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Extended thermodynamics of molecular ideal gases

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The objective of extended thermodynamics of molecular ideal gases is the determination of the 17 fields of *mass density, velocity, energy density, pressure deviator, heat flux, intrinsic energy density and intrinsic heat flux.*

The intrinsic energy represents the rotational or the vibrational energy of the molecules.

The necessary field equations are based upon balance laws and the system of equations is closed by constitutive relations which are characteristic for the gas under consideration.

The generality of the constitutive relations is restricted by *the principle of material frame indifference, and by the entropy principle.*

These principles reduce the constitutive coefficients of all fluxes to the thermal and caloric equation of state of the gas and provide inequalities for the transport coefficients.

The transport coefficients can be related to the shear viscosity, the heat conductivity, and the coefficients of self-diffusion and attenuation of sound waves, so that the field equations become quite specific. The theory is in perfect agreement with the kinetic theory of molecular gases.

It is shown that in non-equilibrium the temperature is discontinuous at thermometric walls. The dynamic pressure and the volume viscosity, are discussed and it is shown how extended thermodynamics and ordinary thermodynamics are related.

1 Introduction

The modern version of extended thermodynamics was recently formulated by Liu & Müller [1] and Kremer [2] as a theory of monatomic gases. The objective of those authors was to obtain a phenomenological theory that is in close agreement with the kinetic theory of gases. And, as such, the theory was successful. Therefore the desire arose to apply the reasoning of extended thermodynamics to a less restricted class of materials and in [3] Kremer worked out the case of real gases, published in [4], and the case of molecular ideal gases, which is described in the present paper.

The objective of extended thermodynamics of molecular gases is the determination of the 17 fields of

$$\begin{aligned}&\textit{mass density } \varrho,\\ &\textit{momentum density } \varrho v_i,\\ &\textit{momentum flux } F_{ij},\\ &\textit{translational energy flux } \tfrac{1}{2} F_{jji},\\ &\textit{intrinsic energy density } \varrho g,\\ &\textit{intrinsic energy flux } G_i.\end{aligned} \tag{1.1}$$

The translational energy density is equal to $\frac{1}{2} F_{ii}$. It is therefore implicitly included in this list of fields. The intrinsic energy density represents the rotational or vibrational energy of the molecules.

The necessary field equations are based upon balance laws, and constitutive equations are formulated to close the system of equations. The constitutive equations are restricted by *the principle of material frame indifference, and by the entropy principle.*

It turns out that all but 6 out of 34 constitutive coefficients can be related to the thermal and caloric equations of state by a careful and systematic exploitation of these principles. The remaining coefficients can either be related to the shear viscosity and heat-conductivity, or they follow from the coefficient of self-diffusion or the absorption and dispersion of sound waves. Alternatively these coefficients may be found by comparison with the kinetic theory of gases, notably with the Eucken formula.

The notation in the paper is the usual indicial notation with summation over repeated indices. Round brackets indicate symmetrization, square brackets antisymmetrization, and angular brackets indicate symmetric and traceless tensors.

2 Thermodynamic processes

All field equations are supposed to be based on balance laws, i.e. differential equations of the generic form

$$\frac{\partial Q}{\partial t} + \frac{\partial Q_i}{\partial x_i} = P, \tag{2.1}$$

where Q, Q_i and P are density, flux and production, respectively.

In particular for the fields (1.1) the balance equations have the form

$$\text{Balance of mass } \frac{\partial \varrho}{\partial t} + \frac{\partial \varrho v_i}{\partial x_i} = 0. \tag{2.2a}$$

$$\text{Balance of momentum } \frac{\partial \varrho v_i}{\partial t} + \frac{\partial F_{ij}}{\partial x_j} = 0. \tag{2.2b}$$

Balance of momentum flux $$\frac{\partial F_{ij}}{\partial t} + \frac{\partial F_{ijk}}{\partial x_k} = P_{ij}. \tag{2.2c}$$

Balance of translational energy flux $$\frac{\partial \frac{1}{2} F_{jji}}{\partial t} + \frac{\partial \frac{1}{2} F_{ijjk}}{\partial x_k} = P_{jji}. \tag{2.2d}$$

Balance of intrinsic energy $$\frac{\partial \varrho g}{\partial t} + \frac{\partial G_i}{\partial x_i} = -\tfrac{1}{2} P_{ii}. \tag{2.2e}$$

Balance of intrinsic energy flux $$\frac{\partial G_i}{\partial t} + \frac{\partial G_{ij}}{\partial x_j} = P_i. \tag{2.2f}$$

The Eq. (2.2a–d) are formally the usual 13 balance equations of extended thermodynamics of monatomic gases with vanishing productions for mass and momentum. The trace of Eq. (2.2c) implies the balance of translational energy whose energy is $\frac{1}{2} F_{ii}$, and $\frac{1}{2} P_{ii}$ is its production. Thus the balance of total energy with density $\varrho g + \frac{1}{2} F_{ii}$ is a conservation law. All tensors are symmetric.

The system of Eq. (2.2) is closed by considering

$$F_{\langle ijk \rangle}, F_{ijjk}, G_{ij}, P_{ij}, P_{jji}, P_i \tag{2.3}$$

as constitutive quantities which—at a given point and time—are related to the values of the fields (1.1) at that point and time in a manner dependent on material. Thus the constitutive equations have the generic form

$$\mathrm{C} = \mathfrak{C}(\varrho, v_i, F_{ij}, F_{jji}, g, G_i) \tag{2.4}$$

where C stands for any one of the quantities (2.3).

If the constitutive functions $\mathfrak{C}$ were known explicitly, we should now have an explicit system of 17 fields equations which are first order differential equations. Every solution of this system is called a *thermodynamic process.*

3 Constitutive theory

3.1 Scope of constitutive theory

In reality the constitutive functions $\mathfrak{C}$ are not known and we must rely on the constitutive theory to restrict their generality and—if possible—to reduce these functions to a few coefficients which can then be measured.

The tools of the constitutive theory are universal physical principles and, above all *the principle of material frame indifference, and the entropy principle.*

I shall state and exploit these principles later in this paper. First, however, I wish to recognize the special role of the velocity in the constitutive functions.

3.2 A reformulation of the problem in terms of non-convective quantities

Instead of the fluxes F_{ij}, F_{ijk}, F_{ijjk}, G_i, G_{ij} and productions P_{jji}, P_i one may introduce *non-convective quantities* denoted as p's, g's and r's in the following equations

$$F_{ij} = \varrho v_i v_j + p_{ij}, \tag{3.1a}$$

$$F_{ijk} = \varrho v_i v_j v_k + 3p_{(ij}v_{k)} + p_{ijk}, \tag{3.1b}$$

$$F_{ijjk} = \varrho v_i v_j v_j v_k + 6p_{(ij}v_j v_{k)} + 4p_{(ijk}v_{j)} + p_{ijjk}, \tag{3.1c}$$

$$G_i = \varrho g v_i + g_i, \tag{3.1d}$$

$$G_{ij} = \varrho g v_i v_j + 2g_{(i}v_{j)} + g_{ij}, \tag{3.1e}$$

$$P_{jji} = 3P_{(ij}v_{j)} + 2r_i^T, \tag{3.1f}$$

$$P_i = -\tfrac{1}{2} P_{jj} v_i + r_i^I. \tag{3.1g}$$

These decompositions render the velocity dependence of the densities, fluxes and productions explicit, because the non-convective quantities are independent of the velocity. This statement is in anticipation of the principle of material frame indifference and I shall come back to it. The complexity of these decompositions, particularly of (3.1 b, c) is motivated by the kinetic theory of gases, but it can also be derived from the requirement of Galilei invariance of the balance laws.

Some special notation is introduced to fit the customary nomenclature. Thus we call

p_{ij} the pressure tensor, (3.2a)

$p = \frac{1}{3} p_{ii}$ the pressure, (3.2b)

$\varepsilon^T = \dfrac{3p}{2\varrho}$ the translational internal energy, (3.2c)

$\varepsilon = \varepsilon^T + g$ the internal energy, (3.2d)

$q_i^T = \frac{1}{2} p_{jji}$ the translational heat flux, (3.2e)

g_i the intrinsic heat flux. (3.2f)

We may replace the F's, G's and P's in the Eq. (2.2) according to (3.1) and (3.2) and introduce the material derivative $\dot a = \dfrac{\partial a}{\partial t} + v_i \dfrac{\partial a}{\partial x_i}$. Thus follows after a little calculation

$$\dot\varrho + \varrho \frac{\partial v_i}{\partial x_i} = 0, \tag{3.3a}$$

$$\varrho \dot v_i + \frac{\partial p_{ij}}{\partial x_j} = 0, \tag{3.3b}$$

$$\dot p_{ij} + p_{ij}\frac{\partial v_k}{\partial x_k} + \frac{\partial p_{\langle ijk\rangle}}{\partial x_k} + \frac{4}{5}\frac{\partial q^T_{(i}}{\partial x_{j)}} + \frac{2}{5}\frac{\partial q^T_k}{\partial x_k}\delta_{ij} + 2p_{k(i}\frac{\partial v_{j)}}{\partial x_k} = P_{ij}, \tag{3.3c}$$

$$\dot q_i^T + \frac{7}{5} q_i^T \frac{\partial v_k}{\partial x_k} + \frac{1}{2}\frac{\partial p_{ijjk}}{\partial x_k} + p_{\langle ijk\rangle}\frac{\partial v_j}{\partial x_k} + \frac{2}{5} q_j^T \frac{\partial v_j}{\partial x_i} + \frac{7}{5} q_j^T \frac{\partial v_i}{\partial x_j}$$
$$- \frac{p_{ij}}{\varrho}\frac{\partial p_{jk}}{\partial x_k} - \frac{p_{jj}}{2\varrho}\frac{\partial p_{ik}}{\partial x_k} = r_i^T, \tag{3.3d}$$

$$\varrho \dot{g} + \frac{\partial g_i}{\partial x_i} = \frac{-1}{2} P_{ii}, \tag{3.3e}$$

$$\dot{g}_i + g_i \frac{\partial v_k}{\partial x_k} + \frac{\partial g_{ij}}{\partial x_j} + g_j \frac{\partial v_i}{\partial x_j} - g \frac{\partial p_{ij}}{\partial x_j} = r_i^I. \tag{3.3f}$$

These equations appear to be more complicated than the original ones in (2.2), in particular they do not reveal the simple balance structure. And yet for the purposes of the constitutive theory they are preferable, because the velocity and its derivatives occur only explicitly.

