Six-field extended thermodynamics models representing molecular energy exchange in a dense polyatomic gas

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Abstract. In the framework of extended thermodynamics, we present three models of a dense polyatomic gases with 6 independent fields. The three models, respectively, represent the relaxation process due to the different molecular energy exchange among the translational, rotational and vibrational energies of a molecule. The characteristic velocities, the local exceptionality and the Maxwellian iteration are also studied. As an example, we study the six-field models of a van der Waals fluid.

1. Introduction
Nonequilibrium phenomena in polyatomic gases, such as absorption and dispersion of ultrasonic waves [1, 2] and shock waves [3], are characterized by the energy exchanges among the translational, rotational, and vibrational modes of a molecule [4]. The energy exchanges are related to the fundamental process for the dynamic (nonequilibrium) pressure [5, 6]. In the past, such phenomena are studied basing on the thermodynamic theory of relaxation processes of internal variables [7, 8, 9] in the framework of the thermodynamics of irreversible processes (TIP) [10] which relies essentially on the assumption of local thermodynamic equilibrium.

Recently, beyond the assumption of the local thermodynamic equilibrium, rational extended thermodynamics (hereafter referred to as ET) [11, 12, 13] has been developed. ET is a thermodynamic theory that adopts dissipative fluxes as independent fields in addition to the usual hydrodynamic fields motivated by the moment system of the kinetic theory [14]. The time evolution of the fields is governed by the system of balance equations which satisfy the Galilean invariance. The constitutive relations in local form are derived by the entropy principle and the causality principle.

ET was firstly proposed for rarefied monatomic gases [12]. Recently, the theory for rarefied polyatomic gases [13] has been established phenomenologically [15, 16, 17, 18] and kinetic-theoretically using the maximum entropy principle [19, 20, 21]. One of the noticeable features of these theories is that the almost all phenomenological coefficients are determined by adopting the thermal and caloric equations of state. The ET theory, in particular, the theory with 14 fields (ET_{14}) which includes the Navier-Stokes-Fourier theory as a special case has been successfully utilized to the study of linear waves [22, 23], shock waves [24, 25], heat conduction [26, 27], and light scattering [28].
In rarefied gases, the dynamic pressure can be identified with the energy exchange between the modes of molecular motion \[18, 29\]. In the case that the molecular internal modes are treated as a unit, the role of the dynamic pressure has been studied most clearly and simply by using the ET theory with 6 fields (ET\(_6\)): mass density, velocity, specific internal energy, and dynamic pressure \[30, 31, 32\]. This theory has one-to-one correspondence with the Meixner theory of a relaxation process \[8, 9\]. The nonlinear constitutive relations were obtained phenomenologically \[33\] and kinetic-theoretically \[34, 35\]. ET\(_6\) is useful, for example, in the study of shock waves \[32, 36\], and the results of which have been confirmed by a kinetic-theoretical study \[37, 38\].

The ET\(_6\) theory of dense polyatomic gases has been proposed by postulating the principle of duality between rarefied and dense gases \[5\]. The physical interpretation of this principle is summarized in \[6\]. In this theory, instead of the dynamic pressure, the nonequilibrium energies which play the role of the thermodynamic potential \[29\] are adopted as independent fields.

In spite of the successful establishment of ET theories of polyatomic gases, there remain nonequilibrium phenomena which are not described well by these theories. In such phenomena, all internal modes can not be treated as a unit. Only recently, for rarefied gases, the ET theory which describes the internal modes individually has been proposed \[18\]. In particular, the ET theory with two molecular relaxation processes for the rotational and vibrational modes (ET\(_7\)) has been constructed. As a limiting case of ET\(_7\), three different ET\(_6\) theories have been proposed depending on the relaxation process due to the energy exchange. The theory which describes the relaxation of the vibrational (rotational) energy individually is referred to ET\(_6^{KR}\) (ET\(_6^{KV}\)), and the previous ET\(_6\) \[30, 31, 33, 5, 39\] in which the energies of the internal modes are treated as a unit is renamed ET\(_6^{RV}\).

