4 Fundamentals of Continuum Thermomechanics

In this Chapter, the laws of thermodynamics are reviewed and formulated for a continuum. The classical theory of thermodynamics, which is concerned with simple compressible systems, is discussed in sections 4.1-4.3, wherein are discussed the concepts of entropy, entropy production and entropy supply, the second law, the notions of reversibility and irreversibility, the thermodynamic potential functions (internal energy, enthalpy and the Gibbs and Helmholtz free energies). Continuum thermomechanics is discussed in section 4.4.

4.1 Classical Thermodynamics: The First Law

As an introduction to the thermomechanics of continua, in this section particularly simple materials undergoing simple deformation and/or heat-transfer processes are considered.

4.1.1 Properties and States

First, here is some essential terminology used to describe thermodynamic processes.

A **property** of a substance is a macroscopic characteristic to which a numerical value can be assigned at a given time. Thus, for example, the mass, volume and energy of a material, or the stress acting on a material, are properties. Work, on the other hand, is not a property, since a material does not "have a certain amount of work" (see the section which follows).

The **state** of a material is the condition of the material as described by its properties. For example a material which has properties volume V_1 and temperature θ_1 could be said to be in state '1' whereas if at some later time it has different properties V_2 and θ_2, it could be said to be in a different state, state '2'.

4.1.2 Work and Path Dependence

For the present purposes, a **system** can be defined to be a certain amount of matter which has fixed or movable boundaries. The state of a system can then be defined by assigning to it properties such as volume, pressure and so on. As will be seen, there are then two ways in which the state of the system can be changed, by interactions with its surroundings through **heat** or through **work**. The notion of heat, although familiar to us, will be defined precisely when the first law of thermodynamics is introduced below. First, consider the system shown below in Fig. 4.1.1, which consists of a block attached to an elastic spring, sliding over a rough surface. A force is applied to the "system" (denoted by the dotted line).

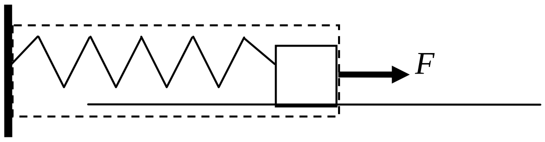

Figure 4.1.1: a spring/block system

The current state of the system can be described by the property *x*, the extension of the spring from its equilibrium position (and its velocity). However, the work done in moving the system from a previous state to the current state is unknown, since the block may have moved directly from its initial position to its current position, or it may have moved over and back many times before reaching the current position. Therefore the work done is **path dependent**. There are many different amounts of work which can be carried out to move a system from one state to another.

4.1.3 Thermal Equilibrium and Adiabatic Processes

Before getting to the first law, it is helpful to consider the notions of **thermal equilibrium** and **adiabatic** processes.

Thermal Equilibrium

Consider the following experiment: two blocks of copper, one of which our senses tell us is "warmer" than the other, are brought into contact and isolated from their surroundings, Fig. 4.2.1a. A number of observations would be made, for example:

(1) the volume of the warmer body decreases with time whereas the volume of the colder body increases, until no further changes take place and the bodies feel equally warm

(2) the electrical resistance of the warmer block decreases with time whereas that of the colder block increases, until the electrical resistances would become constant also.

When these and all such changes in observable properties cease, the interaction is at an end. One says that the two blocks are then in *thermal equilibrium*. In everyday language, one would say that the two blocks have the same **temperature**[1].

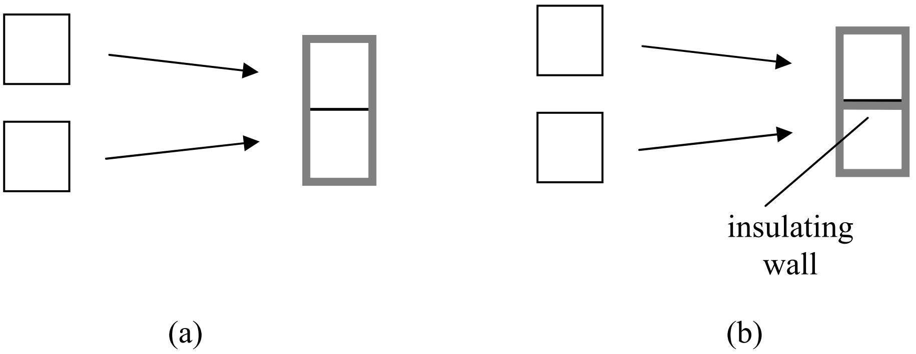

Figure 4.2.1: two blocks of copper brought into contact; (a) no insulating wall, (b) insulating wall

Adiabatic Conditions

Suppose now that, before the blocks are brought together, an **insulating wall** is put in place to separate them, Fig. 4.2.1b. By this is meant that the volume, electrical resistance, etc. of one block does not affect those of the other block. Again, in everyday language, one would simply say that the temperature of one block does not affect the temperature of the other. The term **adiabatic** is used to describe this situation.

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[1] formally, temperature is defined through the **zeroth law of thermodynamics**, which states that if two systems are separately in thermal equilibrium with a third system, then they must be in thermal equilibrium with one another. This statement is tacitly assumed in every measurement of temperature – the third system being the thermometer

4.1.4 The First Law of Thermodynamics

The Experiments of Joule

James Joule carried out some ingenious experiments into the nature of work and heat transfer in materials in the 1840s. In his most famous experiment, Joule filled a container with a fluid and used a rotating paddle wheel, driven by falling weights, to stir the water. The container was thermally insulated and so the process was adiabatic. Joule measured the consequent rise in temperature of the fluid and noted that this change in the fluid's properties was due to the work done by the falling weights.

Further experiments were carried out in which raising the temperature of the thermally insulated fluid was induced by carrying out the necessary work in different ways, for example using electrical means. In all cases, the work required to raise the temperature by a fixed amount was the same.

The series of experiments showed that if a material is thermally insulated, there is only *one* amount of work which brings the material from one state to a second state. If one knows the first state and the second state, one knows the amount of work required to effect the change in state – the work is *path independent*.

It took many years for investigators to absorb the meaning of this experimental result; it was eventually accepted that there must exist a function U, a property of the system, such that

$$W = \Delta U = U_2 - U_1 \qquad \text{(adiabatic process)} \qquad (4.1.1)$$

U is the **internal energy**, and the difference in internal energy between state 2 and state 1 is *defined* as equal to the work done in going from 1 to 2 by *adiabatic* means.

In the case of the stirred fluid, the increase in internal energy is due to the more rapidly moving fluid particles, that is, is equivalent to the increase in kinetic energy of the fluid particles.

Consider again the elastic spring system of Fig. 4.1.1, but now without the sliding over a rough surface, and completely thermally insulated. The work done now depends only on the current state (it equals $\frac{1}{2}kx^2 - \frac{1}{2}kx_0^2$, where k is the spring constant and x_0 is the equilibrium position). The internal energy of the system is seen to be in this case equivalent to the elastic potential energy in the spring.

The First Law

One can imagine now a careful experiment in which a material is thermally insulated from its surroundings and deformed through the work of a set of forces. The material can be deformed into different states, Fig. 4.1.3. The internal energy U will in general be different in each state. U could be measured by carefully recording the work done on the material to reach a given state.

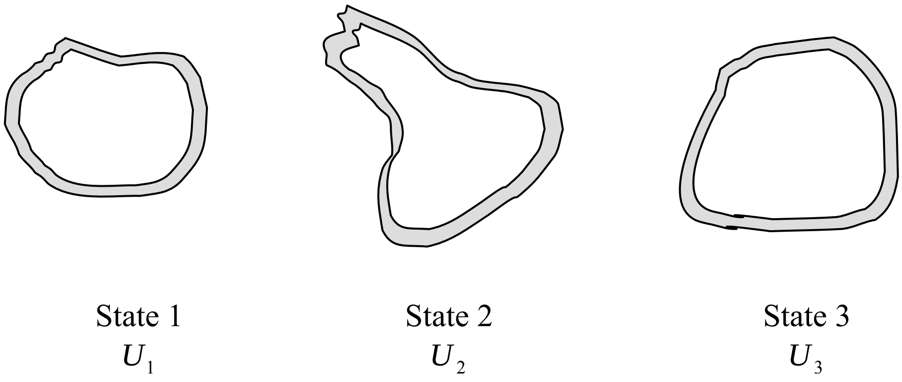

Figure 4.1.3: a thermally insulated material in three different states

Suppose that the internal energy of a material is known at various different states, through the conduction of the aforementioned experiment, in particular one knows the internal energy for the material at two given states, 1 and 2. Relax now the condition that the changes are adiabatic. What this means is that if one now brings the material into contact with another body, the properties of the material *can* be affected. Work is again done to take the material from state 1 to state 2 but it will now be found that, in general,

$$W \neq \Delta U = U_2 - U_1 \tag{4.1.2}$$

The difference between ΔU and W is *defined* as a measure of the *heat Q* which has entered the system in the change. Thus

$$\boxed{W + Q = \Delta U} \qquad \textbf{First Law of Thermodynamics} \tag{4.1.3}$$

This is **the first law of thermodynamics**. In words, t*he change in the internal energy is the sum of the work done plus the heat supplied.*

Note that the concept of heat Q (and internal energy) is introduced and defined with the first law. Like work, heat is a form of energy *transfer*; a body does not *contain* heat. Work is any means of changing the energy of a system other than heat.

Sign Convention for Work and Energy

The following sign convention will be used[2]

$$\begin{array}{ll} Q > 0 \; - & \text{heat enters the system} \\ Q < 0 \; - & \text{heat leaves the system} \\ W > 0 \; - & \text{work done on the system} \\ W < 0 \; - & \text{work done by the system} \end{array} \tag{4.1.4}$$

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[2] many authors use the exact opposite sign convention for work as used here

Other types of Energy

When there are other energies involved, the first law must be amended. For a material moving with a certain velocity, one must also consider its kinetic energy, and the first law reads

$$W + Q = \Delta U + \Delta K \tag{4.1.5}$$

Other types of energy can be incorporated, for example gravitational potential energy and chemical energy[3]. All the different types of energy are often denoted simply by E, so the first law in general reads $W + Q = \Delta E$.

Inside the Black Box

In this continuum treatment of thermodynamics (or **phenomenological thermodynamics**), it is not necessary to look inside and consider the billions of molecules inside the "black box" of a system. However, it is helpful to think of the molecules of a material as having certain micro-velocities and it is the mean velocity of these micro-velocities which manifests itself as the macroscopic velocity property, and the statistical fluctuations of the micro-velocities from the mean velocity are assumed to cancel out, Fig. 4.1.4.

The micro-velocity fluctuations give rise to an *internal* kinetic energy which manifests itself as the macroscopic temperature, as in the stirred fluid mentioned above. The interaction between the elementary particles and the surroundings of the element causes energy to be transferred to the surroundings. This is the **heat flow** through the boundary of the system. This energy exchange can occur even when the shape of the element does not change, whereas a change in potential energy implies a deformation which will induce a re-arrangement of the molecules and change in shape or volume of the system.

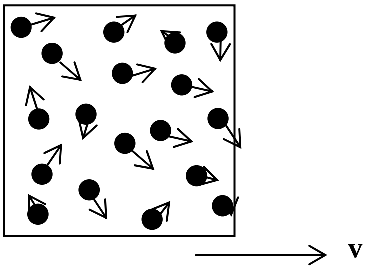

Figure 4.1.4: a system moving with velocity v

The property of pressure or stress of the system is by definition determined by the forces exerted by the elementary particles around the boundary. The fluctuations and micro-movement of the elementary particles will cause stress fluctuations but again these are assumed to cancel out.

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[3] a potential energy which can be accessed when molecular bonds are broken

4.1.5 Simple Compressible Systems

In order to demonstrate the meaning and use of the first law with examples and simple calculations, only **simple systems** will be considered. A simple system is one where there is only *one* possible work interaction. The classic example of a simple compressible system is that of a substance contained within a piston-cylinder apparatus, Fig. 4.1.5. The state of the material can be changed either by heat transfer or by the application of work, and the only work interaction possible is the application of a force to the piston head, compressing or expanding the material. Any effects due to magnetic or electrical interactions, or due to motion or gravity, are ignored.

