

## Research Article

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# A novel construction of thermodynamically compatible models and its correspondence with Boltzmann-equation-based moment-closure hierarchies

**Abstract:** In this article, we propose a novel approach to construct macroscopic balance equations and constitutive equations describing various irreversible phenomena. It is based on the general principles of non-equilibrium thermodynamics and consists of four basic steps: picking suitable state variables, choosing a strictly concave entropy function, properly separating entropy fluxes and production rates, and determining a dissipation matrix. Our approach takes advantage of both extended irreversible thermodynamics and GENERIC formalisms and shows a direct correspondence with Levermore's moment-closure hierarchies for the Boltzmann equation. As a direct application, a new ten-moment model beyond the classical hierarchies is constructed and is shown to recover the Euler equations in the equilibrium state. These interesting results may put various macroscopic modeling approaches, starting from the general principles of non-equilibrium thermodynamics, on a solid microscopic foundation based on the Boltzmann equation.

**Keywords:** Non-equilibrium thermodynamics, constitutive relation, Boltzmann equation, entropy condition

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## 1 Introduction

To derive thermodynamically admissible constitutive relations is a central task of non-equilibrium thermodynamics. In the past decades, various macroscopic thermodynamic approaches, e.g. classical irreversible thermodynamics (CIT), rational thermodynamics, extended irreversible thermodynamics (EIT), GENERIC formalism, have achieved tremendous successes in the mathematical modeling of natural phenomena [1–5], such as polymeric fluids, heat transfer, nanomaterials, ultrasonic waves, second sounds. A common feature of those methods is that they are all starting from the general principles of macroscopic thermodynamics. No details in the microscopic dynamics have been considered during the modeling.

Alternatively, there is another group of so-called kinetic approaches, which seek to construct models based on the microscopic dynamics. Their starting points usually are the Hamiltonian equation, the master equation, the Fokker–Planck equation, the Boltzmann equation, and so on. (To be precise, only the Hamiltonian and Schrödinger equations are widely accepted genuine microscopic models.) Then, with the help of various moment-closure methods, time evolution equations for the macroscopic moments can be directly derived from the microscopic dynamics. A remarkable example is the Chapman–Enskog expansion in the 1910s [6], based on which the classical Navier–Stokes equations, a most famous governing model for the macroscopic fluid mechanics, were derived from the Boltzmann equation for the first time. Later on, a number of different approaches based on the Boltzmann equation were proposed for the same purpose, e.g. the maximal entropy principle [7] and Grad's [8] and Levermore's hierarchies [9]. Now the kinetic approach has already become a standard way to link the macroscopic kinetics with the microscopic dynamics [10]. However, there is no guarantee that the derived macroscopic equations will be thermodynamically admissible automatically.

Apart from moment-closure methods, there is an entire branch of non-equilibrium statistical mechanics dealing with how to eliminate the non-relevant degrees of freedom from microscopic dynamics and obtain

formal macroscopic equations from a statistical aspect. The projection operator technique is such a systematic clear-cut method, which has been first introduced into statistical physics by Nakajima and Zwanzig in the 1960s. In particular, Zwanzig [11] developed it into a powerful tool to derive formal exact equations of motion for classical or quantal probability densities, such as the generalized Fokker–Planck equation and the generalized master equation. Later, Mori [12] applied this method within the Heisenberg picture, which leads to the non-linear generalized quantum Langevin equation. Even in the vicinity of phase transitions or non-equilibrium instabilities, the projection operator techniques have been shown to be effective in many cases [13, 14]. However, because our current study is mainly focused on non-equilibrium thermodynamics, we will not go into details about fruitful results in modern non-equilibrium statistical mechanics. Interested readers may refer to textbooks and monographs in this field [4, 15].

In this article, we propose a novel approach to construct macroscopic balance equations and constitutive equations based on the general principles of non-equilibrium thermodynamics. The four basic elements of our approach: picking suitable state variables, choosing a strictly concave entropy function, properly separating entropy fluxes and production rates, and determining a dissipation matrix are illustrated step by step. As a special example, a new ten-moment model beyond the classical hierarchies is constructed. In the equilibrium state, this model correctly recovers the most familiar Euler equations. Most importantly, from our illustration, a direct correspondence between our macroscopic thermodynamic approach and the Levermore’s moment-closure hierarchies for the Boltzmann equation could be clearly seen. This fact actually points out a possibility of placing various macroscopic modeling approaches starting from the general principles of non-equilibrium thermodynamics on a solid microscopic foundation based on the Boltzmann equation – a long-unsolved problem in this field. Although most previous macroscopic thermodynamic approaches claim their roots in the kinetic theory, this point has never been clearly justified before.

It should be noted that in this article, the Boltzmann equation and the ansatz (2) serve only as a motivation for the governing equation (6), a motivation for providing an example of a solution of the compatibility condition (4), and a setting to explain the physical content of our results (but the physical content is already clear, even without the kinetic theory connection). There is no preference of our formulation for the Boltzmann equation than other microscopic models (in other words, if the underlying Boltzmann equation is replaced by the master equation, Fokker–Planck equation, and so on, a similar approach is still applicable). Readers should always bear this point in mind.

