Chapter 4

Thermodynamics

In the absence of mechanical forces, the first law of thermodynamics states that the time rate of change of the internal energy is equal to the rate of external heat supply which is due to heat generated inside the test volumen ω, and which is described by the heat source density r, and the heat supplied on the surface, which is decribed by the heat flux vector $\boldsymbol{q}$,

$$\frac{d}{dt}\mathcal{U}(t) = \int_{\omega(t)} \varrho(t,\boldsymbol{y})r(t,\boldsymbol{y})\,d\boldsymbol{y} - \int_{\partial\omega(t)} \boldsymbol{q}(t,\boldsymbol{y})\cdot\boldsymbol{n}_y\,ds_{\boldsymbol{y}}\,. \tag{4.1}$$

By using the representation for the internal energy

$$\mathcal{U}(t) = \int_{\omega(t)} \varrho(t,\boldsymbol{y})w(t,\boldsymbol{y})\,d\boldsymbol{y},$$

and the Stokes theorem

$$\int_{\partial\omega(t)} \boldsymbol{q}(t,\boldsymbol{y})\cdot\boldsymbol{n}_y\,ds_{\boldsymbol{y}} = \int_{\omega(t)} \operatorname{div}_y \boldsymbol{q}(t,\boldsymbol{y})\,d\boldsymbol{y},$$

(4.1) is equivalent to

$$\frac{d}{dt}\int_{\omega(t)} \varrho(t,\boldsymbol{y})w(t,\boldsymbol{y})\,d\boldsymbol{y} = \int_{\omega(t)} \varrho(t,\boldsymbol{y})r(t,\boldsymbol{y})\,d\boldsymbol{y} - \int_{\omega(t)} \operatorname{div}_y \boldsymbol{q}(t,\boldsymbol{y})\,d\boldsymbol{y}\,.$$

The application of Reynold's transport theorem, i.e. (2.8), then gives

$$\int_{\omega(t)} \varrho(t,\boldsymbol{y})\frac{d}{dt}w(t,\boldsymbol{y})\,d\boldsymbol{y} = \int_{\omega(t)} \varrho(t,\boldsymbol{y})r(t,\boldsymbol{y})\,d\boldsymbol{y} - \int_{\omega(t)} \operatorname{div}_y \boldsymbol{q}(t,\boldsymbol{y})\,d\boldsymbol{y}.$$

Since this relation holds for all test volumina $\omega(t)$, and by considering continuous functions, this results in

$$\varrho(t,\boldsymbol{y})\frac{d}{dt}w(t,\boldsymbol{y}) = \varrho(t,\boldsymbol{y})r(t,\boldsymbol{y}) - \operatorname{div}_y \boldsymbol{q}(t,\boldsymbol{y}). \tag{4.2}$$

Since the first law of thermodynamics (4.1) is an energy balance, no restrictions on the heat exchange are given. On the other hand, heat can not flow from lower to higher temperatures. To describe the direction and the irreversibility of thermodynamic processes, a new state variable, the entropy $\mathcal{S}$, is introduced,

$$\mathcal{S}(t) = \int_{\omega(t)} \varrho(t, \boldsymbol{y}) s(t, \boldsymbol{y}) \, d\boldsymbol{y}. \tag{4.3}$$

The second law of thermodynamics states that the entropy in a closed system never decreases. The entropy increases in the case of irreversible processes, and the entropy is constant in the case of reversible processes. The time ratio of change of the entropy is given by the sum of some external entropy input rate, and an entropy production rate,

$$\frac{d}{dt}\mathcal{S}(t) = \frac{d}{dt}\mathcal{S}^{(i)}(t) + \frac{d}{dt}\mathcal{S}^{(p)}(t),$$

where the entropy production rate can not be negative,

$$\frac{d}{dt}\mathcal{S}^{(p)}(t) \,\geq\, 0\,.$$

In particular, for reversible processes we have

$$\frac{d}{dt}\mathcal{S}^{(p)}(t) \,=\, 0\,.$$

For a continuous system, the entropy input rate in a control volumina $\omega(t)$ is given by

