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1998

Citation for published version (APA):
Johannesson, B. (1998). *Thermodynamics*. (Report TVBM (Intern 7000-rapport); Vol. 7171). Division of Building Materials, LTH, Lund University.

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Abstract

Thermodynamics and stuff. (mainly taken from; Introduction to the Mechanics of a Continuous Medium, LAWRENCE E. MALVERN, Printice-hall 1969.)

1 Comparison between classical thermodynamics and continuum mechanics

The first law of thermodynamics can be regarded as an expression of the interconvertibility of heat and work, maintaining an energy balance; as such it places no restriction on the direction of the process.

In Classical mechanics of particles and rigid bodies, kinetic energy and potential energy may be fully transformed from one to the other in the *absence* of friction or other dissipative *mechanisms.* Furthermore such processes can equally well proceed in either direction.

When thermal phenomena are involved the situation is quite different. For example, a friction brake on a wheel having a certain kinetic energy (due to its rotating motion) can all be converted into internal energy, if the whole system is insulated, the internal energy remains in the system causing its temperature to rise. As far as the first law of thermodynamics is concerned, the process could equally be reversed; the wheel could be set into motion by converting internal energy into kinetic energy, while the temperature of the system is decreased. Such a reversal never occurs; the frictional dissipation is an *irreversible process.* The second law of thermodynamics puts limits on the direction of such processes.

Another example of the preferred direction is in the flux of heat between two system at different temperatures; the heat never flows spontantaniously from the colder system to the warmer. This is essentially the statement of the second law of thermodynamics given by Clausius in 1850. The gist of the second law of thermodynamics was, however, given by Carnot (1824), but the precise statement is due to Clausius.

This does not mean that heat can never be transferred from a cold system to a hot one; every mechanical refrigerator accomplishes this, but work must be input to do it, and the transfer does not occur spontaneously.

The friction-brake example does not prove that heat can never be converted to into work. Considering, for example, two heat reservoirs at different temperatures. Heat is extracted from the hot reservoir and partly converted into work by the heat engine, but never entirely so, since considerably portion of the energy must always be rejected in the form of heat transfer to the cold reservoir. Loosely speaking, the heat engine cannot function if there is no difference in the temperature between the two reservoirs since no heat flow entering the engine in this case. If this were not the case the cold reservoir would not be needed.

The above examples have been included only to give some feeling for the historical importance of the second law as a law of nature permitting energy transfer to occur spontantaniosly only in certain preferred directions. Here, we are, however, interested in the general mathematical statement of the second law of thermodynamics. To somewhat understand this mathematical statement one must accept that yet another thermal property, namely the entropy, is to be introduced. The entropy is such that it is always nonnegative and is positive for an irreversible process. This inequality, known as the Clasius-Duhem inequality, will be discussed in more detail later.

Unfortunately the concept of entropy is not so readily accessible to intuitions accustomed to mechanical concepts. To get an feeling for its physical significance one may think of matter as molecules The entropy can be

1.1 The reversible process of an ideal gas

The entropy η first appeared in thermodynamics as a state function related to the heat transfer. In classical thermodynamics it is assumed that the specific entropy (or entropy per unit mass) exists, such that in every *reversible* process

$$d\eta = \left(\frac{\hat{d}q}{\theta}\right)_{rev} \tag{1}$$

is a perfect differential. However, in general the heat input $\hat{d}q$ is not a perfect differential. The heat input $\hat{d}q$ is in continuum mechanics the expression; $\hat{d}q = r - \mathrm{div}(\mathbf{q})\,/\rho$.

To illustrate that the reversible process (1) is a perfect differential an example will be considered. Assume that the thermodynamic properties p, v and θ is related as

$$p = \frac{R\theta}{v} \tag{2}$$

that is, by the perfect gas law. The specific volume is $v = 1/\rho$, and R is the gas constant, p is the thermodynamic pressure and θ is the temperature. According to the assumption (2) the fluid cannot sustain any shear stresses i.e.

$$\mathbf{T} = -p\mathbf{I} \tag{3}$$

Further it with assumed that the internal energy is a function of the temperature only, i.e.

$$\varepsilon = \varepsilon(\theta) \tag{4}$$

as suggested by experiments of Joule in 1843. Any process in such an ideal gas is reversible because whenever the independent variables, say specific volume v and temperature θ, return to its initial values, so do the dependent variables, ε and the pressure p.

The energy balance is $\rho\dot{\varepsilon} = \mathrm{tr}\mathbf{T}^{\mathrm{T}}\mathbf{L} - \mathrm{div}\,(\mathbf{q}) + \rho r$ (as expressed in continuum mechanics) ; . It turns out that when having an ideal fluid, i.e. $\mathbf{T} = -p\mathbf{I}$, the term $\mathrm{tr}\mathbf{T}^{\mathrm{T}}\mathbf{L}$ could be simplified by considering instead the volume change $\dot{V}$. To illustrate this consider a 'small' rectangular element with the sides having the length dx_1, dx_2 and dx_3. Hence the volume is given by $V = dx_1dx_2dx_3$ and the volume change can then be expressed as $\dot{V} = d\dot{x}_1dx_2dx_3 + dx_1d\dot{x}_2dx_3 + dx_1dx_2d\dot{x}_3$. The ratio $\dot{V}/V$ becomes

$$\begin{aligned} \frac{\dot{V}}{V} &= \frac{d\dot{x}_1dx_2dx_3}{dx_1dx_2dx_3} + \frac{dx_1d\dot{x}_2dx_3}{dx_1dx_2dx_3} + \frac{dx_1dx_2d\dot{x}_3}{dx_1dx_2dx_3} \\ &= \frac{d\dot{x}_1}{dx_1} + \frac{d\dot{x}_2}{dx_2} + \frac{d\dot{x}_3}{dx_3} \\ &= \mathrm{tr}\mathbf{L} = \mathrm{tr}\mathbf{D} = \mathrm{div}\dot{\mathbf{x}} \end{aligned} \tag{5}$$

That is $\dot{V}/V = \mathrm{tr}\mathbf{L} = \mathrm{div}\dot{\mathbf{x}}$. Consider the mass balance as written within the continuum concept i.e. $\dot{\rho} + \rho\mathrm{div}\dot{\mathbf{x}} = 0$. Here the material time derivative of the mass density, i.e. $\dot{\rho}$ will be identified as the differential $d\rho$ used in classical thermodynamics to yield the mass balance law $d\rho + \rho\mathrm{div}\dot{\mathbf{x}} = 0$. Noting also that a replacement of the material time derivative $\dot{V}$ with the corresponding notation dV one obtain

$$\frac{d\rho}{\rho} = -\frac{dV}{V} \tag{6}$$

from the mass balance $d\rho + \rho\mathrm{div}\dot{\mathbf{x}} = 0$, where $dV/V = \mathrm{div}\dot{\mathbf{x}}$.

