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Extended Thermodynamics of Dense Gases

Dedicated to Prof. Ingo Müller on the occasion of his 75th birthday.

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Abstract We study extended thermodynamics of dense gases by adopting the system of field equations with a different hierarchy structure to that adopted in the previous works. It is the theory of 14 fields of mass density, velocity, temperature, viscous stress, dynamic pressure and heat flux. As a result, most of the constitutive equations can be determined explicitly by the caloric and thermal equations of state. It is shown that the rarefied-gas limit of the theory is consistent with the kinetic theory of gases. We also analyze three physically important systems, that is, a gas with the virial equations of state, a hard-sphere system and a van der Waals fluid, by using the general theory developed in the former part of the present work.

Keywords Extended thermodynamics · Dense gas · Dynamic pressure · Virial equations of state · Hard-sphere system · van der Waals fluid

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1 Introduction

Extended thermodynamics (ET) [1] is a phenomenological field theory capable of describing nonequilibrium phenomena with steep gradients and rapid changes that may be out of local equilibrium. While thermodynamics of irreversible processes (TIP) [2] relies essentially on the assumption of local equilibrium. In this respect, the validity range of ET is wider than that of TIP. Moreover, ET can predict finite speeds of disturbances as its basic system of equations is hyperbolic. On the contrary, TIP predicts infinite speeds of disturbances because of its parabolic character.

A well-known theory of viscous heat-conducting fluids based on TIP is the Navier-Stokes Fourier theory with 5 independent field variables; the mass density, the velocity and the temperature [2, 3]. On the other hand, ET adopts more independent field variables. To be more specific, let us summarize ET

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for rarefied monatomic gases with 13 independent fields; mass density $F(=\rho)$, momentum density F_i , momentum flux F_{ij} , and energy flux F_{ppi} [1,4]. The system of field equations is of balance type such that

$$\begin{aligned}\frac{\partial F}{\partial t} + \frac{\partial F_k}{\partial x_k} &= 0, \\ \frac{\partial F_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} &= 0, \\ \frac{\partial F_{ij}}{\partial t} + \frac{\partial F_{ijk}}{\partial x_k} &= P_{\langle ij \rangle}, \\ \frac{\partial F_{ppi}}{\partial t} + \frac{\partial F_{ppik}}{\partial x_k} &= P_{ppi},\end{aligned}\tag{1}$$

where F_{ijk} and F_{ppik} are the fluxes of F_{ij} and F_{ppi} , respectively, and $P_{\langle ij \rangle}$ and P_{ppi} are the productions with respect to F_{ij} and F_{ppi} , respectively. Here $P_{\langle ij \rangle}$ is a symmetric traceless tensor. The first two equations and the trace part of the third equation represent the conservation laws of mass, momentum and energy, respectively. We notice the hierarchy structure of the system such that: (i) the tensorial rank of the equations increases one by one starting from the mass balance equation, and (ii) the flux in one equation becomes the density in the next equation. Such hierarchy is dictated by the moment equations in the kinetic theory of monatomic gases. As a consequence, $F_{ii}(=\rho v^2 + 3p)$ is, except for a factor 1/2, equal to the energy density, $\rho v^2/2 + \rho\varepsilon$, and therefore $3p = 2\rho\varepsilon$, where v_i , ε and p are the velocity, specific internal energy density and pressure, respectively. Therefore ET with this hierarchy structure is valid only for *rarefied monatomic* gases.

When the hierarchy of the basic equations are truncated as in the system (1), we need, as a closure procedure, constitutive equations for the quantities that are not in the list of the densities (independent field variables). In ET, we assume that such quantities depend locally on the densities. Their functional forms are severely restricted by the universal physical principles; *the principle of objectivity*, *the entropy principle* and *the principle of causality*. Most of the constitutive equations are fully prescribed by the equilibrium properties of gases [1,4].

ET constructed in such a phenomenological way was proved to be consistent with the Grad's procedure in the kinetic theory based on the Boltzmann equation [5]. Moreover, this theory was generalized in order to develop ET with any number of independent variables. These theories of ET have been applied successfully to various nonequilibrium phenomena such as light scattering, sound waves, heat waves (second sound), structure of shock waves [1].

The Navier-Stokes Fourier theory comes out as a limiting case of ET through carrying out the so-called Maxwellian iteration [6]. In this respect, the Navier-Stokes Fourier theory can be seen as an approximation of ET where the relaxation times of dissipative fluxes (viscous stress and heat flux) are negligible (Navier-Stokes Fourier limit).

However, within its validity range, the classical Navier-Stokes Fourier theory is applicable to any fluids that are not necessarily limited to rarefied gases nor to monatomic gases. Therefore, after the successful establishment of ET for rarefied monatomic gases, there appeared many studies of ET for rarefied polyatomic gases [7–9] and also for real gases (or dense gases) [10–15].

In dense gases, no simple relationship between the pressure p and the specific internal energy ε exists, and moreover the so-called dynamic pressure Π (trace of the viscous stress tensor) does not vanish. Taking these facts into account, the previous authors tried to establish ET by postulating a similar hierarchy structure to (1), but with 14 densities including a fourth-rank tensorial density [12, 14, 15]. However, the other feature that a flux in an equation becomes a density in the next equation was abandoned. Because of this generality, the constitutive equations could not be fully determined from the knowledge of the equilibrium properties of gases. Moreover, as we expect, when the Maxwellian iteration procedure is applied, we have to obtain the Navier-Stokes Fourier constitutive equations. The postulation of the fourth-rank tensorial density seems to be not well justified because, as can be seen in the next section, it does not have any straightforward counterpart in the Navier-Stokes Fourier limit.

The objective of the present paper is to propose an ET theory of dense gases by adopting the system of field equations with a different hierarchy structure to (1). We will show that most of the constitutive equations can be determined explicitly by the caloric and thermal equations of state. We will also analyze three physically important systems, that is, a gas with a virial equations of state,

a hard-sphere system and a van der Waals gas, by using the general theory developed in the present paper.

Notations

- A dot on a generic quantity ψ represents the material time derivative:

$$\dot{\psi} \equiv \frac{\partial \psi}{\partial t} + v_i \frac{\partial \psi}{\partial x_i}.$$

- Parentheses around a set of N indices represent the symmetrization with respect to these indices, that is, the sum over all $N!$ permutations of the indices divided by $N!$. For example,

$$\begin{aligned} a_{(i} b_{j)} &= \frac{1}{2!} (a_i b_j + a_j b_i), \\ a_{(i} b_j c_{k)} &= \frac{1}{3!} [a_i (b_j c_k + b_k c_j) + a_j (b_k c_i + b_i c_k) + a_k (b_i c_j + b_j c_i)]. \end{aligned}$$

- Angular brackets denote the symmetric traceless part with respect to these indices (deviatoric part). For example,

$$a_{\langle ij \rangle} = a_{(ij)} - \frac{1}{3} a_{kk} \delta_{ij}.$$

2 Model of dense gases

2.1 Heuristic viewpoint

In order to grasp the structure of the basic system appropriate for ET of dense gases, first of all, let us reconsider the structure of the Navier-Stokes Fourier system. In addition to the usual conservation laws of mass, momentum, and energy:

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_k} (\rho v_k) &= 0, \\ \frac{\partial}{\partial t} (\rho v_i) + \frac{\partial}{\partial x_k} (\rho v_i v_k - t_{ik}) &= 0, \\ \frac{\partial}{\partial t} \left(\frac{\rho v^2}{2} + \rho \varepsilon \right) + \frac{\partial}{\partial x_k} \left[\left(\frac{\rho v^2}{2} + \rho \varepsilon \right) v_k - t_{kj} v_j + q_k \right] &= 0, \end{aligned} \tag{2}$$

we have the constitutive equations:

$$S_{\langle ij \rangle} = 2\mu \frac{\partial v_{\langle i}}{\partial x_{j \rangle}}, \quad \Pi = -\nu \frac{\partial v_k}{\partial x_k}, \quad q_i = -\kappa \frac{\partial T}{\partial x_i}, \tag{3}$$

where t_{ij} is the stress tensor expressed by

$$t_{ij} = -p \delta_{ij} + S_{ij} = -(p + \Pi) \delta_{ij} + S_{\langle ij \rangle} \tag{4}$$

with S_{ij} being the viscous stress tensor and $\Pi (\equiv -S_{ii}/3)$ the dynamic pressure, and q_i is the heat flux. The coefficients μ , ν and κ are the shear viscosity, the bulk viscosity and the heat conductivity, respectively. Here we observe that, as in the paper [16], the equation (3) can be rewritten in the form:

$$\begin{aligned} \frac{\partial}{\partial x_k} \left(v_i \delta_{jk} + v_j \delta_{ik} - \frac{2}{3} v_k \delta_{ij} \right) &= \frac{S_{\langle ij \rangle}}{\mu}, \\ \frac{\partial v_k}{\partial x_k} &= -\frac{\Pi}{\nu}, \\ \frac{\partial T}{\partial x_k} &= -\frac{q_k}{\kappa}. \end{aligned} \tag{5}$$

The system composed of equations (2) and (5) can be seen as a system of 14 equations for the 14 unknown variables: ρ , v_i , ε , q_i , $S_{(ij)}$ and Π . Its mathematical structure is in the form of balance type, but, in eq. (5), we have no term with time derivative. Therefore the system is not hyperbolic but parabolic.

It is, therefore, natural to assume that the mathematical structure of balance laws in ET of dense gases must be of the following type:

$$\begin{aligned} \frac{\partial F}{\partial t} + \frac{\partial F_k}{\partial x_k} &= 0, \\ \frac{\partial F_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} &= 0, & \frac{\partial G_{ii}}{\partial t} + \frac{\partial G_{iik}}{\partial x_k} &= 0, \\ \frac{\partial F_{ij}}{\partial t} + \frac{\partial F_{ijk}}{\partial x_k} &= P_{ij}, & \frac{\partial G_{ppi}}{\partial t} + \frac{\partial G_{ppik}}{\partial x_k} &= Q_{ppi}, \end{aligned} \quad (6)$$

where F is the mass density, F_i is the momentum density, G_{ii} is the energy density, F_{ij} is the momentum flux, and G_{ppi} is the energy flux. And F_{ijk} and G_{ppik} are the fluxes of F_{ij} and G_{ppi} , respectively, and P_{ij} and Q_{ppi} are the productions with respect to F_{ij} and G_{ppi} , respectively. To justify this structure, we observe that equations (2) correspond to (6)_{1,2,3} with the condition that F_{ii} is different from G_{ii} because, as mentioned before, no simple relation exists between the pressure and the internal energy in dense gases. The equation (6)₄ can be split into the deviatoric and trace parts that have the mathematical structure of (5)_{1,2} when the terms with time derivatives are neglected. While equation (6)₅ in the steady case have the mathematical structure of the type of the Fourier's law (5)₃.

We observe also that the structure of (6) is much more restrictive than that adopted in the previous works, and moreover the system does not have the fourth-rank tensor in the set of densities.

To sum up, the hierarchy structure of the system (6) is composed of two parallel series: The one is the series starting from the mass and momentum balance equations (F -series) and the other is from the energy balance equation (G -series). In each series, the flux in one equation becomes the density in the next equation. Such a structure is also completely consistent with the structure of the set of balance equations derived from the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy of many-body distribution functions [17] in statistical mechanics, which is valid not only for rarefied gases but also for dense gases and liquids.

