Abstract

This manuscript is prepared for a Short Course on the variational principle formulated by Onsager based on his reciprocal symmetry for the kinetic coefficients in linear irreversible thermodynamic processes.

Based on the reciprocal relations for kinetic coefficients, Onsager’s variational principle is of fundamental importance to non-equilibrium statistical physics and thermodynamics in the linear response regime. For his discovery of the reciprocal relations, Lars Onsager was awarded the 1968 Nobel Prize in Chemistry. The purpose of this short course is to present Onsager’s variational principle and its applications to first-year graduate students in physics and applied mathematics.

The presentation consists of four units:

1. Review of thermodynamics
2. Onsager’s reciprocal symmetry for kinetic coefficients
3. Onsager’s variational principle
4. Applications:
   4.1 Heat transport
   4.2 Lorentz reciprocal theorem
   4.3 Cross coupling in rarefied gas flows
   4.4 Cross coupling in a mixture of fluids
I. A BRIEF REVIEW OF THERMODYNAMICS

The microcanonical ensemble is of fundamental value while the canonical ensemble is more widely used. For more details, see C. Kittel, *Elementary Statistical Physics*.

The energy is a constant of motion for a conservative system. If the energy of the system is prescribed to be in the range $\delta E$ at $E_0$, we may form a satisfactory ensemble by taking the density as equal to zero except in the selected narrow range $\delta E$ at $E_0$: $P(E) = \text{constant}$ for energy in $\delta E$ at $E_0$ and $P(E) = 0$ outside this range. This particular ensemble is known as the microcanonical ensemble. It is appropriate to the discussion of an isolated system because the energy of an isolated system is a constant.

Let us consider the implications of the microcanonical ensemble. We are given an isolated classical system with constant energy $E_0$. At time $t_0$ the system is characterized by definite values of position and velocity for each particle in the system. The macroscopic average physical properties of the system could be calculated by following the motion of the particles over a reasonable interval of time. We do not consider the time average, but consider instead an average over an ensemble of systems each at constant energy within $\delta E$ at $E_0$. The microcanonical ensemble is arranged with constant density in the region of phase space accessible to the system. Here we have made as a fundamental postulate the assumption of *equal a priori probabilities* for different accessible regions of equal volume in phase space.

A. Entropy

The entropy of the microcanonical ensemble is

$$S = k_B \log \Delta \Gamma,$$

where $\Delta \Gamma$ is the number of states with energy distributed between $E_0$ and $E_0 + \Delta E$. Remember that the general definition of the entropy is $S = -k_B \sum_n w_n \log w_n$, where $k_B$ is the Boltzmann constant and $w_n$ is the distribution function for the system, satisfying $\sum_n w_n = 1$, with $n$ being the set of all quantum numbers which denote the various stationary states of the system. The entropy of the microcanonical ensemble is obtained from a *maximization* of $S = -k_B \sum_n w_n \log w_n$ with respect to $w_n$, subject to the normalization condition $\sum_n w_n = 1$ and the energy condition that $w_n$ is nonzero only if the corresponding energy is in the selected narrow range $\delta E$ at $E_0$. 

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B. Conditions for equilibrium

The entropy is a maximum when a closed system is in equilibrium. The value of $S$ for a system in equilibrium depends on the energy $U$ of the system; on the number $N_i$ of each molecular species $i$ of the system; and on external variables $x_\nu$, such as volume $V$, strain, magnetization. In other words,

$$S = S(U, x_\nu, N_i).$$

We consider the condition for equilibrium in a system made up of two interconnected subsystems, as illustrated in figure 1. Initially the subsystems are separated from each other by an insulating, rigid, and non-permeable barrier.

**Weakly interacting quasi-closed subsystems:** In the following discussion, we consider two weakly interacting quasi-closed subsystems 1 and 2. On the one hand, the two subsystems are quasi-closed, and hence $S_j = S_j(U_j, V_j, N_{ij})$ for $j = 1, 2$ and $S = S_1 + S_2$ from the statistical independence. On the other hand, weak coupling is assumed between the two subsystems. This allows the whole (closed) system to relax towards complete equilibrium (e.g., via energy transfer between the two subsystems) if the total entropy is not maximized (with respect to $U_1$ or $U_2$).

1. **Thermal equilibrium**

Imagine that the barrier is allowed to transmit energy (beginning at one instant of time), with other inhibitions remaining in effect. If the conditions of the two subsystems 1 and 2 do not change, then they are in thermal equilibrium and the entropy of the total system must be a maximum with respect to small transfer of energy from one subsystem to the other. Using the additive property of the entropy,

$$S = S_1 + S_2,$$

we have in equilibrium

$$\delta S = \delta S_1 + \delta S_2 = 0,$$

or

$$\delta S = \left( \frac{\partial S_1}{\partial U_1} \right) \delta U_1 + \left( \frac{\partial S_2}{\partial U_2} \right) \delta U_2 = 0.$$
Because the total system is thermally closed and the total energy is constant, i.e., $\delta U = \delta U_1 + \delta U_2 = 0$, we have

$$\delta S = \left[ \left( \frac{\partial S_1}{\partial U_1} \right) - \left( \frac{\partial S_2}{\partial U_2} \right) \right] \delta U_1 = 0.$$ 

As $\delta U_1$ is an arbitrary variation, we obtain in thermal equilibrium

$$\frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2}.$$ 

Defining the temperature $T$ by

$$\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{x,v,N_i},$$

we obtain $T_1 = T_2$ as the condition for thermal equilibrium.

Suppose that the two subsystems were not originally in thermal equilibrium, but that $T_2 > T_1$. When thermal contact is established to allow energy transmission, the total entropy $S$ will increase. (The removal of any constraint can only increase the volume of phase space accessible to the system.) Thus, after thermal contact is established, $\delta S > 0$, or

$$\left[ \left( \frac{\partial S_1}{\partial U_1} \right) - \left( \frac{\partial S_2}{\partial U_2} \right) \right] \delta U_1 > 0,$$

and

$$\left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \delta U_1 > 0.$$ 

Assuming $T_2 > T_1$, we have $\delta U_1 > 0$. This means that energy passes from the system of high $T$ to the system of low $T$. So $T$ is indeed a quantity that behaves qualitatively like a temperature.

2. **Mechanical equilibrium**

Now imagine that the wall is allowed to move and also transmit energy, but does not pass particles. The volumes $V_1$ and $V_2$ of the two subsystems can readjust to (further) maximize the entropy. In mechanical equilibrium

$$\delta S = \left( \frac{\partial S_1}{\partial V_1} \right) \delta V_1 + \left( \frac{\partial S_2}{\partial V_2} \right) \delta V_2 + \left( \frac{\partial S_1}{\partial U_1} \right) \delta U_1 + \left( \frac{\partial S_2}{\partial U_2} \right) \delta U_2 = 0.$$ 

After thermal equilibrium has been established, we have

$$\left( \frac{\partial S_1}{\partial U_1} \right) \delta U_1 + \left( \frac{\partial S_2}{\partial U_2} \right) \delta U_2 = 0.$$
As the total volume $V = V_1 + V_2$ is constant, we have $\delta V = \delta V_1 + \delta V_2 = 0$, and

$$\delta S = \left[ \left( \frac{\partial S_1}{\partial V_1} \right) - \left( \frac{\partial S_2}{\partial V_2} \right) \right] \delta V_1 = 0.$$  

As $\delta V_1$ is an arbitrary variation, we obtain in mechanical equilibrium

$$\frac{\partial S_1}{\partial V_1} = \frac{\partial S_2}{\partial V_2}.$$  

Defining the pressure $\Pi$ by

$$\frac{\Pi}{T} = \left( \frac{\partial S}{\partial V} \right)_{U,N_i},$$  

we see that for a system in thermal equilibrium (with $T_1 = T_2$), $\Pi_1 = \Pi_2$ is the condition for mechanical equilibrium. In general we define a generalized force $X_{\nu}$ related to the coordinate $x_{\nu}$ by the equation

$$\frac{X_{\nu}}{T} = \left( \frac{\partial S}{\partial x_{\nu}} \right)_{U,N_i}.$$  

It is interesting to note that from the defining equations for $T$ and $\Pi$, we obtain

$$\Pi = \frac{(\partial S/\partial V)_{U,N_i}}{(\partial S/\partial U)_{V,N_i}} = -\left( \frac{\partial U}{\partial V} \right)_{S,N_i}.$$  

This expression for the pressure will be derived again by regarding $U$ as a function of $S$ and $V$.

