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Article

Onsager Variational Principle in Soft Matter Physics

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Abstract

We introduce Onsager variational principle for the derivation of the kinetic equations of purely dissipative systems in the level of Stokesian hydrodynamics. As many soft matter systems belong to this class, the principle can thus be used in the study of soft matter dynamics. In this article, a brief connection between the particles and the thermodynamic systems is presented. We discuss the reciprocal relation which is the important concept of the principle. The relation allows us to write the frictional force in a similar manner of determining the potential force from the gradient of the potential energy. The simplest application of the principle for solving the problem in soft matter dynamics is also shown.

Keywords: Onsager variational principle, Reciprocal relation, Stokesian hydrodynamics, Stochastic processes

Introduction

Onsager variational principle (or "Onsager principle" for short) is a variational principle which can be used as a framework for deriving the equations of motion in various soft matter systems such as diffusion equations for particles in dilute and in concentrated solutions [1,2], kinetic equations in gel dynamics [2,3], Cahn-Hilliard equations in phase separation [4] etc. The principle is proposed by L. Onsager in his papers [5,6]. Originally, Onsager proposed the idea for the systems involving thermodynamically coupled irreversible processes, e.g., the thermoelectric phenomena, heat conduction in an anisotropic medium, and the transference phenomena in electrolytes. Historically, the earlier works showed that such phenomena deduced the reciprocal relations but they were incomplete.[1] Onsager then derived a general class of such reciprocal relations from the principle of

[1] For example, Thomson pointed out the incompleteness in his theory of thermoelectric phenomena and his reciprocal relation was based on experimental basis [7].

microscopic reversibility and theorems from the general theory of fluctuations. Some of his obtained relations can be summarized in a variational principle which is considered as an extension of Rayleigh's principle of the least dissipation of energy in Stokesian hydrodynamics [2].

A system of small particles moving in a viscous fluid can be described by the Onsager principle. For the purely dissipative dynamics, the principle essentially says that the time evolution of the system is the balance between the generalized potential force which drives the system to the state of minimization of the free energy and the generalized frictional force which resists the change. The reciprocal relation is the fundamental concept of the principle. The relation allows us to write the frictional force as the derivative of the dissipation function which is related to the energy dissipated in the system with respect to the generalized velocity. We can justify the Onsager principle if the slow variables specifying slow dynamics of the system[2] are known.

In this article, we shall discuss the Onsager principle of the problem in soft matter physics. We will first give a brief review of Brownian motion of a particle of general shape. The reciprocal relation of the friction coefficient will be stated clearly. Then, we discuss the Onsager principle in soft matter dynamics. Finally, the application of the principle will be demonstrated - translocation of a droplet through a narrow pore.

Brownian Motion of a Particle

Let us consider Brownian motion of a particle which is of a general shape. The configuration of a particle moving in viscous fluid can be described by a set of generalized coordinates $\mathbf{x} = (x_1, x_2, \dots, x_f)$, e.g., a rigid particle can be specified by 6 degrees of freedom of its position and orientation. The generalized potential force of the particle in a potential field $U(\mathbf{x})$ can then be written as

$$F_i = -\frac{\partial U}{\partial x_i}. \tag{1}$$

For a particle moving with small velocity, the generalized frictional force is

$$f_i = -\sum_j \zeta_{ij}\, \dot{x}_j, \tag{2}$$

where ζ_{ij} is the generalized friction coefficient and it is a function of the generalized coordinates describing the configuration of the system. Note that, in general, the frictional force f_i conjugate to the coordinate x_i depends on the velocity of other coordinates $\dot{x}_j (j \neq i)$.

[2] The slow variables are the state variables that specify non-equilibrium systems. The relaxation time of the slow variables is distinctively longer than that of other variables called fast variables.