## 2 Four elements of our approach

Inspired by EIT and GENERIC formalisms, our approach also starts with the general principles of non-equilibrium thermodynamics: the conservation of the total energy and the positiveness of entropy production rates. There are four basic elements in our procedure: (i) choosing suitable state variables (including both conserved and dissipative quantities) that can fully characterize the system under consideration, (ii) constructing a strictly concave entropy function with respect to the chosen state variables, (iii) selecting the proper entropy flux, and (iv) determining a dissipation matrix that characterizes the irreversibility of the system. In the following, we will show how to construct these four elements step by step. Specific attention should be paid to parts (iii) and (iv), which constitute a major difference between ours and other previous studies. In parallel, the Levermore’s moment-closure hierarchies will be referred to from time to time and its underlying correspondence with our macroscopic thermodynamic approach will be revealed and discussed in each step.

For the convenience of following discussions, a brief introduction to the Levermore’s moment-closure hierarchies for the Boltzmann equation is presented before proceeding to our main results. It is well known that the Levermore’s method provides a good coarse-graining way to obtain the desired macroscopic dynamic equations from the microscopic kinetics characterized by the Boltzmann equation. It reads as [9, 16]

$$\frac{\partial}{\partial t} \int c_i f d\vec{\xi} + \nabla \cdot \int \vec{\xi} c_i f d\vec{\xi} = \int c_i (f_* f'_* - ff') B(\vec{\omega}, \vec{\xi}, \vec{\xi}') d\vec{\omega} d\vec{\xi}' d\vec{\xi}, \quad i = 0, 1, \dots, n-1. \quad (1)$$

Here,  $\int c_i f d\vec{\xi}$  is referred to as the  $i$ -th-order moment and  $\{c_i = c_i(\vec{\xi}), i = 0, 1, \dots, n-1\}$  constitutes an admissible space in the sense of [9]. In (1),  $\vec{\xi}$  and  $\vec{\xi}'$  are the velocities of particles before binary collisions,  $\vec{\xi}_*$  and  $\vec{\xi}'_*$  are the velocities of particles after collision,  $f = f(\vec{r}, \vec{\xi}, t)$ ,  $f' = f'(\vec{r}, \vec{\xi}', t)$ ,  $f_* = f_*(\vec{r}, \vec{\xi}_*, t)$ , and  $f'_* = f'_*(\vec{r}, \vec{\xi}'_*, t)$  denote the respective distribution functions of particles in the phase space,  $\vec{\omega}$  denotes the scattering angle, and  $B(\vec{\omega}, \vec{\xi}, \vec{\xi}') = B(\vec{\omega}, \vec{\xi}', \vec{\xi}) = B(\vec{\omega}, \vec{\xi}_*, \vec{\xi}'_*)$  is the collision kernel and is positive almost everywhere in its domain [17]. Let  $\alpha_i = \alpha_i(\vec{r}, t)$  ( $i = 0, 1, \dots, n-1$ ) be an  $i$ -th-order unknown tensor and substitute the ansatz

$$f(\vec{r}, \vec{\xi}, t) = \exp \left[ \sum_{i=0}^{n-1} c_i(\vec{\xi}) \odot \alpha_i \right] \quad (2)$$

introduced in [9] into (1). We get a set of first-order partial differential equations for the unknown parameters  $\alpha_i$ , which are Galilean invariant thanks to the admissibility of  $\{c_i\}$ . Here,  $\odot$  denotes the tensor product, i.e.

$$A \odot B = \sum_{b_1, b_2, \dots, b_m} A_{a_1 a_2 \dots a_n b_1 b_2 \dots b_{m-1} b_m} B_{b_m b_{m-1} \dots b_2 b_1}.$$

Note the Einstein summation convention is adopted automatically in the article. For the Levermore's moment-closure hierarchies, the state variables and the entropy function are already given, whereas the other two steps will be illustrated in what follows.

## 2.1 State variables

The choice of a suitable set of state variables, which can fully characterize the desired kinetic details of the system under study, is a prerequisite for the mathematical modeling of non-equilibrium processes. Using different state variables may lead to different governing equations, and suitable state variables are expected to give simple governing equations that can directly reveal physical insights of the processes. Based on their different dynamic behaviors, state variables can be classified into conserved and dissipative ones. Conserved variables are relatively simple and determined through the underlying conservation laws or symmetry properties of the system, whereas the choice of dissipative variables is usually non-unique and much harder. Until now, there is no general rule for this purpose. EIT suggested to use the unknown variables that appeared in the conservation equations directly [2]. However, in our recent works, we found that the use of conjugated variables with respect to the pre-specified entropy may be better in some way [18].

Motivated by the moment-closure method mentioned above, here we consider an isolated thermodynamic system and assume that it can be fully characterized by state variables  $\phi \equiv \{\phi_0, \phi_1, \dots, \phi_{n-1}\}$ . The subscripts 0 to  $n-1$  denote the different tensor orders of the state variables, like the scalar, vector, tensor, and so on. However, how to choose these state variables properly is not a major task of our current study. Interested readers may refer to the related works we mentioned above.

These variables correspond to the moments defined in (1) as  $\phi_i = \int c_i f d\vec{\xi}$  ( $i = 0, 1, \dots, n-1$ ), with  $\{c_i\}$  an admissible space in the sense of [9], ensuring the Galilean invariance of the derived moment-closure system. Actually, through these normalization conditions, the unknown parameters  $\alpha_i$  in the ansatz (2) can be well determined in terms of the  $\phi_i$ 's. In the kinetic theory, the moments up to order 3 are usually taken as the density  $\rho = \int f d\vec{\xi}$ , the momentum  $M_i = \int \xi_i f d\vec{\xi}$ , the second-order stress tensor  $P_{ij} = \int \xi_i \xi_j f d\vec{\xi}$ , and the third-order heat flux tensor  $Q_{ijk} = \int \xi_i \xi_j \xi_k f d\vec{\xi}$ , where the particle mass is assumed to be 1.