Suppose that the two subsystems in thermal equilibrium were not originally in mechanical equilibrium, but that $\Pi_1 > \Pi_2$. When the wall is allowed to move, the total entropy $S$ will increase. (The removal of any constraint can only increase the volume of phase space accessible to the system.) From

$$\delta S = \left[ \left( \frac{\partial S_1}{\partial V_1} \right) - \left( \frac{\partial S_2}{\partial V_2} \right) \right] \delta V_1 = \frac{1}{T} [\Pi_1 - \Pi_2] \delta V_1 > 0,$$

we see that $\Pi_1 > \Pi_2$ requires $\delta V_1 > 0$: the subsystem of the higher pressure expands in volume. So $\Pi$ is indeed a quantity that behaves qualitatively like a pressure.

### 3. Particle equilibrium

Now imagine that the wall allows diffusion through it of molecules of the $i$th chemical species. Suppose thermal equilibrium and mechanical equilibrium have already been established. From $\delta N_{i1} + \delta N_{i2} = 0$ and

$$\delta S = \left[ \left( \frac{\partial S_1}{\partial N_{i1}} \right) - \left( \frac{\partial S_2}{\partial N_{i2}} \right) \right] \delta N_{i1} = 0,$$


we obtain
\[ \frac{\partial S_1}{\partial N_{i_1}} = \frac{\partial S_2}{\partial N_{i_2}}, \]
as the condition for particle equilibrium. Defining the chemical potential \( \mu_i \) by
\[ -\mu_i T = \left( \frac{\partial S}{\partial N_i} \right)_{U,x}, \]
we see that for a system in both thermal equilibrium \( (T_1 = T_2) \) and mechanical equilibrium \( (\Pi_1 = \Pi_2) \), \( \mu_{i_1} = \mu_{i_2} \) is the condition for particle equilibrium. It is easy to show that particles tend to move from a region of higher chemical potential to that of a lower chemical potential as the system approaches equilibrium \( (\delta S > 0) \).

C. Connection between statistical and thermodynamical quantities

For a system in equilibrium, \( S = S(U, x_\nu, N_i) \), where \( U \) is the energy, \( x_\nu \) denotes the set of external parameters describing the system, and \( N_i \) is the number of molecules of the \( i \)-th species. If the conditions are changed slightly, but reversibly in such a way that the resulting system is also in equilibrium, we have
\[ dS = \left( \frac{\partial S}{\partial U} \right) dU + \sum_\nu \left( \frac{\partial S}{\partial x_\nu} \right) dx_\nu + \sum_i \left( \frac{\partial S}{\partial N_i} \right) dN_i = \frac{dU}{T} + \frac{1}{T} \sum_\nu X_\nu dx_\nu - \frac{1}{T} \sum_i \mu_i dN_i, \]
which may be rewritten as
\[ dU = TdS - \sum_\nu X_\nu dx_\nu + \sum_i \mu_i dN_i. \]
Consider that the number of particles is fixed and the volume is the only external parameter: \( dN_i = 0 \); \( x_\nu \equiv V \); \( X_\nu \equiv \Pi \). Then,
\[ dU = TdS - \Pi dV. \]
We see that the change of internal energy consists of two parts. The term \( TdS \) represents the change in \( U \) when the external parameters are kept constant \( (dV = 0) \). This is what we mean by heat. Thus
\[ DQ = TdS \]
is the quantity of heat added to the system in a reversible process. The symbol \( D \) is used instead of \( d \) because \( DQ \) is not an exact differential — that is, \( Q \) is not a state function. The
term $-\Pi dV$ is the change in internal energy caused by the change in external parameters; this is what we mean by mechanical work, and

$$DW = -\Pi dV$$

is the work done on the system through the volume change $dV$. By elementary mechanics $DW = -pdV$, hence $\Pi \equiv p$. Therefore the change in internal energy may be expressed as

$$dU = DQ + DW,$$

which is The First Law of Thermodynamics.

That $dS = DQ/T$ is an exact differential in a reversible process is a statement of The Second Law of Thermodynamics. That is, $DQ/T$ is a differential of a state function, entirely defined by the state of the system. Now we know that state function is the entropy.

**On $S = S(U,V)$:** Here the discussion on various thermodynamic quantities starts from $S = S(U,V)$ in equilibrium and $dS = dU/T + pdV/T$ for reversible processes. The evaluation of $S$ as a function of $U$ and $V$ can be carried out using the microcanonical ensemble which is characterized by $U$ and $V$.

We are ready to express $U$ as a function of $S$ and $V$: $U = U(S,V)$. Other quantities of interest are then obtained from $U(S,V):$

$$dU = TdS - pdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV,$$

from which

$$T = \left(\frac{\partial U}{\partial S}\right)_V;$$

and

$$p = -\left(\frac{\partial U}{\partial V}\right)_S.$$ 

(Note that the expression for $p$ has been obtained before by starting from $S = S(U,V)$.) However, $S$ and $V$ are often inconvenient independent variables — it is more convenient to work with $(T,V)$ or $(T,p)$. For this purpose we introduce some thermodynamic potentials: $F$ and $G$.

1. **Helmholtz free energy**

When the temperature $T$ is set, it is convenient to introduce the Helmholtz free energy $F$ which is defined as $F \equiv U - TS$, regardless of whether the system is in equilibrium or not
(as long as the entropy can be defined via partial equilibria). For a system in equilibrium, the macroscopic state is completely determined by $T$ and $V$, and $F$ may be expressed as a function of these two independent variables describing the equilibrium state, i.e.,

$$F(T,V) \equiv U - TS,$$

where $T = \left( \frac{\partial U}{\partial S} \right)_V$ has been used to replace $S$ as an independent variable. From $dU = TdS - pdV$ and

$$dF = dU - TdS - SdT = -SdT - pdV = \left( \frac{\partial F}{\partial T} \right)_V dT + \left( \frac{\partial F}{\partial V} \right)_T dV,$$

we obtain

$$-S = \left( \frac{\partial F}{\partial T} \right)_V,$$

and

$$-p = \left( \frac{\partial F}{\partial V} \right)_T.$$

Therefore, if the Helmholtz free energy $F$ is expressed as a function of independent variables $T$ and $V$, then $S$ and $p$ are readily calculated from its partial derivatives.

**On the Helmholtz free energy $F$:** While the definition of $F \equiv U - TS$ is applicable to arbitrary macroscopic states (so long as there is partial equilibrium and hence the entropy can be defined), the total differential $dF = -SdT - pdV$ is obtained for reversible processes only. That is, $-S = (\partial F/\partial T)_V$ and $-p = (\partial F/\partial V)_T$ are relations for equilibrium states only. For an equilibrium system of fixed $T$ and $V$, $F(T,V)$ can be obtained from the partition function of canonical ensemble.

Consider a thermodynamic process at constant temperature $T$. The change in $F$ is given by $\Delta F = \Delta U - T\Delta S = (\Delta Q - T\Delta S) + \Delta W$. For a reversible process, $\Delta Q = T\Delta S$, and hence $\Delta F = \Delta W$. For an irreversible process, however, $\Delta Q < T\Delta S$ according to the second law of thermodynamics, and hence $\Delta F < \Delta W$. That $-\Delta W \leq -\Delta F$ means the maximum work which can be done by the system is the decrease of $F$. If the volume is fixed, then $\Delta W = 0$ and $\Delta F \leq 0$. That is, at constant temperature and volume, the Helmholtz free energy varies towards a minimum, which is just $F(T,V)$ for the final equilibrium state.

**On $\Delta Q \leq T\Delta S$:** Consider a system in contact with a large heat bath such that a constant temperature $T$ is maintained. If $\Delta Q$ is the heat received by the system from the heat bath, then the heat received by the heat bath from the system is $-\Delta Q$. Assuming that the (very small)
change in the (very large) heat bath is reversible, we have $-\Delta Q/T$ as the change of its entropy. That the total entropy tends to increase means $-\Delta Q/T + \Delta S \geq 0$, i.e., $\Delta Q \leq T\Delta S$.