The Langevin equation is the balance of the potential force, the frictional force, and the random force:[3]

$$-\sum_j \zeta_{ij}\,\dot{x}_j - \frac{\partial U}{\partial x_i} + \mathfrak{F}_i(t) = 0, \tag{3}$$

where $\mathfrak{F}_i(t)$ is the random force with zero mean and satisfies the fluctuation-dissipation theorem

$$\langle \mathfrak{F}_i(t)\mathfrak{F}_j(t')\rangle = 2\zeta_{ij}k_BT\delta(t-t'). \tag{4}$$

Reciprocal relation

The friction coefficient ζ_{ij} satisfies the following two properties:

(i) the Lorentz reciprocal relation

$$\zeta_{ij} = \zeta_{ji} \tag{5}$$

(ii) the positive definiteness, i.e., for any $\dot{x}_i$,

$$\sum_{i,j} \zeta_{ij}\dot{x}_i\dot{x}_j \geq 0 \tag{6}$$

Onsager Principle in Soft Matter Physics

In the dynamics of particle-fluid system, e.g., particles sedimenting in a viscous fluid under a gravitational field, the time evolution of the system is determined by the balance between the potential and frictional forces, which can be translated into a variational principle due to the reciprocal relation of the friction coefficient. Onsager's works have shown that, for a non-equilibrium system, the kinetic equations that have the same structure as that of the particle-fluid system can also be written in the form of a variational principle based on the result of the time reversal symmetry of the fluctuations at equilibrium. We shall call this the "Onsager principle". As we have discussed above most soft matter systems satisfy the balance between the potential force, the frictional force, and the random force, however, if the particles are sufficiently large, the random force can be ignored. Consequently, the time evolution of the system will fall into the same structure

[3] We have made the assumption that the velocity correlation time τ defined by $\tau = m/\zeta$, where m is the mass of the particle and ζ is the friction coefficient, is much smaller than the characteristic relaxation time t of the system, i,e, $\tau \ll t$. We, thus, shall consider the limit $\tau \to 0$ in which the inertia term may be ignored. Note that many soft matter systems satisfy this assumption [1].

as of the particle-fluid system. This is the reason why one can use the Onsager principle for studying soft matter dynamics.

Variational Principle in Particle-Fluid System

Here we will show that the time evolution equation for a particle-fluid system can be translated into a variational principle. An example of such a system is the sedimentation of particles under the gravitational force. If the configuration of particles is described by coordinates $\mathbf{x} = (x_1, x_2, \dots, x_f)$, as we described above, the time evolution equation of particles is the balance between the potential force and the frictional force[4]

$$\sum_j \zeta_{ij}\dot{x}_j = -\frac{\partial U(\mathbf{x})}{\partial x_i}, \tag{7}$$

where $U(\mathbf{x})$ is the potential energy. Let us define $(\zeta^{-1})_{ij}$ as the ij-component of the inverse of the matrix ζ. Thus, the equation (7) gives a time evolution equation for x_i

$$\frac{dx_i}{dt} = -\sum_j (\zeta^{-1})_{ij}\frac{\partial U(\mathbf{x})}{\partial x_j}. \tag{8}$$

Since the friction coefficient ζ_{ij} obeys the reciprocal relation, this allows us to write the frictional force as

$$f_i = -\frac{\partial \Phi}{\partial \dot{x}_i}, \tag{9}$$

where Φ is called the Rayleigh's dissipation function defined by[5]

$$\Phi = \frac{1}{2}\sum_{i,j} \zeta_{ij}\dot{x}_i\dot{x}_j. \tag{10}$$

In order to translate the equation of evolution Eq. (8) into variational principle, we first construct the Rayleighian of the system which is sum of the dissipation function and time derivative of the potential energy:

[4] We have assumed that the particles are macroscopic objects. The random force is negligible.

[5] Note that, in order to get the frictional force in the form of Eq. (2), the reciprocal relation is needed.

$$\Re = \Phi + \dot{U}$$

$$= \frac{1}{2}\sum_{i,j} \zeta_{i,j}\dot{x}_i\dot{x}_j + \sum_i \frac{\partial U}{\partial x_i}\dot{x}_i. \quad (11)$$

It can be easily shown that minimization of the Rayleighian gives the time evolution equation Eq. (8). Since, for any $\dot{x}_i, \sum_{i,j}\zeta_{ij}\dot{x}_i\dot{x}_j \geq 0, \Re(\dot{\mathbf{x}})$ has a unique minimum as a function of $\dot{\mathbf{x}} = (\dot{x}_1, \dot{x}_2, \ldots, \dot{x}_f)$ when $\partial\Re/\partial\dot{x}_i = 0$are satisfied. This variational principle is called the principle of least energy dissipation [8].