2.2 Statement of the model of dense gases

We can now definitely formulate the thermodynamic model for ET of dense gases as follows: The basic system of field equations is of balance type given by (6) with 14 independent field variables,

$$\begin{aligned} \text{mass density:} & \quad F \quad (= \rho), \\ \text{momentum density:} & \quad F_i \quad (= \rho v_i), \\ \text{energy density:} & \quad G_{ii}, \\ \text{momentum flux:} & \quad F_{ij}, \\ \text{energy flux:} & \quad G_{ppi}. \end{aligned} \quad (7)$$

2.3 Galilean invariance

We decompose $F_{i_1 \dots i_n k}$ and $G_{i_1 \dots i_n k}$ into the convective and non-convective parts:

$$\begin{aligned} F_{i_1 \dots i_n k} &= F_{i_1 \dots i_n} v_k + H_{i_1 \dots i_n k}, \\ G_{i_1 \dots i_n k} &= G_{i_1 \dots i_n} v_k + J_{i_1 \dots i_n k}. \end{aligned}$$

In particular, the quantities F_{ijk} and G_{ppik} are decomposed as follows: $F_{ijk} = F_{ij} v_k + H_{ijk}$ and $G_{ppik} = G_{ppi} v_k + J_{ppik}$.

The balance equations (6) should be invariant under the Galilean transformation. The general theory of the invariance with respect to the Galilean transformation was given in [18]. As the present

balance equations have a natural order like a moment-theory, we assume that the Galilean invariant form of one equation depends only on its previous ones in the order, and in agreement with the result of [18] we have the *unique* polynomial dependence of the quantities on the velocity expressed by

$$\begin{aligned}
G_{ii} &= \rho v_i v_i + m_{ii}, \\
F_{ij} &= \rho v_i v_j + M_{ij}, \\
G_{ppi} &= \rho v_p v_p v_i + m_{pp} v_i + 2v_p M_{pi} + m_{ppi}, \\
H_{ijk} &= 2v_{(i} M_{j)k} + M_{ijk}, \\
J_{ppik} &= 3v_{(p} v_p M_{i)k} + 2v_p M_{pik} + v_i m_{ppk} + m_{ppik}, \\
Q_{ppi} &= Q_i + 2v_p P_{pi},
\end{aligned} \tag{8}$$

where m_{ii} , M_{ij} , m_{ppi} , M_{ijk} and m_{ppik} do not depend on the velocity, and the productions P_{ij} and Q_i are also independent of the velocity. Moreover the term $v_p M_{pi}$, by taking into account that the tensor M_{pi} can be represented as the sum of its deviatoric and trace parts, can be written as $v_p M_{\langle pi \rangle} + (1/3)v_i M_{pp}$. Similarly we have $v_p M_{pik} = v_p M_{\langle pik \rangle} + (1/3)v_i M_{ppk}$.

With Eq. (8), the balance equations (6) can be rewritten as

$$\begin{aligned}
\dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} &= 0, \\
\rho \dot{v}_i + \frac{\partial M_{ij}}{\partial x_j} &= 0, \\
\dot{m}_{ii} + m_{ii} \frac{\partial v_k}{\partial x_k} + \frac{\partial m_{iik}}{\partial x_k} + 2 \frac{\partial v_i}{\partial x_k} M_{ik} &= 0, \\
\dot{M}_{ii} + M_{ii} \frac{\partial v_k}{\partial x_k} + \frac{\partial M_{iik}}{\partial x_k} + 2 \frac{\partial v_i}{\partial x_k} M_{ik} &= P_{ii}, \\
\dot{M}_{\langle ij \rangle} + M_{\langle ij \rangle} \frac{\partial v_k}{\partial x_k} + \frac{\partial M_{\langle ij \rangle k}}{\partial x_k} + 2 \frac{\partial v_{\langle i}}{\partial x_k} M_{j \rangle k} &= P_{\langle ij \rangle}, \\
\dot{m}_{ppi} + m_{ppi} \frac{\partial v_k}{\partial x_k} + \frac{\partial m_{ppik}}{\partial x_k} + 2 \frac{\partial v_p}{\partial x_k} M_{pik} + \frac{\partial v_i}{\partial x_k} m_{ppk} + 2M_{pi} \dot{v}_p + m_{pp} \dot{v}_i &= Q_i.
\end{aligned} \tag{9}$$

As the first three equations represent the conservation laws of mass, momentum and energy, the quantities M_{ij} , m_{ii} and m_{ppi} have the following conventional meanings:

$$\text{stress tensor:} \quad t_{ij} = -M_{ij} \quad (= -(p + \Pi) \delta_{ij} + S_{\langle ij \rangle}), \tag{10}$$

$$\text{specific internal energy:} \quad \varepsilon = \frac{1}{2\rho} m_{ii}, \tag{11}$$

$$\text{heat flux:} \quad q_i = \frac{1}{2} m_{ppi}, \tag{12}$$

where the pressure p depends only on ρ and m_{ii} . We will see in Section 3.3 that the decomposition in Eq. (10) is consistent in the present theory. M_{ij} is symmetric because we deal with non-polar materials. Therefore P_{ij} is symmetric and M_{ijk} is symmetric only with respect to the first two indices.

We may adopt $\{\rho, v_i, m_{ii}, \Pi, M_{\langle ij \rangle}, m_{ppi}\}$ as a set of independent variables instead of $\{F, F_i, G_{ii}, F_{ii}, F_{\langle ij \rangle}, G_{ppi}\}$. The balance equation of M_{ii} (Eq.(9)₄) is then rewritten as follows:

$$\begin{aligned}
\dot{\Pi} + \left(\frac{5}{3} p - \rho \frac{\partial p}{\partial \rho} - (m_{rr} + 2p) \frac{\partial p}{\partial m_{qq}} \right) \frac{\partial v_k}{\partial x_k} + \left(\frac{5}{3} - 2 \frac{\partial p}{\partial m_{qq}} \right) \Pi \frac{\partial v_k}{\partial x_k} \\
+ 2 \left(\frac{1}{3} - \frac{\partial p}{\partial m_{qq}} \right) \frac{\partial v_r}{\partial x_k} M_{\langle rk \rangle} + \frac{1}{3} \frac{\partial M_{rrk}}{\partial x_k} - \frac{\partial p}{\partial m_{qq}} \frac{\partial m_{rrk}}{\partial x_k} = \frac{P_{rr}}{3}.
\end{aligned} \tag{13}$$

3 Constitutive equations

We need the constitutive equations in order to set up the closed system of field equations. We assume that the constitutive quantities at one point and time depend on the independent fields at that point and time, i.e., local and instantaneous, therefore we have

$$\Psi = \hat{\Psi}(\rho, m_{ii}, \Pi, M_{\langle ij \rangle}, m_{ppi}), \quad (14)$$

where Ψ is one of the constitutive quantities $\{M_{ijk}, m_{ppik}, P_{ij}, Q_i\}$.

We apply to the present case the constitutive theory established in ET [1] where we impose the following universal physical principles on the constitutive equations:

- *Material frame indifference principle:*

The proper constitutive equations are independent of an observer. The material frame indifference principle together with the requirement of the Galilean invariance of balance laws constitute the so-called objectivity principle (the principle of relativity).

- *Entropy principle:*

All solutions of the system of field equations must satisfy the entropy balance with a non-negative entropy production:

$$\frac{\partial h}{\partial t} + \frac{\partial(hv_k + \varphi_k)}{\partial x_k} = \Sigma \geq 0 \quad \Leftrightarrow \quad \dot{h} + h \frac{\partial v_k}{\partial x_k} + \frac{\partial \varphi_k}{\partial x_k} = \Sigma \geq 0, \quad (15)$$

where h is the entropy density, h_k is the entropy flux ($h_k = hv_k + \varphi_k$: φ_k is the non-convective entropy flux), and Σ is the entropy production. Here h and φ_k are constitutive quantities:

$$\begin{aligned} h &= h(\rho, m_{ii}, \Pi, M_{\langle ij \rangle}, m_{ppi}), \\ \varphi_k &= \varphi_k(\rho, m_{ii}, \Pi, M_{\langle ij \rangle}, m_{ppi}). \end{aligned} \quad (16)$$

- *Causality:*

This requires the concavity of the entropy density and guarantees the hyperbolicity of the system of field equations. This also ensures the well-posedness (local in time) of a Cauchy problem and the finiteness of the propagation speeds of disturbances.

3.1 Relations derived from the entropy principle

The entropy principle can be expressed that the following inequality with Lagrange multipliers Λ , Λ_i , λ , Λ_{ij} and λ_i must be satisfied for all fields, ρ through m_{ppi} [19]:

$$\begin{aligned} & \dot{h} + h \frac{\partial v_k}{\partial x_k} + \frac{\partial \varphi_k}{\partial x_k} - \Lambda \left[\dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} \right] - \Lambda_i \left[\rho \dot{v}_i + \frac{\partial M_{ij}}{\partial x_j} \right] \\ & - \lambda \left[\dot{m}_{ii} + m_{ii} \frac{\partial v_k}{\partial x_k} + \frac{\partial m_{iik}}{\partial x_k} + 2 \frac{\partial v_i}{\partial x_k} M_{ik} \right] \\ & - \Lambda_{ii} \left[\dot{\Pi} + \left(\frac{5}{3} p - \rho \frac{\partial p}{\partial \rho} - (m_{rr} + 2p) \frac{\partial p}{\partial m_{qq}} \right) \frac{\partial v_k}{\partial x_k} + \left(\frac{5}{3} - 2 \frac{\partial p}{\partial m_{qq}} \right) \Pi \frac{\partial v_k}{\partial x_k} \right. \\ & \quad \left. + 2 \left(\frac{1}{3} - \frac{\partial p}{\partial m_{qq}} \right) \frac{\partial v_r}{\partial x_k} M_{\langle rk \rangle} + \frac{1}{3} \frac{\partial M_{rrk}}{\partial x_k} - \frac{\partial p}{\partial m_{qq}} \frac{\partial m_{rrk}}{\partial x_k} - \frac{P_{rr}}{3} \right] \\ & - \Lambda_{\langle ij \rangle} \left[\dot{M}_{\langle ij \rangle} + M_{\langle ij \rangle} \frac{\partial v_k}{\partial x_k} + \frac{\partial M_{\langle ij \rangle k}}{\partial x_k} + 2 \frac{\partial v_{\langle i}}{\partial x_k} M_{j \rangle k} - P_{\langle ij \rangle} \right] \\ & - \lambda_i \left[\dot{m}_{ppi} + m_{ppi} \frac{\partial v_k}{\partial x_k} + \frac{\partial m_{ppik}}{\partial x_k} + 2 \frac{\partial v_p}{\partial x_k} M_{pik} + \frac{\partial v_i}{\partial x_k} m_{ppk} + 2 M_{ip} \dot{v}_p + m_{pp} \dot{v}_i - Q_i \right] \\ & \geq 0. \end{aligned}$$

