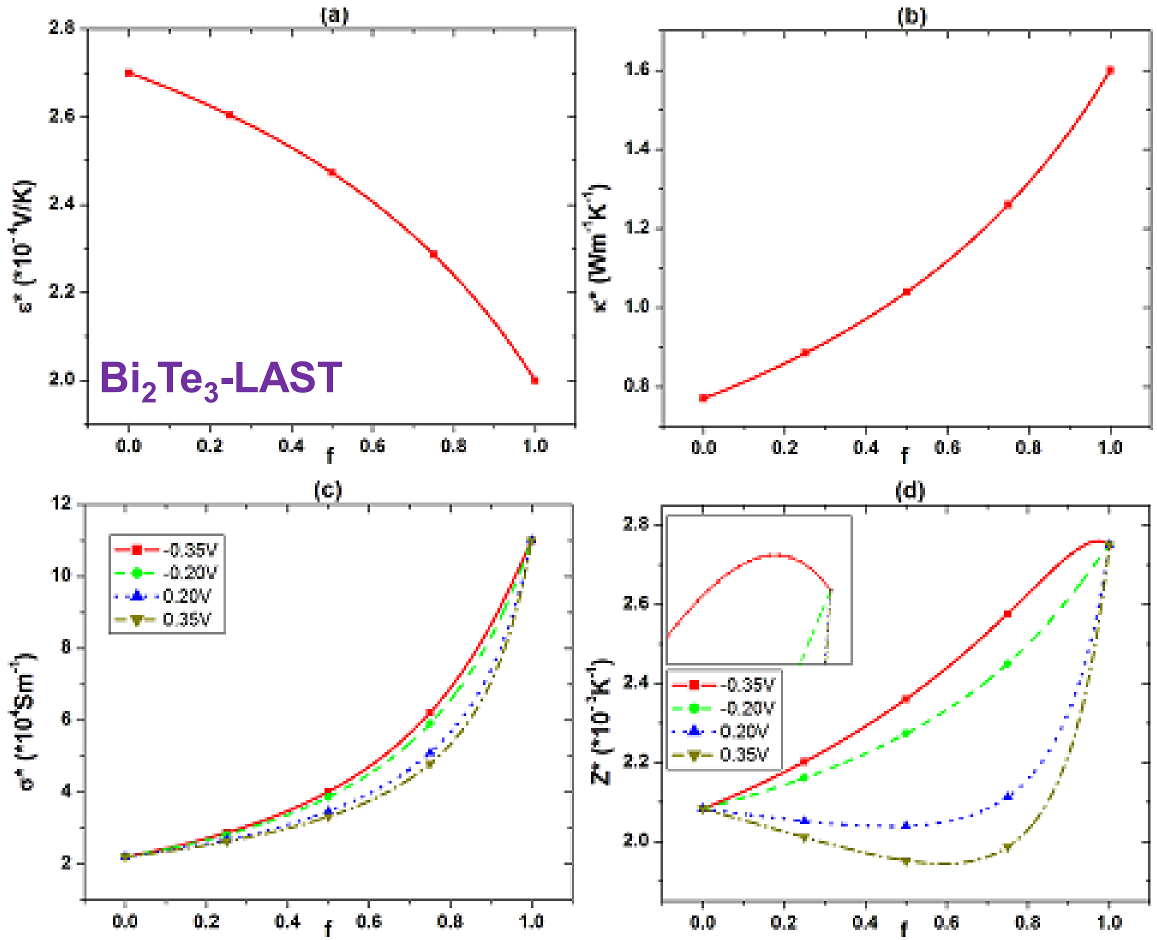




Under identical boundary conditions of temperature and electric potential, the composite and homogenized medium would have: (1) identical current density and (2) identical energy flux.

