

Chapter 3

Generalized Onsager Principle and Its Applications



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Abstract We review the established nonequilibrium thermodynamical principle based on the Onsager linear response theory for irreversible processes, known as the Onsager principle for dissipative systems, firstly. We present it in two different forms: (1) the constructive formulation of the Onsager principle encompassing the kinetic equation, the reciprocal relation on the mobility and the maximum entropy principle; (2) the variational formulation in which the Onsager-Machlup action potential is maximized, or equivalently the Rayleighian is minimized in the isothermal case. Then, we generalize the Onsager principle in its constructive form to allow both reversible and irreversible processes to be modeled as well as mobility coefficient dependent on thermodynamical variables, which is termed the generalized Onsager principle (GOP). We carry out derivations of a plethora of thermodynamical and generalized hydrodynamical theories using the Onsager principle and the generalized Onsager principle to demonstrate their usefulness in establishing new models for nonequilibrium thermodynamical systems.

Keywords General Onsager principle · Onsager Machlup action potential · Generalized hydrodynamics · Non-equilibrium thermodynamical system

3.1 Introduction

Theories for equilibrium thermodynamics have been well developed based on the three fundamental thermodynamical laws: the first, the second and the third law of thermodynamics [8, 16, 17]. For nonequilibrium systems, however, theories are not quite so soundly developed in that there does not exist any physical laws like the three fundamental thermodynamical laws in nonequilibrium mechanics [3, 11]. For thermodynamical systems near equilibrium, the second law of thermodynamics in the form of the Clausius-Duhem inequality and the Onsager linear response theory

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serve as corner stones for the development of many nonequilibrium theories for such systems [12–15]. In this chapter, we review the Onsager linear response theory for nonequilibrium systems, known as the Onsager principle [5], and make a contact with the second law of thermodynamics. The Onsager principle implies the second law of thermodynamics in the form of the Clausius-Duhem inequality. It is in fact more general in that it defines the dissipation mechanism that characterizes the constitutive relation for any matter systems. In the maximum Onsager-Machlup action potential principle, it provides a way to compute the dissipative force and match it up with the other non-dissipative forces. We then discuss how to generalize the Onsager principle to not only allow quasi-linear dependence of the mobility operator on thermodynamical variables in a functional way, but also to allow certain reversible processes directly related to the elastic force to be included in the model [21]. This allows one to apply the generalized Onsager Principle (GOP) to many complex systems beyond what the original Onsager principle was intended for. The organization of the chapter is as follows. In Sect. 3.2, we review the Onsager principle for dissipative systems in two equivalent yet distinct forms. In Sect. 3.3, we discuss the generalized Onsager principle. In Sect. 3.4, we derive a host of thermodynamical models including generalized hydrodynamical theories to show their variational and dissipative structures.

3.2 Onsager Principle for Dissipative Systems

We discuss the Onsager linear response theory for a purely dissipative system in details in this section. We proceed with it in a closed system first and then discuss it in an open system. We give two distinct formulations of the Onsager linear response theory together with the Onsager reciprocal relation in the name of the Onsager principle. The first formulation is constructive and the second is variational. Various applications of the Onsager principle in derivation of nonequilibrium thermodynamical models will be discussed as examples at the end of the section.

3.2.1 Constructive Onsager Principle

We consider a closed thermodynamical system not far from equilibrium $\mathbf{x} = 0$, whose state is described by a set of coarse-grained, thermodynamical variables $\mathbf{x}(t) = (x_1, \dots, x_n)^T$ or fluctuations measured relative to equilibrium value $\mathbf{x} = 0$. Onsager states that entropy of the system S , which is assumed a function of \mathbf{x} , reaches its maximum value S_e at the equilibrium [13–15]. We expand the entropy function in its Taylor series at the equilibrium to arrive at the following approximation up to the quadratic term

$$S = S_e + \Delta S(\mathbf{x}) + o(\|\mathbf{x}\|^2), \quad \Delta S = -\frac{1}{2} \mathbf{x}^T \cdot \mathbf{H} \cdot \mathbf{x}, \quad (3.1)$$

where \mathbf{H} is the negative Hessian matrix of the entropy function, which is a symmetric and positive definite matrix ($\mathbf{H} > 0$) at the maximum when S 应为斜体 has the continuous second order derivatives. In fact, we can introduce a change of variables near the equilibrium so that the entropy function is exactly a quadratic form of a new set of thermodynamic variables \mathbf{x}' in a neighborhood of the maximum. So, without loss of generality, we assume the entropy function is a quadratic function of thermodynamical variable \mathbf{x} near the equilibrium. We note that this is plausible so long as we are interested in the near equilibrium behavior of the thermodynamical system. The probability density of thermodynamical variable \mathbf{x} near the equilibrium (when they are viewed as random fluctuations/variables) is related to $\Delta S(\mathbf{x})$ via $f(\mathbf{x}) = \frac{1}{Z} \exp[\Delta S(\mathbf{x})/k_B T]$, where k_B is the Boltzmann constant, T the absolute temperature and Z is the partition function.

When the system deviates from equilibrium, spontaneous irreversible processes arise in response to the generalized thermodynamic force \mathbf{X} conjugate to \mathbf{x} defined by

$$\mathbf{X} = \left(\frac{\partial \Delta S}{\partial \mathbf{x}} \right) = -\mathbf{H} \cdot \mathbf{x}. \quad (3.2)$$

The force is created by the gradient in the entropy function. It's role is to drive the system in nonequilibrium back to its stable equilibrium state which we describe it as “relaxing” back to the equilibrium. The force vanishes at the equilibrium and this process is irreversible. The entropy production during the process, i.e., the entropy deviated from the equilibrium value, is given by

$$\Delta S = -\frac{1}{2} \mathbf{x}^T \cdot \mathbf{H} \cdot \mathbf{x} = \frac{1}{2} \mathbf{x}^T \cdot \mathbf{X}. \quad (3.3)$$

We note that the entropy production is the half of the inner product of the conjugate variable and the original thermodynamical variable (or fluctuation).

For a small deviation from the equilibrium, the system is assumed to be in the linear response regime, where the state $\mathbf{x}(t)$ evolves according to the following kinetic equation

$$\dot{\mathbf{x}} = \mathbf{L} \cdot \mathbf{X}, \quad (3.4)$$

or, equivalently,

$$\mathbf{X} = \mathbf{L}^{-1} \cdot \dot{\mathbf{x}}, \quad (3.5)$$

where the coefficient $\mathbf{L} = (L_{ij})$, called the mobility, is an invertible matrix and its inverse is the friction coefficient matrix $\mathbf{R} = \mathbf{L}^{-1}$. Off-diagonal entries (L_{ij}) and (R_{ij}) are referred to as cross-coupling coefficients between different irreversible thermodynamical variables. Dynamics described by the kinetic equation is also known as the friction dynamics in Newtonian mechanics [4], which states that the velocity

of the motion in the dynamics is linearly proportional to the force acting on it. In the framework of the classical mechanics (Newtonian mechanics), this is equivalent to setting inertia to zero while retaining the friction force, which is assumed linear in $\dot{\mathbf{x}}$, and all the other external forces in the momentum balance equation. This system subject to friction is also known as the over-damped system in mechanics. Hence, the kinetic equation defines *relaxation dynamics* for how the nonequilibrium system relaxes back to the equilibrium in the linear response theory. Different mobility matrices define different dynamics although the entropy function of the system remains the same. It is therefore the crucial component in any nonequilibrium dynamical model.

Now that mobility defines actual dynamics of the system while relaxing back to equilibrium. We will relate the entropy production rate to the mobility coefficient explicitly in the irreversible process so that which dynamics the system adopts is fully determined by either specifying the mobility or the energy dissipation rate.

Remark 3.2.1 The linear response adopted in this formulation is an assumption which dictates the development of the entire nonequilibrium theory. There is no reason why this cannot be modified to arrive at a truly nonlinear response and thereby yielding nonlinear, nonequilibrium response theories. However, this has not been explored in depth so far. For instance, the friction force might well be a nonlinear response function given by

$$\mathbf{X} = \mathbf{h}(\dot{\mathbf{x}}), \quad (3.6)$$

where $\mathbf{h}(\dot{\mathbf{x}})$ is a nonlinear function of $\dot{\mathbf{x}}$. Assuming \mathbf{h} is invertible (for example, \mathbf{h} is monotonic), we have

$$\dot{\mathbf{x}} = \mathbf{h}^{-1}(\mathbf{X}), \quad (3.7)$$

where \mathbf{h}^{-1} is the inverse of \mathbf{h} . In order for the system to be dissipative, some constraint must be imposed on the function \mathbf{h} . To a large extent, how to proceed with this remains an open problem.

On the other hand, the mobility can be a function of the thermodynamical variable \mathbf{x} . So, the kinetic equation for the linear response can in fact be a nonlinear equation of \mathbf{x} . However, we hope one should keep in mind that the quasi-linear relation between the flux and the force in the linear response can deduce a nonlinear equation for the thermodynamical variables, but a nonlinear relation between $\dot{\mathbf{x}}$ and \mathbf{x} may not always be a consequence of the linear response theory.

Under the condition that S is quadratic in \mathbf{x} , i.e., the sign of S remains invariant under a time-reversal operation, Onsager derived the well-known reciprocal relation

$$L_{ij} = L_{ji}, \quad (3.8)$$

and, consequently, $R_{ij} = R_{ji}$, from the microscopic reversibility, which states that for any $t > 0$ and τ ,

$$\langle \mathbf{x}(t) \mathbf{x}^T(t + \tau) \rangle = \langle \mathbf{x}(t + \tau) \mathbf{x}^T(t) \rangle, \quad (3.9)$$

where the ensemble is taken with respect to the probability density function $f(\mathbf{x}(t))$ and $f(\mathbf{x}(t + \tau))$, respectively, and $\mathbf{x}(t) \mathbf{x}^T(t + \tau)$ is the tensor product between the two vectors, known as the correlation matrix or tensor [12, 15].

Assuming $\mathbf{x}(t)$ is governed by kinetic equation (3.4), we have for small $|\tau|$

$$\mathbf{x}(t + \tau) = \mathbf{x}(t) + \mathbf{L} \cdot \mathbf{X}(t) \tau + O(\tau^2). \quad (3.10)$$

Substituting (3.10) into (3.9), we obtain

$$\langle (\mathbf{x}(t) + \mathbf{L} \cdot \mathbf{X}(t) \tau) \mathbf{x}^T(t) \rangle = \langle \mathbf{x}(t) (\mathbf{x}^T(t) + \mathbf{X}^T(t) \cdot \mathbf{L}^T \tau) \rangle + O(\tau^2). \quad (3.11)$$

We cancel the equal terms on both sides, divide the above equation by τ , and then take limit $\tau \rightarrow 0$ to obtain

$$\langle \mathbf{L} \cdot \mathbf{X} \mathbf{x}^T - \mathbf{x} \mathbf{X}^T \cdot \mathbf{L}^T \rangle = 0. \quad (3.12)$$

We next evaluate $\langle \mathbf{X} \mathbf{x}^T \rangle$

$$\langle \mathbf{X} \mathbf{x}^T \rangle = \int \mathbf{X} \mathbf{x}^T f(\mathbf{x}) d\mathbf{x}, \quad (3.13)$$

where $f(\mathbf{x}) = \frac{1}{Z} e^{\Delta S(\mathbf{x})/k_B T}$. Then,

$$\begin{aligned} \int \mathbf{X} \mathbf{x}^T f(\mathbf{x}) d\mathbf{x} &= \frac{1}{Z} \int \frac{\partial \Delta S}{\partial \mathbf{x}} \mathbf{x}^T e^{\Delta S(\mathbf{x})/k_B T} d\mathbf{x} \\ &= \frac{1}{Z} \int \mathbf{x}^T \frac{\partial}{\partial \mathbf{x}} e^{\Delta S(\mathbf{x})/k_B T} d\mathbf{x} = -\frac{1}{Z} \int \mathbf{I} e^{\Delta S(\mathbf{x})/k_B T} d\mathbf{x} = -\mathbf{I}. \end{aligned} \quad (3.14)$$

It follows that

$$\mathbf{L} = \mathbf{L}^T, \quad (3.15)$$

i.e., L is symmetric. It is worth emphasizing that this derivation does not require detailed knowledge of the irreversible process.