The variables and constitutive quantities are now chosen to be

$$\varrho, v_i, p_{ij}, q_i^T, g, g_i, \tag{3.4}$$

and

$$p_{\langle ijk \rangle}, p_{ijjk}, g_{ij}, P_{ii}, P_{\langle ij \rangle}, r_i^T, r_i^I. \tag{3.5}$$

respectively, and, of course, these sets are equivalent to the original ones in (1.1) and (2.3). Thus the constitutive relations read

$$\hat{C} = \hat{\mathfrak{C}}(\varrho, p_{ij}, q_i^T, g, g_i), \tag{3.6}$$

where $\hat{C}$ stands for any one of the quantities (3.5) and where I have anticipated that the non-convective quantities are independent of v_i.

3.3 *Definition of equilibrium*

Equilibrium is defined as a process in which all productions vanish, so that there are 12 conditions

$$P_{ij}|_E = 0, \quad r_i^T|_E = 0, \quad r_i^I|_E = 0. \tag{3.7}$$

It seems inevitable that these conditions imply the vanishing of the pressure deviator $p_{\langle ij \rangle}$ and of the heat fluxes q_i^T and g_i but there must be one more relation as these are only 11 in number. Therefore in equilibrium the remaining variables g, ϱ and p must be related. I write this condition as

$$g|_E = \varepsilon^I(\varrho, p) \tag{3.8}$$

and conclude that in equilibrium the intrinsic energy is determined by ϱ and p.

In non-equilibrium one may write

$$g = \varepsilon^I(\varrho, p) + \Delta \tag{3.9}$$

which gives—in Δ—an additional variable along with $p_{\langle ij \rangle}$, q_i^T and g_i, that vanishes in equilibrium. The constitutive relations (3.6) may thus be written as

$$\hat{C} = \tilde{\mathfrak{C}}(\varrho, p, p_{\langle ij \rangle}, q_i^T, \Delta, g_i). \tag{3.10}$$

3.4 *Entropy principle*

Let the entropy density be denoted by h and the entropy flux by φ_k. I decompose φ_k into a convective and a non-convective part according to the equation

$$\varphi_k = h v_k + \phi_k . \tag{3.11}$$

h and ϕ_k are constitutive quantities of the generic type (3.10).

The most important part of the entropy principle is the entropy inequality

$$\frac{\partial h}{\partial t} + \frac{\partial \varphi_k}{\partial x_k} \geqq 0 \quad \text{or} \quad \dot{h} + h\frac{\partial v_k}{\partial x_k} + \frac{\partial \phi_k}{\partial x_k} \geqq 0, \tag{3.12}$$

and that inequality must hold for all *thermodynamic processes.*

According to a lemma proved by Liu [5] an equivalent statement is that the following inequality must hold *for all arbitrary fields* (3.4). This new inequality results from (3.12) by adding on its left-hand side the balance laws (3.3), each one multiplied by a Lagrange multiplier Λ that may depend on the same variables as the constitutive quantities $\hat{C}$ in (3.10). Thus we have

$$\begin{aligned}
&\dot{h} + h\frac{\partial v_k}{\partial x_k} + \frac{\partial \phi_k}{\partial x_k} - \Lambda\left(\dot{\varrho} + \varrho\frac{\partial v_i}{\partial x_i}\right) - \Lambda_i^v\left(\varrho\dot{v}_i + \frac{\partial p_{ij}}{\partial x_j}\right) \\
&\quad - \Lambda_{ij}\left(\dot{p}_{ij} + p_{ij}\frac{\partial v_k}{\partial x_k} + \frac{\partial p_{\langle ijk\rangle}}{\partial x_k} + \tfrac{4}{5}\frac{\partial q_{(i}^T}{\partial x_{j)}} + \tfrac{2}{5}\frac{\partial q_k^T}{\partial x_k}\delta_{ij} + 2p_{k(i}\frac{\partial v_{j)}}{\partial x_k} - P_{ij}\right) \\
&\quad - \Lambda_i\left(\dot{q}_i^T + \tfrac{7}{5}\, q_i^T\frac{\partial v_k}{\partial x_k} + \tfrac{1}{2}\frac{\partial p_{ijjk}}{\partial x_k} + p_{\langle ijk\rangle}\frac{\partial v_j}{\partial x_k} + \tfrac{2}{5}\, q_j^T\frac{\partial v_j}{\partial x_i} + \tfrac{7}{5}\, q_j^T\frac{\partial v_i}{\partial x_j}\right. \\
&\quad \left. - \frac{p_{ij}}{\varrho}\frac{\partial p_{jk}}{\partial x_k} - \frac{p_{jj}}{2\varrho}\frac{\partial p_{ik}}{\partial x_k} - r_i^T\right) \\
&\quad - \lambda\left(\varrho\dot{\varepsilon}^I + \varrho\dot{\Delta} + \frac{\partial g_i}{\partial x_i} + \tfrac{1}{2}P_{ii}\right) \\
&\quad - \lambda_i\left(\dot{g}_i + g_i\frac{\partial v_k}{\partial x_k} + \frac{\partial g_{ij}}{\partial x_j} + g_j\frac{\partial v_i}{\partial x_j} - (\varepsilon^I + \Delta)\frac{\partial p_{ij}}{\partial x_j} - r_i^I\right) \geqq 0 .
\end{aligned} \tag{3.13}$$

If we insert all constitutive relations into (3.13) and perform all indicated differentiations we obtain an inequality whose left-hand side is explicitly linear in the derivatives

$$\begin{gathered}
\dot{v}_i,\ \dot{\varrho},\ \dot{p}_{ij},\ \dot{q}_i^T,\ \dot{\Delta},\ \dot{g}_i, \\
\frac{\partial v_i}{\partial x_j},\ \frac{\partial \varrho}{\partial x_i},\ \frac{\partial p_{ij}}{\partial x_k},\ \frac{\partial q_i^T}{\partial x_j},\ \frac{\partial \Delta}{\partial x_i},\ \frac{\partial g_i}{\partial x_j} .
\end{gathered} \tag{3.14}$$

Since the fields are arbitrary, so are these derivatives and therefore the inequality cannot be valid unless all factors of the derivatives (3.14) vanish. This requirement implies the conditions

$$0 = \Lambda_i^v, \quad \frac{\partial h}{\partial \varrho} = \Lambda + \varrho\lambda \frac{\partial \varepsilon^I}{\partial \varrho}, \quad \frac{\partial h}{\partial p_{ij}} = \Lambda_{ij} + \tfrac{1}{3}\, \varrho\lambda \frac{\partial \varepsilon^I}{\partial p}\, \delta_{ij}, \tag{3.15a-c}$$

$$\frac{\partial h}{\partial q_i^T} = \Lambda_i, \quad \frac{\partial h}{\partial \Delta} = \varrho\lambda, \quad \frac{\partial h}{\partial g_i} = \lambda_i, \tag{3.15e-f}$$

$$\begin{aligned} h\, \delta_{ij} = {} & (\varrho\Lambda + \Lambda_{rs} p_{rs} + \tfrac{7}{5}\, \Lambda_r q_r^T + \lambda_r g_r)\, \delta_{ij} + 2\Lambda_{ki} p_{jk} \\ & + \Lambda_r p_{\langle rij \rangle} + \tfrac{2}{5}\, \Lambda_j q_i^T + \tfrac{7}{5}\, \Lambda_i q_j^T + \lambda_i g_j, \end{aligned} \tag{3.16a}$$

$$\frac{\partial \phi_k}{\partial \varrho} = \Lambda_{rs} \frac{\partial p_{\langle rsk \rangle}}{\partial \varrho} + \tfrac{1}{2}\, \Lambda_r \frac{\partial p_{rssk}}{\partial \varrho} + \lambda_r \frac{\partial g_{rk}}{\partial \varrho}, \tag{3.16b}$$

$$\begin{aligned} \frac{\partial \phi_k}{\partial p_{ij}} = {} & \Lambda_{rs} \frac{\partial p_{\langle rsk \rangle}}{\partial p_{ij}} + \tfrac{1}{2}\, \Lambda_r \frac{\partial p_{rssk}}{\partial p_{ij}} + \lambda_r \frac{\partial g_{rk}}{\partial p_{ij}} - \Lambda_r \frac{p_{r(i}}{\varrho}\, \delta_{j)k} \\ & - \frac{p_{rr}}{2\varrho}\, \Lambda_{(i}\, \delta_{j)k} - (\varepsilon^I + \Delta)\, \lambda_{(i}\, \delta_{j)k}, \end{aligned} \tag{3.16c}$$

$$\frac{\partial \phi_k}{\partial q_i^T} = \Lambda_{rs} \frac{\partial p_{\langle rsk \rangle}}{\partial q_i^T} + \tfrac{1}{2}\, \Lambda_r \frac{\partial p_{rssk}}{\partial q_i^T} + \lambda_r \frac{\partial g_{rk}}{\partial q_i^T} + \tfrac{4}{5}\, \Lambda_{ik} + \tfrac{2}{5}\, \Lambda_{rr}\, \delta_{ik}, \tag{3.16d}$$

$$\frac{\partial \phi_k}{\partial \Delta} = \Lambda_{rs} \frac{\partial p_{\langle rsk \rangle}}{\partial \Delta} + \tfrac{1}{2}\, \Lambda_r \frac{\partial p_{rssk}}{\partial \Delta} + \lambda_r \frac{\partial g_{rk}}{\partial \Delta}, \tag{3.16e}$$

$$\frac{\partial \phi_k}{\partial g_i} = \Lambda_{rs} \frac{\partial p_{\langle rsk \rangle}}{\partial g_i} + \tfrac{1}{2}\, \Lambda_r \frac{\partial p_{rssk}}{\partial g_i} + \lambda_r \frac{\partial g_{rk}}{\partial g_i} + \lambda\, \delta_{ik}. \tag{3.16f}$$

There remains the residual inequality

$$\Sigma = \Lambda_{\langle ij \rangle} P_{\langle ij \rangle} + (\tfrac{1}{3}\, \Lambda_{rr} - \tfrac{1}{2}\, \lambda)\, P_{ss} + \Lambda_i r_i^T + \Lambda_i r_i^I \geqq 0, \tag{3.17}$$

whose left-hand side is the entropy production. It contains 4 terms reflecting the productions of the pressure deviator, the translational energy and the two heat fluxes.

In principle it is now obvious how to proceed: From (3.15) we calculate the Lagrange multipliers in terms of h. These are introduced into (3.16) which provides relations between the constitutive relations $p_{\langle ijk \rangle}$, p_{iijk}, g_{ij} and h, ϕ_k. Between those relations it is possible to eliminate h and ϕ_k and obtain restrictions on $p_{\langle ijk \rangle}$, p_{iijk}, g_{ij}.

3.5 Principle of material frame indifference

The principle of material frame indifference requires that the constitutive functions of the non-convective quantities are invariant under Euclidean transformations, or, in other words, the constitutive functions have the same form in an inertial and in a non-inertial frame.