$$\frac{d}{dt}\mathcal{S}^{(i)}(t) \,=\, \int_{\omega(t)} \frac{\varrho(t, \boldsymbol{y}) r(t, \boldsymbol{y})}{\theta(t, \boldsymbol{y})} \, d\boldsymbol{y} - \int_{\partial\omega(t)} \frac{\boldsymbol{q}(t, \boldsymbol{y}) \cdot \boldsymbol{n}_y}{\theta(t, \boldsymbol{y})} \, ds_{\boldsymbol{y}}, \tag{4.4}$$

which reflects that, in a closed and reversible system, the heat supply is proportional to the absolute temperature θ which is strictly positive. Hence we can rewrite the second law of thermodynamics by the Claudius–Duhem inequality

$$\frac{d}{dt}\int_{\omega(t)} \varrho(t, \boldsymbol{y}) s(t, \boldsymbol{y}) \, d\boldsymbol{y} \,\geq\, \int_{\omega(t)} \frac{\varrho(t, \boldsymbol{y}) r(t, \boldsymbol{y})}{\theta(t, \boldsymbol{y})} \, d\boldsymbol{y} - \int_{\partial\omega(t)} \frac{\boldsymbol{q}(t, \boldsymbol{y}) \cdot \boldsymbol{n}_y}{\theta(t, \boldsymbol{y})} \, ds_{\boldsymbol{y}}. \tag{4.5}$$

With Reynold's transport theorem, i.e. (2.8), we have

$$\frac{d}{dt}\int_{\omega(t)} \varrho(t, \boldsymbol{y}) s(t, \boldsymbol{y}) \, d\boldsymbol{y} \,=\, \int_{\omega(t)} \varrho(t, \boldsymbol{y}) \frac{d}{dt} s(t, \boldsymbol{y}) \, d\boldsymbol{y},$$

while with the Stokes theorem we have

$$\int_{\partial\omega(t)} \frac{\boldsymbol{q}(t, \boldsymbol{y}) \cdot \boldsymbol{n}_y}{\theta(t, \boldsymbol{y})} \, ds_{\boldsymbol{y}} \,=\, \int_{\omega(t)} \operatorname{div}_y \frac{\boldsymbol{q}(t, \boldsymbol{y})}{\theta(t, \boldsymbol{y})} \, d\boldsymbol{y} \,=\, \int_{\omega(t)} \left[\frac{\operatorname{div}_y \boldsymbol{q}(t, \boldsymbol{y})}{\theta(t, \boldsymbol{y})} - \frac{\boldsymbol{q}(t, \boldsymbol{y}) \cdot \nabla_y \theta(t, \boldsymbol{y})}{[\theta(t, \boldsymbol{y})]^2} \right] d\boldsymbol{y}.$$

Hence, (4.5) is equivalent to

$$\int_{\omega(t)} \varrho(t, \boldsymbol{y}) \frac{d}{dt} s(t, \boldsymbol{y}) \, d\boldsymbol{y} \,\geq\, \int_{\omega(t)} \left[\frac{\varrho(t, \boldsymbol{y}) r(t, \boldsymbol{y})}{\theta(t, \boldsymbol{y})} - \frac{\operatorname{div}_y \boldsymbol{q}(t, \boldsymbol{y})}{\theta(t, \boldsymbol{y})} + \frac{\boldsymbol{q}(t, \boldsymbol{y}) \cdot \nabla_y \theta(t, \boldsymbol{y})}{[\theta(t, \boldsymbol{y})]^2} \right] d\boldsymbol{y}.$$

Since this holds for all control volumina $\omega(t)$,

$$\varrho(t,\boldsymbol{y})\frac{d}{dt}s(t,\boldsymbol{y}) \;\geq\; \frac{\varrho(t,\boldsymbol{y})r(t,\boldsymbol{y})}{\theta(t,\boldsymbol{y})} - \frac{\mathrm{div}_y\boldsymbol{q}(t,\boldsymbol{y})}{\theta(t,\boldsymbol{y})} + \frac{\boldsymbol{q}(t,\boldsymbol{y})\cdot\nabla_y\theta(t,\boldsymbol{y})}{[\theta(t,\boldsymbol{y})]^2}$$

follows. For positive temperatures $\theta(t,\boldsymbol{y})$ this is equivalent to

$$\varrho(t,\boldsymbol{y})\theta(t,\boldsymbol{y})\frac{d}{dt}s(t,\boldsymbol{y}) - \varrho(t,\boldsymbol{y})r(t,\boldsymbol{y}) + \mathrm{div}_y\boldsymbol{q}(t,\boldsymbol{y}) - \frac{\boldsymbol{q}(t,\boldsymbol{y})\cdot\nabla_y\theta(t,\boldsymbol{y})}{\theta(t,\boldsymbol{y})} \;\geq\; 0\,. \tag{4.6}$$