The mass density ρ and the specific volume v can be expressed with the volume V and with the mass m, as

$$\rho = \frac{m}{V}; \qquad v = \frac{V}{m} \tag{7}$$

Mass cannot be 'destroyed' leading to the conclusion that $m = const.$ i.e. $\dot{m} = 0$. That is, the expression (6) and (7) combines to yield

$$\frac{d\rho}{\rho} = -\frac{dV}{V} = -\frac{mdv}{mv} = -\frac{dv}{v} \tag{8}$$

Now the energy balance, $\rho\dot{\varepsilon} = \mathrm{tr}\mathbf{T}^{\mathrm{T}}\mathbf{L} - \mathrm{div}(\mathbf{q}) + \rho r$ will be rewritten by replacing the material time derivative $\dot{\varepsilon}$ by the differential $d\varepsilon$, i.e. $d\varepsilon = \mathrm{tr}\mathbf{T}^{\mathrm{T}}\mathbf{L}/\rho - \mathrm{div}(\mathbf{q})/\rho + r$. Recall, also that the energy input $\hat{d}q$ is defined as $\hat{d}q = r - \mathrm{div}(\mathbf{q})/\rho$. That is the energy balance or equally the first law of thermodynamics can be written as $d\varepsilon = \mathrm{tr}\mathbf{T}^{\mathrm{T}}\mathbf{L}/\rho + \hat{d}q$. When only considering fluids having the stress tensor given by $\mathbf{T} = -p\mathbf{I}$, the first law then becomes

$$d\varepsilon = -\frac{\mathrm{tr}(p\mathbf{L})}{\rho} + \hat{d}q \tag{9}$$

But from (5) it was concluded that $dV/V = \mathrm{tr}\mathbf{L}$ and from (8) one obtained that $dV/V = dv/v$. The first law (9) (valid for perfect fluids only) then takes the form

$$d\varepsilon = -p\frac{\frac{dv}{v}}{\rho} + \hat{d}q \tag{10}$$

Noting from (7) that the term $v\rho$ cancels, one obtain

$$d\varepsilon = -pdv + \hat{d}q \tag{11}$$

which is the form often presented of the first law of thermodynamics. Not that this form is only valid for perfect fluids.

For a *constant-volume process* the internal energy ε can be related to the temperature θ with the specific heat at constant volume C_v, as

$$d\varepsilon = \hat{d}q = C_v d\theta \tag{12}$$

where the general assumption (4) and the first law (11) was used. Since the assumption of ε only involves a dependence of the temperature, i.e. assumption (4), the specific heat can only be a function of temperature, i.e.

$$d\varepsilon = C_v\left(\theta\right) d\theta \tag{13}$$

Returning to the second law (4) which together with the assumption (2), i.e. $p = R\theta/v$ gives

$$d\varepsilon = -\frac{R\theta}{v}dv + \hat{d}q \tag{14}$$

for a any process (volume not constant) for an ideal gas. The use of (13) and (14) yields an expression for the heat input $\hat{d}q$, as

$$\hat{d}q = C_v\left(\theta\right) d\theta + \frac{R\theta}{v}dv \tag{15}$$

Division by θ gives

$$\frac{\hat{d}q}{\theta} = C_v\left(\theta\right)\frac{d\theta}{\theta} + R\frac{dv}{v} \tag{16}$$

which shows that $\hat{d}q/\theta$ is a perfect differential, in this case, since (16) can be integrated from a reference state described by θ_o and v_o, i.e.

$$\int\limits_{\theta_o,v_o}^{\theta,v} \frac{\hat{d}q}{\theta} = \int\limits_{\theta_o}^{\theta} C_v\left(\theta\right)\frac{d\theta}{\theta} + \int\limits_{v_o}^{v} R\frac{dv}{v} \tag{17}$$

Having the specific heat constant C_v constant, expression (17) reduces to

$$\int\limits_{\theta_o,v_o}^{\theta,v} \frac{\hat{d}q}{\theta} = C_v \ln\left(\frac{\theta}{\theta_o}\right) + R\ln\left(\frac{v}{v_o}\right) \tag{18}$$

Not that the assumption of irreversibility of the system i.e. the assumption (1), makes it possible to express the 'change' of entropy $\Delta\eta$ with an exact function, i.e.

$$\int_{\theta_o,v_o}^{\theta,v} \frac{q}{\theta} = \int_{\theta_o,v_o}^{\theta,v} d\eta = \Delta\eta = \eta - \eta_o = C_v \ln\left(\frac{\theta}{\theta_o}\right) + R\ln\left(\frac{v}{v_o}\right) \tag{19}$$

where (18) was used. This gives the change in entropy for any process (necessarily reversible) in a ideal gas. It should be observed that only two material constants C_v and R is used.

For this case the entropy is evidently a state function, returning to its initial value whenever the temperature returns to its initial value, as it does according to the expression (2), whenever p and v return to its initial values.

In statistical physics the Boltzmann's principle postulate that entropy of a state is proportional to the logarithm of its probability.. Elementary statistic mechanics based on considering a gas as a collection of rigid molecules leads to an expression of the following form for the total entropy S of a sample of gas containing N molecules

$$S = kN\left[\ln V + \tfrac{3}{2}\ln\theta\right] + C \tag{20}$$

where V is the volume, θ the absolute temperature, k is Boltzmann's constant, and C is a constant for which a definite value is obtained only by means of quantum theory. And the total entropy S is related to the specific entropy η by $S = \int_V \rho\eta dV$. It is seen that the expression for the entropy in (19) and (20) has the same form. The identity in the forms of (19) and (20) suggests that entropy in statistical physics and thermodynamic entropy are really the same thing. The statistical physics interpretation in terms of probability and tendency toward disordered macrostates furnishes a physical significance for the otherwise rather abstract thermodynamical concept. Of course, the identity of the two forms has been displayed here only for a very special case, the ideal gas, i.e. for a case where the stress tensor is $\mathbf{T} = -p\mathbf{I}$.

For more general materials, explicit formulas for the entropy are not easy to come by either in thermodynamics or in statistical mechanics. However, the main use of the thermodynamic concept of entropy and the second axiom of thermodynamics is to check that the introduced material functions fulfill the second law.

