Chapter 1

Onsager’s Variational Principle in Soft Matter Dynamics

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It is shown that Onsager’s variational principle gives us a unified framework in discussing various dynamics of soft matter such as diffusion, rheology and their coupling. The variational principle gives kinetic equations which satisfy Onsager’s reciprocal relation. With many examples, it is shown that the kinetic equations are usually written as non-linear partial differential equations for state variables and can describe various non-linear and non-equilibrium phenomena in soft matter. The physics underlying the variational principle is discussed.

1. Introduction

Soft matter is characterized by strongly non-linear and non-equilibrium responses to external fields. For example, polymer solutions show various non-linear viscoelastic behaviors such as shear thinning, stress relaxation and Weissenberg effect etc.1–3 Liquid crystals show dramatic change of their optical properties under weak external fields (of mechanical, electrical or magnetic nature).4 Gels shows various spatial patterns due to the coupled effects of solvent permeation and gel deformation.5

Various equations have been proposed to describe such phenomena. Examples are the Smoluchowskii equation in the dynamics of polymer solutions,1–3 Leslie-Ericksen equation in the dynamics of liquid crystals,4 and the gel-dynamics equations.6 These equations have been, so far, proposed for each problems. In this paper, I will show that these equations are derived from a common framework, the Onsager’s variational principle.

The variational principle was proposed by Onsager in his celebrated paper on the reciprocal relation in the kinetic equations for irreversible

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As Onsager stated in the paper, the variational principle is an extension of Rayleigh’s least energy dissipation principle. The least energy dissipation principle is known as the principle in determining the steady state in linear systems such as viscous flow in Newtonian fluid, and electric current in Ohmic devices. The Onsager’s variational principle which will be discussed in this paper, however, refers to a principle slightly different from this (although they are connected). It is a principle to derive the time evolution equation in irreversible processes. The equations derived from the variational principle is equivalent to Onsager’s kinetic equation.

Although the variational principle, or the kinetic equations, of Onsager represents a linear relation between forces and fluxes, the derived equations are usually non-linear time evolution equations and can describe non-linear phenomena. It will be shown that Onsager’s variational principle gives us various merits, not only to simplify calculations, but also to give us new insight to understand the problem. The purpose of this paper is to explain and to demonstrate these merits. Earlier version of this work was published in.

The construction of this paper is as follows. First, the least energy dissipation principle in hydrodynamics is discussed since I think that it is the earlier version of Onsager’s principle and includes the essential physics underlying Onsager’s theory. Second, Onsager’s variational principle is discussed in a general (and somewhat abstract) form. After this, various applications of Onsager’s principle are discussed. These sections will demonstrate the convenience and the usefulness of Onsager’s variational principle.

2. Particle Motion in Viscous Fluid

2.1. Stokesian hydrodynamics

Consider particles moving in viscous fluid subject to some potential forces, for example, particles sedimenting in a gravitational field, or particles attracting each other via interparticle potential. For small particle of colloidal dimension, one can assume that the velocity field \( \mathbf{v}(\mathbf{r}) \) of the fluid surrounding the particle obeys the Stokes equation:

\[
\eta \nabla^2 \mathbf{v} = \nabla p, \quad \nabla \cdot \mathbf{v} = 0
\]

where \( \eta \) is the viscosity of the surrounding fluid and \( p \) is the pressure. The Stokes equation is the limit of zero Reynolds number of Navier Stokes
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The Stokes equation, and represents the situation that the fluid flow is in a steady state for given boundary condition. The first equation of the Stokes equation represents the force balance for each fluid element, and the second equation represents the incompressible condition for the fluid.

In the Stokes limit, the hydrodynamic drag acting on particles is proportional to the particle velocity. This gives a variational principle which we shall refer to as the hydrodynamic variational principle.

![Diagram of force balance of a sphere moving in a potential field](image)

Fig. 1. Force balance of a sphere moving in a potential field $U(x)$.

Let us consider a very simple situation, i.e., a one-dimensional motion of a spherical particle in a viscous fluid driven by some potential field $U(x)$ (see Fig.1), where $x$ stands for the position of the particle. Since the inertia effect is assumed to be negligibly small in the Stokesian hydrodynamics, the particle motion is determined by the condition that the total force acting on the particle is zero. In the present problem, two forces are acting on the particle. One is the potential force given by

$$F(x) = -\frac{\partial U}{\partial x}$$

and the other is the frictional force which is proportional to the particle velocity $\dot{x}$

$$F_H = -\zeta \dot{x}$$

The friction coefficient $\zeta$ can be calculated by the Stokes equation, and is given by $\zeta = 6\pi \eta a$ where $a$ is the radius of the particle.

The force balance equation is then written as

$$\zeta \ddot{x} = -\frac{\partial U}{\partial x}$$

This equation describes the time evolution of the particle position $x(t)$:

$$\frac{dx}{dt} = -\frac{1}{\zeta} \frac{\partial U}{\partial x}$$
Equation (4) can be cast in the form of a variational principle. If one defines a function \( R(\dot{x}) \) by
\[
R(\dot{x}) = \frac{1}{2} \zeta \dot{x}^2 + \frac{\partial U}{\partial x} \dot{x}
\] (6)

Equation (4) is equivalent to the condition that \( R \) be minimized with respect to \( \dot{x} \), i.e., \( \partial R / \partial \dot{x} = 0 \). The function \( R \) is called Rayleighian.

The Rayleighian consists of two terms. The first term
\[
\Phi(\dot{x}) = \frac{1}{2} \zeta \dot{x}^2
\] (7)
is called the energy dissipation function. When a particle moves with velocity \( \dot{x} \) in a viscous fluid, it does a work to the fluid per unit time \(-F_H \dot{x} = \zeta \dot{x}^2\), which is immediately dissipated into heat. Therefore the energy dissipation function \( \Phi(\dot{x}) \) stands for the half of the energy dissipation rate (the energy dissipated in the viscous fluid per unit time) when the particle moves with velocity \( \dot{x} \). (The coefficient 1/2 is put by historical reason.)

The second term in the Rayleighian represents the rate of the potential energy change when the particle moves with velocity \( \dot{x} \). We shall write this term as \( \dot{U}(\dot{x}) \):
\[
\dot{U}(\dot{x}) = \frac{\partial U}{\partial x} \dot{x}
\] (8)

Given \( \Phi \) and \( \dot{U} \), the Rayleighian is written as
\[
R(\dot{x}) = \Phi(\dot{x}) + \dot{U}(\dot{x})
\] (9)
and the actual velocity \( \dot{x} \) is determined by the condition \( \partial R / \partial \dot{x} = 0 \).

2.2. Hydrodynamic reciprocal relation

The above rewriting of the force balance equation into the variational principle is trivial. However, in more complex systems, the variational principle represents a non-trivial law in Stokesian hydrodynamics.

Consider a system of particles having many degrees of freedom, and let \( x_i \) \( (i = 1, 2, \ldots, f) \) be the set of variables describing the state of the system. For example, the state of a rigid particle is specified by six variables, three to specify the position, and the other three to specify the orientation. For \( N \) particle systems, \( 6N \) variables are needed.

Suppose that the state of the particles changes with rate \( \dot{x}_i \), then there will be a frictional force exerted on the particles by the surrounding fluid.
Let $F_{Hi}$ be the frictional force conjugate to $\dot{x}_i$ i.e., the work done to the fluid per unit time is written as

$$2\Phi = -\sum_i F_{Hi} \dot{x}_i$$

(10)

In the Stokesian hydrodynamics, the frictional force is always written as a linear function of $\dot{x}_i$:

$$F_{Hi} = -\sum_j \zeta_{ij} \dot{x}_j$$

(11)

The coefficients $\zeta_{ij}$ are called friction coefficients, and can be calculated by solving the Stokes equation (see Appendix A).

The friction coefficients $\zeta_{ij}$ have an important property: they are symmetric, and positive definite, i.e.,

$$\zeta_{ij} = \zeta_{ji},$$

(12)

and

$$\sum_{ij} \zeta_{ij} \dot{x}_i \dot{x}_j \geq 0 \quad \text{for any } \dot{x}_i$$

(13)

The proof of these relations is given in Appendix A.

The reciprocal relation (12) is not a trivial relation. For example, consider the motion of a rod-like particle caused by a force $F$ applied at the center of the particle. For rod-like particle, the velocity $V$ is in general not parallel to the force $F$. As it is shown in Fig.2(a), the force $F_x$ in $x$ direction causes a velocity component $V_y$ in $y$ direction, and as shown in Fig.2(b), the force $F_y$ causes a velocity component $V_x$. The reciprocal relation (12) indicates that $V_y/F_x$ is equal to $V_x/F_y$. This relation can be proven by symmetry argument for rod, but for a particle of general shape, validity of the relation $V_y/F_x = V_x/F_y$ is not obvious. For more complex shaped particles, the reciprocal relation gives more surprising result. As it is shown in Fig.2(c), a force $F$ acting on a helical particle causes a rotational angular velocity $\omega$ of the particle, and as shown in Fig.2(d), a torque $T$ causes a translational velocity $V$. The reciprocal relation indicates the equality $\omega/F = V/T$, which is quite non-trivial.

2.3. Hydrodynamic variational principle

Now consider that the motion of the particles is driven by a potential $U(x)$, then the potential force conjugate to $x_i$ is given by $F_i = -\partial U/\partial x_i$. There-
Fig. 2. Hydrodynamic reciprocal relation. Suppose that a force $F_x$ in $x$-direction causes the $y$ component velocity $V_y$ as in (a), then a force $F_y$ in $y$ direction causes a $x$ component velocity given by $V_x = (V_y/F_x)F_y$ as in (b). Suppose that a force $F$ causes a rotation of helical particle with angular velocity $\omega$ as in (c), then a torque $T$ causes a translational velocity $V = (\omega/F)T$ as in (d).