We next calculate the time rate of change of entropy,

$$\dot{S} = -\dot{\mathbf{x}}^T \cdot \mathbf{H} \cdot \mathbf{x} = \dot{\mathbf{x}}^T \cdot \mathbf{X} = \dot{\mathbf{x}}^T \cdot \mathbf{R} \cdot \dot{\mathbf{x}} = \mathbf{X}^T \cdot \mathbf{L} \cdot \mathbf{X}. \quad (3.16)$$

So, for a positive definite $\mathbf{L} > \mathbf{0}$, the entropy production rate is positive for any $\mathbf{X} \neq 0$. We identify $\dot{\mathbf{x}}$ as the generalized flux given its time reversal property.

The maximum entropy assumption, the Onsager reciprocal relation and the kinetic equation defines entire near equilibrium dynamics for the thermodynamical system. These are collectively called the constructive Onsager principle. We next state the **Onsager principle** as follows:

1. the entropy is maximum at the equilibrium, i.e., the entropy production rate is nonnegative, which is ensured by the nonnegative definiteness of \mathbf{L} ;
2. dynamics near equilibrium is given by a linear response, i.e., kinetic equation (3.4);
3. the mobility coefficient matrix satisfies the reciprocal relation $\mathbf{L} = \mathbf{L}^T$.

We note that mobility in the original Onsager principle is assumed independent of \mathbf{x} . In modern applications, this has been generalized to allow L to be functional of \mathbf{x} . We will discuss this when we generalize the Onsager principle in the next chapter.

3.2.2 Onsager Principle Accounting for Inertia

The Onsager principle alluded to earlier applies to purely dissipative systems, in which inertia effect is not accounted for. We now turn to the system with non-negligible inertia and discuss how to incorporate the inertia effect into the Onsager principle. We consider a thermodynamical system in contact with its surrounding. Let U be its internal energy, E_k the kinetic energy corresponding to the inertia effect, Q its heat, and W the work the system does to the surrounding, the first law of thermodynamics states that

$$E_k + U = Q - W. \quad (3.17)$$

We note that the kinetic energy is a part of the total free energy which is independent of entropy. Let S be its entropy and T the absolute temperature defined from the second and the third law of thermodynamics, respectively. According to the second law, for a reversible process,

$$dS = \frac{dQ}{T}; \quad (3.18)$$

for an irreversible process on the other hand,

$$dS = \frac{dQ}{T} + \frac{dQ'}{T}, \quad (3.19)$$

where dQ' is the energy (in the form of heat) lost internally during the irreversible process. Recall that the Helmholtz free energy of the matter system is defined by

$$F = U - TS. \quad (3.20)$$

Hence,

$$d(E_k + F) = d(E_k + U) - TdS - SdT = -dW - dQ' - SdT. \quad (3.21)$$

For an isothermal system, $dT = 0$. Then,

$$d(E_k + F) = d(E_k + U) - TdS = -dW - dQ'. \quad (3.22)$$

The term on the right hand side is the energy loss to the surrounding and internally while the term on the left is the kinetic energy plus the Helmholtz free energy, termed the generalized free energy. The right hand side is termed energy loss or energy dissipation. It then follows that

$$\frac{d}{dt}(E_k + F) = -\frac{d(W + Q')}{dt}, \quad (3.23)$$

called the energy dissipation rate. This is consistent with the second law of thermodynamics.

By definition,

$$\frac{d}{dt}(E_k + F) = \frac{d}{dt}(E_k + U) - T \frac{dS}{dt} = \frac{d}{dt}(E_k + U) - T \mathbf{X}^T \cdot \mathbf{L} \cdot \mathbf{X}. \quad (3.24)$$

For a closed isothermal system, the total energy never changes, i.e., $\frac{d}{dt}(E_k + U) = 0$. Then,

$$\frac{d}{dt}(E_k + F) = -T \frac{dS}{dt} = -T \mathbf{X}^T \cdot \mathbf{L} \cdot \mathbf{X}. \quad (3.25)$$

The energy dissipation rate is the negative of the entropy production rate. Let \mathbf{X} is the total generalized force. We adopt the kinetic equation from the linear response theory

$$\dot{\mathbf{x}} = \mathbf{L} \cdot \mathbf{X}. \quad (3.26)$$

From (3.61), we deduce

$$\frac{d}{dt}(E_k + F) = \left[\frac{\partial}{\partial \mathbf{x}} F + \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}} \right] \cdot \dot{\mathbf{x}} = -T \dot{\mathbf{x}}^T \cdot \mathbf{X}, \quad (3.27)$$

where $E_k = \rho \|\dot{\mathbf{x}}\|^2/2$ is used. This implies

$$\mathbf{X} = -\frac{1}{T} \left[\frac{\partial}{\partial \mathbf{x}} F + \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}} \right] \quad (3.28)$$

So, in the thermodynamical system with inertia, the Onsager principle can be modified to accommodate the inertia. This version of the kinetic equation incorporates the force balance among the inertia, dissipative and the potential force, which generalizes the classical Onsager principle alluded to earlier.

In the constructive Onsager linear response theory, the entropy function is specified a priori and the dissipation functional is derived from the Onsager principle. In some cases however, we are given the system's dissipation function. In that case, how do we derive the kinetic equation for the system? We next give another equivalent approach to derive (3.4). I.e., we will show that the kinetic equation (3.4), can be derived via a variational principle provided the dissipation functional is known a priori. This is the variational version of the Onsager principle.

3.2.3 Variational Onsager Principle

We assume that we know the entropy production rate functional \dot{S} already and define

$$\Phi_S(\dot{\mathbf{x}}, \mathbf{x}) = \frac{1}{2} \dot{S} \quad (3.29)$$

as half of the entropy production rate functional depending on the generalized flux $\dot{\mathbf{x}}$ and \mathbf{x} . Note that this is a quadratic function of $\dot{\mathbf{x}}$ with a coefficient that can be functionals of \mathbf{x} . We then consider its Legendre transform with respect to $\dot{\mathbf{x}}$ while treating \mathbf{x} as parameters:

$$O = \mathbf{X} \cdot \dot{\mathbf{x}} - \Phi_S = \dot{S} - \Phi_S. \quad (3.30)$$

Here \mathbf{X} is introduced as a conjugate variable to generalized flux $\dot{\mathbf{x}}$. The time integral of the functional is known as the Onsager-Matchup action potential [18]:

$$OM = \int_{t_0}^t O[\dot{\mathbf{x}}(\tau), \mathbf{x}(\tau)] d\tau, \quad (3.31)$$

where t_0 is a fixed initial time.

We note that Φ_S is a convex function since $\Phi_S(\dot{\mathbf{x}}, \mathbf{x})$ is as a negative definite quadratic functional of $\dot{\mathbf{x}}$. Viewing density function O as a function of $(\mathbf{X}, \dot{\mathbf{x}})$, we calculate its critical point with respect to $\dot{\mathbf{x}}$ via variational principles to arrive at

$$\mathbf{X} - \frac{\partial}{\partial \dot{\mathbf{x}}} \Phi_S = \mathbf{X} - \mathbf{R} \cdot \dot{\mathbf{x}} = 0. \quad (3.32)$$

Equivalently,

$$\dot{\mathbf{x}} = \mathbf{L} \cdot \mathbf{X}. \quad (3.33)$$

This is kinetic equation (3.4). This indicates that the kinetic equation in Onsager linear response theory can be recovered from the maximum of the Onsager-Matchup action potential. Of course, the Onsager-catchup action potential can be constructed conversely when the mobility is known.

In fact, if $\mathbf{R} = \mathbf{L}^{-1} > 0$ and \mathbf{R} is symmetric, $\mathbf{R} = (\mathbf{R}^{1/2})^2$. Then,

$$\begin{aligned} OM &= \int_{t_0}^t [\mathbf{X} \cdot \dot{\mathbf{x}} - \frac{1}{2} \dot{\mathbf{x}}^T \cdot \mathbf{R} \cdot \dot{\mathbf{x}}] d\tau \\ &= \int_{t_0}^t [\mathbf{X} \cdot \dot{\mathbf{x}} - \frac{1}{2} \|\mathbf{R}^{1/2} \cdot \dot{\mathbf{x}}\|^2] d\tau \\ &= \int_{t_0}^t [\frac{1}{2} \|\mathbf{R}^{-1/2} \cdot \mathbf{X}\|^2 - \frac{1}{2} \|\mathbf{R}^{1/2} \cdot \dot{\mathbf{x}} - \mathbf{R}^{-1/2} \cdot \mathbf{X}\|^2] d\tau. \end{aligned} \quad (3.34)$$

The maximum of OM is achieved at (3.33) given the generalized force \mathbf{X} .

Notice that E_k is a quadratic function of $\dot{\mathbf{x}}$ and F is a function of \mathbf{x} . So, when the inertia is considered,

$$\begin{aligned} \mathbf{X} \cdot \dot{\mathbf{x}} = \dot{S} &= -\frac{1}{T} \frac{d}{dt} (E_k + F) = -\frac{1}{T} [\frac{\partial E_k}{\partial \dot{\mathbf{x}}} \ddot{\mathbf{x}} + \frac{\partial F}{\partial \mathbf{x}} \dot{\mathbf{x}}] \\ &= -\frac{1}{T} [\frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}} + \frac{\partial F}{\partial \mathbf{x}}] \dot{\mathbf{x}}. \end{aligned} \quad (3.35)$$

This implies

$$\mathbf{X} = -\frac{1}{T} [\frac{\partial F}{\partial \mathbf{x}} + \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}}] \quad (3.36)$$

Notice that we used the fact that for $E_k = \frac{\rho}{2} \|\dot{\mathbf{x}}\|^2$,

$$\frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}} = \rho \frac{d\dot{\mathbf{x}}}{dt}, \quad (3.37)$$

which is the inertia force. Hence, the generalized force \mathbf{X} is proportional to the external forces minus the inertia force.