It follows that the constitutive quantities (3.5) cannot depend on the velocity, a result which I have already anticipated in (3.6). Moreover, the constitutive functions must be isotropic functions of their variables.

There are representation theorems on isotropic functions, e.g. see [6]. Here these theorems shall not be of interest in their full generality, because I limit the attention to processes in the neighbourhood of equilibrium, i.e. with small values of $p_{\langle ij\rangle}$, q_i^T, g_i and Δ. Therefore I write

linear representations for $p_{\langle ijk\rangle}$, p_{ijjk}, g_{ij}, P_{ii}, $P_{\langle ij\rangle}$, r_i^T, r_i^I

a quadratic representation for ϕ_i

a third order representation for h, viz.

$$p_{\langle ijk\rangle} = 0, \tag{3.18a}$$

$$p_{ijjk} = (\beta_0 + \beta_1 \Delta)\,\delta_{ik} + \gamma p_{\langle ik\rangle}, \tag{3.18b}$$

$$g_{ik} = (\nu_0 + \nu_1 \Delta)\,\delta_{ik} + \mu p_{\langle ik\rangle}, \tag{3.18c}$$

$$P_{ii} = \xi \Delta, \tag{3.18d}$$

$$P_{\langle ij\rangle} = \sigma p_{\langle ij\rangle}, \tag{3.18e}$$

$$r_i^T = \alpha_1 q_i^T + \alpha_2 g_i, \tag{3.18f}$$

$$r_i^I = \chi_1 q_i^T + \chi_2 g_i, \tag{3.18g}$$

$$\phi_k = (\varphi_1 + \varphi_2 \Delta)\, q_k^T + (\varphi_3 + \varphi_4 \Delta)\, g_k + \varphi_5 p_{\langle kr\rangle} q_r^T + \varphi_6 p_{\langle kr\rangle} g_r, \tag{3.19}$$

$$\begin{aligned} h = {} & \varrho s + h_1 \Delta + h_2 \Delta^2 + h_3 \Delta^3 + (h_4 + h_5 \Delta)\, p_{\langle rs\rangle} p_{\langle rs\rangle} \\ & + (h_6 + h_7 \Delta)\, q_r^T q_r^T + (h_8 + h_9 \Delta)\, g_r g_r + (h_{10} + h_{11} \Delta)\, q_r^T g_r \\ & + h_{12} p_{\langle rs\rangle} p_{\langle sk\rangle} p_{\langle kr\rangle} + h_{13} p_{\langle rs\rangle} q_r^T q_s^T + h_{14} p_{\langle rs\rangle} q_r^T g_s + h_{15} p_{\langle rs\rangle} g_r g_s . \end{aligned} \tag{3.20}$$

All coefficients β_0 through h_{15} may depend on ϱ and p.

A remark seems necessary about why I choose different orders in the representations of $p_{\langle ijk\rangle}, \ldots, r_i^I$, and ϕ_k, and h. Let us consider: What I wish to have in the end, if possible, is knowledge about $p_{\langle ijk\rangle}$ through r_i^I, because these quantities occur in the field equations (3.3). Within a linear theory I should therefore like to known the explicit form of the functions $\beta_0(\varrho, p)$ through $\chi_2(\varrho, p)$. But it turns out, in the evaluation of the conditions (3.15) and (3.16), that the properties of these functions are linked to the coefficients h and φ of non-linear terms in (3.19) and (3.20) in multiple ways. Therefore I must take account of the non-linear representations for h and ϕ_k.

The reader who is sufficiently interested in this subject is invited to turn to the Appendix A1 where the conditions (3.15), (3.16) and (3.17) are exploited in detail. In the main part of the paper I proceed to introduce the absolute temperature but otherwise I merely summarize and discuss the results obtained in the appendix.

4 Results of the constitutive theory

4.1 *Identification of absolute temperature*

Taking into account the representation (3.20) for h we conclude from (3.15) that among all Lagrange multipliers only Λ, Λ_{ii} and λ have a non-vanishing equilibrium value. Indeed we get

$$\Lambda|_E = \frac{\partial \varrho\, s}{\partial \varrho} - h_1 \frac{\partial \varepsilon^I}{\partial \varrho}, \quad \Lambda_{ii}|_E = \frac{\partial \varrho\, s}{\partial p} - h_1 \frac{\partial \varepsilon^I}{\partial p}, \quad \lambda|_E = \frac{h_1}{\varrho}. \tag{4.1}$$

Therefore there is only one linear term in the residual inequality (3.17) and, by use of (3.18d), one may write

$$\Sigma = \left[\tfrac{1}{3}\left(\frac{\partial \varrho\, s}{\partial p} - h_1 \frac{\partial \varepsilon^I}{\partial p}\right) - \frac{h_1}{2\varrho}\right] \xi \Delta + \begin{pmatrix}\text{non-linear terms in} \\ p_{\langle ij\rangle}, q_i^T, g_i, \Delta\end{pmatrix} \geqq 0. \tag{4.2}$$

But Σ has a minimum in equilibrium, namely zero. Therefore it cannot have a linear term. The square bracket in (4.2) must vanish and we have

$$h_1 = \frac{\tfrac{2}{3}\varrho \dfrac{\partial \varrho\, s}{\partial p}}{1 + \tfrac{2}{3}\varrho \dfrac{\partial \varepsilon^I}{\partial p}}. \tag{4.3}$$

The equilibrium part of the trace of (3.16a) reads

$$\Lambda|_E = s - \tfrac{5}{3}\Lambda_{ii}|_E \frac{p}{\varrho}. \tag{4.4}$$

Elimination of h_1 and $\Lambda|_E$ between (4.1a, b), (4.3) and (4.4) gives two equations for $\frac{\partial s}{\partial \varrho}$ and $\frac{\partial s}{\partial p}$ which may be combined as

$$ds = \tfrac{2}{3}\Lambda_{ii}|_E \left\{\frac{\partial}{\partial p}\left(\frac{3p}{2\varrho} + \varepsilon^I\right) dp + \left[\frac{\partial}{\partial \varrho}\left(\frac{3p}{2\varrho} + \varepsilon^I\right) - \frac{p}{\varrho^2}\right] d\varrho\right\},$$

or by (3.2)

$$ds = \tfrac{2}{3}\Lambda_{ii}|_E \left(d\varepsilon|_E - \frac{p}{\varrho^2}\, d\varrho\right). \tag{4.5}$$

Thus by comparison with the Gibbs equation $\tfrac{2}{3}\Lambda_{ii}|_E$ is recognized as $\frac{1}{T}$ where T is the absolute temperature

$$\tfrac{2}{3}\Lambda_{ii}(\varrho, p)|_E = \frac{1}{T}. \tag{4.6}$$

Once the absolute temperature is introduced in this way, it is now possible to replace the pair (ϱ, p) of equilibrium variables by the more familiar pair (ϱ, T) and I shall do this in the sequel.

There is one immediate consequence: The Gibbs equation, i.e. (4.5) and (4.6) joined together in the form

$$ds = \frac{1}{T}\left(d\varepsilon|_E - \frac{p}{\varrho^2}\,d\varrho\right), \tag{4.7}$$

implies the integrability condition

$$\left(\frac{\partial\varepsilon}{\partial\varrho}\right)_T = \frac{1}{\varrho^2}\left[p - T\left(\frac{\partial p}{\partial T}\right)_\varrho\right]. \tag{4.8}$$

Here we are dealing with an ideal gas where

$$p = \frac{k}{m}\varrho T \quad \text{and} \quad \varepsilon^T = \frac{3k}{2m}T \tag{4.9}$$

hold. Therefore (4.8) implies

$$\left(\frac{\partial\varepsilon^I}{\partial\varrho}\right)_T = 0, \tag{4.10}$$

i.e., the specific intrinsic energy is independent of ϱ, it may only depend on the absolute temperature.

4.2 Summary of results

As shown in the appendices A.1 and A.2 the constitutive functions for (3.18a–c), and (3.19), (3.20) obtain the following explicit forms as a result of the entropy principle

$$p_{\langle ijk\rangle} = 0, \tag{4.11a}$$

$$p_{iijk} = \left[\frac{5p^2}{\varrho}\left(1 + \frac{a_1 T^{5/2}}{7p}\right) + a_2\right]\delta_{ik} + \frac{7p}{\varrho}\left(1 + \frac{a_1 T^{5/2}}{7p}\right)p_{\langle ik\rangle}, \tag{4.11b}$$

$$g_{ik} = (p\varepsilon^I + p\,\Delta + a_3)\,\delta_{ik} + \varepsilon^I p_{\langle ik\rangle}, \tag{4.11c}$$

$$\phi_k = \frac{1}{T}(q_k^T + g_k) - \frac{1}{T^2\varepsilon_T^I}\Delta g_k - \frac{2}{5pT}p_{\langle kr\rangle}q_r^T, \tag{4.12}$$

$$\begin{aligned} h = \varrho\left(\frac{k}{m}\ln\frac{T^{3/2}}{\varrho} + \int\frac{\varepsilon_T^I}{T}\,dT + a_4\right) + \frac{\varrho}{T}\Delta - \frac{\varrho}{2T^2\varepsilon_T^I}\Delta^2 \\ + \frac{\varrho}{3T^3(\varepsilon_T^I)^2}\left(1 + \frac{T}{2\varepsilon_T^I}\frac{d\varepsilon_T^I}{dT}\right)\Delta^3 - \frac{1}{4pT}p_{\langle rs\rangle}p_{\langle rs\rangle} \\ - \frac{\varrho}{5p^2T}\left(1 + \frac{a_1 T^{5/2}}{2p}\right)^{-1} q_r^T q_r^T - \frac{1}{2pT^2\varepsilon_T^I}g_r g_r \end{aligned}$$

$$+\frac{1}{2T^2p(\varepsilon_T^I)^2}\left(\frac{2}{T}+\frac{1}{\varepsilon_T^I}\frac{d\varepsilon_T^I}{dT}\right)\Delta g_r g_r+\frac{1}{6p^2T}p_{\langle rs\rangle}p_{\langle sk\rangle}p_{\langle kr\rangle}$$
$$+\frac{9\varrho}{25p^3T}\left(1+\frac{a_1T^{5/2}}{2p}\right)^{-1}p_{\langle rs\rangle}q_r^Tq_s^T+\frac{1}{2p^2T^2\varepsilon_T^I}p_{\langle rs\rangle}g_rg_s\,. \tag{4.13}$$

ε_T^I stands for $\frac{d\varepsilon^I}{dT}$ and a_1 through a_4 are constants of integration.

