Non-equilibrium thermodynamics

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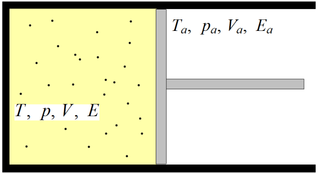
Outline

Thermodynamics		
Equilibrium	$T, E, T(E)$	statics
Ordinary	$E(t), T(E(t))$	homogeneous
Non-equilibrium	$e(t, x^i), T(e(t, x^i))$	field theory

Field theories: relative/Galilean relativistic/special relativistic/general relativistic

Simple system:



Thermostatics - potentials

Extensivity

Existence of densities and specific quantities. Transition to local, field quantities.

Gibbs relation

$$dE = TdS - pdV + \mu dM, \qquad dM = 0.$$

Meaning: Entropy, $S(E, V)$, is a potential.

$$\partial_E S = \frac{1}{T}(E, V), \qquad \partial_V S = \frac{p}{T}(E, V)$$

Vector field, integrating multiplier.

Example: ideal gas

$$E = cMT, \qquad pV = MRT$$

Thermostatics - extensivity

Bulk relations

$$dE = TdS - pdV + \mu dM, \qquad E = TS - pV + \mu M.$$

Specific quantitities: $E = Me, S = Ms, V = Mv$

$$\mu := e - Ts + pv, \qquad \text{definition!}$$

Specific relations

$$de = Tds - pdv, \qquad \mu := e - Ts + pv$$

Density relations

$$d\rho_E = Td\rho_S + \mu d\rho, \qquad \rho_e + p = \rho_h = T\rho_s + \mu\rho$$

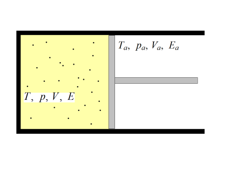
Ordinary thermodynamics

Processes:

$$\dot{E} = (c\dot{T(t)}) = -\alpha(T(t) - T_a), \quad T(0) = T_i.$$
$$T(t) = T_a + (T_i - T_a)e^{-\frac{\alpha}{c}t}$$

System paradox

Body and environment



$$\dot{E} = \hat{Q} + \hat{W} \qquad ? \qquad \dot{E} = T\dot{S} - p\dot{V}$$

Evolution equation:

$$\dot{E} = \hat{Q} + \hat{W} \qquad \dot{V} = \hat{F}.$$

Stability and second law

Second law:

- $S(E, V)$ is potential,
- $S(E, V)$ is concave (thermodynamic stability),
- $S(E, V)$ is increasing (?!, insulated).

Similarity:

Ljapunov theorem:

$\dot{x} = f(x), \quad f(x_0) = 0$ autonomous d.e., x_0 equilibrium.

- There is a Ljapunov function $L(x)$, of x_0 of the d.e.
- L has a strict maximum at equilibrium ($DL_0 = 0, D^2 L_0$ is concave) ,
- L is monotonously increasing along the d.e., DL has a strict max.

Intensives and equilibrium.

Evolution equation

Equation of 'motion':

$$\dot{E} = \hat{Q} - p\hat{F}, \qquad \dot{V} = \hat{F};$$

classical work, volume evolution, $\hat{Q}$, $\hat{F}$ are constitutive
Equilibrium: $T = T_0$, $p = p_0$, $(\hat{Q}, \hat{F})(T, T_0, p, p_0)$ (derived).
Entropy? But: $\dot{S} = ... = \frac{\hat{Q}}{T}$

Ljapunov function:

$$L(E, V) = S(E, V) - \frac{1}{T_0}E - \frac{p_0}{T_0}V$$

Equilibrium! $DL(E, V) = \left(\frac{1}{T} - \frac{1}{T_0}, \frac{p}{T} - \frac{p_0}{T_0}\right)$
Conditions of increasing:
$\dot{L}(E, V) = DL \cdot (\dot{E}, \dot{V}) = \left(\frac{1}{T} - \frac{1}{T_0}, \frac{p}{T} - \frac{p_0}{T_0}\right) \cdot \left(\hat{Q} - p\hat{F}, \hat{F}\right) = ... =$
$= \left(\frac{1}{T} - \frac{1}{T_0}\right) \hat{Q} + \frac{1}{T_0}(p - p_0)\hat{F} \geq 0.$
It is simple and reasonable.

Second Law

Requirement of stability:

$$\dot{E} = \hat{Q} - p\hat{F}, \qquad \dot{V} = \hat{F};$$

$$\left[L(E,V) = S(E,V) - \frac{1}{T_0}E - \frac{p_0}{T_0} \right]$$

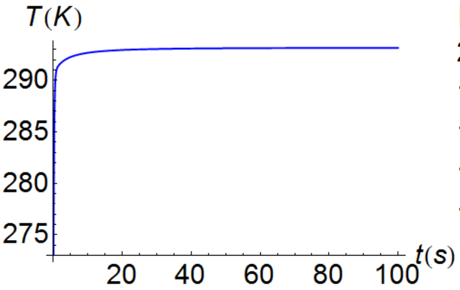
$$\left(\frac{1}{T} - \frac{1}{T_0}\right)\hat{Q} + \frac{1}{T_0}(p - p_0)\hat{F} \geq 0.$$

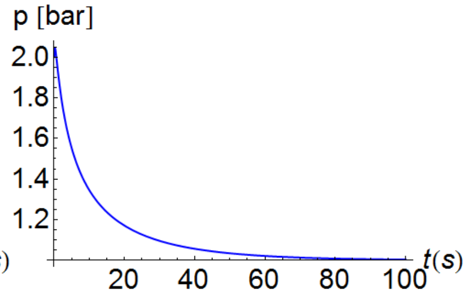
Linear relations, Onsager.