In practice, when inertia is considered, we use

$$O = \dot{S}(\mathbf{X}, \dot{\mathbf{x}}) - \Phi_S(\dot{\mathbf{x}}, \dot{\mathbf{x}}) = -\frac{d}{dt} [\frac{1}{T} (E_k + F)] - \Phi_S \quad (3.38)$$

when differentiating it with respect to rate $\{\dot{\mathbf{x}}\}$ while assuming \mathbf{X} is independent of $\dot{\mathbf{x}}$. It yields

$$\frac{\delta}{\delta \dot{\mathbf{x}}} (\dot{S} - \Phi_S) = \mathbf{X} - \mathbf{R} \cdot \dot{\mathbf{x}} = 0, \quad \Leftrightarrow \quad \dot{\mathbf{x}} = \mathbf{L} \cdot \mathbf{X}, \quad (3.39)$$

which is the kinetic equation in the Onsager principle.

Based on the above discussion, we state the variational form of the Onsager principle as follows:

Onsager Principle in the variational form:

- Given a dissipation functional, $2\Phi_S$, as a quadratic function of $\dot{\mathbf{x}}$, we construct the Legendre transform of Φ_S with respect to $\dot{\mathbf{x}}$:

$$O = \mathbf{X} \cdot \dot{\mathbf{x}} - \Phi_S = \dot{S} - \Phi_S, \dot{S} = -\frac{1}{T} \left[\frac{\delta F}{\delta \mathbf{x}} + \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}} \right] \dot{\mathbf{x}}. \quad (3.40)$$

The time integral of this functional is called the Onsager-Machlup action potential.

- Differentiating O with respect to $\dot{\mathbf{x}}$, one derives the kinetic equation for the system:

$$\frac{\delta O}{\delta \dot{\mathbf{x}}} = 0. \quad (3.41)$$

The kinetic equation is given explicitly by

$$\mathbf{X} = \frac{\delta \Phi_S}{\delta \dot{\mathbf{x}}} \Leftrightarrow \dot{\mathbf{x}} = L \left[-\frac{1}{T} \left[\frac{\delta F}{\delta \mathbf{x}} + \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}} \right] \right]. \quad (3.42)$$

We note that the force \mathbf{X} is equal to the dissipative or frictional force. So, the Onsager principle gives one a way to calculate the dissipative force given the dissipation function and equates it to the other forces (conservative minus the inertia force) acted to the matter system. The Onsager principle in this variational form yields a force balance among all the forces acted to the system.

In a closed system, we have given two formulations of the Onsager principle: one in a constructive form, where the direct linear response theory is formulated, and the other in a variational form with a quadratic dissipation functional. These two formulations are equivalent. We next explore how we formulate the Onsager principle in an open system.

3.2.4 Onsager Principle in an Open System

For an open system under the isothermal condition, the rate of the total energy loss (internal+kinetic energy) is given by

$$\frac{d}{dt}(E_k + U) = -T \frac{dS^*}{dt}, \quad (3.43)$$

where S^* is the entropy lost to the surrounding. Here, we have to use the total entropy $S_{total} = S + S^*$ in place of the entropy S in the closed system. We assume S_{total} is still a quadratic functional of \mathbf{x} and denote the conjugate force by $\mathbf{X} = \frac{\partial(S+S^*)}{\partial \mathbf{x}}$ as well. We once again arrive at

$$\frac{d}{dt}(E_k + F) = \frac{d}{dt}(E_k + U - TS) = -T \frac{dS_{total}}{dt} = -T \mathbf{X}^T \cdot \mathbf{L} \cdot \mathbf{X}. \quad (3.44)$$

So, the energy dissipation rate is proportional negatively to the entropy production rate. It can be shown that the Onsager principle for irreversible thermodynamic processes is equivalent to the second law of thermodynamics in this case as well.

In an open system, we also have to determine the matter system more carefully. For example, when we consider a material domain Ω , we must consider it as a closed domain with boundaries. The boundary of Ω , denoted as $\partial\Omega$, itself constitutes a sub-matter system on which thermodynamics can take place. In this case, Onsager principle would have to be applied to both the interior of Ω as well as its boundary $\partial\Omega$. This is especially important when we deal with free boundaries.

Consider the equivalent formulation in terms of the Onsager maximum action potential principle. For an open system, we must use the total entropy S_{total} in the Onsager-Machlup action potential density

$$O = \dot{S}_{total} - \Phi_S(\dot{\mathbf{x}}, \dot{\mathbf{x}}). \quad (3.45)$$

We assume S_{total} is a quadratic functional of \mathbf{x} . Then, \dot{S}_{total} is bilinear in $\dot{\mathbf{x}}$ and \mathbf{X} . The Onsager variational principle states that for an open system, the state evolution equations can be obtained by differentiating Onsager-Machlup action potential density O with respect to flux $\dot{\mathbf{x}}$ while viewing \mathbf{X} as independent of $\dot{\mathbf{x}}$. This principle serves as a general framework for describing irreversible processes in the linear response regime for an open system as well.

The Onsager variational principle is an extension of Rayleigh's principle of least energy dissipation and, naturally, it reduces to the latter in isothermal systems. In an isothermal system, the rate of entropy production given by the system to the environment can be expressed as

$$\dot{S}^* = -\frac{\dot{Q}}{T} = -\frac{\overline{\dot{U} + E_k}}{T}, \quad (3.46)$$

where T is the system temperature, \dot{Q} is the rate of heat transfer from the environment to the system, and $\overline{\dot{U} + E_k}$ is the rate of change of the system total energy, with $\dot{Q} = \overline{\dot{U} + E_k}$ according to the first law of thermodynamics, assuming no work is done during the process and the process is reversible. We note that The rate of energy change $\overline{\dot{U} + E_k}$ must come from the surrounding in the open system since it is zero for a closed system. Using the Helmholtz free energy, $F = U - TS$, the Onsager-Machlup action potential density is rewritten into

$$O = \dot{S}_{total} - \Phi_S = \dot{S} + \dot{S}^* - \Phi_S = -\frac{\overline{\dot{F} + E_k}}{T} - \Phi_S, \quad (3.47)$$

where $\dot{F} = \dot{U} - T\dot{S}$ in isothermal systems. We define the Rayleighian as

$$R = -TO = \dot{F}(\mathbf{x}) + \dot{E}_k(\dot{\mathbf{x}}, \dot{\mathbf{x}}) + \Phi_F(\dot{\mathbf{x}}, \dot{\mathbf{x}}), \quad (3.48)$$

where the dissipation function $\Phi_F(\dot{\mathbf{x}}, \dot{\mathbf{x}}) = T\Phi_S(\dot{\mathbf{x}}, \dot{\mathbf{x}})$. The maximization of the Onsager-Machlup action potential is equivalent to the minimization of the so-called time integral of the Rayleighian, which implies

$$\frac{\partial R}{\partial \dot{\mathbf{x}}} = 0 \Leftrightarrow -\frac{1}{T} \left[\frac{\delta F}{\delta \mathbf{x}} + \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}} \right] = L^{-1} \cdot x. \quad (3.49)$$

Here, we use

$$\overline{\dot{E}_k + F} = \overline{\dot{E}_k + U} - T \dot{S} = -T(\dot{S} + \dot{S}^*) = -T \dot{S}_{total}. \quad (3.50)$$

Notice that \dot{F} is linear in \mathbf{X} and $\dot{\mathbf{x}}$, while \dot{E}_k and Φ_F are quadratic in $\dot{\mathbf{x}}$. If we substitute the kinetic equation ($\mathbf{X} = \mathbf{L} \cdot \dot{\mathbf{x}}$) into \dot{F} , we obtain $\overline{\dot{E}_k + F} = -2\Phi_F$ under this dynamics or at the maximum of the Onsager-Machlup action potential density. This indicates that the time rate of change of the total free energy or the free energy dissipation rate is twice as large as the energy dissipation functional along the dynamical path of the nonequilibrium system. For isothermal systems, the Rayleighian is given explicitly by

$$R = \frac{\delta F}{\delta \mathbf{x}_i} \dot{\mathbf{x}}_i + \dot{E}_k(\dot{\mathbf{x}}, \dot{\mathbf{x}}) + \frac{1}{2} R_{T,ij} \dot{\mathbf{x}}_i \dot{\mathbf{x}}_j, \quad (3.51)$$

where $\mathbf{R}_T = T\mathbf{R}$ is the rescaled friction coefficient, the generalized force is given by $-\frac{\delta F}{\delta \mathbf{x}} - \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}}$. The first two terms in the right-hand side are $\overline{\dot{E}_k + F}$ and the third term is $\Phi_F(\dot{\mathbf{x}}, \dot{\mathbf{x}})$, which is in a quadratic form with the friction coefficients \mathbf{R}_T forming a symmetric and positive-definite matrix. Minimization of R with respect to rate $\dot{\mathbf{x}}$ gives the kinetic equation

$$T\mathbf{X} = -\frac{\delta F}{\delta \mathbf{x}} - \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}} = \mathbf{R}_T \cdot \dot{\mathbf{x}}, \quad (3.52)$$

which can be interpreted as a balance between the reversible force $-\frac{\delta F}{\delta \mathbf{x}} - \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}}$ and the dissipative or friction force linear in the flux.

If we represent the generalized force by $T\mathbf{X}$, the Rayleighian is given by

$$\begin{aligned} R &= -T\mathbf{X} \cdot \dot{\mathbf{x}} + \frac{1}{2} \dot{\mathbf{x}} \cdot \mathbf{R}_T \cdot \dot{\mathbf{x}} \\ &= -\frac{T}{2} \|\mathbf{R}^{-1/2} \cdot \mathbf{X}\|^2 + \frac{1}{2} \|\mathbf{R}^{1/2} \cdot \dot{\mathbf{x}} - (T\mathbf{R})^{-1/2} \cdot \mathbf{X}\|^2. \end{aligned} \quad (3.53)$$

The minimal Rayleighian corresponds to

$$T\mathbf{X} = \mathbf{L} \cdot \dot{\mathbf{x}}. \quad (3.54)$$

It is worth emphasizing that although the variational principle is equivalent to the kinetic equation combined with the reciprocal relation, the former possesses a notable advantage in some cases. The variational form allows flexibility in the choice of state variables. Once these variables are chosen, the conjugate forces are generated automatically via calculus of variations.

In summary, the extremal conditions on the Onsager-Machlup action potential density or the Rayleighian yields the force balance for the nonequilibrium system in isothermal case among the dissipative force, the inertia and the conservative forces. We next consider how to add external forces to the Onsager principle formulation when the force is nonconservative.

3.2.5 Effect of External Forces

If there exists an external body force to the system denoted as \mathbf{G} , we amend the Rayleighian by

$$R = \dot{\mathbf{x}} \cdot \left(\frac{\delta F}{\delta \mathbf{x}} - \mathbf{G} \right) + \dot{E}_k + \Phi_F. \quad (3.55)$$

Taking its derivative with respect to flux $\dot{\mathbf{x}}$, we obtain the force balance equation

$$T\mathbf{X} = \mathbf{R} \cdot \dot{\mathbf{x}} = -\frac{\delta F}{\delta \mathbf{x}} + \mathbf{G} - \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}}. \quad (3.56)$$

Guided by this, we state the constructive Onsager principle for an open system with an external force \mathbf{G} is thus stated as follows:

1. the kinetic equation is given by $\dot{\mathbf{x}} = \mathbf{L} \cdot \mathbf{X}$, where generalized force is given by $\mathbf{X} = \frac{1}{T} \left[-\frac{\delta F}{\delta \mathbf{x}} + \mathbf{G} - \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}} \right]$;
2. the reciprocal property $\mathbf{L} = \mathbf{L}^T$ applies to the mobility;
3. the nonnegative definiteness of \mathbf{L} warrants positive entropy production.