## 2.2 Entropy function

In the next step, we need to pick an entropy function  $S = S(\phi_0, \phi_1, \dots, \phi_{n-1})$ , which is strictly concave with respect to the pre-chosen state variables  $\phi_i$  ( $i = 0, 1, \dots, n-1$ ). Non-local dependence is not considered here (e.g.  $S$  depends on  $\nabla \phi_i$ ). If yes, the following calculations have to be modified. Except for these, the entropy function is not further specified because it sensitively depends on the details of the problem to be modeled. In the literature, the Boltzmann entropy and the Tsallis entropy are the two most widely referred forms. The

former adopts a log form and is addable, whereas the latter takes a polynomial form and is non-addable [19]. As a special example, here we take  $S = -k_B \int (f \ln f - f) d\tilde{\xi}$  in accordance with the Boltzmann equation, where  $f$  is defined in (2).

Set  $S_{\phi_i} \equiv (\partial S / \partial \phi_i)_{\phi_0, \dots, \phi_{i-1}, \phi_{i+1}, \dots, \phi_{n-1}}$ . We have the generalized Gibbs relation [2]

$$dS = \sum_{i=0}^{n-1} S_{\phi_i}^T \odot d\phi_i$$

and therefore, the evolution equation for entropy

$$\frac{\partial S}{\partial t} = \sum_{i=0}^{n-1} S_{\phi_i}^T \odot \frac{\partial \phi_i}{\partial t} = -\nabla \cdot \vec{j}^S + \sigma^S$$

with

$$\sigma^S \equiv \nabla \cdot \vec{j}^S + \sum_{i=0}^{n-1} S_{\phi_i}^T \odot \frac{\partial \phi_i}{\partial t}.$$

Here  $\vec{j}^S$  stands for the entropy flux and  $\sigma^S$  is the entropy production rate, which should always be non-negative according to the second law of thermodynamics [1, 2].

A proper choice of the entropy flux  $\vec{j}^S$  is crucial for the modeling. However, in previous studies, the entropy flux is usually taken for granted. Few systematic constraints or general guiding principles have been put forward on this point [2]. Here we treat this part more carefully. We split the entropy flux into two parts, i.e.  $\vec{j}^S = \vec{j}_1^S + \vec{j}_2^S$ . Inspired by the moment method for the Boltzmann equation, we take the first part as

$$\vec{j}_1^S = \sum_{i=0}^{n-1} S_{\phi_i}^T \odot \phi_{i+1},$$

where the unknown tensor  $\phi_n$  now can be regarded as the coefficient of  $S_{\phi_{n-1}}$  in the entropy flux  $\vec{j}_1^S$ . Later, it will be seen that  $\phi_n$  is the flux of the state variable  $\phi_{n-1}$ . The second part of the entropy flux  $\vec{j}_2^S$  will be determined in the next section. Now the entropy production rate becomes

$$\sigma^S = \sum_{i=0}^{n-1} S_{\phi_i}^T \odot \left( \frac{\partial \phi_i}{\partial t} + \nabla \cdot \phi_{i+1} \right) + \sum_{i=0}^{n-1} \nabla S_{\phi_i}^T \odot \phi_{i+1} + \nabla \cdot \vec{j}_2^S. \quad (3)$$

## 2.3 Entropy flux

As the first part is fixed, the entropy flux will be totally determined if we can properly set its second part. A direct way, which we will see is also quite meaningful both mathematically and physically, is to require the sum of last two terms in formula (3) to vanish, i.e.

$$\sum_{i=0}^{n-1} \nabla S_{\phi_i}^T \odot \phi_{i+1} + \nabla \cdot \vec{j}_2^S = 0. \quad (4)$$

Or equivalently,

$$\sum_{i=0}^{n-1} S_{\phi_i \phi_j}^T \odot \phi_{i+1} + \partial \vec{j}_2^S / \partial \phi_j = 0 \quad \text{for all } j = 0, \dots, n-1, \quad (5)$$

owing to the generality of state variable  $\phi_j$ . It is a central equation to determine the two unknowns  $\phi_n$  and  $\vec{j}_2^S$  as functions of  $(\phi_0, \phi_1, \dots, \phi_{n-1})$ . In such a way, the  $n$ -th-order tensor  $\phi_n$  can be expressed in terms of other known lower-order state variables and obtain the so-called constitutive equations. Until now, we only know that the above equation admits at least one solution (see the discussions below on the Boltzmann equation). However, in general, under which condition this solution will be unique is still an open problem. If (4) admits other solutions, one would have alternative ways for moment-closure and thus other possibilities of constitutive equations. Such an example is given in Section 4. Further discussions are beyond the scope of this article.

It is easily seen that the requirement imposed by (4) corresponds to the well-known entropy condition for conservation laws  $\partial\phi_i/\partial t + \nabla \cdot \phi_{i+1} = 0$  by multiplying  $S_{\phi_i}^T$  on both sides. This entropy condition, due to Godunov [20], Friedrichs and Lax [21], and others [22], was first proposed for symmetrical hyperbolic systems of first-order PDEs. It is well recognized in mathematics that hyperbolicity is a substantial requirement for systems of first-order PDEs to be well posed [23]. Based on our current macroscopic thermodynamic approach, the hyperbolicity of the resultant PDEs is clearly verified with the help of (4), whereas no other extended theory until now can reach this point in general.