The amazing feature of these results is there specific nature: All coefficients in (3.18a–c) and (3.19), (3.20)—some, or most of them coefficients of non-equilibrium terms—are specifically related to the thermal and caloric equation of state $p(\varrho, T)$ and $\varepsilon^I(T)$ except for the constants a. This specific nature of the results is a recurring feature of extended thermodynamics, first observed by Liu & Müller [1].

However, not everything is quite so specific. Indeed the 6 constitutive coefficients of the productions

$$r_i^T=\alpha_1q_i^T+\alpha_2g_i,\quad P_{\langle ij\rangle}=\sigma p_{\langle ij\rangle}, \tag{4.14a, b}$$

$$r_i^I=\chi_1q_i^T+\chi_2g_i,\quad P_{ii}=\xi\Delta \tag{4.14c, d}$$

are only restricted by some inequalities, viz.

$$\chi_2\leqq 0,\ \alpha_1\left(1+\frac{a_1T^{5/2}}{2p}\right)^{-1}\leqq 0,\quad \sigma\leqq 0,\quad \xi\leqq 0, \tag{4.15a–d}$$

$$\alpha_1\chi_2-\frac{m\varepsilon_T^I}{10k}\left(\alpha_2+\frac{5k}{2m\varepsilon_T^I}\chi_1\right)^2\geqq 0. \tag{4.15e}$$

In the next Section I shall discuss ways on how to identify the remaining unknown coefficients α_1, α_2, χ_1, χ_2, σ, and ξ. These are called the transport coefficients.

If we take the intrinsic energy to be the vibrational energy of the molecules, it is possible to show that the above results of extended thermodynamics are identical to those of statistical thermodynamics, if only the constants a_1, a_2 and a_3 are set equal to zero, see [7]. Therefore in the further development of this paper I shall ignore these constants. In fact, several contributions from a_1 were already ignored in writing (4.15e) in order to make that inequality less cumbersome.

In conclusion I list the field equations, i.e. the balance laws (3.3) combined with the constitutive Eqs. (4.11) and (4.14).

$$\dot\varrho+\varrho\frac{\partial v_i}{\partial x_i}=0, \tag{4.16a}$$

$$\varrho\dot v_i+\frac{\partial p_{ij}}{\partial x_j}=0, \tag{4.16b}$$

$$\varrho\dot\varepsilon+\frac{\partial q_i^T}{\partial x_i}+\frac{\partial g_i}{\partial x_i}+p_{ij}\frac{\partial v_i}{\partial x_j}=0, \tag{4.16c}$$

$$\dot p_{\langle ij\rangle}+p_{\langle ij\rangle}\frac{\partial v_k}{\partial x_k}+\tfrac{4}{5}\frac{\partial q_{\langle i}^T}{\partial x_{j\rangle}}+2p_{k\langle i}\frac{\partial v_{j\rangle}}{\partial x_k}=\sigma p_{\langle ij\rangle}, \tag{4.16d}$$

$$\dot{q}_i^T + \tfrac{7}{5}\, q_i^T \frac{\partial v_k}{\partial x_k} + \tfrac{4}{5}\, q_j^T \frac{\partial v_{(i}}{\partial x_{j)}} + q_j^T \frac{\partial v_i}{\partial x_j} + \frac{5p^2}{2\varrho T} \frac{\partial T}{\partial x_i} - \frac{p_{\langle ij\rangle}}{\varrho} \frac{\partial p_{jk}}{\partial x_k}$$

$$+ \frac{7p}{2\varrho T} p_{\langle ik\rangle} \frac{\partial T}{\partial x_k} + \frac{p}{\varrho} \frac{\partial p_{\langle ik\rangle}}{\partial x_k} = \alpha_1 q_i^T + \alpha_2 g_i, \tag{4.16e}$$

$$\varrho \left(1 - \frac{\varepsilon_T^I}{\varepsilon_T}\right) \dot{\Delta} + \left(1 - \frac{\varepsilon_T^I}{\varepsilon_T}\right) \frac{\partial g_i}{\partial x_i} - \frac{\varepsilon_T^I}{\varepsilon_T} \frac{\partial q_i^T}{\partial x_i} - \frac{\varepsilon_T^I}{\varepsilon_T} p_{ij} \frac{\partial v_i}{\partial x_j} = -\tfrac{1}{2}\, \xi\, \Delta, \tag{4.16f}$$

$$\dot{g}_i + g_i \frac{\partial v_k}{\partial x_k} + g_j \frac{\partial v_i}{\partial x_j} + p\varepsilon_T^I \frac{\partial T}{\partial x_i} + p \frac{\partial \Delta}{\partial x_i} - \Delta \frac{\partial p_{\langle ij\rangle}}{\partial x_j}$$

$$+ \varepsilon_T^I p_{\langle ik\rangle} \frac{\partial T}{\partial x_k} = \chi_1 q_i^T + \chi_2 g_i. \tag{4.16g}$$

I have reordered these equations somewhat compared to (3.3) with respect to the equations of balance of energy. Thus (4.16c) is the balance of internal energy, viz. the sum of the trace of (3.3c) and of (3.3e). Also I have used (4.16c) to eliminate $\dot{T}$ from the balance (3.3e) of intrinsic energy. This was done in order to facilitate a subsequent argument. ε_T in (4.16f) stands for the derivative of $\varepsilon|_E = \frac{3p}{2\varrho} + \varepsilon^I(T)$ with respect to temperature.

Note that the left-hand sides of Eqs. (4.16) are explicit in the variables

$$\varrho,\ v_i,\ T,\ p_{\langle ij\rangle},\ q_i^T,\ \Delta,\ g_i,$$

provided we know $\varepsilon^I = \varepsilon^I(T)$. Of course, p is always equal to $\frac{k}{m}\varrho T$.

5 Identification of transport coefficients

5.1 The limit of ordinary thermodynamics

It is a most natural question, of course, to ask how to get back from extended to ordinary thermodynamics of a molecular gas. In ordinary thermodynamics, instead of the set (1.1), or (3.4) we should have the basic fields

$$\varrho,\ v_i,\ p \ (\text{or } T)$$

and there would be conservation laws of mass, momentum and energy, or the balance of internal energy

$$\dot{\varrho} + \varrho \frac{\partial v_i}{\partial x_i} = 0, \tag{5.1a}$$

$$\varrho \dot{v}_i + \frac{\partial p_{ij}}{\partial x_j} = 0, \tag{5.1b}$$

$$\varrho \dot{\varepsilon} + \frac{\partial q_i}{\partial x_i} + p_{ij} \frac{\partial v_i}{\partial x_j} = 0. \tag{5.1c}$$

To close the system of equations, in ordinary thermodynamics we must have constitutive equations for

the pressure deviator $p_{\langle ij \rangle}$

the heat flux $q_i = q_i^T + g_i$

the internal energy $\varepsilon = \dfrac{3p}{2\varrho} + \varepsilon^I(T) + \Delta$.

Adapting an iterative scheme from the kinetic theory—the so-called Maxwellian iteration, see [8]—we derive the desired constitutive equations from the Eqs. (4.16d–g) in an approximate manner as follows: In the first step we introduce equilibrium values for $p_{\langle ij \rangle}$, q_i^T, Δ and g_i on the left-hand sides of (4.16d–g) and calculate first iterates.

$$\overset{(1)}{p}_{\langle ij \rangle} = 2\frac{p}{\sigma}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}}, \tag{5.2a}$$

$$\alpha_1 \overset{(1)}{q}{}_i^T + \alpha_2 \overset{(1)}{g}_i = \frac{5p^2}{2\varrho T}\frac{\partial T}{\partial x_i}, \tag{5.2b}$$

$$\overset{(1)}{\Delta} = \frac{2p\varepsilon_T^I}{\xi\varepsilon_T}\frac{\partial v_k}{\partial x_k}, \quad \text{i.e.} \quad \overset{(1)}{\varepsilon} = \frac{3p}{2\varrho} + \varepsilon^I + \frac{2p\varepsilon_T^I}{\xi\varepsilon_T}\frac{\partial v_k}{\partial x_k}, \tag{5.2c, d}$$

$$\chi_1 \overset{(1)}{q}{}_i^T + \chi_2 \overset{(1)}{g}_i = p\varepsilon_T^I \frac{\partial T}{\partial x_i}. \tag{5.2e}$$

The iteration proceeds by putting these first iterates into the left-hand sides of (4.16d–g) and calculating second iterates, etc. However, I shall not go beyond the first step. Therefore in the sequel I omit the superposed index (1) in the equations (5.2).

From (5.2b, e) one gets for $q_i = q_i^T + g_i$

$$q_i = -p\frac{k}{m}\frac{\frac{m}{k}\varepsilon_T^I(\alpha_1 - \alpha_2) - \frac{5}{2}(\chi_1 - \chi_2)}{\alpha_2\chi_1 - \alpha_1\chi_2}\frac{\partial T}{\partial x_i}. \tag{5.3}$$

Thus with (5.2a), (5.2c) and (5.3) we have the desired constitutive equations which can be used to close the system (5.1).

Equations (5.2a) and (5.3) are recognized as the constitutive relations of Navier-Stokes and Fourier, respectively, and we conclude that $-\dfrac{p}{\sigma}$ is the coefficient of shear viscosity μ while the factor of $-\dfrac{\partial T}{\partial x_i}$ in (5.3) is the coefficient of heat conductivity $\varkappa$

$$\mu = -\frac{p}{\sigma}, \quad \varkappa = p\frac{k}{m}\frac{\frac{m}{k}\varepsilon_T^I(\alpha_1 - \alpha_2) - \frac{5}{2}(\chi_1 - \chi_2)}{\alpha_2\chi_1 - \alpha_1\chi_2}. \tag{5.4a, b}$$

Since μ and $\varkappa$ are measurable quantities, these equations permit the determination of σ and provide a restriction on the transport coefficients α_1, α_2, χ_1, and χ_2. Thus there remain four unknowns in the theory at this stage.

5.2 Comparison with the kinetic theory. Eucken formulae

In the literature there is considerable interest in the ratio $\varkappa/\mu$ which indicates the relative efficiency of heat and momentum transfer. According to the elementary kinetic theory we should have

$$\frac{\varkappa}{\mu} = \frac{5}{2}\,\varepsilon_T^T + \varepsilon_T^I \tag{5.5}$$

where ε_T^T stands for the derivative of the translational internal energy ε^T with respect to the temperature. This reflects the fact that momentum exchange in a gas and the exchange of intrinsic energy are less effective than the exchange of translational energy by a factor $\frac{2}{5}$, e.g. see [9], p. 279. Equation (5.5) is called the Eucken formula and it has been revised several times as the kinetic theory has become more and more sophisticated. Thus there is a proposition by Chapman and Cowling [10] which reads

$$\frac{\varkappa}{\mu} = \frac{5}{2}\,\varepsilon_T^T + \frac{\varrho D}{\mu}\,\varepsilon_T^I. \tag{5.6}$$

Here D is the coefficient of self-diffusion. There is also a more complex formula, due to Wang Chang and Uhlenbeck [11] which reads

$$\frac{\varkappa}{\mu} = A\left\{1 - \frac{4}{5}\,\frac{m}{k}\,B\varepsilon_T^I + \frac{4}{25}\left(\frac{m}{k}\right)^2 C(\varepsilon_T^I)^2\right\}, \tag{5.7}$$

in which the coefficients are definite expressions that follow from the Chapman-Enskog solution of the Boltzmann equation for molecular gases.