Moreover, energy dissipation rate given by (3.61) is modified to

$$\frac{d}{dt}(E_k + F) = -T\mathbf{X}^T \cdot \mathbf{L} \cdot \mathbf{X} + \mathbf{G} \cdot \dot{\mathbf{x}} = \left[-\frac{\delta F}{\delta \mathbf{x}} - \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}} + \mathbf{G} \right] \cdot \dot{\mathbf{x}}. \quad (3.57)$$

The external force \mathbf{G} can be a conservative or a nonconservative force. In the former case, there exists a potential such that

$$\mathbf{G} = -\nabla h. \quad (3.58)$$

For example, the gravitational potential is $h = g\mathbf{x} \cdot \mathbf{n}$, where \mathbf{n} is the direction of the gravity and g is the gravitational acceleration. In this case, we effectively classify $-\mathbf{G} \cdot \dot{\mathbf{x}}$ as a part of $T\dot{S}^*$.

3.2.6 Extension of Onsager Principle to Spatially Inhomogeneous Systems

In the presentation of the Onsager principle so far, we have assumed the entropy and the entropy production rate (analogously free energy and the energy dissipation rate) are functions of the thermodynamical variables. This applies to spatially homogeneous systems only. Realistically, most matter systems are spatially inhomogeneous. We can extend the Onsager principle to spatially inhomogeneous systems where potentials and mobility are functionals of the thermodynamical variables. Specifically, we assume the entropy, free energy and internal energy are functionals of the thermodynamical variables and the entropy production rate (or the energy dissipation rate) are functionals of the thermodynamical variables and quadratic functions of their corresponding invariant time derivatives. Under these assumptions, the thermodynamical principles mentioned above are still valid.

We generalize the dissipation functional to cases where the coefficients of the quadratic form in $\dot{\mathbf{x}}$ depend on the thermodynamical variables and their spatial derivatives and/or integrals. Then, the kinetic equation derived from the Rayleighian is given by

$$T\mathbf{X} = \frac{\partial \Phi_F}{\partial \dot{\mathbf{x}}} = -\frac{\delta F}{\delta \mathbf{x}} + \mathbf{G} - \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}}, \quad (3.59)$$

where the free energy functional, kinetic energy, and the dissipation functionals are given by

$$F[\mathbf{x}] = \int f(\mathbf{x}, \nabla \mathbf{x}, \dots) d\mathbf{r}, \quad E_k = \int \frac{\rho}{2} \|\dot{\mathbf{x}}\|^2 d\mathbf{r}, \quad \Phi_S = \frac{1}{2} \int \dot{\mathbf{x}} \cdot \mathbf{R} \cdot \dot{\mathbf{x}} d\mathbf{r}, \quad (3.60)$$

where f is the free energy density, ρ is the density of the matter system, r is the spatial variable, \mathbf{R} is the friction coefficient which can be functions of \mathbf{x} and its spatial derivatives. This yields all the transport equations for the system. Notice that this is a force balance equation that includes all the forces in the system: dissipative force $-\frac{\delta \Phi_F}{\delta \dot{\mathbf{x}}}$, elastic force $-\frac{\delta F}{\delta \mathbf{x}}$, external force \mathbf{G} , and the inertia force $-\frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}}$.

In practice, we either apply the Onsager principle directly to arrive at the constitutive relation by constructing the mobility matrix \mathbf{L} to define the kinetic equation:

$$\mathbf{X} = \mathbf{L} \cdot \dot{\mathbf{x}}, \quad (3.61)$$

or maximize the Onsager-Machlup action potential (or minimize the time integral of the Rayleighian) to arrive at the same relation when the dissipation functional Φ_S is available. In the latter case, after we obtain the energy dissipation functional Φ_S and the Helmholtz free energy F , the Rayleighian is defined by

$$R = \overline{E_k + F} - \mathbf{G} \cdot \dot{\mathbf{x}} + \Phi_F, \quad \phi_F = -T\Phi_S. \quad (3.62)$$

Minimizing the functional, we obtain

$$\mathbf{X} = \frac{1}{T} \left[-\frac{\delta F}{\delta \mathbf{x}} + \mathbf{G} - \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}} \right] = L^{-1} \cdot \dot{\mathbf{x}}, \quad (3.63)$$

where L is a functional of \mathbf{x} . In a nutshell, the Onsager maximum action potential principle basically calculates the dissipative force and balances it with all the other forces.

Remark 3.2.2 The Onsager maximum action potential approach only works for a purely dissipative system. The constructive Onsager principle can be extended to account for reversible process as well, which we will consider in the generalized Onsager principle next.

In the following, we consider a series of well-known models and demonstrate how they can be derived using Onsager principles.

Example 3.2.1 (Very viscous incompressible fluid model-Stokes equation) We consider a very viscous incompressible fluid in a domain Ω where inertia can be effectively ignored. The dissipation functional is given by

$$\Phi = - \int_{\Omega} 2\eta \mathbf{D} : \mathbf{D} d\mathbf{x}, \quad (3.64)$$

where η is the shear viscosity. Let $\mathbf{x}(\mathbf{x}_0, t)$ is the position vector in the fluid at time t and \mathbf{x}_0 is its Lagrange coordinate in a reference coordinate at $t = 0$. The fluid is incompressible means the Jacobian is a constant

$$J(\mathbf{x}, \mathbf{x}_0) = \left| \frac{\partial \mathbf{x}}{\partial \mathbf{x}_0} \right| = 1. \quad (3.65)$$

We differential this identity to obtain a constraint on the velocity

$$\nabla \cdot \mathbf{v} = 0. \quad (3.66)$$

The free energy for the system is consisted exclusively the constraint with a lagrange multiplier p

$$F = - \int_{\mathbf{x}^{-1}(\Omega, t)} p J(\mathbf{x}, \mathbf{x}_0) d\mathbf{x}_0. \quad (3.67)$$

The time rate of change of the free energy is given by

$$\dot{F} = - \int_{\Omega} p \nabla \cdot \mathbf{v} d\mathbf{x} \quad (3.68)$$

The Rayleighian is then given by

$$R = \dot{F} + \frac{\Phi}{2}. \quad (3.69)$$

Applying the Onsager principle in variational form, we obtain

$$0 = -\nabla p + 2\eta \nabla \cdot \mathbf{D}. \quad (3.70)$$

This together with (3.66) constitute the Stokes equation for very viscous incompressible fluid flows.

Example 3.2.2 (Incompressible viscous fluid model-Navier-Stokes equation) We consider an incompressible viscous fluid with a constant density ρ and incompressible constraint (3.66). The dissipation rate is given by (3.64). The Rayleighian is defined by

$$R = \int_{\Omega} \left[\frac{d}{dt} \left(\frac{\rho}{2} \|\mathbf{v}\|^2 \right) - p \nabla \cdot \mathbf{v} \right] d\mathbf{x} + \Phi/2, \quad (3.71)$$

where $\dot{\mathbf{v}} = \frac{d}{dt} = \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) \mathbf{v}$ is the material derivative of \mathbf{v} . Applying the Onsager principle, we arrive at

$$0 = \rho \dot{\mathbf{v}} + \nabla p - 2\eta \nabla \cdot \mathbf{D}. \quad (3.72)$$

This together with (3.66) constitutes the Navier-Stokes equation for the incompressible viscous fluid flow.

Example 3.2.3 (Compressible viscous fluid model) For a compressible viscous fluid, the free energy is given by

$$F = \int_{\Omega} f(\rho) d\mathbf{x}, \quad (3.73)$$

where f is the free energy density, a function of density ρ . The energy dissipation functional is given by

$$\Phi = - \int_{\Omega} [2\eta \mathbf{D} : \mathbf{D} + 2\nu (\nabla \cdot \mathbf{v})^2] d\mathbf{x}, \quad (3.74)$$

where ν is the volumetric viscosity. The Rayleighian is defined by

$$\begin{aligned} R &= \int_{\Omega} \left(\frac{d}{dt} + \nabla \cdot \mathbf{v} \right) \left[\frac{\rho}{2} \|\mathbf{v}\|^2 + f(\rho) \right] d\mathbf{x} + \Phi/2 \\ &= \int_{\Omega} \left[\dot{\rho} \frac{\|\mathbf{v}\|^2}{2} + \rho \mathbf{v} \cdot \dot{\mathbf{v}} + \frac{\rho}{2} \|\mathbf{v}\|^2 \nabla \cdot \mathbf{v} + f'(\rho)(\dot{\rho}) + f(\rho) \nabla \cdot \mathbf{v} \right] d\mathbf{x} + \Phi/2, \end{aligned} \quad (3.75)$$

where $\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$ is the material derivative.

We enforce mass conservation for the system

$$\dot{\rho} + \rho \nabla \cdot \mathbf{v} = 0. \quad (3.76)$$

The Rayleighian reduces to

$$R = \int_{\Omega} [\rho \mathbf{v} \cdot \dot{\mathbf{v}} + f'(\rho)(-\rho \nabla \cdot \mathbf{v}) + f(\rho) \nabla \mathbf{v}] d\mathbf{x} + \Phi/2. \quad (3.77)$$

Applying the Onsager principle, i.e, differentiating R with respect to \mathbf{v} , we have

$$-2\eta \nabla \cdot \mathbf{D} - 2\nu \nabla \cdot (\nabla \cdot \mathbf{v} \mathbf{I}) - \nabla(f + \frac{\rho}{2} \|\mathbf{v}\|^2) + \frac{d}{dt}(\rho \mathbf{v}) = 0. \quad (3.78)$$

The force balance equation reduces to

$$\frac{d}{dt}(\rho \mathbf{v}) = 2\eta \nabla \cdot \mathbf{D} + 2\nu \nabla \cdot (\nabla \cdot \mathbf{v} \mathbf{I}) + \nabla(f(\rho) - \rho f'(\rho)) \quad (3.79)$$

We define

$$p = \rho f'(\rho) - f(\rho) \quad (3.80)$$

as the Osmotic pressure. We arrive ta the compressible Navier-Stokes equation

$$\frac{d}{dt}(\rho \mathbf{v}) = 2\eta \nabla \cdot \mathbf{D} + 2\nu \nabla \cdot (\nabla \cdot \mathbf{v} \mathbf{I}) - \nabla p. \quad (3.81)$$

This together with (3.76) constitutes the model for the compressible viscous fluid flow.

