CHAPTER 10

THERMODYNAMICS OF SPATIALLY UNIFORM SYSTEMS

In this first chapter of Part III, I am going to develop an approach to the thermodynamics of spatially uniform fluid systems and processes which has been inspired by continuum thermodynamics.[1] It demonstrates the application of the laws of balance as the starting point of a description of nature. In contrast to the method used in Part II, it does not assume the form of the relationship between currents of entropy and of energy in heating and in cooling. Moreover, it does not follow the historical path of using power cycles for developing the theory, as is common in thermodynamics.

The following sections can be taken as a proof that the ideal gas temperature is the natural measure of the thermal potential. The method presented here will give you a firmer grounding in thermodynamics, and it will prepare you for the simple examples of continuum physics discussed in the following two chapters.

After developing the model of the dynamics of heat of a single viscous fluid, I will repeat the approach for fluids undergoing chemical change. We will start with phase changes and then move to proper reactions. The development should allow you to formulate equivalent models for other materials such as elastic bodies.

10.1 THERMODYNAMICS OF A SINGLE VISCOUS FLUID

I will introduce a generalized approach to thermodynamic theory here by applying it to a simple fluid, namely a single viscous uniform body that cannot change its phase. With the exception of viscosity, this is the example of a material we have encountered in Chapter 5 and again in Chapter 8 (for open systems) where we have assumed constitutive relations allowing only for ideal processes. We have seen that a theory of thermodynamics of such ideal fluids leads to the same relations known from thermostatics, as you can verify by comparison with standard texts on this subject. In other words, the ideal fluids considered so far attain the same properties during dynamical processes as in equilibrium states. The materials for which the theory holds obey such simple constitutive laws as to deliver results independent of the speed and other details of processes. Even though the derivation is one of a theory of dynamics, time apparently drops out of the equations in the end.

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[1] See I. Müller: *Thermodynamics* (1985).

H.U. Fuchs, *The Dynamics of Heat: A Unified Approach to Thermodynamics and Heat Transfer*, Graduate Texts in Physics, DOI 10.1007/978-1-4419-7604-8_11,

If you change the conditions just a little bit, for example by introducing a viscous pressure term, time appears explicitly in the results. This is what I would like to demonstrate on the following pages. The previous results will then be obtained in the limit of vanishing viscosity.

10.1.1 Viscous Pressure

First we should discuss how to include viscosity in the constitutive laws describing the behavior of the fluid. This will tell us something about the particular form the assumptions should take upon which we will base the following development.

Imagine a viscous fluid. Naturally, the effect of viscosity will be felt only as long as the fluid flows. In the case of a uniform body this means that its volume must change. As long as viscous effects are neglected, we would assume the pressure of the fluid to be expressed as a function of temperature and of volume; now, however, we will assume the pressure, which is equivalent to the momentum current density across a surface, to also depend upon the speed of the process:

$$P\left(V,T,\dot{V}\right) = P\big|_E\left(V,T\right) + a\dot{V} \tag{10.1}$$

$P|_E$ is the static pressure of the fluid, i.e., the value of the pressure attained when the volume does not change, or if viscosity is neglected. As you can see, the rate of change of the volume of the body is therefore included as one of the independent variables of the theory. This will have important consequences for the assumptions to be made regarding the behavior of the fluid.

10.1.2 Assumptions

We need to make a number of assumptions to develop a theory of thermodynamics of a particular type of material. Basically, the fundamental laws used so far, with the exception of the relation between currents of entropy and of energy in heating, and with Equ.(1) replacing a simpler form of the equation of state, will furnish the foundation. Naturally, leaving out one assumption calls for a replacement, unless it was an unnecessary one to begin with:

1. First, we have to agree on the independent variables of the theory. As before, they will be the volume and the temperature of the uniform fluid, which now will be joined by the rate of change of the volume. Therefore, entropy, energy, pressure, and other quantities will be functions of *V, T*, and *dV/dt:*

   $$S = S\left(V,T,\dot{V}\right) \quad , \quad E = E\left(V,T,\dot{V}\right) \quad , \quad P = P\left(V,T,\dot{V}\right) \quad , \quad \ldots$$

   This requirement carries over to quantities such as the entropy capacitance and the latent entropy.

2. While we do not take the relation between currents of entropy, currents of energy, and temperature for granted (i.e., we do not assume the important law $I_{E,th} = T\,I_S$, with T the ideal gas temperature, to hold), we accept a constitutive law for the flux of energy in heating which makes it proportional to the flux of entropy.[2] If we heat twice as fast, i.e., if we double the current of entropy, we also double the current

of energy associated with the heating:

$$I_{E,th} \propto I_S \tag{10.2}$$

We see that this is a particular constitutive assumption. The flux of energy associated with compression and expansion of the uniform fluid, on the other hand, is well known:

$$I_{E,comp} = -P\dot{V} \tag{10.3}$$

3. The additional assumption needed in place of knowledge of the full relation between the currents of entropy and of energy in heating can be furnished as follows. We introduce ideal walls separating different fluid systems.[3] Ideal walls are defined to be those which do not contribute to thermal processes; i.e., they do not produce entropy. This means that as part of the definition, the entropy flux across an ideal wall is continuous:

$$I_S(\mathrm{I}) = I_S(\mathrm{II}) \tag{10.4}$$

where the roman numerals refer to the fluids separated by the wall. As the actual assumption, we take for granted that two fluids separated by an ideal wall will have the same temperature at the wall:

$$T(\mathrm{I}) = T(\mathrm{II}) \tag{10.5}$$

Naturally, the flux of energy is continuous across this wall as well (remember the discussion in Section 4.8). Assuming the existence of such walls is necessary for the measurement of temperature to work the way we know it: one of the fluids separated by the wall would be the fluid of the thermometer, the other would be the body whose temperature we wish to measure. Only the fluids, not the wall separating them, may have an influence upon the temperatures (see Fig. 10.1).

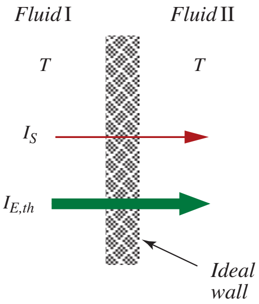

Figure 10.1: Two fluids of the same type are separated by an ideal wall. Across such a wall, entropy and energy flux are continuous. Also, it is assumed that the temperature is the same on both sides.