With μ and $\varkappa$ given by (5.4) we obtain in the present theory

$$\frac{\varkappa}{\mu} = \frac{\sigma}{\alpha_1\chi_2 - \alpha_2\chi_1}\left[\frac{5k}{2m}(\chi_2 - \chi_1) + \varepsilon_T^I(\alpha_1 - \alpha_2)\right] \tag{5.8}$$

and, if we abbreviate the positive expression on the left-hand side of (4.15e) by δ we can recast (5.7) in the form

$$\frac{\varkappa}{\mu} = a\left\{1 - \frac{4}{5}\,\frac{m}{k}\,b\varepsilon_T^I + \frac{4}{25}\left(\frac{m}{k}\right)^2 c(\varepsilon_T^I)^2\right\}, \tag{5.9}$$

where a, b, c stand for

$$a = \frac{5k\sigma(2\chi_2 - \chi_1)^2}{8m\chi_2(\alpha_1\chi_2 - \alpha_2\chi_1)}, \quad b = \frac{\alpha_2}{2\chi_2 - \chi_1} - \frac{2\delta\chi_2^2}{(2\chi_2 - \chi_1)^2}, \quad c = \frac{\alpha_2^2}{(2\chi_2 - \chi_1)^2}. \tag{5.10a–c}$$

Note that (5.9) has the same form as the Eucken formula in the Wang Chang-Uhlenbeck generalization. A comparison between (5.7) and (5.9) would allow us to have three restrictions on the values of the transport coefficients α_1, α_2, χ_1 and χ_2 so that now only one transport coefficient remains unknown in the theory, say ξ.

There is a tempting special case to be considered, namely the case

$$\alpha_2 = 0 \quad \text{and} \quad \chi_1 = 0 \tag{5.11a, b}$$

so that the two equations (5.2b, e) uncouple. We call this case the case of negligible coupling between translational and intrinsic energy. The ratio $\frac{\varkappa}{\mu}$ in (5.8) becomes

$$\frac{\varkappa}{\mu} = \frac{-\dfrac{5p^2}{2\varrho T\alpha_1}}{\mu} - \frac{p}{\mu\chi_2}\varepsilon_T^I. \tag{5.12}$$

By comparison with (5.2b) the numerator of the first term is seen to be equal to the "translational heat conductivity". If we accept, again from the kinetic theory (e.g. see [10], p. 247) that this heat conductivity is very close to $\frac{15k}{4m}\mu$, we may write

$$\frac{\varkappa}{\mu} = \tfrac{5}{2}\,\varepsilon_T^T - \frac{p}{\mu\chi_2}\varepsilon_T^I. \tag{5.13}$$

This formula compares well with the Eucken formula (5.6) in the Chapman and Cowling generalization and we conclude that there is a relation between χ_2 and the measurable coefficient of self-diffusion, viz.

$$-\chi_2 = \frac{p}{\varrho}D. \tag{5.14}$$

Note that, here again, with the assumptions (5.11) and the identification (5.14) of χ_2, we now have only one remaining unknown transport coefficient, viz. ξ. One way of determining that coefficient is the measurement of the attenuation of sound waves. I proceed to show this.

5.3 *Plane harmonic waves of small amplitude*

I investigate solutions of the system (4.16) in the form of plane harmonic waves of small amplitude propagating in the x-direction and having the frequency ω and the complex wave number $k^c = k^r + ik^i$. I consider a constant reference state with $\tilde{\varrho}$, $\tilde{T}$ and vanishing values of Δ, v_x, q_x^T, g_x and $p_{\langle xx\rangle}$

$$\varrho = \tilde{\varrho} + \bar{\varrho}e^{i(\omega t - k^c x)}, \qquad v_x = \bar{v}e^{i(\omega t - k^c x)}, \tag{5.15a, b}$$

$$T = \tilde{T} + \bar{T}e^{i(\omega t - k^c x)}, \qquad \Delta = \bar{\Delta}e^{i(\omega t - k^c x)}, \tag{5.15c, d}$$

$$q_x^T = \bar{q}e^{i(\omega t - k^c x)}, \qquad g_x = \bar{g}e^{i(\omega t - k^c x)}, \tag{5.15e, f}$$

$$p_{\langle xx\rangle} = \bar{p}e^{i(\omega t - k^c x)}. \tag{5.15g}$$

The barred quantities $\bar{\varrho}$ through $\bar{p}$ are the amplitudes, products of them are neglected. The phase speed V and the coefficient of attenuation α^* are given by

$$V = \frac{\omega}{k^r} \quad \text{and} \quad \alpha^* = -k^i. \tag{5.16a, b}$$

For simplicity I shall consider the special case (5.11) of negligible coupling. Insertion of (5.15) into (4.16) gives a system of linear homogeneous equations for the amplitudes, viz.

$$\begin{bmatrix} 1 & -\tilde{\varrho}\frac{k^c}{\omega} & 0 & 0 & 0 & 0 & 0 \\ -\frac{k\tilde{T}}{m}\frac{k^c}{\omega} & \tilde{\varrho} & -\frac{k\tilde{\varrho}}{m}\frac{k^c}{\omega} & -\frac{k^c}{\omega} & 0 & 0 & 0 \\ 0 & -\frac{k\tilde{\varrho}\tilde{T}}{m}\frac{k^c}{\omega} & \frac{3k\tilde{\varrho}}{2m} & 0 & -\frac{k^c}{\omega} & i\frac{\tilde{\xi}}{2\omega} & 0 \\ 0 & 0 & \tilde{\varrho}\tilde{\varepsilon}_T^I & 0 & 0 & \tilde{\varrho} - i\frac{\tilde{\xi}}{2\omega} & -\frac{k^c}{\omega} \\ 0 & 0 & -\frac{5}{2}\left(\frac{k}{m}\right)^2\tilde{\varrho}\tilde{T}\frac{k^c}{\omega} & -\frac{k\tilde{T}}{m}\frac{k^c}{\omega} & 1 + i\frac{\tilde{\alpha}_1}{\omega} & 0 & 0 \\ 0 & 0 & -\frac{k\tilde{\varrho}\tilde{T}}{m}\tilde{\varepsilon}_T^I\frac{k^c}{\omega} & 0 & 0 & -\frac{k\tilde{\varrho}\tilde{T}}{m}\frac{k^c}{\omega} & 1 + i\frac{\tilde{\chi}_2}{\omega} \\ 0 & -\frac{4k\tilde{\varrho}\tilde{T}}{3m}\frac{k^c}{\omega} & 0 & 1 + i\frac{\tilde{\sigma}}{\omega} & -\frac{8}{15}\frac{k^c}{\omega} & 0 & 0 \end{bmatrix} \begin{bmatrix} \bar{\varrho} \\ \bar{v} \\ \bar{T} \\ \bar{p} \\ \bar{q} \\ \bar{\Delta} \\ \bar{g} \end{bmatrix} = 0. \tag{5.17}$$

The determinant must vanish for this system to have a non-trivial solution and that requirement leads to a dispersion relation which has the general form of a bi-cubic equation for (k^c/ω).

$$\left(\frac{k^c}{\omega}\right)^6 + X_1\left(\frac{k^c}{\omega}\right)^4 + X_2\left(\frac{k^c}{\omega}\right)^2 + X_3 = 0 \tag{5.18}$$

where the X's are complex coefficients which are not given here. For the case of small frequency, which is the usual case of sound waves one obtains a solution for

$$\frac{k^c}{\omega} = \frac{1}{V_0}\left\{1 - i\omega\frac{\mu}{2V_0^2\varrho}\frac{k/m}{\varepsilon_T}\left[\frac{15}{4}\frac{1}{m\varepsilon_T/k + 1} + \frac{\varepsilon_T^I}{\varepsilon_T + k/m}\frac{\varrho D}{\mu}\right.\right.$$
$$\left.\left. + \frac{\varepsilon_T^I}{\varepsilon_T}\frac{p}{\mu}\frac{2\varrho}{\xi} + \frac{4}{3}\frac{m\varepsilon_T}{k}\right]\right\}, \tag{5.19}$$

where V_0 is the adiabatic speed of sound, i.e. $V_0 = \left[\left(1 + \frac{k}{m\varepsilon_T}\right)\frac{kT}{m}\right]^{1/2}$, and D is the coefficient of self-diffusion that was introduced earlier. I have dropped the tildes from (5.19).

From (5.19) one may easily calculate the absorption coefficient (5.16 b) which is a measurable quantity and turns out to be a function of ξ. Inversely we may write

$$\xi = \frac{\frac{2\varrho^2 T}{\mu}\left(\frac{k}{m}\right)^2 \frac{\varepsilon_T^I}{\varepsilon_T^2}}{\frac{2V_0^3\varrho\alpha^*}{\omega^2\mu} - \frac{15k}{4m}\frac{1}{\varepsilon_T(m\varepsilon_T/k+1)} - \frac{\varepsilon_T^I}{\varepsilon_T(m\varepsilon_T/k+1)}\frac{\varrho D}{\mu} - \frac{4}{3}}. \tag{5.20}$$

Thus we have identified the last remaining unknown transport coefficient of the theory.

If I had not restricted the attention to the case of negligible coupling in the above analysis of waves, the absorption and dispersion of sound waves should have provided information about other transport coefficients as well.

6 Final remarks

6.1 The role of temperature

The reason why temperature is such an appropriate variable in thermodynamics is that it is considered to be easily measurable and the reason for that is its continuity at a thermometric (sic!) wall. Let us consider how this stands in non-equilibrium.

A thermometric wall does not actively participate in the processes on either side, in particular it does not produce or store entropy so that the entropy flux coming in on one side is going out on the other side. Thus, if e_i is the unit normal to the wall, we have

$$[\![\phi_i]\!]\, e_i = 0. \tag{6.1}$$

The brackets denote the difference of the bracketed quantity on the two sides.