1.2 The Gibbs relation, entropy is a variable conjugate to temperature

Here the underlying assumption of the Gibbs relation will be discussed. the important difference between extensive and intensive variables will also be dealt with.

For a reversible process we have

$$d\eta = \left(\frac{\hat{d}q}{\theta}\right)_{rev} \quad ; \quad \text{or} \quad \hat{d}q = \theta d\eta \tag{21}$$

The simplified energy equation or the first law for an ideal fluid is

$$d\varepsilon = -pdv + \hat{d}q \tag{22}$$

Hence, the expression (21b) and (22) combines to yield

$$d\varepsilon = -pdv + \theta d\eta; \quad \text{(necessarily reversible)} \tag{23}$$

which is the so-called Gibbs relation (only valid for reversible ideal fluids). For a homogeneous system in equilibrium the Gibbs relation can be written as, $dU = -pdV + \theta dS$ where, $S = \int_V \rho\eta dV$ and, $U = \int_V \rho\varepsilon dV$. This shows that the entropy S is the *extensive* conjugate to the *intensive* variable θ (for calculating the thermal energy input), and the volume V is the *extensive* variable conjugate to the stress -p (for calculating the mechanical energy input). An *extensive variable* is one that in a homogeneous system is proportional to the total mass; in general the total amount of it in the system is the sum of amounts in all its parts, e.g., $S = \int_V \rho\eta dV$. An *intensive variable*, on the other hand, has the same value at all points in a homogeneous system in equilibrium, in general the point value of an intensive variable does not depend on the size of the system. The densities of extensive variable e.g. ε, η and v are intensive variables. Since in continuum mechanics one mainly work with densities, the distinction between extensive and intensive variables tends to be obscure.

Considering, again, a reversible ideal gas where the change of internal energy density $d\varepsilon$ can be formulated, as

$$d\varepsilon = -pdv + C_v d\theta + R\theta\frac{dv}{v}; \quad \text{(necessarily reversible)} \tag{24}$$

where (16) and (23) has been used. Using also the perfect gas law, i.e. $p = R\theta/v$, the expression (24) takes the form

$$d\varepsilon = -R\theta\frac{dv}{v}+C_v d\theta + R\theta\frac{dv}{v}; \quad \text{(necessarily reversible)} \tag{25}$$

i.e.

$$d\varepsilon = C_v d\theta \tag{26}$$

and it is concluded that also the Gibbs relation results in that the change of the internal energy density $d\varepsilon$ can only be a function of the temperature in an reversible ideal gas or fluid.

1.3 Entropy change in an irreversible process

Only reversible processes are possible in the ideal gas of equations (2) and (4). This shows that the in the ideal gas the entropy is a state function. Classical thermodynamics postulates that the entropy of an equilibrium state is a state function, determined by the equilibrium values of the independent state variables. Although explicit formulas for either ε or η in terms of the independent state variables are rare, the *first law* still furnishes a method for calculating the change in ε by recording the work input and the heat input for the process. And equation (1) furnishes a method for computing the change in η if we know the heat-input and the temperature history for any (possibly hypothetical) *reversible process* between the same two states. Unfortunately, this may not be a use method for, for example, inelastic deformation processes in materials.

For a reversible process undergoing a cycle returning to its initial state , we have

$$\oint^{cyclic} d\eta = \oint^{cyclic} \left(\frac{\hat{d}q}{\theta}\right)_{rev} = 0 \tag{27}$$

But for a irreversible process we still have

$$\oint^{cyclic} d\eta = 0; \quad \text{reversible and irreversible} \tag{28}$$

(since the entropy η is assumed to be a perfect differential returning to its initial value), but

$$\oint^{cyclic} \left(\frac{\hat{d}q}{\theta}\right)_{irrev} \neq 0; \quad \text{irreversible} \tag{29}$$

In fact, experiments indicates that in general

$$\oint^{cyclic} \left(\frac{\hat{d}q}{\theta}\right)_{irrev} < 0 \tag{30}$$

One interpret the $\hat{d}q/\theta$ as the entropy input from outside (or in continuum mechanics, input from the neighboring points in the material) carried by the heat input $\hat{d}q$; thus in a *irreversible cycle* the *net* entropy input is negative. This means that in a irreversible process where a change from a state 1 to 2 (not a whole cycle) is performed, the entropy increase is greater than the entropy input by heat transfer, i.e.

$$\Delta s > \oint_{1}^{2} \left(\frac{\hat{d}q}{\theta}\right)_{irrev} \tag{31}$$

because the internal entropy production, which is always positive in an irreversible process.

In isolated systems, i.e., one with no heat transfer, reversible processes do not change the entropy, while irreversible processes always increase the entropy. all real processes are irreversible, but in some special cases the dissipation is small enough to be negligeable.. It is clear that when studying cases where the heat input to a point is due to a heat flux $\mathbf{q}$ (remember that $\hat{d}q = r - \operatorname{div}(\mathbf{q})/\rho$) the assumption of a reversible system is irrelevant due to the entropy increase being greater than the input due to $\hat{d}q$ (in the reversible system these to must always equal).

Within the continuum mechanic approach one usually adopt the general inequality of the form (2) to check that introduced material assumptions do not violate the second axiom of thermodynamics. Such methods will be analyzed in detail later.

1.4 Example of ideal gases and van der Waals' gases

A *pure substance* is one which is chemically homogeneous and remains invariant in chemical composition during the process. Experience indicates that in the absence of motion, gravity, capillarity, electricity, and magnetism the state of a pure substance in the form of a fluid is completely determined by any two independent properties. Assuming that this is strictly correct, then the various other properties are in principle expressible as functions of two chosen independent properties by *equations of state*. For example, if temperature θ and specific volume $v = 1/\rho$ are chosen as independent properties, then

$$\varepsilon = \varepsilon\left(\theta, v\right); \qquad \text{and} \qquad p = p\left(\theta, v\right). \tag{32}$$

Alternatively, we may invert the second equation to obtain

$$v = v\left(\theta, p\right) \tag{33}$$

whence, the first equation becomes

$$\varepsilon = \varepsilon\left(\theta, v\left(\theta, p\right)\right) \tag{34}$$

expressing the specific internal energy ε as a function of θ and the thermodynamic pressure p.

The following examples are concerned with substances which are assumed to obey such equations of state. Both ideal gases and van der Waals' gases are considered.