The purpose of the present paper is to propose the ET\(_6\) theories of dense polyatomic gases, in particular, the dense gas theories of ET\(_6^{KR}\) and ET\(_6^{KV}\), and to reveal their characteristic features. In the previous study of ET\(_6^{KR}\) and ET\(_6^{KV}\) \[18\], the field equations for the moments of the velocity distribution function were closed by means of the maximum entropy principle since the rarefied gas was considered. In the present paper, we adopt the phenomenological closure by means of the entropy principle with a model of the energy exchange. This is because no reliable kinetic theory exists for dense gases.

The paper is organized as follows: In Section 2, we present the system of balance equations of three ET\(_6\) theories and the requirement of the entropy principle. With an energy-exchange model, the constitutive relations are determined. In Section 3, we study the characteristic velocities, local exceptionality and Maxwellian iteration of ET\(_6\) theories. In Section 4, as an example, ET\(_6\) theories of a nonpolytropic van der Waals fluid (vdW) are developed. The last section is devoted to the concluding remarks.

2. Closed system of field equations with 6 independent fields

2.1. Thermal and caloric equations of state

We study dense polyatomic gases with the Hamiltonian in the form:

\[ H = H^{K+U} + H^R + H^V, \]

where \(H^{K+U} = (K + U)\) is the Hamiltonian of the subsystem, say \((K + U)\)-system, having the kinetic energy \(K\) of molecular translational motion and the intermolecular potential energy \(U\), \(H^R\) is the one of the subsystem, say \(R\)-system, having the energy of the rotational motion of constituent molecules and \(H^V\) is the one of the subsystem, say \(V\)-system, having the energy of the vibrational motion of constituent molecules. For rarefied polyatomic gases, the intermolecular potential energy \(U\) is ignored.

The thermal and caloric equations of state in terms of the mass density \(\rho\) and the temperature
$T$ are expressed as

$$p = \tilde{p}(\rho, T), \quad \varepsilon = \tilde{\varepsilon}(\rho, T),$$

(2)

where $p$ is the pressure and $\varepsilon$ is the specific internal energy. From (1), the pressure $p$ can be divided into three parts: the pressure $p^{K+U}$ due to $H^{K+U}$, the pressure $p^R$ due to $H^R$ and the pressure $p^V$ due to $H^V$. Since $p^R = 0$ and $p^V = 0$, we have

$$p = p^{K+U}; \quad p^{K+U} = \tilde{p}^{K+U}(\rho, T).$$

(3)

Similarly we have

$$\varepsilon = \varepsilon^{K+U} + \varepsilon^R + \varepsilon^V; \quad \varepsilon^{K+U} = \tilde{\varepsilon}^{K+U}(\rho, T), \quad \varepsilon^R = \tilde{\varepsilon}^R(T), \quad \varepsilon^V = \tilde{\varepsilon}^V(T).$$

(4)

Note that $\varepsilon^R$ and $\varepsilon^V$ depend only on $T$ [40]. We will use also the expression of the pressure in terms of $\rho$ and $\varepsilon^{K+U}:

$$p = \tilde{p}(\rho, \varepsilon^{K+U}) = \tilde{\rho}^{K+U}(\rho, \varepsilon^{K+U}),$$

(5)

where

$$p = \tilde{\rho}^{K+U}(\rho, T) = \tilde{\rho}^{K+U}(\rho, \tilde{\varepsilon}^{K+U}(\rho, T)).$$

(6)

2.2. System of balance equations of $ET_6$

A dissipative process in a polyatomic gas is mainly caused by the energy exchanges among the $(K + U)$, $R$ and $V$ subsystems [18, 5, 6]. Let $\mathcal{E}^{K+U}$, $\mathcal{E}^R$ and $\mathcal{E}^V$ denote the specific energies of $(K + U)$, $R$ and $V$ subsystems, respectively. In an equilibrium state, these energies coincide, respectively, with $\varepsilon^{K+U}$, $\varepsilon^R$ and $\varepsilon^V$. The time evolutions of $\mathcal{E}^{K+U}$, $\mathcal{E}^R$ and $\mathcal{E}^V$ are studied by $ET_7$ which adopts $\rho$, $v$ (velocity), $\mathcal{E}^{K+U}$, $\mathcal{E}^R$ and $\mathcal{E}^V$ as independent fields [18].

