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Onsager's variational principle in soft matter

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Abstract

In the celebrated paper on the reciprocal relation for the kinetic coefficients in irreversible processes, Onsager (1931 *Phys. Rev.* **37** 405) extended Rayleigh's principle of the least energy dissipation to general irreversible processes. In this paper, I shall show that this variational principle gives us a very convenient framework for deriving many established equations which describe the nonlinear and non-equilibrium phenomena in soft matter, such as phase separation kinetics in solutions, gel dynamics, molecular modeling for viscoelasticity nemato-hydrodynamics, etc. Onsager's variational principle can therefore be regarded as a solid general basis for soft matter physics.

1. Introduction

Soft matter represents a large class of materials, polymers, colloids, liquid crystals, and surfactants. Though they are diverse, they have a common feature that they all consist of large structural units, and show large responses to weak external perturbations.

The response of soft matter is characterized by its strong nonlinear and non-equilibrium nature. For example, the viscosity of polymer solutions is not constant, but decreases with increase of shear rate, and depends on the past history of shearing. In liquid crystals, the rotation of the molecular axis (the director) is coupled with macroscopic flow, and their optical response to electric field is strongly nonlinear. Stretched gels show very slow stress relaxation associated with the diffusion of solvent. Quenched solutions show quite complex structural evolution in the process of phase separation.

To describe such nonlinear, non-equilibrium phenomena, various kinetic equations have been proposed. Examples are (i) the Smoluchowski equation for the conformational change of polymers under flow [1, 2], (ii) the Ericksen–Leslie equation for the flow of liquid crystals [3], (iii) the gel dynamics equations [4], (iv) the phase separation dynamics of solutions [5], etc.

In this paper, I will show that these equations are derived from a variational principle which I shall call Onsager's variational principle. The variational principle is the same as that proposed by Onsager in his celebrated paper on the reciprocal relation in the phenomenological kinetic equations for irreversible processes [6]. As Onsager stated in the paper,

the variational principle is an extension of Rayleigh's principle of the least energy dissipation [7]. The least energy dissipation principle is well known in various linear systems such as viscous flow in Newtonian fluid, and electric current in ohmic devices. However, it should be emphasized that Onsager's phenomenological equation can give nonlinear time evolution equations [8–10], and that therefore the variational principle can be used to describe nonlinear phenomena.

Since the classical work of Onsager, various extensions and reformulations have been made for his work, and there are now several ways of deriving the phenomenological equations for the irreversible processes [8–10, 13]. In this paper, I will use the original formulation of Onsager and show that it gives us a simple and unified way of deriving various basic equations known in soft matter. The derivation presented here is not entirely new: various parts have already been published [2, 11, 12], and similar methods may have been already used in other contexts. However, to my knowledge, the presentation given here has not been published previously.

In order to make the argument as simple as possible, I shall limit the discussion to (i) isothermal systems (the temperature of the system is assumed to be constant), and (ii) slow kinetics (the inertia effect is assumed to be negligible). These effects may be taken into account in the same way as in [9, 13], but will not be discussed here.

2. Hydrodynamic variational principle

Onsager's variational principle is an extension of Rayleigh's principle of the least energy dissipation. Therefore this principle is discussed first.

To be clear, let us consider a motion of a rigid particle moving in a viscous fluid under the influence of some external force. The state of the particle is specified by six coordinates, three coordinates denoting the position of the center of mass, and three coordinates specifying the particle orientation. Let X_i ($i = 1, 2, \dots, 6$) be such generalized coordinates. Suppose that the external forces derive from a potential $U(X)$

$$F_i = -\frac{\partial U}{\partial X_i}. \quad (1)$$

This is a generalized force and F_i stands for usual force or torque. Under such forces, the particle moves. Let $V_i = \dot{X}_i$ be the generalized velocity of the particle. If the particle moves in a Newtonian fluid, the fluid exerts a frictional force on the particle. In the limit of small Reynolds number, the fluid motion is described by the Stokes equation, and the frictional force is written as a linear function of V_i [14, 15]

$$F_{Hi} = -\sum_j \zeta_{ij} V_j. \quad (2)$$

The coefficients ζ_{ij} are called friction coefficients, and can be calculated by solving the equations in Stokesian hydrodynamics.

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

$$\zeta_{ij} = \zeta_{ji} \quad \text{and} \quad \sum_{ij} \zeta_{ij} V_i V_j \geq 0 \quad \text{for any } V_i. \quad (3)$$

Notice that the relation $\zeta_{ij} = \zeta_{ji}$ is highly non-trivial. For example it states that if a torque T acting on a point P of a particle induces a velocity V of the point P, a force F acting on P induces an angular velocity ω of the particle around P and that the coefficients are equal to each other. Equation (3) can be proved by Stokesian hydrodynamics, and is called the Lorentz reciprocal relation [14].

Since the inertia effect is negligibly small in the usual motion of small particles, one can assume that the frictional force is always balanced with the potential force:

$$\sum_j \zeta_{ij} V_j = -\frac{\partial U}{\partial X_i}. \quad (4)$$

Let $(\zeta^{-1})_{ij}$ be the inverse of the matrix ζ_{ij} , then equation (4) gives a time evolution equation for X_i :

$$\frac{dX_i}{dt} = -\sum_j (\zeta^{-1})_{ij} \frac{\partial U}{\partial X_j}. \quad (5)$$

Notice that ζ_{ij} , $(\zeta^{-1})_{ij}$, and U are functions of X_i . Therefore, equation (5) is, in general, a rather complex nonlinear equation for X_i .