4. With these preliminaries, we can state the laws of balance which we take to be valid in the current case. They are the expressions of balance of entropy (for the ther-

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[2] In continuum physics, we have Fourier's law for the entropy flux density for fluids such as those described by the Navier-Stokes-Fourier equations:

$$j_S = -\varphi(T,\rho)\frac{dT}{dx}$$

The same type of equation also applies to the thermal energy flux density:

$$j_{E,th} = -\beta(T,\rho)\frac{dT}{dx}$$

Hence, the requirement of proportionality between these fluxes is satisfied. (See Chapter 12 for a more detailed discussion.) We have previously assumed constitutive laws of heating of uniform fluids for which this requirement is fulfilled as well.

[3] For a discussion, see Müller (1985), p. 168–169. The assumption of the continuity of temperature at an ideal wall, Equ.(10.5), replaces other assumptions which are made in different approaches to thermodynamics.

mal process), and of momentum (for the mechanical process). Therefore, we postulate that

$$\begin{aligned} \dot{S} &= I_S + \Pi_S \\ \dot{p} &= I_p \end{aligned} \tag{10.6}$$

Obviously, we should include the effect of irreversibility as a consequence of the viscosity of the material. Since the fluids are basically at rest, the balance of momentum is trivial and will not be explicitly required any longer.

5. Processes also satisfy the requirement of the balance of energy, in addition to the laws of balance for the special processes taking place. Since the particular fluids under investigation allow for thermal and mechanical changes only, the equation of balance of energy takes the form

$$\dot{E} = I_{E,comp} + I_{E,th} \tag{10.7}$$

Remember that this law does not distinguish between different types of physical processes; that is the responsibility of the other laws of balance.

10.1.3 Consequences of the Energy Principle

The crucial point about processes undergone by physical systems is that in addition to the proper laws of balance, they always satisfy the energy principle, i.e., the law of balance of energy, as well. This requirement may be expressed as follows:

> *Physical processes obey the energy principle. If these processes are required to be thermal, they also satisfy the balance of entropy; the law is then said to be a restriction upon the processes. If the phenomena are also supposed to be mechanical, a second restriction applies to them, namely the law of balance of momentum. Each particular law of balance serves as a restriction upon the form the laws governing a process may take.*

Now, such restrictions can be taken into account using Lagrange multipliers;[4] both Equations $(10.6)_1$ and (10.7) are satisfied simultaneously if and only if[5]

$$\dot{E} - I_{E,comp} - I_{E,th} - \lambda^S\left[\dot{S} - I_S - \Pi_S\right] = 0 \tag{10.8}$$

(Remember that we do not have to explicitly take the law of balance of momentum into consideration here.) This is the starting point of one of the approaches developed in continuum thermodynamics, which for lack of a better name, is called *thermodynamics with Lagrange multipliers*. Equ.(10.8) is obtained by subtracting the entropy principle (multiplied by a Lagrange multiplier) from the law of balance of energy. Naturally, λ^S must have the dimension of temperature for the equation to be dimensionally correct.

The next steps consist of expressing the mechanical current of energy, which is a result of changes of volume, and determining the time derivatives of the energy and entropy functions. Since these quantities are functions of volume, temperature, and rate of change of volume, we can write Equ.(10.8) as follows:

$$\begin{aligned}&\frac{\partial E}{\partial V}\dot{V}+\frac{\partial E}{\partial T}\dot{T}+\frac{\partial E}{\partial \dot{V}}\ddot{V}+\left(P\big|_E+a\dot{V}\right)\dot{V}-I_{E,th}\\&\qquad-\lambda^S\left[\frac{\partial S}{\partial V}\dot{V}+\frac{\partial S}{\partial T}\dot{T}+\frac{\partial S}{\partial \dot{V}}\ddot{V}-I_S-\Pi_S\right]=0\end{aligned} \tag{10.9}$$

To obtain this result, the derivatives of $E(V,T,dV/dt)$ and $S(V,T,dV/dt)$ have been written in terms of their partial derivatives, and the law for the mechanical (compressional) energy flux for uniform viscous fluids has been applied (remember Section 2.3.2 and Equ.(10.3)). If we combine terms which are explicitly linear in the time derivatives of the independent variables V, T, and dV/dt, Equ.(10.9) becomes

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4. Lagrange multipliers are known from extremal problems. Assume that a function $f(x_1,x_2,x_3)$ is to be maximized under the additional assumption that the two relations $g_i(x_1,x_2,x_3) = 0$, $i = 1,2$, have to be satisfied. These requirements mean that the three total derivatives have to be zero:

$$\begin{aligned}\frac{\partial f}{\partial x_1}\dot{x}_1+\frac{\partial f}{\partial x_2}\dot{x}_2+\frac{\partial f}{\partial x_3}\dot{x}_3&=0\\ \frac{\partial g_1}{\partial x_1}\dot{x}_1+\frac{\partial g_1}{\partial x_2}\dot{x}_2+\frac{\partial g_1}{\partial x_3}\dot{x}_3&=0\\ \frac{\partial g_2}{\partial x_1}\dot{x}_1+\frac{\partial g_2}{\partial x_2}\dot{x}_2+\frac{\partial g_2}{\partial x_3}\dot{x}_3&=0\end{aligned}$$

The dot denotes a derivative with respect to some parameter. The restrictions are taken into consideration using Lagrange multipliers λ^1 and λ^2. The last two equations are each multiplied by one of the factors and then added to the first. This leads to

$$\begin{aligned}&\left[\frac{\partial f}{\partial x_1}+\lambda^1\frac{\partial g_1}{\partial x_1}+\lambda^2\frac{\partial g_2}{\partial x_1}\right]\dot{x}_1+\left[\frac{\partial f}{\partial x_2}+\lambda^1\frac{\partial g_1}{\partial x_2}+\lambda^2\frac{\partial g_2}{\partial x_2}\right]\dot{x}_2\\&\qquad+\left[\frac{\partial f}{\partial x_3}+\lambda^1\frac{\partial g_1}{\partial x_3}+\lambda^2\frac{\partial g_2}{\partial x_3}\right]\dot{x}_3=0\end{aligned}$$