Therefore the force balance equation is written as

$$\sum_j \zeta_{ij} \dot{x}_j = -\frac{\partial U}{\partial x_i} \quad (14)$$

Let $(\zeta^{-1})_{ij}$ be the inverse of the matrix $\zeta_{ij}$, then Eq. (14) gives the following time evolution equation for $x_i$:

$$\frac{dx_i}{dt} = -\sum_j (\zeta^{-1})_{ij} \frac{\partial U}{\partial x_j} \quad (15)$$

Notice that $\zeta_{ij}$, $(\zeta^{-1})_{ij}$, and $U$ are functions of $x_i$. Therefore, Eq. (15) is, in general, rather complex non-linear equations for $x_i$.

Using the reciprocal relation (12), the time evolution equation (14) can be cast into a variational principle. Let $\Phi$ and $\dot{U}$ be defined by

$$\Phi = \frac{1}{2} \sum_{i,j} \zeta_{ij} \dot{x}_i \dot{x}_j \quad (16)$$

$$\dot{U} = \sum_i \frac{\partial U}{\partial x_i} \dot{x}_i \quad (17)$$

and the function $R$ be defined by

$$R = \Phi + \dot{U} = \frac{1}{2} \sum_{i,j} \zeta_{ij} \dot{x}_i \dot{x}_j + \sum_i \frac{\partial U}{\partial x_i} \dot{\tilde{x}}_i \quad (18)$$
then the force balance equation (14) is equivalent to the condition \( \partial R/\partial \dot{x}_i = 0 \), i.e., the velocity \( \dot{x}_i \) is determined by the condition that \( R \) be minimum with respect to \( \dot{x}_i \). This is the general form of the hydrodynamic variational principle.

It should be noted that the rewriting of the force balance equation (14) to the variational principle is justified only when the reciprocal relation \( (\zeta_{ij} = \zeta_{ji}) \) is satisfied.

3. Onsager’s Variational Principle

3.1. Onsager’s kinetic equation

Onsager showed that the above variational principle holds for general irreversible processes. Let \( x = (x_1, x_2, ...) \) be the set of variables describing the non-equilibrium state of the system, and let us assume that the evolution law of the state can be written in the form

\[
\frac{dx_i}{dt} = \sum_j L_{ij} \frac{\partial S(x)}{\partial x_j}
\]

where \( S(x) \) is the entropy of the system, and \( L_{ij} \) are the phenomenological kinetic coefficients. Equation (19) is called Onsager’s kinetic equation. Many equations known in physics and chemistry can be written in this form as it will be shown later. At this point, let us proceed assuming the validity of Eq. (19).

Using the time reversal symmetry in the fluctuation at equilibrium state, Onsager proved that the coefficients \( L_{ij} \) in Eq. (19) must be symmetric

\[
L_{ij} = L_{ji}
\]  

(20)

This reciprocal relation allows us to write the kinetic equation (19) in the form of a variational principle: the time evolution of the system is determined by minimizing

\[
\tilde{R} = \frac{1}{2} \sum_{i,j} (L^{-1})_{ij} \dot{x}_i \dot{x}_j - \frac{\partial S}{\partial x_i} \dot{x}_i
\]

(21)

This principle is called Onsager’s variational principle. The second term in Eq. (21) stands for the reversible entropy change i.e., the entropy change caused by infinitely slow process (the quasi-equilibrium processes). On the

\[\text{Here we are assuming that the state variables } x_i \text{ are invariant under time reversal transformation, and that there is no magnetic field.}\]
other hand, the first term stands for the half of of irreversible entropy change caused by a process having finite speed.

Onsager’s variational principle has a structure very similar to hydrodynamic variational principle. In fact, if the temperature of the system is constant, thermodynamic force $F_i$ conjugate to the variable $x_i$ is given by

$$F_i = -\frac{\partial A}{\partial x_i} = T \frac{\partial S}{\partial x_i} \quad (22)$$

where $A$ is the free energy of the system and Onsager’s variational principle is written in the same form as the hydrodynamic variational principle.

$$R = \frac{1}{2} \sum_j \zeta_{ij} \dot{x}_i \dot{x}_j + \frac{\partial A}{\partial x_i} \dot{x}_i \quad (23)$$

The difference between Eq. (23) and (18) is that $x_i$ in Eq. (23) stands for a general coordinate specifying the non-equilibrium state, and that the potential energy $U$ is replaced by the free energy $A$. The relation between the Onsager’s variational principle and the hydrodynamic variational principle will be discussed in more detail in the next section.

In the following discussion, we shall assume that the temperature of the system is constant, and use Onsager’s variational principle in the form of Eq. (23). The kinetic equation of Onsager is then given by

$$\frac{dx_i}{dt} = -\sum_j (\zeta^{-1})_{ij} \frac{\partial A}{\partial x_j} \quad (24)$$

3.2. Validity of the variational principle

As we have seen, Onsager’s variational principle is equivalent to Onsager’s kinetic equation with symmetric coefficient $\zeta_{ij}$. Therefore the validity of Onsager’s variational principle entirely depends on the validity of the kinetic equation. Let us therefore spend some time to discuss the base of this equation.

Usual argument to derive the kinetic equation (19) is as follows. If the system is at equilibrium, the entropy takes the maximum value and the state does not change, i.e., both $\partial S(x)/\partial x_i$ and $dx_i/dt$ are equal to zero. If the system is not at equilibrium, both $\partial S(x)/\partial x_i$ and $dx_i/dt$ are not equal to zero. If the deviation from the equilibrium state is small, one can assume a linear relation between $\partial S(x)/\partial x_i$ and $dx_i/dt$, which is equation (19).

This argument presumes that the deviation of $x_i$ from the equilibrium value $x_{i,eq}$ is small, and that the kinetic equation (19) is a linear equation.
for $x_i - x_{i,eq}$. In fact, Onsager used this assumption to prove the reciprocal relation.

On the other hand, it is known that in many systems, the time evolution equations for the state variables are written in the form of Eq. (19) even when the equations become non-linear equations for $x_i - x_{i,eq}$, yet the reciprocal relation (20) are satisfied. We have seen this in the case of particle motion in viscous fluid. Other example is the usual diffusion equation for the particle concentration $n(x,t)$

$$\frac{\partial n}{\partial t} = \frac{\partial n}{\partial x} \left( D(n) \frac{\partial n}{\partial x} \right)$$

which comes from the Fuch's law for the diffusion flux $j = -D(\partial n/\partial x)$.

Equation (25) is in general a non-linear partial differential equation for $n$ since the diffusion coefficient $D$ can be a function of $n$. It will be shown later (see Sec. 4), that Eq. (25) can be written in the form of the kinetic equation (19) with symmetric coefficients ($\zeta_{ij} = \zeta_{ji}$).

It is now generally accepted\textsuperscript{10-12} that Onsager’s theory is valid even when the kinetic equation becomes a non-linear equation for $x_i$. The non-linearity comes from two sources: one is that the forces $\partial S(x)/\partial x_i$ (or $\partial A(x)/\partial x_i$) can be non-linear functions of $x$, and the other is that the kinetic coefficients $L_{ij}$ (or $\zeta_{ij}$) can be a function of $x$.

How can we justify the reciprocal relation in the situation that the time evolution equation becomes a non-linear equation for the state variable $x = (x_1, x_2, ... x_f)$? This question can be cast in a more specific question: is the hydrodynamic reciprocal relation (12) a special case of Onsager’s reciprocal relation? The latter question has been discussed by hydrodynamicists\textsuperscript{16} who raised several questions for the assertion that the hydrodynamic reciprocal relation is a special case of Onsager’s reciprocal relation.

One can justify this assertion in the following way. Although the friction coefficients $\zeta_{ij}$ depend on the particle configuration $x$, they are independent of the potential force which drives the particle motion. Therefore, in proving the reciprocal relation, one can generally assume that there are some hypothetical forces acting on the particles, and that the state $x$ is close to equilibrium (under the given hypothetical forces). Therefore it is justified to use Onsager’s argument to prove the reciprocal relation for the friction coefficients. In this sense, one can regard the hydrodynamic reciprocal relation as a special case of Onsager’s reciprocal relation. In general, as far as the kinetic coefficients $L_{ij}(x)$ is independent of the driving force $\partial S/\partial x_i$, one can justify Onsager’s argument to prove the the reciprocal relation.
The underlying assumption for the kinetic equations (24) is that there is a set of slow variables \( x = (x_1, x_2, \ldots, x_f) \), the relaxation time of which are distinctively longer than those of other fast variables. The free energy \( A(x) \) can be defined only for such systems; in fact, \( A(x) \) can be calculated by statistical mechanics assuming that the fast variables are in equilibrium for given values of slow variables. If the slow variables change with the rate \( \dot{x} \), the fast variables will not be in equilibrium, but as long as the deviation of fast variables from their equilibrium state is small, one can assume a linear relation between the rate of state change and the driving force, and can use Onsager’s argument to justify the reciprocal relation. This is the reason why we can use Onsager’s variational principle for the system whose time evolution equation becomes a non-linear equation for the slow variables.

3.3. **Merit of the variational principle**

The variational principle we have discussed is a simple rewriting of the kinetic equation for the state variables. However, formulating the evolution law in the variational principle has several advantages.