Using the expressions (14) and (16) and taking into account the fact that the following derivatives,

$$\dot{\rho}, \dot{v}_i, \dot{m}_{ll}, \dot{II}, \dot{M}_{\langle ij \rangle}, \dot{m}_{ppi}, \frac{\partial \rho}{\partial x_k}, \frac{\partial v_i}{\partial x_k}, \frac{\partial m_{ll}}{\partial x_k}, \frac{\partial II}{\partial x_k}, \frac{\partial M_{\langle ij \rangle}}{\partial x_k}, \frac{\partial m_{ppi}}{\partial x_k}, \quad (17)$$

can have any values, we obtain the relations:

$$dh = \Lambda d\rho + \lambda dm_{ii} + \Lambda_{ii} dII + \Lambda_{\langle ij \rangle} dM_{\langle ij \rangle} + \lambda_i dm_{ppi}, \quad (18)$$

$$\begin{aligned} d\varphi_k &= \Lambda_k dp + \Lambda_k dII + \Lambda_i dM_{\langle ik \rangle} + \left(\lambda - \Lambda_{ll} \frac{\partial p}{\partial m_{qq}} \right) dm_{iik} \\ &\quad + \frac{\Lambda_{ll}}{3} dM_{iik} + \Lambda_{\langle ij \rangle} dM_{\langle ij \rangle k} + \lambda_i dm_{ppik}, \end{aligned} \quad (19)$$

and

$$\Lambda_i = -\frac{1}{\rho} (\lambda_i m_{kk} + 2\lambda_j M_{ij}), \quad (20)$$

$$\begin{aligned} &\left[h - \Lambda\rho - \lambda(m_{ss} + 2p) - 2\lambda II - \Lambda_{ll} \left(\frac{5}{3}p - \rho \frac{\partial p}{\partial \rho} - (m_{ss} + 2p) \frac{\partial p}{\partial m_{rr}} \right) \right. \\ &\quad \left. - \Lambda_{ll} II \left(\frac{5}{3} - 2 \frac{\partial p}{\partial m_{rr}} \right) - \Lambda_{\langle rs \rangle} M_{\langle rs \rangle} - \lambda_r m_{ssr} \right] \delta_{ik} \\ &\quad - 2\lambda M_{\langle ik \rangle} + 2 \frac{\partial p}{\partial m_{rr}} M_{\langle ik \rangle} \Lambda_{ll} - 2\lambda_j M_{\langle ij \rangle k} - \frac{2}{3} \lambda_i M_{llk} \\ &\quad - \lambda_i m_{llk} - 2\Lambda_{\langle ir \rangle} M_{\langle rk \rangle} - \frac{2}{3} \Lambda_{ll} M_{\langle ik \rangle} - 2\Lambda_{\langle ik \rangle} (p + II) = 0. \end{aligned} \quad (21)$$

The residual inequality is given by

$$\Sigma = \frac{1}{3} \Lambda_{ii} P_{jj} + \Lambda_{\langle ij \rangle} P_{\langle ij \rangle} + \lambda_i Q_i \geq 0. \quad (22)$$

3.2 Equilibrium

Equilibrium is defined as a process in which the productions P_{ii} , $P_{\langle ij \rangle}$ and Q_i vanish. The entropy production Σ becomes minimum and vanishes in equilibrium, and then we obtain the necessary conditions:

$$\Lambda_{ii}^E = 0, \quad \Lambda_{\langle ij \rangle}^E = 0, \quad \lambda_i^E = 0, \quad (23)$$

where index E denotes equilibrium. Therefore the Lagrange multipliers Λ_{ii} , $\Lambda_{\langle ij \rangle}$ and λ_i play a role of characterizing nonequilibrium phenomena, and will be called nonequilibrium variables.

From Eq. (18) and $m_{ii} = 2\rho\varepsilon$, we have the relation:

$$dh^E = \Lambda^E d\rho + 2\lambda^E d(\rho\varepsilon). \quad (24)$$

On the other hand, taking into account that $h^E = \rho s$ where s is the entropy density and that $Tds = d\varepsilon - (p/\rho^2)d\rho$ (the Gibbs equation), we have

$$dh^E = -\frac{g}{T} d\rho + \frac{1}{T} d(\rho\varepsilon), \quad (25)$$

where $g (= \varepsilon + p/\rho - Ts)$ is the chemical potential and T the absolute temperature. Now, by comparison, we conclude that

$$\Lambda^E = -\frac{g}{T}, \quad \lambda^E = \frac{1}{2T}. \quad (26)$$

We observe that the trace part of Eq. (21) in equilibrium becomes an identity.

3.3 Derivation of the constitutive equations

In order to transform the independent variables from $\{\rho, m_{ii}, \Pi, M_{\langle ij \rangle}, m_{ppi}\}$ to $\{\Lambda, \lambda, \Lambda_{ii}, \Lambda_{\langle ij \rangle}, \lambda_i\}$, we introduce the new potentials h' and φ'_k as follows:

$$h' = \Lambda\rho + \lambda m_{ii} + \Lambda_{ii}\Pi + \Lambda_{\langle ij \rangle}M_{\langle ij \rangle} + \lambda_i m_{ppi} - h, \quad (27)$$

$$\varphi'_k = \lambda m_{iik} + \frac{1}{3}\Lambda_{ll}M_{iik} + \Lambda_{\langle ij \rangle}M_{\langle ij \rangle k} + \lambda_i m_{ppik} - \varphi_k. \quad (28)$$

Then we have

$$dh' = \rho d\Lambda + m_{ii}d\lambda + \Pi d\Lambda_{ll} + M_{\langle ij \rangle}d\Lambda_{\langle ij \rangle} + m_{ppi}d\lambda_i, \quad (29)$$

$$\begin{aligned} d\varphi'_k = & -\Lambda_k(dp + d\Pi) - \Lambda_i dM_{\langle ik \rangle} + \frac{\partial p}{\partial m_{jj}}\Lambda_{ll}dm_{ppk} \\ & + m_{ppk}d\lambda + \frac{1}{3}M_{iik}d\Lambda_{ll} + M_{\langle ij \rangle k}d\Lambda_{\langle ij \rangle} + m_{ppik}d\lambda_i. \end{aligned} \quad (30)$$

By using the representation theorem that ensures the principle of objectivity, the potentials h' and φ'_k are expanded around an equilibrium state with respect to the nonequilibrium variables $\{\Lambda_{kk}, \Lambda_{\langle ij \rangle}, \lambda_i\}$ as follows:

$$\begin{aligned} h' = h'^E & + h_1\Lambda_{kk} + h_2\Lambda_{kk}^2 + h_3\Lambda_{\langle ij \rangle}\Lambda_{\langle ij \rangle} + h_4\lambda_i\lambda_i + h_5\Lambda_{kk}^3 + h_6\Lambda_{kk}\Lambda_{\langle ij \rangle}\Lambda_{\langle ij \rangle} \\ & + h_7\Lambda_{\langle ij \rangle}\Lambda_{\langle in \rangle}\Lambda_{\langle nj \rangle} + h_8\Lambda_{kk}\lambda_i\lambda_i + h_9\lambda_i\lambda_j\Lambda_{\langle ij \rangle} + O(4), \end{aligned} \quad (31)$$

$$\varphi'_k = (\beta_1 + \beta_2\Lambda_{ll})\lambda_k + \beta_3\Lambda_{\langle ki \rangle}\lambda_i + O(3), \quad (32)$$

where the coefficients h_1, \dots, h_9 and $\beta_1, \beta_2, \beta_3$ are the functions of Λ and λ . From Eqs. (26)-(27), we have the relation:

$$h'^E = \Lambda^E \rho + \lambda^E m_{ii} - h^E = -\frac{p^E}{T}. \quad (33)$$

From Eqs. (31) and (32), we obtain

$$\begin{aligned} dh' = dh'^E & + \Lambda_{kk}dh_1 + \Lambda_{kk}^2dh_2 + \Lambda_{\langle ij \rangle}\Lambda_{\langle ij \rangle}dh_3 + \lambda_i\lambda_i dh_4 + \Lambda_{kk}^3dh_5 \\ & + \Lambda_{kk}\Lambda_{\langle ij \rangle}\Lambda_{\langle ij \rangle}dh_6 + \Lambda_{\langle ij \rangle}\Lambda_{\langle in \rangle}\Lambda_{\langle nj \rangle}dh_7 + \Lambda_{kk}\lambda_i\lambda_i dh_8 + \lambda_i\lambda_j\Lambda_{\langle ij \rangle}dh_9 \\ & + (h_1 + 2h_2\Lambda_{kk} + 3h_5\Lambda_{kk}^2 + h_6\Lambda_{\langle ij \rangle}\Lambda_{\langle ij \rangle} + h_8\lambda_i\lambda_i) d\Lambda_{ll} \\ & + (2h_3\Lambda_{\langle ij \rangle} + 3h_7\Lambda_{\langle in \rangle}\Lambda_{\langle jn \rangle} + 2h_6\Lambda_{kk}\Lambda_{\langle ij \rangle} + h_9\lambda_i\lambda_j) d\Lambda_{\langle ij \rangle} \\ & + (2h_4\lambda_i + 2h_8\Lambda_{kk}\lambda_i + 2h_9\Lambda_{\langle ij \rangle}\lambda_j) d\lambda_i + O(4), \end{aligned} \quad (34)$$

$$\begin{aligned} d\varphi'_k = & \lambda_k d\beta_1 + \Lambda_{ll}\lambda_k d\beta_2 + \Lambda_{\langle ki \rangle}\lambda_i d\beta_3 + (\beta_1 + \beta_2\Lambda_{ll})d\lambda_k \\ & + \beta_3\Lambda_{\langle ki \rangle}d\lambda_i + \beta_2\lambda_k d\Lambda_{ll} + \beta_3\lambda_i d\Lambda_{\langle ki \rangle} + O(3). \end{aligned} \quad (35)$$

Comparing two expressions of $\frac{\partial h'}{\partial \Lambda_{ll}}$ derived from Eqs. (29) and (34) with each other, we obtain

$$\Pi = h_1 + 2h_2\Lambda_{kk} + 3h_5\Lambda_{kk}^2 + h_6\Lambda_{\langle ij \rangle}\Lambda_{\langle ij \rangle} + h_8\lambda_i\lambda_i + O(3). \quad (36)$$