Using the reciprocal relation (3), the time evolution equation (4) can be cast into a variational principle. Let W and \dot{U} be defined by

$$W = \sum_{i,j} \zeta_{ij} V_i V_j \quad (6)$$

$$\dot{U} = \sum_i \frac{\partial U}{\partial X_i} V_i \quad (7)$$

and the function R be defined by

$$R = \frac{1}{2}W + \dot{U} = \frac{1}{2} \sum_{i,j} \zeta_{ij} V_i V_j + \sum_i \frac{\partial U}{\partial X_i} V_i \quad (8)$$

then it is easy to see that the force balance equation (4) is equivalent to the condition $\partial R / \partial V_i = 0$, i.e. the velocity V_i is determined by the condition that R be minimum with respect to V_i . This principle is called the principle of least energy dissipation.

It should be noted that the basis of the variational principle is the reciprocity and the positive definiteness of ζ_{ij} (equation (3)). As far as these conditions are satisfied, the time evolution equation can be cast in the variational principle. Using the Stokes equation, it can be proved that equation (3) is valid for any objects moving in Newtonian fluids. Therefore the variational principle holds quite generally. For example, the principle holds for objects with many degrees of freedom (such as polymers or membranes), or for the mixture of such objects (such as concentrated solutions of particles or polymers).

The function R is called a Rayleighian. The Rayleighian consists of two terms W and \dot{U} . W is a quadratic function of V_i , and stands for the work done to the fluid per unit time when the particle moves with velocity V_i . The function $(1/2)W$ is called the energy dissipation function. The function \dot{U} is a linear function of V_i and stands for the change of the potential energy of the particle when it moves with velocity V_i .

3. Onsager's variational principle

Onsager showed that the above principle holds for general irreversible processes. Let X_i be the set of variables describing the non-equilibrium state of the system, and let us assume that the time evolution of the state can be written in the form

$$\frac{dX_i}{dt} = \sum_j L_{ij} \frac{\partial S(X)}{\partial X_j} \quad (9)$$

where $S(X)$ is the entropy of the system, and L_{ij} are the phenomenological kinetic coefficients. Using the time reversal symmetry in the equilibrium state, Onsager proved that L_{ij} is symmetric¹

$$L_{ij} = L_{ji}. \quad (10)$$

This reciprocal relation allows us to write the time evolution equation (9) in the form of a variational principle. In the original paper [6], Onsager formulated the variational principle as the maximization of the function $T\dot{S} - (1/2)W$. For isothermal systems, this principle can be shown to reduce to the principle of least energy dissipation: the time evolution of the system is determined by minimizing

$$R = \frac{1}{2} \sum_{i,j} \zeta_{ij} \dot{X}_i \dot{X}_j + \sum_i \frac{\partial A}{\partial X_i} \dot{X}_i \quad (11)$$

¹ Here we are assuming that the state variables X_i are invariant under time reversal transformation, and that there is no magnetic field.

with respect to \dot{X}_i . In equation (11), A is the free energy for the non-equilibrium state, and the second term stands for \dot{A} , the time derivative of A . The difference between equations (8) and (11) is that X_i now stands for the general state variables specifying the non-equilibrium state, and $A(X)$ is the free energy of the system.

Onsager's variational principle is equivalent to the kinetic equation

$$\dot{X}_j = - \sum_j (\zeta^{-1})_{ij} \frac{\partial A}{\partial X_j} \quad (12)$$

but the variational principle has several advantages. This will be demonstrated in the following sections.

4. Diffusion

As a simple application of the variational principle, let us first consider the collective motion of particles in suspensions. Consider the situation that there are many particles moving together (diffusing or sedimenting) in a viscous fluid. In such a situation, it is not sensible to focus on the dynamics of individual particles; it is more important to focus on the behavior of particles as a whole, for example how the concentration of particles evolves in time, or how the orientational distribution of particles evolves in time. Onsager's variational principle gives us a convenient tool to answer these questions.

First let us consider a simple situation that the solution is macroscopically at rest and that the individual particle is a sphere of radius a . Let $n(\mathbf{r}, t)$ be the number density of the particle at point \mathbf{r} and time t . The volume fraction of the particle is given by

$$\phi(\mathbf{r}, t) = v_c n(\mathbf{r}, t) \quad (13)$$

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

The non-equilibrium state of the system is described by $\phi(\mathbf{r}, t)$, and our task is to derive a time evolution equation for ϕ . Since ϕ satisfies the conservation equation

$$\dot{\phi} = -\nabla \cdot (\mathbf{v}_p \phi) \quad (14)$$

we shall determine \mathbf{v}_p , the mean velocity of particles at \mathbf{r} , by the variational principle.

When particles move with velocity \mathbf{v}_p in a quiescent solution, the energy dissipation is given by

$$W = \int d\mathbf{r} \xi(\phi) \mathbf{v}_p^2 \quad (15)$$

where $\xi(\phi)$ is the friction constant for the collective motion of particles per unit volume. If the suspension is dilute, $\xi(\phi)$ is simply given by $6\pi\eta a n = 6\pi\eta a \phi/v_c$. If the suspension is not dilute, $\xi(\phi)$ is not easy to calculate due to hydrodynamic interaction, but many studies have been made and an approximate formula for $\xi(\phi)$ is known [14, 15].