The restrictions introduced here mean that two of the unknown functions x_i could be expressed in terms of the third. One may therefore chose the Lagrange multipliers such that the first two terms in brackets are equal to zero. (These are equations for the two unknowns.) As a result, the third term in brackets must also be equal zero. We therefore obtain three new relations

$$\begin{aligned}\frac{\partial f}{\partial x_1}+\lambda^1\frac{\partial g_1}{\partial x_1}+\lambda^2\frac{\partial g_2}{\partial x_1}&=0\\ \frac{\partial f}{\partial x_2}+\lambda^1\frac{\partial g_1}{\partial x_2}+\lambda^2\frac{\partial g_2}{\partial x_2}&=0\\ \frac{\partial f}{\partial x_3}+\lambda^1\frac{\partial g_1}{\partial x_3}+\lambda^2\frac{\partial g_2}{\partial x_3}&=0\end{aligned}$$

which have to be satisfied together with the two restrictions. In summary, we have five equations for the unknowns x_i, and for the Lagrange multipliers λ^i. Because of the similarity of their approach with the classical method of Lagrange multipliers, Liu and Müller (see Müller, 1985) have chosen to call the λ's Lagrange multipliers.

$$\begin{aligned}&\left[\frac{\partial E}{\partial V}-\lambda^s\frac{\partial S}{\partial V}+P\big|_E\right]\dot{V}+\left[\frac{\partial E}{\partial T}-\lambda^s\frac{\partial S}{\partial T}\right]\dot{T}\\&\qquad+\left[\frac{\partial E}{\partial\dot{V}}-\lambda^S\frac{\partial S}{\partial\dot{V}}\right]\ddot{V}-I_{E,th}+\lambda^S I_S+a\dot{V}^2+\lambda^S\Pi_S=0\end{aligned}\qquad(10.10)$$

This equation must hold for all imaginable processes; i.e., it must be satisfied for all values of the derivatives of the independent variables. Assume this to be the case for a set of such values. Now change one of them just a little bit: in general, Equ.(10.9) will not be satisfied anymore unless the factor multiplying this derivative is set equal to zero. Since this reasoning applies to all terms explicitly involving the derivatives, the following three equations must hold:

$$\begin{aligned}&\frac{\partial E}{\partial V}-\lambda^S\frac{\partial S}{\partial V}+P\big|_E=0\\&\frac{\partial E}{\partial T}-\lambda^S\frac{\partial S}{\partial T}=0\\&\frac{\partial E}{\partial\dot{V}}-\lambda^S\frac{\partial S}{\partial\dot{V}}=0\end{aligned}\qquad(10.11)$$

This leaves us with the residual equation

$$-I_{E,th}+\lambda^S I_S+a\dot{V}^2+\lambda^S\Pi_S=0$$

We can say a couple of things about this equation. For one, the assumption that the fluxes of entropy and of energy in heating are proportional requires

$$I_{E,th}=\lambda^S I_S\qquad(10.12)$$

which at the same time means that

$$\Pi_S=-\frac{a}{\lambda^S}\dot{V}^2\qquad(10.13)$$

Obviously, the production of entropy is a direct consequence of the viscosity of the fluid. Clearly, *a* must be negative or zero.

10.1.4 Determination of the Lagrange Multiplier

Equations (10.11) through (10.13) are the preliminary results of our theory. If we manage to determine the multiplier λ^S in terms of physical quantities, we will have the basis for deriving all desired results about the particular material investigated.

There are still a couple of assumptions we have not used so far. First, we shall make use of the idea regarding ideal walls. Imagine two uniform ideal fluids (I and II) to be

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5. This proof, and the proof of the equivalence of these expressions to the requirement presented in Equ.(10.11), has been given by Liu (1972) for the general case. See also Müller (1985, p. 170).

separated by an ideal wall that only lets entropy and energy pass (see Fig. 10.1). Equ.(10.12) holds for both fluids which means that

$$I_{E,th}(\mathrm{I}) - \lambda^S\left(V_{\mathrm{I}}, T_{\mathrm{I}}, \dot{V}_{\mathrm{I}}\right) I_S(\mathrm{I}) = I_{E,th}(\mathrm{II}) - \lambda^S\left(V_{\mathrm{II}}, T_{\mathrm{II}}, \dot{V}_{\mathrm{II}}\right) I_S(\mathrm{II}) \tag{10.14}$$

Since both fluxes and the temperature are continuous across the wall, this condition reduces to

$$\lambda^S\left(V_{\mathrm{I}}, T, \dot{V}_{\mathrm{I}}\right) = \lambda^S\left(V_{\mathrm{II}}, T, \dot{V}_{\mathrm{II}}\right) \tag{10.15}$$

The volume and the rate of change of the volume of the two fluids are independent and can be given any values; this means that the Lagrange multiplier may only be a function of temperature, and not of the other two independent variables. We have

$$\lambda^S = \lambda^S(T) \tag{10.16}$$

The multiplier is a universal function of temperature, the same for all fluids of the type considered here.

We have to perform one more step before we can apply the results to the ideal gas and find the Lagrange multiplier. Since λ^S only depends upon the temperature of the fluid, Equ.(10.11)$_{(3)}$ reduces to

$$\frac{\partial}{\partial \dot{V}}\left(E - \lambda^S S\right) = 0$$

which means that $E - \lambda^S S$ is independent of dV/dt. Next, Equ.(10.11)$_{(2)}$ is transformed into

$$\frac{\partial}{\partial T}\left(E - \lambda^S S\right) = -S\frac{d\lambda^S}{dT}$$