(a) The variational principle gives kinetic equations which automatically satisfy Onsager’s reciprocal relation. In the usual formulation of irreversible thermodynamics, careful considerations are needed to identify proper set of variables to ensure the reciprocal relation. This task becomes even more complicated if there are certain constraints such as the incompressible condition or conservation law. If one uses the variational principle, proper kinetic equations are obtained easily. It will be shown (Sec. 3.4) that the equations obtained by the variational principle generally satisfy the reciprocal relation. Examples of this merit will be demonstrated in the problem of diffusion (Sec. 4) and nematodynamics (Sec. 8).

(b) The variational principle allows us flexibility in choosing state variables and gives us new approaches for the problems. Any set of variables \( x \) can be chosen for state variables as long as their time derivatives \( \dot{x} \) are uniquely determined by the state variables. Examples of this merit will be seen in the discussion of diffusion (Sec. 4) and rotational Brownian motion (Sec. 5).

(c) The variational principle gives us a convenient formula to find out the forces needed to cause certain control parameters such as the system volume, or shear strain. The mathematical base for this
usage is explained in Sec. 3.5, and its application will be shown in Sec. 4.3 and Sec. 5.5.

In the following, these points are explained in more detail.

3.4. **Reciprocal relation in the kinetic equation**

First, a general reason is given for why the reciprocal relation is guaranteed for the equations obtained by the variational principle.

If both \( \Phi(\dot{x}) \) and \( \dot{A}(\dot{x}) \) are given explicitly as a function of \( \dot{x} = (\dot{x}_1, \dot{x}_2, ...) \) as in Eq.(23), it is obvious that the variational principle \( \partial R/\partial \dot{x}_i = 0 \) gives equations which satisfy the reciprocal relation. In many situations, however, although \( \dot{A}(\dot{x}) \) is obtained easily, \( \Phi(\dot{x}) \) is not easily found. It quite often happens that the energy dissipation function \( \Phi(\dot{x}) \) can be expressed as a function of other variables \( \dot{y} \) which determine \( \dot{x} \), i.e., the dissipation function is expressed as

\[
\Phi = \frac{1}{2} \sum_{ij} \zeta_{ij} \dot{y}_i \dot{y}_j \tag{26}
\]

and \( \dot{x}_i \) is determined by

\[
\dot{x}_i = \sum_j a_{ij} \dot{y}_j \tag{27}
\]

In Eq.(27), \( a_{ij} \) are certain coefficients (which can be a function of \( x \)). The matrix \( (a_{ij}) \) need not be a square matrix: the number of variables \( \dot{y}_i \) can be different from the number of variables \( \dot{x}_i \).

An example of such situation is seen in the problem of diffusion. The non-equilibrium state of the system is described by the concentration profile \( n(x) \). The free energy \( A \) is expressed easily as a functional of \( n(x) \), while the energy dissipation function \( \Phi \) cannot be expressed by \( \dot{n}(x) \): \( \Phi \) is expressed as a functional of the flux \( j(x) \) which determines \( \dot{n}(x) \).

It is easy to prove the reciprocal relation for the kinetic equations derived from the variational principle. The Rayleighian is given by

\[
R = \Phi + \sum_i \frac{\partial A}{\partial x_i} \dot{x}_i = \frac{1}{2} \sum_{ij} \zeta_{ij} \dot{y}_i \dot{y}_j + \sum_{ij} \frac{\partial A}{\partial x_i} a_{ij} \dot{y}_j \tag{28}
\]

Minimization of \( R \) gives

\[
\dot{y}_i = \sum_{jk} (\zeta^{-1})_{ij} \frac{\partial A}{\partial x_k} a_{kj} \tag{29}
\]
This gives the following kinetic equation
\[ \dot{x}_i = \sum_j L_{ij} \frac{\partial A}{\partial x_j} \] (30)
with
\[ L_{ij} = \sum_{l,k} a_{ik} a_{jl} (\zeta^{-1})_{kl} \] (31)
which satisfies the reciprocal relation.

The reciprocal relation can also be proven in the situation that \( \dot{y}_i \) are not independent of each other, but are subject to a set of constraints
\[ \sum_i b_i^{(p)} \dot{y}_i = 0, \quad p = 1, 2, ... \] (32)
With such constraints, the Rayleighian becomes
\[ R = \frac{1}{2} \sum_{ij} \zeta_{ij} \dot{y}_i \dot{y}_j + \sum_j \frac{\partial A}{\partial x_i} a_{ij} \dot{y}_j - \sum_p \lambda^{(p)} \sum_i b_i^{(p)} \dot{y}_i \] (33)
where \( \lambda^{(p)} \ (p = 1, 2, ...) \) are the Lagrange multipliers for the constraints. Minimization of Eq.(33) gives the following kinetic coefficients:
\[ L_{ij} = \sum_{l,k} a_{ik} a_{jl} (\zeta^{-1})_{kl} - \sum_{p,q} c_i^{(p)} c_j^{(q)} (A^{-1})_{pq} \] (34)
where
\[ c_i^{(p)} = \sum_{i,j,k} a_{ij} (\zeta^{-1})_{jk} b_i^{(p)} F \] (35)
and \( (A^{-1})_{pq} \) is the inverse of the matrix
\[ A_{pq} = \sum_{i,j} b_i^{(p)} b_j^{(p)} (\zeta^{-1})_{ij} \] (36)
It is easy to verify that \( L_{ij} \) is a symmetric matrix.

### 3.5. Forces needed to control the state variables
Certain state variables in the Rayleighian can be changed externally. For example, the particle position shown in Fig. 1 can be changed by applying a certain force on the particle. It can be shown that the force \( F_i^{(c)} \) needed to change the parameter \( x_i \) with the rate \( \dot{x}_i \) is given by
\[ F_i^{(c)} = \frac{\partial R}{\partial x_i} \] (37)
For example, if one moves the particle with velocity $\dot{x}$, one has to apply an extra force on the particle

$$F^{(e)} = \zeta \dot{x} + \frac{\partial U}{\partial x}$$

which is equal to $\partial R/\partial \dot{x}$.

Equation (37) can be shown as follows. Suppose that the variables $x_i$ ($i = 1, 2, ... f$) are the internal variables (the time evolution of which is given by $\partial R/\partial \dot{x}_i = 0$), and the other variables $x_i$ ($i = f + 1, f + 2, ... g$) are the externally controllable variables. For such system, the force balance equations are written as

$$\sum_{j=1}^{g} \zeta_{ij} \dot{x}_j = -\frac{\partial A}{\partial x_i}, \quad i = 1, 2, ... f$$

(39)

$$\sum_{j=1}^{g} \zeta_{ij} \dot{x}_j = -\frac{\partial A}{\partial x_i} + F^{(e)}_i, \quad i = f + 1, ... g$$

(40)

which gives Eq. (37).

Examples of the situation where Eq. (37) is useful are shown in Fig. 3. In Fig.3 (a), a semi-permeable membrane separating the colloidal solution from pure solvent is moved with velocity $\dot{L}$. The force $F(t)$ needed to cause such motion is calculated by $\partial R/\partial \dot{L}$. In Fig.3 (b), a gel placed between two plates is squeezed. The force acting at the plate can be calculated by $\partial R/\partial \dot{h}$. In Fig.3(c), a solution of rod-like polymers is sheared with shear rate $\dot{\gamma}$. The shear stress is calculated by $\partial R/\partial \dot{\gamma}$. Actual calculation for these quantities will be shown later.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig3.png}
\caption{Examples of external parameters and their conjugate forces, (a) position $L(t)$ of semi-permeable membrane separating the solution from pure solvent (b) vertical position $h(t)$ of a wall sandwiching a gel, (c) horizontal position $x(t)$ of a wall containing a solution of rod-like molecules. The conjugate forces $F(t)$ are shown in the figure.}
\end{figure}
4. Brownian Motion

4.1. Diffusion equation

As a simple application of Onsager’s variational principle, we first discuss the Brownian motion of an isolated particle. The Brownian motion of a particle can be described by the Langevin equation, which represents the stochastic motion of the particle position \( x(t) \). The Brownian motion can also be described by the time evolution of the probability distribution function \( \psi(x; t) \) which represents the probability of finding the particle at position \( x \). The time evolution equation for \( \psi(x; t) \) is deterministic, and can be derived by the variational principle.

The essential point of this derivation is to regard \( \psi(x) \) as state variables.

If we imagine an ensemble of many realization of Brownian motion, we can define the free energy of such ensemble. Alternatively, we can imagine a very dilute dispersion of particles (see Fig. 4 (a)), and regard \( \psi(x) \) as a quantity proportional to the number density \( n(x) \) of particles i.e., \( \psi(x) = n(x)/N_{\text{tot}} \) where \( N_{\text{tot}} \) is the total number of particles in the system. In the following, we shall take the latter viewpoint and derive the time evolution equation for \( n(x, t) \).

Now \( n \) has to satisfy the conservation equation

\[
\dot{n} = -\frac{\partial j}{\partial x} \tag{41}
\]

where \( j \) is the flux of particles. Equation (41) represents a constraint for the time evolution of \( n \): the constraint is that instantaneous transportation of particles from one place to other remote places cannot take place. To
account for the constraint, we define the velocity $v$ by $v = \frac{j}{n}$ (42)

and determine $v$ by the variational principle.