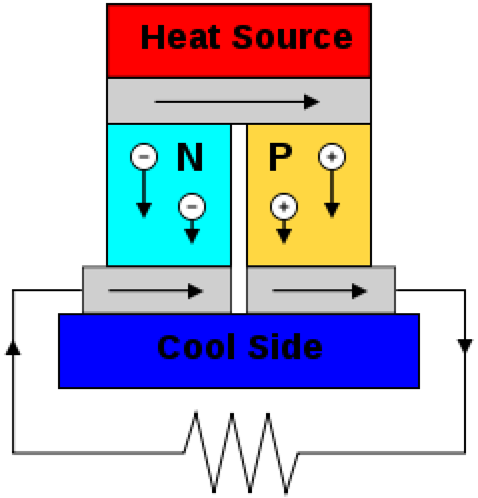
Yang et al (2012)

Enhanced Effective Figure of Merit



Due to nonlinearity, the effective properties depend on boundary conditions

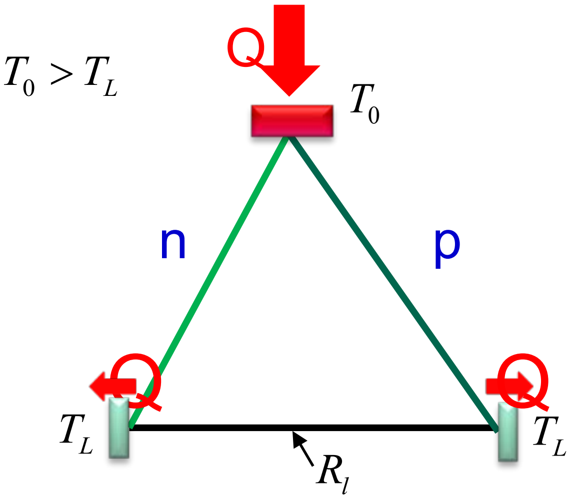
Conversion Efficiency Analysis

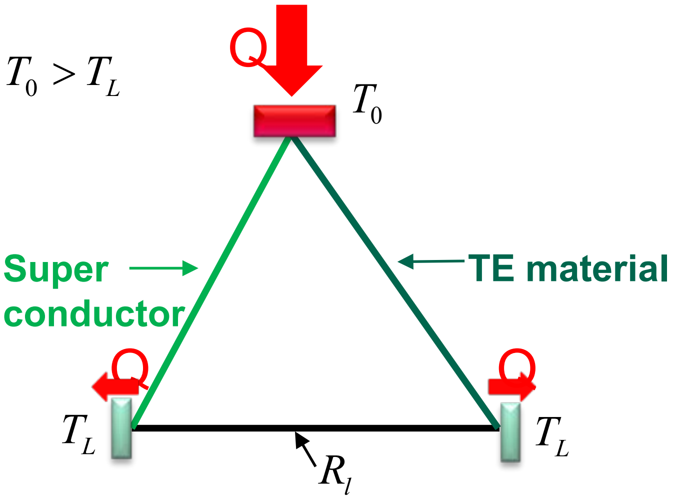


$$H_L = \frac{I^2 R_l}{\dot{E}_0}$$

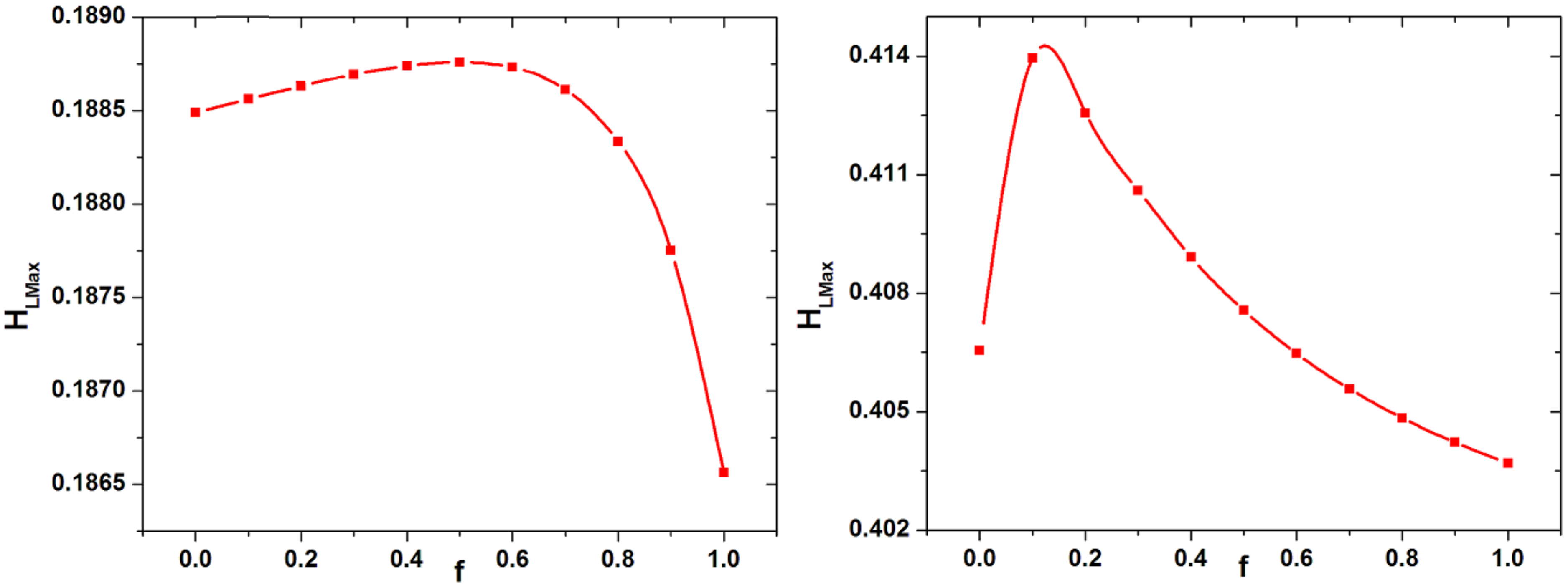
$$\dot{E}_0 = \sum S J_U \Big|_{x=0}$$

$$J_U = -\kappa \nabla T + \alpha T J + \phi J$$





Enhanced Conversion Efficiency



Z of constituent phases is fixed, but individual coefficients are allowed to vary

Enhanced Conversion Efficiency