In the case of the Boltzmann equation, as  $f = \exp(\sum_{i=0}^{n-1} c_i \odot \alpha_i)$ ,  $\phi_i = \int c_i f d\vec{\xi}$  ( $i = 0, 1, \dots, n-1$ ) and  $S = -k_B \int (f \ln f - f) d\vec{\xi}$ , it is easy to verify that

$$\begin{aligned} \sum_{i=0}^{n-1} \nabla S_{\phi_i}^T \odot \phi_{i+1} &= \sum_{i=0}^{n-1} \nabla \left( \sum_{j=0}^{n-1} \frac{\partial S}{\partial \alpha_j} \frac{\partial \alpha_j}{\partial \phi_i} \right)^T \odot \phi_{i+1} \\ &= \sum_{i=0}^{n-1} \nabla \left[ -k_B \sum_{j=0}^{n-1} \left( \sum_{k=0}^{n-1} \alpha_k \int c_j c_k f d\vec{\xi} \right) \left( \int c_i c_j f d\vec{\xi} \right)^{-1} \right]^T \odot \left( \int \vec{\xi} c_i f d\vec{\xi} \right) \\ &= \sum_{i=0}^{n-1} -k_B \nabla \alpha_i^T \odot \frac{\partial \vec{B}}{\partial \alpha_i} = -k_B \nabla \cdot \vec{B}, \end{aligned}$$

where  $\vec{B} = \int \vec{\xi} f d\vec{\xi}$ . Therefore, the entropy condition (4) is solved by

$$\phi_n = \int \vec{\xi} c_{n-1} f d\vec{\xi} \quad \text{and} \quad \vec{J}_2^S = k_B \int \vec{\xi} f d\vec{\xi}.$$

## 2.4 Dissipation matrix

To keep the entropy production rate non-negative ( $\sigma^s \geq 0$ ), consistent with the second law of thermodynamics, it is natural to take

$$\frac{\partial \phi_i}{\partial t} + \nabla \cdot \phi_{i+1} = \sum_{j=0}^{n-1} \lambda_{\phi_i \phi_j} S_{\phi_j}, \quad i = 0, \dots, n-1 \quad (6)$$

in which the dissipation matrix  $\lambda = (\lambda_{\phi_i \phi_j})$  is symmetric and positive semi-definite. Furthermore, we require the null space of  $\lambda$  to be independent of the  $\phi_i$ 's. As pointed out in [24], this requirement is important for the stability of non-equilibrium processes and it reveals the fact that physical laws of conservation hold true, no matter what state the underlying thermodynamical system is in (equilibrium or non-equilibrium). The formulas in (6) are known as the balance equations. Together with the constitutive equations, they constitute a closed system once the entropy function  $S$  and the dissipation matrix  $\lambda$  are specified.

Now we show that the collision integrals on the right-hand side of Levermore's moment-closure hierarchies for the Boltzmann equation can be reformulated into the form defined in (6). To do this, we substitute the ansatz (2) into (1) and define

$$Q(\vec{\alpha}) \equiv \int \vec{c}^T(\vec{\xi}) \left\{ \exp[\vec{c}(\vec{\xi}_*) \cdot \vec{\alpha} + \vec{c}(\vec{\xi}'_*) \cdot \vec{\alpha}] - \exp[\vec{c}(\vec{\xi}) \cdot \vec{\alpha} + \vec{c}(\vec{\xi}') \cdot \vec{\alpha}] \right\} B d\vec{\omega} d\vec{\xi}' d\vec{\xi},$$

where  $\vec{c}(\vec{\xi}) = (c_0, c_1, \dots, c_{n-1})$ ,  $\vec{\alpha} = (\alpha_0, \alpha_1, \dots, \alpha_{n-1})^T$  and  $\vec{c}(\vec{\xi}) \cdot \vec{\alpha} = \sum_{k=0}^{n-1} c_k(\vec{\xi}) \odot \alpha_k(\vec{r}, t)$ . With the celebrated identity [17]

$$4 \int c_i(\vec{\xi})(f_* f'_* - ff') B d\vec{\omega} d\vec{\xi}' d\vec{\xi} = \int [c_i(\vec{\xi}) + c_i(\vec{\xi}') - c_i(\vec{\xi}_*) - c_i(\vec{\xi}'_*)](f_* f'_* - ff') B d\vec{\omega} d\vec{\xi}' d\vec{\xi},$$

which holds for any continuous function  $c_i(\vec{\xi})$ , we can rewrite

$$Q(\vec{\alpha}) = -\frac{1}{4} \int [\vec{c}^T(\vec{\xi}_*) + \vec{c}^T(\vec{\xi}'_*) - \vec{c}^T(\vec{\xi}) - \vec{c}^T(\vec{\xi}')] \left\{ \exp[\vec{c}(\vec{\xi}_*) \cdot \vec{\alpha} + \vec{c}(\vec{\xi}'_*) \cdot \vec{\alpha}] - \exp[\vec{c}(\vec{\xi}) \cdot \vec{\alpha} + \vec{c}(\vec{\xi}') \cdot \vec{\alpha}] \right\} B d\vec{\omega} d\vec{\xi}' d\vec{\xi}.$$