This means that both the entropy and the energy of the fluid must be independent of the rate of change of the volume, and Equ.(10.11)$_{(3)}$ can be dropped from the list of results. These are strong restrictions upon the behavior of the material. We can say that

$$\begin{aligned} S &= S(V,T) \\ E &= E(V,T) \end{aligned} \tag{10.17}$$

Now we are ready to determine the Lagrange multiplier. For the moment, we will set the parameter a, which describes the effects of viscosity in Equ.(10.1), equal to zero. Since we have additional constitutive information about the ideal gas, let us apply the results to this body. We solve the first two parts in Equ.(10.11) for the derivatives of the energy function, and take the derivative with respect to the other independent variable:

$$\begin{aligned} \frac{\partial}{\partial T}\left(\frac{\partial E}{\partial V}\right) &= \frac{\partial}{\partial T}\left(\lambda^S \frac{\partial S}{\partial V} - P\big|_E\right) = \lambda^S \frac{\partial^2 S}{\partial V \partial T} + \frac{d\lambda^S}{dT}\frac{\partial S}{\partial V} - \frac{\partial P\big|_E}{\partial T} \\ \frac{\partial}{\partial V}\left(\frac{\partial E}{\partial T}\right) &= \frac{\partial}{\partial V}\left(\lambda^S \frac{\partial S}{\partial T}\right) = \lambda^S \frac{\partial^2 S}{\partial T \partial V} \end{aligned}$$

If the functions are assumed to be sufficiently smooth, the mixed derivatives must be equal. Therefore, we obtain the condition

$$\frac{d\lambda^S}{dT}\frac{\partial S}{\partial V} = \frac{\partial P|_E}{\partial T}$$

or

$$\frac{d\lambda^S}{dT}\left(\frac{\partial E}{\partial V} + P|_E\right)\frac{1}{\lambda^S} = \frac{\partial P|_E}{\partial T}$$

This finally leads to

$$\frac{1}{\lambda^S}\frac{d\lambda^S}{dT} = \frac{\partial P|_E/\partial T}{\partial E/\partial V + P|_E} \tag{10.18}$$

This still holds for all fluids. In the case of the ideal gas, however, the special properties show that the right-hand side of Equ.(10.18) is equal to the inverse of the ideal gas temperature. Remember that the energy of the ideal gas depends only upon temperature:

$$\frac{1}{\lambda^S}\frac{d\lambda^S}{dT} = \frac{1}{T} \tag{10.19}$$

Integration of this result shows that the unknown Lagrange multiplier is the ideal gas temperature:

$$\lambda^S = T \tag{10.20}$$

In other words, the ideal gas temperature takes the role of the thermal potential. This concludes the proof of the relation between currents of entropy and of energy in heating of uniform fluids. Considering that we allow for irreversibility, the result is even more interesting than the equivalent statement which is traditionally derived for ideal fluids by analyzing cyclic processes (see the Interlude of the First Edition).

10.1.5 Results for Uniform Viscous Fluids

Now that the main unknown factor of the theory has been determined, we can collect the results and derive some more important expressions. First, the fluxes of entropy and of energy in heating are related by

$$I_{E,th} = T\,I_S \tag{10.21}$$

Second, the rate of production of entropy as a consequence of viscous pressure is

$$\Pi_S = -\frac{a}{T}\dot{V}^2 \tag{10.22}$$

Since Π_S cannot be negative, we conclude that the parameter *a* in the law of viscous pressure cannot take positive values:

$$\Pi_S \geq 0 \quad \Rightarrow \quad a \leq 0 \tag{10.23}$$

Furthermore, the properties of the fluids are such that the partial derivatives of energy and of entropy are related by

$$\begin{aligned} \frac{\partial E(V,T)}{\partial V} &= T\,\frac{\partial S(V,T)}{\partial V} - P\big|_E(V,T) \\ \frac{\partial E(V,T)}{\partial T} &= T\,\frac{\partial S(V,T)}{\partial T} \end{aligned} \tag{10.24}$$

This is a consequence of Equ.(10.11). This result can be used to derive the Gibbs fundamental form of the fluid. Since the time derivative of the energy is composed of partial derivatives, according to

$$\dot{E} = \frac{\partial E(V,T)}{\partial V}\dot{V} + \frac{\partial E(V,T)}{\partial T}\dot{T}$$

this quantity can be expressed using Equ.(10.24) to yield

$$\dot{E} = T\,\dot{S} - P\big|_E\,\dot{V} \tag{10.25}$$

Finally, if we introduce the entropy capacitance and the latent entropy; i.e., if we write

$$\begin{aligned} K_V &= \frac{\partial S(V,T)}{\partial T} \\ \Lambda_V &= \frac{\partial S(V,T)}{\partial V} \end{aligned} \tag{10.26}$$

we see that the flux of entropy in heating can be expressed as follows:

$$I_S = \Lambda_V \dot{V} + K_V \dot{T} + \frac{a}{T}\dot{V}^2 \tag{10.27}$$

Obviously, in the case of viscous fluids, heating depends upon the speed of the process; in other words, it is no longer reversible. If you calculate processes undergone by the fluids described in this section, time will appear explicitly in the equations; we will have standard initial value problems that are absent from traditional thermodynamics.

The results we have come across before in Chapter 5 can be derived as the limit of the present theory for vanishing viscosity: if you set $a = 0$, you will obtain the previous results. Aside from the inclusion of irreversibility, the new approach taken to thermodynamics is the most important aspect of this section; in particular, it demonstrates how we can derive the forms of potentials, such as the thermal potential which relates fluxes of entropy and of energy. Remember that historically, the route via the properties of heat engines was chosen. Today, we trust the law of balance of entropy as a general expression of the second law of thermodynamics; therefore, the development presented here seems to flow naturally from what we have learned about thermal processes. Moreover, note how time appears naturally in our relations: we have standard initial value problems to solve.

10.2 IDEAL FLUIDS WITH PHASE TRANSFORMATIONS

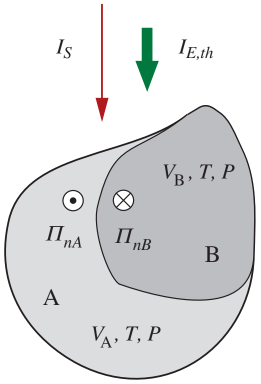

Figure 10.2: A system composed of two phases of the same fluid is heated. In addition to changes of volume and temperature, this case includes changes of amount of substance of the parts A and B. (When A loses an amount of substance, B gains just that much.) Temperature and pressure of the parts are assumed to be the same.

Consider a fluid composed of two phases of the same substance (Fig. 10.2). Both phases are assumed to have the same temperature and pressure. Basically, this sounds like the prescription for two unrelated, non-interacting fluids of the kind described in the previous section (if you disregard viscosity). However, in this case, the parts of the fluid are supposed to interact through a change of phase: one component can disappear while the amount of the other phase increases.