The heat flux $q_i = q_i^T + g_i$—or rather its normal component—is also continuous on a thermometric wall, since such a wall does not store energy either. Therefore insertion of (4.12) into (6.1) gives

$$\left[\!\!\left[\frac{1}{T}\right]\!\!\right] q_i e_i = \left[\!\!\left[\frac{1}{T^2\varepsilon_T^I}\Delta g_i\right]\!\!\right] e_i + \left[\!\!\left[\frac{2}{5pT}p_{\langle ir\rangle}q_r^T\right]\!\!\right] e_i. \tag{6.2}$$

If we neglect non-linear terms, the right-hand side is zero and (6.2) implies that indeed the temperature is continuous. That result, however, is only as good as the linear approximation, because—according to (6.2)—there is a jump of T, if on either or both sides of the wall the bracketed expressions cannot be neglected. In such a case, the temperature looses much of its value as a suitable variable.

6.2 The dynamic pressure

We recall (5.2d) where $\varepsilon^T = \frac{3p}{2\varrho} = \frac{3k}{2m} T$ and $\varepsilon^I = \varepsilon^I(T)$ holds and write

$$\varepsilon = \frac{3k}{2m} T + \varepsilon^I(T) + 2 \frac{p}{\xi} \frac{\varepsilon_T^I}{\varepsilon_T} \frac{\partial v_i}{\partial x_i}. \tag{6.3}$$

Thus ε contains a term proportional to $\frac{\partial v_i}{\partial x_i}$. In the kinetic theory of polyatomic gases, e.g. the works of Wang Chang, Uhlenbeck and de Boer [11] or of Waldmann [12], this is not done. Rather these authors define ε as

$$\varepsilon = \varepsilon^T + \varepsilon^I \quad \text{hence} \quad \varepsilon^T = \frac{3p}{2\varrho} = \varepsilon - \varepsilon^I. \tag{6.4a, b}$$

Elimination of $(\varepsilon - \varepsilon^I)$ from (6.3) and (6.4) leads to

$$p = \frac{k}{m} \varrho T - \zeta \frac{\partial v_i}{\partial x_i} \quad \text{where} \quad \zeta = -\tfrac{4}{3} \frac{k}{m} \frac{\varrho^2 T}{\xi} \frac{\varepsilon_T^I}{\varepsilon_T}, \tag{6.5a, b}$$

if non-linear terms in $\frac{\partial v_i}{\partial x_i}$ are neglected.

It is customary to call the term $-\zeta \frac{\partial v_i}{\partial x_i}$ the *dynamic pressure* and ζ is the *volume viscosity*. By (4.15d) ζ is non-negative.

Thus it is possible to have either ε or p depend on $\frac{\partial v_i}{\partial x_i}$. Both versions are possible and equivalent as was already remarked by Kogan [13].

Appendices

Appendix 1. Consequences of the entropy inequality

The Lagrange multipliers follow by insertion of the representation (3.20) of h into (3.15)

$$\begin{aligned} \Lambda = {} & \left(\frac{\partial \varrho s}{\partial \varrho} - h_1 \frac{\partial \varepsilon^I}{\partial \varrho}\right) + \left(\frac{\partial h_1}{\partial \varrho} - 2h_2 \frac{\partial \varepsilon^I}{\partial \varrho}\right) \Delta + \left(\frac{\partial h_2}{\partial \varrho} - 3h_3 \frac{\partial \varepsilon^I}{\partial \varrho}\right) \Delta^2 \\ & + \left(\frac{\partial h_4}{\partial \varrho} - h_5 \frac{\partial \varepsilon^I}{\partial \varrho}\right) p_{\langle rs \rangle} p_{\langle rs \rangle} + \left(\frac{\partial h_6}{\partial \varrho} - h_7 \frac{\partial \varepsilon^I}{\partial \varrho}\right) q_r^T q_r^T \\ & + \left(\frac{\partial h_8}{\partial \varrho} - h_9 \frac{\partial \varepsilon^I}{\partial \varrho}\right) g_r g_r + \left(\frac{\partial h_{10}}{\partial \varrho} - h_{11} \frac{\partial \varepsilon^I}{\partial \varrho}\right) q_r^T g_r, \end{aligned} \tag{A.1}$$

$$\Lambda_{ii} = \left(\frac{\partial \varrho s}{\partial p} - h_1 \frac{\partial \varepsilon^I}{\partial p}\right) + \left(\frac{\partial h_1}{\partial p} - 2h_2 \frac{\partial \varepsilon^I}{\partial p}\right) \Delta + \left(\frac{\partial h_2}{\partial p} - 3h_3 \frac{\partial \varepsilon^I}{\partial p}\right) \Delta^2$$
$$+ \left(\frac{\partial h_4}{\partial p} - h_5 \frac{\partial \varepsilon^I}{\partial p}\right) p_{\langle rs\rangle} p_{\langle rs\rangle} + \left(\frac{\partial h_6}{\partial p} - h_7 \frac{\partial \varepsilon^I}{\partial p}\right) q_r^T q_r^T$$
$$+ \left(\frac{\partial h_8}{\partial p} - h_9 \frac{\partial \varepsilon^I}{\partial p}\right) g_r g_r + \left(\frac{\partial h_{10}}{\partial p} - h_{11} \frac{\partial \varepsilon^I}{\partial p}\right) q_r^T g_r, \tag{A.2}$$

$$\Lambda_{\langle ij\rangle} = 2(h_4 + h_5 \Delta)\, p_{\langle ij\rangle} + 3h_{12} p_{\langle r\langle i\rangle} p_{\langle j\rangle r\rangle} + h_{13} q^T_{\langle i} q^T_{j\rangle} + h_{14} q^T_{\langle i} g_{j\rangle} + h_{15} g_{\langle i} g_{j\rangle}, \tag{A.3}$$

$$\Lambda_i = 2(h_6 + h_7 \Delta)\, q_i^T + (h_{10} + h_{11} \Delta)\, g_i + 2h_{13} p_{\langle ir\rangle} q_r^T + h_{14} p_{\langle ir\rangle} g_r, \tag{A.4}$$

$$\lambda_i = (h_{10} + h_{11} \Delta)\, q_i^T + 2(h_8 + h_9 \Delta)\, g_i + h_{14} p_{\langle ir\rangle} q_r^T + 2h_{15} p_{\langle ir\rangle} g_r, \tag{A.5}$$

$$\varrho\lambda = h_1 + 2h_2 \Delta + 3h_3 \Delta^2 + h_5 p_{\langle rs\rangle} p_{\langle rs\rangle} + h_7 q_r^T q_r^T + h_9 g_r g_r + h_{11} q_r^T g_r. \tag{A.6}$$

On the other hand, the trace, the symmetric traceless part and the antisymmetric part of Eq. (3.16a) read

$$h = \varrho\Lambda + \tfrac{5}{9}\, p_{rr} \Lambda_{ss} + \tfrac{5}{3}\, p_{\langle rs\rangle} \Lambda_{\langle rs\rangle} + 2\Lambda_r q_r^T + \tfrac{4}{3}\, \lambda_r g_r, \tag{A.7a}$$

$$2\Lambda_{k\langle i} p_{j\rangle k} + \Lambda_r p_{\langle rij\rangle} + \tfrac{9}{5}\, \Lambda_{\langle i} q^T_{j\rangle} + \lambda_{\langle i} g_{j\rangle} = 0, \tag{A.7b}$$

$$2\Lambda_{r[i} p_{j]r} + \Lambda_{[i} q^T_{j]} + \lambda_{[i} g_{j]} = 0. \tag{A.7c}$$

The substitution of the representation (3.20) of h and of the Lagrange multipliers (A.1) through (A.6) into (A.7a) leads to a polynomial in q_i^T, g_i, $p_{\langle ij\rangle}$ and Δ, which is equal to zero, so all its coefficients must be equal to zero

$$\varrho s = \varrho \left(\frac{\partial \varrho s}{\partial \varrho} - h_1 \frac{\partial \varepsilon^I}{\partial \varrho}\right) + \tfrac{5}{3}\, p \left(\frac{\partial \varrho s}{\partial p} - h_1 \frac{\partial \varepsilon^I}{\partial p}\right), \tag{A.8}$$

$$h_1 = \varrho \left(\frac{\partial h_1}{\partial \varrho} - 2h_2 \frac{\partial \varepsilon^I}{\partial \varrho}\right) + \tfrac{5}{3}\, p \left(\frac{\partial h_1}{\partial p} - 2h_2 \frac{\partial \varepsilon^I}{\partial p}\right), \tag{A.9}$$

$$h_2 = \varrho \left(\frac{\partial h_2}{\partial \varrho} - 3h_3 \frac{\partial \varepsilon^I}{\partial \varrho}\right) + \tfrac{5}{3}\, p \left(\frac{\partial h_2}{\partial p} - 3h_3 \frac{\partial \varepsilon^I}{\partial p}\right), \tag{A.10}$$

$$h_4 = \varrho \left(\frac{\partial h_4}{\partial \varrho} - h_5 \frac{\partial \varepsilon^I}{\partial \varrho}\right) + \tfrac{5}{3}\, p \left(\frac{\partial h_4}{\partial p} - h_5 \frac{\partial \varepsilon^I}{\partial p}\right) + \tfrac{10}{3}\, h_4, \tag{A.11}$$

$$h_6 = \varrho \left(\frac{\partial h_6}{\partial \varrho} - h_7 \frac{\partial \varepsilon^I}{\partial \varrho}\right) + \tfrac{5}{3}\, p \left(\frac{\partial h_6}{\partial p} - h_7 \frac{\partial \varepsilon^I}{\partial p}\right) + 4h_6, \tag{A.12}$$

$$h_8 = \varrho \left(\frac{\partial h_8}{\partial \varrho} - h_9 \frac{\partial \varepsilon^I}{\partial \varrho}\right) + \tfrac{5}{3}\, p \left(\frac{\partial h_8}{\partial p} - h_9 \frac{\partial \varepsilon^I}{\partial p}\right) + \tfrac{8}{3}\, h_8, \tag{A.13}$$

$$h_{10} = \varrho \left(\frac{\partial h_{10}}{\partial \varrho} - h_{11} \frac{\partial \varepsilon^I}{\partial \varrho}\right) + \tfrac{5}{3}\, p \left(\frac{\partial h_{10}}{\partial p} - h_{11} \frac{\partial \varepsilon^I}{\partial p}\right) + \tfrac{10}{3}\, h_{10}. \tag{A.14}$$

In the same manner, we get from (A.7b) and (A.1) through (A.6)

$$h_4 = \frac{-1}{6p}\left(\frac{\partial \varrho s}{\partial p} - h_1 \frac{\partial \varepsilon^I}{\partial p}\right), \quad h_5 = \frac{-1}{6p}\left(\frac{\partial h_1}{\partial p} - 2h_2 \frac{\partial \varepsilon^I}{\partial p}\right), \tag{A.15a, b}$$

$$h_{12} = \frac{-2}{3p} h_4, \quad h_{13} = \frac{-9}{5p} h_6, \quad h_{14} = \frac{-7}{5p} h_{10}, \quad h_{15} = \frac{-1}{p} h_8. \tag{A.15c–f}$$

Equation (A.7c) is identically satisfied.