TABLE I. Maximum single element efficiencies for thermoelectric generators. $u(T_c)$ is the relative current density that gives the maximum efficiency.

Material	Efficiency (%)	T_c (°C)	$T_{interface}$ (°C)	T_h (°C)	$u(T_c)$ (V^{-1})
p-TAGS	10.45	100		525	2.97
p-TAGS/PbTe	10.33	100	525	600	2.33
p-TAGS/SnTe	11.09	100	525	600	2.84
p-TAGS/$CeFe_4Sb_{12}$	11.87	100	525	600	2.94
p-TAGS/$CeFe_4Sb_{12}$	13.56	100	525	700	2.88
p-SiGe	4.23	525		1000	0.85
p-TAGS/SiGe	9.89	100	525	1000	1.12
n-PbTe	9.87	100		600	−2.00
n-pbTe/$CoSb_3$	11.30	100	600	700	−1.97
n-PbTe/SiGe	13.76	100	600	1000	−1.46
n-PbTe/La_2Te_3	15.56	100	600	1000	−1.80
n-SiGe	5.44	600		1000	−1.29

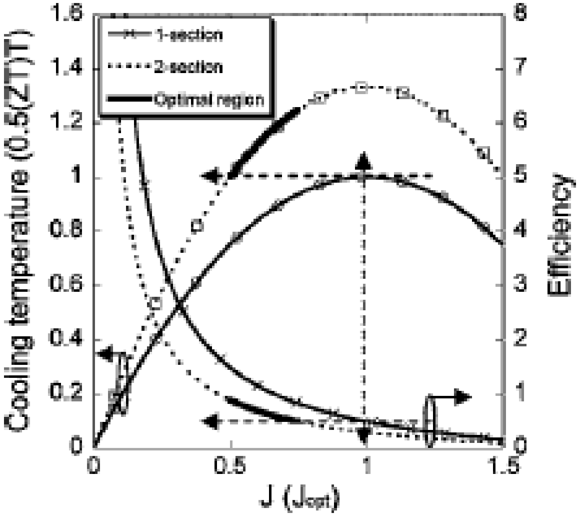
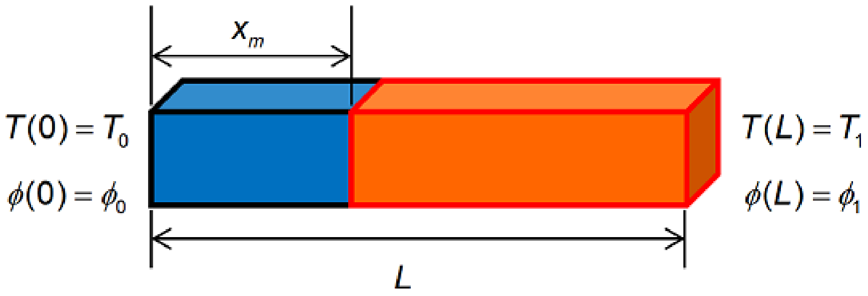