Onsager Principle

As we have shown that the time evolution equation for a particle-fluid system can be translated into the variational principle, we now turn our intention to a non-equilibrium system. Let us consider a non-equilibrium system specified by a set of state variables $\mathbf{x} = (x_1, x_2, \ldots, x_f)$. We assume that the time evolution equation of the system is in the form:

$$\frac{dx_i}{dt} = -\sum_j \lambda_{ij}\frac{\partial A(\mathbf{x})}{\partial x_j}, \quad (12)$$

where $A(\mathbf{x})$ is the free energy. λ_{ij} is the kinetic coefficient and it is related to the friction coefficient ζ_{ij} through

$$\sum_k \zeta_{ik}\lambda_{kj} = \delta_{ij}. \quad (13)$$

Thus, we can see clearly that Eq. (12) can also be written in the form of the balance between two forces as in Eq. (7):

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

Onsager has shown that, for a system described by the time evolution equation of Eq. (12) or Eq. (14), the reciprocal relations are needed which is the result of the time reversal symmetry at equilibrium of the time correlation function. This argument allows us to translate the kinetic equation in the form of Eq. (12) or Eq. (14) into the variational principle. Then, the Rayleighian can be constructed as

$$\Re = \Phi + \dot{A}$$

$$= \frac{1}{2}\sum_{i,j} \zeta_{ij}\, \dot{x}_i \dot{x}_j + \sum_i \frac{\partial A}{\partial x_i}\dot{x}_i. \qquad (15)$$

By minimizing the Rayleighian with respect to $\dot{x}_i$, i.e., $\partial\Re/\partial\dot{x}_i = 0$, this yields the evolution equation Eq. (12). This is the Onsager principle and it can be considered as an extension of Rayleigh's principle of the least dissipation of energy.

The Simplest Example: Translocation of a Droplet Through a Narrow Pore

Within the framework of the Onsager principle, we now consider the simplest problem-the translocation of a liquid droplet through a pore across a rigid wall due to pressure difference [9].

Theory of a droplet

The translocation of a droplet through a narrow pore across a rigid wall is illustrated schematically in Figure 1. A translocating droplet is modeled by two connected spheres where the receiver and donor compartments have radii $r_1(t)$ and $r_2(t)$, respectively. The initial size of the droplet is denoted by R_0 where we assume that R_0 is much larger than the size of the pore and the thickness of the wall is very small. Thus, we can neglect the structure of the pore and the pore is considered as a circle with radius a. The droplet is assumed to be incompressible fluid with viscosity η. We assume that the pressure inside the droplet is constant everywhere and the pressure difference between inside and outside of the droplet is determined by the Laplace pressure. The liquid flow velocity is very small and most of the energy dissipates at the pore when the liquid is flowing through.

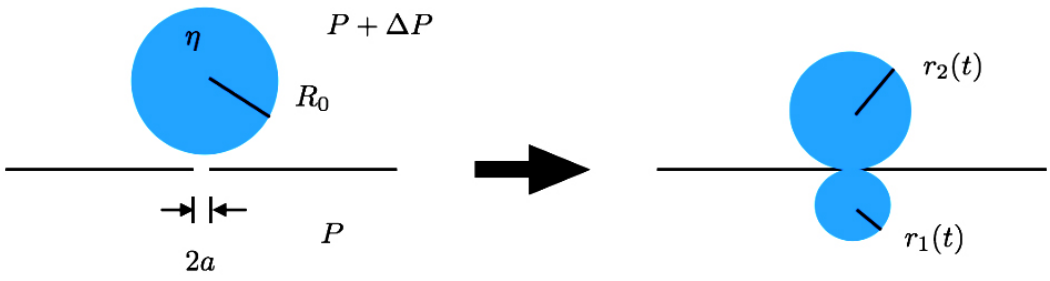

Figure 1 Model of a translocating droplet.

