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A principle in dynamic coarse graining–Onsager principle and its applications

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Abstract. Dynamic coarse graining is a procedure to map a dynamical system with large degrees of freedom to a system with smaller degrees of freedom by properly choosing coarse grained variables. This procedure has been conducted mainly by empiricisms. In this paper, I will discuss a theoretical principle which may be useful for this procedure. I will discuss how to choose coarse grained variables (or slow variables), and how to set up their evolution equations. To this end, I will review the classical example of dynamic coarse graining, i.e., the Brownian motion theory, and show a variational principle for the evolution of the slow variables. The principle, called the Onsager principle, is useful not only to derive the evolution equations, but also to solve the problems.

1 Introduction

Coarse graining is a procedure needed in multi-scale modeling [1,2]. It is an operation of reducing the degrees of freedom of the original system in such a way that the new system with less degrees of freedom behaves in the same way as the original on large length and time scales. For example, in the study of polymers (see Fig. 1), one can use an atomistic model in which the polymer molecule is represented by a set of chemically bonded atoms (Fig. 1(a)). Alternatively, one can use the coarse grained model, in which the polymer is represented by simplified objects, for example, beads and springs (Fig. 1(b)) where the beads represent a group of atoms (for example, the atoms encircled by the dashed lines) and the springs represent the effective connection between them. Such coarse grained model is expected to represent the behavior of the polymer molecule on large length and time scales. A natural question is how to construct such a model.

Coarse graining has two features, static and dynamic. In the static coarse graining, the objective is to construct a model which reproduces the equilibrium properties, while in the dynamic coarse graining, the objective is to reproduce both equilibrium and non-equilibrium properties. Various methods have been proposed and tested for static coarse graining [3–5]. On the other hand, not many studies have been done for dynamic coarse graining [6].

In this paper, I will discuss some theoretical basis for dynamic coarse graining. For this purpose, I will first revisit the Brownian motion theory, the classical example of dynamic coarse graining, and review the argument used in deriving evolution equations for coarse grained variables. I will then show that the evolution law for

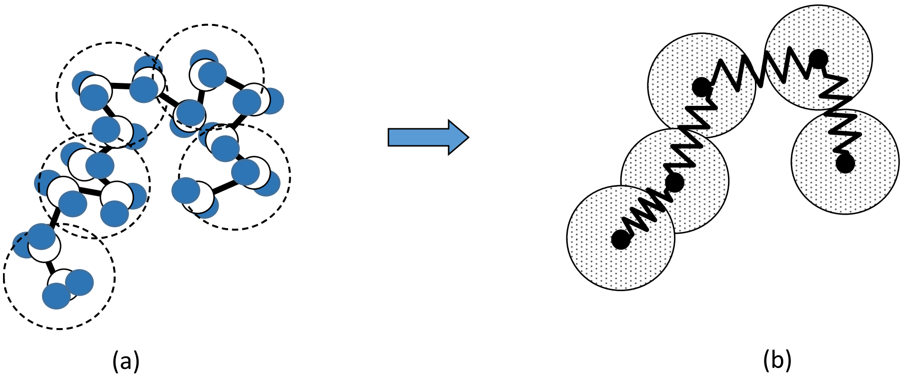

Fig. 1. Model of a polymer molecule (a) atomistic model, (b) coarse grained model.

the coarse grained variables can be stated in a variational principle, called Onsager principle [7–9], which is useful not only in deriving the evolution equations, but also in solving the equations.

2 Brownian motion theory

2.1 Hydrodynamic description

Consider small particles moving in a viscous fluid (see Fig. 2). If the particles are macroscopic, their dynamics is described by hydrodynamics: the fluid is regarded as a continuum with viscosity η and the evolution of particle position and orientation are calculated by solving the hydrodynamic equation. Let $x = (x_1, x_2, ...x_n)$ be the set of parameters representing the configuration of the particles. The particles are subject to two kinds of forces, the potential forces (the forces arising from the interaction potential between particles, and/or the gravitational potential), and the frictional forces exerted by the fluid. The former is represented by the potential energy of the system $U(x)$ as