Next, we obtain by insertion of (3.18), (3.19) and (A.1) through (A.6) into (3.16b–f)

$$\frac{\partial \varphi_1}{\partial \varrho} = h_6 \frac{\partial \beta_0}{\partial \varrho} + h_{10} \frac{\partial \nu_0}{\partial \varrho}, \tag{A.16}$$

$$\frac{\partial \varphi_2}{\partial \varrho} = h_7 \frac{\partial \beta_0}{\partial \varrho} + h_{11} \frac{\partial \nu_0}{\partial \varrho} + h_6 \frac{\partial \beta_1}{\partial \varrho} + h_{10} \frac{\partial \nu_1}{\partial \varrho}, \tag{A.17}$$

$$\frac{\partial \varphi_3}{\partial \varrho} = \tfrac{1}{2} h_{10} \frac{\partial \beta_0}{\partial \varrho} + 2h_8 \frac{\partial \nu_0}{\partial \varrho}, \tag{A.18}$$

$$\frac{\partial \varphi_4}{\partial \varrho} = \tfrac{1}{2} h_{11} \frac{\partial \beta_0}{\partial \varrho} + 2h_9 \frac{\partial \nu_0}{\partial \varrho} + \tfrac{1}{2} h_{10} \frac{\partial \beta_1}{\partial \varrho} + 2h_8 \frac{\partial \nu_1}{\partial \varrho}, \tag{A.19}$$

$$\frac{\partial \varphi_5}{\partial \varrho} = h_{13} \frac{\partial \beta_0}{\partial \varrho} + h_{14} \frac{\partial \nu_0}{\partial \varrho} + h_6 \frac{\partial \gamma}{\partial \varrho} + h_{10} \frac{\partial \mu}{\partial \varrho}, \tag{A.20}$$

$$\frac{\partial \varphi_6}{\partial \varrho} = \tfrac{1}{2} h_{14} \frac{\partial \beta_0}{\partial \varrho} + 2h_{15} \frac{\partial \nu_0}{\partial \varrho} + \tfrac{1}{2} h_{10} \frac{\partial \gamma}{\partial \varrho} + 2h_8 \frac{\partial \mu}{\partial \varrho}, \tag{A.21}$$

$$\frac{\partial \varphi_1}{\partial p} = h_6 \left(\frac{\partial \beta_0}{\partial p} - \frac{5p}{\varrho}\right) + h_{10} \left(\frac{\partial \nu_0}{\partial p} - \varepsilon^I\right), \tag{A.22}$$

$$\frac{\partial \varphi_2}{\partial p} = h_7 \left(\frac{\partial \beta_0}{\partial p} - \frac{5p}{\varrho}\right) + h_{11} \left(\frac{\partial \nu_0}{\partial p} - \varepsilon^I\right) + h_6 \frac{\partial \beta_1}{\partial p} + h_{10} \left(\frac{\partial \nu_1}{\partial p} - 1\right), \tag{A.23}$$

$$\frac{\partial \varphi_3}{\partial p} = \tfrac{1}{2} h_{10} \left(\frac{\partial \beta_0}{\partial p} - \frac{5p}{\varrho}\right) + 2h_8 \left(\frac{\partial \nu_0}{\partial p} - \varepsilon^I\right), \tag{A.24}$$

$$\frac{\partial \varphi_4}{\partial p} = \tfrac{1}{2} h_{11} \left(\frac{\partial \beta_0}{\partial p} - \frac{5p}{\varrho}\right) + 2h_9 \left(\frac{\partial \nu_0}{\partial p} - \varepsilon^I\right) + \tfrac{1}{2} h_{10} \frac{\partial \beta_1}{\partial p} + 2h_8 \left(\frac{\partial \nu_1}{\partial p} - 1\right), \tag{A.25}$$

$$\frac{\partial \varphi_5}{\partial p} = h_{13} \left(\frac{\partial \beta_0}{\partial p} - \frac{5p}{\varrho}\right) + h_{14} \left(\frac{\partial \nu_0}{\partial p} - \varepsilon^I\right) + h_{10} \frac{\partial \mu}{\partial p} + h_6 \left(\frac{\partial \gamma}{\partial p} - \frac{2}{\varrho}\right), \tag{A.26}$$

$$\frac{\partial \varphi_6}{\partial p} = \tfrac{1}{2} h_{14} \left(\frac{\partial \beta_0}{\partial p} - \frac{5p}{\varrho}\right) + 2h_{15} \left(\frac{\partial \nu_0}{\partial p} - \varepsilon^I\right) + 2h_8 \frac{\partial \mu}{\partial p} + \tfrac{1}{2} h_{10} \left(\frac{\partial \gamma}{\partial p} - \frac{2}{\varrho}\right), \tag{A.27}$$

$$\varphi_5 = h_6 \left(\gamma - \frac{5p}{\varrho}\right) + h_{10} (\mu - \varepsilon^I), \quad \varphi_6 = \tfrac{1}{2} h_{10} \left(\gamma - \frac{5p}{\varrho}\right) + 2h_8(\mu - \varepsilon^I), \tag{A.28a, b}$$

$$\varphi_1 = \tfrac{2}{3}\left(\frac{\partial \varrho s}{\partial p} - h_1 \frac{\partial \varepsilon^I}{\partial p}\right), \quad \varphi_2 = \tfrac{2}{3}\left(\frac{\partial h_1}{\partial p} - 2h_2 \frac{\partial \varepsilon^I}{\partial p}\right), \quad \varphi_5 = \tfrac{8}{5} h_4, \tag{A.29a–c}$$

$$\varphi_2 = h_6\beta_1 + h_{10}\nu_1, \quad \varphi_4 = \tfrac{1}{2} h_{10}\beta_1 + 2h_8\nu_1, \tag{A.30a, b}$$

$$\varphi_3 = \frac{h_1}{\varrho}, \quad \varphi_4 = \frac{2h_2}{\varrho}, \quad \varphi_6 = 0. \tag{A.31a–c}$$

The residual inequality (3.17) reads

$$\begin{aligned}\Sigma = {} & 2h_4\sigma p_{\langle rs\rangle} p_{\langle rs\rangle} + \left[\tfrac{1}{3}\left(\frac{\partial \varrho s}{\partial p} - h_1 \frac{\partial \varepsilon^I}{\partial p}\right) - \frac{h_1}{2\varrho}\right] \xi \Delta \\ & + \left[\tfrac{1}{3}\left(\frac{\partial h_1}{\partial p} - 2h_2 \frac{\partial \varepsilon^I}{\partial p}\right) - \frac{h_2}{\varrho}\right] \xi \Delta^2 + (2h_6\alpha_1 + h_{10}\chi_1)\, q_r^T q_r^T \\ & + (2h_8\chi_2 + h_{10}\alpha_2)\, g_r g_r + [2h_6\alpha_2 + 2h_8\chi_1 + h_{10}(\alpha_1 + \chi_2)]\, q_r^T g_r \geqq 0,\end{aligned} \tag{A.32}$$

where use has been made of the Eqs. (3.18d–g) and (A.1) through (A.6). In (A.32) I have omitted terms that are more than quadratic in $\{q_i^T, g_i, \Delta, p_{\langle ij\rangle}\}$.

$$\Sigma = \hat{\Sigma}(\varrho, p, p_{\langle ij\rangle}, q_i^T, \Delta, g_i)$$

assumes its minimum in equilibrium so that we have

$$\Sigma|_E = \hat{\Sigma}(\varrho, p, 0, 0, 0, 0) = 0. \tag{A.33}$$

The necessary conditions for Σ to be a minimum in equilibrium are

$$\left.\frac{\partial \Sigma}{\partial X_A}\right|_E = 0 \quad \text{and} \quad \left\| \left.\frac{\partial^2 \Sigma}{\partial X_A\, \partial X_B}\right|_E \right\| \quad \text{is non-negative definite} \tag{A.34a, b}$$

where $X_A = \{p_{\langle ij\rangle}, q_i^T, \Delta, g_i\}$.

From the first of these conditions we conclude that

$$h_1 = \frac{\tfrac{2}{3}\varrho \dfrac{\partial \varrho s}{\partial p}}{1 + \tfrac{2}{3}\varrho \dfrac{\partial \varepsilon^I}{\partial p}}, \tag{A.35}$$

and from the second

$$h_4\sigma \geqq 0, \quad \xi\left[\tfrac{1}{3}\left(\frac{\partial h_1}{\partial p} - 2h_2 \frac{\partial \varepsilon^I}{\partial p}\right) - \frac{h_2}{\varrho}\right] \geqq 0, \tag{A.36a, b}$$

$$2h_6\alpha_1 + h_{10}\chi_1 \geqq 0, \quad 2h_8\chi_2 + h_{10}\alpha_2 \geqq 0, \tag{A.36c, d}$$

$$(2h_6\alpha_1 + h_{10}\chi_1)(2h_8\chi_2 + h_{10}\alpha_2) \geqq \left[h_6\alpha_2 + h_8\chi_1 + h_{10}\left(\frac{\alpha_1 + \chi_2}{2}\right)\right]^2. \tag{A.36e}$$