It follows from the mean value theorem that

$$\exp[\vec{c}(\vec{\xi}_*) \cdot \vec{\alpha} + \vec{c}(\vec{\xi}'_*) \cdot \vec{\alpha}] - \exp[\vec{c}(\vec{\xi}) \cdot \vec{\alpha} + \vec{c}(\vec{\xi}') \cdot \vec{\alpha}] = M[\vec{c}(\vec{\xi}_*) + \vec{c}(\vec{\xi}'_*) - \vec{c}(\vec{\xi}) - \vec{c}(\vec{\xi}')] \cdot \vec{\alpha},$$

where

$$M(\vec{\alpha}, \vec{\xi}, \vec{\xi}', \vec{\xi}_*, \vec{\xi}'_*) = \int_0^1 \exp\left\{\tau[\vec{c}(\vec{\xi}_*) + \vec{c}(\vec{\xi}'_*) - \vec{c}(\vec{\xi}) - \vec{c}(\vec{\xi}')] \cdot \vec{\alpha} + [\vec{c}(\vec{\xi}) + \vec{c}(\vec{\xi}')] \cdot \vec{\alpha}\right\} d\tau.$$

Then the dissipation matrix is found to be

$$\lambda(\vec{\alpha}) = \frac{1}{4} \int [\vec{c}^T(\vec{\xi}_*) + \vec{c}^T(\vec{\xi}'_*) - \vec{c}^T(\vec{\xi}) - \vec{c}^T(\vec{\xi}')] MB[\vec{c}(\vec{\xi}_*) + \vec{c}(\vec{\xi}'_*) - \vec{c}(\vec{\xi}) - \vec{c}(\vec{\xi}')] d\vec{\omega} d\vec{\xi}' d\vec{\xi},$$

which is symmetric and positive semi-definite. Moreover, it is well known that mass, moment, and energy are the only three conservation laws for the Boltzmann equation [8], which leads to the conclusion that the null space

$$\left\{ \vec{\alpha} \in R^n : \int |[\vec{c}(\vec{\xi}_*) + \vec{c}(\vec{\xi}'_*) - \vec{c}(\vec{\xi}) - \vec{c}(\vec{\xi}')] \cdot \vec{\alpha}|^2 d\vec{\omega} d\vec{\xi}' d\vec{\xi} = 0 \right\}$$

of  $\lambda(\vec{\alpha})$  is independent of  $\phi$ . Thus, the collision integrals are

$$Q(\vec{\alpha}) = -\lambda(\vec{\alpha}) \cdot \vec{\alpha} = \lambda(\vec{\alpha}(\vec{\phi})) \cdot S_{\vec{\phi}},$$

by noting the identity  $\vec{\alpha} = -S_{\vec{\phi}}$ .

In the literature, there is an alternative way to write dissipation terms, in particular the non-linear dissipation terms arising in chemical kinetics, and consequently, also the Boltzmann collision term, which can be seen as the term arising in chemical kinetics for binary chemical reactions with species labeled by velocities. This alternative way, consisting of using the notion of dissipation potential, appears to be more “restricted” and “physical”. Interested readers may see, as an example, [25] for general chemical kinetics and [26] for the Boltzmann collision term.

### 3 Orthogonal conditions

Now we try to show that the general principles of non-equilibrium thermodynamics are fulfilled in our formalism. Notice that the above balance equations could be rewritten into a compact form:

$$\frac{\partial \vec{\phi}}{\partial t} = \vec{J}_c^\phi + \vec{J}_d^\phi.$$

Here the vector for state variables is

$$\vec{\phi} = (\phi_0, \phi_1, \dots, \phi_{n-1})^T,$$

the conserved energetic flows are

$$\vec{J}_c^\phi = -\nabla \cdot (\phi_1, \phi_2, \dots, \phi_n)^T,$$

and the dissipative entropic flows are

$$\vec{J}_d^\phi = \lambda \odot S_{\vec{\phi}}.$$

In view of the kinetic theory, we write the density  $\rho = \phi_0$ , the momentum  $\vec{M} = \rho \vec{v} = \phi_1$ , the second-order stress tensor  $\mathbf{P} = \phi_2$ , and the third-order heat flux tensor  $\mathbf{Q} = \phi_3$  and introduce  $U = \text{tr } \mathbf{P}/2 - \vec{M}^2/(2\rho)$  as the internal energy. Then the following relations can be verified:

$$\begin{aligned} U_{\vec{\phi}}^T \cdot \vec{J}_c^\phi &= -\nabla \cdot (U\vec{v}) - \nabla \cdot \vec{q} - \mathbf{p}^T : \nabla \vec{v}, \\ U_{\vec{\phi}}^T \cdot \vec{J}_d^\phi &= \frac{1}{2} v_i^2 \sum_{j=0}^{n-1} \lambda_{\rho\phi_j} \odot S_{\phi_j} - v_i \sum_{j=0}^{n-1} \lambda_{M_i\phi_j} \odot S_{\phi_j} + \frac{\delta_{ki}}{2} \sum_{j=0}^{n-1} \lambda_{P_{ik}\phi_j} \odot S_{\phi_j}, \end{aligned} \quad (7)$$

where  $p_{ij} = P_{ij} - \rho v_i v_j$  and  $q_i = Q_{jji}/2 - P_{ij} v_j - P_{jj} v_i/2 + \rho v_j^2 v_i$  are recognized as the traditional pressure and heat flux tensors, respectively. To recover the first law of thermodynamics, which states that the change in the internal energy is equal to the amount of heat flux plus the amount of work done by its surroundings, terms