Example 1a. *A specific heat is defined by the ratio* $\hat{d}q/\theta$, *which in a fluid pure substance is equal to* $\left(d\varepsilon + pdv\right)/d\theta$ *by the first law. It turns out that the specific heat at constant pressure is* $c_p = \left(\partial\varepsilon/\partial\theta\right)_p + p\left(\partial v/\partial\theta\right)_p$. *The subscript indicates that the variable held constant. To show this consider:*

From (32) and (33) we have

$$\varepsilon = \varepsilon\left(\theta, p\right); \qquad v = v\left(\theta, p\right) \tag{35}$$

Differentiation of (35a) gives (not that the pressure is constant)

$$d\varepsilon = \left(\frac{\partial\varepsilon}{\partial\theta}\right)_p d\theta + \left(\frac{\partial\varepsilon}{\partial p}\right)_\theta dp = \left(\frac{\partial\varepsilon}{\partial\theta}\right)_p d\theta \tag{36}$$

and differentiation of (35b) gives

$$dv = \left(\frac{\partial v}{\partial\theta}\right)_p d\theta + \left(\frac{\partial v}{\partial p}\right)_\theta dp = \left(\frac{\partial v}{\partial\theta}\right)_p d\theta \tag{37}$$

Then $\left(d\varepsilon + pdv\right)/d\theta$ which is the specific heat c_p for a pure substans, becomes

$$c_p = \left(\left(\frac{\partial\varepsilon}{\partial\theta}\right)_p d\theta + p\left(\frac{\partial v}{\partial\theta}\right)_p d\theta\right)/d\theta = \left(\frac{\partial\varepsilon}{\partial\theta}\right)_p + p\left(\frac{\partial v}{\partial\theta}\right)_p \tag{38}$$

which was the relation to be shown.

Example 1b. *Show that* $(\partial\varepsilon/\partial\theta)_p = (\partial\varepsilon/\partial\theta)_v + (\partial\varepsilon/\partial v)_\theta\,(\partial v/\partial\theta)_p$ *and hence that* $c_p - c_v = [p + (\partial\varepsilon/\partial v)_\theta]\,(\partial v/\partial\theta)_p$ *where* c_v *is defined as* $c_v = (\partial\varepsilon/\partial\theta)_v$.

The expression (36) is

$$d\varepsilon = \left(\frac{\partial\varepsilon}{\partial\theta}\right)_p d\theta + \left(\frac{\partial\varepsilon}{\partial p}\right)_\theta dp \tag{39}$$

and (34) is

$$\varepsilon = \varepsilon\left(\theta, v\left(\theta, p\right)\right) \tag{40}$$

Differentiation of (40), gives

$$d\varepsilon = \left(\frac{\partial\varepsilon}{\partial\theta}\right)_v d\theta + \left(\frac{\partial\varepsilon}{\partial v}\right)_\theta dv\left(\theta, p\right) \tag{41}$$

and, further differentiation of $v\left(\theta, p\right)$, gives

$$dv = \left(\frac{\partial v}{\partial\theta}\right)_p d\theta + \left(\frac{\partial v}{\partial p}\right)_\theta dp \tag{42}$$

Combine (41) and (42), to yield

$$d\varepsilon = \left(\frac{\partial\varepsilon}{\partial\theta}\right)_v d\theta + \left(\frac{\partial\varepsilon}{\partial v}\right)_\theta \left(\left(\frac{\partial v}{\partial\theta}\right)_p d\theta + \left(\frac{\partial v}{\partial p}\right)_\theta dp\right) \tag{43}$$

The following is to be shown

$$\left(\frac{\partial\varepsilon}{\partial\theta}\right)_p = \left(\frac{\partial\varepsilon}{\partial\theta}\right)_v + \left(\frac{\partial\varepsilon}{\partial v}\right)_\theta \left(\frac{\partial v}{\partial\theta}\right)_p \tag{44}$$

From (38) we have the expression for c_p, i.e.

$$c_p = \left(\frac{\partial\varepsilon}{\partial\theta}\right)_p + p\left(\frac{\partial v}{\partial\theta}\right)_p \tag{45}$$

and c_v is defined as

$$c_v = \left(\frac{\partial\varepsilon}{\partial\theta}\right)_v \tag{46}$$

Hence

$$c_p - c_v = \left(\frac{\partial \varepsilon}{\partial \theta}\right)_p + p\left(\frac{\partial v}{\partial \theta}\right)_p - \left(\frac{\partial \varepsilon}{\partial \theta}\right)_v \tag{47}$$

By using (44) and (47) one obtain

$$c_p - c_v = \left(\frac{\partial \varepsilon}{\partial \theta}\right)_p + p\left(\frac{\partial v}{\partial \theta}\right)_p - \left(\left(\frac{\partial \varepsilon}{\partial \theta}\right)_p - \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta \left(\frac{\partial v}{\partial \theta}\right)_p\right) \tag{48}$$

which can be rearanged to yield the expression

$$c_p - c_v = p\left(\frac{\partial v}{\partial \theta}\right)_p + \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta \left(\frac{\partial v}{\partial \theta}\right)_p = \left[p + \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta\right]\left(\frac{\partial v}{\partial \theta}\right)_p \tag{49}$$

This is the result to be shown in this example.

Example 1c. *Show that* $c_p - c_v = [p + (\partial\varepsilon/\partial v)_\theta]\,(\partial v/\partial\theta)_p$ *can be brought to the form* $c_p - c_v = pv\beta + v\beta\,(\partial\varepsilon/\partial v)_\theta$*, where* $\beta = (\partial v/\partial\theta)_p/v$*.*

Condisider (49), i.e.

$$c_p - c_v = p\left(\frac{\partial v}{\partial \theta}\right)_p + \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta \left(\frac{\partial v}{\partial \theta}\right)_p \tag{50}$$

Insert the expressions for β into the above relation to yield

$$c_p - c_v = pv\beta + v\beta\left(\frac{\partial \varepsilon}{\partial v}\right)_\theta \tag{51}$$

Example 2. *Evaluate* $c_p - c_v$ *for the ideal gas defined by* $pv = R\theta$ *and* $\varepsilon = \varepsilon(\theta)$*.*

For an ideal gas we have

$$v = R\frac{\theta}{p}; \qquad \left(\frac{\partial v}{\partial \theta}\right)_p = \frac{R}{p} \tag{52}$$

The derivative β is according to example 1c, in this case, given as

$$\beta = \frac{R}{pv} \tag{53}$$

And (51) gives $c_p - c_v$ for an ideal gas, as

$$c_p - c_v = pv\beta = R \tag{54}$$

which was to be shown.