In [18], it has been revealed that the order of the relaxation times of the processes due to the energy exchanges is different and depends on the situations under study. In the present paper, let us study the relaxation process with a time scale in which an energy exchange between two of the three subsystems relaxes quickly and therefore such energy exchange can be ignored. Then these two subsystems can be regarded as a unit, say subsystem $A$, and the thermodynamic process is dominantly characterized by the time evolution of the remaining subsystem, say subsystem $B$, of which energy exchange with subsystem $A$ is slow. Let $\mathcal{E}^A$ and $\mathcal{E}^B$ denote the energies of subsystems $A$ and $B$, respectively. Then the specific internal energy $\varepsilon$ can be divided as follows:

$$\varepsilon = \mathcal{E}^A + \mathcal{E}^B.$$

(7)

Note that we consider the processes that, as usual, the energy related to the molecular internal motion (rotational and/or vibrational modes) relaxes slowly. Therefore this kind of energy is involved in $\mathcal{E}^B$ and the energy of the molecular translational motion is involved in $\mathcal{E}^A$. As shown in Table 1, there are three possible choices of the subsystems $A$ and $B$ (see also [18]): (i) $R$ and $V$ systems are treated as a unit and relax slowly ((RV)-process), (ii) $(K + U)$ and $R$ systems are treated as a unit and $V$-system relaxes slowly ((KR)-process), and (iii) $(K + U)$ and $V$ systems treated as a unit and $R$-system relaxes slowly ((KV)-process). The energies $\mathcal{E}^A$ and $\mathcal{E}^B$ are expressed as the sum of the energies of constituent subsystems. For example, for (KR)-process, we have $\mathcal{E}^A = \mathcal{E}^{K+U+R} = \mathcal{E}^{K+U} + \mathcal{E}^R$. 

3
Table 1. Three possible choices of the subsystem A and B

| Process | A  | B  |
|---------|----|----|
| (i) ET$_R^V$ (RV) | $K + U$ | $R + V$ |
| (ii) ET$_R^K$ (KR) | $K + U + R$ | $V$ |
| (iii) ET$_R^K$ (KV) | $K + U + V$ | $R$ |

ET$_R^V$, ET$_R^K$ and ET$_R^K$ are the theories which describe the (RV), (KR) and (KV)-process, respectively. These ET$_R$ theories adopt $\rho$, $v_i$, $\mathcal{E}^A$ and $\mathcal{E}^B$ as independent fields and the system of field equations is expressed, as studied in [29], by

$$
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho v_i) = 0,
$$

$$
\frac{\partial \rho v_i}{\partial t} + \frac{\partial}{\partial x_i}(\rho v_i v_j + P \delta_{ij}) = 0,
$$

$$
\frac{\partial}{\partial t}(2\rho \mathcal{E}^A + \rho v^2) + \frac{\partial}{\partial x_i}\{(2\rho \mathcal{E}^A + \rho v^2 + 2P) v_i\} = \dot{P}_l,
$$

$$
\frac{\partial}{\partial t}(2\rho \mathcal{E}^B) + \frac{\partial}{\partial x_i}(2\rho \mathcal{E}^B v_i) = -\dot{P}_l,
$$

where $P$ is the pressure, which is composed of the equilibrium pressure $p$ and the dynamic pressure $\Pi$, and $\dot{P}_l$ ($-\dot{P}_l$) is the production of $\rho \mathcal{E}^A$ ($\rho \mathcal{E}^B$). By the Galilean invariance of the system [41, 5, 29], the fluxes of $\rho \mathcal{E}^A$ and $\rho \mathcal{E}^B$ are determined strictly, and it is determined that the production term $\dot{P}_l$ is a velocity-independent quantity. The first two equations are the conservation laws of mass and momentum. The third and forth equations are, respectively, the relaxation equation of the energies $\rho \mathcal{E}^A$ and $\rho \mathcal{E}^B$. Since sum of them represents the conservation law of the energy, the productions of $\rho \mathcal{E}^A$ and $\rho \mathcal{E}^B$ are chosen as in (8). For (RV)-process, the system (8) coincides with the previous dense gas theory [5].

The constitutive relation of $P$ which is assumed to depend on the independent fields locally and instantaneously:

$$
P = P(\rho, \mathcal{E}^A, \mathcal{E}^B)
$$

is determined by the entropy principle with an energy-exchange model in Sec. 2.4. The explicit expression of $\dot{P}_l$ is evaluated approximately by the Maxwellian iteration in Sec. 3.