With (4.2), i.e.

$$\varrho(t,\boldsymbol{y})\frac{d}{dt}w(t,\boldsymbol{y}) = \varrho(t,\boldsymbol{y})r(t,\boldsymbol{y}) - \mathrm{div}_y\,\boldsymbol{q}(t,\boldsymbol{y}),$$

we further conclude

$$\varrho(t,\boldsymbol{y})\left[\theta(t,\boldsymbol{y})\frac{d}{dt}s(t,\boldsymbol{y}) - \frac{d}{dt}w(t,\boldsymbol{y})\right] - \frac{\boldsymbol{q}(t,\boldsymbol{y})\cdot\nabla_y\theta(t,\boldsymbol{y})}{\theta(t,\boldsymbol{y})} \;\geq\; 0\,. \tag{4.7}$$

Note that (4.7) describes a relation between the internal energy w, the entropy s, and the temperature θ. Hence we may consider

$$w(t,\boldsymbol{y}) = W(s(t,\boldsymbol{y})), \tag{4.8}$$

to compute

$$\frac{d}{dt}w(t,\boldsymbol{y}) = W'(s)\,\frac{d}{dt}s(t,\boldsymbol{y})\,. \tag{4.9}$$

With this we conclude from (4.7)

$$\varrho(t,\boldsymbol{y})\Big[\theta(t,\boldsymbol{y}) - W'(s)\Big]\,\frac{d}{dt}s(t,\boldsymbol{y}) - \frac{\boldsymbol{q}(t,\boldsymbol{y})\cdot\nabla_y\theta(t,\boldsymbol{y})}{\theta(t,\boldsymbol{y})} \;\geq\; 0\,.$$

For

$$W'(s)_{|s=s(t,\boldsymbol{y})} = \theta(t,\boldsymbol{y}) \tag{4.10}$$

we therefore conclude

$$-\frac{\boldsymbol{q}(t,\boldsymbol{y})\cdot\nabla_y\theta(t,\boldsymbol{y})}{\theta(t,\boldsymbol{y})} \;\geq\; 0\,.$$

Since the absolute temperature $\theta(t,\boldsymbol{y})$ is strictly positive, this inequality implies

$$\boldsymbol{q}(t,\boldsymbol{y})\cdot\nabla_y\theta(t,\boldsymbol{y}) \;\leq\; 0\,,$$

which means that heat flux can only flow from higher to lower temperatures. Thus the second law of thermodynamics implies restrictions on the direction of heat transfer. The simplest relation which fulfills the above relation is Fourier's law of heat conduction,

$$\boldsymbol{q}(t,\boldsymbol{y}) \;=\; -\boldsymbol{\kappa}(t,\boldsymbol{y})\nabla_y\theta(t,\boldsymbol{y}), \tag{4.11}$$

where $\boldsymbol{\kappa}(t,\boldsymbol{y})$ is the symmetric and positive definite tensor of thermal conductivity. Note that (4.9) and (4.10) also imply

$$\frac{d}{dt}w(t,\boldsymbol{y}) = W'(s)\,\frac{d}{dt}s(t,\boldsymbol{y}) = \theta(t,\boldsymbol{y})\,\frac{d}{dt}s(t,\boldsymbol{y})\,,$$

and for the partial differential equation (4.2) we therefore conclude

$$\varrho(t,\boldsymbol{y})\,\theta(t,\boldsymbol{y})\frac{d}{dt}s(t,\boldsymbol{y}) = \varrho(t,\boldsymbol{y})r(t,\boldsymbol{y}) + \mathrm{div}_y[\boldsymbol{\kappa}(t,\boldsymbol{y})\nabla_y\theta(t,\boldsymbol{y})]. \tag{4.12}$$