2. **Gibbs free energy**

When the temperature $T$ and the pressure $p$ are both set, it is convenient to introduce the Gibbs free energy $G$ which is defined as $G \equiv F + pV = U - TS + pV$, regardless of whether the system is in equilibrium or not (as long as the entropy can be defined via partial equilibria). For a system in equilibrium, the macroscopic state is completely determined by $T$ and $p$, and $G$ may be expressed as a function of these two independent variables describing the equilibrium state, i.e.,

$$G(T, p) \equiv U - TS + pV;$$

where $T = \left(\frac{\partial U}{\partial S}\right)_V$ and $p = -\left(\frac{\partial U}{\partial V}\right)_S$ has been used to replace $S$ and $V$ as the two independent variables. From $dU = TdS - pdV$ and

$$dG = dU - TdS - SdT + pdV + Vdp = -SdT + Vdp = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp,$$

we obtain

$$-S = \left(\frac{\partial G}{\partial T}\right)_p,$$

and

$$V = \left(\frac{\partial G}{\partial p}\right)_T.$$ 

Therefore, if the Gibbs free energy $G$ is expressed as a function of independent variables $T$ and $p$, then $S$ and $V$ are readily calculated from its partial derivatives.

Consider a thermodynamic process at constant temperature $T$ and pressure $p$. The change in $G$ is given by $\Delta G = \Delta U - T\Delta S + p\Delta V = (\Delta Q - T\Delta S) + \Delta W + p\Delta V = \Delta Q - T\Delta S$. For a reversible process, $\Delta Q = T\Delta S$, and hence $\Delta G = 0$. For an irreversible process, $\Delta Q < T\Delta S$, and hence $\Delta G < 0$. Therefore, at constant temperature and pressure, the Gibbs free energy tends to a minimum. This minimum is $G(T, p)$ for the equilibrium state at the given temperature and pressure.
II. ONSAGER’S VARIATIONAL PRINCIPLE

A. Reciprocal relations for linear irreversible thermodynamic processes

The heat flux $\vec{J}$ induced by temperature gradient $\nabla T$ is given by the constitutive equations

$$J_i = -\sum_{j=1}^{3} \lambda_{ij} \nabla_j T \quad (i = 1, 2, 3),$$

where $\lambda_{ij}$ are coefficients of heat conductivity. The heat conductivity tensor is symmetric even in crystals of low symmetry (Stokes 1851).

B. Onsager’s reciprocal symmetry derived from microscopic reversibility

For a closed system, consider the fluctuations of a set of (macroscopic) variables $\alpha_i (i = 1, ..., n)$ with respect to their most probable (equilibrium) values. The entropy of the system $S$ has a maximum $S_e$ at equilibrium so that $\Delta S = S - S_e$ can be written in the quadratic form,

$$\Delta S (\alpha_1, ..., \alpha_n) = -\frac{1}{2} \sum_{i,j=1}^{n} \beta_{ij} \alpha_i \alpha_j,$$

where $\beta$ is symmetric and positive definite. The probability density at $\alpha_i (i = 1, ..., n)$ is given by

$$f (\alpha_1, ..., \alpha_n) = f (0, ..., 0) e^{\Delta S/k_B}$$

where $k_B$ is the Boltzmann constant. The forces conjugate to $\alpha_i$ are defined by

$$X_i = \frac{\partial \Delta S}{\partial \alpha_i} = -\sum_{j=1}^{n} \beta_{ij} \alpha_i$$

which are linear combinations of $\alpha_i$ not far from equilibrium.

Following the above definition of the forces, the equilibrium average (over the distribution function $f (\alpha_1, ..., \alpha_n)$) of $\alpha_i X_j$ is given by

$$\langle \alpha_i X_j \rangle = -k_B \delta_{ij}.$$  

Microscopic reversibility leads to the equality

$$\langle \alpha_i (t) \alpha_j (t + \tau) \rangle = \langle \alpha_j (t) \alpha_i (t + \tau) \rangle$$
for time correlation functions. In a certain domain not far from equilibrium, the macroscopic variables $\alpha_i (i = 1, \ldots, n)$ satisfy the linear equations

$$\frac{d}{dt}\alpha_i (t) = - \sum_{k=1}^{n} M_{ik} \alpha_k (t) = \sum_{j=1}^{n} L_{ij} X_j (t).$$

Here the Onsager kinetic coefficient matrix $L$ is related to the rate coefficient matrix $M$ via the relation $L \beta = M$.

*Onsager’s hypothesis is that fluctuations evolve in the mean according to the same macroscopic laws.* Therefore, in evaluating the correlation function $\langle \alpha_i (t) \alpha_j (t + \tau) \rangle$ for a short time interval $\tau$ (a hydrodynamic time scale which is macroscopically short but microscopically long), $\alpha_j (t + \tau)$ is given by

$$\alpha_j (t + \tau) = \alpha_j (t) + \tau \frac{d}{dt}\alpha_j (t) = \alpha_j (t) + \tau \sum_{k=1}^{n} L_{jk} X_k (t).$$

It is worth pointing out that $\tau$ is macroscopically short for the linear expansion but microscopically long for the applicability of the macroscopic laws. It follows that $\langle \alpha_i (t) \alpha_j (t + \tau) \rangle$ is given by

$$\langle \alpha_i (t) \alpha_j (t + \tau) \rangle = \langle \alpha_i (t) \alpha_j (t) \rangle + \tau \sum_{k=1}^{n} L_{jk} \langle \alpha_i (t) X_k (t) \rangle$$

$$= \langle \alpha_i (t) \alpha_j (t) \rangle - \tau k_B L_{ji}$$

Similarly, $\langle \alpha_j (t) \alpha_i (t + \tau) \rangle$ is given by

$$\langle \alpha_j (t) \alpha_i (t + \tau) \rangle = \langle \alpha_j (t) \alpha_i (t) \rangle - \tau k_B L_{ij}.$$  

Comparing the above two time correlation functions, we obtain the reciprocal relations

$$L_{ij} = L_{ji}$$

from microscopic reversibility. Note that $\langle \alpha_i (t) \alpha_j (t) \rangle = \langle \alpha_j (t) \alpha_i (t) \rangle$ by definition.

**C. Onsager’s variational principle based on the reciprocal symmetry**

For small deviation from equilibrium, the system is in the linear response regime, where the state variables $\alpha_i (i = 1, \ldots, n)$ evolve according to the kinetic equations

$$\dot{\alpha}_i = L_{ij} X_j,$$  

(1)
or equivalently
\[ X_i = R_{ij} \dot{\alpha}_j, \quad (2) \]
where the kinetic coefficients \( L_{ij} \) form a symmetric and positive definite matrix, and so do the coefficients \( R_{ij} \), with \( L_{ij} R_{jk} = \delta_{ik} \). Off-diagonal entries \( L_{ij} \) and \( R_{ij} \) are referred to as cross-coupling coefficients between different irreversible processes labeled by \( i \) and \( j \). Under the condition that the variables \( \alpha \) are even, \( i.e., \) their signs remain invariant under time reversal operation, Onsager derived the reciprocal relations
\[ L_{ij} = L_{ji}, \quad (3) \]
and consequently \( R_{ij} = R_{ji} \), from the microscopic reversibility. It is worth emphasizing that his derivation does not require detailed knowledge of the irreversible processes.

Based on Onsager’s reciprocal relations (3), the kinetic equations (2) can be used to formulate a variational principle governing the irreversible processes. This variational principle states that for a closed system, the state evolution equations can be obtained by maximizing the action function (or functional)
\[ \hat{S} (\alpha, \dot{\alpha}) - \Phi_S (\dot{\alpha}, \dot{\alpha}) \]
with respect to the rates \( \{\dot{\alpha}_i\} \). Here \( \dot{S} = X_i \dot{\alpha}_i \) is the rate of change of the entropy, and the dissipation function \( \Phi_S (\dot{\alpha}, \dot{\alpha}) = R_{ij} \dot{\alpha}_i \dot{\alpha}_j / 2 \) is half the rate of entropy production. For an open system, however, there is an additional term \( \dot{S}^* \), which is the rate of entropy given by the system to the environment, added to the action (4), leading to
\[ \mathcal{O} = \dot{S} + \dot{S}^* - \Phi_S (\dot{\alpha}, \dot{\alpha}), \quad (5) \]
which is called the Onsager-Machlup action. Note that \( \dot{S} + \dot{S}^* \) is still linear in \( \{\dot{\alpha}_i\} \). Onsager’s variational principle states that for an open system, the state evolution equations can be obtained by maximizing the Onsager-Machlup action \( \mathcal{O} \) with respect to the rates \( \{\dot{\alpha}_i\} \). This principle serves as a general framework for describing irreversible processes in the linear response regime.