**Remark.** In general, there is also the relaxation process due to the energy exchange between $K$ and $U$. However, in the present analysis, we assume that $K$ and $U$ are treated as a unit. As discussed in [5], this assumption indicates that we consider the energy exchanges among $H^{K+U}$, $H^R$ and $H^V$ are the most dominant mechanism of the emergence of the dynamic pressure. In the monatomic-gas limit, this mechanism predicts that the dynamic pressure disappears.

### 2.3. Entropy principle

The entropy principle requires the following inequality [12, 13] with $h (= \rho \eta)$ being the entropy density ($\eta$: specific entropy), $h_i$ the entropy flux ($h_i = h v_i + \varphi_i$; $\varphi_i$ is the non-convective entropy flux), and $\Sigma$ the entropy production:

$$
\frac{\partial h}{\partial t} + \frac{\partial h_i}{\partial x_i} = \Sigma \geq 0
$$
for any solution of the system. We assume that \( h, \varphi_i \) and \( \Sigma \) are constitutive quantities:

\[
\eta = \eta(\rho, \mathcal{E}_A, \mathcal{E}_B), \quad \varphi_i = \varphi_i(\rho, \mathcal{E}_A, \mathcal{E}_B), \quad \Sigma = \Sigma(\rho, \mathcal{E}_A, \mathcal{E}_B). \tag{11}
\]

As the result of the exploitation of the entropy principle, we obtain the following partial differential equation for \( \eta \) [5, 29]:

\[
\eta_\rho + \frac{\mathcal{P}}{\rho^2} \eta_{\mathcal{E}_A} = 0, \tag{12}
\]

where a subscript attached to \( \eta \) indicates a partial derivative. The nonequilibrium temperatures \( \vartheta \) and \( \Theta \) which are, respectively, related to \( \mathcal{E}_A \) and \( \mathcal{E}_B \) (see (21)) can be introduced through the nonequilibrium entropy density as follows [5, 13, 18, 29]:

\[
\frac{1}{\vartheta} = \eta_{\mathcal{E}_A}, \quad \frac{1}{\Theta} = \eta_{\mathcal{E}_B}. \tag{13}
\]

In equilibrium, \( \vartheta \) and \( \Theta \) coincide with the equilibrium temperature \( T \) since \( \mathcal{E}_A \) and \( \mathcal{E}_B \) coincide with \( \varepsilon_A \) and \( \varepsilon_B \). By using (12) and (13), the derivative of the nonequilibrium entropy density is obtained as follows:

\[
d\eta = -\frac{\mathcal{P}}{\rho^2 \vartheta} d\rho + \frac{1}{\vartheta} d\mathcal{E}_A + \frac{1}{\Theta} d\mathcal{E}_B. \tag{14}
\]

The entropy principle also requires that the entropy production satisfies the following relation [5, 29]:

\[
\Sigma = \frac{1}{2} \left( \frac{1}{\vartheta} - \frac{1}{\Theta} \right) \tilde{P}_{lb} \geq 0. \tag{15}
\]

In addition, from the representation theorem, we have \( \varphi_i = 0 \).

### 2.4. A model of nonequilibrium entropy and pressure

Except for the production term, there remain two constitutive quantities, that is, \( \eta \) and \( \mathcal{P} \) which are related to each other by the relation (12). In the previous studies of ET\(_6\)RV, two equivalent models to determine the constitutive relations have been proposed. The one is a model of the pressure [5, 6] which assumes that the dynamic pressure is caused by the energy exchange between the subsystems. The other one is a model of the nonequilibrium entropy density [29] which assumes on the basis of the energy-exchange model that \( \eta \) is the sum of the entropy densities of the subsystems.