We construct a dynamical equation for our model system from the Onsager principle. The principle states that if a non-equilibrium system is described by a set of slow variables $\mathbf{x} =$

$(x_1, x_2, \ldots x_f)$, the time evolution equation of the system can be obtained by minimization of Rayleighian defined by

$$\Re = \Phi + \dot{F}, \tag{16}$$

with respect to $\dot{x}$, where Φ is the energy dissipation function and $\dot{F}$ is the time derivative of the free energy. What are the slow variables for the translocating droplet? When the droplet is translocating through the pore, $r_1(t)$ and $r_2(t)$ are the slow variables. However, we can simply assume that during the process the volume of the droplet is preserved such that $R_0^3 = r_1^3 + r_2^3$. Thus, we can reduce the degrees of freedom to one. Since the translocation time depends on the initial size R_0 as well as the pressure difference ΔP, we, then, introduce dimensionless parameters a/R_0 and $\Delta P a/\gamma$, where γ is the surface tension between the droplet and the surrounding liquid.

A. The free energy

The free energy of the translocating droplet is the sum of the surface tension energy and the work done by the pressure difference:

$$F = 4\pi\gamma(r_1^2 + r_2^2) - \frac{4\pi}{3}\Delta P(r_1^3 - r_2^3). \tag{17}$$

Equation (17) can be rewritten in terms of the dimensionless variables x defined by $x = (r_1/R_0)^3$. Then, the potential energy is rewritten as

$$F\left(x; \frac{a}{R_0}; \frac{\Delta P a}{\gamma}\right) = a^2\gamma\left[4\pi\left(\frac{R_0}{a}\right)^2\left(x^{2/3} + (1-x)^{2/3}\right) - \frac{4\pi}{3}\left(\frac{R_0}{a}\right)^3\left(\frac{\Delta P a}{\gamma}\right)(2x-1)\right]. \tag{18}$$

B. The energy dissipation function

In the limit of small Reynolds number, the energy dissipation function for the droplet is given by

$$\Phi = \frac{1}{2}\zeta a^2 v_l^2, \tag{19}$$

where ζ is the friction coefficient. Generally, ζ should be function of the slow variable. It can be derived from the Stokesian hydrodynamics. However, in this article, we simply assume it as a constant. Note that the friction coefficient has the unit of $\mathrm{kg{\cdot}m^{-2}{\cdot}s^{-1}}$. The liquid flow velocity v_l is defined by $v_l = (2r_1/a)^2\dot{r}_1$. By using the dimensionless variable x defined above, the dissipation function can be rewritten as

$$\Phi\left(\dot{x};\frac{a}{R_0}\right)=\frac{8}{9}a^4\zeta\left(\frac{R_0}{a}\right)^6\dot{x}^2. \quad (20)$$

C. The droplet's evolution equation

The Rayleighian of the system is given by

$$\Re=\Phi+\dot{F},$$

$$=\frac{8}{9}a^4\zeta\left(\frac{R_0}{a}\right)^6\dot{x}^2+a^2\gamma\left[\left(\frac{R_0}{a}\right)^2\frac{8\pi}{3}\left(x^{-1/3}-(1-x)^{-1/3}\right)\dot{x}-\frac{8\pi}{3}\left(\frac{R_0}{a}\right)^3\left(\frac{\Delta Pa}{\gamma}\right)\dot{x}\right]. \quad (21)$$

The evolution of x is determined by the condition that $\Re$ is minimized with respect to $\dot{x}$, i.e., $\partial\Re/\partial\dot{x}=0$. This is the Onsager principle. Then, we obtain

$$\frac{dx}{d\tau'}=-\frac{3\pi}{2}\left(\frac{a}{R_0}\right)^4\left[x^{-\frac{1}{3}}-(1-x)^{-\frac{1}{3}}-\left(\frac{R_0}{a}\right)\left(\frac{\Delta Pa}{\gamma}\right)\right], \quad (22)$$

where $\tau'=t/\tau$ is a droplet-dimensionless time and we have defined $\tau=\zeta a^2/\gamma$. At the initial state, the receiver compartment is assumed to be a sphere with radius a. Thus, we will have $x(\tau'=0)=(a/R_0)^3$.