Onsager’s variational principle is an extension from Rayleigh’s principle of least energy dissipation, and naturally it reduces to the latter for isothermal systems. In an isothermal system, the rate of entropy given by the system to the environment can be expressed as
\[ \dot{S}^* = -\dot{Q}/T = -\dot{U}/T, \]
where \( T \) is the system temperature, \( \dot{Q} \) is the rate of heat transfer
from the environment to the system, and $\dot{U}$ is the rate of change of the system energy, with $\dot{Q} = \dot{U}$ according to the first law of thermodynamics. Note that $T$ is constant here. The maximization of the Onsager-Machlup action (5) is equivalent to the minimization of the so-called Rayleighian

$$\mathcal{R} = \dot{F}(\alpha, \dot{\alpha}) + \Phi_F(\dot{\alpha}, \dot{\alpha}),$$

(6)

with respect to the rates $\{\dot{\alpha}_i\}$. Here $\dot{F} \equiv \dot{U} - T\dot{S} = -T\left(\dot{S} + \dot{S}^*\right)$ is the rate of change of the Helmholtz free energy of the system, and the dissipation function $\Phi_F(\dot{\alpha}, \dot{\alpha}) \equiv T\Phi_S(\dot{\alpha}, \dot{\alpha})$ is half the rate of free energy dissipation. As $\dot{F}$ is linear while $\Phi_F$ is quadratic in the rates $\{\dot{\alpha}_i\}$, the principle of least energy dissipation leads to $\dot{F} = -2\Phi_F$. For isothermal systems, the Rayleighian can be written as

$$\mathcal{R} = \frac{\partial F}{\partial \alpha_i} \dot{\alpha}_i + \frac{1}{2} \zeta_{ij} \dot{\alpha}_i \dot{\alpha}_j,$$

(7)

where the first term in the right hand side is $\dot{F}$ and the second term is $\Phi_F(\dot{\alpha}, \dot{\alpha})$, which is in a quadratic form with the friction coefficients $\zeta_{ij}$ forming a symmetric and positive definite matrix. Minimization of $\mathcal{R}$ with respect to the rates gives the kinetic equations

$$-\frac{\partial F}{\partial \alpha_i} = \zeta_{ij} \dot{\alpha}_j,$$

(8)

which can be interpreted as a balance between the reversible force $-\partial F/\partial \alpha_i$ and the dissipative force linear in the rates.

It is worth emphasizing that although the variational principle is equivalent to the kinetic equations combined with the reciprocal relations, the former possesses a notable advantage: 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.

III. APPLICATIONS

A. Heat transport

Consider the heat transport in a crystal. The “forces” and “rates” (“velocities”) are related by the constitutive equations

$$-\frac{1}{T^2} \nabla_i T = X_i = \sum_{j=1}^3 R_{ij} J_j,$$
where $X_i (i = 1, 2, 3)$ are the forces and the components of the heat flux $J_j (j = 1, 2, 3)$ are the rates. Here the matrix $R$ is the inverse of the Onsager coefficient matrix $L$, which is also symmetric. The dissipation function $\phi \left( \vec{J}, \vec{J} \right)$ is introduced in the form of

$$\phi \left( \vec{J}, \vec{J} \right) \equiv \frac{1}{2} \sum_{i,j=1}^{3} R_{ij} J_i J_j.$$  

It is worth emphasizing that $\phi$ can be defined in this quadratic form because of the symmetry in the matrices $R$ and $L$. It is observed that substituting the constitutive equations into the quadratic expression for $\phi$ yields

$$2\phi \left( \vec{J}, \vec{J} \right) \equiv \sum_{i,j=1}^{3} R_{ij} J_i J_j = \sum_{i=1}^{3} J_i X_i = \sum_{i=1}^{3} J_i \nabla_i \left( \frac{1}{T} \right),$$  

which equals the rate of entropy production per unit volume due to heat transport.

Let $s$ denote the local entropy density in the system. Then, under the assumption of local equilibrium, the rate of change of $s$ is given by

$$\frac{ds}{dt} = \frac{1}{T} \left( -\nabla \cdot \vec{J} \right),$$  

where $-\nabla \cdot \vec{J}$ is the rate of local accumulation of heat. The rate of change of the total entropy $S$ is the volume integral

$$\dot{S} = \int \frac{ds}{dt} \, dV = \int \left( -\frac{1}{T} \nabla \cdot \vec{J} \right) \, dV.$$  

The rate of the entropy given off to the surrounding environment is given by the surface integral

$$\dot{S}^* = \int \left( \frac{J_n}{T} \right) \, dA,$$  

where $J_n$ is the outward normal component of the heat flux at the boundary. It follows that

$$\dot{S} + \dot{S}^* = \int \left( -\frac{1}{T} \nabla \cdot \vec{J} \right) \, dV + \int \left( \frac{J_n}{T} \right) \, dA$$  
$$= \int \left( -\frac{1}{T} \nabla \cdot \vec{J} \right) \, dV + \int \nabla \cdot \left( \frac{\vec{J}}{T} \right) \, dV = \int \vec{J} \cdot \nabla \left( \frac{1}{T} \right) \, dV.$$  

It can be shown that the constitutive equations for heat transport can be derived from the variational principle

$$\Phi \left( \vec{J}, \vec{J} \right) - \left[ \dot{S} \left( \vec{J} \right) + \dot{S}^* \left( J_n \right) \right] = \text{minimum},$$

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where the temperature distribution is prescribed, and the rates, \( i.e \), the heat flux \( \vec{J} \), are varied. Here \( \Phi (\vec{J}, \vec{J}) \) is defined by
\[
\Phi (\vec{J}, \vec{J}) = \int \phi (\vec{J}, \vec{J}) \, dV = \int \left( \frac{1}{2} \sum_{i,j=1}^{3} R_{ij} J_i J_j \right) \, dV,
\]
\( \dot{S} (\vec{J}) \) is defined by
\[
\dot{S} (\vec{J}) = \int \left( -\frac{1}{T} \nabla \cdot \vec{J} \right) \, dV,
\]
and \( \dot{S}^* (J_n) \) is defined by
\[
\dot{S}^* (J_n) = \int \left( \frac{J_n}{T} \right) \, dA,
\]
with
\[
\dot{S} (\vec{J}) + \dot{S}^* (J_n) = \int \vec{J} \cdot \nabla \left( \frac{1}{T} \right) \, dV.
\]
The variation of \( \Phi (\vec{J}, \vec{J}) - [\dot{S} (\vec{J}) + \dot{S}^* (J_n)] \) is given by
\[
\delta \left\{ \Phi (\vec{J}, \vec{J}) - [\dot{S} (\vec{J}) + \dot{S}^* (J_n)] \right\} = \int \sum_k \left[ \frac{\partial}{\partial J_k} \phi (\vec{J}, \vec{J}) - \nabla_k \left( \frac{1}{T} \right) \right] \delta J_k \, dV,
\]
from which we have
\[
\frac{\partial}{\partial J_k} \phi (\vec{J}, \vec{J}) = \nabla_k \left( \frac{1}{T} \right) \equiv X_k
\]
according to the variational principle. We note that these are exactly the constitutive equations
\[
\sum_j R_{kj} J_j = \nabla_k \left( \frac{1}{T} \right).
\]
As shown already, inserting the constitutive equations into the quadratic expression for \( \phi \) yields the equality
\[
2\phi (\vec{J}, \vec{J}) = \sum_k J_k \frac{\partial}{\partial J_k} \phi (\vec{J}, \vec{J}) = \sum_k J_k \nabla_k \left( \frac{1}{T} \right),
\]
and hence the integral form
\[
2\Phi (\vec{J}, \vec{J}) = \dot{S} (\vec{J}) + \dot{S}^* (J_n).
\]
Note that \( \dot{S} (\vec{J}) + \dot{S}^* (J_n) \) is the rate of change of the entropy in the system and the surrounding environment. Therefore, the rate of entropy production \( 2\Phi (\vec{J}, \vec{J}) \) is equal to the rate of change of the total entropy \( \dot{S} (\vec{J}) + \dot{S}^* (J_n) \) in an irreversible process governed by the constitutive equations.
B. Stokes equation and Navier slip boundary condition

The variational principle is now fully employed to investigate the Stokes flows with boundary slip. Below is a brief review, showing that the Stokes equation and the Navier slip boundary condition can be derived from the principle of least energy dissipation.