$$F_{pi} = -\frac{\partial U(x)}{\partial x_i}\cdot \tag{1}$$

This represents the generalized force conjugate to x_i. The frictional forces exerted by the fluid are calculated by Stokesian hydrodynamics for small particles of colloidal size. As a result, the forces are obtained as linear functions of the particle velocity $\dot{x} = (\dot{x}_1, \dot{x}_2, \ldots \dot{x}_n)$:

$$F_{fi} = -\sum_j \zeta_{ij}(x)\dot{x}_j \tag{2}$$

ζ_{ij} is called friction coefficient, which is, in general, a function of the particle configuration x. It is known that the matrix made of $\zeta_{ij}(x)$ is symmetric and positive definite, i.e.,

$$\zeta_{ij}(x) = \zeta_{ji}(x), \qquad \sum_{ij} \zeta_{ij}\dot{x}_i\dot{x}_j \geq 0 \quad \text{for any } \dot{x}_i. \tag{3}$$

The reciprocal relation $\zeta_{ij} = \zeta_{ji}$ can be proved starting from the Stokes equation and is called Lorentz reciprocal relation.

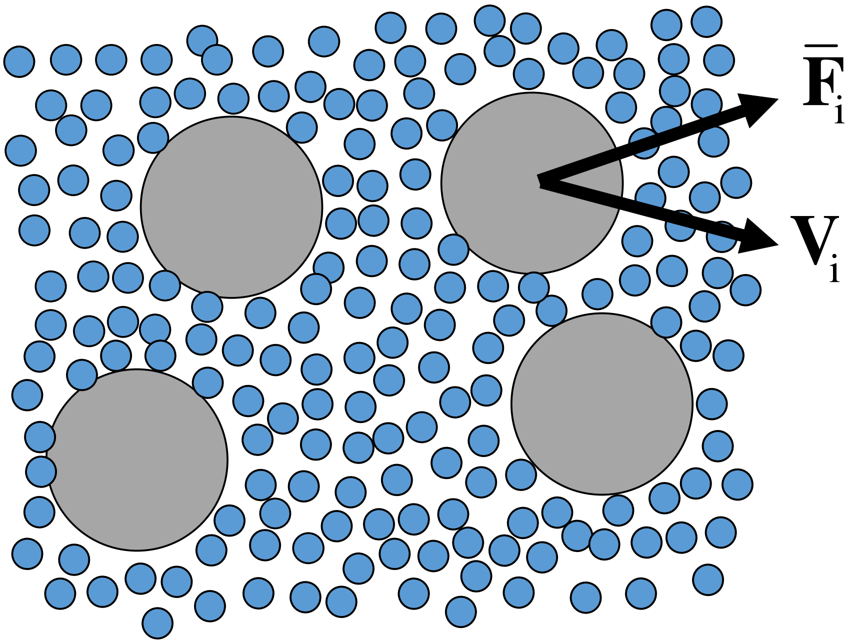

Fig. 2. Molecular representations of a suspension. Particles are moving at constant speed V_i among fluid molecules. The average of the force F_i exerted on the particle is calculated either by macroscopic hydrodynamics or by statistical mechanics. This gives the connection between macroscopic description and molecular description.

The evolution equation of the particle configuration is given by the force balance equation $F_{pi} + F_{fi} = 0$, or

$$\sum_j \zeta_{ij}(x)\dot{x}_j = -\frac{\partial U(x)}{\partial x_i}\cdot \tag{4}$$

This is a non-linear equation for x, and therefore can be used to study the complex non-linear behaviors of suspensions [10,11].

2.2 Mesoscopic description

If particle size becomes small, the particles start to show Brownian motion. Phenomenologically, the Brownian motion can be described by the Langevin equation

$$\sum_j \zeta_{ij}(x)\dot{x}_j = -\frac{\partial U(x)}{\partial x_i} + F_{ri}(t) \tag{5}$$

where $F_{ri}(t)$ is a stochastic force representing the fluctuating part of the force exerted on the particle by fluid molecules. Since the average part of this force is already in the left hand side of Eq. (5), the average of $F_{ri}(t)$ is zero; $\langle F_{ri}(t)\rangle = 0$. The variance of $F_{ri}(t)$ is determined by the condition that the statistical distribution of x at equilibrium is given by the Boltzmann distribution $\psi_{eq}(x) \propto \exp(-\beta U(x))$, where $\beta = 1/(k_B T)$. The second condition requires that the time correlation of the random forces must satisfy [9]