10.2.1 Assumptions

The assumptions that will be made in the course of the following derivation are mostly the same as those introduced above in Section 10.1. In particular, we are again dealing with ideal fluids and processes which do not produce entropy. Experience tells us that fluxes of entropy are reversed upon reversal of the changes undergone by the two phase fluids in chemical equilibrium shown in Fig. 10.2. Therefore, the equation of balance of entropy looks like the one used above:

$$\dot{S} = I_S \tag{10.28}$$

where the entropy of the system is now the sum of the entropies of the two phases A and B:

$$S(V,T,n) = S_A(V_A,T,n_A) + S_B(V_B,T,n_B) \tag{10.29}$$

Note that in the current case, the independent variables include the amounts of substance of the components.

Currents of entropy and of energy in heating are again taken to be proportional, as in Equ.(10.2), and we take the existence of ideal walls for granted.

We now have to add equations of balance for the two species A and B. There is no flow of any substance across system boundaries, but both A and B can undergo phase changes, leading to the production or destruction of the species. Therefore, the equations of balance read

$$\begin{aligned} \dot{n}_A &= \Pi_{nA} \\ \dot{n}_B &= \Pi_{nB} \end{aligned} \tag{10.30}$$

(Neglecting transports of the substances across the system boundary in Fig. 10.2 is of no fundamental significance.) Since the chemical reactions taking place are of a very special nature—when a unit of one phase disappears, exactly one unit of the other phase is produced—the rates of production and destruction are related by

$$\Pi_{nA} + \Pi_{nB} = 0 \tag{10.31}$$

Except for the balance of momentum, which, again, is trivial and does not have to be considered separately, these are the laws of balance of the processes taking place in the two phase fluids discussed here. As always, the processes also must satisfy the energy principle. The energy of the system can be changed only by energy flows due to heating or cooling and compression or expansion.

10.2.2 Consequences of the Balance of Energy

Even though we have extended the nature of the fluids under investigation, the law of balance of energy looks just like it did in the case of the single phase fluid. Since, with the exception of energy, the only physical quantities exchanged across the boundary of the system are entropy and momentum, the only energy currents are the thermal and the mechanical ones; the latter is related to compression or expansion:

$$\dot{E}_{\mathrm{A}} + \dot{E}_{\mathrm{B}} - I_{E,comp} - I_{E,th} = 0 \tag{10.32}$$

The expression for the exchange of energy in the compressional process is the same one used for the power of non-viscous uniform fluids. This time, however, we can write it with the volumes of both components in mind:

$$I_{E,comp} = -P\left(\dot{V}_{\mathrm{A}} + \dot{V}_{\mathrm{B}}\right) \tag{10.33}$$

The method of taking the balance of energy into account simultaneously with the balance of all other relevant quantities, once more requires the introduction of Lagrange multipliers. There is one such multiplier for every basic law of balance that is added to the list, including the energy principle. In our case, this means that we have to introduce three such factors, which we label λ^S, $\lambda^{n\mathrm{A}}$, and $\lambda^{n\mathrm{B}}$, respectively. The relation to be satisfied then takes the form:

$$\begin{aligned} &\dot{E}_{\mathrm{A}} + \dot{E}_{\mathrm{B}} + P\left(\dot{V}_{\mathrm{A}} + \dot{V}_{\mathrm{B}}\right) - I_{E,th} \\ &\quad - \lambda^S\left[\dot{S}_{\mathrm{A}} + \dot{S}_{\mathrm{B}} - I_S\right] - \lambda^{n\mathrm{A}}\left[\dot{n}_{\mathrm{A}} - \Pi_{n\mathrm{A}}\right] - \lambda^{n\mathrm{B}}\left[\dot{n}_{\mathrm{B}} - \Pi_{n\mathrm{B}}\right] = 0 \end{aligned} \tag{10.34}$$

The following steps in evaluating the consequences of the energy principle are similar to those in the case of the single phase fluid. However, they involve some more algebra. First, we introduce the derivatives of the energy and the entropy with respect to the independent variables. After collecting the terms that are explicitly linear in the time derivatives of these independent variables, we obtain

$$\begin{aligned} &\left[\frac{\partial E_{\mathrm{A}}}{\partial V_{\mathrm{A}}} - \lambda^S \frac{\partial S_{\mathrm{A}}}{\partial V_{\mathrm{A}}} + P\right]\dot{V}_{\mathrm{A}} + \left[\frac{\partial E_{\mathrm{B}}}{\partial V_{\mathrm{B}}} - \lambda^S \frac{\partial S_{\mathrm{B}}}{\partial V_{\mathrm{B}}} + P\right]\dot{V}_{\mathrm{B}} + \left[\frac{\partial E_{\mathrm{A}}}{\partial T} - \lambda^S \frac{\partial S_{\mathrm{A}}}{\partial T}\right]\dot{T} \\ &\left[\frac{\partial E_{\mathrm{B}}}{\partial T} - \lambda^S \frac{\partial S_{\mathrm{B}}}{\partial T}\right]\dot{T} + \left[\frac{\partial E_{\mathrm{A}}}{\partial n_{\mathrm{A}}} - \lambda^S \frac{\partial S_{\mathrm{A}}}{\partial n_{\mathrm{A}}} - \lambda^{n\mathrm{A}}\right]\dot{n}_{\mathrm{A}} + \left[\frac{\partial E_{\mathrm{B}}}{\partial n_{\mathrm{B}}} - \lambda^S \frac{\partial S_{\mathrm{B}}}{\partial n_{\mathrm{B}}} - \lambda^{n\mathrm{B}}\right]\dot{n}_{\mathrm{B}} \\ &-\left[I_{E,th} - \lambda^S I_S\right] - \left[\lambda^{n\mathrm{A}}\Pi_{n\mathrm{A}} + \lambda^{n\mathrm{B}}\Pi_{n\mathrm{B}}\right] = 0 \end{aligned}$$