on the right-hand side of (7) should vanish. Therefore, the energetic forces  $U_{\phi_j}$ , defined as the gradient of the internal energy with respect to state variables, and the dissipative entropic flows are orthogonal. Physically, this orthogonal relation means that the energetic forces do not contribute to the dissipative entropic flows, such that the corresponding state variables will be conserved. Owing to the arbitrariness of velocity  $v_i$ ,

$$\sum_{j=0}^{n-1} \lambda_{\rho\phi_j} \odot S_{\phi_j} = \sum_{j=0}^{n-1} \lambda_{M_i\phi_j} \odot S_{\phi_j} = \sum_{j=0}^{n-1} \sum_{i=1}^3 \lambda_{P_i\phi_j} \odot S_{\phi_j} = 0$$

are required by the Galilean invariance in general. In this way, the classical conservation laws for mass, momentum, and total energy are recovered.

Additionally, we have

$$S_{\phi}^T \cdot \vec{J}_c^{\phi} = -\nabla \cdot \vec{J}^S, \quad (8)$$

$$S_{\phi}^T \cdot \vec{J}_d^{\phi} = \sigma^S. \quad (9)$$

The first formula shows another orthogonal relation between the conserved energetic flows and the entropic forces (the gradient of entropy with respect to state variables). Physically, it means that the entropic forces do not disturb the conserved energetic flows, which in turn guarantees the conservation of mass, momentum, and total energy during the irreversible processes. It is noted that (8) and (9) together guarantee the second law of thermodynamics, namely the entropy of an isolated system never decreases.

## 4 Application: A ten-moment model beyond classical hierarchies

As an example, here we are going to construct a ten-moment model with state variables given as the density  $\phi_0 \equiv \rho$ , momentum  $\phi_1 \equiv \rho\vec{v}$  and symmetric pressure tensor  $\phi_2 \equiv \mathbf{P}$ . Specifically, we set the entropy function as  $S = k_B \rho [\ln \det \Theta - 2 \ln \rho + 3 \ln(2\pi) + 3]/2$ , where  $\Theta = \rho^{-1} \mathbf{P} - \vec{v}\vec{v}$ . It is a direct generalization of the well-known entropy in the equilibrium state. Furthermore, it is noted that the entropy function thus defined is a strictly concave function with respect to  $\rho$ ,  $\rho\vec{v}$ , and  $\mathbf{P}$ .

In this case, the balance equations is given by

$$\begin{aligned} \frac{\partial}{\partial t} \rho + \nabla \cdot (\rho\vec{v}) &= 0, \\ \frac{\partial}{\partial t} (\rho\vec{v}) + \nabla \cdot \mathbf{P} &= 0, \\ \frac{\partial}{\partial t} \mathbf{P} + \nabla \cdot \phi_3 &= \lambda_{\mathbf{P}\mathbf{P}} : \Theta^{-1}. \end{aligned}$$

Now the only remaining thing is to determine the constitutive relation  $\phi_3 = \phi_3(\rho, \rho\vec{v}, \mathbf{P})$  to be exact.

By noting

$$\begin{aligned} S_{\phi_0\phi_0}/k_B &= -\rho^{-1}\vec{v}\vec{v} : \Theta^{-1} - \rho^{-1} - \rho/2[\Theta^{-1} : (\partial\Theta/\partial\rho)]^2, \\ S_{\phi_0\phi_1}/k_B &= \rho^{-1}\vec{v} \cdot \Theta^{-1} + \vec{v} \cdot \Theta^{-2} : (\partial\Theta/\partial\rho), \\ S_{\phi_0\phi_2}/k_B &= -1/2\Theta^{-2} : (\partial\Theta/\partial\rho), \\ S_{\phi_1\phi_1}/k_B &= -\rho^{-1}\Theta^{-1} - 2\rho^{-1}\vec{v}\vec{v} : \Theta^{-2}, \\ S_{\phi_1\phi_2}/k_B &= \rho^{-1}\vec{v} \cdot \Theta^{-2}, \\ S_{\phi_2\phi_2}/k_B &= -1/2\rho^{-1}\Theta^{-2}, \end{aligned}$$

we find that the entropy condition (5) turns to be

$$\begin{aligned} k_B \{ -\rho^{-1}\vec{v}\vec{v} : \Theta^{-1} - \rho^{-1} - \rho/2[\Theta^{-1} : (\partial\Theta/\partial\rho)]^2 \} \rho\vec{v} + k_B [\rho^{-1}\vec{v} \cdot \Theta^{-1} + \vec{v} \cdot \Theta^{-2} : (\partial\Theta/\partial\rho)] \cdot \mathbf{P} \\ + k_B [-1/2\Theta^{-2} : \partial\Theta/\partial\rho] : \phi_3 + \partial\vec{J}_2^S/\partial\rho = 0, \end{aligned}$$

$$\begin{aligned}
& k_B[\rho^{-1}\vec{v} \cdot \Theta^{-1} + \vec{v} \cdot \Theta^{-2} : (\partial\Theta/\partial\rho)]\rho\vec{v} + k_B[-\rho^{-1}\Theta^{-1} - 2\rho^{-1}\vec{v}\vec{v} : \Theta^{-2}] \cdot \mathbf{P} \\
& \quad + k_B[\Theta^{-2} : \partial\Theta/\partial(\rho\vec{v})] : \phi_3 + \partial\vec{J}_2^S/\partial(\rho\vec{v}) = 0, \\
& k_B[-1/2\Theta^{-2} : (\partial\Theta/\partial\rho)]\rho\vec{v} + k_B[\rho^{-1}\vec{v} \cdot \Theta^{-2}] \cdot \mathbf{P} + k_B[-1/2\Theta^{-2} : \partial\Theta/\partial\mathbf{P}] : \phi_3 + \partial\vec{J}_2^S/\partial\mathbf{P} = 0.
\end{aligned}$$