$$\langle F_{ri}(t)F_{rj}(t')\rangle_x = 2\zeta_{ij}(x)k_B T\delta(t-t') \tag{6}$$

where $\langle ... \rangle_x$ stands for the average for the state where particle configuration is fixed at x. Equation (6) is obtained by combining macroscopic phenomenological equation (i.e., the Stokes equation) with statistical theory (i.e., the Boltzmann distribution). Notice that the reciprocal relation and the positive definiteness of ζ_{ij}, represented by Eq. (3), are also derived from this relation.

2.3 Molecular description

The set of equations appearing in the phenomenological theory can be derived directly from the first principle of statistical mechanics, i.e., from the Liouville equation. Let $\Gamma = (q_1, q_2, \dots q_f, p_1, p_2, \dots p_f)$ be the set of generalized coordinates and generalized momenta of the fluid molecules. The Hamiltonian of the system can be written as $H(\Gamma; x)$. (Note that here the variables $x = (x_1, \dots x_n)$ representing the particle configuration are treated as external parameters appearing in the Hamiltonian.)

Given the Hamiltonian, the force acting on the particle in the microscopic state Γ is calculated by

$$\hat{F}_i(\Gamma; x) = -\frac{\partial H(\Gamma; x)}{\partial x_i} \cdot \tag{7}$$

To relate this molecular description to hydrodynamic description, we consider that the particles are slowly moving at rate $\dot{x}$ driven by some external forces, and ask what is the average of the microscopic force $\hat{F}_i$. The average can be calculated straightforwardly by statistical mechanics.

First consider the case that the particle configuration is fixed, i.e., the case of $\dot{x} = 0$. In this case, the fluid molecules are in equilibrium for given x, and their distribution is given by

$$\psi_{eq}(\Gamma; x) = \frac{e^{-\beta H(\Gamma; x)}}{\int d\Gamma \; e^{-\beta H(\Gamma; x)}} \cdot \tag{8}$$

The average of $\hat{F}_i$ for this state is easily calculated as

$$\langle \hat{F}_i \rangle_x = \int d\Gamma \hat{F}_i \psi_{eq}(\Gamma; x) = -\frac{\int d\Gamma \; \frac{\partial H}{\partial x_i} e^{-\beta H(\Gamma; x)}}{\int d\Gamma \; e^{-\beta H(\Gamma; x)}} = -\frac{\partial A(x)}{\partial x_i} \tag{9}$$

where $A(x)$ is the free energy of the system when x is fixed.

$$A(x) = -\frac{1}{\beta} \ln \left[\int d\Gamma \; e^{-\beta H(\Gamma; x)} \right] \cdot \tag{10}$$

Now let us consider that particles start to move with constant velocity $\dot{x}$ at time $t = 0$. The distribution function of fluid molecules $\psi(\Gamma, t; x, \dot{x})$ is obtained by solving the Liouville equation with the initial condition $\psi(\Gamma, 0; x, \dot{x}) = \psi_{eq}(\Gamma; x)$. If $\dot{x}$ is small enough, the Liouville equation can be solved by perturbation method, i.e., by writing $\psi(\Gamma, t; x, \dot{x})$ as

$$\psi(\Gamma, t; x, \dot{x}) = \psi_{eq}(\Gamma; x) + \sum_i \psi_i(\Gamma, t; x) \dot{x}_i + \dots \tag{11}$$

The average of the force acting on the particle at time t is then calculated by

$$\langle \hat{F}_i \rangle_{x, \dot{x}} = \int d\Gamma \hat{F}_i \left[\psi_{eq}(\Gamma; x) + \sum_i \psi_i(\Gamma, t; x) \dot{x}_i + \dots \right] \cdot \tag{12}$$

The result can be written as [9]

$$\langle \hat{F}_i \rangle_{x,\dot{x}} = -\frac{\partial A(x)}{\partial x_i} - \sum_j \tilde{\zeta}_{ij}(x,t)\dot{x}_j + \dots \tag{13}$$

The first term on the right hand side represents the force in the case of $\dot{x} = 0$, and the second term represents the first order correction to this for small $\dot{x}$. By straightforward calculation, one can show that $\tilde{\zeta}_{ij}(x,t)$ is given by [9]

$$\tilde{\zeta}_{ij}(x,t) = \beta \int_0^t dt' \langle F_{ri}(t') F_{rj}(0) \rangle_x \tag{14}$$

where

$$F_{ri} = \hat{F}_i(\Gamma; x) - \langle \hat{F}_i \rangle_x \tag{15}$$

is the fluctuating part of the microscopic force acting on the particle.