The free energy A of the system can be expressed as a functional of ϕ :

$$A = \int d\mathbf{r} f(\phi(\mathbf{r})) \quad (16)$$

where $f(\phi)$ stands for the free energy per unit volume of the suspension, and we have assumed that the effect of gravity is negligible. From equation (16), \dot{A} can be calculated by using equation (14):

$$\begin{aligned} \dot{A} &= \int d\mathbf{r} f'(\phi) \dot{\phi} = - \int d\mathbf{r} f'(\phi) \nabla \cdot (\mathbf{v}_p \phi) \\ &= \int d\mathbf{r} \mathbf{v}_p \phi \cdot \nabla f'(\phi) \end{aligned} \quad (17)$$

where we have used integration by parts.

The Rayleighian is then given by

$$R = \frac{1}{2} \int d\mathbf{r} \xi(\phi) \mathbf{v}_p^2 + \int d\mathbf{r} \mathbf{v}_p \phi \cdot \nabla f'(\phi). \quad (18)$$

The minimization of R with respect to \mathbf{v}_p gives the following:

$$\mathbf{v}_p = -\frac{\phi}{\xi} \nabla f'(\phi). \quad (19)$$

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

$$\Pi = \phi f'(\phi) - f(\phi) \quad (20)$$

as

$$\mathbf{v}_p = -\frac{1}{\xi} \nabla \Pi. \quad (21)$$

Equations (14) and (21) give the following diffusion equation:

$$\frac{\partial \phi}{\partial t} = \nabla \cdot [D(\phi) \nabla \phi] \quad (22)$$

where $D(\phi)$ is given by

$$D(\phi) = \frac{\phi}{\xi} \frac{\partial \Pi}{\partial \phi}. \quad (23)$$

This gives a diffusion constant in concentrated solution. It is easy to confirm that in the case of dilute solution equation (23) gives the Einstein formula $D = k_B T / (6\pi\eta a)$.

In the above example of diffusion, the variable X_i which specifies the non-equilibrium state of the system is the spatial distribution of the volume fraction of the particles $\phi(\mathbf{r})$. Hence the suffix i is replaced by the spatial coordinate \mathbf{r} . The diffusion equation is a special form of Onsager's kinetic equation. Indeed, equation (22) can be written in the form of the kinetic equation shown in equation (12):

$$\dot{\phi}(\mathbf{r}) = - \int d\mathbf{r}' L(\mathbf{r}, \mathbf{r}') \frac{\delta A}{\delta \phi(\mathbf{r}')} \quad (24)$$

where the kernel $L(\mathbf{r}, \mathbf{r}')$ is given by

$$L(\mathbf{r}, \mathbf{r}') = -\nabla \cdot \left[\frac{\phi(\mathbf{r})^2}{\xi(\phi(\mathbf{r}))} \nabla \delta(\mathbf{r} - \mathbf{r}') \right]. \quad (25)$$

The kernel $L(\mathbf{r}, \mathbf{r}')$ is symmetric, i.e., for any functions $\phi_1(\mathbf{r})$ and $\phi_2(\mathbf{r})$, the following identity holds:

$$\begin{aligned} \int d\mathbf{r} d\mathbf{r}' L(\mathbf{r}, \mathbf{r}') \phi_1(\mathbf{r}) \phi_2(\mathbf{r}') \\ = \int d\mathbf{r} d\mathbf{r}' L(\mathbf{r}', \mathbf{r}) \phi_1(\mathbf{r}) \phi_2(\mathbf{r}'). \end{aligned} \quad (26)$$

Notice that in the above application of the variational principle, what is determined by the variational principle is not the time derivative of the state variable $\dot{\phi}$, but the velocity v_p which determines $\dot{\phi}$, yet the reciprocal relation for the kinetic coefficients is satisfied (see equation (26)). As far as the time evolution equation is obtained by the variational principle, the final kinetic equations satisfy Onsager's reciprocal relation. This fact can be proved quite generally.

Suppose that the time derivative of the state variable \dot{X}_i is written as a linear combination of some generalized velocities V_i :

$$\dot{X}_i = \sum_j a_{ij} V_j \quad (27)$$

where a_{ij} is a certain coefficient². The matrix (a_{ij}) needs not be a square matrix: the number of velocity variables V_i can be different from the number of state variables X_i . Suppose that the energy dissipation function is written as a quadratic function of V_i and that the Rayleighian is given by

$$R = \frac{1}{2} \sum_{ij} \tilde{\zeta}_{ij} V_i V_j + \sum_{ij} \frac{\partial A}{\partial X_i} a_{ij} V_j. \quad (28)$$

Minimization of R gives

$$V_i = \sum_{jk} (\tilde{\zeta}^{-1})_{ij} \frac{\partial A}{\partial X_k} a_{kj}. \quad (29)$$

This gives the following kinetic equation:

$$\dot{X}_i = \sum_j L_{ij} \frac{\partial A}{\partial X_j} \quad (30)$$

with

$$L_{ij} = \sum_{l,k} a_{ik} a_{jl} (\tilde{\zeta}^{-1})_{kl} \quad (31)$$

which satisfies the reciprocal relation ($L_{ij} = L_{ji}$) and positive definiteness $\sum_{i,j} x_i x_j L_{ij} \geq 0$.