As Π vanishes in equilibrium, $h_1 \equiv 0$. In a similar way, we compare two expressions of $\frac{\partial h'}{\partial \Lambda}$, $\frac{\partial h'}{\partial \lambda}$, $\frac{\partial h'}{\partial \Lambda_{\langle ij \rangle}}$ and $\frac{\partial h'}{\partial \lambda_i}$ derived from Eqs. (29) and (34) with each other, then we obtain

$$\begin{aligned} \rho = \rho^E & + \frac{\partial h_2}{\partial \Lambda}\Lambda_{kk}^2 + \frac{\partial h_3}{\partial \Lambda}\Lambda_{\langle ij \rangle}\Lambda_{\langle ij \rangle} + \frac{\partial h_4}{\partial \Lambda}\lambda_i\lambda_i + \frac{\partial h_5}{\partial \Lambda}\Lambda_{kk}^3 + \frac{\partial h_6}{\partial \Lambda}\Lambda_{kk}\Lambda_{\langle ij \rangle}\Lambda_{\langle ij \rangle} \\ & + \frac{\partial h_7}{\partial \Lambda}\Lambda_{\langle ij \rangle}\Lambda_{\langle in \rangle}\Lambda_{\langle jn \rangle} + \frac{\partial h_8}{\partial \Lambda}\Lambda_{kk}\lambda_i\lambda_i + \frac{\partial h_9}{\partial \Lambda}\lambda_i\lambda_j\Lambda_{\langle ij \rangle} + O(4), \\ m_{ii} = m_{ii}^E & + \frac{\partial h_2}{\partial \lambda}\Lambda_{kk}^2 + \frac{\partial h_3}{\partial \lambda}\Lambda_{\langle ij \rangle}\Lambda_{\langle ij \rangle} + \frac{\partial h_4}{\partial \lambda}\lambda_i\lambda_i + \frac{\partial h_5}{\partial \lambda}\Lambda_{kk}^3 + \frac{\partial h_6}{\partial \lambda}\Lambda_{kk}\Lambda_{\langle ij \rangle}\Lambda_{\langle ij \rangle} \\ & + \frac{\partial h_7}{\partial \lambda}\Lambda_{\langle ij \rangle}\Lambda_{\langle in \rangle}\Lambda_{\langle jn \rangle} + \frac{\partial h_8}{\partial \lambda}\Lambda_{kk}\lambda_i\lambda_i + \frac{\partial h_9}{\partial \lambda}\lambda_i\lambda_j\Lambda_{\langle ij \rangle} + O(4), \\ M_{\langle ij \rangle} = & 2h_3\Lambda_{\langle ij \rangle} + 3h_7\Lambda_{\langle in \rangle}\Lambda_{\langle jn \rangle} + 2h_6\Lambda_{kk}\Lambda_{\langle ij \rangle} + h_9\lambda_i\lambda_j + O(3), \\ m_{ppi} = & 2h_4\lambda_i + 2h_8\Lambda_{kk}\lambda_i + 2h_9\Lambda_{\langle ij \rangle}\lambda_j + O(3), \end{aligned} \quad (37)$$

where $\rho^E = \rho^E(\Lambda, \lambda)$ and $m_{ii}^E = m_{ii}^E(\Lambda, \lambda) = 2\rho^E(\Lambda, \lambda)\varepsilon^E(\Lambda, \lambda)$. From Eqs. (37)_{1,2}, we can represent the pressure p as follows:

$$\begin{aligned} p(\rho, m_{ii}) &= p^E(\rho^E, m_{ii}^E) + \left(\left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}} \left(\frac{\partial h_2}{\partial \Lambda} \right)_\lambda + \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_\rho \left(\frac{\partial h_2}{\partial \lambda} \right)_\Lambda \right) \Lambda_{kk}^2 \\ &+ \left(\left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}} \left(\frac{\partial h_3}{\partial \Lambda} \right)_\lambda + \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_\rho \left(\frac{\partial h_3}{\partial \lambda} \right)_\Lambda \right) \Lambda_{\langle ij \rangle} \Lambda_{\langle ij \rangle} \\ &+ \left(\left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}} \left(\frac{\partial h_4}{\partial \Lambda} \right)_\lambda + \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_\rho \left(\frac{\partial h_4}{\partial \lambda} \right)_\Lambda \right) \lambda_i \lambda_i + O(3). \end{aligned} \quad (38)$$

From equations (37)_{1,2} and (38), we notice an important point that we have a nonequilibrium density ρ and an equilibrium density ρ^E , and that the difference $\rho - \rho^E$ is in the second order of magnitude with respect to the nonequilibrium variables. This justifies the equality, $\rho = \rho^E$, as far as the linear theory with respect to the nonequilibrium variables is concerned. The same is true for the quantities m_{ii} and p . This point will play a crucial role in the next subsection.

Next we compare two expressions of $\frac{\partial \varphi'_k}{\partial \Lambda}$, $\frac{\partial \varphi'_k}{\partial \lambda}$, $\frac{\partial \varphi'_k}{\partial \Lambda_{ll}}$, $\frac{\partial \varphi'_k}{\partial \Lambda_{\langle ij \rangle}}$ and $\frac{\partial \varphi'_k}{\partial \lambda_i}$ derived from Eqs. (30) and (35) with each other, then we obtain

$$\begin{aligned} 0 &= \left[\frac{\partial \beta_1}{\partial \Lambda} - 2 \frac{\partial p}{\partial \Lambda} \left(\varepsilon + \frac{p}{\rho} \right) \right] \lambda_k \\ &+ \left[\frac{\partial \beta_2}{\partial \Lambda} - \frac{4h_2}{\rho} \frac{\partial p}{\partial \Lambda} - 2 \frac{\partial p}{\partial m_{ii}} \frac{\partial h_4}{\partial \Lambda} - 2 \frac{\partial h_4}{\partial \Lambda} \left(\varepsilon + \frac{p}{\rho} \right) \right] \Lambda_{ll} \lambda_k \\ &+ \left[\frac{\partial \beta_3}{\partial \Lambda} - 4 \frac{h_3}{\rho} \frac{\partial p}{\partial \Lambda} - 2 \frac{\partial h_3}{\partial \Lambda} \left(\varepsilon + \frac{p}{\rho} \right) \right] \lambda_i \Lambda_{\langle ik \rangle} + O(3), \\ 0 &= \left[\frac{\partial \beta_1}{\partial \lambda} - 2h_4 - 2 \frac{\partial p}{\partial \lambda} \left(\varepsilon + \frac{p}{\rho} \right) \right] \lambda_k \\ &+ \left[\frac{\partial \beta_2}{\partial \lambda} - 2h_8 - \frac{4h_2}{\rho} \frac{\partial p}{\partial \lambda} - 2 \frac{\partial p}{\partial m_{ii}} \frac{\partial h_4}{\partial \lambda} - 2 \frac{\partial h_4}{\partial \lambda} \left(\varepsilon + \frac{p}{\rho} \right) \right] \Lambda_{ll} \lambda_k \\ &+ \left[\frac{\partial \beta_3}{\partial \lambda} - 2h_9 - 4 \frac{h_3}{\rho} \frac{\partial p}{\partial \lambda} - 2 \frac{\partial h_3}{\partial \lambda} \left(\varepsilon + \frac{p}{\rho} \right) \right] \lambda_i \Lambda_{\langle ik \rangle} + O(3), \\ M_{iik} &= 3 \left[\beta_2 - 2h_2 \left(\varepsilon + \frac{p}{\rho} \right) \right] \lambda_k + O(2), \\ M_{\langle ij \rangle k} &= \left[\beta_3 - 2h_3 \left(\varepsilon + \frac{p}{\rho} \right) \right] \lambda_{\langle i} \delta_{j \rangle k} + O(2), \\ m_{ppik} &= \left[\beta_1 + \left\{ \beta_2 - 2h_4 \left(\frac{\partial p}{\partial m_{pp}} \right)_\rho \right\} \Lambda_{ll} \right] \delta_{ik} + \beta_3 \Lambda_{\langle ik \rangle} + O(2). \end{aligned} \quad (39)$$

We now derive the relations among the coefficients h_2, \dots, h_9 and $\beta_1, \beta_2, \beta_3$. By substituting Eqs. (37), (39)_{3,4} and (31) into Eq.(21), we have

$$\begin{aligned}
h_2 &= \frac{1}{4\lambda} \left(-\frac{5}{3} p^E + \left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}^E} \rho^E + \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} m_{rr}^E + 2 \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} p^E \right), \\
h_3 &= -\frac{p^E}{2\lambda}, \\
h_5 &= \left(2 \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} - \frac{7}{6} \right) \frac{h_2}{3\lambda} - \frac{1}{3} \left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}^E} \left(\frac{\partial h_2}{\partial \Lambda} \right)_\lambda - \frac{1}{3} \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} \left(\frac{\partial h_2}{\partial \lambda} \right)_\Lambda, \\
h_6 &= \frac{1}{4\lambda^2} \left(\frac{7}{3} p^E - \left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}^E} \rho^E - \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} m_{rr}^E - 4 \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} p^E \right), \\
h_7 &= \frac{p^E}{3\lambda^2}, \\
h_8 &= -\frac{1}{3\lambda} \left[\frac{5}{3} \beta_3 + \beta_2 - \frac{1}{\rho^E} \left(\frac{10}{3} h_3 + 2h_2 \right) (m_{ii}^E + 2p^E) \right] \\
&\quad - \frac{5}{6\lambda} h_4 - \left(\frac{\partial p^E}{\partial \rho^E} \right)_{m_{ii}^E} \left(\frac{\partial h_4}{\partial \Lambda} \right)_\lambda - \lambda \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} \left(\frac{\partial h_4}{\partial \lambda} \right)_\Lambda, \\
h_9 &= -\frac{1}{\lambda} \left[\frac{\beta_3}{6} + \beta_2 - \frac{1}{\rho^E} \left(\frac{h_3}{3} + 2h_2 \right) (m_{ii}^E + 2p^E) \right] - \frac{h_4}{\lambda}.
\end{aligned} \tag{40}$$

From Eqs. (39)_{1,2}, we have the relations:

$$\begin{aligned}
\frac{\partial \beta_1}{\partial \Lambda} &= 2 \frac{\partial p^E}{\partial \Lambda} \left(\varepsilon^E + \frac{p^E}{\rho^E} \right), \\
\frac{\partial \beta_2}{\partial \Lambda} &= \frac{4h_2}{\rho^E} \frac{\partial p^E}{\partial \Lambda} + 2 \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} \frac{\partial h_4}{\partial \Lambda} + 2 \frac{\partial h_4}{\partial \Lambda} \left(\varepsilon^E + \frac{p^E}{\rho^E} \right), \\
\frac{\partial \beta_3}{\partial \Lambda} &= 4 \frac{h_3}{\rho^E} \frac{\partial p^E}{\partial \Lambda} + 2 \frac{\partial h_3}{\partial \Lambda} \left(\varepsilon^E + \frac{p^E}{\rho^E} \right), \\
\frac{\partial \beta_1}{\partial \lambda} &= 2h_4 + 2 \frac{\partial p^E}{\partial \lambda} \left(\varepsilon^E + \frac{p^E}{\rho^E} \right), \\
\frac{\partial \beta_2}{\partial \lambda} &= 2h_8 + \frac{4h_2}{\rho^E} \frac{\partial p^E}{\partial \lambda} + 2 \left(\frac{\partial p^E}{\partial m_{ii}^E} \right)_{\rho^E} \frac{\partial h_4}{\partial \lambda} + 2 \frac{\partial h_4}{\partial \lambda} \left(\varepsilon^E + \frac{p^E}{\rho^E} \right), \\
\frac{\partial \beta_3}{\partial \lambda} &= 2h_9 + 4 \frac{h_3}{\rho^E} \frac{\partial p^E}{\partial \lambda} + 2 \frac{\partial h_3}{\partial \lambda} \left(\varepsilon^E + \frac{p^E}{\rho^E} \right)
\end{aligned} \tag{41}$$

Note that the coefficient h_4 appears only in (40)_{6,7} and in (41)_{2,4,5}.

3.4 Definitions of the temperature and the chemical potential in nonequilibrium

As explained before, from Eqs. (37)_{1,2} and (38), we notice the following two points: (i) The density ρ and the internal energy m_{ii} at a nonequilibrium state with $(\Lambda, \lambda, \Lambda_{kk}, \Lambda_{ij}, \lambda_i)$ are equal to the equilibrium quantities ρ^E and m_{ii}^E at (Λ, λ) to within second-order terms. This means that, as far as the linear constitutive equations are concerned, the values of (Λ, λ) are exactly those of the associated local equilibrium state [20] with the nonequilibrium state. Therefore we can use the relations (26), and can introduce the temperature T and the chemical potential g into the nonequilibrium state through the following relations:

$$\Lambda = -\frac{g}{T}, \quad \lambda = \frac{1}{2T}. \tag{42}$$

Hereafter we will use T and g with this understanding. (ii) The pressure p is also equal to the local equilibrium quantity p^E to within second-order terms. Thus we assure the adequateness of the decomposition prescribed in Eq. (10).

