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

Liping Liu
Department of Mechanical & Aerospace Engineering
Department of Mathematics
Rutgers University

Coworker: Hanxiong Wang

Seminar at IPAM, UCLA, November 21, 2013
Bottom-up vs. Top-down

Figure from http://eng.jhu.edu/wse/civil/page/mechanics-of-materials
Main problem

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

- Kinematics: thermodynamic variables to describe the system \((\mu, T)\)
- Balance / conservation Laws: \(\text{Div}(\mathbf{\Sigma} + \mathbf{\Sigma}_M) = 0, \quad \text{Div}\mathbf{D} = 0, \quad \text{etc}\)
- Constitutive Relations:
  - Frame indifference
  - Material symmetries
  - Laws of thermodynamics
Why multiscale modeling?

- Constitutive laws: \( \sigma = CE \quad D = \varepsilon E \quad B = \frac{1}{\mu} \)

  ➢ Multifunctional: \( c(\Sigma, F, \tilde{D}, \tilde{E}, \tilde{P}) = 0 \)

- 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

Figure from http://www.icams.de/content/research-at-icams/research-index.html
Bridging scales and disciplines: materials genome initiative

Materials Genome Initiative: A Renaissance of American Manufacturing

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

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...
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):
  \[ s = -\frac{k_b}{2e} = -0.43e - 4 \text{V/K} \]

• Free electron gas (FD statistics):
  \[ s = -\frac{k_b \pi^2 k_b T}{2e \cdot 3\varepsilon_F} = -0.43e - 6 \text{V/K} \]

• Band theory for semi-conductor (MB statistics):
  \[ s = \frac{k_b}{q^*} \left( \frac{E_c - \varepsilon_F}{k_b T} + \delta_n \right) \sim -0.43e - 4 \text{V/K} \]
Figure of merits and power factor

- Power factor:
  \[ W_{\text{max}} = \frac{\alpha_z^2 \delta T^2}{4 \sigma_z L^2} = \frac{P_f}{4} \left(\frac{\delta T}{L}\right)^2 \]
  \[ P_f = s^2 \sigma \]

- 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:
  \[ \dot{W}_{\text{max}} = \frac{\alpha_z^2 \delta T^2}{4\sigma_z L^2} = \frac{P_f}{4} \left( \frac{\delta T}{L} \right)^2 \]

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- \[ ZT_0 = T_0 s^2 \sigma / \kappa \]

\[ Q \]

Heat reservoirs

\( T_2, \mu_0 \)

\( T_1, -\mu_0 \)

\( e_z \)
Usable energy content in ocean

- Second Law of thermodynamics:

\[ \eta_{\text{carnot}} = \frac{T_h - T_c}{T_h} \]

- Usable energy per ton water:

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

\[ \propto (T_h - T_c)^2 \]

1 Megawatt \( \sim 180 \text{ l/s} \) \( \sim 1-2 \text{ Million USD} \)

Kitchen faucet \( \sim 0.1 \text{ l/s} \)

- 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

\[
L_1 = \begin{pmatrix}
    T \sigma & T \sigma s \\
    \beta \sigma & \kappa + \beta \sigma s
\end{pmatrix}
\]

\[
\sigma = \sigma^T, \beta = T s^T, \kappa = \kappa^T
\]

- Positive-definite of the material coefficient tensor

\[
L_1 > 0
\]
Empirical constitutive relations

\[ j_1 = L_1 f_1 \]

\[ j_1 = \begin{pmatrix} j_e \\ j_s \end{pmatrix}: \text{flux} \]

\[ f_1 = \frac{1}{T} \begin{pmatrix} e \\ g \end{pmatrix}: \text{driving forces} \]

\[ L_1 = \begin{pmatrix} T\sigma & T\sigma s \\ \beta\sigma & \kappa + \beta\sigma s \end{pmatrix} \]

- 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:
  \[ q = -\kappa \nabla T, \quad j_e = 0 \]

\[ e = -\nabla \mu, g = -\nabla T, j_e, j_s = \frac{q}{T}: \text{entropy flux, } j_u = q + \mu e: \text{energy flux} \]
Constitutive model

- Choices of “driving-forces”:
  \[ e = - \nabla \mu, \quad g = - \nabla T, \quad f_1 = \frac{1}{T} \begin{pmatrix} e \\ g \end{pmatrix} \rightarrow f = \Lambda f_1 \]

- Choices of “fluxes”:
  \[ q, \quad j_e, \quad j_s = \frac{q}{T}: \text{entropy flux}, \quad j_u = q + \mu e: \text{energy flux} \]

  \[ j_1 = \begin{pmatrix} j_e \\ j_s \end{pmatrix} \rightarrow j = \Gamma j_1 \]

  \[ L_1 \rightarrow L = \Gamma L_1 \Lambda^{-1} \]
An alternative viewpoint

- **Near-equilibrium thermodynamics:**
  
  **State variables:**
  \[ \nabla \mathbf{u} = (\nabla u_1, \ldots, \nabla u_m) =: F \]

  **Rate of entropy generation:**
  \[ \gamma = \gamma(u, F) = \gamma(u, 0) + F \cdot B(u, 0) + F \cdot C(u, 0) + \cdots \]

  \[ \gamma(u, F) \geq 0 \]
  \[ \gamma(u, 0) = 0, \quad B(u, 0) = 0, \quad C(u, 0) > 0 \]