The above example demonstrates an advantage of the variational principle. If it is difficult to write down the energy dissipation as a function of \dot{X}_i , one can choose any set of variables V_i which describe the time evolution of the system and determine them by the variational principle. This flexibility is quite useful, and will be seen further in the following examples.

5. Coupling between flow and particle motion

5.1. Colloidal suspensions

In section 4, it is assumed that the solution is at rest as a whole. This assumption is not always correct. When colloidal particles move relative to the 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. A certain part starts to sediment faster than the other, and forms 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 the fluid flow as a whole. Let $v(\mathbf{r}, t)$ be the macroscopic velocity of the solution (v is defined as the volume averaged velocity $v = \phi v_p + (1 - \phi) v_s$). If we assume that the colloidal solution is regarded as a Newtonian fluid with effective viscosity $\eta(\phi)$, the energy dissipation function is written as

$$W = \int d\mathbf{r} \xi(\phi) (v_p - v)^2 + \frac{1}{2} \int d\mathbf{r} \eta(\phi) \left(\frac{\partial v_\alpha}{\partial r_\beta} + \frac{\partial v_\beta}{\partial r_\alpha} \right)^2 \quad (32)$$

where the indices α, β denote the x, y, z components of vectors and Einstein's convention, that summation is taken over repeatedly appearing indices, is used. The first term v_p^2 in equation (15) has been replaced by $(v_p - v)^2$, and the second term has been added to account for the energy dissipation caused by the velocity gradient of the solution.

With the gravitational energy taken into account, the free energy A of the solution is now given by

$$A = \int d\mathbf{r} [f(\phi) - \rho_1 \phi \mathbf{g} \cdot \mathbf{r}] \quad (33)$$

where $\rho_1 = \rho_p - \rho_s$ is the density difference between the particle and solvent. The time derivative of (33) is

$$\begin{aligned} \dot{A} &= \int d\mathbf{r} (f'(\phi) - \rho_1 \mathbf{g} \cdot \mathbf{r}) \dot{\phi}(\mathbf{r}) \\ &= \int d\mathbf{r} v_p \phi \cdot (\nabla f'(\phi) - \rho_1 \mathbf{g}). \end{aligned} \quad (34)$$

Since the solution is incompressible, v has to satisfy the constraint

$$\nabla \cdot v = 0. \quad (35)$$

Therefore the Rayleighian is given by

$$R = \frac{1}{2} W + \dot{A} + \int d\mathbf{r} p(\mathbf{r}) \nabla \cdot v \quad (36)$$

where the last term stands for the effect of constraint (35). The conditions $\delta R / \delta v_p = 0$ and $\delta R / \delta v = 0$ give the following equations:

$$\xi(v_p - v) = -\phi \nabla f'(\phi) + \rho_1 \phi \mathbf{g} \quad (37)$$

$$\nabla \eta \cdot [\nabla v + (\nabla v)'] + \xi(v - v_p) = \nabla p. \quad (38)$$

Equations (35), (37), (38) and (14) give a closed set of equations which describes the coupling between the particle motion (diffusion and sedimentation) and macroscopic flow.

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

$$\dot{\phi}(\mathbf{r}) = - \int d\mathbf{r}' L(\mathbf{r}, \mathbf{r}') \frac{\delta A}{\delta \phi(\mathbf{r}')} \quad (39)$$

with symmetric kernel $L(\mathbf{r}, \mathbf{r}')$.

It should be emphasized that the state variable in solutions is $\phi(\mathbf{r})$, and v_p and v are auxiliary variables introduced to

² Notice that equation (14) can be written as $\dot{\phi}(\mathbf{r}) = \int d\mathbf{r}' a(\mathbf{r}, \mathbf{r}') v_p(\mathbf{r}')$ with $a(\mathbf{r}, \mathbf{r}') = -\nabla[\delta(\mathbf{r} - \mathbf{r}')\phi(\mathbf{r})]$ and is a special form of equation (27).

describe the time evolution of $\phi(\mathbf{r})$. Equations (14) and (37) can be written as

$$\dot{\phi}(\mathbf{r}) = -\nabla \cdot (\mathbf{v}\phi) + \nabla \cdot \left[\frac{\phi}{\xi} \nabla \frac{\delta A}{\delta \phi(\mathbf{r})} \right]. \quad (40)$$

In some of the literature, the first term on the right-hand side is called the ‘reversible part’. This terminology is misleading, since there is no reason to discriminate the variable \mathbf{v} from other variable \mathbf{v}_p : both velocities are determined by the balance of the dissipative force and the potential force.

5.2. Phase separation

A special case of the above coupled equation for flow and diffusion is the equation used to describe the phase separation kinetics in solution. Suppose a homogeneous solution is brought into the state where $D(\phi)$ is negative, then the solution starts to separate into two phases, the concentrated phase and the dilute phase. The kinetics of phase separation has been extensively discussed in statistical mechanics [5]. The equations used there can be obtained by a minor modification of the above equations.