For convenience, we take $\{\rho, T\}$ as independent variables instead of $\{\mathcal{A}, \lambda\}$. Then the relations (40) are rewritten in terms of $\{\rho, T\}$ as follows:

$$\begin{aligned}
h_2 &= -\frac{5}{6}Tp + \frac{\rho T}{2} \left(\frac{\partial p}{\partial \rho} \right)_T + \frac{T^2}{2\rho} \frac{\left(\frac{\partial p}{\partial T} \right)_\rho^2}{\left(\frac{\partial \varepsilon}{\partial T} \right)_\rho}, \\
h_3 &= -Tp, \\
h_5 &= \frac{2Th_2}{3} \left(-\frac{7}{6} + \frac{\left(\frac{\partial p}{\partial T} \right)_\rho}{\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho} \right) + \frac{\rho T}{3} \left(\frac{\partial h_2}{\partial \rho} \right)_T + \frac{T^2}{3} \left(\frac{\partial h_2}{\partial T} \right)_\rho \frac{\left(\frac{\partial p}{\partial T} \right)_\rho}{\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho}, \\
h_6 &= \frac{7}{3}pT^2 - \rho T^2 \left(\frac{\partial p}{\partial \rho} \right)_T - T^2 \left(p + T \left(\frac{\partial p}{\partial T} \right)_\rho \right) \frac{\left(\frac{\partial p}{\partial T} \right)_\rho}{\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho}, \\
h_7 &= \frac{4}{3}T^2p, \\
h_8 &= -\frac{2}{3}T\beta_2 - \frac{10}{9}T\beta_3 - \frac{5}{3}Th_4 + \rho T \left(\frac{\partial h_4}{\partial \rho} \right)_T + T^2 \left(\frac{\partial h_4}{\partial T} \right)_\rho \frac{\left(\frac{\partial p}{\partial T} \right)_\rho}{\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho} \\
&\quad + \frac{8T}{3} \left(\varepsilon + \frac{p}{\rho} \right) \left(h_2 - \frac{5}{3}Tp \right), \\
h_9 &= -2T\beta_2 - \frac{T}{3}\beta_3 - 2Th_4 + 4T \left(\varepsilon + \frac{p}{\rho} \right) \left(2h_2 - \frac{Tp}{3} \right).
\end{aligned} \tag{43}$$

And the relations (41) are rewritten as follows:

$$\begin{aligned}
\frac{\partial \beta_1}{\partial \rho} &= 2 \left(\varepsilon + \frac{p}{\rho} \right) \left(\frac{\partial p}{\partial \rho} \right)_T, \\
\frac{\partial \beta_2}{\partial \rho} &= 4 \frac{h_2}{\rho} \left(\frac{\partial p}{\partial \rho} \right)_T + 4 \left(\varepsilon + \frac{p}{\rho} \right) \left(\frac{\partial h_2}{\partial \rho} \right)_T + \left(\frac{\partial h_4}{\partial \rho} \right)_T \frac{\left(\frac{\partial p}{\partial T} \right)_\rho}{\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho}, \\
\frac{\partial \beta_3}{\partial \rho} &= -4T \left(\varepsilon + 2\frac{p}{\rho} \right) \left(\frac{\partial p}{\partial \rho} \right)_T, \\
\frac{\partial \beta_1}{\partial T} &= 2 \left(\varepsilon + \frac{p}{\rho} \right) \left(\frac{\partial p}{\partial T} \right)_\rho - \frac{h_4}{T^2}, \\
\frac{\partial \beta_2}{\partial T} &= \frac{2}{3T}\beta_2 + \frac{10}{9T}\beta_3 + \frac{5}{3T}h_4 - \frac{\rho}{T} \left(\frac{\partial h_4}{\partial \rho} \right)_T - h_2 \left[\frac{8}{3T} \left(\varepsilon + \frac{p}{\rho} \right) - \frac{4}{\rho} \left(\frac{\partial p}{\partial T} \right)_\rho \right] \\
&\quad + 4 \left(\varepsilon + \frac{p}{\rho} \right) \left[\frac{10}{9}p + \left(\frac{\partial h_2}{\partial T} \right)_\rho \right], \\
\frac{\partial \beta_3}{\partial T} &= \frac{2}{T}\beta_2 + \frac{1}{3T}\beta_3 + \frac{2}{T}h_4 - 8 \left(\varepsilon + \frac{p}{\rho} \right) \left(\frac{p}{3} + \frac{h_2}{T} \right) - 4T \left(\varepsilon + 2\frac{p}{\rho} \right) \left(\frac{\partial p}{\partial T} \right)_\rho.
\end{aligned} \tag{44}$$

We will show in Sections 7 and 8 that, by using the relations (43), (44) and the equations of state ($\varepsilon = \hat{\varepsilon}(\rho, T)$, $p = \hat{p}(\rho, T)$), we can derive uniquely the explicit expressions of these coefficients except for the integration constants.

3.5 Linear constitutive equations

From Eqs. (37) and (39)_{3,4,5}, the linear constitutive equations are summarized as follows:

$$\begin{aligned}
\Pi &= 2h_2\Lambda_{kk}, \\
M_{\langle ij \rangle} &= 2h_3\Lambda_{\langle ij \rangle}, \\
m_{ppi} &= 2h_4\lambda_i, \\
M_{iik} &= 3 \left[\beta_2 - 4h_2 \left(\varepsilon + \frac{p}{\rho} \right) \right] \lambda_k, \\
M_{\langle ij \rangle k} &= \left[\beta_3 - 4h_3 \left(\varepsilon + \frac{p}{\rho} \right) \right] \lambda_{\langle i} \delta_{j \rangle k}, \\
m_{ppik} &= \left[\beta_1 + \left\{ \beta_2 - h_4 \frac{(\frac{\partial p}{\partial T})_\rho}{\rho(\frac{\partial \varepsilon}{\partial T})_\rho} \right\} \Lambda_{ll} \right] \delta_{ik} + \beta_3 \Lambda_{\langle ik \rangle}.
\end{aligned} \tag{45}$$

It is usually more convenient to take $\{\rho, T, S_{\langle ij \rangle}, \Pi, q_i\}$ as independent variables instead of $\{\rho, T, \Lambda_{\langle ij \rangle}, \Lambda_{ll}, \lambda_i\}$. From Eqs. (45)_{1,2,3}, (10) and (11), the Lagrange multipliers are expressed by

$$\Lambda_{kk} = \frac{1}{2h_2}\Pi, \quad \Lambda_{\langle ij \rangle} = -\frac{1}{2h_3}S_{\langle ij \rangle}, \quad \lambda_i = \frac{1}{h_4}q_i. \tag{46}$$

Then we may express the linear constitutive equations as follows:

$$\begin{aligned}
M_{iik} &= 3Lq_k, \\
M_{\langle ij \rangle k} &= Kq_{\langle i} \delta_{j \rangle k}, \\
m_{ppik} &= \left[\beta_1 + \left\{ \frac{h_4}{2h_2} \left(L - \frac{(\frac{\partial p}{\partial T})_\rho}{\rho(\frac{\partial \varepsilon}{\partial T})_\rho} \right) + 2 \left(\varepsilon + \frac{p}{\rho} \right) \right\} \Pi \right] \delta_{ik} - \left(\frac{h_4}{2h_3}K + 2 \left(\varepsilon + \frac{p}{\rho} \right) \right) S_{\langle ik \rangle},
\end{aligned} \tag{47}$$

where the coefficients h_2, h_3, h_4 and $\beta_1, \beta_2, \beta_3$ are the functions of ρ and T . And instead of β_2 and β_3 , we introduce the coefficients L and K that are the functions of ρ and T defined by

$$L = \frac{1}{h_4} \left[\beta_2 - 4h_2 \left(\varepsilon + \frac{p}{\rho} \right) \right], \quad K = \frac{1}{h_4} \left[\beta_3 - 4h_3 \left(\varepsilon + \frac{p}{\rho} \right) \right]. \tag{48}$$

3.6 Entropy density and entropy flux

With Eqs. (27), (28), (31), (32) and the constitutive equations (47), the entropy density and the entropy flux are expressed as

$$h = h^E + \frac{1}{4h_2}\Pi^2 + \frac{1}{4h_3}S_{\langle ij \rangle}S_{\langle ij \rangle} + \frac{1}{h_4}q_i q_i + O(3), \tag{49}$$

$$\varphi_k = \frac{1}{T}q_k + \frac{1}{2h_2} \left(L - \frac{(\frac{\partial p}{\partial T})_\rho}{\rho(\frac{\partial \varepsilon}{\partial T})_\rho} \right) \Pi q_k - \frac{K}{2h_3}q_i S_{\langle ik \rangle} + O(3). \tag{50}$$

3.7 Productions

The productions are also expanded with respect to the nonequilibrium variables $\{\Lambda_{kk}, \Lambda_{\langle ij \rangle}, \lambda_i\}$ around an equilibrium state. In the linear approximation, we have

$$P_{\langle ij \rangle} = \sigma \Lambda_{\langle ij \rangle}, \quad P_{ii} = 3\zeta \Lambda_{kk}, \quad Q_i = \tau \lambda_i. \tag{51}$$

Then we obtain

$$\Sigma = \sigma \Lambda_{\langle ij \rangle} \Lambda_{\langle ij \rangle} + \zeta \Lambda_{kk}^2 + \tau \lambda_i \lambda_i \geq 0. \tag{52}$$

There are three conditions for the coefficients:

$$\sigma > 0, \quad \zeta > 0, \quad \tau > 0. \quad (53)$$

The constitutive equations (51) may also be expressed as

$$P_{\langle ij \rangle} = -\frac{\sigma}{2h_3} S_{\langle ij \rangle}, \quad P_{ii} = \frac{3\zeta}{2h_2} \Pi, \quad Q_i = \frac{\tau}{h_4} q_i. \quad (54)$$

4 Concavity of the entropy density and causality

The system (6) must be symmetric hyperbolic so as to ensure the causality. Near equilibrium this requirement corresponds to the condition of the concavity of the entropy density [1, 21].¹

As the second derivative of the entropy density h near equilibrium is given by

$$d^2h = d^2h^E + \frac{1}{4h_2}(d\Pi)^2 + \frac{1}{4h_3}dS_{\langle ij \rangle}dS_{\langle ij \rangle} + \frac{1}{h_4}dq_idq_i, \quad (55)$$

the condition is satisfied when h^E is a concave function with respect to $\{\rho, m_{ii}\}$ and the following inequalities are fulfilled:

$$h_2 < 0, \quad h_3 < 0, \quad h_4 < 0. \quad (56)$$

Using the well-known results of thermodynamic stability in equilibrium thermodynamics and the relations (43)_{2,3} and (44)₄, the concavity condition is expressed as follows:

$$\begin{aligned} p > 0, \quad \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho > 0, \quad \left(\frac{\partial p}{\partial \rho}\right)_T > 0, \\ -\frac{5}{6}Tp + \frac{\rho T}{2} \left(\frac{\partial p}{\partial \rho}\right)_T + \frac{\frac{T^2}{2\rho} \left(\frac{\partial p}{\partial T}\right)_\rho^2}{\left(\frac{\partial \varepsilon}{\partial T}\right)_\rho} < 0, \\ 2T^2 \left(\varepsilon + \frac{p}{\rho}\right) \left(\frac{\partial p}{\partial T}\right)_\rho - T^2 \left(\frac{\partial \beta_1}{\partial T}\right)_\rho < 0. \end{aligned} \quad (57)$$

¹ The entropy density used in the mathematical community has usually opposite sign to the present entropy density. As a consequence, they speak about convexity instead of concavity.