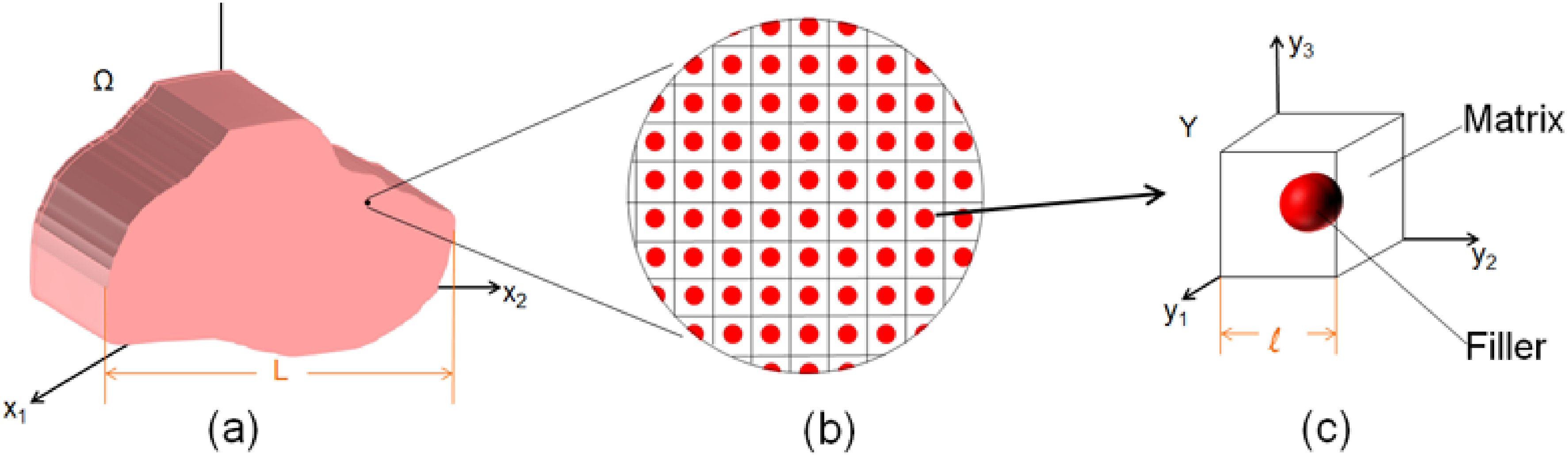
FIG. 2. Cooling temperature and the efficiency for the staircase material in case 2 with one or two sections, respectively.

Snyder (2004)

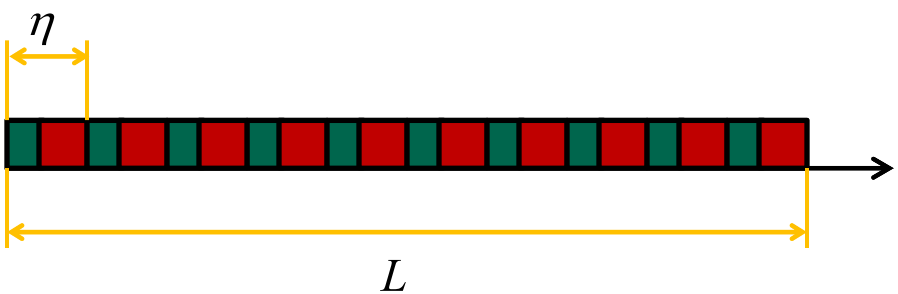
Bian and Shakouri (2006)