If the particle at $x$ moves with velocity $v(x)$, the energy dissipation is given by $\zeta v(x)^2$. Thus the energy dissipation function of the system is given by

$$\Phi = \frac{1}{2} \int dx \ z(x)^2 v(x)^2$$ (43)

On the other hand, if the concentration profile of particles is $n(x)$, the free energy of the system is given by

$$A = \int dx \ [k_B T n(x) \ln n(x) + n(x) U(x)]$$ (44)

The time derivative of $A$ can be calculated by Eqs. (41) and (44);

$$\dot{A} = \int dx \ [k_B T \dot{n}(\ln n + 1) + \dot{n} U(x)]$$

$$= - \int dx \ \frac{\partial n}{\partial x} [k_B T (\ln n + 1) + U]$$

$$= \int dx \ v n \frac{\partial}{\partial x} (k_B T \ln n + U)$$ (45)

where integral by parts has been used.

From Eq. (43) and (45), the Rayleighian is give by

$$R = \frac{1}{2} \int dx \ z n v^2 + \int dx \ v n \frac{\partial}{\partial x} (k_B T \ln n + U)$$ (46)

Minimizing this with respect to $v$, we have

$$v = - \frac{1}{\zeta} \frac{\partial}{\partial x} (k_B T \ln n + U)$$ (47)

Equations (41) and (47) give the following time evolution equation for $n(x, t)$

$$\frac{\partial n}{\partial t} = D \frac{\partial}{\partial x} \left( \frac{\partial n}{\partial x} + \frac{n}{k_B T} \frac{\partial U}{\partial x} \right)$$ (48)

and the Einstein relation

$$D = \frac{k_B}{\zeta}$$ (49)

Equation (48) is the diffusion equation in the potential field $U(x)$. 

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4.2. Reciprocal relation in the diffusion equation

The diffusion equation (48) does not look-like Onsager’s kinetic equation Eq. (24), but it is indeed a special form of it. In fact, Eq. (48) can be written as

$$\dot{n}(x) = -\int dx'L(x,x') \frac{\delta A}{\delta n(x')}$$  \hspace{1cm} (50)

where the kernel $L(x,x')$ is given by

$$L(x,x') = -\frac{\partial}{\partial x} \left[ \frac{n(x)}{\zeta} \frac{\partial}{\partial x'} \delta(x - x') \right],$$  \hspace{1cm} (51)

The kernel $L(x,x')$ is symmetric, i.e., for any functions $n_1(x)$ and $n_2(x)$, the following identity holds.

$$\int dx \int dx' L(x,x')n_1(x)n_2(x') = \int dx \int dx' L(x',x)n_1(x)n_2(x')$$  \hspace{1cm} (52)

Thus the diffusion equation satisfy the reciprocal relation.

4.3. Forces acting on the semi-permeable membrane

Let us now discuss the force needed to control the position of the semi-permeable membrane shown in Fig. 3(a). Since the integral in Eq. (44) is done between $0$ and $L(t)$, $\dot{A}$ is calculated as

$$\dot{A} = \dot{L}[k_B T n(L) \ln n(L) + n(L) U(L)] + \int_0^{L(t)} dx \dot{n} k_B T [\ln n + 1 + U(x)]$$  \hspace{1cm} (53)

Using Eq. (42) and integral by parts, we have,

$$\dot{A} = \dot{L}[k_B T n(L) \ln n(L) + n(L) U(L)] - v(L)n(L) k_B T [\ln n(L) + U(L)] + \int_0^{L(t)} dx \frac{\partial}{\partial x} [k_B T (\ln n + 1) + U(x)]$$

$$= -\dot{L} n(L) k_B T + \int_0^{L(t)} dx v n(x) \frac{\partial}{\partial x} [k_B T (\ln n + 1) + U(x)]$$  \hspace{1cm} (54)

where we have used the condition that the velocity $v$ satisfies $v(L) = \dot{L}$.

On the other hand, the energy dissipation function is given by

$$\Phi = \frac{\zeta}{2} \int_0^{L(t)} dx v^2 n(x) + \frac{1}{2} \xi_m \dot{L}^2$$  \hspace{1cm} (55)
The second term represents the extra energy dissipation caused by the solvent flow through the membrane ($\xi_m$ is the friction constant of the membrane.) The force $F(t)$ acting on the semi-permeable membrane is given by $\frac{\partial R}{\partial \dot{L}}$, and is equal to

$$F(t) = \frac{\partial}{\partial \dot{L}} (\Phi + \dot{A}) = \xi_m \dot{L} - n(L) k_B T$$

(56)

If the membrane is fixed (i.e., $L = 0$), the force is given by the osmotic pressure of the solution near the membrane. Notice that the potential $U(x)$ does not enter in the expression.

5. Rotational Brownian Motion

5.1. State variables of a rod-like particle

To demonstrate the merit of the flexibility in choosing state variables, we now discuss the rotational Brownian motion of a rod-like particle. The orientation of a rod can be specified by two angular coordinates $\theta$ and $\phi$ defined in Fig. 5. Alternatively, the orientation can be specified by a vector $\mathbf{u}$ parallel to the rod axis. The $x, y, z$ components of $\mathbf{u}$ is given by

$$u_x = u \sin \theta \cos \phi$$
$$u_y = u \sin \theta \sin \phi$$
$$u_z = u \cos \theta$$

(57)

where $u = |\mathbf{u}|$.

The rotational Brownian motion can be described by the time evolution equation for the distribution function $\psi(\theta, \phi; t)$ or $\psi(\mathbf{u}; t)$. We shall first derive these equations.
5.2. Diffusion equation for $\psi(\theta, \phi)$

The distribution function $\psi(\theta, \phi)$ is defined as follows. The probability of finding the angular coordinate of rod in the area $dS = \sin \theta d\theta d\phi$ is given by $\psi(\theta, \phi) dS$. The normalization condition for $\psi$ is

$$\int dS \psi = \int_0^\pi d\theta \int_0^{2\pi} d\phi \sin \theta \psi(\theta, \phi) = 1 \quad (58)$$

The conservation equation for such probability is written as

$$\dot{\psi} = -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \dot{\theta} \psi) - \frac{\partial}{\partial \phi} (\dot{\phi} \psi) \quad (59)$$

Now if the rod rotates with angular velocity $\omega$ normal to the axis, the surrounding fluid exerts a frictional torque $-\zeta_r \omega$ on the rod, where $\zeta_r$ is the rotational friction constant\(^\dagger\). The energy dissipation for this motion is $\zeta_r \omega^2$ and therefore the energy dissipation function of the system (per unit volume) is given by

$$\Phi = \frac{n \zeta_r}{2} \int dS \omega^2 \psi \quad (61)$$

where $n$ is the number density of particles in the system.

Since $\omega^2 = \dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2$, Equation (61) is written as

$$\Phi = \frac{n \zeta_r}{2} \int dS (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \psi \quad (62)$$

On the other hand, the free energy of the system (per unit volume) is given by

$$A = nk_B T \int dS \psi \ln \psi \quad (63)$$

(Here, the term of external potential has been dropped for simplicity.) Using Eq. (59), the time derivative of $A$ is calculated as

$$\dot{A} = nk_B T \int dS \dot{\psi} (\ln \psi + 1)$$

$$= nk_B T \int d\theta d\phi \sin \theta \left[ -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \dot{\theta} \psi) - \frac{\partial}{\partial \phi} (\dot{\phi} \psi) \right] (\ln \psi + 1)$$

$$= nk_B T \int d\theta d\phi \sin \theta \left( \dot{\psi} \frac{\partial}{\partial \theta} + \psi \dot{\phi} \frac{\partial}{\partial \phi} \right) (\ln \psi + 1) \quad (64)$$

\(^\dagger\)For a rod of length $L$ and diameter $b$, hydrodynamic calculation gives\(^3\)

$$\zeta_r = \frac{\pi \eta L^3}{3(\ln(L/b) - 0.8)} \quad (60)$$
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Minimization of $\Phi + \dot{A}$ with respect to $\dot{\theta}$ and $\dot{\phi}$ gives

$$\zeta_r \dot{\theta} \psi = -k_BT \frac{\partial \psi}{\partial \theta}$$  \hspace{1cm} (65)

$$\zeta_r \dot{\phi} \psi = -k_BT \frac{\partial \psi}{\sin^2 \theta \partial \phi}$$  \hspace{1cm} (66)

The time evolution equation for $\psi$ is determined by Eqs. (59), (65) and (66):

$$\frac{\partial \psi}{\partial t} = D_r \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta}\right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2}\right]$$  \hspace{1cm} (67)

where

$$D_r = \frac{k_BT}{\zeta_r}$$  \hspace{1cm} (68)

Equation (67) is the rotational diffusion equation for a rod-like particle.\textsuperscript{1}

5.3. Diffusion equation for $\psi(u)$

The rotational diffusion equation can also be written in $u$ space, where $u$ represents a vector parallel to the rod axis. The length $u = |u|$ of the vector does not matter, and can be taken to be unity, but here we assume that $u$ takes some constant value. Let $\psi(u)du$ be the probability of finding the rod in the volume element $du$ in $u$ space. The conservation equation is written as

$$\dot{\psi} = -\frac{\partial}{\partial u} (\dot{u}\psi)$$  \hspace{1cm} (69)

We shall determine $\dot{u}$ by the variational principle. Since $u^2 = \text{constant}$, $\dot{u}$ has to satisfy the following constraint

$$\dot{u} \cdot u = 0$$  \hspace{1cm} (70)

Since $\dot{u} = \omega \times u$ and $\omega \cdot u = 0$, the energy dissipation function of the system can be written as

$$\Phi = \frac{n}{2} \int du \zeta_r \frac{\dot{u}^2}{u^2} \psi$$  \hspace{1cm} (71)

On the other hand, the time derivative of the free energy is calculated as

$$\dot{A} = n k_BT \int du \dot{\psi}(\ln \psi + 1)$$

$$= n k_BT \int du \dot{u} \psi \cdot \frac{\partial \ln \psi}{\partial u}$$  \hspace{1cm} (72)
Therefore the Rayleighian of the present system becomes
\[
R = \frac{n}{2} \int du \zeta \frac{u^2}{u^2} \psi + nk_BT \int du \dot{u} \psi \cdot \frac{\partial \ln \psi}{\partial u} - \int du \lambda(u) \dot{u} \cdot u
\] (73)
The last term in Eq. (73) stands for the constraint (70).