Example 3. *In an adiabatic process, i.e.* $\hat{d}q = 0$, *with an ideal gas, i.e.* $pv = R\theta$ *and* $\varepsilon = \varepsilon(\theta)$, *an equation* $(c_p - R)\, pdv + c_v vdp = 0$ *can be obtained, by using the first law of thermodynamics i.e.* $(d\varepsilon + pdv)/d\theta = 0$ *(observe that* $\hat{d}q = 0$ *in this assumed case) and* $d\varepsilon = c_v d\theta$.

Consider a differentiation of the ideal gas law as

$$d(pv) = d(R\theta) \tag{55}$$

i.e.

$$pdv + vdp = Rd\theta \tag{56}$$

The 'adiabatic' first law ('adiabatic' energy balance) is

$$\frac{d\varepsilon}{d\theta} + p\frac{dv}{d\theta} = 0 \tag{57}$$

see the information in the example. Inserting $d\varepsilon = c_v d\theta$ in (57) gives

$$c_v + p\frac{dv}{d\theta} = 0; \quad \text{or} \quad d\theta = -\frac{pdv}{c_v} \tag{58}$$

The temperature is a function of specific volume and pressure, differentiation gives

$$\theta = \theta(v, p); \quad d\theta = \left(\frac{\partial \theta}{\partial v}\right)_p dv + \left(\frac{\partial \theta}{\partial p}\right)_v dp \tag{59}$$

For a ideal gas we, hence, have

$$\theta = \frac{pv}{R}; \quad \left(\frac{\partial \theta}{\partial v}\right)_p = \frac{p}{R}; \quad \left(\frac{\partial \theta}{\partial p}\right)_v = \frac{v}{R} \tag{60}$$

From (56) one conclude that

$$d\theta = \frac{p}{R}dv + \frac{v}{R}dp \tag{61}$$

Inserting the expression for $d\theta$ in (58b), gives

$$-\frac{pdv}{c_v} = \frac{p}{R}dv + \frac{v}{R}dp \tag{62}$$

Rearangement, yield

$$-Rpdv = c_v pdv + c_v vdp \tag{63}$$

i.e.

$$(c_p - R)\, p dv + c_v v dp = 0 \tag{64}$$

Which was the result to be derived.

Example 4. *Show that in a fluid pure substance where* $\varepsilon = \varepsilon(\theta, v)$*, the total differential* $d\varepsilon$ *is given by* $d\varepsilon = c_v d\theta + ((c_p - c_v)/v\beta - p)\, dv$*. See example 1c.*

Differentiation of $\varepsilon = \varepsilon(\theta, v)$ is

$$\varepsilon = \varepsilon(\theta, v)\,; \quad d\varepsilon = \left(\frac{\partial \varepsilon}{\partial \theta}\right)_v d\theta + \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta dv \tag{65}$$

The parameter c_v is accoding to example 1b defined as

$$c_v = \left(\frac{\partial \varepsilon}{\partial \theta}\right)_v \tag{66}$$

$$\frac{c_p - c_v}{v} = \left(p + \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta\right)$$

$$\frac{c_p - c_v}{v\beta} - p = \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta$$

$$d\varepsilon = \left(\frac{\partial \varepsilon}{\partial \theta}\right)_v d\theta + \left(\frac{c_p - c_v}{v\beta} - p\right) dv$$

$$d\varepsilon = c_v d\theta + \left(\frac{c_p - c_v}{v\beta} - p\right) dv$$

Example 5. *Use the results of Example 4 to show that* $\varepsilon = \varepsilon_o + \int_{\theta_o}^{\theta} c_v d\theta + a(1/v_o - 1/v)$ *in a van der Waals' gas defined by* $(p + a/v^2)(v - b) = R\theta$ *and* $(\partial\varepsilon/\partial v)_\theta = a/v^2$*, where a, b and R are constants.*

$$c_p - c_v = pv\beta + v\beta\left(\frac{\partial \varepsilon}{\partial v}\right)_\theta ; \quad \beta = \left(\frac{\partial v}{\partial \theta}\right)_p / v$$

$$\left(\frac{\partial \varepsilon}{\partial v}\right)_\theta = \frac{a}{v^2}$$

$$c_p - c_v = pv\beta + v\beta a/v^2$$

$$\frac{(c_p - c_v)}{v\beta} - p = \frac{a}{v^2} = \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta$$

$$\varepsilon = \varepsilon\left(\theta, v\right); \quad d\varepsilon = \left(\frac{\partial \varepsilon}{\partial \theta}\right)_v d\theta + \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta dv$$

$$d\varepsilon = \left(\frac{\partial \varepsilon}{\partial \theta}\right)_v d\theta + \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta dv$$

$$c_v = \left(\frac{\partial \varepsilon}{\partial \theta}\right)_v$$

$$d\varepsilon = c_v d\theta + \left(\frac{a}{v^2}\right) dv$$

$$\varepsilon = \varepsilon_o + \int_{\theta_o}^{\theta} c_v d\theta + a\left(\frac{1}{v_o} - \frac{1}{v}\right)$$

Example 6a. *When the equations of state relating three variables such as* p, v, θ *are invertible some important relationships among the partial derivatives can be derived. For example, from* $v = v\left(\theta, p\left(\theta, v\right)\right)$ *one can establish that* $1 \equiv (\partial v/\partial v)_\theta = (\partial v/\partial p)_\theta\,(\partial p/\partial v)_\theta$ *and* $0 \equiv (\partial v/\partial \theta)_v = (\partial v/\partial \theta)_p + (\partial v/\partial p)_\theta\,(\partial p/\partial \theta)_v$ *this the second relation can be verified as follows:*

$$v = v\left(\theta, p\left(\theta, v\right)\right); \quad dv = \left(\frac{\partial v}{\partial \theta}\right)_p d\theta + \left(\frac{\partial v}{\partial p}\right)_\theta d\left(p\left(\theta, v\right)\right)$$

$$p\left(\theta, v\right); \quad dp = \left(\frac{\partial p}{\partial \theta}\right)_v d\theta + \left(\frac{\partial p}{\partial v}\right)_\theta dv$$

$$dv = \left(\frac{\partial v}{\partial \theta}\right)_p d\theta + \left(\frac{\partial v}{\partial p}\right)_\theta \left(\left(\frac{\partial p}{\partial \theta}\right)_v d\theta + \left(\frac{\partial p}{\partial v}\right)_\theta dv\right)$$

$$dv = \left(\frac{\partial v}{\partial \theta}\right)_p d\theta + \left(\frac{\partial v}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial \theta}\right)_v d\theta + \left(\frac{\partial v}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial v}\right)_\theta dv$$

$$\left(\frac{\partial v}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial v}\right)_\theta = 1$$

$$dv = \left(\frac{\partial v}{\partial \theta}\right)_p d\theta + \left(\frac{\partial v}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial \theta}\right)_v d\theta + dv$$

$$1 = \left(\frac{\partial v}{\partial \theta}\right)_p \frac{d\theta}{dv} + \left(\frac{\partial v}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial \theta}\right)_v \frac{d\theta}{dv} + 1$$

$$\left(\frac{\partial v}{\partial \theta}\right)_p + \left(\frac{\partial v}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial \theta}\right)_v = 0$$