Example 3.2.4 (Incompressible binary viscous fluid model) We consider a binary viscous fluid of two viscous fluid components with the same densities. We denote the volume fraction of one fluid component as ϕ . For the incompressible binary viscous fluid model in a domain V , the kinetic energy is given by $E_k = \int_V \frac{\rho}{2} \|\mathbf{v}\|^2 d\mathbf{x}$, the incompressibility condition is given by $\nabla \cdot \mathbf{v} = 0$, the dissipation functional is given by $\Phi_F = \frac{1}{2} \int_V [\eta \|\nabla \mathbf{v}\|^2 + \gamma \|\mathbf{v}\|^2 + \dot{\phi} M^{-1} \dot{\phi} - p \nabla \cdot \mathbf{v}] d\mathbf{x}$, where p is the pressure, M is the mobility operator, the free energy density is given by $F[\phi] = \int_V f(\phi, \nabla \phi) d\mathbf{x}$. The Rayleighian of the system is given by

$$R = \Phi_F + \overline{\dot{F} + \dot{E}_k}. \quad (3.82)$$

The kinetic equations for the incompressible fluid flows are given by

$$\begin{aligned}
\frac{\delta R}{\delta \mathbf{v}} &= -[\eta \nabla \cdot \nabla \mathbf{v} - \nabla p - \gamma \mathbf{v} - \rho \dot{\mathbf{v}}] + \nabla \phi M^{-1} \dot{\phi} = 0, \\
\frac{\delta R}{\delta p} &= \nabla \cdot \mathbf{v} = 0, \\
\frac{\delta R}{\delta \phi} &= \dot{\phi} + M\mu = 0,
\end{aligned} \tag{3.83}$$

where

$$\mu = \frac{\delta F}{\delta \phi}. \tag{3.84}$$

This system of equations can be simplified into

$$\begin{aligned}
\frac{d}{dt} \rho \mathbf{v} &= \eta \nabla \cdot \nabla \mathbf{v} - \nabla p - \gamma \mathbf{v} + \mu \nabla \phi, \\
\nabla \cdot \mathbf{v} &= 0, \\
\dot{\phi} + M\mu &= 0.
\end{aligned} \tag{3.85}$$

Here, $(\dot{\bullet})$ must be the time invariant derivative, i.e., the material derivative.

Remark 3.2.3 The mobility can be viewed as a differential operator. The time derivative is taken as the material derivative. If we set $\phi = 1$ and the free energy as zero, we recover the transport equation for the incompressible viscous fluid. When the inertia term and the friction term are neglected, we recover the Stokes equation

$$\eta \nabla \cdot \nabla \mathbf{v} - \nabla p = 0. \tag{3.86}$$

When the inertia and the viscous stress is neglected, we recover the Darcy's law for fluid flows in the porous media

$$-\nabla p - \gamma \mathbf{v} = 0. \tag{3.87}$$

This equation can also be derived from the constructive Onsager principle directly by calculating the time rate of change of the total free energy and then apply the linear response theory. However, for the Stokes equation and the Darcy's law, the free energy simply consists of the Lagrange multiplier term for the constraint.

3.2.7 Lagrange Mechanics-A Complementary Formulation

We have learned that the Onsager principle provides a way for one to calculate the dissipative force and then put it against the other forces in a force balance equation for developing nonequilibrium models. Traditionally, there is yet another method

that one has used to derive mechanical models using Lagrangian mechanics for mechanical systems without dissipation. Let \mathcal{L} be the Lagrangian of the system defined by

$$\mathcal{L}[\mathbf{x}, \dot{\mathbf{x}}] = \int_{t_0}^{t_1} [E_k(\dot{\mathbf{x}}) - F[\mathbf{x}]] dt, \quad (3.88)$$

where $[t_0, t_1]$ is a fixed time interval, $E_k = \int \frac{\rho}{2} \|\mathbf{v}\|^2 d\mathbf{x}$ is the kinetic energy and $F = \int f d\mathbf{x}$ is the free energy of the system. The variation of \mathcal{L} with respect to \mathbf{x} is given by

$$\frac{\delta \mathcal{L}}{\delta \mathbf{x}} = -\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\mathbf{x}}} + \frac{\partial \mathcal{L}}{\partial \mathbf{x}} = -\frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}} - \frac{\partial F}{\partial \mathbf{x}}. \quad (3.89)$$

In a system without an external nonconservative force, this is the total non-dissipative force. The above expression equals zero is known as the Euler-Lagrange equation for the system. This gives the governing system of equation for a nondissipative system. It does not apply to systems with dissipation.

If we balance this force with the other forces in a dissipative system including the dissipative force ($\frac{\partial \Phi_F}{\partial \dot{\mathbf{x}}}$) and the nonconservative forces ($-\mathbf{G}$), we end up with the force balance equation, i.e., the momentum balance equation

$$\frac{\delta \mathcal{L}}{\delta \mathbf{x}} + \mathbf{G} = T\mathbf{X} \quad (3.90)$$

for the dissipative system. This application extends the use of Lagrangian. The force $T\mathbf{X}$ is the dissipative force, which is given by other means than the variation of the Lagrangian. If one has the ability to obtain the dissipative force by other means, the Lagrangian mechanics formulation can help us to obtain the non-dissipative forces. The dynamics of the system is determined through balancing the forces.

3.3 Generalized Onsager Principle

The Onsager reciprocal relation is valid for dissipative systems. In many nonequilibrium systems, the Onsager reciprocal relation does not hold or does not have to hold, for instance, conservative Hamiltonian systems, the active matter systems and viscoelastic fluid systems with microstructures etc. where irreversible and reversible processes coexist and intertwine with nonlocal interactions. For the systems, we have to extend the Onsager principle by allowing the mobility matrix to be non-symmetric and nonlinear and in the meantime the free energy to include nonlocal interactions. If we modify the mobility and free energy or entropy this way, we arrive at the generalized Onsager principle.

In the generalization of the Onsager principle, we assume the existence of a kinetic energy functional (E_k), an entropy functional or a free energy functional (F). Given a nonconservative external forces \mathbf{G} , the generalized force \mathbf{X} is given by

$$T\mathbf{X} = -\frac{\delta F}{\delta \mathbf{x}} + \mathbf{G} - \frac{d}{dt} \frac{\partial E_k}{\partial \dot{\mathbf{x}}}, \quad (3.91)$$

where T is the absolute temperature. The generalized Onsager principle states as follows.

1. There exists a mobility operator \mathbf{L} such that $\dot{\mathbf{x}} = \mathbf{L}[\mathbf{x}] \cdot \mathbf{X}$, where \mathbf{L} is a functional of \mathbf{x} ;
2. mobility operator $\mathbf{L} = \mathbf{M}_{sym} + \mathbf{M}_{anti}$, where $\mathbf{M}_{sym} = \mathbf{M}_{sym}^T \geq 0$ and $\mathbf{M}_{anti}^T = -\mathbf{M}_{anti}$, may be functions of \mathbf{x} ;
3. the nonnegative definiteness of $\mathbf{M}_{sym} \geq 0$ ensure the free energy is dissipative absent of any external forces in the isothermal cases

$$\frac{d}{dt}(F + E_k) = -T\mathbf{X}^T \cdot \mathbf{M}_{sym} \cdot \mathbf{X} + \mathbf{G} \cdot \dot{\mathbf{x}}, \quad (3.92)$$

or the entropy production is increasing

$$\frac{d}{dt} S_{total} = \mathbf{X}^T \cdot \mathbf{M}_{sym} \cdot \mathbf{X} - \frac{1}{T} \mathbf{G} \cdot \dot{\mathbf{x}}. \quad (3.93)$$

The antisymmetric part \mathbf{M}_{anti} corresponds to the reversible process that is non-energetic and not built in the Onsager-Machlup maximum action potential nor the Rayleighian so that the variational version of the Onsager principle can not be generalized. Thus, the generalized Onsager principle does not have an equivalent variational counterpart. By allowing antisymmetric mobility operators, we are able to handle energy conservative systems, like Hamiltonian systems. In the generalized Onsager principle, we basically say that the constitutive relation includes not only the dissipative force but also the nondissipative force!

Remark 3.3.1 We have presented two distinct formulations of the Onsager principle for dissipative systems. One is in the form of the kinetic equation, maximum entropy principle and the Onsager reciprocal relation; and the other is in the form of the maximum Onsager-Machlup action potential or equivalently the minimum Rayleighian. In the presentation, we have clearly identified the thermodynamic variables or fluctuations away from the equilibrium as \mathbf{x} and assumed the entropy is given by a functional of these variables. Moreover, we assume the dissipation functional is given by a quadratic functional of flux variable $\dot{\mathbf{x}}$.

However, many dissipation functionals given for hydrodynamic theories in fluid systems are not given as functionals of $\dot{\mathbf{x}}$, but rather functionals of their spatial gradients in the Eulerian coordinate, like in the viscous fluid flows. For these systems, the corresponding generalized force is the stress tensor instead of the force. Normally,

there is no problem when identifying the thermodynamic variables and their conjugate variables if we apply the generalized Onsager principle directly to arrive at the kinetic equation. If one were to use the variational Onsager principle, one has to justify what is the thermodynamical variable whose variation needs to be considered. For the variational Onsager principle, regardless how the dissipation functional is defined, one should always minimize the Rayleighian with respect to $\dot{\mathbf{x}}$.

3.4 Applications of the Generalized Onsager Principle

The generalized Onsager principle provides a mathematical description for any thermodynamical systems near equilibrium. Here, we demonstrate how to apply it to derive thermodynamical models and hydrodynamical models for nonhomogeneous systems that satisfy the second law of thermodynamics.

3.4.1 Dissipative Thermodynamical Models for Nonequilibrium Systems

We consider a nonequilibrium thermodynamical system with N internal variables to describe its state. The free energy of the system is given by

$$F = \int f(\{\phi_i\}, \{\nabla\phi_i\}, \{\nabla^2\phi_i\}, \dots) d\mathbf{x}, \quad (3.94)$$

where $\phi_i, i = 1, \dots, N$ are the internal variables. The energy dissipation rate of the system is given by

$$\frac{dF}{dt} = \int (\mu_1, \dots, \mu_N) \cdot (\dot{\phi}_1, \dots, \dot{\phi}_N)^T d\mathbf{x}. \quad (3.95)$$

where $\mu_i = \frac{\delta f}{\delta \phi_i}, i = 1, \dots, N$ are chemical potentials. We also consider the generalized inertia in the system corresponding to the kinetic energy

$$\int \frac{1}{2} \sum_{i,j=1}^N \phi_{i,t} \mathbf{C}_{ij} \phi_{j,t} d\mathbf{x}, \quad (3.96)$$

where $\mathbf{C} > 0$ a constant “mass” matrix.

Generalized Onsager principle then implies

$$(\dot{\phi}_1, \dots, \dot{\phi}_N)^T = -\mathbf{M} \cdot [(\mu_1, \dots, \mu_N)^T + \mathbf{C} \cdot (\phi_{1,tt}, \dots, \phi_{N,tt})^T], \quad (3.97)$$

where \mathbf{M} is the mobility matrix. If we choose

$$\mathbf{M} = \sum_{k=0}^n \nabla^k \cdot \mathbf{L}_k \nabla^k, \quad (3.98)$$

where \mathbf{L}_k are symmetric tensor, the energy dissipation rate is given by

$$\begin{aligned} \frac{dF}{dt} = & - \int_{\Omega} \sum_{k=0}^n [\nabla^k [(\mu_1, \dots, \mu_m) + (\mathbf{C} \cdot (\phi_{1,tt}, \dots, \phi_{N,tt})^T)^T] \cdot \mathbf{L}_k \cdot \nabla^k [(\mu_1, \dots, \mu_m)^T + \\ & \mathbf{C} \cdot (\phi_{1,tt}, \dots, \phi_{N,tt})^T]] dx + \int_{\partial\Omega} g ds, \end{aligned} \quad (3.99)$$

where g is the energy dissipation rate across the surface. By choosing proper boundary conditions so that $g = 0$ on the boundary, we arrive at the bulk energy dissipation rate equation/formula

$$\begin{aligned} \frac{dF}{dt} = & - \int_{\Omega} \sum_{k=0}^n [\nabla^k [(\mu_1, \dots, \mu_m) + (\mathbf{C} \cdot (\phi_{1,tt}, \dots, \phi_{N,tt})^T)^T] \cdot \mathbf{L}_k \cdot \nabla^k [(\mu_1, \dots, \mu_m)^T + \\ & \mathbf{C} \cdot (\phi_{1,tt}, \dots, \phi_{N,tt})^T]] dx. \end{aligned} \quad (3.100)$$

It is dissipative provided the quadratic form in the density is positive semi-definite. If $\mathbf{C} = 0$, this reduces to the dissipative model, also known as the gradient flow model. There are two well-known special cases:

- $n = 0$, it yields the Allen-Cahn system.
- $n = 1$ and $\mathbf{L}_0 = \mathbf{0}$, it is the Cahn-Hilliard system.