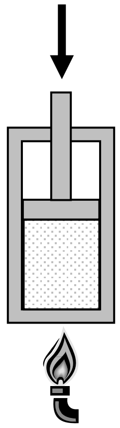

Figure 4.1.5: A simple piston-cylinder system

A **pure substance** is one which has a uniform and invariable chemical composition. In theory this could include different phases of the same substance (e.g. water and steam for H_2O).

In what follows, only pure substances in the context of simple compressible systems will be considered.

Work

If p is the pressure at the piston face, and dV is a small change in volume of the material, Fig. 4.1.5, then the work done in compressing/expanding the material is

$$\delta W = -p\,dV\,, \tag{4.1.6}$$

the minus sign because a positive work is done when the volume gets smaller. The total work done during a compression/expansion of the material is then

$$W = \int \delta W = -\int_{p_1,V_1}^{p_2,V_2} p\,dV \tag{4.1.7}$$

The symbol δ is used here to indicate that the small amount of work δW is not a true differential[4]; it cannot be integrated to a function which is evaluated at only the initial and final states, $W \neq \int_{p_1,V_1}^{p_2,V_2} dW = W(p_2,V_2) - W(p_1,V_1)$, since the work done is process/path. To illustrate this path dependence, consider the $p-V$ graph in Fig. 4.1.6, which shows three different process paths between states 1 (p_1,V_1) and 2 (p_2,V_2). For path ABC, the work done is $p_2(V_2 - V_1)$. For path $\mathrm{AB'C}$, the work done is $p_1(V_2 - V_1)$. The work for the third, curved, path requires an integration along AC and will in general be different from both the other results.

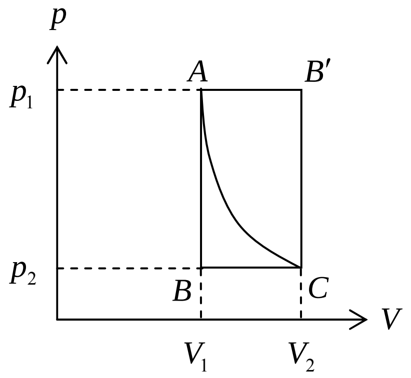

Figure 4.1.6: a p-V diagram

The first law states that $dU = \delta W + \delta Q$ which can now be re-written as

$$\boxed{dU = -pdV + \delta Q} \quad \textbf{First Law for a Simple Compressible System} \quad (4.1.8)$$

4.1.6 Quasi-Static Processes

A system is said to be in **equilibrium** when it experiences no change over time – it is in a **steady state**. Full **thermodynamic equilibrium** of a system requires thermal equilibrium with any surroundings and also mechanical equilibrium[5].

Much of the theory developed here requires that the system be in a certain state with certain properties. If a property such as temperature is varying throughout the material, one cannot easily speak of its “state”. Thus when a material is undergoing some process, for example it is being deformed or heated, it is often necessary to assume that it is a **quasi-static** (or **quasi-equilibrium**) process. This means that the process takes place so slowly that the rate of change of the process is slow relative to the time taken for the properties to reach equilibrium. For example, if one heats water in the piston-cylinder arrangement of Fig. 4.1.5 by putting it directly over a hot flame, the water near the base will heat up first and cause convection currents and the water will not be anywhere near an equilibrium state. On the other hand, one could imagine heating the water extremely

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[4] but not to be confused with the use of this symbol to represent a variation, as in the context of the principle of virtual work

[5] and also **chemical equilibrium**, where there are no net reactions taking place

slowly with a low flame, so that at any time instant the water temperature is very nearly constant throughout.

To examine what this might mean in the case of the work performed, consider Fig. 4.1.7, which shows the system pressure p and the external pressure p_{ext} – the pressure exerted by the surroundings. Assuming thermal equilibrium, if $p = p_{ext}$ then there is full equilibrium. If, however, there is an appreciable difference between the two, for example if a large external pressure is suddenly applied, the piston head will depress rapidly and pressure will not remain uniform throughout the system. However, if the pressures differ by a small amount dp, the work done is

$$W = -\int pdV = -\int (p_{ext} \pm dp)dV = -\int p_{ext}dV \mp \int dpdV = -\int p_{ext}dV \qquad (4.1.9)$$

provided dp is extremely small. The smaller dp, the closer the system will be to mechanical equilibrium. As with the heat transfer, this implies that quasi-equilibrium is maintained provided the piston is moved extremely slowly by incrementally increasing the pressure by very small amounts. (It is often suggested that this might be achieved by repeatedly placing individual grains of sand on the piston head.)

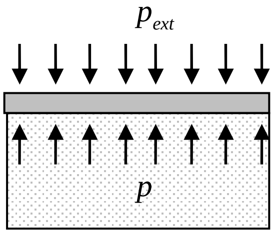

Figure 4.1.7: pressures exerted on a piston head

Unless otherwise stated, it will be assumed that the material at any instance is in quasi-equilibrium. If the system is *not* in equilibrium, Eqn. 4.1.8, $dU = -pdV + \delta Q$, does not make much sense, and one would have to use the more general version $dU = \delta W + \delta Q$.

Example

A gas is contained in a rigid thermally insulated container. It is then allowed to expand into a similar container initially evacuated, Fig. 4.1.8. There is no heat transfer and so $Q = 0$. Since a vacuum provides no resistance to an expanding gas, there is no pressure and hence no work done. Therefore there is no change in the internal energy of the gas. This is *not* a quasi-static process.

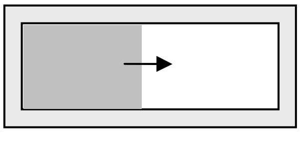

Figure 4.1.8: a thermally insulated gas expanding in an evacuated container

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Example

Consider the cylinder arrangement of Fig. 4.1.9, which shows a gas contained by a weight. The gas is heated and this causes the weight to rise. The pressure is constant and so the work done is $p\Delta V = p(V_2 - V_1)$. This example shows a system taking heat as input and performing work as output, with no necessary internal energy change.

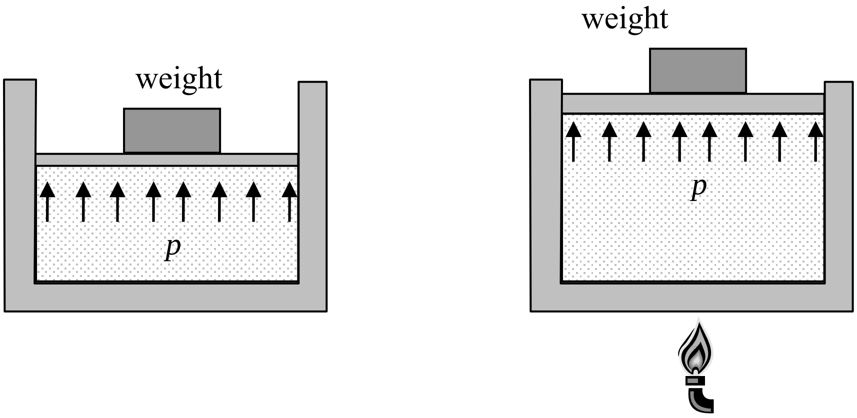

Figure 4.1.9: a heated gas causing a weight to move

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The opposite process, whereby work is converted purely into heat is called **dissipation** (for example, as can occur in a frictional brake).

4.1.7 State Variables and State Functions

Now a general guide known as the **state principle** says that there is one independent property for each way a system's energy can be varied independently. For a simple compressible system, there are two ways of varying the energy and so the material has *two* **independent properties**[6]. One can take any two of, for example, the temperature[7] θ, pressure *p*, volume *V* or internal energy *U*. The two chosen independent properties are the **state variables** of the system. The state of the system is completely described by these state variables.

Other properties of the system can be expressed as **state functions** of the state variables. For example, suppose that one takes the temperature and volume to be the state variables. Then the relations

$$p = p(\theta, V), \quad U = U(\theta, V) \tag{4.1.10}$$

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[6] this is not always the case; it should be emphasised that the number of state variables needed to completely characterise a material undergoing a certain process is, in the final analysis, determined from experiment

[7] the symbol θ denotes the **absolute temperature**, with $\theta > 0$

are state functions for the pressure and internal energy. Equations involving the various properties of a system, as in 4.1.10, are also called **equations of state**. The first of these, relating force variables (in this simple case, the pressure *p*) to kinematic variables (in this case, the volume *V*) and temperature, is called a **thermodynamic** (or **thermal**) **equation of state**. The second, relating the internal energy to a thermal variable (here temperature) and a kinematic variable, is called a **caloric equation of state**.

Different sets of state variables may be chosen. For example, taking p and θ to be the state variables, the state functions would be

$$V = V(p,\theta), \quad U = U(p,\theta) \tag{4.1.11}$$

A key feature of a state function is that its value is determined from the values of the state variables; its value does not depend on the particular path taken to reach the current state. For example, the internal energy is a state function (by its own definition); if one chooses the state variables to be (p,V), the change in internal energy between states '1' and '2' is (compare with Eqn. 4.1.7)

$$\Delta U = \int_{p_1,V_1}^{p_2,V_2} dU = U(p_2,V_2) - U(p_1,V_1) \tag{4.1.12}$$

The value of ΔU depends only on the values of the state variables, in other words its value is the same no matter what path is taken between A and C in Fig. 4.1.6.

$U = U(p,V)$ defines a surface U in $p-V$ space. The total differential of U is then[8]

$$dU = \left(\frac{\partial U}{\partial p}\right)_V dp + \left(\frac{\partial U}{\partial V}\right)_p dV \tag{4.1.13}$$

Although the partial differentiation here means differentiation with respect to one variable only, it is conventional in classical thermodynamics to include a subscript to explicitly indicate this, as here – the subscript emphasises the variable which is held constant. This notation helps avoid confusion when the set of state variables being used is changed during an analysis.

These partial derivatives are themselves state functions; since the function U is known for all (p,V), so are its slopes.

4.1.8 Specific Properties

Specific properties are properties *per unit mass*. They are usually denoted by lower case letters. For example, the specific volume (reciprocal of the density) and specific internal energy are

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[8]

$$v = \frac{V}{m}, \quad u = \frac{U}{m} \tag{4.1.14}$$

where m is the mass of the system. The properties V and U are **extensive properties**, meaning they depend on the amount of substance in the system. The specific properties on the other hand are **intensive properties**, meaning they do not depend on the amount of substance. Other intensive properties are the temperature θ and pressure p.

One can also express the heat and work as per unit mass:

$$\delta q = \frac{\delta Q}{m}, \quad \delta w = \frac{\delta W}{m} \tag{4.1.15}$$

4.1.9 Heat Capacity

Specific Heat and the Enthalpy

The **heat capacity** is defined as *the amount of heat required to raise the system by one unit of temperature*, so the higher the heat capacity, the more the heat required to increase the temperature. For example, water has a very high heat capacity, so it requires a lot of heating to increase its temperature. By the same token, it can give out a lot of heat without dropping in temperature too quickly (hence its use in hot water bottles).

The amount of heat required to raise the temperature by a fixed amount is path-dependent, depending as it does on the amount of accompanying work carried out, so the heat capacity as defined above is ambiguous. To remove this ambiguity, one can specify the path taken during which the heat is added; the two common paths chosen are those at constant volume and at constant pressure.

From Eqn. 4.1.8, the **heat capacity at constant volume** is, by definition,

$$C_V \equiv \left(\frac{\delta Q}{d\theta} \right)_V = \left(\frac{\partial U}{\partial \theta} \right)_V \tag{4.1.16}$$

In this case, all the supplied thermal energy goes into raising the temperature of the body. Note that C_V is a state function; this is clear from the fact that there is no path dependence involved in its evaluation.

The question arises: what is the volume which is held "constant"? Although C_V will in general depend on the V chosen, this dependence is very weak for many materials; a material is usually assigned a value for C_V without reference to the volume at which it is measured.

The **heat capacity at constant pressure** is by definition

$$C_p \equiv \left(\frac{\delta Q}{d\theta}\right)_p = \left(\frac{\partial U}{\partial \theta} + p\frac{\partial V}{\partial \theta}\right)_p = \left(\frac{\partial H}{\partial \theta}\right)_p \tag{4.1.17}$$

where H is the **enthalpy**, defined by

$$H = U + pV \tag{4.1.18}$$

In this case, some of the thermal energy is converted into work, and so $C_p \geq C_V$.