By generalizing the latter model, we propose the following nonequilibrium entropy density:

\[
\eta = s^A(\rho, \mathcal{E}_A) + s^B(\mathcal{E}_B), \tag{16}
\]

where \( s^A \) and \( s^B \) are the nonequilibrium entropy densities of the subsystem which satisfy the Gibbs relations of each subsystem:

\[
\vartheta ds^A = d\mathcal{E}_A - \frac{\tilde{p}(\rho, \mathcal{E}_A)}{\rho^2} d\rho, \quad \Theta ds^B = d\mathcal{E}_B \tag{17}
\]

with the nonequilibrium temperatures defined in (13). Note that \( s^B \) depends only on \( \mathcal{E}_B \) because the subsystem \( B \) is related to only the internal modes. The nonequilibrium temperatures are expressed in this case as follows:

\[
\frac{1}{\vartheta} = s^A_{\mathcal{E}_A}, \quad \frac{1}{\Theta} = s^B_{\mathcal{E}_B}. \tag{18}
\]
From (12), we obtain
\[
\mathcal{P} = \tilde{p}(\rho, \mathcal{E}^A),
\]
then we also obtain the dynamic pressure as follows:
\[
\Pi = \mathcal{P} - p = \tilde{p}(\rho, \mathcal{E}^A) - \tilde{p}(\rho, \varepsilon^A).
\] (20)

Let us adopt \(\{\rho, v_i, \vartheta, \Theta\}\) as independent variables instead of \(\{\rho, v_i, \mathcal{E}^A, \mathcal{E}^B\}\). From (18), \(\mathcal{E}^A\) depends on \(\rho\) and \(\vartheta\), while \(\mathcal{E}^B\) depends only on \(\Theta\). Since \(\mathcal{E}^A\) and \(\mathcal{E}^B\), respectively, coincide with \(\varepsilon^A = \tilde{\varepsilon}^A(\rho, T)\) and \(\varepsilon^B = \tilde{\varepsilon}^B(T)\) in equilibrium in which \(\vartheta\) and \(\Theta\) coincide with \(T\), we notice that \(\mathcal{E}^A\) and \(\mathcal{E}^B\) follow the caloric equations of state of each subsystem:
\[
\mathcal{E}^A = \tilde{\varepsilon}^A(\rho, \vartheta), \quad \mathcal{E}^B = \tilde{\varepsilon}^B(\Theta).
\] (21)

From (7), the total internal energy \(\varepsilon\) is given by
\[
\tilde{\varepsilon}(\rho, T) = \tilde{\varepsilon}^A(\rho, \vartheta) + \tilde{\varepsilon}^B(\Theta).
\] (22)

This gives the relationship among the three temperatures \(T\), \(\vartheta\), and \(\Theta\). From (20), the dynamic pressure is expressed as follows:
\[
\Pi = \tilde{p}(\rho, \vartheta) - \tilde{p}(\rho, T).
\] (23)

The entropy density is restricted by the thermodynamic stability condition, which requires that the entropy must be convex with respect to the densities. In the present case, this condition is given by [29]
\[
\tilde{p}_\rho(\rho, \vartheta) > 0, \quad c^A_v(\rho, \vartheta) > 0, \quad c^B_v(\Theta) > 0,
\] (24)
where \(c^A_v\) and \(c^B_v\) are the specific heats of the two subsystems defined by \(c^A_v(\rho, \vartheta) = \partial \tilde{\varepsilon}^A(\rho, \vartheta)/\partial \vartheta\) and \(c^B_v(\Theta) = d\tilde{\varepsilon}^B(\Theta)/d\Theta\).

**Remark.** Instead of the model of the entropy density (16), it is possible to adopt a model of the pressure. In [18], for rarefied gases, the expression of \(\mathcal{P}\) is obtained in the form of (19) without the contribution of \(U\). The principle of duality between rarefied and dense gases [5] states that the nonequilibrium pressure is caused by the energy exchange between the subsystems whether the contribution of \(U\) exists or not. In other words, the pressure evaluated with \(K\) in rarefied gases is replaced by the pressure evaluated with \((K + U)\) in dense gases. From this principle, we have (19) in dense gases. Then, we obtain (16) as a result.

### 3. Characteristic velocities, local exceptionality and Maxwellian iteration

The characteristic velocities \(\mathcal{V}\) associated to the hyperbolic system (8) are obtained as
\[
\mathcal{V} = v_n \text{ (multiplicity 4), } v_n \pm \mathcal{U} \quad \text{with} \quad \mathcal{U}^2 = p_\rho(\rho, \vartheta) + \frac{\partial p_\rho^2(\rho, \vartheta)}{\rho^2 c^A_v(\rho, \vartheta)},
\] (25)
where \(v_n\) is the velocity in normal direction to the wave front. Note that \(\mathcal{U}\) satisfies the subcharacteristic condition [42] with respect to the Euler system. This condition ensures that ETa includes the Euler system as a principal subsystem.