  "Conjugate variables":
  \[ S = \frac{\partial}{\partial F} \gamma(u, F) \]

  Indeed, by the first law we have
  \[ \gamma = j_1 \cdot f_1 \]

  \[ j_1 = \begin{pmatrix} j_e \\ j_s \end{pmatrix}, \quad f_1 = \frac{1}{T} \begin{pmatrix} e \\ g \end{pmatrix} \]
Implication of Gauge symmetry

• Invariance of entropy generation rate:

\[ \gamma = \gamma(\mu, T; F) = \gamma(\mu + c, T; F) \]

\[
L_1 = \begin{pmatrix}
T\sigma & T\sigma s \\
T s^T \sigma & \kappa + T s^T \sigma s \\
\end{pmatrix}
\]

independent of \( \mu \)
**Conservation laws**

- **Steady states:**
  
  \[
  \begin{align*}
  \text{div } j_e &= 0 \\
  \text{div } j_u &= 0
  \end{align*}
  \]

  \[
  j = \begin{pmatrix} j_e \\ j_u \end{pmatrix} = \Lambda j_1, \\
  \Lambda = \begin{pmatrix} I & 0 \\ \mu I & T I \end{pmatrix}
  \]

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

  \[
  f = \Lambda^{-T} f_1 \quad \Rightarrow \quad L = \Lambda L_1 \Lambda^T
  \]

  \[
  L = \begin{pmatrix}
  T \sigma & \mu T \sigma + T^2 \sigma S \\
  \mu T \sigma + T^2 \sigma S & \mu^2 T \sigma + \mu T^2 (s^T \sigma + \sigma S) + T^2 (k + Ts^T \sigma S)
  \end{pmatrix}
  \]

  \[
  j_1 = \begin{pmatrix} j_e \\ j_s \end{pmatrix} \\
  f_1 = \frac{1}{T} \begin{pmatrix} e \\ g \end{pmatrix}
  \]
Field equations

- Steady states:
  - \( \text{div } Lf = 0 \)

\[
f = \begin{pmatrix}
-\nabla \frac{\mu}{T} \\
\nabla \frac{1}{T}
\end{pmatrix}
\]

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

- The above system of equations are intrinsically nonlinear since it is not possible to eliminate the \( \mu \)-dependence of \( L \)
Linearization

- Small temperature difference and $\mu$ variations:

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

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

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

$${\text{div}} \ Lf = 0$$
Figure of merits and power factor

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

- **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: \[ \dot{W}_{\text{max}} = \frac{P_f K_n \left( \frac{R_2}{R_1} \right)}{4} \left( \frac{\delta T}{R_2 - R_1} \right)^2 \]

- Figure of merit remains the same.

- More general geometries and boundary conditions?
Homogenization

(a)

\[ \Omega_1 \quad \Omega_2 \quad \Omega_3 \quad \Omega_4 \]

\[ \cdots \]

- Unit cell problem:

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

- Variational formulation:

\[
F \cdot C^e F = \min_{v \in \mathcal{W}} \left\{ \int_Y (\nabla v + F) \cdot C(x)(\nabla v + F) \right\}
\]

\[
f = \begin{pmatrix}
-\nabla \frac{\mu}{T} \\
\nabla \frac{1}{T}
\end{pmatrix}
\]

\[
L(0, T_0; x) = \begin{pmatrix}
T_0 \sigma & T^2 \sigma s \\
T_0^2 \sigma s & T_0^2 (\kappa + T_0 s^T \sigma s)
\end{pmatrix}
\]
Closed-form solutions: laminates

![Diagram of laminates](image)

\[ A^e := \begin{bmatrix} T_0 \sigma_z & T_0^2 \alpha_z \\ T_0^2 \alpha_z & T_0^2 \kappa'_z \end{bmatrix} = (\theta_1 A_1^{-1} + \theta_2 A_2^{-1})^{-1}. \]

- 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

\[ \begin{cases} \Delta u = \chi_\Omega & \text{on } \mathbb{R}^n \\ \text{boundary conditions} & \text{at } \infty \end{cases} \]

- Maxwell-Eshelby’s solution

\[ \nabla \nabla u = Q \quad \text{on } \Omega \]
Closed-form solutions: E-inclusions

Definition:

\[
\begin{align*}
\nabla^2 \phi &= \theta - \chi \Omega_2 \\
\nabla \nabla \phi &= -(1 - \theta) Q \\
\text{periodic boundary conditions} & \quad \text{on } \partial Y,
\end{align*}
\]

Closed-form solution can be obtained for TE composites with microstructures of periodic E-inclusions.
Designing TE composites (1)

\[ C^e = C_1 + \theta[(1 - \theta)\Delta CR - \mathbb{I}]^{-1}\Delta C \]
Designing TE composites (2)

\[ C^e = C_1 + \theta[(1 - \theta)\Delta CR - \mathbb{I}]^{-1}\Delta C \]
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 1 Megawatt power gain (10K-difference)

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

\[ P_f = s^2 \sigma \]

Annual cost: 2 Million $
Large-scale power plants by TE effects

- Geothermal sources

- Number of TE tubes:

\[ \sim \frac{1}{\delta T^2} \]