The enthalpy is a state function, since U, p and V are (either state functions or state variables). As with $C_V = (\partial U / \partial \theta)_V$, the heat capacity $C_p = (\partial H / \partial \theta)_p$ is also state function.

Note that, for an incompressible material, $C_V = C_p = \partial U / \partial \theta$ and there is no ambiguity as to its meaning. Most fluids are incompressible, or nearly so, and solids are also often approximated as incompressible for heat capacity measurements. The case of gases will be discussed below.

Internal Energy Measurements

Suppose now that the heat capacity at constant volume has been carefully measured over a given temperature range, by recording the heat required to effect increments in temperature. The internal energy changes within that range can then be found from

$$\Delta U = U_2 - U_1 = \int_{\theta_1}^{\theta_2} C_V d\theta \qquad \text{(constant volume)} \tag{4.1.18}$$

Although this measurement technique requires constant volume processes, since internal energy is a property the results apply to *all* processes.

Some values for the specific internal energy and enthalpy of steam for a range of temperatures, pressures and specific volumes are given in Table 4.1.1 below. The reference state for internal energy (where u is chosen to be zero) is for saturated water at 0.01°C. The corresponding reference state for the enthalpy is obtained from 4.1.17[9].

θ (^0C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)
120	1.793	2537.3	2716.6
200	2.172	2658.1	2875.3
280	2.546	2779.6	3034.2
360	2.917	2904.2	3195.9

Table 4.1.1a: Properties for steam at pressure $p = 0.1\text{MPa}$

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[9] note that u and h can take on negative values, depending on the reference state chosen

p (MPa)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)
0.035	6.228	2660.4	2878.4
0.100	2.172	2658.1	2875.3
0.300	0.716	2650.7	2865.5
0.500	0.425	2642.9	2855.4

Table 4.1.1b: Properties for steam at temperature $\theta = 200^0\,\mathrm{C}$

4.1.10 The Ideal Gas

A **thermally perfect gas** is one for which the thermal equation of state is

$$pV = mR\theta \quad \text{or} \quad pv = R\theta \tag{4.1.19}$$

where R is the universal gas constant. Further, an **ideal gas** is a thermally perfect gas whose internal energy depends on the temperature only, that is, its caloric equation of state is of the form

$$U = U(\theta) \tag{4.1.20}$$

To justify this expression from a physical point of view, consider a gas at the microscopic level. Internal energy and pressure are related through intermolecular forces. If the pressure is very low, the internal energy is no longer affected by these forces, since the molecules are so far apart, but only by their kinetic energy of motion, i.e. the temperature. Moderate changes in volume will not bring the molecules of gas close enough together to alter this sole dependence on temperature.

When the internal energy is a function of θ *and V*, one has

$$dU = \left(\frac{\partial U}{\partial \theta}\right)_V d\theta + \left(\frac{\partial U}{\partial V}\right)_\theta dV = C_V d\theta + \left(\frac{\partial U}{\partial V}\right)_\theta dV \tag{4.1.21}$$

Thus for an ideal gas

$$dU = C_V d\theta\,. \tag{4.1.22}$$

Example

Consider an ideal gas undergoing a volume change under **isothermal**, i.e. constant temperature, conditions. From 4.1.19, the quantity $pV = p_1V_1 = p_2V_2$ is a constant $mR\theta$. This constrains the process to lie on one particular path in a $p - V$ diagram. Also, from 4.1.22, $dU = 0$ and so $\delta Q = -\delta W$. If an ideal gas expands at constant temperature then the heat input exactly equals the work done against an incrementally changing external pressure.

■

Consider now a process involving work and heat transfer. One has $\delta Q = C_V d\theta + pdV$ and the total heat input is

$$Q = \int \delta Q = \int_{\theta_1}^{\theta_2} C_V(\theta) d\theta + \int_{p_1, V_1}^{p_2, V_2} pdV \tag{4.1.23}$$

The second integral here clearly depends on the exact combination of pressure and volume during the process, so the heat input Q is path dependent, as expected. However, consider the following:

$$\begin{aligned} \int \frac{\delta Q}{\theta} &= \int_{\theta_1}^{\theta_2} \frac{C_V(\theta)}{\theta} d\theta + \int_{p_1, v_1}^{p_2, V_2} \frac{pdV}{\theta} \\ &= \int_{\theta_1}^{\theta_2} \frac{C_V(\theta)}{\theta} d\theta + mR \int_{V_1}^{V_2} \frac{dV}{V} \\ &= \int_{\theta_1}^{\theta_2} \frac{C_V(\theta)}{\theta} d\theta + mR \ln(V_2 / V_1) \end{aligned} \tag{4.1.24}$$

The quantity on the right is now path independent. In fact, for the simple case where C_V is independent of θ, a good approximation for many "near-ideal" gases, one has

$$\int \frac{\delta Q}{\theta} = C_V \ln(\theta_2 / \theta_1) + mR \ln(V_2 / V_1) \tag{4.1.25}$$

This expression means that, *for an ideal gas undergoing a quasi-static process*, although the quantity Q depends on the process, $\int \delta Q / \theta$ does not and so is a property. This property is called the **entropy** of the gas.

4.1.11 Problems

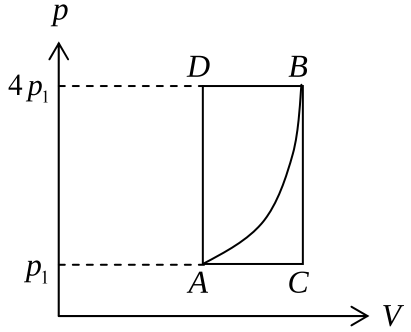
1. A gas is contained in a thermally insulated cylinder. It is very rapidly compressed so that its temperature rises sharply. Has there been a transfer of heat to the gas? Has work been done? Is the process quasi-static?

2. A gas expands from an initial state where $p_1 = 500\,\text{kPa}$ and $V_1 = 0.1\text{m}^3$ to a final state where $p_2 = 100\,\text{kPa}$. The relationship between pressure and volume during the particular process is $pV = k$, a constant. Sketch the process on a $p - V$ diagram and determine the work, in kJ. Interpret the + or – sign on your result.

3. A system, whose equation of state depends only on the volume V, temperature θ and pressure p, is taken (quasi-statically) from state A to state B along the path ACB at the pressures indicated in the figure below. In this process 40J of heat enter the system and 20J of work are done by the system.
   (a) evaluate ΔU
   (b) how much heat enters the system along the path ADB?

(c) if the system goes from B to A by the curved path indicated schematically on the figure, the work done on the system is 30J. How much heat enters or leaves the system?

(d) If the internal energy at A is denoted by U_A, etc., suppose that $U_D - U_A = 20J$. What then is the heat transfer involved in the processes AD and DB?



4. Air is contained in a vertical piston-cylinder assembly by a piston of mass $100\,\text{kg}$ and having a face area of $0.01\,\text{m}^2$. The mass of the air is 5 g, and initially the air occupies a volume of 0.005 m^3. The atmosphere exerts a pressure of $100\,\text{kPa}$ on the top of the piston. Heat transfer of magnitude $2\,\text{kJ}$ occurs slowly from the air to the surroundings, and the volume of the air decreases to $0.002\,\text{m}^3$. Neglecting friction between the piston and the cylinder wall, determine the change in specific internal energy of the air, in kJ/kg. [Note that the pressure is constant on the piston-head, and consists of the piston-weight and the atmospheric pressure.]

5. A closed system, i.e. one which can exchange heat or work with its surroundings, but not matter, undergoes a **thermodynamic cycle**[10] consisting of the following processes:

Process 1-2: adiabatic compression with $pV^{1.4} = \text{const.}$ from $p_1 = 344.74\,\text{kPa}$, $V_1 = 0.084951\,\text{m}^3$ to $V_2 = V_1/3$
Process 2-3: constant volume
Process 3-1: constant pressure, $U_1 - U_3 = 49.27317\,\text{kJ}$

There are no significant changes in kinetic or gravitational potential energy.

(a) sketch the cycle on a $p-V$ diagram
(b) calculate the net work for the cycle
(c) calculate the heat transfer for process $2-3$

6. How could you use the definition of the specific heat capacity at constant pressure to evaluate the internal energy of a material?

7. Show that for a system (not necessarily an ideal gas) undergoing a constant pressure process, the heat input is equal to the change in enthalpy.

8. Show that, for an ideal gas, $R = C_p - C_V$

---

[10] meaning the substance is brought back to its initial state at the end of the process; state variables resume their initial values

9. Use the result of problem 8 to show that, when an ideal gas undergoes an adiabatic quasi-static change, $pV^{\gamma} = \text{const.}$ where $\gamma = C_p / C_V$.

10. In Table 4.1.1:
    (a) Does the steam behave like an ideal gas? Nearly? (Note the internal energies in Table 4.1.1b)
    (b) The internal energy decreases as the steam is compressed. Is this what you would expect? Comment.

4.2 Classical Thermodynamics: The Second Law

4.2.1 A Qualitative Sketch of the Second Law and Entropy

The first law of thermodynamics is concerned with the conservation of energy. The second law of thermodynamics is concerned with how that energy is transferred between systems. Its relevance to everyday experience can be seen from the following examples:

- Ice is placed in a glass of water. It melts.
- A hot metal tray is taken out of the oven and placed on a bench top. It cools.
- A brittle plate is dropped from a height onto a hard floor. It smashes into small pieces.
- A piece of iron is left outside. It rusts.
- A bicycle tyre is pumped to high pressure and punctured. The air rushes out.

The common factor in all these examples is that energy is spreading out *in a certain direction*.

- The energy in more rapidly moving warm air molecules disperses to the ice and breaks the intermolecular hydrogen bonds, allowing the water molecules in the ice to move more freely.
- The hot metal contains a relatively large amount of energy due to its vibrating atoms and this energy is transferred to the surrounding air molecules and thereby dispersed.
- The potential energy in the plate disperses through a heating of the surrounding air, the ground and the plate as it smashes.
- The iron atoms and oxygen molecules in the air have chemical (potential) energy stored in their bonds. When iron and oxygen react, lower energy iron oxide bonds are formed and the energy difference is dispersed as heat[1].
- The relatively large energy of the pressurized air in the tyre disperses when the tyre is punctured.

Very qualitatively, the second law says that *energy tends to spontaneously disperse unless hindered from doing so*.

If any of these processes were filmed and the tape accidentally played backwards, the mistake would immediately be evident. However, no physical law (apart from the second law) would be broken if the events happened in reverse. For example, the plate falls because there is a gravitational force pulling it down. However, beginning at the end and working back, it is theoretically possible for the many billions of air (and ground) molecules, which are now moving more rapidly due to the breaking plate, to interact in such a perfect way that the dispersed heat flows back towards the broken pieces and so provides enough energy for the pieces to fly together and gain a kinetic energy to lift off the ground, rise up and eventually slow until it reaches its precise original position off the ground. The second law says that this will not happen; energy does not spontaneously, that is without outside interference, gather together and concentrate in a small locality.

---

[1] most spontaneous reactions of this type require a certain energy to get started, the **activation energy**, and this hinders the second law from wreaking havoc

Entropy is closely associated with the second law. Again, qualitatively, entropy is *a measure of how dispersed energy is*. Each system has a certain entropy and as energy disperses, the entropy increases. When the air rushes out of the tyre, the entropy of the air and its surroundings increases. When the hot tray cools, the entropy of the tray and surrounding air increases. When the iron and oxygen react, entropy increases.

Entropy can also be defined in terms of probabilities. To take a classic example, consider a box with a shutter splitting it in two. A gas occupies one half of the box (as in Fig. 4.1.8). The shutter is then removed. What will happen? The gas will of course expand to completely fill the box. What are the chances of this happening in reverse? The gas molecules are constantly moving, but the probability of them moving about the box in such a way that all gas molecules would somehow occupy only one half of the box, with no gas in the other half of the box, is zero. As the gas expands, it moves to a more probable state, and the entropy increases.

The Second Law and Maximum Work

When heat is supplied to the confined gas of Fig. 4.1.9, work is done when the gas expands and raises the weight. However, if the flame is not placed under the apparatus but simply left to burn, the heat energy, according to the second law, will disperse into the air. It will not ever *spontaneously* gather back again in a small locality where it could again be used to do some work. The only way to get it back into a small locality again is to input even more energy. In this sense the second law tells us that if we want to maximize the amount of work we can do, we need to use heat energy productively, and if any heat energy escapes it is not possible to use it again without expending more energy. In this sense, entropy can be regarded as a measure of a system’s energy unavailable for conversion into work.