In the final state of phase separation, the concentrated region and the dilute region coexist with each other. At the boundary between the two regions, concentration changes very rapidly over the molecular length scale. In such a case, the total free energy cannot be written in the form of equation (16). There is an extra energy which corresponds to the interfacial energy between the two regions. The effect of the interfacial energy can be accounted for by replacing equation (16) by

$$A = \int d\mathbf{r} [f(\phi) + \frac{1}{2}\kappa_s(\nabla\phi)^2] \quad (41)$$

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

$$\dot{A} = \int d\mathbf{r} \frac{\delta A}{\delta \phi(\mathbf{r})} \dot{\phi}(\mathbf{r}) = \int d\mathbf{r} (f'(\phi) - \kappa_s \nabla^2 \phi) \dot{\phi}(\mathbf{r}). \quad (42)$$

The phase separation kinetics has been discussed by the set of equations (14), (37) and (38) with $f'(\phi)$ being replaced by $f'(\phi) - \kappa_s \nabla^2 \phi$.

6. Gel dynamics

Gel is a homogeneous mixture of elastic material and fluid. A typical gel, polymeric 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 the polymer network is coupled with the transport of the solvent. For example, when a gel is compressed, solvent bleeds out from the gel. Equations which describe the coupled phenomena of network deformation and solvent permeation can be derived from the variational principle [4, 12]. The derivation is the same as for solutions. The only 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 gradient of the polymer network.

The state variable in a gel is the displacement vector $\mathbf{u}(\mathbf{r}, t)$ which represents the displacement of the point on the network located at \mathbf{r} in a certain reference state. If the displacement is small, the free energy is given in the same form as the elastic energy of deformation:

$$A = \int d\mathbf{r} \left[\frac{1}{2}K \left(\frac{\partial u_\alpha}{\partial r_\alpha} \right)^2 + \frac{1}{4}G \left(\frac{\partial u_\alpha}{\partial r_\beta} + \frac{\partial u_\beta}{\partial r_\alpha} - \frac{2}{3}\delta_{\alpha\beta} \frac{\partial u_\gamma}{\partial r_\gamma} \right)^2 \right] \quad (43)$$

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

On the other hand, the energy dissipation is given by

$$W = \int d\mathbf{r} \xi (\dot{\mathbf{u}} - \mathbf{v}_s)^2 \quad (44)$$

where \mathbf{v}_s stands for the velocity of the solvent.

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 solvent from the surroundings, or bringing out solvent to the surroundings). This constraint is expressed as

$$\phi \nabla \cdot \dot{\mathbf{u}} + (1 - \phi) \nabla \cdot \mathbf{v}_s = 0 \quad (45)$$

where ϕ is the volume fraction of solvent (which may be assumed to be constant in the present consideration of small deformation).

The Rayleighian is thus constructed as

$$R = \frac{1}{2} \int d\mathbf{r} \xi (\dot{\mathbf{u}} - \mathbf{v}_s)^2 + \int d\mathbf{r} \frac{\delta A}{\delta \mathbf{u}} \cdot \dot{\mathbf{u}} + \int d\mathbf{r} p(\mathbf{r}) [\phi \nabla \cdot \dot{\mathbf{u}} + (1 - \phi) \nabla \cdot \mathbf{v}_s]. \quad (46)$$

The last term comes from the constraint (45). The conditions $\delta R / \delta \dot{\mathbf{u}} = 0$ and $\delta R / \delta \mathbf{v}_s = 0$ give the following set of equations:

$$(K + \frac{1}{3}G) \nabla (\nabla \cdot \mathbf{u}) + G \nabla^2 \mathbf{u} = \nabla p \quad (47)$$

and

$$\nabla \cdot \mathbf{u} = \kappa \nabla^2 p \quad (48)$$

where

$$\kappa = \frac{(1 - \phi)^2}{\xi}. \quad (49)$$

Equations (47) and (48) are the basic equations which describe the coupling of deformation and diffusion in gels. Application of these equations is discussed in [4].

7. Viscoelasticity of fluid

So far, we have assumed that the material is either a viscous fluid of constant viscosity or an elastic material of constant modulus. Actual soft matters are usually viscoelastic: they have both viscosity and elasticity [1, 16], and the relation between the stress and strain (or strain rate) is nonlinear. Describing the complex flow and deformation behavior of soft matter has been a central issue in rheology [1, 16]. Here I shall

show that the complex rheological properties of soft matter can again be handled by the variational principle. As an example, I take a solution of rod-like polymers.

Consider first a dilute solution of rod-like polymers. Suppose that the solution is uniform and flowing with macroscopic velocity

$$\mathbf{v}(\mathbf{r}) = \boldsymbol{\kappa} \cdot \mathbf{r} \quad (50)$$

where $\boldsymbol{\kappa}$ stands for the velocity gradient tensor:

$$\kappa_{\alpha\beta} = \frac{\partial v_\alpha}{\partial r_\beta}. \quad (51)$$

The viscosity of the solution depends on the orientational distribution of the polymers. Let $\psi(\mathbf{u}, t)$ be the probability of finding a polymer in the direction of unit vector \mathbf{u} . The time derivative of $\psi(\mathbf{u}, t)$ satisfies the conservation equation

$$\dot{\psi} = -\frac{\partial}{\partial \mathbf{u}} \cdot (\psi \dot{\mathbf{u}}) \quad (52)$$

and $\dot{\mathbf{u}}$ is determined by the variational principle.