Thermoelectric Composite

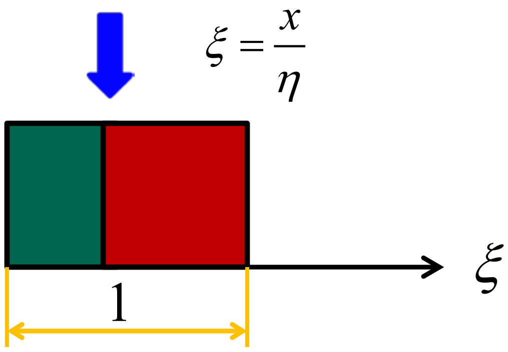




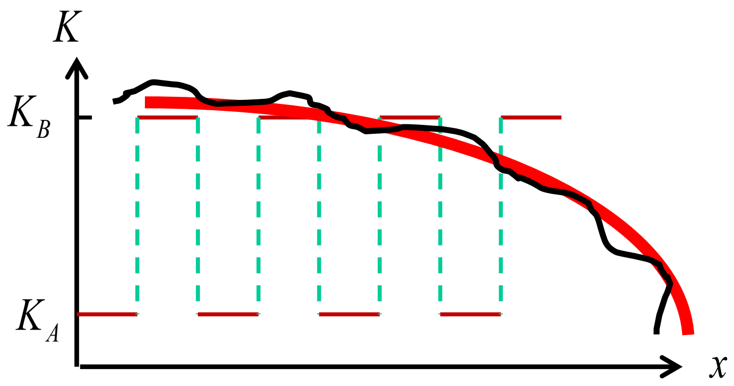
One-dimensional Asymptotic Analysis



***x*: slow or macroscopic variable**



ξ: fast or microscopic variable



$$T(x,\xi) = T_0(x,\xi) + \eta T_1(x,\xi) + \eta^2 T_2(x,\xi) + \ldots$$

$$\phi(x,\xi) = \phi_0(x,\xi) + \eta \phi_1(x,\xi) + \eta^2 \phi_2(x,\xi) + \ldots$$

Asymptotic Analysis

η^{-2}

$$\boxed{\frac{\partial}{\partial \xi}(\kappa \frac{\partial T_0}{\partial \xi}) = 0}$$

η^{-1}

$$\sigma \frac{\partial \phi_0}{\partial \xi} + \sigma\alpha \frac{\partial T_0}{\partial \xi} = 0$$

$$\frac{\partial}{\partial x}(\kappa \frac{\partial T_0}{\partial \xi}) + \frac{\partial}{\partial \xi}(-\alpha J T_0 + \kappa \frac{\partial T_0}{\partial x} + \kappa \frac{\partial T_1}{\partial \xi}) = \frac{\partial \phi_0}{\partial \xi} J$$

η^{0}

$$-J = \sigma \frac{\partial \phi_0}{\partial x} + \sigma \frac{\partial \phi_1}{\partial \xi} + \sigma\alpha \frac{\partial T_0}{\partial x} + \sigma\alpha \frac{\partial T_1}{\partial \xi}$$

$$\frac{\partial}{\partial x}(-\alpha J T_0 + \kappa \frac{\partial T_0}{\partial x} + \kappa \frac{\partial T_1}{\partial \xi}) + \frac{\partial}{\partial \xi}(-\alpha J T_1 + \kappa \frac{\partial T_1}{\partial x} + \kappa \frac{\partial T_2}{\partial \xi})$$

$$= (\frac{\partial \phi_0}{\partial x} + \frac{\partial \phi_1}{\partial \xi}) J$$

Homogenized Equations

$$T(x,\xi) = T_0(x,\xi) + \eta T_1(x,\xi) + \eta^2 T_2(x,\xi) + \ldots \qquad \phi(x,\xi) = \phi_0(x,\xi) + \eta\phi_1(x,\xi) + \eta^2\phi_2(x,\xi) + \ldots$$

Homogenized

$$\boxed{\frac{d^2T_0}{dx^2} - \left(<\frac{\alpha}{\kappa}>^2 - <\frac{\alpha^2}{\kappa}><\frac{1}{\kappa}>\right)J^2T_0 + <\frac{1}{\sigma}><\frac{1}{\kappa}>J^2 = 0}$$