What is L?

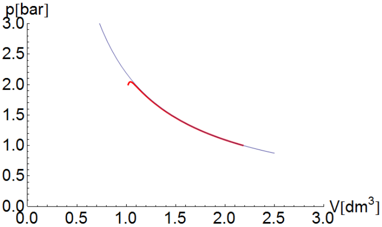
- Entropy of a reservoir.
- Exergy.

Example 1.1

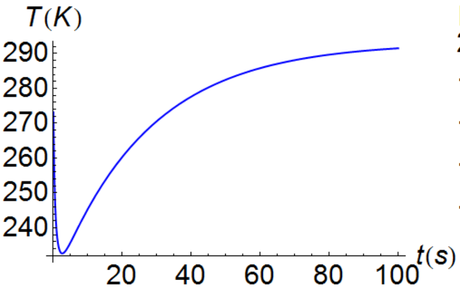


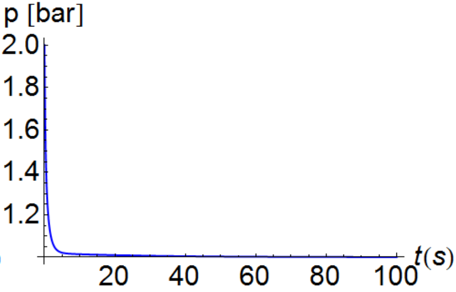


Fast thermal and slow mechanical equilibration

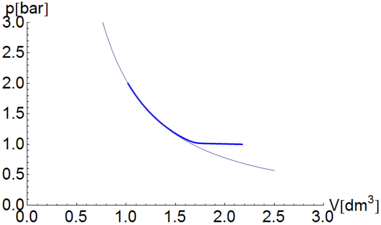


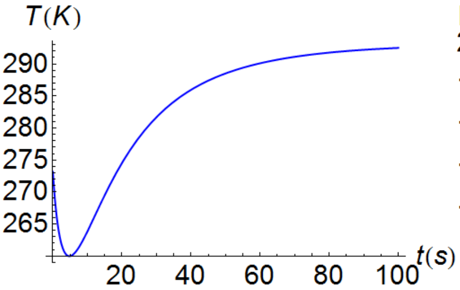
Example 1.2

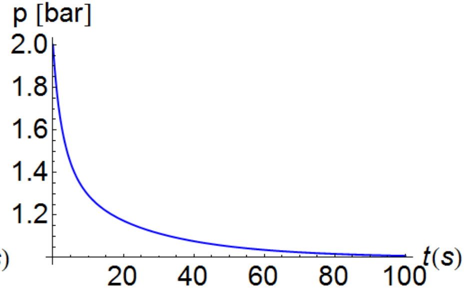




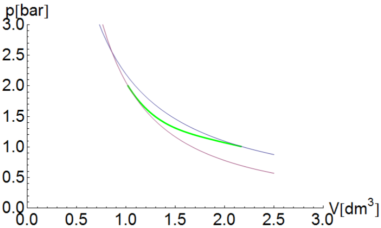
Fast mechanical equilibration : adiabatic process followed by an isobaric one



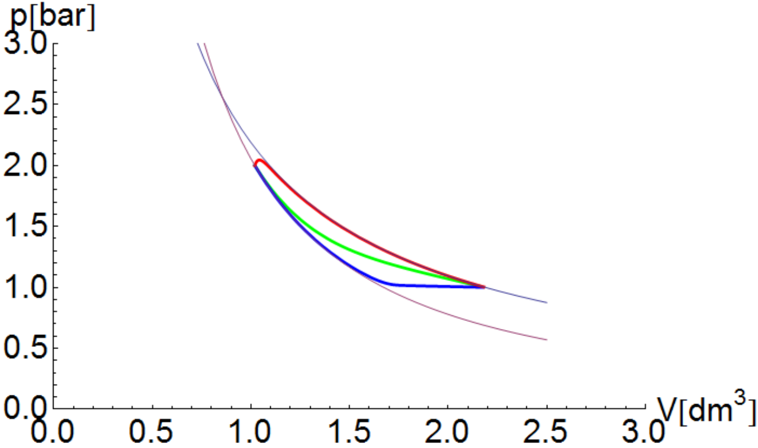




Intermediate speed.



Example 1.4



The isothermal (red), adiabatic-isobaric blue and mixed (green) processes together with the $T = T_a$ isotherm and $p = p_i(V/V_i)^\kappa$ adiabatic curves (thin lines) on the p-V plane.

Ordinary thermomechanics I.

Equation of 'motion':

$$\dot{E} = \hat{Q} - p\hat{F} + MU\hat{G}, \qquad \dot{V} = \hat{F}, \qquad \dot{U} = \hat{G}.$$

total energy $E_T = E + M\frac{U^2}{2}$; $\hat{Q}$, $\hat{F}$, $\hat{G}$ are constitutive
Equilibrium: $T = T_0$, $p = p_0$, $U = 0$, $(\hat{Q}, \hat{F}, \hat{G})(T, T_0, p, p_0, U)$ (derived).