The same arguments that led to Equations (10.11) and (10.12) also apply here. Starting with the second one, the fluxes of entropy and of energy will be proportional if

$$I_{E,th} = \lambda^S I_S \tag{10.35}$$

For the remainder of the equation, we can say that it has to be satisfied for all possible values of the rates of change of the independent variables. Since this requirement can easily be violated unless all factors are identically zero, we end up with the following relations:

$$\begin{aligned}
&\frac{\partial E_\mathrm{A}}{\partial V_\mathrm{A}} - \lambda^S \frac{\partial S_\mathrm{A}}{\partial V_\mathrm{A}} + P = 0 \\
&\frac{\partial E_\mathrm{B}}{\partial V_\mathrm{B}} - \lambda^S \frac{\partial S_\mathrm{B}}{\partial V_\mathrm{B}} + P = 0 \\
&\frac{\partial E_\mathrm{A}}{\partial T} - \lambda^S \frac{\partial S_\mathrm{A}}{\partial T} = 0 \\
&\frac{\partial E_\mathrm{B}}{\partial T} - \lambda^S \frac{\partial S_\mathrm{B}}{\partial T} = 0 \\
&\frac{\partial E_\mathrm{A}}{\partial n_\mathrm{A}} - \lambda^S \frac{\partial S_\mathrm{A}}{\partial n_\mathrm{A}} - \lambda^{n\mathrm{A}} = 0 \\
&\frac{\partial E_\mathrm{B}}{\partial n_\mathrm{B}} - \lambda^S \frac{\partial S_\mathrm{B}}{\partial n_\mathrm{B}} - \lambda^{n\mathrm{B}} = 0
\end{aligned} \tag{10.36}$$

and, for the production rates of the species:

$$\lambda^{n\mathrm{A}} \Pi_{n\mathrm{A}} + \lambda^{n\mathrm{B}} \Pi_{n\mathrm{B}} = 0 \tag{10.37}$$

This last relation will prove to be important when we interpret the meaning of the Lagrange multipliers that go with the species A and B. For now, we will use the reasoning presented when the Lagrange multiplier λ^S was determined. We start with a single-phase fluid for which the result of the previous section applies: λ^S is equal to the temperature. Then, a fluid (II) of this type is brought in contact with the two-phase fluid (I) via an ideal wall. Again, the argument which led to Equ.(10.14) is used; here it means that

$$\lambda^S(\mathrm{II}) = \lambda^S(\mathrm{I}) = T \tag{10.38}$$

All that remains to be done is to determine the multipliers λ^{nA} and λ^{nB}.

10.2.3 The Chemical Potential of Pure Fluids

Take a closer look at Equ.(10.37). If we combine it with the relation between the production rates, i.e., with Equ.(10.31), we see that the Lagrange multipliers of the two phases of the fluid must be equal:

$$\left(\lambda^{n\mathrm{A}} - \lambda^{n\mathrm{B}}\right)\Pi_{n\mathrm{A}} = 0 \quad \Rightarrow \quad \lambda^{n\mathrm{A}} = \lambda^{n\mathrm{B}} \tag{10.39}$$

Since the phases are in chemical equilibrium, it makes sense to interpret the as yet unknown factors as the chemical potentials of the fluid:

$$\lambda^{n\mathrm{A}} = \mu_\mathrm{A} \quad , \quad \lambda^{n\mathrm{B}} = \mu_\mathrm{B} \tag{10.40}$$

The rest of the equations derived above provide a means of relating the chemical potentials to other variables of the fluids. By introducing the Lagrange multipliers into the intermediate results, we obtain the laws that govern the behavior of pure fluids that may undergo phase transformations. First, the fluxes of entropy and of energy in heating must be related by the ideal gas temperature:

$$I_{E,th} = T\, I_S \tag{10.41}$$

Then, the partial derivatives of the energy and the entropy functions satisfy the relations presented in Equ.(10.36). For each of the phases, we may now write

$$\begin{aligned}
\frac{\partial E(V,T,n)}{\partial V} &= T\,\frac{\partial S(V,T,n)}{\partial V} - P(V,T,n)\\
\frac{\partial E(V,T,n)}{\partial T} &= T\,\frac{\partial S(V,T,n)}{\partial T}\\
\frac{\partial E(V,T,n)}{\partial n} &= T\,\frac{\partial S(V,T,n)}{\partial n} + \mu(V,T,n)
\end{aligned} \tag{10.42}$$

10.2.4 The Gibbs Fundamental Form and the Chemical Potential

Since the energy is a function of volume, temperature, and amount of substance, its time derivative is

$$\dot{E} = \frac{\partial E(V,T,n)}{\partial V}\dot{V} + \frac{\partial E(V,T,n)}{\partial T}\dot{T} + \frac{\partial E(V,T,n)}{\partial n}\dot{n}$$

Introducing the laws derived in Equ.(10.42) and collecting terms leads to the *Gibbs fundamental form* for fluids whose amount of substance may change:

$$\dot{E} = T\,\dot{S} - P\dot{V} + \mu\dot{n} \tag{10.43}$$

This is an extension of the form used for single-phase fluids. Again, there is one such relation for each of the phases. Now, we are ready to derive the relationship between the chemical potential and other variables of the fluid. We write each of the extensive quantities in Equ.(10.43) as the product of its density and the volume:

$$\frac{d}{dt}(\rho_E V) - T\,\frac{d}{dt}(\rho_S V) + P\frac{d}{dt}V - \mu\frac{d}{dt}(\rho_n V) = 0$$

Taking the derivatives leads to

$$[\rho_E - T\rho_S + P - \mu\rho_n]\dot{V} + [\dot{\rho}_E - T\dot{\rho}_S - \mu\dot{\rho}_n]V = 0$$

Since this relation must be satisfied for all possible (independent) values of the volume and its time derivative, both factors in brackets must be identically zero. Otherwise, the equation could be violated. The result of these considerations are the Gibbs fundamental form written in terms of the densities, and the relations between energy, entropy, density, and chemical potential:

$$\dot{\rho}_E = T\dot{\rho}_S + \mu\dot{\rho}_n \tag{10.44}$$

and

$$\bar{e} = T\,\bar{s} - P\bar{\upsilon} + \mu \tag{10.45}$$

The last formula has been rewritten by using molar quantities (see Equ.(8.46)).

10.2.5 Temperature and Pressure Dependence of the Chemical Potential

We have made extensive use of the dependence of the chemical potential upon temperature and pressure in the course of the applications presented in the previous sections. There, the proof was performed for special cases, but now we are in a position to deliver a general derivation.