The energy dissipation function is written as a quadratic function of $\dot{\mathbf{u}}$ and $\boldsymbol{\kappa}$. If the polymer follows the macroscopic flow, its direction changes according to

$$\dot{\mathbf{u}}_{\text{flow}} = \left(\mathbf{I} - \frac{\mathbf{u}\mathbf{u}}{u^2} \right) \cdot \boldsymbol{\kappa} \cdot \mathbf{u}. \quad (53)$$

Deviation of $\dot{\mathbf{u}}$ from $\dot{\mathbf{u}}_{\text{flow}}$ causes extra energy dissipation. For a slender rod, the energy dissipation per unit volume is shown to be given by [2]

$$W = \frac{1}{2} \eta_0 (\boldsymbol{\kappa} + \boldsymbol{\kappa}^t) : (\boldsymbol{\kappa} + \boldsymbol{\kappa}^t) + n \zeta_r \int d\mathbf{u} \psi \left[(\dot{\mathbf{u}} - \dot{\mathbf{u}}_{\text{flow}})^2 + \frac{1}{2} (\mathbf{u} \cdot \boldsymbol{\kappa} \cdot \mathbf{u})^2 \right] \quad (54)$$

where η_0 is the viscosity of solvent, $\boldsymbol{\kappa}^t$ is the transpose of the tensor $\boldsymbol{\kappa}$, n is the number density of particles, and ζ_r is the rotational friction constant of the polymer. The first term on the right-hand side represents the energy dissipation caused by solvent viscosity, and the second term represents the dissipation due to the presence of rod-like polymers.

In dilute solutions, the free energy A is entirely due to the orientational entropy, and is written as

$$A = nk_B T \int d\mathbf{u} \psi \ln \psi. \quad (55)$$

From equations (52) and (55), \dot{A} is calculated as

$$\begin{aligned} \dot{A} &= nk_B T \int d\mathbf{u} (\dot{\psi} \ln \psi + \dot{\psi}) \\ &= nk_B T \int d\mathbf{u} \dot{\mathbf{u}} \psi \frac{\partial \ln \psi}{\partial \mathbf{u}}. \end{aligned} \quad (56)$$

Since \mathbf{u} is a unit vector, $\dot{\mathbf{u}}$ has to satisfy the constraint

$$\dot{\mathbf{u}} \cdot \mathbf{u} = 0. \quad (57)$$

Thus the Rayleighian (per unit volume) is

$$\begin{aligned} R &= n \int d\mathbf{u} \psi \left[\frac{\zeta_r}{2} (\dot{\mathbf{u}} - \dot{\mathbf{u}}_{\text{flow}})^2 + \frac{\zeta_r}{4} (\mathbf{u} \cdot \boldsymbol{\kappa} \cdot \mathbf{u})^2 \right. \\ &\quad \left. + \dot{\mathbf{u}} k_B T \frac{\partial \ln \psi}{\partial \mathbf{u}} + \lambda(\mathbf{u}) \mathbf{u} \cdot \dot{\mathbf{u}} \right] \\ &\quad + \frac{1}{4} \eta_0 (\boldsymbol{\kappa} + \boldsymbol{\kappa}^t) : (\boldsymbol{\kappa} + \boldsymbol{\kappa}^t). \end{aligned} \quad (58)$$

The condition $\delta R / \delta \mathbf{u} = 0$ and the constraint (57) give

$$\dot{\mathbf{u}} = -(\mathbf{u}^2 \mathbf{I} - \mathbf{u}\mathbf{u}) \cdot \left(\frac{k_B T}{\zeta_r} \frac{\partial \ln \psi}{\partial \mathbf{u}} \right) + \dot{\mathbf{u}}_{\text{flow}}. \quad (59)$$

Equations (59) and (52) give the following time evolution equation for $\psi(\mathbf{u}, t)$:

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial \mathbf{u}} \cdot (\mathbf{u}^2 \mathbf{I} - \mathbf{u}\mathbf{u}) \cdot \left(D_r \frac{\partial \psi}{\partial \mathbf{u}} - \frac{\boldsymbol{\kappa} \cdot \mathbf{u}}{u^2} \psi \right) \quad (60)$$

where $D_r = k_B T / \zeta_r$ is the rotational diffusion constant.

Equation (60) determines the orientational distribution of rod-like polymers in the flow field. The macroscopic stress tensor can be calculated by the following equation [2]:

$$\sigma_{\alpha\beta} = \frac{\partial R}{\partial \kappa_{\alpha\beta}}. \quad (61)$$

Equation (61) is derived according to the following reasoning. Though we have regarded the solution velocity \mathbf{v} as a given quantity in the above treatment, \mathbf{v} is in fact a quantity to be determined by the variational principle as we have seen in sections 5 and 5.2. The total Rayleighian is written as

$$R_{\text{total}} = \int d\mathbf{r} R[\psi(\mathbf{u}; \mathbf{r}), \mathbf{v}(\mathbf{r})]. \quad (62)$$

Since R depends on $\mathbf{v}(\mathbf{r})$ through $\kappa_{\alpha\beta} = \partial v_\alpha / \partial r_\beta$, the condition $\delta R_{\text{total}} / \delta v_\alpha(\mathbf{r}) = 0$ gives

$$\frac{\partial}{\partial r_\beta} \left(\frac{\partial R}{\partial \kappa_{\alpha\beta}} \right) = 0. \quad (63)$$

Comparing this with the force balance equation for the macroscopic stress $\partial \sigma_{\alpha\beta} / \partial r_\beta = 0$, we get equation (61).