This method can be used to derive thermodynamically consistent models for any material systems.

3.4.2 Gross-Pitaevskii Equations

Let $u(\mathbf{x}, t)$ be a complex valued function. Consider the energy given by

$$F = \int [\nabla u \cdot \nabla \bar{u} - V_0(\mathbf{x})|u|^2 + V(|u|)] dx, \quad (3.101)$$

where $V_0(\mathbf{x})$ is the trapping potential and $V(|u|)$ is a nonlinear potential function for interactions. The energy dissipation rate is calculated as follows

$$\frac{dF}{dt} = \int [u_t(-\nabla^2 \bar{u} - V_0 \bar{u} + \frac{\partial V}{\partial |u|^2} \bar{u}) + \bar{u}_t(-\nabla^2 u - V_0 u + \frac{\partial V}{\partial |u|^2} u)] dx. \quad (3.102)$$

We set

$$u_t = M(-\nabla^2 u - V_0 u + \frac{\partial V}{\partial |u|^2} u). \quad (3.103)$$

If we impose that the energy is conserved, i.e., $\frac{dF}{dt} = 0$. Then, it follows that

$$M = \pm i. \quad (3.104)$$

This gives rise to the Gross-Pitaevskii equation:

$$iu_t = \nabla^2 u + V_0 u - \frac{\partial V}{\partial |u|^2} u. \quad (3.105)$$

This is also known as the nonlinear Schrodinger equation. We can extend this derivation to a vector of complex valued function \mathbf{u} for multi-component Gross-Pitaevskii equations.

3.4.3 Generalized Hydrodynamic Theories

We consider a binary mixture of complex fluids consisting of polymers and solvent. The microstructure in the complex fluid is described by the low moments of a polymer distribution density function $f(\mathbf{r}, \hat{\mathbf{v}}, t)$:

$$c_n(\mathbf{r}, t) = \int_{\mathbf{S}} f(\mathbf{r}, \hat{\mathbf{v}}, t) d\hat{\mathbf{v}}, \quad \mathbf{p}(\mathbf{r}, t) = \frac{1}{c_n} \int_{\mathbf{S}} \hat{\mathbf{v}} f(\mathbf{r}, \hat{\mathbf{v}}, t) d\hat{\mathbf{v}}, \quad \mathbf{Q}(\mathbf{r}, t) = \frac{1}{c_n} \int_{\mathbf{S}} (\hat{\mathbf{v}}\hat{\mathbf{v}} - \frac{1}{d}) f(\mathbf{r}, \hat{\mathbf{v}}, t) d\hat{\mathbf{v}}, \quad (3.106)$$

where \mathbf{r} is the position vector, $\hat{\mathbf{v}}$ is the orientation of the polymer, \mathbf{S} is the admissible space for $\hat{\mathbf{v}} \in \mathbf{s}$ and d is the dimensionality.

We note that (i) hydrodynamics is described by low moments of a distribution function in any fluid systems; the momentum, density and energy are low moments of a distribution function; (ii) a generalized hydrodynamic model can be derived using either f or only the first a few low moments; (iii). hydrodynamics and microstructure couplings are via the low moments!

Let ρ , \mathbf{v} , σ and \mathbf{F}_e be the density, mass average velocity, total stress, and total body force of the mixture system. We then have the following conservation laws.

• **Mass conservation:**

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (3.107)$$

• **Momentum conservation:**

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \nabla \cdot (\rho \mathbf{v} \mathbf{v}) = \nabla \cdot \sigma + \mathbf{F}_e. \quad (3.108)$$

- Constitutive equation accounting for the microstructure of the system for σ and \mathbf{F}_e . These include: σ and \mathbf{F}_e , and transport equations for the internal variables $(c, \mathbf{p}, \mathbf{Q})$.

The singular limits of the momentum equation like the Stokes equation for very viscous mixtures are derived by taking the respective singular limits of the full equation.

Consider a mixture of complex fluids, whose micro-structures are described by the first 3 moments $(c, \mathbf{p}, \mathbf{Q})$ of a microstructural distribution function and solvent with the total mass density ρ and mass averaged velocity \mathbf{v} . The mass conservation is given by (3.107). The number density of the microscopic constituent c in the complex fluid is described by the following equation

$$\partial_t c + \nabla \cdot (c\mathbf{v} + \mathbf{j}) = 0, \quad (3.109)$$

where \mathbf{j} is an extra diffusive flux.

The momentum equation is given by (3.108). The above equations need to be augmented by the constitutive equations. Namely, we need to derive evolution equations for $c, \mathbf{p}, \mathbf{Q}$ and constitutive equation for flux \mathbf{j} , stress σ and \mathbf{F}_e .

Constitutive equations:

We assume the free energy of the mixture system is given by

$$F = F[c, \nabla c, \mathbf{p}, \nabla \mathbf{p}, \mathbf{Q}, \nabla \mathbf{Q}] = \int_V f(c, \nabla c, \mathbf{p}, \nabla \mathbf{p}, \mathbf{Q}, \nabla \mathbf{Q}) dV, \quad (3.110)$$

where f is the free energy density per unit volume. The total free energy is defined by the sum of the kinetic energy and the free energy:

$$E^{total} = \int_V [\frac{\rho}{2} \|\mathbf{v}\|^2 + f] dV. \quad (3.111)$$

The energy dissipation rate at a constant temperature T is calculated as follows

$$\begin{aligned} \frac{dE^{total}}{dt} &= \int_V \left\{ \frac{1}{2} \frac{\partial(\rho \|\mathbf{v}\|^2)}{\partial t} + \frac{\partial f}{\partial t} \right\} dV = \\ &= \int_V [-\nabla \cdot (\frac{\rho \mathbf{v}}{2} \|\mathbf{v}\|^2) + \mathbf{v} \cdot (\nabla \cdot \sigma + \mathbf{F}_e) + \mu \frac{\partial c}{\partial t} - \mathbf{h} \cdot \frac{\partial \mathbf{p}}{\partial t} - \mathbf{G} : \frac{\partial \mathbf{Q}}{\partial t}] dV = \\ &= \int_V [-\nabla \cdot (\frac{\rho \mathbf{v}}{2} \|\mathbf{v}\|^2) + \mathbf{v} \cdot (\nabla \cdot \sigma + \mathbf{F}_e) + \mu (\dot{c} - \nabla \cdot (c\mathbf{v})) - \mathbf{h} \cdot (\dot{\mathbf{p}} - \mathbf{v} \cdot \nabla \mathbf{p} - \Omega \cdot \mathbf{p}) - \\ &\quad \mathbf{G} : (\dot{\mathbf{Q}} - \mathbf{v} \cdot \nabla \mathbf{Q} - \Omega \cdot \mathbf{Q} + \mathbf{Q} \cdot \Omega)] dV = \\ &= \int_{\partial V} [-\frac{\rho \mathbf{n} \cdot \mathbf{v}}{2} \|\mathbf{v}\|^2 + \mathbf{v} \cdot \sigma \cdot \mathbf{n}] ds + \int_V [(-\nabla \mathbf{v} : \sigma + \mathbf{h} \cdot \Omega \cdot \mathbf{p} + \mathbf{G} : (\Omega \cdot \mathbf{Q} - \mathbf{Q} \cdot \Omega)) + \\ &\quad (\mathbf{v} \cdot \mathbf{F}_e - \mathbf{v} \cdot \nabla c + \mathbf{h} \cdot \mathbf{v} \cdot \nabla \mathbf{p} + \mathbf{G} : \mathbf{v} \cdot \nabla \mathbf{Q}) + \mu \dot{c} - \mathbf{h} \cdot \dot{\mathbf{p}} - \mathbf{G} : \dot{\mathbf{Q}} - r\hat{\mu}] dV = \\ &= \int_{\partial V} [-\frac{\rho \mathbf{n} \cdot \mathbf{v}}{2} \|\mathbf{v}\|^2 + \mathbf{v} \cdot \sigma \cdot \mathbf{n} - \mathbf{n} \cdot \mathbf{j} \mu] ds + \int_V [-\mathbf{D} : \sigma^s + \nabla \mu \cdot \mathbf{j} - \mathbf{h} \cdot \dot{\mathbf{p}} - \mathbf{G} : \dot{\mathbf{Q}}] dV, \end{aligned} \quad (3.112)$$

where $\mu = \frac{\delta F}{\delta c}$, $\mathbf{h} = -\frac{\delta F}{\delta \mathbf{p}}$, and $\mathbf{G} = -\frac{\delta F}{\delta \mathbf{Q}}$ are the variation of the free energy with respect to the three internal variables, σ^a is the antisymmetric part of the stress, σ_e is the Ericksen stress, σ_s is the symmetric part of the stress,

$$\begin{aligned}
\sigma_{\alpha\beta}^s &= \sigma_{\alpha\beta} - \sigma_{\alpha\beta}^e - \sigma_{\alpha\beta}^a, \\
\sigma_{\alpha\beta}^a &= \frac{1}{2}(p_\alpha h_\beta - p_\beta h_\alpha) + (Q_{\alpha\gamma} G_{\gamma\beta} - G_{\alpha\gamma} Q_{\gamma\beta}), \\
\partial_\beta \sigma_{\alpha\beta}^e &= -(c \partial_\alpha \mu + h_\gamma \partial_\alpha p_\gamma + G_{\beta\gamma} \partial_\alpha Q_{\gamma\beta}).
\end{aligned} \tag{3.113}$$