It can be verified that the above equations are solved by

$$(\phi_3)_{ijk} = v_i P_{jk} + v_j P_{ik} + v_k P_{ij} - 2\rho v_i v_j v_k + 2\Theta^2 : \partial\vec{g}(\Theta)/\partial\Theta \quad \text{and} \quad \vec{J}_2^S = k_B\rho\vec{v} + \vec{g}(\Theta),$$

where  $\vec{g}(\Theta)$  is an arbitrary vector function of  $\Theta$ .

Additionally, we can determine the entropic fluxes as  $\vec{J}_1^S = S\vec{v} - k_B\rho\vec{v}$  and  $\vec{J}^S = S\vec{v} + \vec{g}(\Theta)$ . Therefore, the evolution equation for the entropy is given by

$$\frac{\partial}{\partial t} S = -\nabla \cdot [\vec{v}S + \vec{g}(\Theta)] + \Theta^{-1} : \lambda_{\mathbf{P}\mathbf{P}} : \Theta^{-1}.$$

Compared to classical results, an additional term  $\vec{g}(\Theta)$  is added to the entropy flux in our new model. This new term allows us great flexibility in the modeling of various irreversible processes characterized through the constitutive relations, but clearly has no effect on the entropy production rate and thereby the non-equilibrium thermodynamics underlying.

Now we are going to show how our new model reduces to the most familiar Euler equations in the equilibrium state. We split the pressure tensor into two parts  $\mathbf{P} = 2\mathbf{E} + \boldsymbol{\tau}$ , where  $\mathbf{E} = (\rho\mathbf{I} + \rho\vec{v}\vec{v})/2$  with  $p$  as the equilibrium pressure, then the last two balance equations become

$$\begin{aligned}
\frac{\partial}{\partial t}(\rho\vec{v}) + \nabla \cdot \mathbf{P} &= \frac{\partial}{\partial t}(\rho\vec{v}) + \nabla \cdot (\rho\vec{v}\vec{v}) + \nabla p + \nabla \cdot \boldsymbol{\tau} = 0, \\
\frac{\partial}{\partial t}\mathbf{P} + \nabla \cdot \phi_3 &= 2\left[\frac{\partial}{\partial t}\mathbf{E} + \nabla \cdot (\vec{v}\mathbf{E} + \frac{1}{3}\vec{v}p\mathbf{I})\right] + \left[\frac{\partial}{\partial t}\boldsymbol{\tau} + \nabla \cdot (\vec{v}\boldsymbol{\tau}) + (\nabla\vec{v}) \cdot \boldsymbol{\tau} + \boldsymbol{\tau} \cdot (\nabla\vec{v})^T + \vec{v}\nabla \cdot \boldsymbol{\tau} + (\nabla \cdot \boldsymbol{\tau})\vec{v}\right] \\
&\quad + 2\nabla \cdot [\Theta^2 : \partial\vec{g}(\Theta)/\partial\Theta] = \rho\lambda_{\mathbf{P}\mathbf{P}} : (\rho\mathbf{I} + \boldsymbol{\tau})^{-1}.
\end{aligned}$$

By taking traces on both sides of the last equation and noting that

$$\text{tr } E|_e = (3p/2 + \rho\vec{v}^2/2)|_e = \rho e, \quad \boldsymbol{\tau}|_e = 0, \quad \lambda_{p_i p_{jj}} = 0,$$

we will arrive at the Euler equations in the equilibrium state as long as  $\nabla \cdot [\Theta^2 : \partial\vec{g}(\Theta)/\partial\Theta] = 0$ . The latter condition can be achieved by properly choosing the function  $\vec{g}(\Theta)$  and will not be addressed here. Furthermore, it is easy to verify that the entropy function defined above for the ten-moment model reduces to the classical one  $S|_e = k_B\rho(3 \ln T - 2 \ln \rho + 3 \ln(2\pi k_B) + 3)/2$  in the equilibrium state, where  $T = (2e - \vec{v}^2)/(3k_B)$  stands for the temperature.

Interestingly, the macroscopic formulation above has good microscopic correspondence. If we take the distribution function as the multi-dimensional gaussian distribution, i.e.

$$f = \rho(2\pi)^{-3/2}(\det \Theta)^{-1/2} \exp[-(\vec{\xi} - \vec{v}) \cdot \Theta^{-1} \cdot (\vec{\xi} - \vec{v})/2],$$

then it can be shown that the entropy function defined above is given by the Boltzmann formula

$$S = -k_B \int (f \ln f - f) d\vec{\xi},$$

while the macroscopic state variables are fully consistent with the Levermore's ansatz, i.e.

$$\rho = \int f d\vec{\xi}, \quad \rho\vec{v} = \int \vec{\xi} f d\vec{\xi}, \quad \mathbf{P} = \int \vec{\xi}\vec{\xi} f d\vec{\xi}, \quad \phi_3 = \int \vec{\xi}\vec{\xi}\vec{\xi} f d\vec{\xi},$$

providing  $\vec{g}(\Theta) \equiv 0$ . However, once  $\vec{g}(\Theta) \neq 0$ , the above solutions will go beyond either Levermore's or Grad's classical results and present a completely new model. Further analysis and applications of this new model are under discussion.