Minimizing \(R\) with respect to \(\dot{u}\) and determining \(\lambda\) by Eq. (70), we have
\[
\dot{u} = -\frac{k_BT}{\zeta_r} \left( u^2I - uu \right) \cdot \frac{\partial \ln \psi}{\partial u}
\] (74)
where \(I\) is the unit tensor \((I_{\alpha\beta} = \delta_{\alpha\beta})\). The time evolution equation is now given by
\[
\frac{\partial \psi}{\partial t} = D_r \frac{\partial}{\partial u} \left[ \left(u^2I - uu\right) \cdot \left(\frac{\partial \psi}{\partial u}\right)\right]
\] (75)
Using the relation (57), one can confirm that Eq. (75) is equivalent to Eq. (67). It will be shown that Eq. (75) is more convenient than Eq. (67) for practical calculation.

5.4. Diffusion equation in flow field

The rotational Brownian motion of particles gives viscoelasticity to the solution. This has been discussed in the molecular theory of rheology.\(^1\)\(^-\)\(^3\) Here the main point of the theory is discussed based on the variational principle.

Suppose that a solution of rod-like particles is placed in a velocity field
\[
v(r) = \kappa \cdot r
\] (76)
or
\[
v_\alpha(r) = \kappa_{\alpha\beta} r_\beta
\] (77)
where Greek indices \(\alpha, \beta\) stand for the \(x, y, z\) components, and Einstein’s convention that summation is taken over repeatedly appearing indices has been used. The tensor
\[
\kappa_{\alpha\beta} = \frac{\partial v_\alpha}{\partial r_\beta}
\] (78)
is called the velocity gradient tensor.

The incompressible condition for the fluid velocity \(v(r)\) gives the following condition for \(\kappa_{\alpha\beta}\)
\[
\kappa_{\alpha\alpha} = 0
\] (79)
Now, if the solution does not contain particles, the energy dissipation per unit volume of the solution is given by

$$2\Phi_0 = \frac{1}{2} \eta (\kappa_{\alpha\beta} + \kappa_{\beta\alpha})^2$$  \hspace{1cm} (80)

where $\eta$ is the viscosity of solvent.

![Fig. 6. The change of the vector $\mathbf{u}$ when the rod is placed in a velocity gradient $\kappa$. If $\mathbf{u}$ follows the flow field completely, it changes with velocity $\kappa \cdot \mathbf{u}$, but since the length $|\mathbf{u}|$ cannot change, the actual velocity is given by $\mathbf{u}_{\text{flow}} = (I - uu/u^2) \cdot \kappa \cdot \mathbf{u}$.

If the solution contains a rod rotating with speed $\dot{\mathbf{u}}$, there is an extra energy dissipation. The energy dissipation can be calculated again by solving the Stokes equation, and is written as a quadratic function of $\dot{\mathbf{u}}$ and $\kappa$. For slender rod, hydrodynamic calculation gives the following energy dissipation function:

$$\Phi = \Phi_0 + \frac{n}{2} \zeta r \int d\mathbf{u} \psi \left[ \frac{(\dot{\mathbf{u}} - \dot{\mathbf{u}}_{\text{flow}})^2}{u^2} + \frac{1}{2} \frac{(u \cdot \kappa \cdot u)}{u^4} \right]$$  \hspace{1cm} (81)

where $\dot{\mathbf{u}}_{\text{flow}}$ stands for the velocity induced by the macroscopic flow (see Fig. 6)

$$\dot{\mathbf{u}}_{\text{flow}} = \left( I - uu/u^2 \right) \cdot \kappa \cdot \mathbf{u}$$  \hspace{1cm} (82)

On the other hand, expression for $\dot{A}$ is given by the same form as Eq. (72). Hence the Rayleighian is given by

$$R = \Phi_0 + \frac{n}{2} \zeta r \int d\mathbf{u} \psi \left[ \frac{(\dot{\mathbf{u}} - \dot{\mathbf{u}}_{\text{flow}})^2}{u^2} + \frac{1}{2} \frac{(u \cdot \kappa \cdot u)}{u^4} \right]$$

$$+ k_B T n \int d\mathbf{u} \dot{\mathbf{u}} \psi \frac{\partial \ln \psi}{\partial \mathbf{u}} - \int d\mathbf{u} \lambda(\mathbf{u}) \dot{\mathbf{u}} \cdot \mathbf{u}$$  \hspace{1cm} (83)

This gives the following equation for $\dot{\mathbf{u}}$:

$$\dot{\mathbf{u}} = - \frac{k_B T}{\zeta r} \left( u^2 I - uu \right) \cdot \frac{\partial \ln \psi}{\partial \mathbf{u}} + \dot{\mathbf{u}}_{\text{flow}}$$  \hspace{1cm} (84)
and the equation for $\dot{\psi}$

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial \mathbf{u}} \cdot \left( (\mathbf{u}^2 \mathbf{I} - \mathbf{uu}) \cdot \left( D \frac{\partial \psi}{\partial \mathbf{u}} - \frac{1}{\mathbf{u}^2} \kappa \cdot \mathbf{u} \psi \right) \right)$$

(85)

Equation (85) determine the orientational distribution of rod-like polymers in flow field.

5.5. Expression for the stress tensor

The macroscopic stress tensor $\sigma_{\alpha\beta}$ can be calculated by the formula (37). Since $\sigma_{\alpha\beta}$ is the force conjugate to the velocity gradient tensor $\kappa_{\alpha\beta}$, we have

$$\sigma_{\alpha\beta} = \frac{\partial R}{\partial \kappa_{\alpha\beta}}$$

(86)

For the Rayleighian (83), Eq.(86) gives the following expression for the stress tensor

$$\sigma_{\alpha\beta} = n \int d\mathbf{u} \psi \left[ -\zeta \frac{(\dot{\mathbf{u}}_\alpha - \dot{\mathbf{u}}_{\text{flow},\alpha}) u_\beta}{u^2} + \frac{1}{2} \zeta \frac{u_\alpha u_\beta u_\mu u_\nu \kappa_{\mu\nu}}{u^4} \right]
+ \eta_0 (\kappa_{\alpha\beta} + \kappa_{\beta\alpha})$$

(87)

The first term can be rewritten by the use of Eq.(84):

$$- \int d\mathbf{u} \psi \zeta \frac{(\dot{\mathbf{u}}_\alpha - \dot{\mathbf{u}}_{\text{flow},\alpha}) u_\beta}{u^2}
= k_B T \int d\mathbf{u} \left( \delta_{\alpha\mu} \frac{u_\alpha u_\mu}{u^2} \right) \frac{\partial \psi}{\partial u_\mu} u_\beta
= -k_B T \int d\mathbf{u} \psi \frac{\partial}{\partial u_\mu} \left[ u_\beta \left( \delta_{\alpha\mu} - \frac{u_\alpha u_\mu}{u^2} \right) \right]
= k_B T \int d\mathbf{u} \psi \left( 3 \frac{u_\alpha u_\beta}{u^2} - \delta_{\alpha\beta} \right)
= 3k_B T (\mathbf{\hat{u}}_\alpha \mathbf{\hat{u}}_\beta - \frac{1}{3} \delta_{\alpha\beta})$$

(88)

where $\mathbf{\hat{u}} = \mathbf{u}/|\mathbf{u}|$ is the unit vector in the direction of $\mathbf{u}$, and $\langle ... \rangle$ stands for the average for $\mathbf{u}$ with the distribution function $\psi(\mathbf{u})$.

From Eqs.(87) and (88), the stress tensor is given by

$$\sigma_{\alpha\beta} = 3nk_B T (\mathbf{\hat{u}}_\alpha \mathbf{\hat{u}}_\beta - \frac{1}{3} \delta_{\alpha\beta}) + \frac{m}{2} \zeta \langle \dot{\mathbf{u}}_\alpha \dot{\mathbf{u}}_\beta \mathbf{\hat{u}}_\mu \mathbf{\hat{u}}_\nu \kappa_{\mu\nu} \rangle + \eta_0 (\kappa_{\alpha\beta} + \kappa_{\beta\alpha})$$

(89)

Equation (89) indicates that the stress tensor of the solution of rod-like particles has two origins. One is the kinetic origin arising from the rotational Brownian motion of particles, and the other is the hydrodynamic origin arising from the extra energy dissipation caused by the rod.
Equations (85) and (89) give the constitutive equation: for given velocity gradient, $\psi(u; t)$ can be obtained by solving Eq.(85), and then the stress can be calculated by Eq.(89). The constitutive equation describes the non-linear viscoelasticity of the solution of rod-like polymers.\textsuperscript{1,3}

6. Coupling between Diffusion and Flow

6.1. Diffusion in concentrated solutions

In Sec. 4, we have discussed the diffusion of particles in dilute solution. Now we discuss the diffusion in concentrated solutions. In dilute solutions, the motion of particles is independent of each other. In concentrated solutions, interaction between particles gives new features to the diffusion.