Ljapunov function:

$$L(E, V) = S\left(E_T - M\frac{U^2}{2}, V\right) - \frac{1}{T_0}E - \frac{p_0}{T_0}V$$

Equilibrium! $DL(E, V, U) = \left(\frac{1}{T} - \frac{1}{T_0}, \frac{p}{T} - \frac{p_0}{T_0}, -\frac{MU}{T}\right)$
Conditions of increasing: $\dot{L}(E, V, U) = DL \cdot (\dot{E}, \dot{V}, \dot{U}) =$
$= \left(\frac{1}{T} - \frac{1}{T_0}, \frac{p}{T} - \frac{p_0}{T_0}, -\frac{MU}{T}\right) \cdot \left(\hat{Q} - p\hat{F} + mU\hat{G}, \hat{F}, \hat{G}\right) = ... =$
$= \left(\frac{1}{T} - \frac{1}{T_0}\right)\hat{Q} + \frac{1}{T_0}(p - p_0)\hat{F} - \frac{MU}{T_0}\hat{G} \geq 0.$

Ordinary thermomechanics II.

Equation of 'motion':

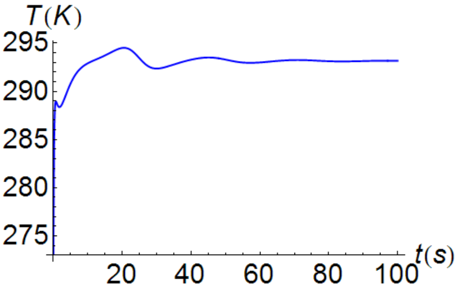
$$\dot{E} = \hat{Q} - p\hat{F} + MU\hat{G}, \qquad \dot{V} = \hat{F}, \qquad \dot{U} = \hat{G}.$$

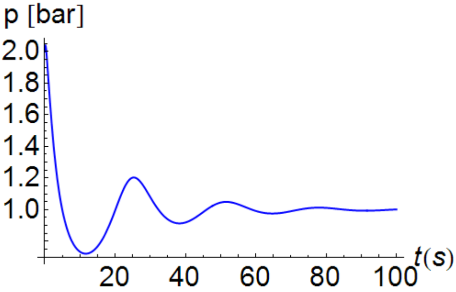
Linear, simplified constitutive equations:

$$\begin{aligned}
\hat{Q} &= -\alpha(T - T_0), \\
\hat{F} &= \beta_1(p - p_0) - b_{12}MU, \\
\hat{G} &= \beta_{21}(p - p_0) - b_2 MU.
\end{aligned}$$

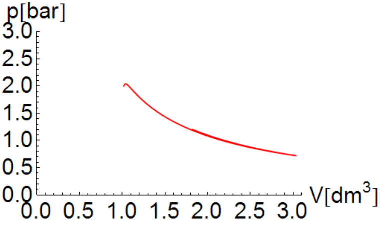
Pure mechanics: $\alpha = 0$
Usual dissipative mechanics: $\alpha = 0, \beta_{12} = -\beta_{12}, \beta_1 = 0$
Usual ideal mechanics: $\alpha = 0, \beta_{12} = -\beta_{12}, \beta_1 = \beta_2 = 0$

Example 2.1

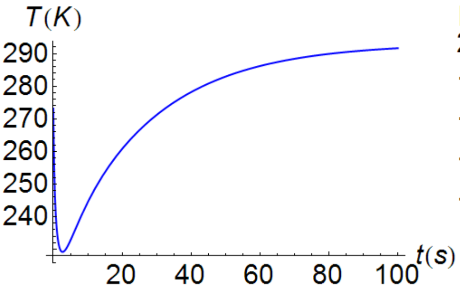


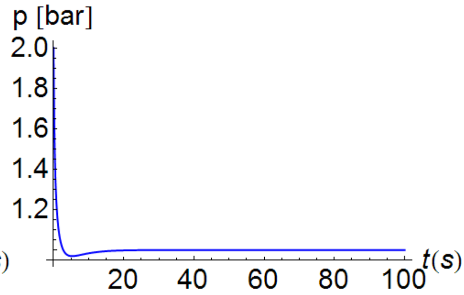


Fast thermal and slow mechanical equilibration: isothermal oscillations

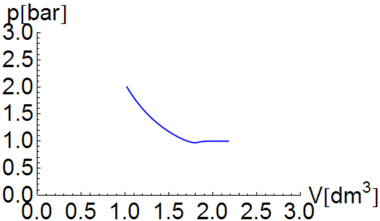


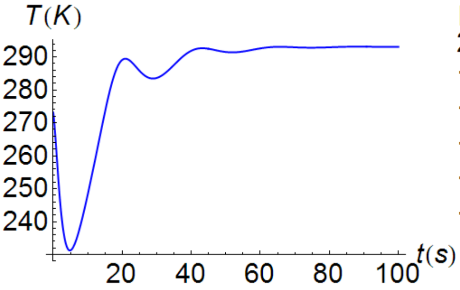
Example 2.2

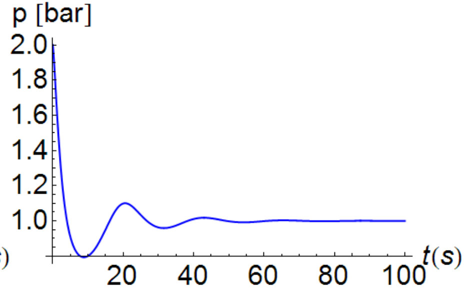




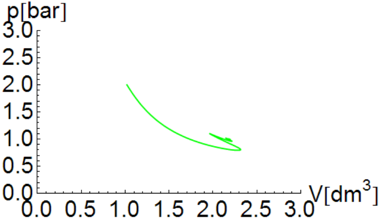
Fast mechanical equilibration: adiabatic process followed by an isobaric one: no oscillations