D. The droplet's trajectory in τ'–x plane

The droplet's evolution equation Eq. (22) can be solved numerically. We have employed the Runge-Kutta method and the droplet's trajectory in the τ'–x plane has been shown. Firstly, we have evaluated the critical pressure. The ratio R_0/a is selected to be 10.0. Our result suggests the critical pressure $\Delta P_c=0.9\gamma/a$ as shown in Figure 2(a). Naturally, in the absence of the pressure difference, the free energy is symmetric around $x=0.5$. Increasing the pressure will reduce the energy barrier. Necessarily, the energy barrier disappears when $\Delta P\geq\Delta P_c$. Above the critical pressure, the droplet can be succeeded in the translocation process. Secondly, it is clear that the translocation time (as indicated when $x=1.0$) is reduced when the pressure difference across the wall increases. The result is shown in Figure 2(b).

We have used the experiments done by Cumming *et al.* [10] to verify our critical pressure. In their work, the rejection of oil drop from a dilute emulsion of oil in water using Nuclepore filters with different pore sizes is investigated. The oil/water emulsion is kerosene dispersed in water. The authors have shown that, for example, for the pore size with radius $2.5\,\mu$m, the oil rejection is about 90-95% where the ratio of the oil drop size to the pore size is in the range of 0.4-16 and the interfacial tension $\gamma=5.1$ mN•m^{-1} is used. The authors' result is valid for the critical pressure ranging from 500 to around 1,800 Pa. While our predicted critical pressure is $\Delta P_c=1{,}836$ for the

ratio of the oil drop size to the pore size is 10. This discrepancy can be originated from many reasons. One possible thing is that, in our model, the translocating droplet is simply modeled as two connected spheres. However, the experiments done in [10] have suggested that the (large) deformation of the droplet during the filtration process can occur.

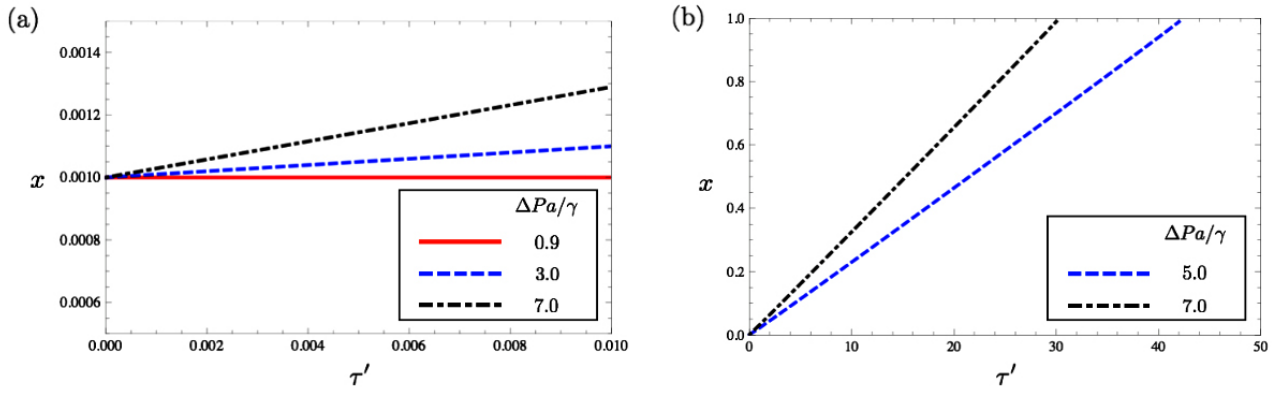

Figure 2 The critical pressure is found to be $0.9\gamma/a$ *(solid red line) as shown in the evolution of the droplet at short time scale (a). The translocation time (indicated when* $x = 1.0$*) is decreased when the pressure difference across the wall increases as shown in the plot for long time scale (b).*

Conclusions

In this article, we have shown that the kinetic equations in soft matter systems with purely dissipative dynamics can be translated into the variational principle called the Onsager principle. The basic concepts in the principle are the reciprocal relation and the existence of the slow variables. Our simplest example shows clearly that the physical variables of interest can be studied in the framework of the principle. Many authors also demonstrated that the principle can be used for studying the dynamics of various soft matter systems such as lipid bilayer vesicle [11,12], nematic liquid crystal [13], droplet of binary solution [14] etc.

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