The time invariant derivatives are defined by

$$\begin{aligned}
D_{\alpha\beta} &= \frac{1}{2}(\partial_\alpha v_\beta + \partial_\beta v_\alpha), \quad \Omega_{\alpha\beta} = \frac{1}{2}(\partial_\alpha v_\beta - \partial_\beta v_\alpha), \\
\dot{c} &= \partial_t c + \nabla \cdot (\mathbf{v}c), \quad \dot{P}_\alpha = \partial_t p_\alpha + v_\beta \partial_\beta p_\alpha + \Omega_{\alpha\beta} p_\beta, \\
\boxed{\mathbf{Q}} &= \frac{\partial \mathbf{Q}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{Q} + [\Omega \cdot \mathbf{Q} - \mathbf{Q} \cdot \Omega],
\end{aligned} \tag{3.114}$$

where \mathbf{D} is the strain rate tensor, Ω is the vorticity of the velocity field \mathbf{v} , P_α is the convected co-rotational derivative of \mathbf{p} , $\boxed{\mathbf{Q}}$ is the convected co-rotational derivative of \mathbf{Q} . If we choose the boundary condition of \mathbf{v} and \mathbf{j} so that the boundary integral contribution to the energy dissipation is zero, the time derivative of the total energy reduces to

$$\dot{E}^{total} = - \int_V (\sigma^s, \boxed{\mathbf{Q}}, \dot{\mathbf{P}}, \mathbf{j}) \cdot (\mathbf{D}, \mathbf{G}, \mathbf{h}, -\nabla \mu)^T dV, \tag{3.115}$$

where

$$\begin{array}{ccc}
\text{Flux} & \longleftrightarrow & \text{Force} \\
(\sigma_{\alpha\beta}^s, \boxed{Q_{\alpha\beta}}, \dot{P}_\alpha, j_\alpha) & \longleftrightarrow & (D_{\alpha\beta}, G_{\alpha\beta}, h_\alpha, -\partial_\alpha \mu).
\end{array} \tag{3.116}$$

with this, we propose the following constitutive relation using the generalized Onsager principle:

$$\text{Fluxes} = [\mathbf{M}_{sym} + \mathbf{M}_{anti}] \cdot \text{Force}. \tag{3.117}$$

The total free energy dissipation rate is then given by

$$\frac{d}{dt} \int_V E^{total} d\mathbf{x} = - \int_V T \dot{S} d\mathbf{x} = - \int \text{Force} \cdot \mathbf{M}_{sym} \cdot \text{Forced} \mathbf{x}. \tag{3.118}$$

It is negative provided the symmetric part of the mobility matrix is positive semi-definite. We give some examples to show how the well-known hydrodynamical models are related to the generalized Onsager principle.

Example 3.4.1 (Binary incompressible viscous fluid mixture model) We have presented some derivations of hydrodynamical models using the variational Onsager principle in the previous section. We now derive it using the constructive Onsager principle approach. We ignore \mathbf{p} and \mathbf{Q} and only consider c as the internal variable. We assume the density is a constant and propose the mobility matrix as follows:

$$\begin{pmatrix} \sigma^v \\ \mathbf{j} \end{pmatrix} = \mathbf{M} \cdot \begin{pmatrix} \mathbf{D} \\ -\nabla\mu \end{pmatrix}, \sigma^a = 0, \nabla \cdot \sigma^e = -c\nabla\mu, \sigma^s = -p\mathbf{I} + \sigma^v, \quad (3.119)$$

where

$$\mathbf{M} = \begin{pmatrix} 2\eta\delta_{\alpha k}\delta_{\beta l} & 0 \\ 0 & \lambda\delta_{\alpha k} \end{pmatrix}, \quad (3.120)$$

η is the shear viscosity coefficient and λ is the mobility for the concentration variable c . The governing system of equations is summarized as follows.

$$\begin{aligned} \frac{\partial c}{\partial t} + \nabla(c\mathbf{v}) + \nabla \cdot \lambda \cdot \nabla\mu &= 0, \\ \nabla \cdot \mathbf{v} &= 0, \\ \rho\left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla\mathbf{v}\right) &= -\nabla p - c\nabla\mu + \nabla \cdot \sigma^s, \end{aligned} \quad (3.121)$$

where ρ is a constant density. This is known as the Navier-Stokes-Cahn-Hilliard system.

The energy dissipation of the system is given by

$$\frac{d}{dt}E = - \int [2\eta\mathbf{D} : \mathbf{D} + \lambda\|\nabla\mu\|^2]d\mathbf{x}, \quad (3.122)$$

where $E = \int [\frac{\rho}{2}\|\mathbf{v}\|^2 + f(\phi)]d\mathbf{x}$ is the total free energy. In the Stokes limit, the inertia terms are dropped and the force balance is given by

$$0 = -\nabla p - c\nabla\mu + \nabla \cdot \sigma^s. \quad (3.123)$$

The same energy dissipation rate applies.

Example 3.4.2 (Quasilinear incompressible model for viscoelastic fluids) We consider only \mathbf{Q} as the internal variable and ignore the density variation and the polar effect. We apply the Onsager principle to the flux and force pair to arrive at

$$\sigma^s = \sigma^v - p\mathbf{I}, \begin{pmatrix} \sigma^v \\ \mathbf{Q} \end{pmatrix} = \mathbf{M} \cdot \begin{pmatrix} \mathbf{D} \\ \mathbf{G} \end{pmatrix}, \quad (3.124)$$

where

$$\mathbf{M}_{sym} = \begin{pmatrix} 2\eta\delta_{\alpha k}\delta_{\beta l} & 0 \\ 0 & \frac{1}{\lambda}\delta_{\alpha k}\delta_{\beta l} \end{pmatrix}, \quad (3.125)$$

λ is the relaxation time of the polymer.

$$\mathbf{M}_{anti} = \begin{pmatrix} 0 & -A_1 \\ A_1 & 0 \end{pmatrix}, \quad (3.126)$$

$$A_1 = a[Q_{\alpha k} \delta_{\beta l} + \delta_{\alpha k} Q_{\beta l}],$$

$a \in [-1, 1]$ is a rate parameter. The governing system of equations is given by

$$\begin{aligned} \square \mathbf{Q} - a[\mathbf{D} \cdot \mathbf{Q} + \mathbf{Q} \cdot \mathbf{D}] - \frac{1}{\lambda} \mathbf{G} &= 0, \\ \nabla \cdot (\mathbf{v}) &= 0, \\ \rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) &= -\nabla p + \nabla \cdot (\sigma^s - \sigma^e - \sigma^a), \end{aligned} \quad (3.127)$$

where ρ is a constant density.

The energy dissipation is given by

$$\frac{d}{dt} E = - \int [2\eta \mathbf{D} : \mathbf{D} + \frac{1}{\lambda} \mathbf{G} : \mathbf{G}] d\mathbf{x}, \quad (3.128)$$

where $E = \int [\frac{\rho}{2} \|\mathbf{v}\|^2 + f(\mathbf{Q})] d\mathbf{x}$ is the total energy. If a quadratic free energy density is given, the Oldroyd B model is recovered [2],

$$f(\mathbf{Q}) = \frac{\gamma}{2} tr(\mathbf{Q}^2), \quad (3.129)$$

where γ is the elastic modulus. If a cubic free energy density is given, the Giesekus model is obtained

$$f(\mathbf{Q}) = \frac{\gamma}{2} tr(\mathbf{Q}^2) + \frac{\gamma_2}{3} tr(\mathbf{Q}^3), \quad (3.130)$$

where $\gamma_{1,2}$ are elastic moduli. If we choose the free energy density as

$$f(\mathbf{Q}) = \gamma_1 tr(\mathbf{Q}^2) + \gamma_2 (tr(\mathbf{Q}))^2, \quad (3.131)$$

the linear Phan-Thien Tanner model is recovered.

Example 3.4.3 (Model for nematic liquid crystal solutions) For liquid crystal solutions, we use the polarity vector \mathbf{p} and the nematic order tensor \mathbf{Q} . The generalized Onsager principle yields the following constitutive equation.

$$\begin{aligned} (\sigma^s, \square \mathbf{Q}, \dot{\mathbf{P}}, \mathbf{j})^T &= [\mathbf{M}_{sym} + \mathbf{M}_{anti}] \cdot (\mathbf{D}, \mathbf{G}, \mathbf{h}, -\nabla \mu)^T \\ \mathbf{M}_{sym} &= \begin{pmatrix} A_0 & 0 & 0 & 0 \\ 0 & \frac{1}{\gamma_2} \delta_{\alpha k} \delta_{\beta l} & \frac{\chi_1}{2} A & \frac{\chi_2}{2} A \\ 0 & \chi_1 p_\beta \delta_{\alpha k} \delta_{\beta l} & \frac{1}{\gamma_1} \delta_{\alpha k} & \lambda \delta_{\alpha k} \\ 0 & \chi_2 p_\beta \delta_{\alpha k} \delta_{\beta l} & \lambda \delta_{\alpha k} & \gamma \delta_{\alpha k} \end{pmatrix}, \end{aligned} \quad (3.132)$$

where

$$\begin{aligned} A_0 &= 2\eta\delta_{\alpha k}\delta_{\beta l} + (\bar{\eta} - \frac{2}{3}\eta)\delta_{\gamma k}\delta_{\gamma l}\delta_{\alpha\beta} + \alpha_1(Q_{\alpha k}\delta_{\beta l} + \delta_{\alpha k}Q_{\beta l}) \\ &+ \alpha_2 Q_{kl}Q_{\alpha\beta} + \alpha_3(p_{\alpha}p_k\delta_{\beta l} + \delta_{\alpha k}p_{\beta}p_l) + \alpha_4 p_k p_l p_{\alpha} p_{\beta}, \quad A = (p_{\alpha}\delta_{\beta k} + p_{\beta}\delta_{\alpha k}). \end{aligned} \quad (3.133)$$

The coefficient matrix is symmetric and positive definite to ensure energy dissipation.

$$\mathbf{M}_{anti} = \begin{pmatrix} 0 & -A_1 & -A_2 & -A_3 \\ A_1 & 0 & 0 & 0 \\ A'_2 & 0 & 0 & 0 \\ A'_3 & 0 & 0 & 0 \end{pmatrix}, \quad (3.134)$$

$$\begin{aligned} A_1 &= v_0 + a[Q_{\alpha k}\delta_{\beta l} + \delta_{\alpha k}Q_{\beta l}] + v_3(Q_{kl}Q_{\alpha\beta}) + \theta_1\delta_{kl}\delta_{\alpha\beta}, \\ A_2 &= \frac{v_1}{2}(p_{\beta}\delta_{\alpha k} + p_{\alpha}\delta_{\beta k}) + \theta_2 p_k\delta_{\alpha\beta}, \quad A'_2 = v_1 p_{\beta}\delta_{\alpha k}\delta_{\beta l} + \theta_2 p_{\alpha}\delta_{kl}, \\ A_3 &= \frac{v_2}{2}(p_{\beta}\delta_{\alpha k} + p_{\alpha}\delta_{\beta k}) + \theta_3 p_k\delta_{\alpha\beta}, \quad A'_3 = v_2 p_{\beta}\delta_{\alpha k}\delta_{\beta l} + \theta_3 p_{\alpha}\delta_{kl}. \end{aligned}$$

The coefficient matrix is antisymmetric so that the corresponding part does not contribute to energy dissipation. When the free energy of the liquid crystal is specified, these together with the momentum balance equation and continuity equation $\nabla \cdot \mathbf{v} = 0$ gives the governing system of equations for the liquid crystal system.

3.4.4 Kinetic Theory for Liquid Crystalline Polymer Solutions

The generalized Onsager principle can be applied to mesoscopic modeling. We illustrate it to derive the kinetic equation for liquid crystalline polymers. We model liquid crystalline polymers as rigid rods suspended in a solution. The rod or filament particles are described by their aspect ratio a and axis of symmetry \mathbf{m} , with $||\mathbf{m}|| = 1$, and the spatial coordinates \mathbf{x} of the center of mass. Thus the microstructure configuration space is the sphere \mathbf{S}^2 (for polar rods) or the hemisphere (for apolar rods), and physical space is a domain in \mathbf{R}^3 .