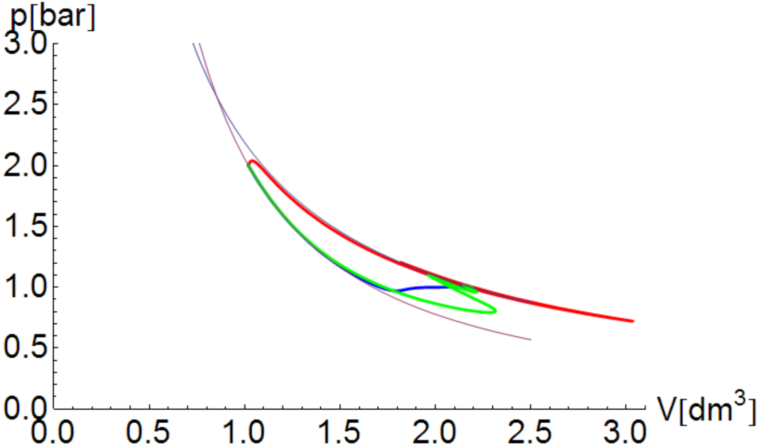






Intermediate speed, with oscillations.





The isothermal (red), adiabatic-isobaric blue and mixed (green) processes together with the $T = T_a$ isotherm and $p = p_i(V/V_i)^\kappa$ adiabatic curves (thin lines) on the p-V plane. Oscillations galore.

Heat conduction

Heat conduction theory - Fourier

Balance of internal energy

$$\rho\dot{e} + \partial_i q^i = 0$$

ρ density, e specific internal energy, q^i conductive current density of the internal energy, heat flux, rigid conductors: $\dot{} = \partial_t$, $\rho = const.$.
Thermodynamics: $s(e)$, $de = Tds$

Entropy balance

$$\rho\dot{s} + \partial_i J^i \geq 0$$

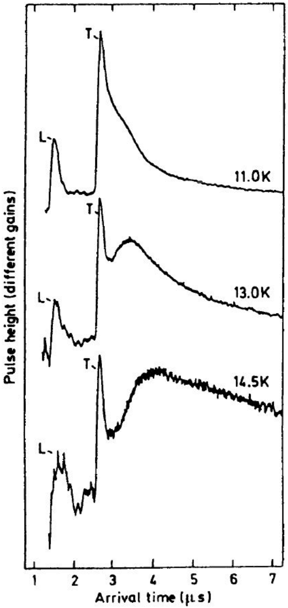
s specific entropy, J^i entropy flux. Assumption: $J^i = \frac{q^i}{T}$

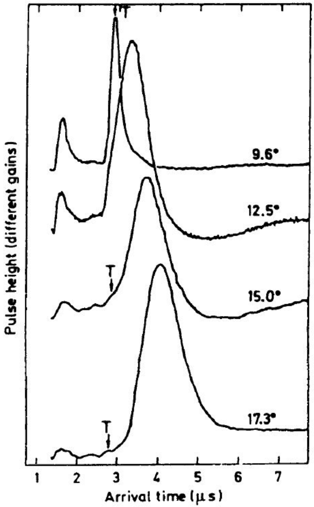
Entropy production

$$\rho\dot{s}e + \partial_i \frac{q^i}{T} = .. = q^i \partial_i \frac{1}{T} \geq 0$$