(a) Due to the interaction, the diffusion constant $D$ now becomes a function of concentration. Accordingly, the diffusion equation becomes a non-linear equation for the particle concentration.

(b) The diffusion of particles generally induces flow of solvent, and can cause macroscopic flow in solutions. If particle concentration is low, this effect can be negligible, but if concentration is high, the effect can be important.

We shall discuss these two issues separately. In this section we shall discuss the effect of interaction on the diffusion constant assuming that there is no macroscopic flow, i.e., we consider the diffusion of particles in a quiescent solutions (see Fig. 4(b)).

To denote the concentration of particles, we use volume fraction $\phi(r; t)$, which is related to the number density $n(r, t)$ by

$$\phi(r, t) = v_c n(r, t)$$

where $v_c = 4\pi a^3/3$ is the volume of the particle.

Time evolution equation for $\phi$ can be obtained in the same way as in the dilute case. Let $v_p$ be the particle velocity, then the conservation equation is written as

$$\dot{\phi} = -\nabla \cdot (v_p \phi)$$

When particles move with velocity $v_p$ in a quiescent solution, the energy dissipation is given by

$$\Phi = \frac{1}{2} \int d\mathbf{r} \xi(\phi) v_p^2$$
where $\xi(\phi)$ is the friction constant (per unit volume) for the collective motion of particles. If the solution is dilute, $\xi(\phi)$ is simply given by $n\zeta = (\phi/v_c)\zeta$. If the solution is concentrated, $\xi(\phi)$ is not expressed by a simple function, but many studies have been done to calculate $\xi(\phi)$ theoretically.\textsuperscript{16,17} Also $\xi(\phi)$ can be measured experimentally by the method shown in Fig. 7.

![Fig. 7. Experimental set up to measure the friction constant $\xi(\phi)$. The particles are contained in a box made of porous walls fixed to the side wall. The solvent is transported from bottom container to top container by a pressure difference $\Delta P$. If the fluid velocity is $v$, the friction constant is given by $\xi = \Delta P/(hv)$, where $h$ is the thickness of the box. In practice, the pressure drop in the top and bottom container, and that across the porous walls has to be taken into account to obtain $\xi(\phi)$ accurately.](image)

The free energy $A$ of the system can be expressed as a functional of $\phi(r)$.

$$A = \int dr f(\phi(r))$$

(93)

where $f(\phi)$ stands for the free energy (per unit volume) of the solution of concentration $\phi$, and we have assumed that the effect of gravity is negligible. From Eq. (93), $\dot{A}$ can be calculated by using Eq. (91),

$$\dot{A} = \int dr f'(\phi) \dot{\phi} = -\int dr f'(\phi) \nabla \cdot \{v_p \phi\} = \int dr v_p \phi \cdot \nabla f'(\phi)$$

(94)

The minimization of $R = \Phi + \dot{A}$ with respect to $v_p$ gives

$$v_p = -\frac{\phi}{\xi} \nabla f'(\phi)$$

(95)

The right hand side can be rewritten by using the osmotic pressure $\Pi(\phi)$ of the solution

$$\Pi(\phi) = \phi f'(\phi) - f(\phi) + f(0)$$

(96)
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as

\[ v_p = -\frac{1}{\xi} \nabla \Pi \quad (97) \]

Equations (91) and (97) give the following diffusion equation

\[ \frac{\partial \phi}{\partial t} = \nabla [D(\phi) \nabla \phi] \quad (98) \]

where \( D(\phi) \) is given by

\[ D(\phi) = \frac{\phi \partial \Pi}{\xi \partial \phi} \quad (99) \]

This gives a diffusion constant in concentrated solution. In the case of dilute solution, Eq. (99) reduces to the Einstein relation (49).

The force \( F(t) \) acting on the semi-permeable membrane can be calculated by the same way as in Sec. 4.3, and it is given by \( \xi_m \dot{L} - \Pi(\phi(L)). \)

6.2. Coupling between solute diffusion and solution flow

In the previous section, it is assumed that the solution is at rest as a whole. This assumption is not always correct. When solute moves relative to solvent, it generally induces a macroscopic flow of solutions. For example, when a colloidal suspension initially placed on top of a pure solvent starts to sediment, the particles do not sediment homogeneously (see Fig. 4(c)). Certain part starts to sediment faster than the other, and form a lane where the particles and solvent move downward, while the solvent in the other part moves upward.

In order to describe such phenomena, it is necessary to take into account of the solution velocity \( v(r, t) \) which is defined as the volume averaged velocity

\[ v = \phi v_p + (1 - \phi) v_s \quad (100) \]

where \( v_s \) is the velocity of the solvent. If we assume that the solution is regarded as a Newtonian fluid with effective viscosity \( \eta(\phi) \), the energy dissipation function is written as

\[ \Phi = \frac{1}{2} \int d\mathbf{r} \xi(\phi)(v_p - v)^2 + \frac{1}{4} \int d\mathbf{r} \eta(\phi) \left( \frac{\partial v_\alpha}{\partial r_\beta} + \frac{\partial v_\beta}{\partial r_\alpha} \right)^2 \quad (101) \]

The first term in Eq.(101) stands for the dissipation due to the relative motion between solute and solution, and the second term represents the dissipation caused by velocity gradient of the solution.
The free energy $A$ of the solution is now given by

$$A = \int dr [f(\phi) - \rho_1 \phi g \cdot r]$$

(102)

where the gravitational energy has been added to discuss the problem of sedimentation ($\rho_1 = \rho_p - \rho_s$ is the density difference between the particle and solvent). The time derivative of Eq.(102) is given by

$$\dot{A} = \int dr [f'(\phi) - \rho_1 g \cdot r] \dot{\phi}(r) = \int dr v_p \phi \cdot (\nabla f'(\phi) - \rho_1 g)$$

(103)

Since the solution is incompressible, $\mathbf{v}$ has to satisfy the constraint

$$\nabla \cdot \mathbf{v} = 0$$

(104)

Therefore the Rayleighian is given by

$$R = \Phi + \dot{A} - \int dr p(r) \nabla \cdot \mathbf{v}$$

(105)

where the last term stands for the constraint (104). The conditions $\delta R/\delta v_p = 0$ and $\delta R/\delta \mathbf{v} = 0$ give the following equations

$$\xi (v_p - \mathbf{v}) = -\phi \nabla f'(\phi) + \rho_1 \phi g$$

(106)

$$-\nabla \eta \cdot [\nabla \mathbf{v} + (\nabla \mathbf{v})^t] + \xi (\mathbf{v} - v_p) = -\nabla p$$

(107)

Equations (104)–(107) and Eq. (91) give the following set of equations.

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot (\mathbf{v} \phi) + \nabla \left[ \frac{\phi}{\xi} (\nabla \Pi - \rho_1 g \phi) \right]$$

(108)

$$\nabla \eta \cdot [\nabla \mathbf{v} + (\nabla \mathbf{v})^t] = \nabla (p - \Pi) - \rho_1 g \phi$$

(109)

and

$$\nabla \cdot \mathbf{v} = 0$$

(110)

Again one can show that the above set of equations can be written in the form of Onsager's kinetic equation:

$$\frac{\partial \phi}{\partial t} = -\int dr' L(r,r') \frac{\delta A}{\delta \phi(r')}$$

(111)

with symmetric kernel $L(r,r')$.

It should be emphasized that the state variable in the present problem is $\phi(r)$, and $v_p$ and $\mathbf{v}$ are auxiliary variables introduced to determine $\dot{\phi}(r)$. In some literatures, the first term on the right hand side of Eq.(108) is called “reversible part”. This terminology is misleading, since there is no reason to discriminate the velocity $\mathbf{v}$ from the velocity $v_p$: both velocities are determined by the balance of the dissipative force and the potential force.
6.3. Phase separation

A special case of the above coupled equations for diffusion and flow is the equations used to describe the phase separation kinetics in solution. Suppose a homogeneous solution is brought into the state where $\partial \Pi / \partial \phi$ is negative, then the solution starts to separate into two phases, concentrated phase and dilute phase. The kinetics of phase separation has been extensively discussed in statistical mechanics. The equations used there can be obtained by a minor modification of the above equations.

In the final state of phase separation, concentrated region and dilute region coexist with each other. At the boundary between the two regions, solute concentration changes very rapidly over molecular length scale. In such a case, the total free energy cannot be written in the form of Eq.(93). There is an extra energy which corresponds to the interfacial energy between the two regions. The interfacial energy can be accounted for by the following free energy functional

$$ A = \int dr \left[ f(\phi) + \frac{1}{2} \kappa_s (\nabla \phi)^2 \right] $$

(112)

where $\kappa_s$ is a positive constant. Then $\dot{A}$ is given by

$$ \dot{A} = \int dr \frac{\delta A}{\delta \phi(r)} \dot{\phi}(r) = \int dr (f'(\phi) - \kappa_s \nabla^2 \phi) \dot{\phi}(r) $$

(113)

The phase separation kinetics can be discussed by Eqs.(106) and (107) with $f'(\phi)$ being replaced by $f'(\phi) - \kappa_s \nabla^2 \phi$. This gives the following set of equations

$$ \frac{\partial \phi}{\partial t} = -\nabla \cdot (\nu \phi) + \nabla \left[ \frac{\phi}{\xi} (\nabla \Pi - \rho_1 g \phi - \phi \kappa_s \nabla^2 \phi) \right] $$

(114)

$$ \nabla \eta \cdot [\nabla v + (\nabla v)^t] = \nabla (p - \Pi) - \rho_1 g \phi - \phi \kappa_s \nabla^2 \phi $$

(115)

Outcomes of these equations are discussed in.