If the correlation times of the random forces are much smaller than the characteristic times of particles, $\tilde{\zeta}_{ij}(x,t)$ approaches to the asymptotic value $\tilde{\zeta}_{ij}(x,\infty)$ before x changes by any appreciable amount. In this case, Eq. (13) can be simplified as

$$\langle \hat{F}_i \rangle_{x,\dot{x}} = -\frac{\partial A(x)}{\partial x_i} - \sum_j \zeta_{ij}(x)\dot{x}_j + \dots \tag{16}$$

where

$$\zeta_{ij}(x) = \tilde{\zeta}_{ij}(x,\infty) = \beta \int_0^\infty dt' \langle F_{ri}(t') F_{rj}(0) \rangle_x . \tag{17}$$

In the above discussion, we considered the situation that the particles are forced to move at a given rate $\dot{x}$ by some external forces. If there are no external forces, the motion of the particles is determined by the condition that the average force $\langle \hat{F}_i \rangle_{x,\dot{x}}$ is zero. This condition gives

$$\sum_j \zeta_{ij}(x)\dot{x}_j = -\frac{\partial A(x)}{\partial x_i} \cdot \tag{18}$$

This is equivalent to Eq. (4), where the potential energy $U(x)$ is now replaced by the free energy $A(x)$ since the potential energy $U(x)$ in a macroscopic system is in fact the free energy. Therefore the equations in the phenomenological theory are derived straightforwardly from statistical mechanics.

3 Onsager principle

3.1 Variational principle in the evolution law

The argument in the previous section shows that as long as x is a proper set of slowly varying variables, their evolution equations are written in the form of Eq. (18). We call such variables slow variables. In the case of suspensions, slow variables are the particle coordinates, and the other fast variables are Γ, but there is nothing to restrict the argument to this case. The only requirement for x is that they change slowly in time: the characteristic time of x, which is determined by the kinetic Eq. (18), is much longer than the correlation time of the forces created by other variables. As long as this condition is satisfied, the rewriting of Eq. (13) into Eq. (16) is justified, ant the time evolution (18) is justified.

The generality of the argument in the Brownian motion theory was noted by Onsager [7,8], and he used this argument to prove his celebrated reciprocal relation: if the kinetic equation for an irreversible system is written in the form (18), the equality $\zeta_{ij} = \zeta_{ji}$ holds. He then showed that due to the reciprocal relation, the kinetic Eq. (18) can be generally written in a form of variational principle. Consider the following quadratic function of $\dot{x}$, called Rayleighian

$$R(x, \dot{x}) = \frac{1}{2}\sum_{i,j} \zeta_{ij}(x)\dot{x}_i\dot{x}_j + \sum_i \frac{\partial A}{\partial x_i}\dot{x}_i. \tag{19}$$

The kinetic Eq. (18) is then obtained by minimizing R with respect to $\dot{x}_i$, i.e., by the condition $\partial R/\partial \dot{x}_i = 0$. We shall call this principle Onsager principle. [The Onsager principle discussed here is a special case of Onsager's original one. His original variational principle uses entropy production rather than energy dissipation. The present variational principle is valid for isothermal system where the temperature is constant throughout the system].

The Rayleighian consists of two parts. The first part

$$\Phi = \frac{1}{2}\sum_{i,j} \zeta_{ij}(x)\dot{x}_i\dot{x}_j \tag{20}$$

is called the dissipation function and the second part

$$\dot{A} = \sum_i \frac{\partial A}{\partial x_i}\dot{x}_i \tag{21}$$

is called the free energy change rate.