A more formal and quantitative treatment of the second law will now be given.

4.2.2 Entropy and the Second Law

Entropy

The entropy S of a system is a property of that system. The change in entropy dS is due to two quantities. First, define the **entropy supply** $\delta S^{(r)}$ (an increment) through

$$\delta S^{(r)} = \frac{\delta Q}{\theta} \tag{4.2.1}$$

where Q is the heat supply; one can imagine the entropy “flowing” into the system. Define also the **entropy production** $\delta S^{(i)}$ (also an increment) to be the difference between the increment of entropy and the entropy supply:

$$dS = \delta S^{(r)} + \delta S^{(i)} \tag{4.2.2}$$

Thus the entropy change in a material is due to two components: the entropy supply, “carried” into the material with the heat supply, and the entropy production, which is produced *within* the material. (The reason for the "*r*" and "*i*" superscripts is given further below.)

Note that, whereas the entropy S is a state function (a property), the entropy supply and entropy production are not, since they depend on the particular process by which the state has changed, and hence the use of the symbol "δ" for these functions. (Compare 4.2.2 with the first law, $dU = \delta W + \delta Q$.)

The Second Law

The second law of thermodynamics states that the entropy production is a non-negative quantity,

$$\boxed{\delta S^{(i)} \geq 0} \qquad \textbf{The Second Law} \qquad (4.2.3)$$

Regarding 4.2.2, the Second Law states that the increase in entropy of a system must be at least as great as the entropy flowing into that system.

In terms of the entropy, the first law can be written as

$$\begin{aligned} dU &= \delta W + \theta \delta S^{(r)} \\ &= \delta W + \theta dS - \theta \delta S^{(i)} \end{aligned} \qquad (4.2.4)$$

or, including the second law,

$$\delta W = dU - \theta dS + \theta \delta S^{(i)} \qquad \text{with} \qquad \delta S^{(i)} \geq 0 . \qquad (4.2.5)$$

A process is termed **reversible** if the equality holds, $\delta S^{(i)} = 0$, so that there is no entropy production, in which case $dS = \delta S^{(r)}$. Otherwise it is termed an **irreversible** process, in which case $dS = \delta S^{(r)} + \delta S^{(i)}$. The superscript "*r*" on the entropy supply is to indicate that the entropy supply is equivalent to the change of entropy in a *reversible* process. The superscript "*i*" on the entropy production is to indicate that entropy production is associated with *irreversible* processes.

Alternative Statements of the Second Law

There are many different statements of the second law and each can be "derived" from the others (there is no one agreed version). Another useful definition is that *the heat input to the system in transforming from state A to state B is bounded from above*, according to

$$\delta Q \leq \theta dS \qquad (4.2.6)$$

The maximum possible heat input is θdS, in which case the entropy change is due entirely to entropy supply, with no entropy production – a reversible process. It can be seen that the statement $\delta Q \leq \theta dS$ is equivalent to the statement $\delta S^{(i)} \geq 0$.

A re-arrangement of Eqn. 4.2.6 gives the classic **Clausius's inequality**:

$$dS \geq \frac{\delta Q}{\theta} \tag{4.2.7}$$

4.2.3 Reversibility

Pure Heating

As an example of a reversible process, consider a **pure heating** (or cooling) process, where the volume is held constant, Fig. 4.2.1. Taking the two state variables to be θ and V, it follows from 4.2.5 that the work increment can be expressed as

$$\delta W = \left(\frac{\partial U}{\partial V} - \theta \frac{\partial S}{\partial V} \right)_{\theta} dV + \left(\frac{\partial U}{\partial \theta} - \theta \frac{\partial S}{\partial \theta} \right)_{V} d\theta + \theta \delta S^{(i)} \tag{4.2.8}$$

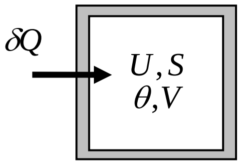


Figure 4.2.1: Pure heating

With $\delta W = dV = 0$, this reduces to

$$\left(\frac{\partial U}{\partial \theta} - \theta \frac{\partial S}{\partial \theta} \right)_{V} d\theta + \theta \delta S^{(i)} = 0 \tag{4.2.9}$$

Now *U* and *S* are state functions, and the partial derivatives and, in particular, the term inside the brackets are also properties of the system. Further, $\delta S^{(i)} \geq 0$, $\theta > 0$, and $d\theta$ can be positive, negative or zero. Since $d\theta$ can be assigned a value completely independently of the value of the term inside the brackets, the equality in Eqn. 4.2.9 can only be satisfied *in general* if both

$$\left(\frac{\partial U}{\partial \theta} - \theta \frac{\partial S}{\partial \theta} \right)_{V} = 0 \quad \text{and} \quad \delta S^{(i)} = 0 \tag{4.2.10}$$

The second equality shows that *a quasi-static pure heating process is always reversible*. As mentioned, the first equality is a relation between state functions and is not path-dependent and hence holds for *all* processes, not just for pure heating.

In reality there is never any such thing as a completely reversible process – in the case of pure heating, a reversible process would require that the temperature at any instant is uniform throughout the material, which will never be exactly true. It will be shown below that if there is any appreciable temperature gradient within a material then there will be entropy production.

Reversible Processes

To be precise, a process is reversible when both the system *and its surroundings* can be returned to their original states. For example, if the material in a piston-cylinder arrangement is compressed quasi-statically and there is no friction between the piston and cylinder walls, then the process is reversible – the load can be reduced by very small amounts and the material will "push back" on the piston returning it to its original configuration, with no net work done or heat supplied to the system.

Irreversible Processes

An irreversible process is one for which there is entropy production, $\delta S^{(i)} > 0$. In practice, irreversibilities are introduced into systems whenever there is spontaneity:

- unrestrained expansion of a gas/liquid to a lower pressure – for example when the lid is taken off a gas at high pressure, and is allowed to escape into the atmosphere
- heat transfer from one part of a material to another part at a lower temperature (except in the ideal case where the temperature difference is infinitesimal)
- friction (both the sliding friction of solid on solid and the friction that occurs between molecules in the flow of fluids)

The common factor amongst all these is that the system and its surroundings cannot be returned to their original configurations. For example, with the piston-cylinder arrangement, friction between the piston head and cylinder walls means that further work needs to be expended on the return stroke so that, although the piston-cylinder is returned to its original state, a net amount of work needs to be done and so the "surroundings", or whatever is producing the work, is not back at its original state. Similarly, if the piston was compressed very quickly to its final position, the temperature, momentarily, might well be higher at the piston head than further down in the material. This would produce a spontaneous heat transfer from the upper part of the material to the lower part and it would not be possible to return the system and its surroundings to their original states.

Irreversible Heat Transfer

In the processes studied so far, it has been assumed that all the state functions were uniform throughout the material. In particular, it has been assumed that the temperature is uniform throughout. What if one now has a system whose parts are at different temperatures?

Suppose that a quantity of heat δQ flows from a body at temperature θ_1 to a body at temperature θ_2, Fig. 4.2.2. One can imagine for the sake of argument that the heat capacities of both bodies are sufficiently large that their temperatures are effectively unchanged by the heat flow. The two bodies are insulated from their surroundings.

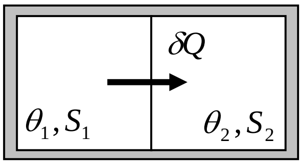


Figure 4.2.2: Heat flow from one body to another

This is pure heating and so the entropy change due to this heat transfer are the entropy supplies $\delta S_1^{(r)} = \delta Q/\theta_1 < 0$ and $\delta S_2^{(r)} = \delta Q/\theta_2 > 0$. Considering now the complete system (both bodies), there is no entropy supply, so any entropy change must be an entropy production

$$\delta S^{(i)} = \frac{\delta Q}{\theta_2} - \frac{\delta Q}{\theta_1} \tag{4.2.11}$$

Since $\delta S^{(i)} \geq 0$, it follows that $\theta_1 > \theta_2$, that is, *heat flows from the warmer body to the colder body*.

In this example there is no work done, no heat transfer and no internal energy change, but there is an entropy change.

If one wants the heat transfer to be very nearly reversible, one can make the entropy production very small. This can be achieved by making the temperature difference between the two bodies very small: by letting $\theta_1 = \theta, \theta_2 = \theta + \Delta\theta$, one has $\delta S^{(i)} \approx -(\delta Q/\theta)(\Delta\theta/\theta)$. Keeping the entropy supply constant, this means that one must make $\Delta\theta/\theta$ as small as possible. Thus heat transfer is reversible *only* if there is an "infinitely small" temperature difference between the two bodies.

Entropy supply is due to heat transfer, but the entropy production here is due to an adiabatic irreversible change.

Entropy Measurements

The entropy of a material can be measured as follows. First, since $dS = \delta Q/\theta + \delta S^{(i)}$, one has $dS = C(d\theta/\theta) + \delta S^{(i)}$ where *C* is the specific heat capacity. Thus, for a *reversible* process, one has

$$\Delta S = \int_{\theta_1}^{\theta_2} C\, d\theta/\theta \qquad \text{(reversible)} \tag{4.2.12}$$

but one must ensure that the entropy production is zero. In practice, what one does is keep $d\theta/\theta$ small enough so that the entropy production is sufficiently small for the accuracy required. Once the entropy change is found, it of course applies to *all* processes, not just the reversible process used in the experiment.

Thermodynamic Equilibrium

Thermodynamic equilibrium has already been mentioned – it occurs when no changes of the state variables can occur. Thus, one requires that $\delta W = \delta Q = dU = 0$. With $\delta Q = 0$, one has $\delta S^{(r)} = 0$ and $dS = dS^{(i)}$. For full equilibrium, one requires that $dS^{(i)} = 0$ but, since entropy production tends always to increase the entropy, thermal equilibrium can only occur if the entropy has reached its *maximum possible value*.

4.2.4 Free Expansion of an Ideal Gas

It was seen that, for an ideal gas undergoing a quasi-static process (see Eqn. 4.1.25),

$$\Delta S = S_2 - S_1 = C_V \ln(\theta_2 / \theta_1) + mR\ln(V_2 / V_1) \tag{4.2.13}$$

and the entropy production is zero. In other words, any quasi-static process involving an ideal gas is reversible.

Consider an isothermal quasi-static process in which an ideal gas is heated very slowly, so that it does work and expands to twice its original volume. One has $\Delta S = mR\ln 2$. This is the change in entropy in the gas; the surroundings has an equal decrease in entropy as heat leaves it so that, by definition, the total entropy change in this reversible process is zero.

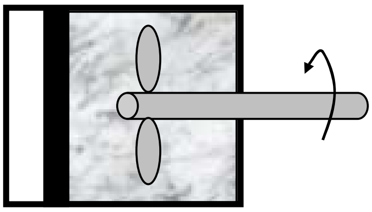
Consider now a thermally insulated container divided by a partition into two parts each of volume V. One of these contains an ideal gas and the other is evacuated. The partition is taken away, so that the gas completely fills the container (see Fig. 4.1.8). During the spontaneous expansion, there is a complex non-equilibrium turbulence. The gas eventually settles down to its new equilibrium position. The initial and final states are as for the reversible heating described above, so the entropy change in the gas must again be $\Delta S = mR\ln 2$. However, here there is no interaction with the surroundings, so this entropy must be entropy production.