Consider an incompressible Newtonian fluid in a region \( \Omega \) with a solid boundary \( \partial \Omega \), and neglect the inertial effect. The incompressibility condition reads \( \nabla \cdot \vec{v} = 0 \), and the boundary is impermeable at which the normal velocity \( v_n\big|_{\partial \Omega} = 0 \). Here the rate is the velocity field \( \vec{v}(\vec{r}) \) and the free energy is constant in time. The dissipation in the bulk region is due to the viscosity \( \eta \), and the corresponding dissipation function is

\[
\Phi_v = \int_\Omega dV \left[ \frac{1}{4} \eta \left( \partial_i v_j + \partial_j v_i \right)^2 \right].
\]  

If boundary slip occurs at the fluid-solid interface, then the corresponding dissipation function is given by

\[
\Phi_s = \int_{\partial \Omega} dS \left[ \frac{1}{2} \beta \left( \vec{v}^{\text{slip}} \right)^2 \right],
\]

where \( \beta \) is the slip coefficient, and \( \vec{v}^{\text{slip}} \) is the slip velocity, defined as the tangential velocity of the fluid relative to the solid at the fluid-solid interface. Here the solid boundary is still, and hence \( \vec{v}^{\text{slip}} = \vec{v} \). The Rayleighian of the system is given by

\[
\mathcal{R} = \Phi_v + \Phi_s = \int_\Omega dV \left[ \frac{1}{4} \eta \left( \partial_i v_j + \partial_j v_i \right)^2 \right] + \int_{\partial \Omega} dS \left[ \frac{1}{2} \beta \vec{v}^2 \right].
\]  

Combining the principle of least energy dissipation with the incompressibility condition, we have \( \delta \left[ \mathcal{R} - \int_\Omega dV \pi \partial_i v_i \right] = 0 \) for any \( \vec{v}(\vec{r}) \rightarrow \vec{v}(\vec{r}) + \delta \vec{v}(\vec{r}) \), with \( \pi \) being the Lagrange multiplier. The Euler-Lagrange equations are the Stokes equation

\[
-\nabla \pi + \nabla \cdot \left[ \eta \left( \nabla \vec{v} + \nabla \vec{v}^T \right) \right] = 0
\]

in the bulk region, and the Navier boundary condition

\[
\hat{n} \cdot \hat{\sigma}^{\text{vis}} \cdot \hat{T} + \beta \vec{v}^{\text{slip}} = 0
\]

at the solid boundary, where \( \hat{\sigma}^{\text{vis}} \equiv \eta \left( \nabla \vec{v} + \nabla \vec{v}^T \right) \) is the viscous stress tensor, and \( \hat{T} \equiv \hat{T} - \hat{n} \hat{n} \) with \( \hat{n} \) being the outward pointing (from fluid into solid) unit vector normal to \( \partial \Omega \). Note that the Lagrange multiplier \( \pi \) is the pressure. The total stress is \( \hat{\sigma} \equiv -\pi \hat{T} + \hat{\sigma}^{\text{vis}} \).
Prior to Onsager's general work, there existed a few specific reciprocal relations studied by Lord Kelvin and Helmholtz. In fluid dynamics, the hydrodynamic reciprocal relations, known as the Lorentz reciprocal theorem, are also regarded as a special form of Onsager's reciprocal relations. Consider an incompressible Stokes flow in a region $\Omega$ with a solid boundary $\partial \Omega$. The velocity field $\vec{v}(\vec{r})$ is governed by the Stokes equation (12), with the no-slip boundary condition at $\partial \Omega$. Suppose that in the same system, two velocity fields $\vec{v}^{(1)}$ and $\vec{v}^{(2)}$ are both the solutions to Eq. (12), with their corresponding stress fields denoted by $\sigma^{(1)}$ and $\sigma^{(2)}$, respectively. The Lorentz reciprocal theorem states that

$$\int_{\partial \Omega} d\vec{S} \hat{n} \cdot \sigma^{(1)} \cdot \vec{v}^{(2)} = \int_{\partial \Omega} d\vec{S} \hat{n} \cdot \sigma^{(2)} \cdot \vec{v}^{(1)},$$

where $\hat{n}$ is the outward pointing (from fluid into solid) unit vector normal to $\partial \Omega$. The proof is as follows. The left hand side of Eq. (14) can be expressed as

$$\int_{\partial \Omega} d\vec{S} \hat{n} \cdot \sigma^{(1)} \cdot \vec{v}^{(2)} = \int_{\Omega} dV \nabla \cdot (\sigma^{(1)} \cdot \vec{v}^{(2)})$$

$$= \int_{\Omega} dV \left( \nabla \cdot \sigma^{(1)} \cdot \vec{v}^{(2)} + \sigma^{(1)} : \nabla \vec{v}^{(2)} \right)$$

$$= \int_{\Omega} dV \left[ -p^{(1)} \delta_{ij} \partial_i v_j^{(2)} + \frac{\eta}{2} \left( \partial_i v_j^{(1)} + \partial_j v_i^{(1)} \right) \left( \partial_i v_j^{(2)} + \partial_j v_i^{(2)} \right) \right],$$

where the Stokes equation, $\nabla \cdot \vec{v} = 0$, and the symmetry of $\sigma$ are used. It is readily seen that the right hand side of of Eq. (14) leads to the same expression. Furthermore, the Lorentz reciprocal theorem (14) can be expressed as

$$F_k^{(1)} \dot{x}_k^{(2)} = F_k^{(2)} \dot{x}_k^{(1)},$$

where $\dot{x}_k$ are the generalized velocities of the solid objects and $F_k$ are the generalized dissipative forces conjugate to $\dot{x}_k$. Note that the no-slip boundary condition is applied to move from $\vec{v}$ of the fluid to $\dot{x}_k$ of the solid. Due to the linearity of the Stokes flows, we have the linear dependence of the forces on the rates:

$$F_k = \zeta_{kl} \dot{x}_l,$$
where the friction coefficients $\zeta_{kl}$ form a positive definite matrix. It follows from Eq. (16) that the Lorentz reciprocal theorem can be expressed as

$$\zeta_{kl} = \zeta_{lk},$$

meaning that the matrix formed by the friction coefficients $\zeta_{kl}$ is symmetric.

In the above discussion, the Lorentz reciprocal theorem expressed in Eqs. (16) and (18) is derived from the Stokes equation and the no-slip boundary condition. We have already shown that the Stokes equation (12) and the Navier boundary condition (13) can be simultaneously obtained from the principle of least energy dissipation. It is therefore expected that the hydrodynamic reciprocal relations can be generalized to describe the Stokes flows with the Navier boundary condition.

Consider the same system with the Navier boundary condition. The velocity of the solid boundary $\partial \Omega$ is denoted by $\vec{W}$. From the Navier boundary condition (13), we readily obtain

$$\int_{\partial \Omega} dS \hat{n} \cdot \sigma^{\leftrightarrow} \cdot \vec{v}_{\text{slip}} = \int_{\partial \Omega} dS \hat{n} \cdot \sigma^{\leftrightarrow} \cdot \vec{W}.$$

Meanwhile, Eq. (14) still holds. Note that $\vec{W} = \vec{v} - \vec{v}_{\text{slip}}$ on $\partial \Omega$. By combining Eqs. (14) and (19), we obtain the generalized form of the hydrodynamic reciprocal relations

$$\int_{\partial \Omega} dS \hat{n} \cdot \sigma^{\leftrightarrow} \cdot \vec{W} = \int_{\partial \Omega} dS \hat{n} \cdot \sigma^{\leftrightarrow} \cdot \vec{V}.$$

Note that the no-slip limit is obtained as $\beta \to \infty$ with $\vec{W} = \vec{v}$ on $\partial \Omega$. With the Lorentz reciprocal theorem generalized from Eq. (14) to (20), it can be further expressed as Eq. (16), which results in the symmetry in Eq. (18). We emphasize that in the presence of boundary slip, we need Eq. (20) in order to arrive at Eqs. (16) and (18). It is remarkable that the reciprocal symmetry is preserved in the Stokes flows with the Navier slip condition.