Fourier law: $q^i = \lambda \partial_i \frac{1}{T} = -\lambda_F \partial_i T$

Heat pulse experiments: low temperature NaF

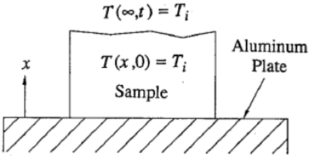


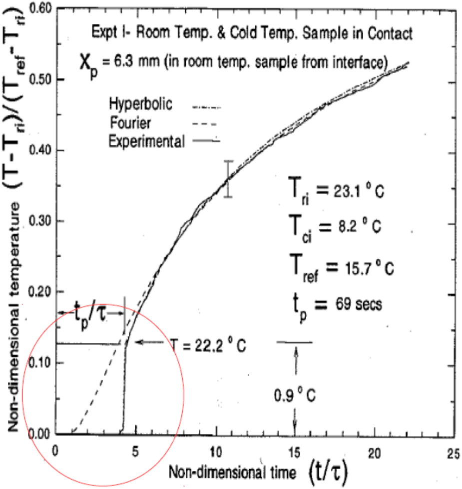


Mitra-Kumar-Vedavarz-Moallemi, 1995

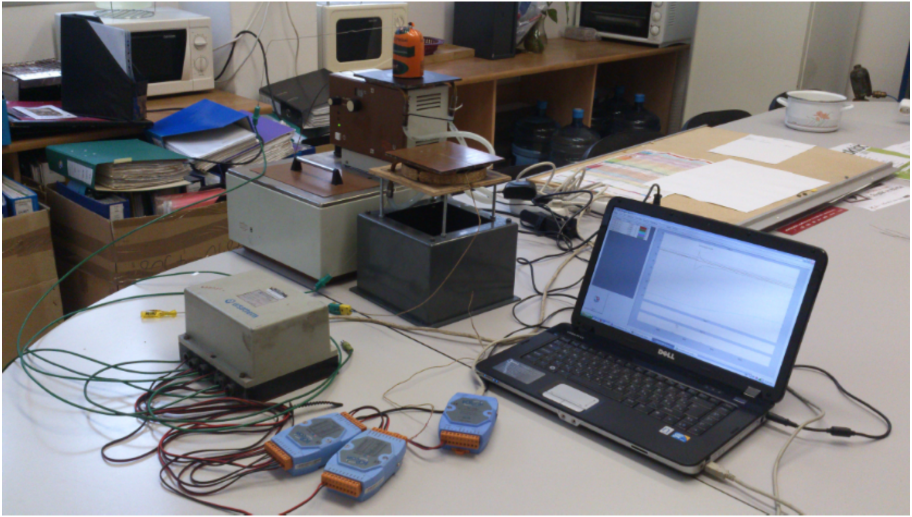
Processed frozen meat:

τ = 20-60 s





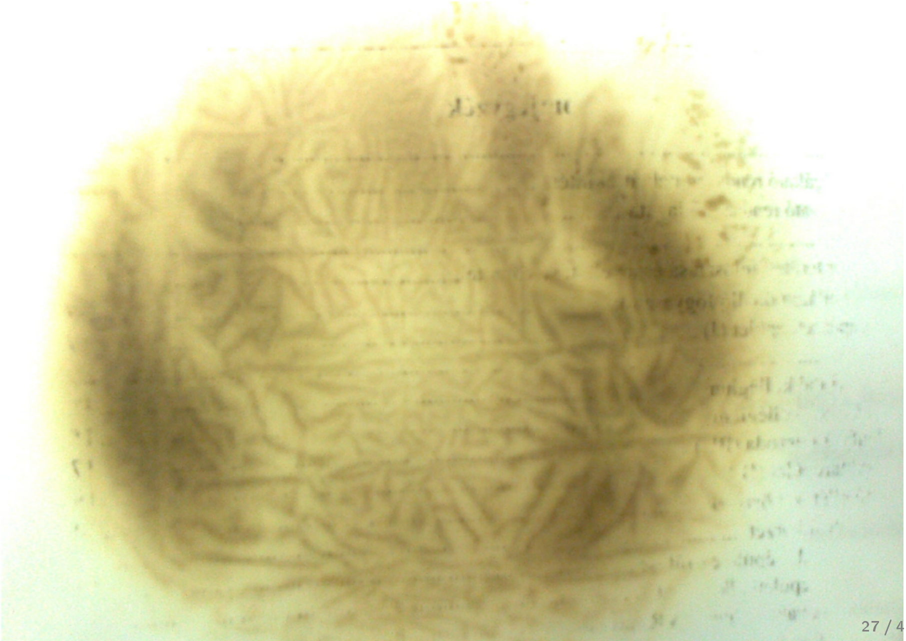
Frozen meat experiment - home version 1



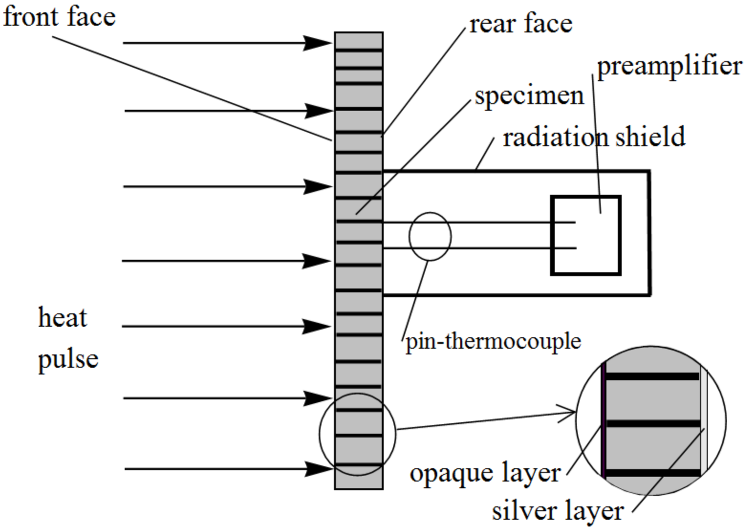
Frozen meat experiment - home version 2

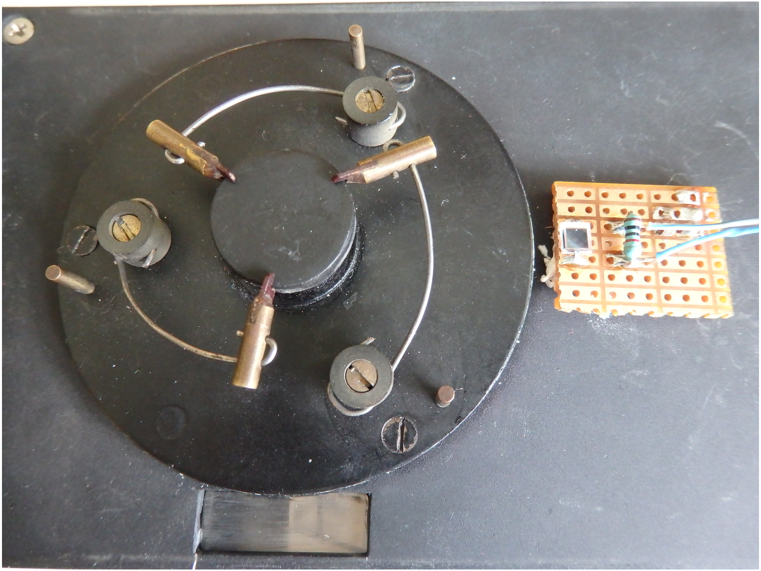
Roasted book experiment

Roasted book experiment - the result

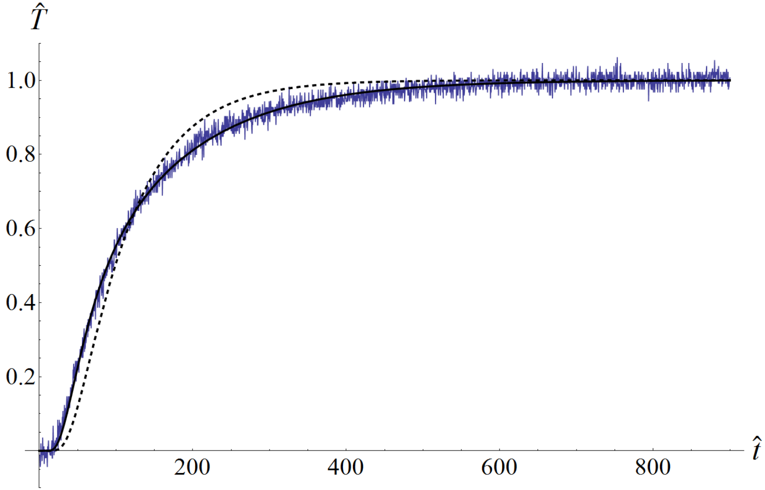


Heat pulse experiment - sketch





Heat pulse experiment - result



Metal-plastic layers, Fourier and GK fits.

Heat conduction theory - beyond Fourier

Balance of internal energy

$$\rho \dot{e} + \partial_i q^i = 0$$

Beyond Fourier: *memory* and *nonlocal* extensions

1. Fourier: $q = \lambda_1 \partial_x T$
2. Maxwell-Cattaneo-Vernotte: $\tau_q \partial_t q + q = \lambda_1 \partial_x T$
3. Jeffreys type (or dual-phase lag): $\tau_q \partial_t q + q = \lambda_1 \partial_x T + \lambda_2 \partial_{tx} T$
4. Guyer-Krumhansl: $\tau_q \partial_t q + q = \lambda_1 \partial_x T + a \partial_{xx} q$
5. Green-Naghdi: $\tau_q \partial_t q = \lambda_1 \partial_x T + a \partial_{xx} q$
6. Cahn-Hilliard type: $q = \lambda_1 \partial_x T + a \partial_{xx} q$
7. There are more ...

Heat conduction beyond Fourier

Internal variable + generalized entropy current:

- ξ^i is an *internal variable*
- entropy density: $s(e, \xi^i) = s_e\left(e - \frac{m}{2}\xi^i \cdot \xi^i\right)$
- entropy current: $J^i = B^{ij} q^j$

Entropy production:

$$\left(B^{ij} - \frac{1}{T}\delta^{ij}\right)\partial_i q_j + q_j \partial_i B^{ij} - \rho \frac{m}{T}\xi_i \dot{\xi}^i \geq 0$$

Isotropic, linear relations between *thermodynamic fluxes* and *forces*:

$$\begin{aligned}
B^{ij} - \frac{1}{T}\delta^{ij} &= k_1 \partial_k q^k \delta^{ij} + k_2 \frac{1}{2}(\partial^i q^j + \partial^j q^i) + k_3 \frac{1}{2}(\partial^i q^j - \partial^j q^i) \\
q^i &= l_1 \partial_j B^{ji} - l_{12}\rho \frac{m}{T}\xi^i \\
\dot{\xi}^i &= l_{21}\partial_j B^{ji} - l_2 \rho \frac{m}{T}\xi^i
\end{aligned}$$

Simplification in 1+1D

The system:

$$\begin{aligned}
\rho c \partial_t T + \partial_x q &= 0, \\
B - \frac{1}{T} &= k \partial_x q \\
q &= l_1 \partial_x B - \hat{l}_{12} \xi \\
\partial_t \xi &= l_{21} \partial_x B - \hat{l}_2 \xi
\end{aligned}$$

General consitutive relation

$$\partial_t q + \hat{l}_2 q - L \partial_x \left(\frac{1}{T} + k \partial_x q \right) - l_1 \partial_x \partial_t \left(\frac{1}{T} + k \partial_x q \right) = 0$$

$L = (l_1 \hat{l}_2 - \hat{l}_{12} l_{21})$

General consitutive relation

$$\tau \partial_t q + q + \lambda_F \partial_x T - a_1 \partial_{xx} q - \lambda_1 \partial_{tx} \left(\tfrac{1}{T} \right) - a_2 \partial_{txx} q = 0$$