In the theory of the hyperbolic system, the local exceptionality (locally linearly degenerate) hyper-surface is crucial to study the admissibility of the shock wave, in particular, rarefaction
shock [43]. It is known that the sound waves can be locally exceptional if \( \delta V = 0 \) for some states. In the present case, when \( \{ \rho, v_i, \eta, \Theta \} \) are adopted as independent fields, the hyper-surface of local exceptionality exists if the following relation is satisfied [5, 18]:

\[
\left( \frac{\partial^2 U}{\partial \rho^2} \right)_{\eta, \Theta} = 0. \tag{26}
\]

The energy exchange between two subsystems is characterized by the following quantity:

\[
\Delta \equiv \mathcal{E}^A - \mathcal{E}^A = -\mathcal{E}^B + \varepsilon^B.
\]

The linearized system around an equilibrium state \((\rho, T)\) is obtained by expanding the system with respect to the energy exchange \(\Delta\) up to the first order. The nonequilibrium temperatures are in terms of \(\Delta\) as follows:

\[
\theta - T = \frac{\Delta}{c_v^A}, \quad \Theta - T = -\frac{\Delta}{c_v^B}, \tag{27}
\]

and, from (23), the dynamic pressure is expressed as follows:

\[
\Pi = p_T (\theta - T) = \frac{p_T}{c_v^A} \Delta. \tag{28}
\]

Here and hereafter we use the notation \(c_v^A\) instead of \(c_v^A(\rho, T)\) and so on for simplicity. The production term is given by

\[
\hat{P}_{II} = -\frac{2\rho}{\tau} \Delta, \tag{29}
\]

where \(\tau = \tau(\rho, T)\) is the relaxation time for \(\Delta\) which is positive from the requirement of the entropy principle (15). It is noted that \(\tau\) is also interpreted as the relaxation time of the dynamic pressure which is studied in previous studies [15, 22, 24, 30, 32]. The system of field equations (8) is rewritten with the independent fields \(\{\rho, v_i, T, \Delta\}\) as follows:

\[
\dot{\rho} + \rho \frac{\partial v_i}{\partial x_i} = 0,
\]

\[
\rho \dot{v}_i + \frac{\partial}{\partial x_i} \left( p + \frac{p_T}{c_v^A} \Delta \right) = 0,
\]

\[
\rho c_v \dot{T} + p_T \left( T + \frac{\Delta}{c_v^A} \right) \frac{\partial v_i}{\partial x_i} = 0,
\]

\[
\dot{\Delta} + \frac{p_T c_v^B}{\rho c_v} \left( T + \frac{\Delta}{c_v^A} \right) \frac{\partial v_i}{\partial x_i} = -\frac{1}{\tau} \Delta,
\]

where \(c_v\) is the specific heat defined by \(c_v(\rho, T) = \partial \mathcal{E}(\rho, T)/\partial T\) which satisfies \(c_v = c_v^A + c_v^B\). By adopting the Maxwellian iteration [44], we obtain the bulk viscosity \(\nu\) in terms of \(\tau\):

\[
\nu = \frac{T p_T^2 c_v^B}{\rho c_v^A}.
\]

The relaxation time \(\tau\) can be estimated by using the experimental data on \(\nu\).
4. ET\textsubscript{6} theories of a van der Waals Fluid

4.1. Equations of state and dynamic pressure

Let us study, as a typical example, a nonpolytropic vdW fluid of which thermal and caloric equations of state are given by

\[ p = \frac{k_B}{m} \frac{T\rho}{1 - b\rho} - a\rho^2, \quad \varepsilon = \varepsilon_r - a\rho, \quad (32) \]

where \( \varepsilon_r \) is the specific internal energy of a rarefied gas and the material-dependent constants \( a \) and \( b \) represent, respectively, a measure of the strength of the attraction between constituent molecules and the effective volume (or exclusion volume) of a molecule. The specific internal energies of subsystems \( \varepsilon^A \) and \( \varepsilon^B \) are expressed with those in rarefied gases as follows:

\[ \varepsilon^A = \tilde{\varepsilon}^A(T) - a\rho, \quad \varepsilon^B = \tilde{\varepsilon}^B(T). \quad (33) \]

In particular, since the specific heat of intermolecular potential is zero, we have

\[ c^A_v(T) = c^A_v(T') - b\rho, \quad c^B_v(T) = c^B_v(T'), \quad (34) \]

where \( c^A_v, c^B_v \) are the specific heats of the subsystem in a rarefied gas.