5 Field equations

The closed system of field equations is obtained by substituting the equations (47) into the system (9):

$$\begin{aligned}
\dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} &= 0, \\
\rho \dot{v}_i + \frac{\partial p}{\partial x_i} + \frac{\partial \Pi}{\partial x_i} - \frac{\partial S_{\langle ij \rangle}}{\partial x_j} &= 0, \\
\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho \dot{T} + \left[p + \Pi - \rho^2 \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T \right] \frac{\partial v_k}{\partial x_k} - \frac{\partial v_i}{\partial x_k} S_{\langle ik \rangle} + \frac{\partial q_k}{\partial x_k} &= 0, \\
\dot{S}_{\langle ij \rangle} - 2p \frac{\partial v_{\langle i}}{\partial x_j \rangle} + S_{\langle ij \rangle} \frac{\partial v_k}{\partial x_k} - 2\Pi \frac{\partial v_{\langle i}}{\partial x_j \rangle} + 2 \frac{\partial v_{\langle i}}{\partial x_k} S_{\langle j \rangle k} - q_{\langle i} \delta_{j \rangle k} \frac{\partial K}{\partial x_k} - K \frac{\partial q_{\langle i}}{\partial x_j \rangle} &= -\frac{1}{\tau_S} S_{\langle ij \rangle}, \\
\dot{\Pi} - \frac{2h_2}{T} \frac{\partial v_k}{\partial x_k} + \left(\frac{5}{3} - \frac{\frac{\partial p}{\partial T}}{\rho \frac{\partial \varepsilon}{\partial T}} \right) \Pi \frac{\partial v_k}{\partial x_k} - \left(\frac{2}{3} - \frac{\frac{\partial p}{\partial T}}{\rho \frac{\partial \varepsilon}{\partial T}} \right) \frac{\partial v_{\langle i}}{\partial x_k} S_{\langle ik \rangle} \\
+ q_k \frac{\partial L}{\partial x_k} + \left(L - \frac{\frac{\partial p}{\partial T}}{\rho \frac{\partial \varepsilon}{\partial T}} \right) \frac{\partial q_k}{\partial x_k} &= -\frac{1}{\tau_\Pi} \Pi, \\
\dot{q}_j + \left(1 + \frac{K}{2} \right) q_j \frac{\partial v_k}{\partial x_k} + \frac{K}{2} q_k \frac{\partial v_k}{\partial x_j} + \left(1 + L - \frac{K}{3} \right) q_k \frac{\partial v_j}{\partial x_k} \\
- \frac{h_4}{2T^2} \frac{\partial T}{\partial x_j} + \frac{h_4}{4h_2} \left(L - \frac{\frac{\partial p}{\partial T}}{\rho \frac{\partial \varepsilon}{\partial T}} \right) \frac{\partial \Pi}{\partial x_j} - \frac{h_4}{4h_3} K \frac{\partial S_{\langle jk \rangle}}{\partial x_k} \\
+ \Pi \left[\left\{ \frac{\partial \varepsilon}{\partial \rho} - \frac{p}{\rho^2} + \frac{\partial}{\partial \rho} \left(\frac{h_4}{4h_2} \left(L - \frac{\frac{\partial p}{\partial T}}{\rho \frac{\partial \varepsilon}{\partial T}} \right) \right) \right\} \frac{\partial \rho}{\partial x_j} \right. \\
+ \left. \left\{ \frac{\partial \varepsilon}{\partial T} + \frac{\partial}{\partial T} \left(\frac{h_4}{4h_2} \left(L - \frac{\frac{\partial p}{\partial T}}{\rho \frac{\partial \varepsilon}{\partial T}} \right) \right) \right\} \frac{\partial T}{\partial x_j} - \frac{1}{\rho} \frac{\partial \Pi}{\partial x_j} + \frac{1}{\rho} \frac{\partial S_{\langle jk \rangle}}{\partial x_k} \right] \\
- S_{\langle jk \rangle} \left[\left\{ \frac{\partial \varepsilon}{\partial \rho} - \frac{p}{\rho^2} + \frac{\partial}{\partial \rho} \left(\frac{h_4}{4h_3} K \right) \right\} \frac{\partial \rho}{\partial x_k} \right. \\
+ \left. \left\{ \frac{\partial \varepsilon}{\partial T} + \frac{\partial}{\partial T} \left(\frac{h_4}{4h_3} K \right) \right\} \frac{\partial T}{\partial x_k} - \frac{1}{\rho} \frac{\partial \Pi}{\partial x_k} + \frac{1}{\rho} \frac{\partial S_{\langle ik \rangle}}{\partial x_i} \right] &= -\frac{1}{\tau_q} q_j,
\end{aligned} \tag{58}$$

where τ_S , τ_Π and τ_q are the relaxation times given by

$$\tau_S = -\frac{2h_3}{\sigma}, \quad \tau_\Pi = -\frac{2h_2}{\zeta}, \quad \tau_q = -\frac{2h_4}{\tau}. \tag{59}$$

6 Relationship between ET and Navier-Stokes-Fourier theory

We carry out the Maxwellian iteration [1, 6] in the system (58): The first iterates $\Pi^{(1)}$, $S_{\langle ij \rangle}^{(1)}$ and $q_i^{(1)}$ are obtained by the substitution of the 0th iterates $S_{\langle ij \rangle}^{(0)} = 0$, $\Pi^{(0)} = 0$ and $q_i^{(0)} = 0$ into the left hand side of (58)_{4,5,6}. Then we obtain

$$S_{\langle ij \rangle}^{(1)} = 2p\tau_S \frac{\partial v_{\langle i}}{\partial x_j \rangle}, \quad \Pi^{(1)} = \frac{2h_2}{T} \tau_\Pi \frac{\partial v_k}{\partial x_k}, \quad q_i^{(1)} = \frac{h_4}{2T^2} \tau_q \frac{\partial T}{\partial x_i}. \tag{60}$$

On the other hand, we have the laws of Navier-Stokes and Fourier expressed by (3). The comparison reveals that

$$\mu = p\tau_S, \quad \nu = -\frac{2h_2}{T} \tau_\Pi, \quad \kappa = -\frac{h_4}{2T^2} \tau_q. \tag{61}$$

We can therefore estimate the values of the relaxation times τ_S , τ_q and τ_Π from the experimental data of the coefficients μ , ν and κ .

The second iterates are obtained by substituting the first iterates into the left hand side of (58)_{4,5,6}, and higher iterates are obtained in a similar way.

In conclusion, the system can be certainly closed by the universal principles except for some nonessential constants, provided that we know the thermal and caloric equations of state and the viscosity and heat conductivity coefficients. This surprising result, which could not be achieved in previous works on this subject, shows clearly the power of our hierarchy assumption.

7 Rarefied-gas limit

It is important to study the rarefied-gas limit of the present theory in order to check its consistency with the results from the kinetic theory of gases [22]. The dependence of the limit on the degrees of freedom of a molecule is also made clear.

7.1 Equations of state

From the ideal gas law with the equipartition law of energy, the thermal and caloric equations of state for a classical rarefied gas are expressed as

$$p = \frac{k_B}{m} \rho T, \quad \varepsilon = \frac{D}{2} \frac{k_B}{m} T, \quad (62)$$

where k_B and m being, respectively, the Boltzmann constant and the mass of a molecule, and D is the degrees of freedom of a molecule, i.e., $D = 3 + f$ where 3 corresponds to the translational motion in the 3-dimensional space and f is the internal degrees of freedom.

7.2 Linear constitutive equations

The coefficients h_2, \dots, h_9 and $\beta_1, \beta_2, \beta_3$ in this case are easily obtained from the relations (43) and (44). We assume that the integration constants in $\beta_1, \beta_2, \beta_3$ vanish. This assumption is reasonable because of the fact that our results below are consistent with those of the kinetic theory [22].

The linear constitutive equations are given by

$$\begin{aligned} M_{ik} &= \frac{10}{D+2} q_k, \\ M_{\langle ij \rangle k} &= \frac{4}{D+2} q_{\langle i} \delta_{j \rangle k}, \\ m_{ppik} &= \frac{k_B}{m} T [(D+2)p + (D+4)\Pi] \delta_{ik} - \frac{k_B}{m} T (D+4) S_{\langle ik \rangle}, \\ P_{ii} &= -\frac{9D\zeta}{2(D-3) \frac{k_B}{m} \rho T^2} \Pi, \\ P_{\langle ij \rangle} &= \frac{\sigma}{2 \frac{k_B}{m} \rho T^2} S_{\langle ij \rangle}, \\ Q_i &= -\frac{\tau}{(D+2) \left(\frac{k_B}{m}\right)^2 \rho T^3} q_i. \end{aligned} \quad (63)$$

We notice a subtle point in Eq. (63)₄ for the case of rarefied monatomic gases where $D = 3$ and as a consequence $\Pi = 0$. Note also that the coefficient h_2 vanishes in this case. We will discuss this point in Section 7.5.

7.3 Concavity of the entropy density

The entropy density and the entropy flux are expressed as

$$h = h^E - \frac{3D}{4(D-3)\frac{k_B}{m}\rho T^2}\Pi^2 - \frac{1}{4\frac{k_B}{m}\rho T^2}S_{\langle ij \rangle}S_{\langle ij \rangle} - \frac{1}{(D+2)\left(\frac{k_B}{m}\right)^2\rho T^3}q_i q_i + O(3), \quad (64)$$

$$\varphi_k = \frac{1}{T}q_k - \frac{D^2 + 6D - 12}{(D-3)(D+2)\frac{k_B}{m}\rho T^2}\Pi q_k + \frac{2}{(D+2)\frac{k_B}{m}\rho T^2}q_i S_{\langle ik \rangle} + O(3). \quad (65)$$

The requirement of the concavity of the entropy density are expressed as

$$\begin{aligned} p > 0, \quad \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho > 0, \quad \left(\frac{\partial p}{\partial \rho}\right)_T > 0, \\ \frac{D}{(D-3)\frac{k_B}{m}\rho T^2} > 0, \quad \frac{1}{(D+2)\left(\frac{k_B}{m}\right)^2\rho T^3} > 0. \end{aligned} \quad (66)$$

It is easy to see that all inequalities are identically satisfied for classical polyatomic gases with $D > 3$. However, as will be discussed in Section 7.5, we should be careful for monatomic gases with $D = 3$.