Guyer-Krumhansl hierarchy

Balance + constitutive, non-dimensional

$$\begin{aligned} \partial_t T + \partial_x q &= 0, \\ \tau \partial_t q + q + \lambda \partial_x T - a \partial_{xx} q &= 0 \end{aligned}$$

Wave form

$$\color{red}{\tau \partial_{tt} T - \lambda_F \partial_{xx} T} + \partial_t T - a \partial_{txx} T = 0$$

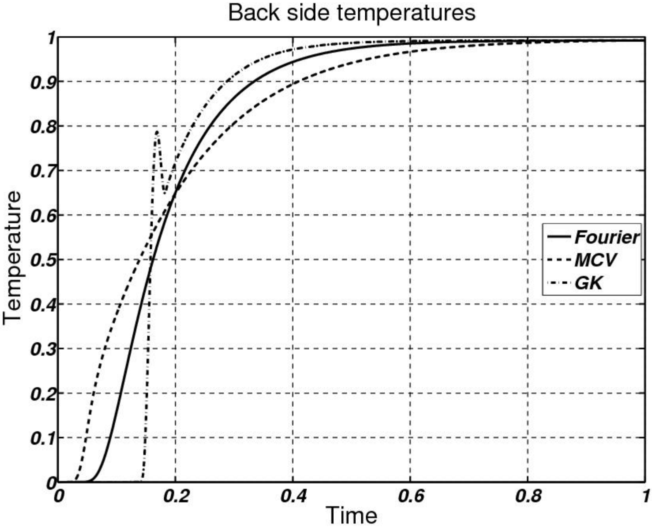
Hierarchy

$$\tau \partial_t \left(\color{blue}{\partial_t T - \frac{a}{\tau} \partial_{xx} T} \right) + \color{blue}{\partial_t T - \lambda \partial_{xx} T} = 0$$

Some solutions are exactly Fourier!

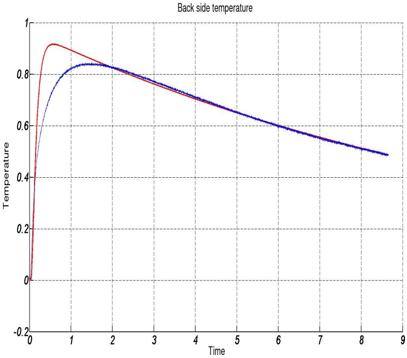
Experiments?

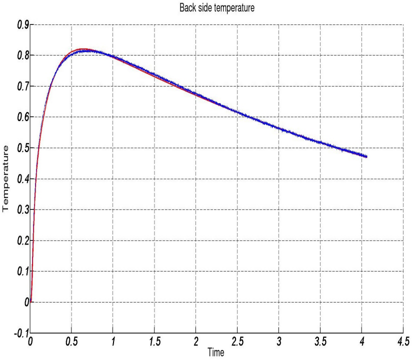
- Fourier, Maxwell-Cattaneo-Vernotte and Guyer-Krumhansl



Experiments?

- Metal foam: Fourier and Guyer-Krumhansl





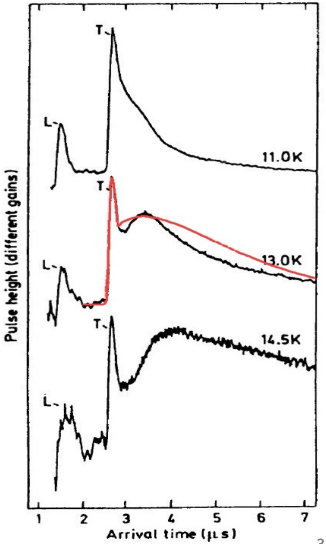
V.P. and Fülöp T. (2012) Ann. Phys., 524(8), 470.

Kovács R. and V.P. (2015), Int. J. Heat and Mass Transfer, 83, p613-620.

Both, S. et al. (2016), J. Non-Equilibrium Thermodynamics, 41(1), p41-48.

Experiments?

Low temperature NaF experiments: ballistic propagation and second sound (courtesy of R. Kovács)



Rheology of solids

Elasticity with an internal variable I

Extended state space and consequences

$$\tilde{s}(e,\epsilon,\xi) = s(e,\epsilon) - \frac{a}{2}\xi^2$$

$$\rho ds = \frac{\rho}{T}de - \frac{\sigma}{T}d\epsilon - \rho a\xi d\xi$$

$$\tilde{\sigma}(e,\epsilon,\xi) = \sigma(e,\epsilon) + \hat{\sigma}(e,\epsilon,\xi)$$

$$\rho\partial_t e + \partial_x q = \tilde{\sigma}\partial_t\epsilon = \sigma\partial_t\epsilon + \hat{\sigma}\partial_t\epsilon$$

Entropy production

$$\rho\partial_t\tilde{s} + \partial_x j_s = \frac{\rho}{T}\partial_t e - \frac{\sigma}{T}\partial_t\epsilon - \rho a\xi\partial_t\xi + \partial_x\frac{q}{T} = q\partial_x\frac{1}{T} + \frac{\hat{\sigma}}{T}\partial_t\epsilon - \rho a\xi\partial_t\xi \geq 0$$

Mechanical part:

$$(\tilde{\sigma} - \underbrace{T\rho\partial_\epsilon s}_{E\epsilon})\partial_t\epsilon - A\xi\partial_t\xi = \hat{\sigma}\partial_t\epsilon - A\xi\partial_t\xi \geq 0$$