Appendix 2. The absolute temperature as variable and the final results

We replace the pair of variables (ϱ, p) by the pair (ϱ, T) and use the relations

$$\left(\frac{\partial f}{\partial \varrho}\right)_p = \left(\frac{\partial f}{\partial \varrho}\right)_T + \left(\frac{\partial f}{\partial T}\right)_\varrho \left(\frac{\partial T}{\partial \varrho}\right)_p \quad \text{and} \quad \left(\frac{\partial f}{\partial p}\right)_\varrho = \left(\frac{\partial f}{\partial T}\right)_\varrho \left(\frac{\partial T}{\partial p}\right)_\varrho, \qquad \text{(A.37a, b)}$$

to rewrite the Eqs. (A.8) through (A.31) in the form

$$h_1 = \frac{\varrho}{T}, \quad h_2 = \frac{-\varrho}{2T^2\varepsilon_T^I}, \qquad \text{(A.38a, b)}$$

$$h_3 = \frac{1}{3T^3(\varepsilon_T^I)^2}\left(1 + \frac{T}{2\varepsilon_T^I}\frac{d\varepsilon_T^I}{dT}\right), \quad h_4 = \frac{-1}{4pT}, \qquad \text{(A.39a, b)}$$

$$h_5 = 0, \quad h_6 = \frac{2\nu_1}{5pTA}, \qquad \text{(A.40a, b)}$$

$$h_8 = \frac{1}{2T^2\varepsilon_T^I A}\left(\gamma - \frac{5p}{\varrho}\right), \quad h_{10} = \frac{-2\beta_1}{5pTA}, \qquad \text{(A.41a, b)}$$

$$h_7 = \frac{2}{5pTA^2\varepsilon_T^I}\biggl[\frac{\beta_1(\mu - \varepsilon^I)\,\nu_1}{T} + \frac{3p\beta_1(\mu - \varepsilon)}{2T} + \nu_1\beta_1\varepsilon_T^I\left(\frac{2\nu_1}{5p} + 1\right)$$

$$+ \beta_1\,(\mu - \varepsilon^I)\frac{\partial \nu_1}{\partial T} - \nu_1(\mu - \varepsilon^I)\frac{\partial \beta_1}{\partial T}\biggr], \qquad \text{(A.42)}$$

$$h_9 = \frac{7\beta_1(\mu - \varepsilon^I)^2}{2T^3A^2(\varepsilon_T^I)^2} + \frac{1}{2T^2A^2(\varepsilon_T^I)^2}\left(\gamma - \frac{5p}{\varrho}\right)\biggl[\frac{3A}{2T} + \frac{3p}{2T}\left(\gamma - \frac{5p}{\varrho}\right)$$

$$\times \left(1 + \frac{2\nu_1}{3p}\right) - \beta_1\varepsilon_T^I\left(\frac{\nu_1}{p} - 1\right) - (\mu - \varepsilon^I)\frac{\partial \beta_1}{\partial T} + \left(\gamma - \frac{5p}{\varrho}\right)\frac{\partial \nu_1}{\partial T} - \frac{A}{\varepsilon_T^I}\frac{d\varepsilon_T^I}{dT}\biggr], \qquad \text{(A.43)}$$

$$h_{11} = \frac{-2}{5pTA^2\varepsilon_T^I}\biggl[\beta_1^2\varepsilon_T^I\left(\frac{2\nu_1}{5p} + 1\right) + \tfrac{3}{2}\,\beta_1\frac{p}{T}\left(\gamma - \frac{5p}{\varrho}\right)\left(\frac{2\nu_1}{3p} + 1\right)$$

$$+ \beta_1\left(\gamma - \frac{5p}{\varrho}\right)\frac{\partial \nu_1}{\partial T} - \nu_1\left(\gamma - \frac{5p}{\varrho}\right)\frac{\partial \beta_1}{\partial T}\biggr], \qquad \text{(A.44)}$$

$$h_{12} = \frac{1}{6p^2T}, \quad h_{13} = \frac{-18\nu_1}{25p^2TA}, \qquad \text{(A.45a, b)}$$

$$h_{14} = \frac{14\beta_1}{25p^2TA}, \quad h_{15} = \frac{-1}{2pT^2\varepsilon_T^I A}\left(\gamma - \frac{5p}{\varrho}\right), \qquad \text{(A.46a, b)}$$

$$\varphi_1 = \frac{1}{T}, \quad \varphi_2 = 0, \quad \varphi_3 = \frac{1}{T}, \qquad \text{(A.47a–c)}$$

$$\varphi_4 = \frac{-1}{T^2\varepsilon_T^I}, \quad \varphi_5 = \frac{-2}{5pT}, \quad \varphi_6 = 0, \qquad \text{(A.48a–c)}$$

$$\beta_1 = \frac{5p}{T\varepsilon_T^I}(\mu - \varepsilon^I), \tag{A.49}$$

$$\frac{\partial\beta_0}{\partial\varrho} = \frac{5p}{\varrho}\frac{\partial p}{\partial\varrho}, \quad \frac{\partial\nu_0}{\partial\varrho} = \varepsilon^I\frac{\partial p}{\partial\varrho}, \tag{A.50a, b}$$

$$\frac{\partial\gamma}{\partial\varrho} = \frac{2}{\varrho}\frac{\partial p}{\partial\varrho} - \frac{1}{\varrho}\left(\gamma - \frac{5p}{\varrho}\right), \quad \frac{\partial\mu}{\partial\varrho} = \frac{-1}{\varrho}(\mu - \varepsilon^I), \tag{A.51a, b}$$

$$\frac{\partial\beta_1}{\partial\varrho} = 0, \quad \frac{\partial\nu_1}{\partial\varrho} = \frac{\partial p}{\partial\varrho}. \tag{A.52a, b}$$

$$\frac{\partial\beta_0}{\partial T} = \frac{5p}{\varrho}\frac{\partial p}{\partial T} + \frac{5p}{2T}\left[\left(\gamma - \frac{5p}{\varrho}\right) + 2(\mu - \varepsilon^I)\right], \tag{A.53}$$

$$\frac{\partial\nu_0}{\partial T} = \varepsilon^I\frac{\partial p}{\partial T} + \nu_1\varepsilon_T^I + \frac{5p}{2T}(\mu - \varepsilon^I), \tag{A.54}$$

$$\frac{\partial\mu}{\partial T} = \frac{3}{2T}(\mu - \varepsilon^I) + \frac{\nu_1\varepsilon_T^I}{p}, \tag{A.55}$$

$$\frac{\partial\gamma}{\partial T} = \frac{2}{\varrho}\frac{\partial p}{\partial T} + \frac{5}{2T}\left(\gamma - \frac{5p}{\varrho}\right) + \frac{7}{T}(\mu - \varepsilon^I), \tag{A.56}$$

$$h_6\frac{\partial\beta_1}{\partial T} + h_{10}\left(\frac{\partial\nu_1}{\partial T} - \frac{\partial p}{\partial T}\right) = \frac{-5p}{2T}h_7\left[\left(\gamma - \frac{5p}{\varrho}\right) + 2(\mu - \varepsilon^I)\right] - h_{11}\left[\varepsilon_T^I\nu_1 + \frac{5p}{2T}(\mu - \varepsilon^I)\right], \tag{A.57}$$

$$h_{10}\frac{\partial\beta_1}{\partial T} + 4h_8\left(\frac{\partial\nu_1}{\partial T} - \frac{\partial p}{\partial T}\right) = \frac{-5p}{2T}h_{11}\left[\left(\gamma - \frac{5p}{\varrho}\right) + 2(\mu - \varepsilon^I)\right] - 4h_9\left[\varepsilon_T^I\nu_1 + \frac{5p}{2T}(\mu - \varepsilon^I)\right] + \frac{2}{T^3\varepsilon_T^I}\left(2 + \frac{T}{\varepsilon_T^I}\frac{d\varepsilon_T^I}{dT}\right). \tag{A.58}$$

In the above equations ε_T^I stands for the derivative of ε^I with respect to the temperature and A is defined by

$$A = \beta_1(\mu - \varepsilon^I) - \nu_1\left(\gamma - \frac{5p}{\varrho}\right). \tag{A.59}$$

Insertion of (A.40b), (A.41b), (A.42) and (A.44) into (A.57) leads to

$$\beta_1 = 0, \tag{A.60}$$

and we get from (A.49), (A.55), (A.41b), (A.42), (A.44) and (A.46a)

$$\mu = \varepsilon^I, \quad \nu_1 = p, \quad h_{10} = h_7 = h_{11} = h_{14} = 0. \tag{A.61a–c}$$

Moreover, Eq. (A.57) is identically satisfied and the other coefficients result from integration of (A.50a), (A.50b), (A.51a), (A.53), (A.54), (A.56) and the

Gibbs Eq. (4.7)

$$\gamma = \frac{7p}{\varrho}\left(1 + \frac{a_1 T^{5/2}}{7p}\right), \quad \beta_0 = \frac{5p^2}{\varrho}\left(1 + \frac{a_1 T^{5/2}}{7p}\right) + a_2, \tag{A.62a, b}$$

$$\nu_0 = p\varepsilon^I + a_3, \quad s = \frac{k}{m}\ln\frac{T^{3/2}}{\varrho} + \int \frac{\varepsilon_T^I}{T}\,dT + a_4. \tag{A.63a, b}$$

a_1 through a_4 are constants of integration.

I summarize the results

$$s = \frac{k}{m}\ln\frac{T^{3/2}}{\varrho} + \int \frac{\varepsilon_T^I}{T}\,dT + a_4, \quad h_1 = \frac{\varrho}{T}, \quad h_2 = \frac{-\varrho}{2T^2\varepsilon_T^I}, \tag{A.64a–c}$$

$$h_3 = \frac{\varrho}{3T^3(\varepsilon_T^I)^2}\left(1 + \frac{T}{2\varepsilon_T^I}\frac{d\varepsilon_T^I}{dT}\right), \quad h_4 = \frac{-1}{4pT}, \quad h_5 = 0, \tag{A.65a–c}$$

$$h_6 = \frac{-\varrho}{5p^2T}\left(1 + \frac{a_1 T^{5/2}}{2p}\right)^{-1}, \quad h_7 = 0, \quad h_8 = \frac{-1}{2pT^2\varepsilon_T^I}, \tag{A.66a–c}$$

$$h_9 = \frac{1}{2T^2p(\varepsilon_T^I)^2}\left(\frac{2}{T} + \frac{1}{\varepsilon_T^I}\frac{d\varepsilon_T^I}{dT}\right), \quad h_{10} = h_{11} = 0, \quad h_{12} = \frac{1}{6p^2T}, \tag{A.67a–c}$$

$$h_{13} = \frac{9\varrho}{25p^3T}\left(1 + \frac{a_1 T^{5/2}}{2p}\right)^{-1}, \quad h_{14} = 0, \quad h_{15} = \frac{1}{2p^2T^2\varepsilon_T^I}, \tag{A.68a–c}$$

$$\varphi_1 = \frac{1}{T}, \quad \varphi_2 = 0, \quad \varphi_3 = \frac{1}{T}, \tag{A.69a–c}$$

$$\varphi_4 = \frac{-1}{T^2\varepsilon_T^I}, \quad \varphi_5 = \frac{-2}{5pT}, \quad \varphi_6 = 0, \tag{A.70a–c}$$

$$\beta_0 = \frac{5p^2}{\varrho}\left(1 + \frac{a_1 T^{5/2}}{7p}\right) + a_2, \quad \beta_1 = 0, \quad \mu = \varepsilon^I, \tag{A.71a–c}$$

$$\gamma = \frac{7p}{\varrho}\left(1 + \frac{a_1 T^{5/2}}{7p}\right), \quad \nu_0 = p\varepsilon^I + a_3, \quad \nu_1 = p. \tag{A.72a–c}$$

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