In the development of the theory we started with temperature, volume, and amount of substance as the independent variables. With the Gibbs fundamental form, on the other hand, energy, temperature, pressure, and the chemical potential are variables of entropy, volume, and amount of substance. Other forms of Equ.(10.43) are based on other sets of independent variables. We need the set that includes temperature and pressure in addition to amount of substance. This transformation is facilitated using the definition of the *Gibbs free energy* function G:

$$G = E + PV - T\,S \tag{10.46}$$

The time derivative of this quantity is equal to

$$\dot{G} = \dot{E} + P\dot{V} + \dot{P}V - T\,\dot{S} - \dot{T}\,S$$

Using Equ.(10.43), this can be written

$$\dot{G} = V\dot{P} - S\dot{T} + \mu\dot{n} \tag{10.47}$$

which is an alternative fundamental form having independent variables P, T, and n. According to Equ.(10.47), the partial derivatives of $G(P,T,n)$ are equal to the volume, the entropy, and the chemical potential, respectively:

$$\frac{\partial G(P,T,n)}{\partial P} = V(P,T,n) = n\overline{v}(P,T,n) \tag{10.48}$$

$$\frac{\partial G(P,T,n)}{\partial T} = -S(P,T,n) = -n\overline{s}(P,T,n) \tag{10.49}$$

$$\frac{\partial G(P,T,n)}{\partial n} = \mu(P,T,n) \tag{10.50}$$

Taking the derivative of Equ.(10.48) with respect to amount of substance, the derivative of Equ.(10.50) with respect to pressure, and equating the mixed derivatives

$$\frac{\partial}{\partial n}\frac{\partial G(P,T,n)}{\partial P} = \overline{v}(P,T)$$
$$\frac{\partial}{\partial P}\frac{\partial G(P,T,n)}{\partial n} = \frac{\partial \mu(P,T,n)}{\partial P}$$

we obtain the first of the desired results:

$$\frac{\partial \mu(P,T,n)}{\partial P} = \overline{v}(P,T) \tag{10.51}$$

The second one is derived in just the same way:

$$\frac{\partial \mu(P,T,n)}{\partial T} = -\bar{s}(P,T) \tag{10.52}$$

These are the relations we used above. They are an example of the restrictions put upon the multitude of quantities used for the description of phenomena; theory limits the number of independent functions which might have to be measured in the lab if property data are required (see Chapter 15).

10.2.6 The Clapeyron Equation

In Chapter 15, we will discuss in much more detail the fact that for phase changes, pressure and temperature are related directly. This is a consequence of the equality of the chemical potentials of both phases at the transition:

$$\mu_{\mathrm{I}}(P,T) = \mu_{\mathrm{II}}(P,T) \tag{10.53}$$

Since this holds for all values of the temperature, the derivative of the difference of the potentials with respect to *T* must be zero:

$$\frac{d(\mu_{\mathrm{II}} - \mu_{\mathrm{I}})}{dT} = 0 \tag{10.54}$$

Performing the differentiation leads to

$$\frac{\partial \mu_{\mathrm{II}}}{\partial T} + \frac{\partial \mu_{\mathrm{II}}}{\partial P}\frac{dP}{dT} - \left(\frac{\partial \mu_{\mathrm{I}}}{\partial T} + \frac{\partial \mu_{\mathrm{I}}}{\partial P}\frac{dP}{dT}\right) = 0$$

We can introduce the temperature and pressure dependence of the chemical potentials according to Equations (10.51) and (10.52), and obtain the Clapeyron equation:

$$-\bar{s}_{\mathrm{II}} + \bar{s}_{\mathrm{I}} + \left[\bar{v}_{\mathrm{II}} - \bar{v}_{\mathrm{I}}\right]\frac{dP}{dT} = 0 \tag{10.55}$$

In Chapter 15, we will make use of this result in the derivation of vapor pressure.

10.3 REACTION IN UNIFORM MIXTURES OF FLUIDS

Let us now treat the special case of reactions occurring in a closed system (no flow). A fluid is composed of several species which may react; it may exchange heat, and it is deformable. Still, we will treat the system as a uniform, non-viscous chunk of matter. The effects of motion will be neglected.

Again, we have to consider the proper expressions of balance which hold for entropy and amount of substance. Since we have *N* different species, we arrive at

$$\begin{aligned} &\dot{S} - I_S = \Pi_S \\ &\dot{n}_1 = \Pi_{n1} \quad , \quad \dots \quad , \quad \dot{n}_N = \Pi_{nN} \end{aligned} \tag{10.56}$$

While we do not allow for convective currents in our model, we can no longer exclude the possibility of entropy being generated; indeed, we know that this is precisely what happens in reacting fluids that cannot undergo other processes; we therefore have an entropy production rate in the balance of entropy. As far as chemical substances are concerned, there is an equation of balance for the amount of substance of each of the species present.

Energy may be exchanged with the surroundings as a consequence of heating and of deformation. Therefore, we have an equation of balance of energy with two terms describing exchange, namely:

$$\dot{E} = I_{E,comp} + I_{E,th} \tag{10.57}$$

For the non-viscous, uniform fluid, the flux of energy due to deformation is

$$I_{E,comp} = -P\dot{V} \tag{10.58}$$

where P is the total pressure of the fluid. Again, we will follow the derivation introduced above, which leads to

$$\dot{E} + P\dot{V} - I_{E,th} - T\left[\dot{S} - I_S - \Pi_S\right] - \sum_{i=1}^{N} \mu_i\left[\dot{n}_i - \Pi_{ni}\right] = 0 \tag{10.59}$$

as a consequence of the fact that all equations of balance should be satisfied simultaneously. To simplify the work, we have assumed the Lagrange multipliers to be known. This equation is easily rearranged as follows:

$$\underbrace{\dot{E} + P\dot{V} - T\dot{S} - \sum_{i=1}^{N} \mu_i \dot{n}_i}_{=0} - \underbrace{I_{E,th} + T I_S}_{=0} + \underbrace{T\Pi_S + \sum_{i=1}^{N} \mu_i \Pi_{ni}}_{=0} = 0 \tag{10.60}$$

For the same reasons as given above, the first and the second terms must be equal to zero, which leads to the main result of the present case:

$$\dot{E} + P\dot{V} - T\dot{S} - \sum_{i=1}^{N} \mu_i \dot{n}_i = 0 \tag{10.61}$$

$$T\Pi_S + \sum_{i=1}^{N} \mu_i \Pi_{ni} = 0 \tag{10.62}$$

The first of these expressions is the Gibbs fundamental form of a fluid composed of different substances, while the second demonstrates how much entropy is produced as a consequence of the irreversible reactions between species.