It remains to desribe the internal energy w and the entropy s by using the temperature θ. From (4.10) we find

$$w(t,\boldsymbol{y}) = W(s(t,\boldsymbol{y})) = \theta(t,\boldsymbol{y})\,s(t,\boldsymbol{y}) + A(\theta(t,\boldsymbol{y})), \tag{4.13}$$

with the Helmholtz free energy

$$A(\theta(t,\boldsymbol{y})) = W(s(t,\boldsymbol{y})) - \theta(t,\boldsymbol{y})\,s(t,\boldsymbol{y})\,. \tag{4.14}$$

With (4.13) we compute

$$\begin{aligned}\frac{d}{dt}w(t,\boldsymbol{y}) &= \frac{d}{dt}\Big[\theta(t,\boldsymbol{y})\,s(t,\boldsymbol{y}) + A(\theta(t,\boldsymbol{y}))\Big]\\ &= \theta(t,\boldsymbol{y})\,\frac{d}{dt}s(t,\boldsymbol{y}) + s(t,\boldsymbol{y})\,\frac{d}{dt}\theta(t,\boldsymbol{y}) + A'(\theta)\,\frac{d}{dt}\theta(t,\boldsymbol{y}),\end{aligned}$$

and when inserting this into (4.7) this gives

$$\begin{aligned}\frac{\boldsymbol{q}(t,\boldsymbol{y})\cdot\nabla_y\theta(t,\boldsymbol{y})}{\theta(t,\boldsymbol{y})} &\le \varrho(t,\boldsymbol{y})\left[\theta(t,\boldsymbol{y})\frac{d}{dt}s(t,\boldsymbol{y}) - \frac{d}{dt}w(t,\boldsymbol{y})\right]\\ &= \varrho(t,\boldsymbol{y})\left[\theta(t,\boldsymbol{y})\frac{d}{dt}s(t,\boldsymbol{y}) - \left(\theta(t,\boldsymbol{y})\,\frac{d}{dt}s(t,\boldsymbol{y}) + s(t,\boldsymbol{y})\,\frac{d}{dt}\theta(t,\boldsymbol{y}) + A'(\theta)\,\frac{d}{dt}\theta(t,\boldsymbol{y})\right)\right]\\ &= -\varrho(t,\boldsymbol{y})\Big[s(t,\boldsymbol{y}) + A'(\theta)\Big]\,\frac{d}{dt}\theta(t,\boldsymbol{y})\,.\end{aligned}$$

For

$$A'(\theta)_{|\theta=\theta(t,\boldsymbol{y})} = -s(t,\boldsymbol{y}) \tag{4.15}$$

we conclude

$$\frac{\boldsymbol{q}(t,\boldsymbol{y})\cdot\nabla_y\theta(t,\boldsymbol{y})}{\theta(t,\boldsymbol{y})} \le 0,$$

which again implies Fourier's law (4.11).

A Taylor expansion for the Helmholtz free energy $A(\theta)$ with respect to some constant reference temperature θ_0 gives

$$A(\theta) \approx A(\theta_0) + A'(\theta_0)\,(\theta-\theta_0) + \frac{1}{2}\,A''(\theta_0)\,(\theta-\theta_0)^2,$$

and from (4.15) we obtain

$$s(t,\boldsymbol{y}) = -A'(\theta(t,\boldsymbol{y})) \approx -A'(\theta_0) - A''(\theta_0)\,(\theta(t,\boldsymbol{y}) - \theta_0),$$

i.e.

$$\frac{d}{dt}s(t,\boldsymbol{y}) = -A''(\theta_0)\,\frac{d}{dt}\theta(t,\boldsymbol{y}), \tag{4.16}$$

and together with (4.12) we conclude the heat equation

$$c(\theta)\frac{d}{dt}\theta(t,\boldsymbol{y}) = \varrho(t,\boldsymbol{y})r(t,\boldsymbol{y}) + \mathrm{div}_y[\boldsymbol{\kappa}(t,\boldsymbol{y})\nabla_y\theta(t,\boldsymbol{y})] \tag{4.17}$$

with the material and temperature dependent heat capacity

$$c(\theta) = -\varrho(t,\boldsymbol{y})\,\theta(t,\boldsymbol{y})\,A''(\theta_0)\,. \tag{4.18}$$