From (23), the dynamic pressure is expressed as follows:

\[ \Pi = \frac{k_B}{m} \frac{\rho}{1 - b\rho} (T - T). \quad (35) \]

The relation between the bulk viscosity and the relaxation time (31) is explicitly obtained as follows:

\[ \nu = \frac{k_B}{m} \frac{c^B_v}{c_v c_v^A (1 - b\rho)^2} \tau. \quad (36) \]

4.2. Nonequilibrium entropy and its convexity in a vdW fluid

From (16) with the equilibrium entropy density of a vdW fluid, the nonequilibrium entropy density \( \eta \) is obtained as follows:

\[ \eta = \frac{k_B}{m} \log \left( \frac{1 - b\rho}{\rho} \right) + \int \varepsilon^A_v(T') dT' + \int \varepsilon^B_v(T') dT' + s_0, \quad (37) \]

where \( s_0 \) is a constant at a reference state.

As the conditions (24)\textsubscript{2,3} are identically satisfied, the convexity condition of the entropy density comes only from (24)\textsubscript{1} and is expressed as

\[ \hat{\rho} (\hat{\rho}, \hat{\vartheta}) > (3 - 2\hat{\rho})\hat{\rho}^2, \quad (38) \]

where we have introduced the following dimensionless variables:

\[ \hat{\rho} = \frac{\rho}{\rho_{cr}}, \quad \hat{\vartheta} = \frac{T}{T_{cr}}, \quad \hat{\Theta} = \frac{\Theta}{T_{cr}}, \quad (39) \]

with \( \rho_{cr} = a/(27b^2), T_{cr} = 8a/(27k_B m b) \) which are the quantities at the critical point. In the \( (\hat{\rho}, \hat{\rho}(\hat{\rho}, \hat{\vartheta})) \)-plane, the boundary (spinodal curve) is independent of \( \hat{\vartheta} \) as similar to
the case of the Euler system in which the spinodal curve for equilibrium pressure is independent of the temperature.

The critical point is the point on the spinodal curve with the condition that the second derivative also vanishes:

$$\left(\frac{\partial^2 p(\rho, \vartheta)}{\partial \rho^2}\right)_{\vartheta} = 0.$$ 

With (38), we have, as the Euler system,

$$\hat{\rho} = 1, \quad \hat{\vartheta} = 1, \quad \hat{p}(\hat{\rho}, \hat{\vartheta}) = 1.$$ (40)

**Remark.** The expressions of the spinodal curve and critical point are independent from the molecular relaxation processes. However, $\vartheta$ depends on the process (see (27) near equilibrium case).

### 4.3. Characteristic velocity and critical derivative in a vdW fluid

In the present case, the characteristic velocity $U$ is obtained as follows:

$$U^2 = \frac{k_B}{m} \frac{\vartheta \gamma^A(\vartheta)}{(1 - b \rho)^2} - 2a \rho,$$ (41)

where $\gamma^A(\vartheta) = \frac{\hat{c}_A^v(\vartheta) + 1}{\hat{c}_A^v(\vartheta)}$ is the ratio of the specific heats of subsystem $A$ with the dimensionless specific heat $\hat{c}_A^v = m c_A^v / k_B$.

The locus of the local exceptionality (26), called critical derivative curve (see [43]), is expressed as, in the dimensionless form with (39),

$$\hat{p}(\hat{\rho}, \hat{\vartheta}) = \hat{\rho}^2 \left\{ \frac{2(3 - \hat{\rho})^2}{\gamma^A(\vartheta)(\gamma^A(\vartheta) + 1) - \frac{\vartheta}{\hat{c}_A^v(\vartheta)} \frac{d \hat{c}_A^v(\vartheta)}{d \vartheta}} - 3 \right\}.$$ (42)