4.2.5 Problems

1. A system undergoes a process in which work is done on the system and the heat transfer Q occurs at a constant temperature θ_b. For each case, determine whether the entropy change of the system is positive, negative, zero or indeterminate:
   (a) reversible process, $Q > 0$
   (b) reversible process, $Q = 0$
   (c) reversible process, $Q < 0$
   (d) irreversible process, $Q > 0$
   (e) irreversible process, $Q = 0$
   (f) irreversible process, $Q < 0$

2. A block of lead at temperature $200\ \text{K}$ has heat capacity $C = 1000\ \text{J K}^{-1}$, which is independent of temperature in the range $100 - 200\ \text{K}$. It is to be cooled to $100\ \text{K}$ in liquid baths, which are large enough that their temperatures do not change. Assume that the only heat transfer which occurs is between the liquid baths and the lead block, and that the lead block changes temperature instantaneously/uniformly (so that there is no entropy production *within* the block). What is the entropy supply for the lead and the liquid bath(s), and the net entropy production, during the following processes: the lead is
   (a) plunged straight into a liquid bath at $100\ \text{K}$
   (b) first cooled in a bath at $150\ \text{K}$ and then in a second bath at $100\ \text{K}$
   (c) cooled using four baths at temperatures $175\ \text{K}$, $150\ \text{K}$, $125\ \text{K}$ and $100\ \text{K}$
   (d) cooled in an infinite number of temperature baths with a continuous range from $200\ \text{K}$ to $100\ \text{K}$
   [hint: no work is done; use the lead's heat capacity to evaluate Q]

3. Consider an *insulated* piston-cylinder assembly which initially contains water as a saturated liquid at $100\ \text{C}$ (373.15 K), as illustrated below. A paddle wheel acts on the water, which undergoes a process to the corresponding saturated vapour state at the *same* temperature, during which the piston moves freely in the cylinder (no friction). Using the data below, determine
   (a) the net work per unit mass done – which is greater, the work done by the paddle wheel or that done by the expanding water?
   (b) the specific entropy supply; the specific entropy production – why do you think it is non-zero?
   Next, consider the case where the initial and final states are the same as before, but the change is now brought about by the supply of *heat only* (with no paddle wheel). Determine
   (c) the work done per unit mass[2]
   (d) the heat transfer per unit mass
   (e) the specific entropy supply and the specific entropy production – is this a surprise?



	u (kJ / kg)	v (m^3 / kg)	s (kJ / kg.K)	p (MPa)
Liquid	400	0.001	1.448	0.1014
Gas	2500	1.6	7.510	0.1014

---

[2] the initial and final temperatures and pressures are $100\ \text{C}$ and $0.1014\ \text{MPa}$ – these are the "end-points" for the initial and final *states* – in general, they may not necessarily be constant throughout the process – we do not know (and don't have to know here) how the temperature and pressure changed *during* the process in parts (a-b); with the paddle wheel, the temperature and pressure are unlikely to be uniform throughout the material. For parts (c-e), it is reasonable to assume that they are constant throughout

4. A certain mass of an ideal gas for which $C_V = 3R/2$, independent of temperature, is taken *reversibly* from $\theta = 100$ K, $p = 10^5$ Pa to $\theta = 400$ K, $p = 8\times 10^5$ Pa by two different paths (1) and (2):
   (1) consisting of (a) at constant volume from $\theta = 100 \to 400$ K, (b) isothermally to the final pressure
   (2) consisting of (a) at constant pressure from $\theta = 100 \to 400$ K, (b) isothermally to the final volume

   Calculate the entropy changes and verify that the total entropy change is the same for both paths. Compare this with the heat absorbed or given out for each of paths (1) and (2) – they even turn out to be of opposite sign.
   [hint: use the ideal gas law and the fact that for a constant volume process, $\delta Q = C_V d\theta$; also, use Eqn. 4.2.13, the fact that $Q_{\text{rev}} = \int_{S_1}^{S_2} \theta \, dS$, and the result of Q.8 from section 4.1]

4.3 Thermodynamic Functions

Four important and useful thermodynamic functions will be considered in this section (two of them have been encountered in the previous sections). These are the **internal energy** U, the **enthalpy** H, the **Helmholtz free energy** (or simply the **free energy**) Ψ and the **Gibbs free energy** (or simply the **Gibbs function**) G. These functions will be defined and examined below for both reversible and irreversible processes.

4.3.1 Reversible Processes

Consider first a reversible process.

The Internal Energy

The internal energy is

$$\begin{aligned} dU &= \delta W + \delta Q \\ &= -p dV + \theta dS \end{aligned} \tag{4.3.1}$$

the second line being valid for quasi-static processes. The properties of a pure compressible substance include V, θ, S and p. From 4.3.1, it is natural to take V and S as the state variables:

$$dU = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS \tag{4.3.2}$$

so that

$$p = -\left(\frac{\partial U}{\partial V}\right)_S, \qquad \theta = \left(\frac{\partial U}{\partial S}\right)_V \tag{4.3.3}$$

Thus $U(V,S)$ contains all the thermodynamic information about the system; given V and S one has an expression for U and can evaluate p and θ through differentiation. U is a **thermodynamic potential**, meaning that it provides information through a differentiation.

V and S are said to be the **canonical** (**natural**) **state variables** for U. By contrast, expressing the internal energy as a function of the volume and temperature, for example, $U = U(V,\theta)$, is not so useful, since this cannot provide all the necessary information regarding the state of the material. A new state function will be introduced below which has V and θ as canonical state variables.

Similarly, the equation of state $\theta(V, p)$ does not contain all the thermodynamic information. For example, there is no information about U or S, and this equation of state must be supplemented by another, just as the ideal gas law is supplemented by the caloric equation of state $U = U(\theta)$.

Returning to the internal energy function, and taking the differential relations between p, θ and U, Eqns. 4.3.3, and differentiating them again, and using the fact that $\partial^2 U / \partial V \partial S = \partial^2 U / \partial S \partial V$, one arrives at the **Maxwell relation**,

$$-\left(\frac{\partial p}{\partial S}\right)_V = \left(\frac{\partial \theta}{\partial V}\right)_S \tag{4.3.4}$$

The Helmholtz Free Energy

Define the **(Helmholtz) free energy function** through

$$\Psi = U - \theta S \tag{4.3.5}$$

One has

$$\begin{aligned} d\Psi &= dU - \theta dS - S d\theta \\ &= dU - \delta Q - S d\theta \quad , \\ &= -pdV - Sd\theta \end{aligned} \tag{4.3.6}$$

the second line being valid for reversible processes. Now V and θ have emerged as the natural state variables. Writing $\Psi = \Psi(V, \theta)$,

$$d\Psi = \left(\frac{\partial \Psi}{\partial V}\right)_\theta dV + \left(\frac{\partial \Psi}{\partial \theta}\right)_V d\theta \tag{4.3.7}$$

so that

$$p = -\left(\frac{\partial \Psi}{\partial V}\right)_\theta, \qquad S = -\left(\frac{\partial \Psi}{\partial \theta}\right)_V \tag{4.3.8}$$

The Enthalpy and Gibbs Free Energy

The enthalpy is defined by Eqn. 4.1.18,

$$H = U + pV \tag{4.3.9}$$

To determine the canonical state variables, evaluate the increment:

$$\begin{aligned} dH &= dU + pdV + Vdp \\ &= \delta W + \delta Q + pdV + Vdp \end{aligned} \tag{4.3.10}$$

and so

$$dH = \theta dS + Vdp \tag{4.3.11}$$

and the natural variables are p and S. Finally, the Gibbs free energy function is defined by

$$G = U - \theta S + pV \tag{4.3.12}$$

and the canonical state variables are p and θ.

The definitions, canonical state variables and Maxwell relations for all four functions are summarised in Table 4.3.1 below.

Thermo-dynamic potential	Symbol and appropriate variables	Definition	Differential relationship	Maxwell relation
Internal energy	$U(S,V)$		$dU = -pdV + \theta dS$	$\theta = \left(\frac{\partial U}{\partial S}\right)_V,\ p = -\left(\frac{\partial U}{\partial V}\right)_S$ $\left(\frac{\partial \theta}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
Enthalpy	$H(S,p)$	$H = U + pV$	$dH = Vdp + \theta dS$	$\theta = \left(\frac{\partial H}{\partial S}\right)_p,\ V = \left(\frac{\partial H}{\partial p}\right)_S$ $\left(\frac{\partial \theta}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
Helmholtz free energy	$\Psi(\theta,V)$	$\Psi = U - \theta S$	$d\Psi = -pdV - Sd\theta$	$S = -\left(\frac{\partial \Psi}{\partial \theta}\right)_V,\ p = -\left(\frac{\partial \Psi}{\partial V}\right)_\theta$ $\left(\frac{\partial S}{\partial V}\right)_\theta = \left(\frac{\partial p}{\partial \theta}\right)_V$
Gibbs free energy	$G(\theta,p)$	$G = U - \theta S + pV$	$dG = Vdp - Sd\theta$	$S = -\left(\frac{\partial G}{\partial \theta}\right)_p,\ V = \left(\frac{\partial G}{\partial p}\right)_\theta$ $\left(\frac{\partial S}{\partial p}\right)_\theta = -\left(\frac{\partial V}{\partial \theta}\right)_p$

Table 4.3.1: Thermodynamic Potential Functions and Maxwell relations

Mechanical variables: whereas the internal energy and the Helmholtz free energy are functions of a kinematic variable (V), the enthalpy and the Gibbs function are functions of a force variable (p).

Thermal variables: whereas the internal energy and the enthalpy are functions of the entropy, the Helmholtz and Gibbs free energy functions are functions of the temperature.

If one is analyzing a process with, for example, *constant* temperature, it makes sense to use either the Helmholtz or Gibbs free energy functions, so that there is only one variable to consider.

Note that the temperature is an observable property and can be controlled to some extent. Values for the entropy, on the other hand, cannot be assigned arbitrary values in experiments. For this reason a description in terms of the free energy, for example, is often more useful than a description in terms of the internal energy.

4.3.2 Irreversible Processes

Consider now an irreversible process.

The Internal Energy

One has $\delta W = dU - \theta dS + \theta \delta S^{(i)}$ and, with the internal energy again a function of the entropy and volume,

$$\delta W = \left[\left(\frac{\partial U}{\partial S} \right)_V - \theta \right] dS + \left(\frac{\partial U}{\partial V} \right)_S dV + \theta \delta S^{(i)} \qquad (4.3.13)$$

Consider the case of pure heating $\delta W = dV = \delta S^{(i)} = 0$, so

$$\theta = \left(\frac{\partial U}{\partial S} \right)_V \qquad (4.3.14)$$

as in the reversible case. This relation between properties is of course valid for any process, not necessarily a pure heating one. Thus

$$\delta W = \left(\frac{\partial U}{\partial V} \right)_S dV + \theta \delta S^{(i)} \qquad (4.3.15)$$

Express the work in the form

$$\boxed{\begin{aligned} \delta W &= dW^{(q)} + \delta W^{(d)} \\ &= A^{(q)} dV + A^{(d)} dV \end{aligned}} \qquad (4.3.16)$$

such that the **quasi-conservative force** $A^{(q)}$ is that associated with the work $W^{(q)}$ which is recoverable, whilst the **dissipative force** A^d produces the work $W^{(d)}$ which is dissipated, i.e. associated with irreversibilities.

From 4.3.15,

$$A^{(q)} = \left(\frac{\partial U}{\partial V} \right)_S \qquad (4.3.17)$$

and the **dissipative work** $\delta W^{(d)}$ is

$$\delta W^{(d)} = A^{(d)} dV = \theta \delta S^{(i)} \geq 0 \qquad (4.3.18)$$

The name *quasi-conservative force* for the $A^{(q)}$ (here, actually a force per area) is in recognition that the internal energy plays the role of a potential in 4.3.17, but it is also a function of the entropy. It can be seen from Eqn. 4.3.17 that the quasi-conservative force is a state function, and equals $-p$ in a fully reversible process.

In the **isentropic** case, $dS = 0$, and one has

$$\delta W = dU + \theta \delta S^{(i)} \tag{4.3.19}$$

This shows that, in the isentropic case, the internal energy is that part of the work which is recoverable.

The Free Energy

Directly from $\Psi = U - \theta S$, with θ and V the independent variables,

$$\frac{\partial \Psi}{\partial \theta} = \left(\frac{\partial U}{\partial \theta} - \theta \frac{\partial S}{\partial \theta} \right) - S, \qquad \frac{\partial \Psi}{\partial V} = \frac{\partial U}{\partial V} - \theta \frac{\partial S}{\partial V} \tag{4.3.20}$$

From the pure heating analysis given earlier, Eqn. 4.2.9-10, the term $\partial U / \partial \theta - \theta \partial S / \partial \theta$ is zero, so

$$S = -\left(\frac{\partial \Psi}{\partial \theta} \right)_V \tag{4.3.21}$$

as in the reversible case and

$$d\Psi = \left(\frac{\partial \Psi}{\partial V} \right)_\theta dV - S d\theta \tag{4.3.22}$$

The work can now be written again as Eqn. 4.3.16, but now with the quasi-conservative force given by {▲Problem 3}

$$A^{(q)} = \left(\frac{\partial \Psi}{\partial V} \right)_\theta \tag{4.3.23}$$

The dissipative work is again given by 4.3.18. Also, $A^{(q)} = -p$ for a reversible process.