For the Rayleighian (58), the stress tensor is given by

$$\begin{aligned} \sigma_{\alpha\beta} &= n \int d\mathbf{u} \psi \left[\zeta_r (\dot{u}_\alpha - \dot{u}_{\text{flow}\alpha}) u_\beta \right. \\ &\quad \left. + \frac{1}{2} \zeta_r u_\alpha u_\beta u_\mu u_\nu \kappa_{\mu\nu} \right] + \eta_0 (\kappa_{\alpha\beta} + \kappa_{\beta\alpha}). \end{aligned} \quad (64)$$

By using equation (59) and integration by parts, it can be shown that (64) is written in the following form:

$$\begin{aligned} \sigma_{\alpha\beta} &= n \int d\mathbf{u} \psi \left[3k_B T (u_\alpha u_\beta - \delta_{\alpha\beta}) \right. \\ &\quad \left. + \frac{1}{2} \zeta_r u_\alpha u_\beta u_\mu u_\nu \kappa_{\mu\nu} \right] + \eta_0 (\kappa_{\alpha\beta} + \kappa_{\beta\alpha}). \end{aligned} \quad (65)$$

Equations (60) and (65) give the constitutive equation: for given velocity gradient, $\psi(\mathbf{u}; t)$ can be obtained by solving equation (60), and then the stress can be calculated by equation (65). The constitutive equation describes the nonlinear viscoelasticity of the dilute solution of rod-like polymers.

It can be easily shown that equation (60) is equivalent to the usual form for the rotational diffusion equation [2]:

$$\frac{\partial \psi}{\partial t} = D_r \mathcal{R}^2 \psi - \mathcal{R} \cdot [(\mathbf{u} \times \boldsymbol{\kappa} \cdot \mathbf{u}) \psi] \quad (66)$$

where $\mathcal{R} = \mathbf{u} \times \partial / \partial \mathbf{u}$ is the rotational differentiation operator.

8. Liquid crystals

8.1. Molecular theory

The theory described in section 7 can be extended for concentrated solutions of rod-like polymers, especially for the liquid crystalline phase. The molecular theory [2, 17] for the rheology of the nematic phase of a rod-like polymer can be formulated in the framework of the variational principle by introducing two modifications to the above theory.

First, the expression for the energy dissipation function must be modified. In concentrated solutions, free Brownian rotation of an individual polymer is strongly prohibited by the surrounding polymers, and therefore the effective rotational friction constant $\tilde{\zeta}_r$ becomes much larger than that in dilute solution (estimation of $\tilde{\zeta}_r$ has been made by the tube model [17, 2]). Hence the energy dissipation is written as

$$W = n \int d\mathbf{u} \psi \tilde{\zeta}_r [\dot{\mathbf{u}} - \dot{\mathbf{u}}_{\text{flow}}]^2. \quad (67)$$

Here, only the dominant term for the energy dissipation is taken into account: the first term in equation (54) which arises from the solvent viscosity, and the last term in the integrand which arises from the inextensibility of the polymer have been ignored in equation (67).

Second, the expression for the free energy must be modified. To describe the ordered state of the nematic phase, it is essential to take into account the interaction between polymers. Let $U(\mathbf{u}, \mathbf{u}')$ be the effective interaction between two polymers directed along \mathbf{u} and \mathbf{u}' , then the free energy is given by

$$A = n \int d\mathbf{u} k_B T \psi \ln \psi(\mathbf{u}) + \frac{n}{2} \int d\mathbf{u} \int d\mathbf{u}' U(\mathbf{u}, \mathbf{u}') \psi(\mathbf{u}) \psi(\mathbf{u}'). \quad (68)$$

Repeating the same calculation as for the dilute solution, we get the following equation for the time evolution of the orientational distribution function:

$$\frac{\partial \psi}{\partial t} = \frac{\partial}{\partial \mathbf{u}} \cdot (\mathbf{u}^2 \mathbf{I} - \mathbf{u} \mathbf{u}) \cdot \left[\tilde{D}_r \left(\frac{\partial \psi}{\partial \mathbf{u}} + \frac{\psi}{k_B T} \frac{\partial U_{mf}}{\partial \mathbf{u}} \right) - \frac{\boldsymbol{\kappa} \cdot \mathbf{u}}{u^2} \psi \right] \quad (69)$$

where $\tilde{D}_r = k_B T / \tilde{\zeta}_r$ is the effective rotational diffusion constant, and $U_{mf}(\mathbf{u})$ is the mean field potential given by

$$U_{mf}(\mathbf{u}) = \int d\mathbf{u}' U(\mathbf{u}, \mathbf{u}') \psi(\mathbf{u}'). \quad (70)$$

The stress tensor is given by

$$\sigma_{\alpha\beta} = n \int d\mathbf{u} \psi \left[3k_B T (u_\alpha u_\beta - \delta_{\alpha\beta}) + \left(\delta_{\alpha\mu} - \frac{u_\alpha u_\mu}{u^2} \right) u_\beta \frac{\partial U_{mf}}{\partial u_\mu} \right]. \quad (71)$$

Equations (69) and (71) give the constitutive equation for liquid crystals.