Consequences of the theory are derived in a manner very similar to what we have seen in Section 10.2. We have taken the energy and the entropy of the fluid to be functions of volume, temperature, and N species. If we perform partial derivatives on the Gibbs fundamental form, Equ.(10.61), and collect the terms, we get

$$\left[\frac{\partial E}{\partial V}-T\frac{\partial S}{\partial V}+P\right]\dot{V}+\left[\frac{\partial E}{\partial T}-T\frac{\partial S}{\partial T}\right]\dot{T}+\sum_{i=1}^{N}\left[\frac{\partial E}{\partial n_i}-T\frac{\partial S}{\partial n_i}-\mu_i\right]\dot{n}_i=0$$

Since every one of the independent variables can be changed independently of the others, each of the terms in brackets must be zero:

$$\begin{aligned}\frac{\partial E\left(V,T,n_1\ldots n_N\right)}{\partial V}&=T\frac{\partial S\left(V,T,n_1\ldots n_N\right)}{\partial V}-P\left(V,T,n_1\ldots n_N\right)\\ \frac{\partial E\left(V,T,n_1\ldots n_N\right)}{\partial T}&=T\frac{\partial S\left(V,T,n_1\ldots n_N\right)}{\partial T}\end{aligned} \tag{10.63}$$

and

$$\frac{\partial E\left(V,T,n_1\ldots n_N\right)}{\partial n_i}=T\frac{\partial S\left(V,T,n_1\ldots n_N\right)}{\partial n_i}+\mu_i\left(V,T,n_1\ldots n_N\right) \tag{10.64}$$

for $i = 1\ldots N$. These relations are similar, but not equal, to what we have derived in Equ.(10.42). In that case, the relations held for each individual phase composed of only one species. In our current case, on the other hand, E and S are the energy and the entropy of the entire mixture, and we have a total of N equations of the form given in Equ.(10.64), where the derivatives of these functions are taken with respect to each of the species of the mixture.

EXERCISES AND PROBLEMS

1. Consider a uniform viscous fluid like the one introduced in Section 10.1. Let the fluid have a pressure, and entropy capacitance, and a latent entropy like the ideal gas, but let friction be present. (a) Show that the energy added in heating of the fluid at constant volume is

$$E_{th}=E\left(V,T_f\right)-E\left(V,T_i\right)$$

where the indices i and f refer to the initial and the final states, respectively. (b) Consider heating at constant pressure. Show that, in this case, the energy added in heating can be expressed as

$$E_{th}=H\left(P,T_f\right)-H\left(P,T_i\right)+\int_{t_i}^{t_f}a\dot{V}^2dt$$

Show that this quantity is always less than the difference of the enthalpies at the end and the beginning. (c) Assume the friction factor a, the rate of change of the volume, and the energy current in heating to be given. Assume the rate of change of the volume to be constant. Show that the initial value problem of the fluid takes the form

$$\begin{aligned}&\frac{C_V}{T}\dot{T}-\frac{1}{T}I_{E,th}\left(t\right)+\frac{a}{T}\dot{V}^2=-\frac{nR}{V_0+\dot{V}t}\dot{V}\\ &T\left(t=0\right)=T_0\end{aligned}$$

where V_0 is the volume at $t = 0$.

2. Consider the uniform viscous fluid described in Problem 1. Show that for isothermal heating at a temperature T with prescribed entropy current $I_S(t)$, the differential equation for the volume becomes

$$\frac{a}{T}\dot{V}^2 + \frac{nR}{V}\dot{V} = I_S(t)$$

3. Derive the initial value problem for adiabatic processes of an ideal gas having internal friction according to the model of Section 10.1. Assume the rate of change of volume to be given as a particular function of time.

4. (a) Show how to obtain the temperature and the pressure of a simple fluid as derivatives of the energy function. (b) Derive the energy of the ideal gas as a function of S and V. Show that you can obtain both the entropy as a function of temperature and volume, and the equation of state of the ideal gas from this information.

5. Isothermal and adiabatic compressibilities, κ_T and κ_S, are defines as follows:

$$\kappa_T = -\frac{1}{V}\frac{\partial V(P,T)}{\partial P} \quad , \quad \kappa_S = -\frac{1}{V}\frac{\partial V(P,S)}{\partial P}$$

Demonstrate that κ_T and κ_S, are related by the factor γ (the ratio of the specific heats).

6. For the uniform fluids treated in Section 10.1, show that

$$\Lambda_V = \frac{\partial P(V,T)}{\partial T}$$

7. The thermal coefficient of expansion is defined as $\alpha_V = (1/V)\partial V(P,T)/\partial T$. Prove the following relationship:

$$K_P - K_V = V\frac{\alpha^2}{\kappa_T}$$

Transform this relation to show that the specific temperature coefficients of enthalpy and of energy are related by

$$c_P = c_V\left(1 + \gamma^* \alpha_V T\right) \quad , \quad \gamma^* = \frac{\alpha_V}{\rho c_V \kappa_T} = \frac{\alpha_V}{\rho c_P \kappa_S}$$

where γ^* is called the Grüneisen ratio. (κ_S is the adiabatic compressibility, respectively.) Show that the Grüneisen ratio for the ideal gas is

$$\gamma^* = \frac{c_P}{c_V} - 1 = \gamma - 1$$

8. Assume that the density $\rho(T)$, the specific entropy capacitance $\kappa_P(T)$ at constant pressure, and the speed of sound c in a fluid are known from experiments as functions of temperature for a given pressure. Determine from these values the ratio of the specific heats γ, the (isothermal) compressibility κ_T, and the latent entropy with respect to volume.

9. Show that the law of adiabatic change of an ideal fluid written with temperature and density as the independent variables is given by

$$\left.\frac{dT}{d\rho}\right|_{ad} = \frac{T}{\rho}\gamma^*$$

where γ^* is the Grüneisen ratio defined in Problem 7.