In the isothermal case, $d\theta = 0$,

$$\delta W = d\Psi + \theta \delta S^{(i)} \tag{4.3.24}$$

This shows that, in the isothermal case, the free energy is that part of the work which is recoverable.

The quasi-conservative forces for the internal energy and free energy are listed in Table 4.3.2. Note that expressions for quasi-conservative forces are not available in the case of the Enthalpy and Gibbs free energy since they do not permit in their expression increments in volume dV, which are required for expressions of work increment.

Thermo-dynamic potential	Differential relationship	Relations
$U(S,V)$	$dU = -pdV + \theta dS - \theta\delta S^{(i)}$	$\theta = \left(\frac{\partial U}{\partial S}\right)_V$, $A^{(q)} = \left(\frac{\partial U}{\partial V}\right)_S$
$\Psi(\theta,V) = U - \theta S$	$d\Psi = -pdV - Sd\theta - \theta\delta S^{(i)}$	$S = -\left(\frac{\partial \Psi}{\partial \theta}\right)_v$, $A^{(q)} = \left(\frac{\partial \Psi}{\partial V}\right)_\theta$

Table 4.3.2: Quasi-Conservative Forces for Irreversible Processes,
$\delta W = A^{(q)}dV + \theta\delta S^{(i)} = -pdV$

4.3.3 The Legendre Transformation

The thermodynamic functions can be transformed into one another using a mathematical technique called the **Legendre Transformation**. The Legendre Transformation is discussed in detail in Part IV, where it plays an important role in Plasticity Theory, and other topics. For the present purposes, note that the Legendre transformation of a function $f(x,y)$ is the function $g(\alpha,\beta)$ where

$$g(\alpha,\beta) = \alpha x + \beta y - f(x,y) \tag{4.3.25}$$

and

$$\alpha = \frac{\partial f}{\partial x}, \beta = \frac{\partial f}{\partial y}, \qquad x = \frac{\partial g}{\partial \alpha}, y = \frac{\partial g}{\partial \beta} \tag{4.3.26}$$

When only one of the two variables is switched, the transform reads

$$g(\alpha,y) = \alpha x - f(x,y) \tag{4.3.27}$$

where

$$\alpha = \frac{\partial f}{\partial x}, \qquad x = \frac{\partial g}{\partial \alpha} \tag{4.3.28}$$

For example, if one has the function $U(S,V)$ and wants to switch the independent variable from S to θ, Eqn. 4.3.27 leads one to consider the new function

$$g(\theta,V) = \theta S - U(S,V) \tag{4.3.29}$$

and Eqns. 4.3.28 give

$$\theta = \left(\frac{\partial U}{\partial S}\right)_V \quad \text{and} \quad S = \left(\frac{\partial g}{\partial \theta}\right)_V \tag{4.3.30}$$

It can be seen that $g(\theta,V)$ is the negative of the Helmholtz free energy and the two differential relations in 4.3.30 are contained in Table 4.3.1.

4.3.4 Problems

1. By considering reversible processes, derive the differential relationships and the Maxwell relations given in Table 4.3.1 for (a) the enthalpy, (b) the Gibbs free energy

2. Let the two independent variables be V and θ. Consider the internal energy, $U = U(V,\theta)$. Use the pure heating example considered in §4.2 to show that the quasi-conservative force of Eqn. 4.3.17 can also be expressed as
$$A^{(q)} = \left(\frac{\partial U}{\partial V} - \theta\frac{\partial S}{\partial V}\right)_\theta$$

3. Show that Eqn. 4.3.22 leads to Eqn. 4.3.23.

4. Use the Legendre Transformation rule to transform the Helmholtz free energy $\Psi(\theta,V)$ into a function of the variables θ and σ. Derive also the two differential relations analogous to Eqns. 4.3.30. Show that this new function is the negative of the Gibbs energy (use the relation $\Psi = U - \theta S$), where $\sigma = -p$, and that the two differential relations correspond to two of the relations in Table 4.3.1.

5. Use the Legendre Transformation rule to transform the enthalpy $H(S,p)$ into a function of the variables S and V. Show that this new function is the negative of the internal energy, and that the two differential relations correspond to two of the relations in Table 4.3.1.

4.4 Continuum Thermomechanics

The classical thermodynamics is now extended to the thermomechanics of a continuum. The state variables are allowed to vary throughout a material and processes are allowed to be irreversible and move far from thermal and mechanical equilibrium. Some schools of thought would question whether entropy is a state function at all under these conditions. Here, we simply accept the fact that it is. This is part of the **rational thermodynamics** approach and is generally accepted in the solid mechanics community.

4.4.1 The First Law

The first law of thermodynamics is, in rate form,

$$P_{ext} + Q^{*} = \dot{U} + \dot{K} \tag{4.4.1}$$

where P_{ext} is the power of the external forces, Q^{*} is the rate at which heat is supplied (called the **thermal power**, the **non-mechanical power**, or the **rate of thermal work**), $\dot{U}$ is the rate of change of the internal energy and $\dot{K}$ is the rate of change of kinetic energy. The superscript "*" is used here and in what follows to indicate rates of change of quantities which are not state functions.

Recall from Part III, Eqn 3.8.2, the mechanical energy balance,

$$P_{\text{ext}} + P_{\text{int}} = \dot{K} \tag{4.4.2}$$

Eliminating P_{ext} and $\dot{K}$ from these equations leads to

$$-P_{\text{int}} + Q^{*} = \dot{U} \tag{4.4.3}$$

Heat supply

It is convenient to write the total heat supply to a finite volume of material as an integral over the volume. This is done by defining the **heat flux q** to be the rate at which heat is conducted from interior to exterior per unit area, Fig. 4.4.1. The rate of heat *entering* is thus $-\int_s \mathbf{q}\cdot\mathbf{n}ds$. Let there also be a source of heat supply inside the material, for example a radiator of heat. Let $\int_v r dv$ be the rate of such heat supply, where the scalar *r* is the **heat source**, the rate of heat generated per unit volume. Thus, with the divergence theorem,

$$Q^{*} = -\int_v \text{div}\mathbf{q}\,dv + \int_v r\,dv \tag{4.4.4}$$

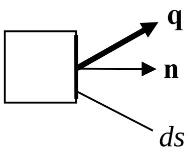


Figure 4.4.1: heat flux vector and normal vector to a surface element

Recall also from Part III, Eqns. 3.8.15, the stress power

$$P_{\text{int}} = -\int_v \boldsymbol{\sigma} : \mathbf{d} dv \tag{4.4.5}$$

Combining Eqns. 4.4.3-5, and expressing the strain energy rate in the form of an integral (see Part III, Eqn. 3.8.15) leads to

$$\int_v \boldsymbol{\sigma} : \mathbf{d} dv - \int_v \text{div}\mathbf{q} dv + \int_v r dv = \int_v \rho \dot{u} dv \tag{4.4.6}$$

Since this holds for all volumes *v*, one has the local form

$$\boxed{\boldsymbol{\sigma} : \mathbf{d} - \text{div}\mathbf{q} + r = \rho \dot{u}} \qquad \textbf{The First Law} \tag{4.4.7}$$

4.4.2 The Second Law

Entropy

The entropy $S(\mathbf{x}, t)$ is defined as the scalar property

$$S = \int_v \rho s dv \tag{4.4.8}$$

where *s* is the specific entropy or **entropy density**. The change in entropy is due to two quantities. First, very like the heat transferred into a body, Eqn. 4.4.4, define the entropy supply $S^{(r)*}$ to be the rate of entropy input,

$$S^{(r)*} = -\int_s \mathbf{s}_\mathbf{q} \cdot \mathbf{n} ds + \int_v s_r dv \tag{4.4.9}$$

where $\mathbf{s}_\mathbf{q}$ is the **entropy flux** through the element surface and s_r is entropy supply due to sources within the element . Further, the entropy flux is taken to be proportional to the heat flux, and the proportionality factor is the reciprocal of the non-negative scalar **absolute temperature** θ (and similarly for the density s_r and the heat supply density *r*) so that, using the divergence theorem,

$$\begin{aligned} S^{(r)*} &= -\int_s \frac{\mathbf{q}}{\theta}\cdot\mathbf{n}\,ds + \int_v \frac{r}{\theta}dv \\ &= -\int_v \operatorname{div}\left(\frac{\mathbf{q}}{\theta}\right)dv + \int_v \frac{r}{\theta}dv \end{aligned} \tag{4.4.10}$$

Define the entropy production $S^{(i)*}$ to be the difference between the rate of change of entropy and the entropy supply:

$$S^{(i)*} = \dot{S} - S^{(r)*} \tag{4.4.11}$$

The second law of thermodynamics states that the entropy production is a non-negative quantity,

$$S^{(i)*} \geq 0 \tag{4.4.12}$$

The Clausius-Duhem Inequality

Thus one has the **Clausius-Duhem inequality**:

$$S^{(i)*} = \frac{d}{dt}\int_v \rho s dv + \int_v \operatorname{div}\left(\frac{\mathbf{q}}{\theta}\right)dv - \int_v \frac{r}{\theta}dv \geq 0 \tag{4.4.13}$$

In local form, the Clausius-Duhem inequality reads as (introducing a specific entropy production, $s^{(i)*}$)

$$s^{(i)*} = \dot{s} + \frac{1}{\rho}\operatorname{div}\left(\frac{\mathbf{q}}{\theta}\right) - \frac{r}{\rho\theta} \geq 0 \tag{4.4.14}$$

or, equivalently {▲Problem 1},

$$\boxed{s^{(i)*} = \dot{s} - \frac{r}{\rho\theta} + \frac{1}{\rho\theta}\operatorname{div}\mathbf{q} - \frac{1}{\rho\theta^2}(\mathbf{q}\cdot\nabla\theta) \geq 0} \quad \textbf{The Second Law} \tag{4.4.15}$$

This is the continuum statement of the Second Law.

4.4.3 The Dissipation Inequality

Eliminating $\operatorname{div}\mathbf{q}$ (and *r*) from both the first and second laws leads to the **dissipation inequality**

$$\boxed{\theta s^{(i)*} = \theta\dot{s} - \dot{u} + \frac{1}{\rho}(\boldsymbol{\sigma}:\mathbf{d}) - \frac{1}{\rho\theta}(\mathbf{q}\cdot\nabla\theta) \geq 0} \quad \textbf{Dissipation Inequality} \tag{4.4.16}$$

The term $\theta\dot{s}^{(i)*}$ is the specific dissipation (or **internal dissipation**) and is denoted by the symbol ϕ. The Clausius-Duhem inequality can simply be written as

$$\phi \equiv \theta\dot{s}^{(i)*} \geq 0 \tag{4.4.17}$$

Multiplying Eqn. 4.4.16 across by the density leads to

$$\rho\theta\dot{s}^{(i)*} = \left[\rho\theta\dot{s} - \rho\dot{u} + \boldsymbol{\sigma} : \mathbf{d}\right] + \left[-\frac{1}{\theta}(\mathbf{q} \cdot \nabla\theta)\right] \geq 0 \tag{4.4.18}$$

Each term here has units of power per unit (current) volume. The term inside the first bracket is called the **mechanical dissipation** (per unit volume). The term inside the second bracket is the dissipation due to temperature gradients, i.e. heat flow, and is called the **thermal dissipation** (per unit volume). Note that the thermal dissipation will always be positive if **q** and $\nabla\theta$ are of opposite sign. Integrating over a volume *v* leads to

$$\underbrace{\int_v \rho\theta\dot{s}^{(i)*} dv}_{\text{dissipation}} = \underbrace{\int_v \{\boldsymbol{\sigma} : \mathbf{d} - \rho\dot{u} + \rho\theta\dot{s}\} dv}_{\text{mechanical dissipation}} + \underbrace{\int_v \left\{-\frac{1}{\theta}(\nabla\theta \cdot \mathbf{q})\right\} dv}_{\text{thermal dissipation}} \tag{4.4.19}$$

The term $\rho\theta\dot{s}^{(i)*}$ in Eqn. 4.4.18 is often denoted by the symbol γ and also termed the dissipation. This is a dissipation per unit volume. When the deformations are small, the volume changes are negligible. When the deformations are appreciable, however, the volume and density change, and it is better to work with specific quantities such as ϕ.