At the kinetic scale, one begins with a microstructure distribution function $f(\mathbf{x}, \mathbf{m}, t)$ for the rodlike molecule ensemble assuming all rods are identical in size and shape, where $f(\mathbf{x}, \mathbf{m}, t)d\mathbf{m}$ gives the number of particles with center of mass \mathbf{x} and orientation \mathbf{m} within the patch $d\mathbf{m}$ at time t . We define the ensemble average in the orientation space $\mathbf{S}^2 = \{\mathbf{m} | ||\mathbf{m}|| = 1\}$ by [2, 4]

$$\langle (\cdot) \rangle = \int_{\mathbf{S}^2} (\cdot) f(\mathbf{m}, \mathbf{x}, t) d\mathbf{m}. \quad (3.135)$$

We denote the zeroth, first, and second moments of f by $c = \langle 1 \rangle$, $\mathbf{p} = \langle \mathbf{m} \rangle$, $\mathbf{M} = \langle \mathbf{m}\mathbf{m} \rangle$, respectively, where c is the *rod number density*, $\mathbf{n} = \frac{1}{c}\mathbf{p}$ is the *polarity vector*, and $\tilde{\mathbf{Q}} = \frac{1}{c}\mathbf{M} - \frac{\mathbf{I}}{3}$ is the *orientation tensor* [1, 6, 7, 9, 19]. (Note: different authors normalize c to get a particle, mass, or volume fraction.)

In rodlike molecule systems, individual rods are transported by a superposition of four effects: (1) macroscopic velocity \mathbf{u} of the fluid mixture, (2) diffusive translational transport in \mathbf{x} -space due to spatial gradients of the chemical potential, (3) rotational velocity induced by the macroscopic flow and modeled by the Jeffery orbit equation in eqn. (3.140), and (4) diffusive rotational transport in \mathbf{m} -space due to rotational gradients of the chemical potential. A key remaining ingredient entails the nonlocal interactions of high aspect ratio rods and filaments, which we now discuss.

The nonlocal microstructure interaction potential has a general form,

$$U = \int_V \int_{\mathbf{S}^2} K(\mathbf{m}, \mathbf{m}', \mathbf{x}, \mathbf{y}) f(\mathbf{m}, \mathbf{y}, t) d\mathbf{m}' d\mathbf{y}, \quad (3.136)$$

where $K(\mathbf{m}, \mathbf{m}', \mathbf{x}, \mathbf{y})$ is an interaction kernel [4, 9, 10, 20] and $V \in \mathbf{R}^3$ is the physical domain for rods in \mathbf{R}^3 . In practice, U is typically approximated by a local representation in terms of low moments (shown here up to 2nd moments) and their derivatives via a truncation of the series expansion of the kernel function:

$$U \approx U(c, \nabla c, \mathbf{p}, \nabla \mathbf{p}, \mathbf{M}, \nabla \mathbf{M}). \quad (3.137)$$

The Onsager and Maier-Saupe excluded-volume potentials for liquid crystals are two classical examples, while Marrucci and Greco [10, 20] extended the potential for nematic polymers to incorporate gradient elasticity (the kinetic analog of Frank elasticity).

Combining the nonlocal potential and the entropy of the system, the *free energy* over the material volume V for the system is given by

$$F[f] = k_B T \int_V \int_{\mathbf{S}^2} \left[\ln f - f + \frac{U}{2} \right] f d\mathbf{m} d\mathbf{x} = k_B T \int_V \left\langle \ln f - f + \frac{U}{2} \right\rangle d\mathbf{x}. \quad (3.138)$$

The *chemical potential* is then given by

$$\mu = k_B T \frac{\delta F}{\delta f} = k_B T [\ln f + U]. \quad (3.139)$$

The transport equation for the probability density function f is given by the *Smoluchowski equation* that couples advection, physical and configurational space diffusion, and rotation by the flow:

$$\frac{\partial f}{\partial t} + \nabla \cdot (\mathbf{u} f) + \mathcal{R} \cdot ((\mathbf{m} \times (\dot{\mathbf{m}} f)) = \nabla \mathbf{j}_x + \mathcal{R} \cdot \mathbf{j}_r,$$

$$\dot{\mathbf{m}} = \Omega \cdot \mathbf{m} + a [\mathbf{D} \cdot \mathbf{m} - \mathbf{D} : \mathbf{m}\mathbf{m}],$$

where operator $\mathcal{R} = \mathbf{m} \times \frac{\partial}{\partial \mathbf{m}}$ is the rotational gradient, $\dot{\mathbf{m}}$ is the Jeffery orbit for the rodlike particle with the aspect ratio a in Stokes flow, $\mathbf{D} = \frac{1}{2}(\nabla \mathbf{u} + \nabla \mathbf{u}^T)$ is the rate of strain tensor, and $\mathbf{\Omega} = \frac{1}{2}(\nabla \mathbf{u} - \nabla \mathbf{u}^T)$ is the vorticity tensor, respectively.

Next, we turn to the remaining hydrodynamic equations and extra stress contributions arising from the microstructure. We assume the mass and momentum conservation equation given by,

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) &= 0, \\ \rho \left[\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right] &= \nabla \cdot (-\Pi \mathbf{I} + \boldsymbol{\tau}) + \mathbf{F}_e, \end{aligned} \quad (3.140)$$

where ρ is the density of the fluid, Π is the hydrostatic pressure, the extra stress is given by

$$\boldsymbol{\tau} = \boldsymbol{\tau}^{sym} + \boldsymbol{\tau}^{antisym}, \quad (3.141)$$

and \mathbf{F}_e is the elastic force. We denote the total energy by

$$E = \int_V \left[\frac{\rho}{2} \|\mathbf{v}\|^2 d\mathbf{x} + F[f] \right]. \quad (3.142)$$

Then, the total energy dissipation is calculated as follows

$$\begin{aligned} \frac{dE}{dt} &= \int_V [\mathbf{v} \cdot \nabla \cdot (-\rho \mathbf{v} \mathbf{v} + \boldsymbol{\tau} - \Pi \mathbf{I} + \mathbf{F}_e) + \int_{S^2} \frac{\delta F}{\delta f} \frac{\partial f}{\partial t} d\mathbf{m}] d\mathbf{x} \\ &= \int_V [\mathbf{v} \cdot \nabla \cdot (-\rho \mathbf{v} \mathbf{v} + \boldsymbol{\tau} - \Pi \mathbf{I} + \mathbf{F}_e) + \int_{S^2} [-\frac{\delta F}{\delta f} \nabla \cdot (\mathbf{v} f) \\ &\quad + \nabla \cdot \mathbf{j}_x - \mathcal{R} \cdot (f \mathbf{m} \times (\mathbf{\Omega} \cdot \mathbf{m} - a \mathbf{D} \cdot \mathbf{m} \mathbf{m}) - \mathbf{j}_m)] d\mathbf{m}] d\mathbf{x} \\ &= - \int_V [\mathbf{D} : (\boldsymbol{\tau}^{sym} + \frac{a}{2} \langle \mathbf{m} \times \mathcal{R} \mathbf{m} + \mathbf{m} \mathbf{m} \times \mathcal{R} \mathbf{m} \rangle - \int_{S^2} (\nabla \mu \cdot \mathbf{j}_x + \mathcal{R} \mu \cdot \mathbf{j}_m) d\mathbf{m})] d\mathbf{x} \\ &\quad + \int_{\partial V} \mathbf{n} \cdot [-\frac{\rho}{2} \|\mathbf{v}\|^2 + \boldsymbol{\tau}^{sym} \cdot \mathbf{v} - p \mathbf{v} - \int_{S^2} (\mathbf{j}_x + \mathbf{v} \mu f) d\mathbf{m}] d\mathbf{x}. \end{aligned} \quad (3.143)$$

We let

$$\begin{aligned} \mathbf{F}_e &= -\langle \nabla \mu \rangle, \\ \boldsymbol{\tau}^{antisym} &= -\frac{1}{2} \langle \mathbf{m} \times \mathcal{R} \mu \mathbf{m} - \mathbf{m} \mathbf{m} \times \mathcal{R} \mu \rangle. \end{aligned} \quad (3.144)$$

We use the generalized Onsager principle to yield the following linear response equation

$$\begin{pmatrix} \boldsymbol{\tau}^{sym} \\ \mathbf{j}_x \\ \mathbf{j}_m \\ r \end{pmatrix} = \begin{bmatrix} C & 0 & 0 \\ 0 & D_s f & 0 \\ 0 & 0 & D_r f \end{bmatrix} \cdot \begin{pmatrix} \mathbf{D} \\ -\nabla \mu \\ -\mathcal{R} \mu \end{pmatrix} \quad (3.145)$$

where C is a fourth order tensor known as the friction coefficient. If we choose $C_{ijkl} = 2\eta\delta_{ik}\delta_{jl} + \nu\delta_{ij}\delta_{kl}$, the coefficient leads to the viscous stress, where η is the shear viscosity and ν the volumetric viscosity. We write the elastic body force \mathbf{F}_e using the *Ericksen stress* τ_e defined by $\nabla \cdot \tau_e = \mathbf{F}_e$.

We summarize the equations in the model as follows.

$$\begin{aligned}\nabla \cdot \tau_e &= -\langle \nabla \mu \rangle, \\ \tau^{sym} &= \tau_e + 2\eta \mathbf{D} + \nu tr(\mathbf{D})\mathbf{I} - a/2[\langle \mathbf{m} \times \mathcal{R}\mu \mathbf{m} + \mathbf{m} \mathbf{m} \times \mathcal{R}\mu \rangle], \\ \tau^{antisym} &= -1/2[\langle \mathbf{m} \times \mathcal{R}\mu \mathbf{m} - \mathbf{m} \mathbf{m} \times \mathcal{R}\mu \rangle], \tau^v = 2\eta \mathbf{D} + \nu tr(\mathbf{D})\mathbf{I}, \quad (3.146) \\ \mathbf{j}_x &= -D_s f \cdot \nabla \mu, \\ \mathbf{j}_m &= -D_r f \cdot \mathcal{R}\mu.\end{aligned}$$

Then, the Smoluchowski equation for f takes a general, transparent, and conservative form:

$$\partial f / \partial t + (\nabla, \mathcal{R}) \cdot (\mathbf{u} f + -D_s f \cdot \nabla \mu, \mathbf{m} \times \dot{\mathbf{m}} f - D_r f \cdot \mathcal{R}\mu) = 0. \quad (3.147)$$

In this way, we have “derived” a kinetic theory for a liquid crystal solution, which is a two scale model. This generalized Onsager relation lays the foundation for multiscale kinetic theories for complex fluids flows, including both solutions and melts.

3.5 Conclusion

We have discussed the Onsager principle for irreversible nonequilibrium processes and the generalized Onsager principle for both reversible and irreversible nonequilibrium processes. The constructive formulation of the Onsager principle applies to general nonequilibrium processes while the Onsager maximum action potential principle only applies to the irreversible processes. We demonstrate by examples that the Onsager principle is an effective modeling tool to develop dynamical theories for any nonequilibrium systems.

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