To use Eq. (18) for the present study, we consider the solid boundary $\partial \Omega$ consisting of the surfaces of $N$ rigid bodies $\partial \Omega^i$ ($i = 1, \ldots, N$), each in a motion described by the translational velocity $\vec{V}^i$ and the angular velocity $\vec{\omega}^i$. The solid velocity at $\vec{r}$ on $\partial \Omega^i$ can be expressed as

$$\vec{W} (\vec{r}) = \vec{V}^i + \vec{\omega}^i \times \delta \vec{r}^i,$$

where $\delta \vec{r}^i$ is measured relative to the center of mass of the $i$-th rigid body. Then we have

$$\int_{\partial \Omega} dS \hat{n} \cdot \sigma^{\leftrightarrow} \cdot \vec{W} = \sum_{i=1}^{N} \left( \int_{\partial \Omega^i} dS \hat{n} \cdot \sigma^{\leftrightarrow} \cdot \vec{V}^i \right) + \sum_{i=1}^{N} \left[ \int_{\partial \Omega^i} dS \delta \vec{r}^i \times (\hat{n} \cdot \sigma^{\leftrightarrow}) \right] \cdot \vec{\omega}^i,$$
where \( \int_{\partial \Omega_i} dS \hat{n} \cdot \tilde{\sigma} \) is the total force by the \( i \)-th rigid body on the fluid, and \( \int_{\partial \Omega_i} dS \delta \hat{r} \times (\hat{n} \cdot \tilde{\sigma}) \) is the total torque by the \( i \)-th rigid body on the fluid. This leads to a specific form of Eq. (16), in which \( \tilde{V}^i \) and \( \tilde{\omega}^i \) \((i = 1, \ldots, N)\) are the generalized velocities of the rigid bodies \( \dot{x}_k \), and \( \int_{\partial \Omega_i} dS \hat{n} \cdot \tilde{\sigma} \) and \( \int_{\partial \Omega_i} dS \delta \hat{r} \times (\hat{n} \cdot \tilde{\sigma}) \) are their conjugate generalized forces \( F_k \).

Finally we emphasize that the Lorentz reciprocal theorem is valid only when the slip length \( l_s = \eta/\beta \) is a material constant, which makes the Navier boundary condition linear.

D. Nematic liquid crystals

The Leslie-Ericksen hydrodynamic theory for nematic liquid crystals gives the dissipative stress tensor \( \tilde{\sigma} \) and the torque density by the director on the fluid \( \tilde{\Gamma} \) as

\[
\tilde{\sigma} = \alpha_1 \left( \tilde{n} \tilde{n} : \nabla \tilde{A} \right) \tilde{n} \tilde{n} + \alpha_2 \tilde{n} \tilde{N} + \alpha_3 \tilde{N} \tilde{n} + \alpha_4 \tilde{A} + \alpha_5 \left( \tilde{n} \cdot \tilde{A} \right) \tilde{n} + \alpha_6 \left( \tilde{n} \cdot \tilde{A} \right) \tilde{n},
\]

\[
\tilde{\Gamma} = \tilde{n} \times \left( \gamma_1 \tilde{N} + \gamma_2 \tilde{A} \cdot \tilde{n} \right),
\]

where \( \alpha_i \) \((i = 1, \ldots, 6)\) are phenomenological parameters, \( \tilde{n} \) is the director, \( \tilde{A} \equiv \frac{1}{2} \left( \nabla \tilde{v} + \nabla \tilde{v}^T \right) \) is the rate-of-strain tensor of flow, and \( \tilde{N} \equiv \tilde{n} - \tilde{v} \times \tilde{n} = (\tilde{\omega} - \tilde{v}) \times \tilde{n} \) is the velocity of the director relative to the fluid, with \( \tilde{\omega} \) being the angular velocity of the director and \( \tilde{v} \equiv \frac{1}{2} \nabla \times \tilde{v} \) being the angular velocity of the fluid. In addition, \( \gamma_1 \) and \( \gamma_2 \) are given by \( \gamma_1 = \alpha_3 - \alpha_2 \) and \( \gamma_2 = \alpha_6 - \alpha_5 \). Only five of the six \( \alpha_i \) \((i = 1, \ldots, 6)\) parameters are independent because of the Parodi relation

\[
\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5,
\]

which results from the Onsager reciprocal relations.

E. Cross coupling in gas flows in micro-channels

In rarefied gases, mass and heat transport processes interfere with each other, leading to the mechano-caloric effect and thermo-osmotic effect, which are of interest to both theoretical study and practical applications. We employ the unified gas-kinetic scheme to investigate these cross coupling effects in gas flows in micro-channels. Our numerical simulations cover channels of planar surfaces and also channels of ratchet surfaces, with Onsager’s reciprocal relation verified for both cases. For channels of planar surfaces, simulations are performed in a wide range of Knudsen number and our numerical results show good agreement with
the literature results. For channels of ratchet surfaces, simulations are performed for both
the slip and transition regimes and our numerical results not only confirm the theoretical
prediction [Phys. Rev. Lett. 107, 164502 (2011)] for Knudsen number in the slip regime but
also show that the off-diagonal kinetic coefficients for cross coupling effects are maximized
at a Knudsen number in the transition regime. Finally, a preliminary optimization study is
carried out for the geometry of Knudsen pump based on channels of ratchet surfaces.

In a closed system out of equilibrium, the rate of entropy production can be expressed as

$$\frac{dS}{dt} = \sum_{i=1}^{N} J_i X_i,$$

(25)

where $S$ is the entropy, $J_i$ are the thermodynamic fluxes, and $X_i$ are the conjugate ther-
modynamic forces. For small deviation away from equilibrium, we have the linear relations
between $J_i$ and $X_i$:

$$J_i = \sum_{j=1}^{N} L_{ij} X_j,$$

(26)

where $L_{ij}$ are the kinetic coefficients. Onsager’s reciprocal relations state that $L_{ij}$ and $L_{ji}$
are equal as a result of microscopic reversibility. Starting from the Gibbs equation, the
thermodynamic fluxes and forces can be identified for gas flows, and the corresponding
constitutive equations can be derived.

A schematic illustration of the cross coupling in a channel of planar surfaces can be
found in figure 2, where a long channel is confined by two parallel solid plates separated by
a distance $H$ and connected with two reservoirs. The left reservoir is maintained at pressure
$p_0 - \Delta p/2$ and temperature $T_0 - \Delta T/2$ while the right reservoir is maintained at $p_0 + \Delta p/2$
and $T_0 + \Delta T/2$. We use $\Delta p < 0$ and $\Delta T > 0$ in our simulations, with $|\Delta p/p_0| \ll 1$ and
$|\Delta T/T_0| \ll 1$ to ensure the linear response. Usually, a mass flux to the right is generated
by the pressure gradient due to $\Delta p < 0$ and a heat flux to the left is generated by the
temperature gradient due to $\Delta T > 0$. For rarefied gas, however, $\Delta p$ also contributes to the
heat flux and $\Delta T$ also contributes to the mass flux. These cross coupling effects are called
the mechano-caloric effect and thermo-osmotic effect respectively.

For a single-component gas, the rate of entropy production can be expressed as

$$\frac{dS}{dt} = J_M \Delta \left( -\frac{\nu}{T} \right) + J_E \Delta \left( \frac{1}{T} \right),$$

(27)

where $\nu$ is the chemical potential per unit mass, $J_E$ and $J_M$ are the energy flux and mass
flux from the left reservoir to the right reservoir, and $\Delta$ means the quantity on the right
minus the quantity on the left. Here $\nu$ and $J_E$ can be written as

$$\nu = h - Ts,$$

$$J_E = J_Q + hJ_M,$$

where $s$ and $h$ are the entropy and enthalpy per unit mass, and $J_Q$ is the heat flux. Together with the Gibbs-Duhem equation

$$d\nu = -sdT + dp/\rho,$$

where $\rho$ is the mass density. Equation (27) becomes

$$\frac{dS}{dt} = -\frac{1}{\rho T} J_M \Delta p - \frac{1}{T^2} J_Q \Delta T.$$  (31)

According to equation (31), the thermodynamic forces and fluxes are connected in the form of

$$\begin{bmatrix} J_M \\ J_Q \end{bmatrix} = \begin{bmatrix} L_{MM} & L_{MQ} \\ L_{QM} & L_{QQ} \end{bmatrix} \begin{bmatrix} -\rho_0^{-1} T_0^{-1} \Delta p \\ -T_0^{-2} \Delta T \end{bmatrix},$$  (32)

with

$$L_{MQ} = L_{QM},$$  (33)

due to Onsager’s reciprocal relations. The detailed mechanism may vary with geometric configuration and rarefaction. Here and throughout the paper, the subscript ‘0’ denotes the reference state from which various deviations (in pressure, temperature, etc) are measured.