The dissipation inequality 4.4.16 is in terms of the internal energy. In terms of the specific free energy $\psi = u - s\theta$, one has

$$\phi = \theta\dot{s}^{(i)*} = -s\dot{\theta} - \dot{\psi} + \frac{1}{\rho}(\boldsymbol{\sigma} : \mathbf{d}) - \frac{1}{\rho\theta}(\mathbf{q} \cdot \nabla\theta) \geq 0 \tag{4.4.20}$$

4.4.4 The Clausius-Plank Inequality

In many applications the thermal dissipation is very much smaller than the mechanical dissipation (in fact it is zero in many important applications – see section 4.4.7 below). If this is the case then the thermal dissipation rate can be ignored, and one has the stronger form of the second law, in terms of internal energy and free energy,

$$\boxed{\begin{aligned}&\phi = \theta\dot{s} - \dot{u} + \frac{1}{\rho}(\boldsymbol{\sigma} : \mathbf{d}) \geq 0\\ &\phi = -s\dot{\theta} - \dot{\psi} + \frac{1}{\rho}(\boldsymbol{\sigma} : \mathbf{d}) \geq 0\end{aligned}} \quad \textbf{Clausius-Plank inequality} \qquad (4.4.21)$$

which is known as the **Clausius-Plank inequality**.

Equivalently, one can argue that the processes of mechanical dissipation and heat flow are independent, so that each are separately required to be non-negative, again leading to Eqn. 4.4.21. This issue will be explored more fully in Part IV, where it will indeed be shown that the thermal dissipation is very often decoupled from the mechanical dissipation, with both being required to be separately positive.

Using the first law, Eqn. 4.4.21 can be rewritten in the alternative form

$$\theta\dot{s} = \phi + \frac{1}{\rho}r - \frac{1}{\rho}\mathrm{div}\mathbf{q} \qquad (4.4.22)$$

which is an **evolution equation** for s (showing how it evolves over time).

4.4.5 Special Thermodynamic Processes

Some important limiting processes are considered next.

Reversible Processes

In a reversible process, $\phi = s^{(i)*} = 0$. The Clausius-Plank inequality now becomes

$$\dot{u} = \theta\dot{s} + \frac{1}{\rho}(\boldsymbol{\sigma} : \mathbf{d}) \quad \text{or} \quad \dot{\psi} = -s\dot{\theta} + \frac{1}{\rho}(\boldsymbol{\sigma} : \mathbf{d}) \qquad (4.4.23)$$

From the First Law,

$$\rho\dot{s} = -\frac{\mathrm{div}\mathbf{q}}{\theta} \qquad (4.4.24)$$

This is the entropy supply (with zero temperature gradients) and corresponds to the classical thermodynamic (for which, also, $\nabla\theta = 0$) expression $dS^{(r)} = \delta Q/\theta$.

Isentropic Conditions

For an isentropic process, the entropy is constant and remains constant, so $\dot{s} = 0$. In this case, the dissipation is

$$\phi = -\dot{u} + \frac{1}{\rho}(\boldsymbol{\sigma} : \mathbf{d}) - \frac{1}{\rho\theta}(\mathbf{q} \cdot \nabla\theta) \geq 0 \qquad (4.4.25)$$

Isothermal Conditions

In an isothermal process, the absolute temperature remains constant, $\dot{\theta} = 0$. This can be achieved, for example, by keeping the material's surroundings at constant temperature, and loading the material very slowly, so that any temperature differences which arise between the material and surroundings are allowed to disappear.

The Clausius-Plank inequality becomes

$$\phi = \theta\dot{s} - \dot{u} + \frac{1}{\rho}(\boldsymbol{\sigma} : \mathbf{d}) \geq 0 \quad \text{or} \quad \phi = -\dot{\psi} + \frac{1}{\rho}(\boldsymbol{\sigma} : \mathbf{d}) \geq 0 \qquad (4.4.26)$$

Equilibrium Conditions

As mentioned in §4.2.3, a material which is unaffected by external conditions has no work done to it or heat supplied and the first law then states that the internal energy is constant. In that case, when the entropy has reached a maximum and the dissipation is zero, there is no more change in any of the state variables, and equilibrium has been reached.

Adiabatic Conditions

In an adiabatic process, $\mathbf{q} = \mathbf{o}$. This can be achieved, for example, by very rapid loading, so that there is no time for heat exchange with the surroundings.

Under these conditions (and taking also $r = 0$), the first law reads $\boldsymbol{\sigma} : \mathbf{d} = \rho\dot{u}$ (recall that the internal energy change is equal to the work done in an adiabatic process). The dissipation inequality reduces to

$$s^{(i)*} = \dot{s} \geq 0 \qquad (4.4.27)$$

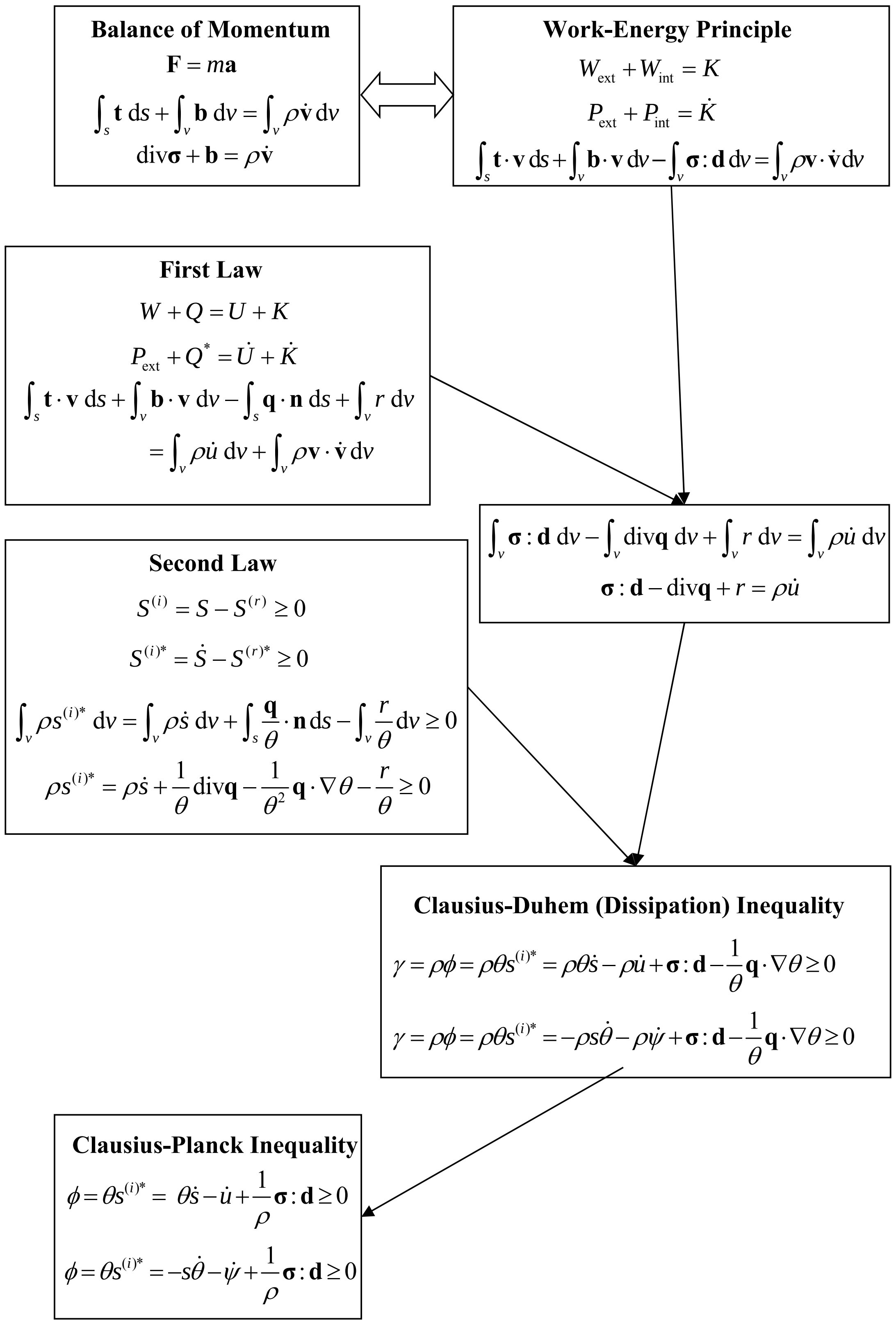
or

$$\phi = \theta\dot{s} \geq 0 \qquad (4.4.28)$$

If the process is both adiabatic and isentropic, then $\phi = \dot{s} = 0$. An adiabatic reversible process is equivalent to an isentropic reversible process.

4.4.6 Summary

A summary of the thermomechanical theory, showing the various laws and relations which are involved, and how they are interconnected, is given in Fig. 4.4.2 below.



Balance of Momentum

$$\mathbf{F} = m\mathbf{a}$$

$$\int_s \mathbf{t}\,\mathrm{d}s + \int_v \mathbf{b}\,\mathrm{d}v = \int_v \rho\dot{\mathbf{v}}\,\mathrm{d}v$$

$$\mathrm{div}\boldsymbol{\sigma} + \mathbf{b} = \rho\dot{\mathbf{v}}$$

Work-Energy Principle

$$W_{\mathrm{ext}} + W_{\mathrm{int}} = K$$

$$P_{\mathrm{ext}} + P_{\mathrm{int}} = \dot{K}$$

$$\int_s \mathbf{t}\cdot\mathbf{v}\,\mathrm{d}s + \int_v \mathbf{b}\cdot\mathbf{v}\,\mathrm{d}v - \int_v \boldsymbol{\sigma}:\mathbf{d}\,\mathrm{d}v = \int_v \rho\mathbf{v}\cdot\dot{\mathbf{v}}\,\mathrm{d}v$$

First Law

$$W + Q = U + K$$

$$P_{\mathrm{ext}} + Q^{*} = \dot{U} + \dot{K}$$

$$\int_s \mathbf{t}\cdot\mathbf{v}\,\mathrm{d}s + \int_v \mathbf{b}\cdot\mathbf{v}\,\mathrm{d}v - \int_s \mathbf{q}\cdot\mathbf{n}\,\mathrm{d}s + \int_v r\,\mathrm{d}v = \int_v \rho\dot{u}\,\mathrm{d}v + \int_v \rho\mathbf{v}\cdot\dot{\mathbf{v}}\,\mathrm{d}v$$

$$\int_v \boldsymbol{\sigma}:\mathbf{d}\,\mathrm{d}v - \int_v \mathrm{div}\mathbf{q}\,\mathrm{d}v + \int_v r\,\mathrm{d}v = \int_v \rho\dot{u}\,\mathrm{d}v$$

$$\boldsymbol{\sigma}:\mathbf{d} - \mathrm{div}\mathbf{q} + r = \rho\dot{u}$$

Second Law

$$S^{(i)} = S - S^{(r)} \geq 0$$

$$S^{(i)*} = \dot{S} - S^{(r)*} \geq 0$$

$$\int_v \rho s^{(i)*}\,\mathrm{d}v = \int_v \rho\dot{s}\,\mathrm{d}v + \int_s \frac{\mathbf{q}}{\theta}\cdot\mathbf{n}\,\mathrm{d}s - \int_v \frac{r}{\theta}\mathrm{d}v \geq 0$$

$$\rho s^{(i)*} = \rho\dot{s} + \frac{1}{\theta}\mathrm{div}\mathbf{q} - \frac{1}{\theta^2}\mathbf{q}\cdot\nabla\theta - \frac{r}{\theta} \geq 0$$

Clausius-Duhem (Dissipation) Inequality

$$\gamma = \rho\phi = \rho\theta s^{(i)*} = \rho\theta\dot{s} - \rho\dot{u} + \boldsymbol{\sigma}:\mathbf{d} - \frac{1}{\theta}\mathbf{q}\cdot\nabla\theta \geq 0$$

$$\gamma = \rho\phi = \rho\theta s^{(i)*} = -\rho s\dot{\theta} - \rho\dot{\psi} + \boldsymbol{\sigma}:\mathbf{d} - \frac{1}{\theta}\mathbf{q}\cdot\nabla\theta \geq 0$$

Clausius-Planck Inequality

$$\phi = \theta s^{(i)*} = \theta\dot{s} - \dot{u} + \frac{1}{\rho}\boldsymbol{\sigma}:\mathbf{d} \geq 0$$

$$\phi = \theta s^{(i)*} = -s\dot{\theta} - \dot{\psi} + \frac{1}{\rho}\boldsymbol{\sigma}:\mathbf{d} \geq 0$$

Figure 4.4.2: Thermomechanics

4.4.7 The use of Thermomechanics in Developing Material Models

Material models and the consequences of the laws of thermomechanics will be discussed in depth in Part IV. Here, as an introduction, the case of small-strain elastic/thermoelastic materials will be touched upon briefly.