Example 6b. *Show that the results of Example 6a imply the cyclic relation* $(\partial v/\partial p)_\theta (\partial p/\partial \theta)_v (\partial \theta/\partial v)_p = -1$.

$$\left(\frac{\partial v}{\partial \theta}\right)_p + \left(\frac{\partial v}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial \theta}\right)_v = 0$$

Multiplication with $(\partial \theta/\partial v)_p$ gives

$$\left(\frac{\partial \theta}{\partial v}\right)_p \left(\frac{\partial v}{\partial \theta}\right)_p + \left(\frac{\partial \theta}{\partial v}\right)_p \left(\frac{\partial v}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial \theta}\right)_v = 0$$

$$1 + \left(\frac{\partial \theta}{\partial v}\right)_p \left(\frac{\partial v}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial \theta}\right)_v = 0$$

$$\left(\frac{\partial \theta}{\partial v}\right)_p \left(\frac{\partial v}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial \theta}\right)_v = -1$$

Example 7a. *The Gibbs relation i.e.* $d\varepsilon = \theta d\eta - p dv$ *is assumed valid for all pure fluid substances, since it is a relationship between state variables, even though it was obtained by using* $\hat{d}q = \theta d\eta$ *which applies only to a reversible process. If* $\varepsilon = \varepsilon(\theta, v)$, *show that the Gibbs relation leads to* $d\eta = \frac{1}{\theta}(\partial\varepsilon/\partial\theta)_v d\theta + \frac{1}{\theta}[p + (\partial\varepsilon/\partial v)_\theta] dv$ *and that this implies that* $(\partial\eta/\partial\theta)_v = \frac{1}{\theta}(\partial\varepsilon/\partial\theta)_v$ *and that* $(\partial\eta/\partial v)_\theta = \frac{1}{\theta}[p + (\partial\varepsilon/\partial v)_\theta]$.

The first law is

$$d\varepsilon = \theta d\eta - p dv$$

For a reversible process

$$\hat{d}q = \theta d\eta$$

further

$$\varepsilon = \varepsilon(\theta, v); \qquad d\varepsilon = \left(\frac{\partial \varepsilon}{\partial \theta}\right)_v d\theta + \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta dv$$

$$\left(\frac{\partial \varepsilon}{\partial \theta}\right)_v d\theta + \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta dv = \theta d\eta - p dv$$

$$d\eta = \frac{1}{\theta}\left(\frac{\partial \varepsilon}{\partial \theta}\right)_v d\theta + \frac{1}{\theta}\left(\left(\frac{\partial \varepsilon}{\partial v}\right)_\theta + p\right)_\theta dv$$

and

$$\eta = \eta(\theta, v); \qquad d\eta = \left(\frac{\partial \eta}{\partial \theta}\right)_v d\theta + \left(\frac{\partial \eta}{\partial v}\right)_\theta dv$$

Therefore

$$\left(\frac{\partial \eta}{\partial \theta}\right)_v = \frac{1}{\theta}\left(\frac{\partial \varepsilon}{\partial \theta}\right)_v; \text{ and } \left(\frac{\partial \eta}{\partial v}\right)_\theta = \frac{1}{\theta}\left(\left(\frac{\partial \varepsilon}{\partial v}\right)_\theta + p\right)_\theta$$

Example 7b. *Use the result of Example 7a to show that the equality of* $\partial^2\eta/\partial\theta\partial v$ *and* $\partial^2\eta/\partial\theta\partial v$ *results in the equation* $p + (\partial\varepsilon/\partial v)_\theta = \theta\,(\partial p/\partial\theta)_v$.

$$\left(\frac{\partial \eta}{\partial \theta}\right)_v = \frac{1}{\theta}\left(\frac{\partial \varepsilon}{\partial \theta}\right)_v; \qquad \frac{\partial^2 \eta}{\partial \theta \partial v} = 0$$

$$\left(\frac{\partial \eta}{\partial v}\right)_\theta = \frac{1}{\theta}\left(\frac{\partial \varepsilon}{\partial v} + p\right)_\theta;$$

$$\frac{\partial^2 \eta}{\partial v \partial \theta} = -\frac{1}{\theta^2}\left(\left(\frac{\partial \varepsilon}{\partial v}\right)_\theta + p\right)_\theta + \frac{1}{\theta}\left(\frac{\partial p}{\partial \theta}\right)_v$$

$$\frac{\partial^2 \eta}{\partial v \partial \theta} = \frac{\partial^2 \eta}{\partial \theta \partial v}$$

$$\frac{1}{\theta}\left(\frac{\partial p}{\partial \theta}\right)_v = \frac{1}{\theta^2}\left(\left(\frac{\partial \varepsilon}{\partial v}\right)_\theta + p\right)_\theta$$

$$p + \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta = \theta\left(\frac{\partial p}{\partial \theta}\right)_v$$

Example 7c. *Use the result of Example 1, Example 6a and Example 7a and the definition of* c_v *i.e.* $c_v = (\partial\varepsilon/\partial\theta)_v$ *and of* $\kappa = -(\partial v/\partial p)_\theta/v$ *i.e. the isothermal compressibility, to obtain:* $d\eta = \frac{c_v}{\theta}d\theta + \frac{\beta}{\kappa}dv$.