7. Gel Dynamics

Gel is a homogeneous mixture of elastic material and fluid. In polymeric gels, gel consists of cross-linked polymer and solvent. The cross-linked polymer forms a three dimensional network and gives an elasticity to the gel.

The deformation of polymer network is coupled with the transport of solvent. For example, when a gel is compressed, solvent bleeds out from
the gel (see Fig. 8(a)). Conversely, when a drop of solvent permeates into a gel, it deforms the gel (Fig. 8(b)). Equations which describe the coupled phenomena of gel deformation and solvent permeation can be derived from the variational principle. The derivation is very similar to that for solutions. The difference is that, in solutions, the free energy is a function of polymer concentration, while in gels, the free energy is a function of the deformation of polymer network.

The state variable in a gel is the displacement field $u(r,t)$ which represents the displacement of the point on the network located at $r$ in a certain reference state. The free energy of the system $A$ is now expressed as a functional of the gradient of the displacement vector, i.e.,

$$ A = \int dr f(e_{\alpha\beta}(r)) $$

where $e_{\alpha\beta}$ is defined by

$$ e_{\alpha\beta} = \frac{\partial u_{\alpha}}{\partial r_{\beta}} $$

If the displacement is small, the free energy density $f$ is given by the same form as the elastic energy of deformation

$$ f = \frac{1}{2}K e_{\alpha\alpha}^2 + \frac{1}{4}G \left( e_{\alpha\beta} + e_{\beta\alpha} - \frac{2}{3}\delta_{\alpha\beta}e_{\gamma\gamma} \right)^2 $$

where $K$ and $G$ are called the osmotic bulk modulus, and the shear modulus respectively.

The time derivative $\dot{A}$ is calculated as

$$ \dot{A} = \int dr \frac{\partial f}{\partial e_{\alpha\beta}} \frac{\partial u_{\alpha}}{\partial r_{\beta}} = \int dr \sigma_{\alpha\beta} \frac{\partial u_{\alpha}}{\partial r_{\beta}} $$

Fig. 8. Examples showing the coupling between solvent motion and deformation of gels. (a) Solvent bleeds out from a squeezed gel. (b) A drop of solvent placed at the top of a gel induces a deformation of the gel.

(a) Solvent bleeds out from a squeezed gel. (b) A drop of solvent placed at the top of a gel induces a deformation of the gel.
where

\[ \sigma^{n}_{\alpha\beta} = \frac{\partial f}{\partial e_{\alpha\beta}} = Ke_{\gamma\gamma}\delta_{\alpha\beta} + G\left(e_{\alpha\beta} + e_{\beta\alpha} - \frac{2}{3}\delta_{\alpha\beta}e_{\gamma\gamma}\right) \] (120)

is called the osmotic stress tensor. The osmotic stress tensor corresponds to the osmotic pressure in solution, and stands for the thermodynamic force acting on the solute (i.e., the polymer network in the present problem).

On the other hand, the energy dissipation function is given by

\[ \Phi = \frac{1}{2} \int d\mathbf{r} \xi (\dot{u} - v_s)^2 \] (121)

where \( v_s \) stands for the velocity of the solvent. In Eq.(121), it is assumed that the energy dissipation in gels arises dominantly from the relative motion between solvent and polymer network; the energy dissipation associated with the velocity gradient is ignored.

In constructing the Rayleighian, one has to take into account of the fact that gel behaves as an incompressible material; i.e., the volume change of a gel can only occur by taking in (or out) solvent from (or to) surrounding. This constraint is expressed as the incompressible condition \( \nabla \cdot \mathbf{v} = 0 \) for the volume average velocity \( \mathbf{v} = \phi \dot{\mathbf{u}} + (1 - \phi)v_s \), or

\[ \phi \nabla \cdot \dot{\mathbf{u}} + (1 - \phi)\nabla \cdot v_s = 0 \] (122)

where the volume fraction of polymer network \( \phi \) is assumed not to change since the deformation is small. The Rayleighian is thus constructed as

\[ R = \frac{1}{2} \int d\mathbf{r} \left\{ \xi (\dot{u}_{\mathbf{r}} - v_{s,\mathbf{r}})^2 + \sigma^{n}_{\alpha\beta} \frac{\partial \dot{u}_{\mathbf{r}}}{\partial \mathbf{r}_{\beta}} - p(\mathbf{r}) \left[ \phi \frac{\partial \dot{u}_{\mathbf{r}}}{\partial \mathbf{r}_{\alpha}} + (1 - \phi)\frac{\partial v_{s,\mathbf{r}}}{\partial \mathbf{r}_{\alpha}} \right] \right\} \] (123)

The last term comes from the constraint (122). The conditions \( \delta R/\delta \dot{u}_{\mathbf{r}} = 0 \) and \( \delta R/\delta v_{s,\mathbf{r}} = 0 \) give the following set of equations:

\[ \xi (\dot{u}_{\mathbf{r}} - v_{s,\mathbf{r}}) - \frac{\partial \sigma^{n}_{\alpha\beta}}{\partial \mathbf{r}_{\beta}} + \phi \frac{\partial p}{\partial \mathbf{r}_{\alpha}} = 0 \] (124)

\[ -\xi (\dot{u}_{\mathbf{r}} - v_{s,\mathbf{r}}) + (1 - \phi) \frac{\partial p}{\partial \mathbf{r}_{\alpha}} = 0 \] (125)

Equations (124) and (125) give

\[ \frac{\partial}{\partial \mathbf{r}_{\beta}} (\sigma^{n}_{\alpha\beta} - p\delta_{\alpha\beta}) = 0 \] (126)

and

\[ v_{s,\alpha} - \dot{u}_{\alpha} = -\frac{1 - \phi}{\xi} \frac{\partial p}{\partial \mathbf{r}_{\alpha}} \] (127)
Equation (126) stands for the balance of forces acting on each volume element of the gel. Notice that the mechanical stress acting on the volume element is given by $\sigma_{\alpha\beta} - p\delta_{\alpha\beta}$. The term $-p\delta_{\alpha\beta}$ represents the contribution from the solvent pressure. In fact, if one calculates the force acting at the wall for the situation shown in Fig.3 (b) using Eq.(37), one can show that the force acting on the wall is given by $(\sigma^n - pI) \cdot n$, where $n$ is a vector normal to the wall.

On the other hand, Eq. (127) represents the permeation of solvent in gel network. Equation (127) indicates that the permeation speed is proportional to the pressure gradient. This is known as Darcy’s law for porous materials.

The dynamics of gels (deformation and solvent permeation) can be described by Eqs. (122), (126) and (127). The equations may be written explicitly as partial differential equations for $u$ and $p$:

$$\left( K + \frac{1}{3} G \right) \nabla (\nabla \cdot u) + G \nabla^2 u = \nabla p$$  \hspace{1cm} (128)

and

$$\nabla \dot{u} = \kappa \nabla^2 p$$  \hspace{1cm} (129)

where

$$\kappa = \frac{(1 - \phi)^2}{\xi}$$  \hspace{1cm} (130)

Application of these equations is discussed in Ref. 6.

8. Liquid Crystals

Liquid crystal is a fluid which has an intermediate order between liquid and crystal. In a typical class of liquid crystals called nematics, molecular orientation is ordered as in a crystal, while molecular positions are random as in a liquid. The direction of the molecular orientation is represented by a unit vector $n$ called director. The director can change in space and time depending on external forces (of mechanical, electrical or magnetic origin).

The continuum mechanics of nematics was established by Leslie and Ericksen.\textsuperscript{4} The Leslie–Ericksen theory describes the time variation of the fluid velocity $v(r,t)$, and the director $n(r,t)$. Here this theory is discussed based on the variational principle.

In the Leslie–Ericksen theory, the state variable is the director field $n(r)$ which stands for the average direction of molecules at point $r$. The energy
dissipation function \( \Phi \) is a quadratic function of \( \dot{n}_\alpha \) and \( \kappa_{\alpha\beta} = \partial v_\alpha / \partial r_\beta \). The explicit form of \( \Phi \) can be determined by symmetry argument. Using the fact that \( \Phi \) vanishes for uniform rotation of the system, one can show that \( \Phi \) is a quadratic function of strain rate

\[
\dot{\epsilon}_{\alpha\beta} = \frac{1}{2} (\kappa_{\alpha\beta} + \kappa_{\beta\alpha})
\]

(131)

and \( \tilde{n}_\alpha \) which is defined by

\[
\tilde{n}_\alpha = \dot{n}_\alpha - \frac{1}{2} (\kappa_{\alpha\beta} - \kappa_{\beta\alpha}) n_\beta
\]

(132)

\( \tilde{n}_\alpha \) represents the deviation of \( \dot{n} \) from the fluid rotation. If one constructs the energy dissipation function \( \Phi \) which is scalar and quadratic in \( \dot{\epsilon}_{\alpha\beta} \) and \( \tilde{n}_\alpha \) with coefficients that may depend on \( n \), one gets

\[
2\Phi = \beta_1 (\dot{\epsilon}_{\alpha\beta} n_\alpha n_\beta)^2 + \beta_2 \dot{\epsilon}_{\alpha\beta}^2 + \beta_3 (\dot{\epsilon}_{\alpha\beta} n_\beta)^2 + \beta_4 \tilde{n}_\alpha^2 + \beta_5 \tilde{n}_\alpha \dot{\epsilon}_{\alpha\beta} n_\beta
\]

(133)

where \( \beta_1, ... \beta_5 \) are constants.