The classical thermodynamic expression for the work done to a system is $\delta W = -pdV$. This was generalised to the continuum statement for the power exerted on an infinitesimal element, $\boldsymbol{\sigma} : \mathbf{d}$. In the same way, the kinematic variable of the classical thermodynamic system, *V*, is generalised to the case of a continuum by considering the state to be a function of the *strains*.

When the strains are small, the rate of deformation is equivalent to the time rate of change of the small strain tensor:

$$\mathbf{d} = \dot{\boldsymbol{\varepsilon}}, \qquad d_{ij} = \dot{\varepsilon}_{ij} \tag{4.4.29}$$

The dissipation inequalities are then

$$\phi = \theta\dot{s} - \dot{u} + \frac{1}{\rho}\sigma_{ij}\dot{\varepsilon}_{ij} - \frac{1}{\rho\theta}q_i\theta_{,i} \ge 0, \qquad \phi = \theta\dot{s} - \dot{u} + \frac{1}{\rho}\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \frac{1}{\rho\theta}\mathbf{q}\cdot\nabla\theta \ge 0$$

or

$$\phi = -s\dot{\theta} - \dot{\psi} + \frac{1}{\rho}\sigma_{ij}\dot{\varepsilon}_{ij} - \frac{1}{\rho\theta}q_i\theta_{,i} \ge 0, \quad \phi = -s\dot{\theta} - \dot{\psi} + \frac{1}{\rho}\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \frac{1}{\rho\theta}\mathbf{q}\cdot\nabla\theta \ge 0 \tag{4.4.30}$$

Reversible Process

In the case of reversible processes:

$$\theta\dot{s} - \dot{u} + \frac{1}{\rho}\sigma_{ij}\dot{\varepsilon}_{ij} - \frac{1}{\rho\theta}q_i\theta_{,i} = 0, \qquad \theta\dot{s} - \dot{u} + \frac{1}{\rho}\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \frac{1}{\rho\theta}\mathbf{q}\cdot\nabla\theta = 0$$

or

$$-s\dot{\theta} - \dot{\psi} + \frac{1}{\rho}\sigma_{ij}\dot{\varepsilon}_{ij} - \frac{1}{\rho\theta}q_i\theta_{,i} = 0, \qquad -s\dot{\theta} - \dot{\psi} + \frac{1}{\rho}\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} - \frac{1}{\rho\theta}\mathbf{q}\cdot\nabla\theta = 0 \tag{4.4.31}$$

Consider now a material whose state is completely defined by the set of state variables $(\theta, \varepsilon_{ij})$, so the free energy state function is $\psi = \psi(\theta, \varepsilon_{ij})$. This defines the **thermoelastic material**. The internal energy is expressed in canonical form as $u = u(s, \varepsilon_{ij})$ (see section 4.3). One then has

$$\dot{u} = \frac{\partial u}{\partial s}\dot{s} + \frac{\partial u}{\partial \varepsilon_{ij}}\dot{\varepsilon}_{ij} \quad \text{and} \quad \dot{\psi} = \frac{\partial \psi}{\partial \theta}\dot{\theta} + \frac{\partial \psi}{\partial \varepsilon_{ij}}\dot{\varepsilon}_{ij} \tag{4.4.32}$$

Thus

$$\left(\theta-\frac{\partial u}{\partial s}\right)\dot{s}+\left(\frac{1}{\rho}\sigma_{ij}-\frac{\partial u}{\partial \varepsilon_{ij}}\right)\dot{\varepsilon}_{ij}+\frac{1}{\rho\theta}q_i\theta_{,i}=0$$
$$\left(\theta-\frac{\partial u}{\partial s}\right)\dot{s}+\left(\frac{1}{\rho}\boldsymbol{\sigma}-\frac{\partial u}{\partial \boldsymbol{\varepsilon}}\right):\dot{\boldsymbol{\varepsilon}}+\frac{1}{\rho\theta}\mathbf{q}\cdot\nabla\theta=0$$
or
$$-\left(s+\frac{\partial \psi}{\partial \theta}\right)\dot{\theta}+\left(\frac{1}{\rho}\sigma_{ij}-\frac{\partial \psi}{\partial \varepsilon_{ij}}\right)\dot{\varepsilon}_{ij}-\frac{1}{\rho\theta}q_i\theta_{,i}=0$$
$$-\left(s+\frac{\partial \psi}{\partial \theta}\right)\dot{\theta}+\left(\frac{1}{\rho}\boldsymbol{\sigma}-\frac{\partial \psi}{\partial \boldsymbol{\varepsilon}}\right):\dot{\boldsymbol{\varepsilon}}-\frac{1}{\rho\theta}\mathbf{q}\cdot\nabla\theta=0$$

(4.4.33)

Consider now the free energy equation here (the argument which follows applies also to the internal energy equation). The state variables are $(\theta, \varepsilon_{ij})$ and the other properties are state functions of these variables; these include all the terms inside the brackets, that is, s, ψ, σ_{ij} and also the partial derivatives. For any particular state, these properties will have certain values. On the other hand, no matter the state, the variables $\dot{\theta}, \dot{\varepsilon}_{ij}, \theta_{,i}$ can (in theory) be assigned arbitrary values: negative, zero or positive. The terms which pre-multiply $\dot{\theta}, \dot{\varepsilon}_{ij}$ are *completely independent* of these variables – indeed, this fact is built into the model under consideration: the state is a function of $(\theta, \varepsilon_{ij})$ only and is not, for example, dependent on the values of $\dot{\theta}, \dot{\varepsilon}_{ij}, \theta_{,i}$. On the other hand, **q** is not a state function and in fact may be a function of the temperature gradients. The only way that Eqn. 4.4.33 can be satisfied in general, then, is for

$$\nabla\theta=0 \qquad (4.4.34)$$

and the following relations must hold (compare these with 4.3.3 and 4.3.8):

$$\boxed{\theta=\frac{\partial u}{\partial s}, \quad \sigma_{ij}=\rho\frac{\partial u}{\partial \varepsilon_{ij}}} \quad \text{and} \quad \boxed{s=-\frac{\partial \psi}{\partial \theta}, \quad \sigma_{ij}=\rho\frac{\partial \psi}{\partial \varepsilon_{ij}}} \qquad (4.4.35)$$

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Note that the density (and volume) changes for small strains may be neglected, so that the density in 4.4.35 can be taken to be the current density or the density in the undeformed configuration, ρ_0.

4.4.8 Thermomechanics in the Material Form

The dissipation inequality is derived here for the case of the material description.

The First Law

In order to rewrite the energy balance equations in material form, first introduce the scalars (what follows is analogous to the definitions of traction and stress with respect to the current and reference configurations)

$$\begin{aligned} q^{(\mathbf{n})} &= -\mathbf{q}\cdot\mathbf{n} \\ Q^{(\mathbf{N})} &= -\mathbf{Q}\cdot\mathbf{N} \end{aligned} \tag{4.4.36}$$

Here **q** is the **Cauchy heat flux** of Eqn. 4.4.4, defined per unit current surface area ds with outward normal **n**, and **Q** the **Piola-Kirchhoff heat flux**, defined per unit reference surface area dS and outward normal **N**.

The rate of heat transfer into the material can now be written as either of

$$-\int_s \mathbf{q}\cdot\mathbf{n}ds = -\int_S \mathbf{Q}\cdot\mathbf{N}dS \tag{4.4.37}$$

Using Nanson's formula, Part III, Eqn. 2.2.59, $\mathbf{n}ds = J\mathbf{F}^{-\mathrm{T}}\mathbf{N}dS$, the Cauchy and Piola-Kirchhoff heat flux vectors are related through $\mathbf{Q} = J\mathbf{F}^{-1}\mathbf{q}$.

The combination of the mechanical energy balance with the first law, i.e. Eqn. 4.4.3, then reads (see also Part III, Eqn. 3.7.26)

$$\int_V \mathbf{P}:\dot{\mathbf{F}}dV - \int_V \mathrm{Div}\mathbf{Q}dV + \int_V RdV = \int_V \rho_0\dot{u}dV \tag{4.4.38}$$

where $\int_V RdV = \int_v rdv$, or, in local form,

$$\mathbf{P}:\dot{\mathbf{F}} - \mathrm{Div}\mathbf{Q} + R = \rho_0\dot{u} \tag{4.4.39}$$

or

$$\mathbf{S}:\dot{\mathbf{E}} - \mathrm{Div}\mathbf{Q} + R = \rho_0\dot{u} \tag{4.4.40}$$

Note that, comparing the spatial and material forms,

$$\int_V \mathrm{Div}\mathbf{Q}dV = \int_v \mathrm{div}\mathbf{q}dv, \quad \mathrm{Div}\mathbf{Q} = J\mathrm{div}\mathbf{q}, \quad \frac{1}{\rho_0}\mathrm{Div}\mathbf{Q} = \frac{1}{\rho}\mathrm{div}\mathbf{q} \tag{4.4.41}$$

The Second Law

Analogous to Eqn. 4.4.13, the second law can be expressed in material form as

$$\frac{d}{dt}\int_V \rho_0 s dV + \int_V \mathrm{Div}\left(\frac{\mathbf{Q}}{\theta}\right) dV - \int_V \frac{R}{\theta} dV \geq 0 \qquad (4.4.42)$$

or, analogous to 4.4.16, one has the dissipation inequality

$$\theta s^{(i)*} = \theta\dot{s} - \dot{u} + \frac{1}{\rho_0}\left(\mathbf{P} : \dot{\mathbf{F}}\right) - \frac{1}{\rho_0 \theta}(\mathbf{Q} \cdot \mathrm{Grad}\theta) \geq 0 \qquad (4.4.43)$$

Isothermal Conditions

In an isothermal process,

$$\phi = \theta\dot{s} - \dot{u} + \frac{1}{\rho_0}\left(\mathbf{P} : \dot{\mathbf{F}}\right) \geq 0 \quad \text{or} \quad \phi = -\dot{\psi} + \frac{1}{\rho_0}\left(\mathbf{P} : \dot{\mathbf{F}}\right) \geq 0 \qquad (4.4.44)$$

The second of these can be written as

$$\mathbf{P} : \dot{\mathbf{F}} = \rho_0 \dot{\psi} + \rho_0 \phi \qquad \text{with} \qquad \phi \geq 0 \qquad (4.4.45)$$

where the rate of free energy $(\rho_0 \dot{\psi})$ and the dissipation $(\rho_0 \phi)$ are per unit reference volume.

4.4.9 Objectivity

By definition, the scalars heat Q, internal energy U, entropy S and temperature θ are objective, that is they remain unchanged under an observer transformation 2.8.7. It follows that the heat flux vector $\mathbf{q}$ is also objective, transforming according to 2.8.10. By definition, the vector entropy flux $\mathbf{s}_\mathbf{q}$ is objective, that is it transforms according to 2.8.10.

4.4.10 Problems

1. Show that $\mathrm{div}\left(\dfrac{\mathbf{q}}{\theta}\right) = \dfrac{1}{\theta}\mathrm{div}\,\mathbf{q} - \dfrac{1}{\theta^2}(\mathbf{q} \cdot \nabla\theta)$

2. Show that the relation $\mathbf{Q} = J\mathbf{F}^{-1}\mathbf{q}$ is consistent with the relation 4.4.41, $\mathrm{Div}\mathbf{Q} = J\mathrm{div}\mathbf{q}$.