$$d\eta = \frac{1}{\theta}\left(\frac{\partial \varepsilon}{\partial \theta}\right)_v d\theta + \frac{1}{\theta}\left(\left(\frac{\partial \varepsilon}{\partial v}\right)_\theta + p\right)_\theta dv$$

$$c_v = \left(\frac{\partial \varepsilon}{\partial \theta}\right)_v; \quad \kappa = -\left(\frac{\partial v}{\partial p}\right)_\theta /v; \quad \beta = \left(\frac{\partial v}{\partial \theta}\right)_p /v$$

$$p + \left(\frac{\partial \varepsilon}{\partial v}\right)_\theta = \theta\left(\frac{\partial p}{\partial \theta}\right)_v$$

$$\frac{1}{\theta}\left(p+\left(\frac{\partial\varepsilon}{\partial v}\right)_{\theta}\right)=\left(\frac{\partial p}{\partial\theta}\right)_{v}$$

$$\left(\frac{\partial v}{\partial\theta}\right)_{p}+\left(\frac{\partial v}{\partial p}\right)_{\theta}\left(\frac{\partial p}{\partial\theta}\right)_{v}=0$$

$$-\frac{\left(\frac{\partial v}{\partial\theta}\right)_{p}}{\left(\frac{\partial v}{\partial p}\right)_{\theta}}=\left(\frac{\partial p}{\partial\theta}\right)_{v}=\frac{\beta}{\kappa}\frac{1}{\theta}\left(p+\left(\frac{\partial\varepsilon}{\partial v}\right)_{\theta}\right)$$

$$d\eta=\frac{c_v}{\theta}d\theta+\frac{\beta}{\kappa}dv$$

Example 8a. *For the van der Waals' gas defined in Example 5, show that:* $\beta=\left(Rv^2\left(v-b\right)\right)/\left(R\theta v^3-2a\left(v-b\right)^2\right)$ *and that the material property* κ *takes the form:* $\kappa=\left(v^2\left(v-b\right)^2\right)/\left(R\theta v^3-2a\left(v-b\right)^2\right)$. *The definition of the coefficient of volume expansion at constant pressure is* $\beta=-\left(\partial v/\partial\theta\right)_p/v$ *and the isothermal compressibility* $\kappa=-\left(\partial v/\partial p\right)_\theta/v$.

$$\left(p+a/v^2\right)\left(v-b\right)=R\theta$$

$$pv-pb=R\theta-\frac{a}{v}+\frac{ab}{v^2}$$

$$p=\frac{R\theta}{\left(v-b\right)}-\frac{a}{v\left(v-b\right)}+\frac{ab}{v^2\left(v-b\right)}$$

$$\left(\frac{\partial p}{\partial\theta}\right)_{v}=\frac{R}{\left(v-b\right)}$$

$$p=\frac{R\theta v^2-av+ab}{v^2\left(v-b\right)}=\frac{R\theta v^2-a\left(v-b\right)}{v^2\left(v-b\right)}$$

$$h\left(v\right)=\frac{f\left(v\right)}{g\left(v\right)};\quad h'\left(v\right)=\frac{g\left(v\right)f'\left(v\right)-f\left(v\right)g'\left(v\right)}{\left(g\left(v\right)\right)^2}$$

$$\left(\frac{\partial p}{\partial v}\right)_{\theta}=\frac{\left[v^2\left(v-b\right)\right]\left[2R\theta v-a\right]-\left[R\theta v^2-a\left(v-b\right)\right]\left[v\left(3v-2b\right)\right]}{v^4\left(v-b\right)^2}$$

$$\left(\frac{\partial p}{\partial v}\right)_{\theta}=\frac{\left[v\left(v-b\right)\right]\left[2R\theta v-a\right]-\left[R\theta v^2-a\left(v-b\right)\right]\left[(3v-2b\right]}{v^3\left(v-b\right)^2}$$

$$\left(\frac{\partial p}{\partial v}\right)_{\theta}=\frac{-R\theta v^3-av^2+abv+3av\left(v-b\right)-2ab\left(v-b\right)}{v^3\left(v-b\right)^2}$$

$$\left(\frac{\partial p}{\partial v}\right)_\theta = \frac{-R\theta v^3 + 2av^2 - 4abv + 2ab^2}{v^3 (v-b)^2}$$

$$\left(\frac{\partial p}{\partial v}\right)_\theta = \frac{-R\theta v^3 + 2a(v-b)^2}{v^3 (v-b)^2}$$

$$\left(\frac{\partial v}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial v}\right)_\theta = 1$$

$$\left(\frac{\partial v}{\partial p}\right)_\theta = \frac{v^3 (v-b)^2}{-R\theta v^3 + 2a(v-b)^2}$$

$$\kappa = -\left(\frac{\partial v}{\partial p}\right)_\theta / v$$

$$\kappa = \frac{v^2 (v-b)^2}{R\theta v^3 - 2a(v-b)^2}$$

$$\left(\frac{\partial p}{\partial \theta}\right)_v = \frac{R}{(v-b)}$$

$$\left(\frac{\partial v}{\partial \theta}\right)_p + \left(\frac{\partial v}{\partial p}\right)_\theta \left(\frac{\partial p}{\partial \theta}\right)_v = 0$$

$$-\frac{\left(\frac{\partial v}{\partial \theta}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_\theta} = \frac{\beta}{\kappa} = \left(\frac{\partial p}{\partial \theta}\right)_v$$

$$\beta = \kappa \left(\frac{\partial p}{\partial \theta}\right)_v = \frac{v^2 (v-b)^2}{R\theta v^3 - 2a(v-b)^2}\left(\frac{R}{(v-b)}\right)$$

$$\beta = \frac{Rv^2 (v-b)}{R\theta v^3 - 2a(v-b)^2}$$

Example 8b. *Use the result from Example 7c and Example 8a to show that,* $\eta - \eta_o = \int_{\theta_o}^{\theta} \frac{c_v}{\theta} d\theta + R \ln\left((v-b) / (v_o - b)\right)$.

$$d\eta = \frac{c_v}{\theta} d\theta + \frac{\beta}{\kappa} dv$$

$$\beta = \frac{Rv^2 (v-b)}{R\theta v^3 - 2a(v-b)^2}; \quad \kappa = \frac{v^2 (v-b)^2}{R\theta v^3 - 2a(v-b)^2}$$

$$d\eta = \frac{c_v}{\theta} d\theta + \left(\frac{R}{(v-b)} \right) dv$$

$$\eta - \eta_o = \int_{\theta_o}^{\theta} \tfrac{c_v}{\theta} d\theta + R \ln \left((v-b) / (v_o - b) \right)$$

1.5 Examples on irreversible processes, the continuum approach,

The example to be dealt with here is an introduction to the thermodynamic methods within the continuum approach. By identifying so-called thermodynamic definitions which make sure that the constitutive relations always will satisfy the second axiom of thermodynamics. Of course, dissipations must be allowed in general models, that is the assumption of reversibility is not introduced.