In comparison with the spinodal curve (38), the condition that the curve of local exceptionality resides in the stable region is

$$\frac{3 - \hat{\rho}}{\gamma^A(\vartheta)(\gamma^A(\vartheta) + 1) - \frac{\vartheta}{\hat{c}_A^v(\vartheta)} \frac{d \hat{c}_A^v(\vartheta)}{d \vartheta}} \geq 1.$$ (43)

For polytropic gases where the specific heats are constant, recalling $\gamma^A > 1$, the condition (43) can be expressed as

$$1 < \gamma^A \leq \sqrt{\frac{13}{4} - \hat{\rho} - \frac{1}{2}}.$$ (44)

The necessary condition that the locus resides in stable region is $\hat{\rho} < 1$. The condition (44) can be rewritten with respect to $\hat{c}_A^v$ as follows:

$$\hat{c}_A^v \geq \frac{1}{\sqrt{\frac{13}{4} - \hat{\rho} - \frac{3}{2}}} \geq \frac{3 + \sqrt{13}}{2}.$$ (45)

As previously studied in [5], in the case of ET$_R^RVI$ in which $\hat{c}_A^v = 3/2$, it is observed that the locus (42) is independent of the nonequilibrium variables. In this case the locus of local exceptionality
coincides with the curve for a monatomic Euler fluid and always resides in the unstable region. On the other hand, in the cases of ET$_6^{KR}$ and ET$_6^{KV}$ in which \( \hat{c}_v^A > \frac{3}{2} \), with a large value of \( \hat{c}_v^A \), there exists a region in the \((\hat{\rho}, \hat{\rho}(\hat{\rho}, \hat{\vartheta}))\)-plane where the local exceptionality curve exists in the stable region. Therefore, in such cases, the rarefaction shock may appear. The same feature is observed in a polyatomic Euler system [43]. The loci of the local exceptionality in the cases that \( \hat{c}_v^A = \frac{3}{2}, \frac{7}{2} \) and \( \frac{11}{2} \) are shown in Figure 1.

\[
\begin{align*}
\text{Spinodal curve} & \quad \hat{\rho}(\hat{\rho}, \hat{\vartheta}) \\
\text{Locus of the local exceptionality} & \quad \hat{c}_v^A = \frac{3}{2} \\
& \quad \hat{c}_v^A = \frac{7}{2} \\
& \quad \hat{c}_v^A = \frac{11}{2}
\end{align*}
\]

Figure 1. Loci of the local exceptionality (42) with \( \hat{c}_v^A = \frac{3}{2} \) (dashed line), \( \frac{7}{2} \) (dot-dashed line) and \( \frac{11}{2} \) (dotted line) and spinodal curve (solid line) in the \((\hat{\rho}, \hat{\rho}(\hat{\rho}, \hat{\vartheta}))\)-plane.

5. Summary and concluding remarks

We have studied three ET$_6$ theories of dense polyatomic gases in which the internal modes of a molecule play a significant role. These theories are based on three different relaxation processes due to the energy exchange between the subsystems. The model of the nonequilibrium entropy density is proposed on the basis of the energy-exchange model and the system of the field equations is phenomenologically closed. The characteristic velocities, the local exceptionality and the Maxwellian iteration have been studied. As an example, ET$_6$ theories of a nonpolytropic vdW fluid is constructed. In particular, it has been elucidated that, in a polytropic vdW fluid, the locus of the local exceptionality of ET$_6^{KR}$ and ET$_6^{KV}$ resides in the stable region with a large value of specific heat of the subsystem \( A \).

Finally, three concluding remarks are made:

(i) The present procedure to obtain the dense gas theory can be applied to the case of ET$_7$. Then the relaxation processes of rotational and vibrational modes are described separately. In ET$_7$ of a polytropic vdW fluid, the existence of the locus of the local exceptionality in the stable region may be suspicious because its characteristic velocities are same as those of ET$_6^{RV}$. These studies will be the subject of the next paper.

(ii) There remains a question how to determine the relaxation process under study. One way is to choose the process which is the most appropriate in comparison with the experimental data. The comparison of the theoretical prediction of the dispersion relation of a sound wave in dense gases by ET with the experimental data will soon be reported elsewhere.

(iii) From an experimental point of view, it is well known that the existence of the rarefaction shock is still controversial. Since the present analysis is based on the simplified theory, the
study of the admissibility of the rarefaction shock by a more realistic ET theory with shear stress and heat flux is the subject for subsequent works.

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