7.4 Field equations

Using the constitutive equations (63), we obtain the closed system of field equations:

$$\begin{aligned} \dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} &= 0, \\ \rho \dot{v}_i + \frac{\partial p}{\partial x_i} + \frac{\partial \Pi}{\partial x_i} - \frac{\partial S_{\langle ij \rangle}}{\partial x_j} &= 0, \\ \dot{T} + \frac{2}{D\frac{k_B}{m}\rho}(p + \Pi) \frac{\partial v_k}{\partial x_k} - \frac{2}{D\frac{k_B}{m}\rho} \frac{\partial v_i}{\partial x_k} S_{\langle ik \rangle} + \frac{2}{D\frac{k_B}{m}\rho} \frac{\partial q_k}{\partial x_k} &= 0, \\ \dot{S}_{\langle ij \rangle} - 2p \frac{\partial v_{\langle i}}{\partial x_j} + S_{\langle ij \rangle} \frac{\partial v_k}{\partial x_k} - 2\Pi \frac{\partial v_{\langle i}}{\partial x_j} + 2 \frac{\partial v_{\langle i}}{\partial x_k} S_{\langle j \rangle k} - \frac{4}{D+2} \frac{\partial q_{\langle i}}{\partial x_j} &= -\frac{1}{\tau_S} S_{\langle ij \rangle}, \\ \dot{\Pi} + \frac{2(D-3)}{3D} p \frac{\partial v_k}{\partial x_k} + \frac{5D-6}{3D} \Pi \frac{\partial v_k}{\partial x_k} - \frac{2(D-3)}{3D} \frac{\partial v_{\langle i}}{\partial x_k} S_{\langle ik \rangle} \\ &+ \frac{4(D-3)}{3D(D+2)} \frac{\partial q_k}{\partial x_k} = -\frac{1}{\tau_\Pi} \Pi, \\ \dot{q}_i + \frac{D+4}{D+2} q_i \frac{\partial v_k}{\partial x_k} + \frac{2}{D+2} q_k \frac{\partial v_k}{\partial x_i} + \frac{D+4}{D+2} q_k \frac{\partial v_i}{\partial x_k} + \frac{D+2}{2} \left(\frac{k_B}{m}\right)^2 \rho T \frac{\partial T}{\partial x_i} \\ &+ \frac{k_B}{m} T \frac{\partial \Pi}{\partial x_i} - \frac{k_B}{m} T \frac{\partial S_{\langle ik \rangle}}{\partial x_k} + \Pi \left[-\frac{\frac{k_B}{m} T}{\rho} \frac{\partial \rho}{\partial x_i} + \frac{D+2}{2} \frac{k_B}{m} \frac{\partial T}{\partial x_i} - \frac{1}{\rho} \frac{\partial \Pi}{\partial x_i} + \frac{1}{\rho} \frac{\partial S_{\langle ik \rangle}}{\partial x_k} \right] \\ &- S_{\langle ik \rangle} \left[-\frac{\frac{k_B}{m} T}{\rho} \frac{\partial \rho}{\partial x_k} + \frac{D+2}{2} \frac{k_B}{m} \frac{\partial T}{\partial x_k} - \frac{1}{\rho} \frac{\partial \Pi}{\partial x_k} + \frac{1}{\rho} \frac{\partial S_{\langle pk \rangle}}{\partial x_p} \right] = -\frac{1}{\tau_q} q_i, \end{aligned} \quad (67)$$

where τ_S , τ_q and τ_Π are the relaxation times given by

$$\tau_S = \frac{2pT}{\sigma}, \quad \tau_\Pi = \frac{2(D-3)pT}{3D\zeta}, \quad \tau_q = \frac{2(D+2)\left(\frac{k_B}{m}\right)^2\rho T^3}{\tau}. \quad (68)$$

The relaxation times are related to the shear and bulk viscosities and the heat conductivity:

$$\mu = p\tau_S, \quad \nu = \frac{2(D-3)}{3D}p\tau_\Pi, \quad \kappa = \frac{D+2}{2} \frac{p^2}{\rho T} \tau_q. \quad (69)$$

7.5 Remarks

Two remarks are made:

(i) For diatomic gases with $D = 5$ where only the rotational degrees of freedom are taken into account, above field equations coincide with those derived from the kinetic theory of diatomic gases [22] except for the expressions of the relaxation times. This shows the soundness of the present theory.

(ii) Equation (67)₅, when $D = 3$, is reduced to $\Pi = 0$, as is expected in rarefied monatomic gases. In this case, Eq. (67)₅ plays no more role. And the theory becomes singular because of the change of the system itself, that is, the change from 14 equations to 13 equations. Therefore, the field equations with $D = 3$ now constitute the same system of field equations as that in ET of rarefied monatomic gases [1]! As mentioned in the Introduction, only in this case, the relation $F_{ii} = G_{ii}$ is satisfied, and then (6)₃ and the trace part of (6)₄ degenerate into one equation. Above observation is evidently consistent with this fact.

8 Application to special systems

The general theory developed so far is applied to three physically important systems: (i) the system with the virial equations of state, (ii) a hard-sphere system, and (iii) a van der Waals fluid. The analysis of the first system shows explicitly the corrections to the results in the rarefied-gas limit when the system is no more dilute enough. As a hard-sphere system plays an important role in the perturbation theory in liquid-state physics [23–25], it seems to be interesting for the researchers in this field to understand ET of the system. A van der Waals fluid is the well-known simple model that can describe real-gas effects including gas-liquid phase transitions.

8.1 System with the virial equations of state

The thermal and caloric equations of state are given in the form of virial expansion:

$$\begin{aligned} p &= \frac{k_B}{m} \rho T (1 + B_2(T)\rho + B_3(T)\rho^2 + \cdots), \\ \varepsilon &= \frac{D}{2} \frac{k_B}{m} T - \frac{k_B}{m} T^2 \rho B'_2(T) - \frac{1}{2} \frac{k_B}{m} T^2 \rho^2 B'_3(T) + \cdots, \end{aligned} \quad (70)$$

where $B_2(T)$, $B_3(T)$, \cdots are the second and third virial coefficients, and so on. Here a prime means a derivative with respect to the temperature T .

Using the equations of state (70), we can obtain the explicit expressions of the coefficients in the constitutive equations in the following way: We obtain $h_2, h_3, h_5, \cdots, h_9$ except for h_4 from (43). Integrating (44)₁ with respect to ρ , we obtain β_1 as follows:

$$\begin{aligned} \beta_1 &= \int_{\rho_0}^{\rho} 2 \left(\varepsilon(\bar{\rho}, T) + \frac{p(\bar{\rho}, T)}{\bar{\rho}} \right) \left(\frac{\partial p(\bar{\rho}, T)}{\partial \bar{\rho}} \right)_T d\bar{\rho} + C_1(\rho_0, T, T_0), \\ &= \left(\frac{k_B}{m} \right)^2 (D+2) T^2 \rho + \left(\frac{k_B}{m} \right)^2 T^2 \rho^2 ((D+3)B_2 - T B'_2) + O(\rho^3) + C_2(\rho_0, T, T_0), \end{aligned}$$

where $C_{1,2}(\rho_0, T, T_0)$ are integration functions, and ρ_0 and T_0 are, respectively, the mass density and temperature in a reference state. As β_1 at an arbitrary value of T must asymptotically approaches $\left(\frac{k_B}{m} \right)^2 (D+2) T^2 \rho$ in the rarefied-gas limit discussed in Sec. 7, we obtain $C_2(\rho_0, T, T_0) = 0$. Now β_1 has been determined within the approximation adopted here, we get the explicit form of h_4 from (44)₄. β_2 and β_3 can be determined in a similar way. We can easily check the consistency that β_2 and β_3 obtained in this way satisfy the remaining relations (44)_{5,6}.

For simplicity, we show the constitutive equations up to the first correction with respect to ρ :

$$\begin{aligned}
M_{iik} &= \left[\frac{10}{D+2} + \frac{5(D+2)TB'_2 + 10T^2B''_2}{(D+2)^2} \rho + O(\rho^2) \right] q_k, \\
M_{\langle ij \rangle k} &= \left[\frac{4}{D+2} + \frac{2(D+2)TB'_2 + 4T^2B''_2}{(D+2)^2} \rho + O(\rho^2) \right] q_{\langle i} \delta_{j \rangle k}, \\
m_{ppik} &= \frac{k_B}{m} T \left[\left\{ \frac{k_B}{m} (D+2) \rho T + \frac{k_B}{m} ((D+3)B_2 - TB'_2) \rho^2 T + O(\rho^3) \right\} \right. \\
&\quad \left. + \left\{ D+4 + \frac{4(D-3)B_2 - 5DTB'_2 - 6T^2B''_2}{2(D-3)} \rho + O(\rho^2) \right\} \Pi \right] \delta_{ik} \\
&\quad - \frac{k_B}{m} T \{ D+4 + \rho(2B_2 - TB'_2) + O(\rho^2) \} S_{\langle ik \rangle}, \\
P_{ii} &= -\frac{9D}{2\frac{k_B}{m}(D-3)\rho T^2} \left[1 + \frac{(D+12)B_2 + \frac{12}{D}(D+2)TB'_2 + \frac{12}{D}T^2B''_2}{2(D-3)} \rho + O(\rho^2) \right] \zeta \Pi, \\
P_{\langle ij \rangle} &= \frac{1}{2\frac{k_B}{m}\rho T^2} [1 - B_2 \rho + O(\rho^2)] \sigma S_{\langle ij \rangle}, \\
Q_i &= -\frac{1}{\left(\frac{k_B}{m}\right)^2 (D+2)\rho T^3} \left[1 - \left(B_2 - \frac{T^2 B''_2}{D+2} \right) \rho + O(\rho^2) \right] \tau q_i.
\end{aligned} \tag{71}$$

As can be seen above, the first correction depends on both the virial coefficients B_2 and the degrees of freedom D .

The closed system of field equations can be easily obtained by using above constitutive equations. We omit its expression for simplicity.

The relaxation times are related to the shear and bulk viscosities and the heat conductivity:

$$\begin{aligned}
\mu &= \frac{k_B}{m} \rho T (1 + B_2(T) \rho + O(\rho^2)) \tau_S, \\
\nu &= \frac{1}{3D} \frac{k_B}{m} \rho T \left[2(D-3) - \left((D+12)B_2 + \frac{12}{D}(D+2)TB'_2 + \frac{12}{D}T^2B''_2 \right) \rho + O(\rho^2) \right] \tau_\Pi, \\
\kappa &= \frac{1}{2} \left(\frac{k_B}{m} \right)^2 \rho T [D+2 + ((D+2)B_2 - T^2 B''_2) \rho + O(\rho^2)] \tau_q.
\end{aligned} \tag{72}$$

8.2 Hard-sphere system

The thermal and caloric equations of state are given by

$$\begin{aligned}
p &= \frac{k_B}{\omega} T \eta \Gamma(\eta), \\
\varepsilon &= \frac{D}{2} \frac{k_B}{m} T,
\end{aligned} \tag{73}$$

where η is the packing fraction related to the mass density ρ by

$$\eta = \frac{\rho \omega}{m}, \tag{74}$$

and $\Gamma(\eta)$ is a function of η determined explicitly by computer experiments [23]. Here ω is the volume of a hard sphere. In this subsection, we use η instead of ρ .