On the other hand, the free energy of nematics is given by the elastic energy of directors

\[
A = \frac{1}{2} K_1 (\nabla \cdot n)^2 + \frac{1}{2} K_2 (n \cdot \nabla \times n)^2 + \frac{1}{2} K_3 (n \times \nabla \times n)^2
\]

(134)

If we define

\[
g_{\alpha\beta} = \frac{\partial n_\beta}{\partial r_\alpha}
\]

(135)

the free energy \( A \) is written as

\[
A = \frac{1}{2} K_1 (g_{\alpha\alpha})^2 + \frac{1}{2} K_2 (g_{\alpha\beta} n_\alpha g_{\beta\gamma})^2 + \frac{1}{2} K_3 (g_{\alpha\beta} n_\beta - g_{\beta\alpha} n_\gamma)^2
\]

(136)

The time derivative \( \dot{A} \) is written as

\[
\dot{A} = \sigma_{\alpha\beta}^{(e)} \kappa_{\alpha\beta} + h_\alpha \tilde{n}_\alpha
\]

(137)

where \( \sigma_{\alpha\beta}^{(e)} \) and \( h_\alpha \) are obtained as:

\[
\sigma_{\alpha\beta}^{(e)} = - \frac{\partial A}{\partial g_{\alpha\gamma}} g_{\gamma\beta}
\]

(138)

\[
h_\alpha = - \frac{\partial A}{\partial n_\alpha} + \frac{\partial}{\partial r_\beta} \left( \frac{\partial A}{\partial g_{\alpha\beta}} \right)
\]

(139)

The Rayleighian therefore becomes

\[
R = \Phi + \sigma_{\alpha\beta}^{(e)} \kappa_{\alpha\beta} + h_\alpha \tilde{n}_\alpha - \lambda n_\alpha \dot{n}_\alpha - \eta_{\alpha\alpha}
\]

(140)
The last two terms arise from the constraints for \( \kappa_{\alpha\beta} \) and \( \tilde{n}_\alpha \).

The time evolution of \( n_\alpha \) is determined by \( \partial R/\partial \dot{n}_\alpha = 0 \), and the stress tensor is given by \( \sigma_{\alpha\beta} = \partial R/\partial \kappa_{\alpha\beta} \). Straightforward calculation gives the following expression for the stress tensor \( \sigma_{\alpha\beta} \) and the time evolution equation for \( n_\alpha \):

\[
\sigma_{\alpha\beta} = \alpha_1 \dot{\epsilon}_{\mu\nu} n_\mu \dot{n}_\nu n_\beta + \alpha_2 n_\alpha \tilde{n}_\beta + \alpha_3 \tilde{n}_\alpha n_\beta + \alpha_4 \kappa_{\alpha\beta} + \alpha_5 n_\alpha n_\mu \dot{\epsilon}_{\mu\beta} + \alpha_6 n_\beta n_\mu \dot{\epsilon}_{\alpha\mu} + \sigma^{(c)}_{\alpha\beta} - p \delta_{\alpha\beta}
\]

where

\[
\gamma_1 \dot{n}_\alpha + \gamma_2 \dot{\epsilon}_{\alpha\beta} n_\beta - h_\alpha = \lambda n_\alpha
\]

Equations (141)-(142) are the Leslie–Ericksen’s equation. Notice that the Parodi’s relation \( \alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \) is automatically satisfied in this derivation.

9. Conclusion

In this paper, I have shown that many equations used in soft matter physics can be derived from Onsager’s variational principle. The variational principle is equivalent to Onsager’s kinetic equation with reciprocal relations, but it has several advantages. The variational principle allows us a great flexibility in choosing state variables, and velocities. Also, the variational principle is quite convenient to deal with systems which have certain constraints, and to calculate the forces needed to change control parameters.

Various time evolution equations used in soft matter physics, such as the diffusion equation, the flow-diffusion coupled equation, the gel dynamics
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Onsager’s variational principle is giving a unified framework for the soft matter dynamics.

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Appendix A. Proof of the Hydrodynamic Reciprocal Relation

The friction coefficient $\zeta_{ij}$ for particles in viscous fluid can be calculated by the following procedure. Consider that the configuration of the particles changes with the rate $\dot{x} = (\dot{x}_1, \dot{x}_2, ...)$. The velocity of a point $r$ on a surface of a particles is a linear function of $\dot{x}$ and can be written as

$$v(r) = \sum_i G_i(r; x) \dot{x}_i$$

The function $G_i(r; x)$ is determined by the shape of the particle. The fluid velocity induced by the particle motion is determined by solving the Stokes equation (1) under the boundary condition (A.1) at the surface of the particles.

The frictional force $f_H(r)$ acting on a unit area at the particle surface at $r$ is given by

$$f_H(r; x) = \sigma \cdot n$$

where

$$\sigma_{\alpha\beta} = \eta \left( \frac{\partial v_\alpha}{\partial r_\beta} + \frac{\partial v_\beta}{\partial r_\alpha} \right) - p \delta_{\alpha\beta}$$

is the $\alpha\beta$ component of the stress tensor of the fluid, and $n$ is a unit vector normal to the surface. The work done to the fluid is therefore calculated by

$$2\Phi = \int dS \sum_i -f_H(r; x) \cdot G_i(r; x) \dot{x}_i = -\sum_i F_{Hi} \dot{x}_i$$
where the integral \( dS \) is done for all surfaces, and the force \( F_{Hi} \) is defined by

\[
F_{Hi} = \int dS f_H(\mathbf{r}; x) \cdot \mathbf{G}_i(\mathbf{r}; x) \quad (A.5)
\]

Equation (A.5) is the definition of the frictional force conjugate to \( \dot{x}_i \).

Since the Stokes equation is a linear equation of \( v \), and the boundary condition for \( v \) is a linear function of \( \dot{x}_i \), the frictional force \( F_{Hi} \) can also be written as a linear function of \( \dot{x}_i \).

\[
F_{Hi} = -\sum_j \zeta_{ij}(x) \dot{x}_j \quad (A.6)
\]

To prove the reciprocal relation \( \zeta_{ij} = \zeta_{ji} \), we consider two situations, one is that the particle state changes with velocity \( \dot{x}_i^{(1)} \), and the other with velocity \( \dot{x}_i^{(2)} \). Let \( F_{Hi}^{(1)} \) \( F_{Hi}^{(2)} \) be the frictional forces for each situations. We shall prove the identity

\[
\sum_i F_{Hi}^{(1)} \dot{x}_i^{(2)} = \sum_i F_{Hi}^{(2)} \dot{x}_i^{(1)} \quad (A.7)
\]

The reciprocal relation follows from this identity.

Let \( \mathbf{v}^{(a)}(\mathbf{r}) \) and \( \sigma^{(a)} \) be the velocity field and the stress field for the two situations ((\( a = 1, 2 \))). By Eqs. (A.3) and (A.5), the left hand side of Eq. (A.7) is written as

\[
I = -\sum_i F_{Hi}^{(1)} \dot{x}_i^{(2)} = -\sum_i \int dS G_{i\alpha}(\mathbf{r}; x) \sigma_{\alpha\beta}^{(1)} n_\beta \dot{x}_i^{(2)} \quad (A.8)
\]

Since the fluid velocity satisfies the boundary condition (A.1),

\[
I = -\int dS v_{\alpha}^{(2)} \sigma_{\alpha\beta}^{(1)} n_\beta \quad (A.9)
\]

Using the Gauss theorem, the surface integral on the right hand side of Eq. (A.9) can be written as

\[
I = \int d\mathbf{r} \frac{\partial}{\partial r_\beta} (v_{\alpha}^{(2)} \sigma_{\alpha\beta}^{(1)}) = \int d\mathbf{r} \left( \frac{\partial v_{\alpha}^{(2)}}{\partial r_\beta} \sigma_{\alpha\beta}^{(1)} + \frac{\partial \sigma_{\alpha\beta}^{(1)}}{\partial r_\beta} v_\alpha^{(2)} \right) \quad (A.10)
\]

The second term in the integrand on the right hand side of Eq. (A.10) vanishes by the Stokes equation. The first term can be written as

\[
I = \frac{1}{2} \int d\mathbf{r} \left( \frac{\partial v_{\alpha}^{(2)}}{\partial r_\beta} + \frac{\partial v_{\beta}^{(2)}}{\partial r_\alpha} \right) \sigma_{\alpha\beta}^{(1)}
= \frac{\eta}{2} \int d\mathbf{r} \left( \frac{\partial v_{\alpha}^{(2)}}{\partial r_\beta} + \frac{\partial v_{\beta}^{(2)}}{\partial r_\alpha} \right) \left( \frac{\partial v_{\alpha}^{(1)}}{\partial r_\beta} + \frac{\partial v_{\beta}^{(1)}}{\partial r_\alpha} \right) \quad (A.11)
\]
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The last expression in this equation is invariant for the exchange of the superscript (1), (2). Therefore the hydrodynamic reciprocal relation Eq. (12) has been proven.

If we put $\dot{x}_i^{(1)} = \dot{x}_i^{(2)} = \dot{x}_i$ in Eq. (A.11), we have

$$-\sum_i F_{Hi} \dot{x}_i = \frac{\eta}{2} \int dr \left( \frac{\partial v_\alpha}{\partial r_\beta} + \frac{\partial v_\beta}{\partial r_\alpha} \right)^2$$

(A.12)

The right hand side of Eq. (A.12) is non-negative. Thus Eq. (13) has been proven.

References