Remark 4.1 *Instead of* (4.8), $w = W(s)$, *we may consider the internal energy* w *as a function of the temperature* θ*,*

$$w(t,\boldsymbol{y}) = \overline{W}(\theta(t,\boldsymbol{y})),$$

which gives

$$\frac{d}{dt}w(t,\boldsymbol{y}) = \overline{W}'(\theta)\,\frac{d}{dt}\theta(t,\boldsymbol{y})\,. \tag{4.19}$$

If we define the heat capacity as

$$c(\theta) = \varrho(t,\boldsymbol{y})\,\overline{W}'(\theta(t,\boldsymbol{y})), \tag{4.20}$$

the heat equation (4.17) *follows from* (4.2) *and* (4.19) *by using Fourier's law* (4.11)*. Note that* (4.10) *may imply at least locally the inverse representation*

$$s(t,\boldsymbol{y}) = W'^{,-1}(\theta(t,\boldsymbol{y})),$$

and therefore

$$w(t,\boldsymbol{y}) = W(s(t,\boldsymbol{y})) = W(W'^{,-1}(\theta(t,\boldsymbol{y}))) =: \overline{W}(\theta(t,))$$

follows.

Example 4.1 *For*

$$w = W(s) = s^2$$

we obtain

$$\theta = W'(s) = 2s, \quad i.e. \quad s = \frac{1}{2}\,\theta\,.$$

Then,

$$\overline{W}(\theta) = W(\frac{1}{2}\theta) = \frac{1}{4}\,\theta^2, \quad c(\theta) = \varrho\,\overline{W}'(\theta) = \frac{1}{2}\,\varrho\,\theta\,.$$

On the other hand, the related Helmholtz free energy is given as

$$A(\theta) = W(s) - \theta s = s^2 - \theta s = \frac{1}{4}\,\theta^2 - \frac{1}{2}\,\theta^2 = -\frac{1}{4}\,\theta^2,$$

implying

$$c(\theta) = -\varrho\,\theta\,A''(\theta) = -\varrho\,\theta\left(-\frac{1}{2}\right) = \frac{1}{2}\,\varrho\,\theta\,.$$

The heat equation as given in (4.17) is formulated in Eulerian coordinates,

$$c(\theta)\Big[\partial_t\theta(t,\boldsymbol{y}) + \boldsymbol{v}(t,\boldsymbol{y})\cdot\nabla_y\theta(t,\boldsymbol{y})\Big] - \mathrm{div}_y[\boldsymbol{\kappa}(t,\boldsymbol{y})\nabla_y\theta(t,\boldsymbol{y})] = \varrho(t,\boldsymbol{y})r(t,\boldsymbol{y}), \tag{4.21}$$

where the deformation $\boldsymbol{y} = \boldsymbol{\varphi}(t,\boldsymbol{x})$ is taken into account. For a fixed body $\Omega(t) = \Omega(t_0)$ for all $t > t_0 = 0$ we have $\boldsymbol{\varphi}(t,\boldsymbol{x}) = \boldsymbol{x}$, implying $\boldsymbol{v}(t,\boldsymbol{y}) = \boldsymbol{0}$. From (4.21) we then conclude the heat equation in Lagrangian coordinates,

$$c(\theta)\partial_t\theta(t,\boldsymbol{x}) - \mathrm{div}_x[\boldsymbol{\kappa}(t,\boldsymbol{x})\nabla_x\theta(t,\boldsymbol{x})] = \varrho(t,\boldsymbol{x})r(t,\boldsymbol{x}). \tag{4.22}$$

When there is no change in time, we end up with the stationary heat equation,

$$-\mathrm{div}_x[\boldsymbol{\kappa}(\boldsymbol{x})\nabla_x\theta(\boldsymbol{x})] = \varrho(\boldsymbol{x})r(\boldsymbol{x}). \tag{4.23}$$

Note that in all cases we have to add appropriate boundary and, except of the statinary case, initial conditions.