8.2. Ericksen–Leslie theory

For nematics made of small molecules, the viscoelastic effect and the nonlinear effect are not important. For such cases, the flow of nematics can be described by the Ericksen–Leslie theory, which can also be derived from the variational principle.

In the Ericksen–Leslie theory, the state variable is the director field $\mathbf{n}(\mathbf{r})$ which stands for the average direction of molecules at point \mathbf{r} . The energy dissipation W is a quadratic function of $\dot{\mathbf{n}}$ and $\boldsymbol{\kappa}$. The explicit form of W can be determined by symmetry arguments. Using the fact that W is zero for uniform rotation of the system, one can show that W is a quadratic function of the strain rate

$$\dot{\epsilon}_{\alpha\beta} = \frac{1}{2}(\kappa_{\alpha\beta} + \kappa_{\beta\alpha}) \quad (72)$$

and the velocity of \mathbf{u} relative to the macroscopic rotation

$$\tilde{\mathbf{n}}_\alpha = \dot{\mathbf{n}}_\alpha - \frac{1}{2}(\kappa_{\alpha\beta} - \kappa_{\beta\alpha})n_\beta. \quad (73)$$

Constructing a quadratic function of $\dot{\epsilon}_{\alpha\beta}$ and $\tilde{\mathbf{n}}_\alpha$, the coefficients of which can depend on \mathbf{n} , we have

$$W = \beta_1 (\dot{\epsilon}_{\alpha\beta} n_\alpha n_\beta)^2 + \beta_2 \dot{\epsilon}_{\alpha\beta}^2 + \beta_3 (\dot{\epsilon}_{\alpha\beta} n_\beta)^2 + \beta_4 \tilde{\mathbf{n}}_\alpha^2 + \beta_5 \tilde{\mathbf{n}}_\alpha \dot{\epsilon}_{\alpha\beta} n_\beta \quad (74)$$

where β_1, \dots, β_5 are constants.

The Rayleighian therefore becomes

$$R = \frac{1}{2} W + h_\alpha \dot{\mathbf{n}}_\alpha - \lambda n_\alpha \dot{\mathbf{n}}_\alpha \quad (75)$$

where h_α stands for the potential force conjugate to n_α . The time evolution of n_α is determined by $\partial R / \partial \dot{\mathbf{n}}_\alpha = 0$, and the stress tensor is given by equation (61). A straightforward calculation gives the following expression for the stress tensor $\sigma_{\alpha\beta}$ and the time evolution equation for n_α :

$$\sigma_{\alpha\beta} = \alpha_1 \dot{\epsilon}_{\mu\nu} n_\mu n_\nu n_\alpha n_\beta + \alpha_2 n_\alpha \tilde{\mathbf{n}}_\beta + \alpha_3 \tilde{\mathbf{n}}_\alpha n_\beta + \alpha_4 \dot{\epsilon}_{\alpha\beta} + \alpha_5 n_\alpha n_\mu \dot{\epsilon}_{\mu\beta} + \alpha_6 n_\beta n_\mu \dot{\epsilon}_{\alpha\mu} \quad (76)$$

$$\gamma_1 \tilde{\mathbf{n}}_\alpha + \gamma_2 \dot{\epsilon}_{\alpha\beta} n_\beta - h_\alpha = \lambda n_\alpha \quad (77)$$

where

$$\begin{aligned} \alpha_1 &= \beta_1 & \alpha_2 &= \frac{1}{2}\beta_4 + \frac{1}{4}\beta_5 \\ \alpha_3 &= -\frac{1}{2}\beta_4 + \frac{1}{4}\beta_5 & \alpha_4 &= \beta_2 \\ \alpha_5 &= \frac{1}{2}\beta_3 + \frac{1}{4}\beta_5 & \alpha_6 &= -\frac{1}{2}\beta_3 - \frac{1}{4}\beta_5 \\ \gamma_1 &= -\beta_4 = \alpha_3 - \alpha_2 & \gamma_2 &= -\frac{1}{2}\beta_5 = \alpha_6 - \alpha_5. \end{aligned} \quad (78)$$

Equations (76) and (77) constitute the Leslie–Ericksen equation [3]. Notice that the Parodi 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 which have been used in soft matter physics can be derived from the classical variational principle proposed by Onsager. The

variational principle is equivalent to Onsager's kinetic equation with reciprocal relations for the kinetic coefficients, but it has several advantages.

(1) The variational principle allows us a great flexibility in choosing state variables, and velocities. Also, the variational principle is quite convenient for systems in which the velocity V_i has to satisfy certain constraints such as the incompressible condition.

(2) The variational principle demonstrates the logical structure of Onsager's theory clearly. The difficult part in the usual kinetic formulation of Onsager's theory is to find a proper set of pairs of velocity and forces. If one uses the variational principle, one obtains such pairs automatically.

The time evolution equations used in soft matter physics, the diffusion equation, the flow–diffusion coupled equation, the gel dynamics equation, the Smoluchowski equation, and the Ericksen–Leslie equation are all derived from the variational principle. Therefore they all belong to the same class of equations represented by Onsager's kinetic equation. This indicates that Onsager's variational principle is an important principle in soft matter physics.

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