In the free molecular regime and with specular reflection on plates, the gas molecules travel ballistically from one side to the other and the distribution function at any point can be treated as a combination of two half-space Maxwellians from the two reservoirs. The kinetic coefficients in equation (32) can be analytically derived in this case, given by

$$\begin{bmatrix} L_{MM} & L_{MQ} \\ L_{QM} & L_{QQ} \end{bmatrix} = \frac{H\rho_0 T_0}{4} \sqrt{\frac{8k_B T_0}{\pi m}} \begin{bmatrix} \rho_0/p_0 & -1/2 \\ -1/2 & 9\rho_0/4\rho_0 \end{bmatrix},$$  (34)

where $k_B$ is the Boltzmann constant and $m$ is the molecular mass.

If the temperature gradient is imposed on the plates and the gas molecules are diffusely reflected, then the mass flux due to the temperature gradient is generated by thermal creep.
on the plates. The kinetic coefficients in this case have been calculated by several authors using different methods. Assuming the length to height ratio of the channel is fixed and noting $\rho \lambda = \text{constant}$ and $\mu \propto \rho^0 T^{1/2}$ for hard-sphere molecules, the average velocity $\bar{U}$ induced by thermal creep can be estimated from the Maxwell slip boundary condition,

$$\bar{U} \sim \frac{\mu_0}{\rho_0 T_0} \nabla T \propto \text{Kn} \frac{\Delta T}{\sqrt{T_0}},$$

where $\lambda$ is the mean free path, $\mu$ is the dynamic viscosity independent of the density, and $\text{Kn} = \lambda_0 / H$ is the Knudsen number. In later sections, we will show that $L_{MQ}$ and $L_{QM}$ are equal and increase with the increasing Kn.

**F. Cross coupling in a mixture of fluids**

1. **Ideal fluids**

The continuity equation is given by

$$\frac{\partial}{\partial t} \rho + \nabla \cdot (\rho \bar{v}) = 0$$

where $\rho$ is the mass density. The momentum equation is given by

$$\frac{\partial}{\partial t} (\rho \bar{v}) + \nabla \cdot (\rho \bar{v} \bar{v}) = \rho \frac{d}{dt} \bar{v} = -\nabla p$$

where $\frac{d}{dt} \bar{v} \equiv \frac{\partial}{\partial t} \bar{v} + \bar{v} \cdot \nabla \bar{v}$ is the rate of change of the velocity of a given fluid particle, and $p$ is the pressure. This is Euler’s equation and is one of the fundamental equations of fluid dynamics. The motion of an ideal fluid is adiabatic and in adiabatic motion the entropy of any fluid particle remains constant as the particle moves about in space. Therefore, the entropy equation is given by

$$\frac{\partial}{\partial t} (\rho s) + \nabla \cdot (\rho s \bar{v}) = 0$$

where $s$ is the entropy per unit mass.

Now we are ready to derive the energy equation. The kinetic energy density is $\frac{1}{2} \rho \bar{v}^2$ and the internal energy density is $\rho \varepsilon$ where $\varepsilon$ is the internal energy per unit mass. Using the continuity equation and the momentum equation, we have

$$\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \bar{v}^2 \right) = -\bar{v} \cdot \nabla p - \nabla \cdot \left[ \left( \frac{1}{2} \rho \bar{v}^2 \right) \bar{v} \right]$$
for the kinetic energy. As to the internal energy, we have \( \frac{d}{dt}(\rho\varepsilon) = \rho T \frac{d}{dt}s + h \frac{d}{dt}\rho = -\rho \bar{v} \cdot \nabla s - h \nabla \cdot (\rho \bar{v}) \)

by use of the entropy equation and the continuity equation. Putting the two energies together, we have

\[
\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \bar{v}^2 + \rho \varepsilon \right) = -\bar{v} \cdot \nabla p - \nabla \cdot \left[ \left( \frac{1}{2} \rho \bar{v}^2 \right) \bar{v} \right] - \rho T \bar{v} \cdot \nabla s - h \nabla \cdot (\rho \bar{v}).
\]

To proceed, we note that from thermodynamics we have \( dh = T ds + \frac{1}{\rho} dp, \rho dh = \rho T ds + dp, \) and hence \( \rho \nabla h = \rho T \nabla s + \nabla p. \) It follows that \( \frac{\partial}{\partial t} \left( \frac{1}{2} \rho \bar{v}^2 + \rho \varepsilon \right) \) can be expressed as

\[
\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \bar{v}^2 + \rho \varepsilon \right) = -\nabla \cdot \left[ \left( \frac{1}{2} \rho \bar{v}^2 + \rho h \right) \bar{v} \right],
\]

which shows that the energy flux is given by \( \left( \frac{1}{2} \rho \bar{v}^2 + \rho h \right) \bar{v}. \) Note that we have \( \rho h \bar{v} \) rather than \( \rho \varepsilon \bar{v} \) in the energy flux because the work done by pressure forces is to be included.

2. Viscous fluids

Now we turn to viscous fluids. The continuity equation remains unchanged and the momentum equation is given by

\[
\frac{\partial}{\partial t} (\rho \bar{v}) + \nabla \cdot (\rho \bar{v} \bar{v}) = \rho \frac{d}{dt} \bar{v} = -\nabla p + \nabla \cdot \bar{\sigma}',
\]

where \( \bar{\sigma}' \) is the viscous stress tensor. The energy equation is given by

\[
\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \bar{v}^2 + \rho \varepsilon \right) = -\nabla \cdot \left[ \left( \frac{1}{2} \rho \bar{v}^2 + \rho h \right) \bar{v} \right] + \nabla \cdot \left( \bar{\sigma}' \cdot \bar{v} \right) - \nabla \cdot \bar{q}
\]

where \( \bar{q} \) is the heat flux. Note that the energy equation for viscous fluids takes into account the work done by viscous forces and the thermal conduction, which are absent in ideal fluids.

The entropy equation can be derived by use of the above equations and thermodynamic relations. The derivation is straightforward and the procedure can be outlined as follows. Using the continuity equation and the momentum equation, we can obtain an equation for \( \frac{\partial}{\partial t} \left( \frac{1}{2} \rho \bar{v}^2 \right). \) Combining the energy equation and the equation for \( \frac{\partial}{\partial t} \left( \frac{1}{2} \rho \bar{v}^2 \right), \) we can obtain an equation for \( \frac{\partial}{\partial t} (\rho \varepsilon): \)

\[
\frac{\partial}{\partial t} (\rho \varepsilon) = -\nabla \cdot (\rho h \bar{v}) + \bar{\sigma}' : \nabla \bar{v} - \nabla \cdot \bar{q} + \bar{v} \cdot \nabla p.
\]
Combining the above equation with \( \frac{\partial}{\partial t} (\rho \varepsilon) = \rho T \frac{\partial}{\partial t} s + h \frac{\partial}{\partial t} \rho \), we obtain

\[
\rho T \frac{\partial}{\partial t} s = \tau_{\varepsilon} : \nabla \vec{v} - \nabla \cdot \vec{q} + \vec{v} \cdot \nabla p - \rho \vec{v} \cdot \nabla h,
\]

which becomes

\[
\rho T \left( \frac{\partial}{\partial t} s + \vec{v} \cdot \nabla s \right) = \tau_{\varepsilon} : \nabla \vec{v} - \nabla \cdot \vec{q},
\]

with the help of \(-\rho \nabla h + \nabla p = -\rho T \nabla s\). Finally we obtain the entropy equation

\[
\frac{\partial}{\partial t} (\rho s) + \nabla \cdot (\rho \vec{v} \vec{v}) = -\nabla \cdot \left( \vec{q} \right) + \frac{1}{T} \tau_{\varepsilon} : \nabla \vec{v} + \vec{q} \cdot \nabla \frac{1}{T},
\]

where \( \vec{q} \) is the entropy flux, \( \frac{1}{T} \tau_{\varepsilon} : \nabla \vec{v} \) is the rate of entropy production due to viscous dissipation, and \( \vec{q} \cdot \nabla \frac{1}{T} \) is the rate of entropy production due to thermal conduction.