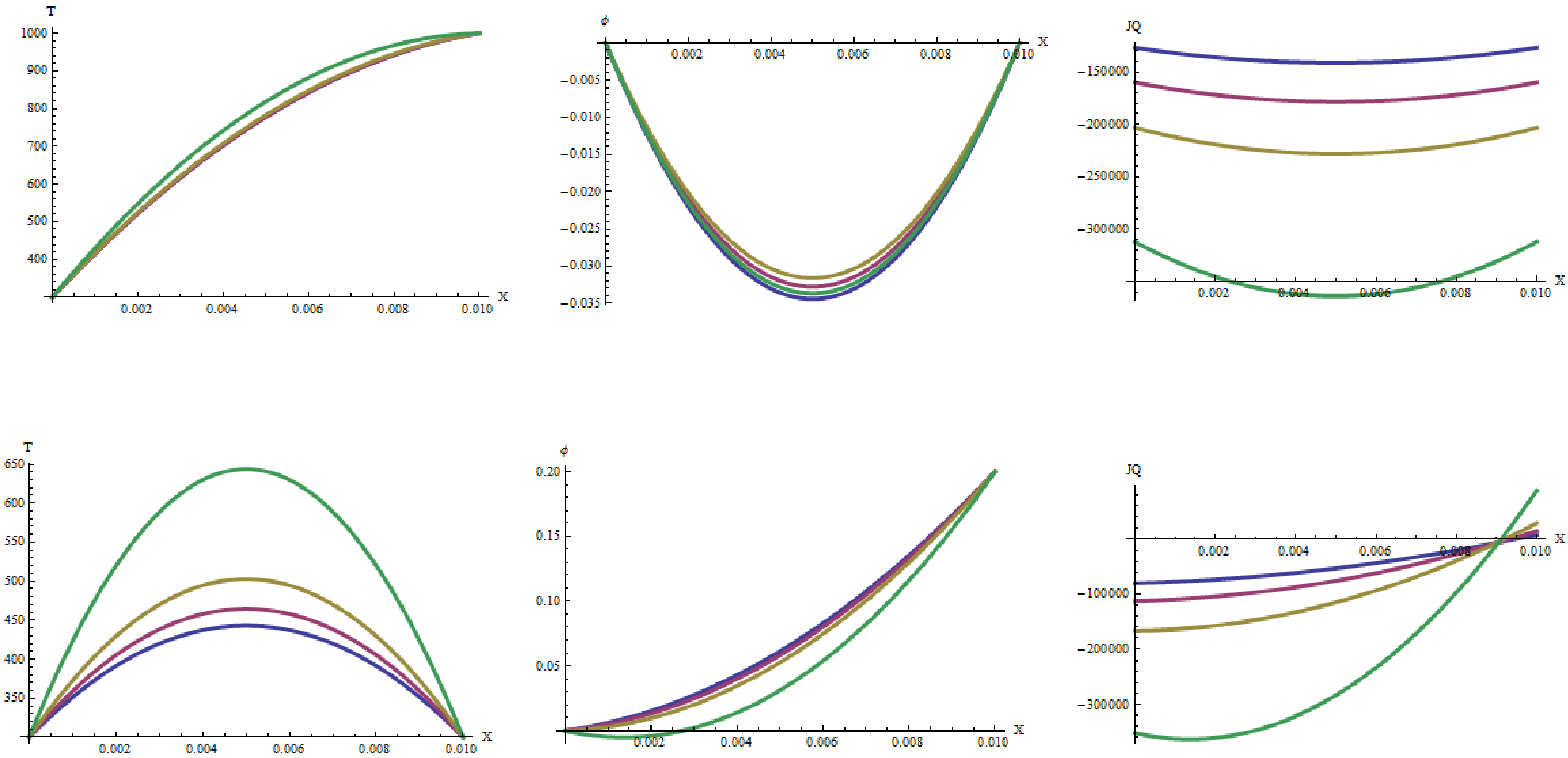
$$\boxed{\begin{aligned}&\frac{d^2\phi_0}{dx^2} + \left(<\frac{\alpha^2}{\kappa}> - <\frac{\alpha}{\kappa}>^2<\frac{1}{\kappa}>^{-1}\right)J\frac{dT_0}{dx}\\ &-\left(<\frac{\alpha^2}{\kappa}><\frac{\alpha}{\kappa}> - <\frac{\alpha}{\kappa}>^3<\frac{1}{\kappa}>^{-1}\right)J^2T_0 - <\frac{1}{\sigma}><\frac{\alpha}{\kappa}>J^2 = 0\end{aligned}}$$

Homogeneous

$$\boxed{\frac{d^2T}{dx^2} + \frac{1}{\sigma\kappa}J^2 = 0} \qquad \boxed{\frac{d^2\phi}{dx^2} - \frac{\alpha}{\sigma\kappa}J^2 = 0}$$

Homogenized and homogeneous materials satisfy different type of governing equations!

Homogenized Solution



Concluding Remarks

Rigorous asymptotic analysis has been developed to predict the effective thermoelectric behaviors of composite materials, and preliminary results suggest that conversion efficiency higher than that of constituents is possible in composites