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Notes on thermomechanics, thermodynamics, statistical mechanics

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Some notes on understanding thermomechanics, thermodynamics, and statistical mechanics

1 The second law in thermomechanics and thermostatics

Let's exclude electromagnetism and materials with intrinsic spin. The general local form of the second law in a generic reference frame can be equivalently written

$$\begin{aligned} \partial_t s + \nabla \cdot (\boldsymbol{v} s) &\geqslant -\frac{1}{T}(\nabla \cdot \boldsymbol{q} + Q) + \frac{1}{T^2}\boldsymbol{q} \cdot \nabla T \\ T\partial_t s &\geqslant -T\nabla \cdot (\boldsymbol{v} s) - \nabla \cdot \boldsymbol{q} - Q + \frac{1}{T}\boldsymbol{q} \cdot \nabla T \end{aligned} \tag{1}$$

where s is the volumic entropy, $\boldsymbol{v}$ the velocity of the material, $T > 0$ the temperature, $\boldsymbol{q}$ the heat flux, and Q the *emitted* volume heating (positive if the material is *releasing* volumic heat).

It should be noted that the heat flux is actually *measured in a frame instantaneously at rest with respect to the material*. This is the reason why different observers agree on its magnitude (frame-indifferent quantity). This is the definition of "heating", as opposed to a generic energy flux.

From this equation it's clear that the rate of change of the *total* entropy in a fixed volume must be larger than the sum of various contributions which come not only from heat flux but also from entropy convection and temperature gradients.

If S is the total entropy in a fixed volume, and *if temperature is uniform throughout the fixed volume*, then the second law has the specialized form

$$T\partial_t S \geqslant -\Phi_S - Q \qquad \text{(uniform } T\text{)} \tag{2}$$

where Φ_S is the total entropy *out*flux and Q is the total heat *leaving* the fixed volume.

If we instead consider a particular body B, the second law for the total entropy S_B of the body, with volume element $\mathrm{d}B$, is

$$\dot{S}_B \geqslant -\int_B \frac{1}{T}(\nabla \cdot \boldsymbol{q} + Q)\,\mathrm{d}B + \int_B \frac{1}{T^2}\boldsymbol{q} \cdot \nabla T\,\mathrm{d}B \tag{3}$$

and *if temperature is uniform throughout the body*:

$$T\dot{S}_B \geqslant -Q_B \qquad \text{(uniform } T\text{)} \tag{4}$$

where Q_B is the total heat *emitted* by the body. The body may be changing shape and volume.

The local form of the energy balance for a generic observer is

$$\partial_t u + \nabla \cdot (\boldsymbol{v} u) = -\nabla \cdot \boldsymbol{q} - Q - \mathrm{tr}(\boldsymbol{T}\,\nabla \boldsymbol{v}^+) \tag{5}$$

where u is the volumic internal energy, $\boldsymbol{T}$ the symmetric (compressive) stress, and $\nabla \boldsymbol{v}^+$ the symmetrized velocity gradient. The term $\mathrm{tr}(\boldsymbol{T}\,\nabla \boldsymbol{v}^+)$ is the local working *done by* the material, and is agreed upon by all observers.

It should be noted that, just like for $\boldsymbol{q}$, also the stress is actually *measured in a frame instantaneously at rest with respect to the material*. This is the reason why different observers agree on its magnitude (frame-indifferent quantity).

The balance of internal energy can be used to express the total heating in terms of energy and work: $-\nabla \cdot \boldsymbol{q} - Q = \partial_t u + \nabla \cdot (\boldsymbol{v} u) + \mathrm{tr}(\boldsymbol{T}\,\nabla \boldsymbol{v}^+)$, leading to alternative forms of inequalities (1), (2), (3), (4):

$$\begin{aligned} \partial_t s + \nabla \cdot (\boldsymbol{v} s) &\geqslant +\frac{1}{T}[\partial_t u + \nabla \cdot (\boldsymbol{v} u) + \mathrm{tr}(\boldsymbol{T}\,\nabla \boldsymbol{v}^+)] + \frac{1}{T^2}\boldsymbol{q} \cdot \nabla T \\ T\partial_t s &\geqslant -T\nabla \cdot (\boldsymbol{v} s) + \partial_t u + \nabla \cdot (\boldsymbol{v} u) + \mathrm{tr}(\boldsymbol{T}\,\nabla \boldsymbol{v}^+) + \frac{1}{T}\boldsymbol{q} \cdot \nabla T\ , \end{aligned} \tag{6}$$

and in a fixed volume:

$$T\partial_t S \geqslant -\mathit{\Phi}_S + \partial_t U + \mathit{\Phi}_U + W \qquad \text{(uniform } T\text{)} \tag{7}$$

where $\mathit{\Phi}_U$ is the *out*flow of internal energy and $W =$ is the total work *done by* the material in the fixed volume. With respect to the body B:

$$\dot{S}_B \geqslant \frac{1}{T}\dot{U}_B + \int_B \mathrm{tr}(\boldsymbol{T}\,\nabla \boldsymbol{v}^+)\,\mathrm{d}B + \int_B \frac{1}{T^2}\boldsymbol{q} \cdot \nabla T\,\mathrm{d}B \tag{8}$$

and *if temperature is uniform throughout the body*:

$$T\dot{S}_B \geqslant \dot{U}_B + W_B \qquad \text{(uniform } T\text{)} \tag{9}$$

The last inequality can also be written

$$\dot{A}_B + \dot{T}S_B + W_B \leqslant 0 \qquad \text{(uniform } T\text{)} \tag{10}$$

with the Helmholtz free energy

$$A_B \coloneqq U_B - T\,S_B \;. \tag{11}$$