3. A mixture of fluids

Let us start from the continuity equations of two miscible components, with one labeled by the subscript “1” and the other labeled by the subscript “2”. They read

\[
\frac{\partial}{\partial t} \rho_1 + \nabla \cdot (\rho_1 \vec{v}_1) = 0
\]

and

\[
\frac{\partial}{\partial t} \rho_2 + \nabla \cdot (\rho_2 \vec{v}_2) = 0,
\]

in which \( \vec{v}_i \) (\( i = 1, 2 \)) is the velocity of a particular species. The mass density \( \rho \) and velocity \( \vec{v} \) of the mixture are defined by \( \rho = \rho_1 + \rho_2 \) and \( \rho \vec{v} = \rho_1 \vec{v}_1 + \rho_2 \vec{v}_2 \). Physically, \( \vec{v} \) is the mass-averaged velocity which is a field variable that enters into the hydrodynamic momentum equation. The local relative concentration \( c \) is defined by \( \rho c = \rho_1 - \rho_2 \). It follows that \( \rho c \vec{v} \) equals \( (\rho_1 - \rho_2) \vec{v} \).

Adding the continuity equations for the two components gives the continuity equation

\[
\frac{\partial}{\partial t} \rho + \nabla \cdot (\rho \vec{v}) = 0
\]

for \( \rho \). The diffusive flux \( \vec{j} \) is defined through the equation \( \rho_1 \vec{v}_1 - \rho_2 \vec{v}_2 = \rho c \vec{v} + \vec{j} \). It follows that \( \vec{j} \) is given by \( \vec{j} = \rho_1 (\vec{v}_1 - \vec{v}) - \rho_2 (\vec{v}_2 - \vec{v}) \). Note that \( \rho_1 (\vec{v}_1 - \vec{v}) + \rho_2 (\vec{v}_2 - \vec{v}) = 0 \) — the diffusion discussed here is defined relative to the motion of the center of mass of a fluid.
element. Rewriting the difference between the continuity equations for the two components as

$$\frac{\partial}{\partial t} (\rho c) + \nabla \cdot \left( \rho c \vec{v} + \vec{j} \right) = 0,$$

we obtain

$$\rho \left( \frac{\partial}{\partial t} c + \vec{v} \cdot \nabla c \right) = \frac{d}{dt} c = -\nabla \cdot \vec{j}.$$

By introducing $\mu$ as an appropriately defined chemical potential of the mixture, we have thermodynamic equations

$$d (\rho \varepsilon) = \rho T ds + h d\rho + \rho \mu d c$$

and

$$\rho dh = \rho T ds + dp + \rho \mu dc$$

for $\varepsilon$ and $h$. They will be used when we derive the entropy equation from the energy equation.

To proceed, we employ the momentum equation

$$\frac{\partial}{\partial t} (\rho \vec{v}) + \nabla \cdot (\rho \vec{v} \vec{v}) = \rho \frac{d}{dt} \vec{v} = -\nabla p + \nabla \cdot \vec{\sigma}$$

and the energy equation

$$\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \vec{v}^2 + \rho \varepsilon \right) = -\nabla \cdot \left[ \left( \frac{1}{2} \rho \vec{v}^2 + \rho h \right) \vec{v} \right] + \nabla \cdot \left( \vec{\sigma} : \nabla \vec{v} - \nabla \cdot \vec{q} + \vec{v} \cdot \nabla p \right),$$

which look the same as those used for viscous fluids of one component. We would like to point out that while $\vec{\sigma}'$ is still the viscous stress tensor, the physical meaning of $\vec{q}$ is not clear at the moment — it is expected to represent the total energy flux due to thermal conduction and diffusion. This is to be clarified by the explicit form of the entropy equation.

In order to derive the entropy equation, we first combine the continuity equation and the momentum equation to obtain an equation for $\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \vec{v}^2 \right)$. We then combine the energy equation and the equation for $\frac{\partial}{\partial t} \left( \frac{1}{2} \rho \vec{v}^2 \right)$ to obtain an equation for $\frac{\partial}{\partial t} (\rho \varepsilon)$:

$$\frac{\partial}{\partial t} (\rho \varepsilon) = -\nabla \cdot (\rho v \vec{v}) + \vec{\sigma}' : \nabla \vec{v} - \nabla \cdot \vec{q} + \vec{v} \cdot \nabla p.$$

Combining the above equation with $\frac{\partial}{\partial t} (\rho \varepsilon) = \rho T \frac{\partial}{\partial t} s + h \frac{\partial}{\partial t} \rho + \rho \mu \frac{\partial}{\partial t} c$ from thermodynamics, we obtain

$$\rho T \frac{\partial}{\partial t} s = \vec{\sigma}' : \nabla \vec{v} - \nabla \cdot \vec{q} + \vec{v} \cdot \nabla p - \rho \vec{v} \cdot \nabla h - \rho \mu \frac{\partial}{\partial t} c,$$

which becomes

$$\rho T \left( \frac{\partial}{\partial t} s + \vec{v} \cdot \nabla s \right) = \vec{\sigma}' : \nabla \vec{v} - \nabla \cdot \vec{q} - \rho \mu \left( \frac{\partial}{\partial t} c + \vec{v} \cdot \nabla c \right),$$
with the help of $-\rho \nabla h + \nabla p = -\rho T \nabla s - \rho \mu \nabla c$. Using $\rho \left( \frac{\partial}{\partial t} c + \vec{v} \cdot \nabla c \right) = -\nabla \cdot \vec{j}$, we have

$$\rho T \left( \frac{\partial}{\partial t} s + \vec{v} \cdot \nabla s \right) = \dot{\varepsilon} : \nabla \vec{v} - \nabla \cdot \vec{q} + \mu \nabla \cdot \vec{j} = \dot{\varepsilon} : \nabla \vec{v} - \nabla \cdot \left( \vec{q} - \mu \vec{j} \right) - \vec{j} \cdot \nabla \mu,$$

which gives the entropy equation

$$\frac{\partial}{\partial t} (\rho s) + \nabla \cdot (\rho s \vec{v}) = -\nabla \cdot \left( \frac{\vec{q} - \mu \vec{j}}{T} \right) + \pi,$$

in which $\frac{\vec{q} - \mu \vec{j}}{T}$ is the entropy flux and $\pi$ is the rate of entropy production per unit volume, given by

$$\pi = \frac{1}{T} \dot{\varepsilon} : \nabla \vec{v} + \left( \vec{q} - \mu \vec{j} \right) \cdot \nabla \frac{1}{T} - \vec{j} \cdot \nabla \mu T.$$

Here $\frac{1}{T} \dot{\varepsilon} : \nabla \vec{v}$ is the rate of entropy production due to viscous dissipation, and $\left( \vec{q} - \mu \vec{j} \right) \cdot \nabla \frac{1}{T} - \vec{j} \cdot \nabla \mu$ is the rate of entropy production due to thermal conduction and diffusion. The latter can be written as

$$\left( \vec{q} - \mu \vec{j} \right) \cdot \left( -\nabla \frac{1}{T^2} \right) + \vec{j} \cdot \left( -\nabla \mu T \right)$$

in which $\left( \vec{q} - \mu \vec{j} \right)$ and $\vec{j}$ are the fluxes associated with thermal conduction and diffusion, and $-\nabla \frac{1}{T^2}$ and $-\nabla \mu T$ are the conjugate forces. Now we are ready to write down the constitutive equations

$$\vec{j} = -\alpha T \left( \nabla \mu \right) - \beta T^2 \left( \nabla \frac{1}{T^2} \right),$$

$$\vec{q} - \mu \vec{j} = -\delta T \left( \nabla \mu \right) - \gamma T^2 \left( \nabla \frac{1}{T^2} \right)$$

with the reciprocal relation $\beta T^2 = \delta T$ for the cross coupling between thermal conduction and diffusion.

**FIGURES**
FIG. 1. A closed system made up of two interconnected subsystems.

\[ p_0 - \Delta p/2 \quad T_0 - \Delta T/2 \]
\[ p_0 + \Delta p/2 \quad T_0 + \Delta T/2 \]

mass flux \( J_M \)

heat flux \( J_Q \)

(\( \Delta p < 0 \))

(\( \Delta T > 0 \))

FIG. 2. A schematic illustration of the cross coupling in a channel of planar surfaces.