Using the expressions of the coefficients in the constitutive equations derived in the same way as above, we obtain the constitutive equations:

$$\begin{aligned}
M_{iik} &= \frac{10 \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta}}{D\eta\Gamma + 2 \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta}} q_k, \\
M_{\langle ij \rangle k} &= \frac{4 \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta}}{D\eta\Gamma + 2 \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta}} q_{\langle i} \delta_{j \rangle k}, \\
m_{ppik} &= \frac{k_B}{m} T \left[\frac{k_B}{\omega} \eta T \left(D\Gamma + \Gamma^2 + \frac{1}{\eta} \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta} \right) \right. \\
&\quad \left. + \left\{ D + 2\Gamma - \frac{6D\Gamma^2 + \frac{2}{\eta}(-5D + 6\Gamma) \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta}}{2D\Gamma - 6\Gamma^2 - 3D\eta\Gamma'} \right\} \Pi \right] \delta_{ik} \\
&\quad - \frac{k_B}{m} T \left(D + 2\Gamma + \frac{2}{\eta\Gamma} \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta} \right) S_{\langle ik \rangle}, \\
P_{ii} &= - \frac{9D\zeta}{\frac{k_B}{\omega} \eta T^2 (2D\Gamma - 6\Gamma^2 - 3D\eta\Gamma')} \Pi, \\
P_{\langle ij \rangle} &= \frac{\sigma}{2 \frac{k_B}{\omega} \eta T^2 \Gamma} S_{\langle ij \rangle}, \\
Q_i &= - \frac{\tau}{\left(\frac{k_B}{m} \right)^2 \frac{m}{\omega} \eta T^3 \left(D\Gamma + \frac{2}{\eta} \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta} \right)} q_i,
\end{aligned} \tag{75}$$

where $\Gamma' = d\Gamma(\eta)/d\eta$.

The relaxation times are related to the shear and bulk viscosities and the heat conductivity:

$$\begin{aligned}
\mu &= p\tau_S, \\
\nu &= \frac{1}{3D} \frac{k_B}{\omega} \eta T (2D\Gamma - 6\Gamma^2 - 3D\eta\Gamma') \tau_\Pi, \\
\kappa &= \left(\frac{k_B}{m} \right)^2 \frac{m}{\omega} \eta \frac{T}{2} \left(D\Gamma + \frac{2}{\eta} \int_0^\eta \Gamma^2(\bar{\eta}) d\bar{\eta} \right) \tau_q.
\end{aligned} \tag{76}$$

The concavity condition of the entropy density in this case can be expressed by only one inequality:

$$-\frac{\Gamma}{3} + \frac{\Gamma^2}{D} + \frac{\eta\Gamma'}{2} < 0. \tag{77}$$

Then we find that there is a critical packing fraction η_C such that the above condition is satisfied in the region $0 < \eta < \eta_C$. In the case of $D = 5$, for example, we can estimate $\eta_C = 0.0447$ by adopting the following functional form of Γ [26]:

$$\Gamma(\eta) = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \tag{78}$$

The dependence of η_C on D is shown in Fig. 1. It is remarkable that $\eta_C = 0$ in the case of $D = 3$.

8.3 van der Waals fluid

The thermal and caloric equations of state are given by

$$\begin{aligned}
p &= \frac{k_B}{m} \frac{T\rho}{1 - b\rho} - a\rho^2, \\
\varepsilon &= \frac{D}{2} \frac{k_B}{m} T - a\rho,
\end{aligned} \tag{79}$$

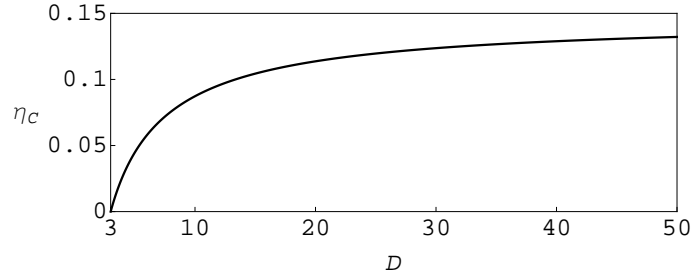


Fig. 1 Dependence of the critical packing fraction η_C on the degrees of freedom D .

where the material-dependent constants a and b represent, respectively, a measure of the attraction between the constituent molecules and the effective volume (or exclusion volume) of a molecule.

The constitutive equations are obtained by using the same procedure as above:

$$\begin{aligned}
M_{iik} &= 10 \frac{\frac{k_B}{m} T + \frac{a}{b^2 \rho} (1 - b\rho)(b\rho + \log(1 - b\rho))}{(D + 2) \frac{k_B}{m} T - D(1 - b\rho)a\rho} q_k, \\
M_{\langle ij \rangle k} &= 4 \frac{\frac{k_B}{m} T + \frac{a}{b^2 \rho} (1 - b\rho)(b\rho + \log(1 - b\rho))}{(D + 2) \frac{k_B}{m} T - D(1 - b\rho)a\rho} q_{\langle i} \delta_{j \rangle k}, \\
m_{ppik} &= \frac{k_B}{m} T \left[(D + 2)p + \frac{k_B}{m} T \frac{b\rho^2}{(1 - b\rho)^2} - 2a\rho^2 \frac{1 + b\rho}{1 - b\rho} + \frac{8}{3} \frac{a^2 \rho^3}{\frac{k_B}{m} T} \right. \\
&\quad + \left\{ \frac{k_B}{m} T \frac{2(D - 3)(D + 4) - (7D^2 + 18D - 12)b\rho + 5D(D + 2)b^2 \rho^2}{1 - b\rho} \right. \\
&\quad + \frac{a}{b} (D(1 - b\rho)^2(10 + Db\rho) + 12b\rho(2 + Db\rho)) - 4D \frac{a^2 \rho^2}{\frac{k_B}{m} T} (1 - b\rho)^2 \\
&\quad \left. \left. + 10D \frac{a}{b^2 \rho} (1 - b\rho)^2 \log(1 - b\rho) \right\} \Pi \right. \\
&\quad \left. \left/ \left\{ \frac{k_B}{m} T (2(D - 3) - 5Db\rho) + Da\rho(1 - b\rho)^2 \right\} \right] \delta_{ik} \right. \\
&\quad - \frac{k_B}{m} T \left\{ \frac{k_B}{m} T \frac{D + 4 - (D + 2)b\rho}{1 - b\rho} + \frac{a}{b} (2 - (D + 8)b\rho + Db^2 \rho^2) \right. \\
&\quad \left. + 4 \frac{a^2 \rho^2}{\frac{k_B}{m} T} (1 - b\rho) + 2 \frac{a}{b^2 \rho} (1 - b\rho) \log(1 - b\rho) \right\} S_{\langle ik \rangle} \\
&\quad \left/ \left\{ \frac{k_B}{m} T - a\rho(1 - b\rho) \right\}, \right. \\
P_{ii} &= - \frac{9D(1 - b\rho)^2}{\frac{k_B}{m} \rho T^2 (2(D - 3) - 5Db\rho) + Da\rho^2 T(1 - b\rho)^2} \zeta \Pi, \\
P_{\langle ij \rangle} &= \frac{1 - b\rho}{2 \frac{k_B}{m} \rho T^2 - 2a\rho^2 T(1 - b\rho)} \sigma S_{\langle ij \rangle}, \\
Q_i &= - \frac{(1 - b\rho)}{\left(\frac{k_B}{m} \right)^2 (D + 2) \rho T^3 - \frac{k_B}{m} D \rho^2 T^2 a(1 - b\rho)} \tau q_i.
\end{aligned} \tag{80}$$

The relaxation times are related to the shear and bulk viscosities and the heat conductivity:

$$\begin{aligned}\mu &= p\tau_S, \\ \nu &= \left(\frac{k_B}{m} \frac{\rho T}{3D(1-b\rho)^2} (2(D-3) - 5Db\rho) + \frac{a\rho^2}{3} \right) \tau_\Pi, \\ \kappa &= \frac{1}{2} \left(\left(\frac{k_B}{m} \right)^2 \frac{D+2}{1-b\rho} \rho T - \frac{k_B}{m} Da\rho^2 \right) \tau_q.\end{aligned}\tag{81}$$

We now study the concavity condition of the entropy density (57). For later convenience, we introduce the dimensionless variables:

$$\hat{p} = \frac{p}{p_{cr}}, \quad \hat{\rho} = \frac{\rho}{\rho_{cr}}, \quad \hat{T} = \frac{T}{T_{cr}},\tag{82}$$

where $\rho_{cr} = 1/(3b)$, $p_{cr} = a/(27b^2)$ and $T_{cr} = 8a/(27\frac{k_B}{m}b)$ are, respectively, the mass density, the pressure and the temperature at the critical point. Then the thermal and caloric equations of state are rewritten in terms of the dimensionless quantities as

$$\begin{aligned}\hat{p} &= \frac{8\hat{T}\hat{\rho}}{3-\hat{\rho}} - 3\hat{\rho}^2, \\ \hat{\varepsilon} &= \frac{\rho_{cr}}{p_{cr}} \varepsilon = \frac{4D\hat{T}}{3} - 3\hat{\rho}.\end{aligned}\tag{83}$$

As the inequality (57)₂ is always satisfied, the concavity condition is now expressed as

$$\begin{aligned}\frac{8\hat{T}\hat{\rho}}{3-\hat{\rho}} - 3\hat{\rho}^2 &> 0, \quad \frac{8\hat{T}}{(3-\hat{\rho})^2} - 2\hat{\rho} > 0, \\ \frac{18 + D(5\hat{\rho} - 6)}{D(\hat{\rho} - 3)^2} \hat{T}^2 \hat{\rho} - \frac{3}{8} \hat{T} \hat{\rho}^2 &< 0, \quad \frac{8(D+2)\hat{T} + 3D(\hat{\rho} - 3)\hat{\rho}}{(\hat{\rho} - 3)} \hat{T}^2 \hat{\rho} < 0.\end{aligned}\tag{84}$$

The condition is satisfied in the shaded regions in Fig. 2 for several values of D . The minimum integer of D for the concavity region to contain the critical point is 8. For purposes of theoretical exploration, we also depict the figure of $D = 100$ as a case of large D .

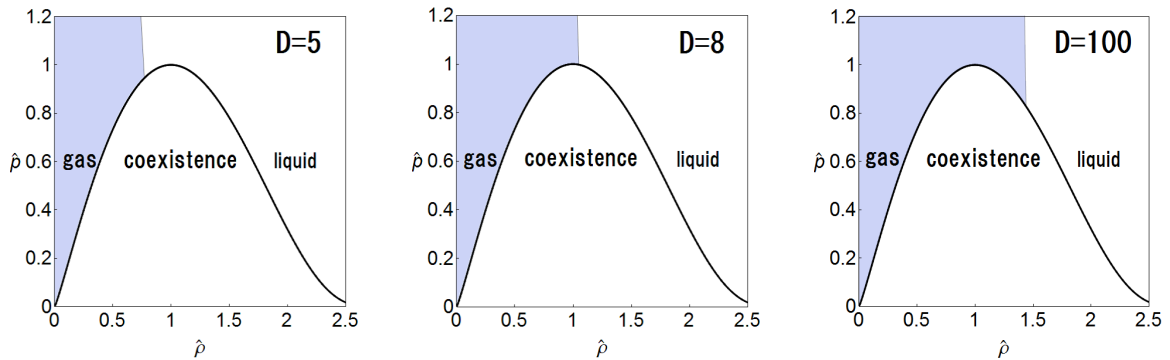


Fig. 2 The concavity condition (84) is satisfied in the shaded region. The degrees of freedom: $D = 5, 8$ and 100 . The curve represents the coexistence curve.

9 Concluding remarks

In conclusion we make the following two remarks:

(i) We have proposed and explained a possible phenomenological model of ET of dense gases. The model has been constructed with no reference to microscopic details of the system such as the internal motion of molecules, i.e., molecular rotation and vibration. In this respect, the standpoint of the present work is purely phenomenological and is quite different from that of the previous works dealing with so-called molecular ET [7–9].

(ii) As discussed in the previous sections, we have understood a subtle point in the present theory in the case of monatomic gases with $D = 3$. This point seems to be interesting from both physical and mathematical viewpoints, and is worthy of further study. This will be the subject for the next paper.

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