Example 1, *Show that a class of viscous fluids assumed defined by four constitutive equations of the form: the stress,* $\mathbf{T} = \mathbf{T}(\eta, 1/\rho, \mathbf{D})$, *heat flux vector* $\mathbf{q} = \mathbf{q}(\eta, 1/\rho, \mathbf{D})$, *internal energy density* $\varepsilon{=}\varepsilon(\eta, 1/\rho, \mathbf{D})$ *and , the temperature* $\theta{=}\theta(\eta, 1/\rho, \mathbf{D})$, *can only respond adiabatically.*

$$\theta \rho \dot{\eta} - \text{ grad } (\theta) \cdot \mathbf{q}/\theta - \rho \dot{\varepsilon} + \text{tr} \left(\mathbf{T}^{\mathrm{T}} \mathbf{L} \right) \geq 0$$

$$\mathbf{T} = \mathbf{T}^{\mathrm{T}}$$

$$\text{tr}(\mathbf{TL}) = \text{tr}(\mathbf{TD})$$

Since tr$(\mathbf{L})$=tr$(\mathbf{D})$

$$\rho (\theta \dot{\eta} - \dot{\varepsilon}) - \text{ grad } (\theta) \cdot \mathbf{q}/\theta + \text{tr}(\mathbf{TD}) \geq 0$$

$$\dot{\rho} + \rho \, \text{div} \dot{\mathbf{x}} = 0; \quad \dot{\rho} + \rho \, \text{tr}(\mathbf{D}) = 0$$

Since div$\dot{\mathbf{x}}$ =tr$(\mathbf{D})$

$$\varepsilon{=}\varepsilon(\eta, 1/\rho, \mathbf{D}); \quad \dot{\varepsilon} = \frac{\partial \varepsilon}{\partial \eta} \dot{\eta} + \frac{\partial \varepsilon}{\partial (1/\rho)} \dot{\overline{(1/\rho)}} + \frac{\partial \varepsilon}{\partial \mathbf{D}} \cdot \dot{\mathbf{D}}$$

$$\theta \rho \dot{\eta} - \text{ grad } (\theta) \cdot \mathbf{q}/\theta - \rho \left(\frac{\partial \varepsilon}{\partial \eta} \dot{\eta} + \frac{\partial \varepsilon}{\partial (1/\rho)} \dot{\overline{(1/\rho)}} + \frac{\partial \varepsilon}{\partial \mathbf{D}} \cdot \dot{\mathbf{D}} \right) + \text{tr}(\mathbf{TD}) \geq 0$$

$$\rho \left(\theta - \frac{\partial \varepsilon}{\partial \eta} \right) \dot{\eta} - \rho \frac{\partial \varepsilon}{\partial (1/\rho)} \dot{\overline{(1/\rho)}} - \rho \frac{\partial \varepsilon}{\partial \mathbf{D}} \cdot \dot{\mathbf{D}} + \text{tr}(\mathbf{TD}) - \text{ grad } (\theta) \cdot \mathbf{q}/\theta \geq 0$$

$$\dot{\overline{(1/\rho)}} = -\frac{\dot{\rho}}{\rho^2}$$

$$\rho\left(\theta - \frac{\partial\varepsilon}{\partial\eta}\right)\dot{\eta} + \frac{\partial\varepsilon}{\partial\left(1/\rho\right)}\frac{\dot{\rho}}{\rho} - \rho\frac{\partial\varepsilon}{\partial\mathbf{D}}\cdot\dot{\mathbf{D}} + \mathrm{tr}\left(\mathbf{TD}\right) - \mathrm{grad}\left(\theta\right)\cdot\mathbf{q}/\theta \geq 0$$

$$\dot{\rho} = -\rho\,\mathrm{tr}\left(\mathbf{D}\right)$$

$$\rho\left(\theta - \frac{\partial\varepsilon}{\partial\eta}\right)\dot{\eta} - \frac{\partial\varepsilon}{\partial\left(1/\rho\right)}\mathrm{tr}\left(\mathbf{D}\right) - \rho\frac{\partial\varepsilon}{\partial\mathbf{D}}\cdot\dot{\mathbf{D}} + \mathrm{tr}\left(\mathbf{TD}\right) - \mathrm{grad}\left(\theta\right)\cdot\mathbf{q}/\theta \geq 0$$

$$\mathbf{T} = -p\mathbf{I}$$

$$\rho\left(\theta - \frac{\partial\varepsilon}{\partial\eta}\right)\dot{\eta} - \left(\frac{\partial\varepsilon}{\partial\left(1/\rho\right)} + p\right)\mathrm{tr}\left(\mathbf{D}\right) - \rho\frac{\partial\varepsilon}{\partial\mathbf{D}}\cdot\dot{\mathbf{D}} - \mathrm{grad}\left(\theta\right)\cdot\mathbf{q}/\theta \geq 0$$

Since, $\mathrm{tr}(-p\mathbf{ID}) = -p\mathrm{tr}(\mathbf{D})$. The change in entropy $\dot{\eta}$, the trace of the symmetric part of the velocity gradient $\mathbf{D}$, i.e. $\mathrm{tr}(\mathbf{D})$, and the rate of change of $\mathbf{D}$ i.e. $\dot{\mathbf{D}}$, must in a general model be allowed to be arbitrary. Therefore one defines the following thermodynamic relations

$$\theta = \frac{\partial\varepsilon}{\partial\eta}$$

$$p = -\frac{\partial\varepsilon}{\partial\left(1/\rho\right)}$$

$$\frac{\partial\varepsilon}{\partial\mathbf{D}} = \mathbf{0}$$

Hence the internal energy ε is independent of $\mathbf{D}$ and therefore is the determination of the thermodynamic temperature θ also independent of $\mathbf{D}$ since the thermodynamic definition of the temperature is a function of the internal energy ε.

The constitutive relations therefore reduces to

$$\varepsilon = \varepsilon\left(\eta, 1/\rho\right); \quad \text{and} \quad \theta = \theta\left(\eta, 1/\rho\right)$$

Indeed, the thermodynamic pressure p must also be independent of $\mathbf{D}$ since ε is independent of $\mathbf{D}$ in this specific example with its choice of constitutive relations and thermodynamic relations, i.e.

$$\mathbf{T} = \mathbf{T}\left(\eta, 1/\rho\right) = -p\left(\eta, 1/\rho\right)\mathbf{I}$$

At last it is concluded that the heat flux $\mathbf{q}$ must be equal to zero $\mathbf{q} = \mathbf{0}$, in this model of a fluid since no restriction is placed on grad(θ). It is concluded that a model defined with the constitutive equations xx-xx, must respond adiabatically. Evidently a more general assumption is needed for a realistic description of a fluid, including grad(θ) among the independent variables, furthermore a sophisticated method to tackle the stresses (not only the thermodynamic pressure p) caused by the motion of the fluid, must be dealt with in a stringent way.