## 5 Conclusion

As a summary, in this article, we have proven the following theorem.

**Theorem.** *Let*

$$\frac{\partial \phi_i}{\partial t} = -\nabla \cdot \phi_{i+1} + \sum_{j=0}^{n-1} \lambda_{\phi_i \phi_j} S_{\phi_j}, \quad i = 0, \dots, n-1 \quad (10)$$

*be equations governing the time evolution of  $n$  fields  $(\phi_0, \phi_1, \dots, \phi_{n-1})$ . The field  $S$  is a given concave function of  $(\phi_0, \phi_1, \dots, \phi_{n-1})$ . The above equations imply*

$$\frac{\partial S}{\partial t} = -\nabla \cdot \left( \sum_{i=0}^{n-1} S_{\phi_i}^T \odot \phi_{i+1} + \vec{j}_2^S \right) + \sum_{i=0}^{n-1} \sum_{j=0}^{n-1} S_{\phi_i}^T \lambda_{\phi_i \phi_j} S_{\phi_j} \quad (11)$$

*provided the compatibility condition*

$$\sum_{i=0}^{n-1} \nabla S_{\phi_i}^T \odot \phi_{i+1} + \nabla \cdot \vec{j}_2^S = 0,$$

*relating two unspecified functions of  $(\phi_0, \phi_1, \dots, \phi_{n-1})$ , namely the scalar field  $\phi_n$  and the vector field  $\vec{j}_2^S$ , hold.*

According to the above theorem, the entropy flux and entropy production rate in the entropy evolution equation (11) are specified to be compatible with the time evolution equations of macroscopic states, and we have shown that the macroscopic balance equations and constitutive equations constructed in this way will not only fully agree with the general principles of non-equilibrium thermodynamics (therefore thermodynamically admissible) but also have a deep microscopic foundation with respect to the Boltzmann equation.

In parallel with Levermore's moment-closure hierarchies for the Boltzmann equation, the four basic steps in our derivation are the choice of suitable state variables, the construction of a strictly concave entropy function, the proper separation of entropy flux and entropy production rate, and the determination of the dissipative structure have been illustrated step by step (see Table 1). As a special example, a new ten-moment model beyond the classical Levermore's or Grad's hierarchies are discussed. Owing to the close linkage between microscopic kinetics and macroscopic dynamics, our derivation may shed light on other macroscopic modeling approaches for irreversible thermodynamics, in which a major bottleneck is knowing how to properly construct those four elements.

Although our current formulation and EIT follow the same procedure of modeling, there are several intrinsic differences between them. First, in EIT, any additional variables beside the traditional mass, momentum, and energy could be included as extended variables, whereas in our formulation, in order to keep the inherent correspondence with the microscopic dynamics, a set of preferred state variables are suggested. Second, there are no systematic constraints or guiding principles on the construction of entropy flux in EIT. On the contrary, the compatibility condition (4) in our approach, based on which the freedom in the separation of entropy flux and entropy production rate is almost completely eliminated, acts a central formula to link the equation of entropy evolution with that of state variable evolution. Finally, EIT puts forward no fine mathematical structure on the entropy production rate as ours.

It is notable that the governing equations (10) obey the structure of conservation-dissipation formalism we have proposed for coarse-grained descriptions of irreversible processes [18]. Thus, they are globally hyperbolic and thereby well posed for initial-value problems, allow a convenient definition of weak solutions, and are amenable to existing numerics. More importantly, a well-behaved short-relaxation-time limit with respect to CIT is ensured automatically. This interesting observation may open a door to explore inherent connections between various non-equilibrium thermodynamic models and theories in the future.

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	Macroscopic thermodynamics	Boltzmann equation
State variables	$\{\phi_0, \dots, \phi_{n-1}\}$	$\left\{ \int c_0 f d\vec{\xi}, \dots, \int c_{n-1} f d\vec{\xi} \right\}$
Entropy function	$S(\phi_0, \dots, \phi_{n-1})$	$S = \int (-k_B f \ln f) d\vec{\xi}$
Entropy flux	$\vec{J}^s = \vec{J}_1^s + \vec{J}_2^s$ $\vec{J}_1^s = \sum_{i=0}^{n-1} S_{\phi_i}^T \odot \phi_{i+1}$ $\sum_{i=0}^{n-1} \nabla S_{\phi_i}^T \odot \phi_{i+1} + \nabla \cdot \vec{J}_2^s = 0$	$\vec{J}^s = \int (-k_B f \ln f) \vec{\xi} d\vec{\xi}$
Entropy production rate	$\sigma^S = S_{\phi}^T \odot \lambda \odot S_{\phi} \geq 0$	$\sigma^S = \frac{k_B}{4} \int \ln [ff' / (f_* f'_*)] \times (ff' - f_* f'_*) B d\vec{\omega} d\vec{\xi}' d\vec{\xi} \geq 0$
Conservation	Conservation laws for mass, momentum, energy	Five collision invariants
Dissipation	Second law of thermodynamics	H-theorem

**Table 1.** The correspondence between our macroscopic thermodynamic approach and the moment-closure hierarchies for the Boltzmann equation.

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