Elasticity with an internal variable II

Linear solution: beyond viscoelasticity

$$\hat{\sigma} = l_{11}\partial_t\epsilon + l_{12}(-A\xi), \qquad \partial_t\xi = l_{21}\partial_t\epsilon + l_{22}(-A\xi)$$

Second law restrictions:

$$l_{11} \geq 0, \quad l_{22} \geq 0, \quad det(L^s) \geq 0.$$

Elimination of the internal variable

$$\tilde{\sigma} + \frac{1}{Al_{22}}\partial_t\tilde{\sigma} = E\epsilon + \left(\frac{det(L)}{l_{22}} + \frac{E}{Al_{22}}\right)\partial_t\epsilon + \frac{l_{11}}{Al_{22}}\partial_{tt}\epsilon$$

Kluitenberg-Verhás body

$$(\tilde{\sigma} - E\epsilon) + \tau\partial_t(\tilde{\sigma} - E_1\epsilon) = E_2\partial_{tt}\epsilon$$

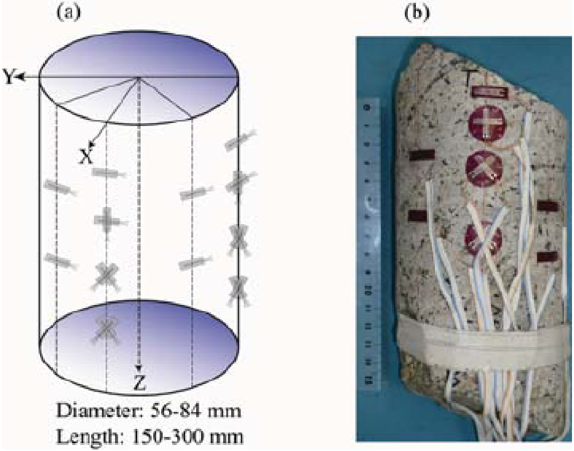
Hooke, Kelvin-Voigt, Poynting-Thomson-Zener (standard) bodies.
Must be doubled in 3D isotropy!

Experiments?

Rock 2

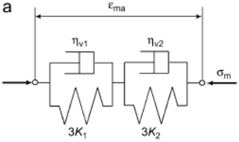
Rock 3

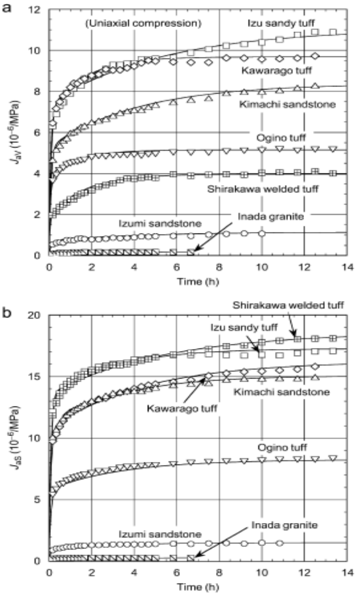
Anelastic Strain Recovery



Deviatoric and volumetric relaxation

Matsuki and Takeuchi (1991-99)
Matsuki (2008), Lin et al. (2010)





Elasticity with an internal variable III

Hierarchy in time:

- Second law: nonnegative coefficients
- Isotropy: separation of deviatoric and spherical parts, like Lamé coefficients or bulk and shear viscosities.
- Spherical and deviatoric Kluitenberg for uniaxial loading:

$$
\begin{aligned}
(\sigma - E\epsilon) + \tau\partial_t(\sigma - E_1\epsilon) + \tau_1\partial_{tt}(\sigma - E_2\epsilon) + \tau_2\partial_{ttt}(\sigma - E_3\epsilon) \\
= E_4\partial_{tttt}\epsilon
\end{aligned}
$$

- Material - apparent: deviatoric Kelvin-Voigt + spherical Hooke = Kluitenberg-Verhás in uniaxial compression.

Asszonyi Cs., Fülöp T. and V.P., Continuum Mechanics and Thermodynamics, (2015), 27, p971-986, (arXiv:1407.0882).

Summary - hierarchies galore

Ordinary thermodynamics

- Thermodynamics is stability
- Inertia leads mechanics

Wave approach to heat conduction

- Current multiplier
- Fourier equation hierarchy

Elasticity with a single internal variable of state

- Kluitenberg body
- Hooke law hierarchy

Elasticity with dual weakly nonlocal internal variables

- Modified entropy current
- Wave equation hierarchy

Thank you for the attention!

Ordinary thermodynamics:

- Truesdell, C. and Bharatha, S., Classical Thermodynamics as a Theory of Heat Engines, Springer, 1977.
- Matolcsi, T., Dynamical laws in thermodynamics, Physics Essays, 1992, 5/3, p320-327.
- Matolcsi, T., Ordinary Thermodynamics, Academic Publisher, Budapest, 2005.

Heat conduction:

- Both et al, Deviation from Fourier law at room temperature heterogeneous materials, Journal of Non-Equilibrium Thermodynamics, (2016), 41/1, 41-48, (arXiv:1506.05764).

Rheology:

- Asszonyi Cs., Fülöp T. and V.P., Distinguished rheological models for solids in the framework of a thermodynamical internal variable theory, Continuum Mechanics and Thermodynamics, (2015), 27, 971-986, (arXiv:1407.0882).