Φ is called dissipation function since 2Φ represents the energy dissipated in the system per unit time when the slow variables are changing at rate $\dot{x}$. This is seen as follows. To change x_i at rate $\dot{x}_i$, we have to apply a force $-(F_{pi} + F_{fi}) = \partial A/\partial x_i + \sum_j \zeta_{ij}\dot{x}_j$. The work done to the system per unit time is $-\sum_i (F_{pi} + F_{fi})\dot{x}_i$. The difference between this work and the free energy change rate $\dot{A}$ is the work dissipated in the system per unit time, which is equal to 2Φ.

The Onsager principle can be state as follows: *Among all possible physical processes, the actual process realized in reality is the process that minimizes the Rayleighian.* Alternatively, it can be stated in the form of minimum energy dissipation principle: *Among all possible physical processes which change the free energy from A to $A + \dot{A}\Delta t$, the actual process realized in reality is the process that minimizes the energy dissipation* 2Φ.

4 How to choose slow variables

The argument in the previous section shows that if the slow variables are properly chosen, the dynamics is determined by the Onsager principle and their time evolution equations are written in the form of Eq. (18) with coefficients satisfying the reciprocal relation $\zeta_{ij} = \zeta_{ji}$. [Note that Eq. (18) can represent partial differential equations since i in Eq. (18) can be a continuous variable, and $A(x)$ can be a functional of a function $x(i)$. Such an example is given in Sect. 5.1, and many other examples are given in Ref. [9]]. In practice, the most difficult part in applying the Onsager principle to practical problems is how to choose slow variables. In principle, the only requisite for slow variables is that they change much more slowly than other variables. This condition is still vague and it is natural to ask how we can choose slow variables, and how we can judge whether the chosen slow variables are proper or not.

At this stage, no clear answers can be given to such questions. However, we can discuss some criteria which are useful in selecting proper slow variables (see also the discussion in [13]).

A simple criteria to judge whether the chosen set of slow variables are proper or not is whether the evolution of the system is determined uniquely if the set of the slow variables x are given. The slow variables have to specify the non-equilibrium state of the system in such a way that, given the state at time t, the state at the next time step $t + \Delta t$ is determined uniquely.

For example, if a macroscopic particle is moving in a viscous fluid, the particle position at time $t + \Delta t$ is determined uniquely if the particle position at time t is given. In this case, the particle position x is a proper slow variable, and the dynamics of the system is described by the evolution equation for x. However, if the particle is moving in a viscoelastic fluid (such as polymer solutions), the particle position x is not enough to determine the time evolution of x because the drag exerted on the particle by viscoelastic fluids depends on the particle velocity in the past. Therefore the evolution equation cannot be written in the form of Eq. (18). Mathematically speaking, this is because the rewriting of Eq. (13) into (16) is not allowed in this case (since the correlation time for the random force is non-negligible in viscoelastic fluids). However, even in this case, if we include inner variables which describe the viscoelasticity (e.g., the variables describing the polymer configuration), it is still possible to discuss the evolution of the system in the framework of the variational principle [13].

Discussion is needed on the applicability of the variational principle for a system in which the Brownian motion is important. In this case, the particle position x is not deterministic, and the evolution equation for x cannot be written in the form of Eq. (18). However, we can still make a statistical prediction on the state of the system. If we know the distribution function $\psi(x,t)$ of the particle at time t, the distribution function at the next time step is determined uniquely. Indeed, its evolution equation for $\psi(x,t)$ can be derived from the variational principle [9,12]. (Example of such treatment is given in Sect. 5.1.)

An important situation where the variational principle clearly breaks down is the case that inertia forces (or accelerations $\ddot{x}$) are non-negligible. In this case, the argument given in Sect. 2.3 is not valid any more. The inertia effect can be included in a more general framework called dissipative Hamiltonian dynamics [13,14].

With these reservations, the dynamics of many soft matter systems obeys the variational principle. Many phenomenological equations in soft matter (diffusion equation, Smoluchowskii equation for Brownian motion, Cahn-Hilliard equation for phase separation, Leslie-Ericksen equation for nematic crystals, gel dynamic equations etc.) have been derived based on this principle [9,12]. On the other hand, clear criteria for slow variables are still lacking, and it is a subject to be explored.

5 Example

5.1 Diffusion of particles

In this section, I demonstrate a usage of the variational principle for a simple problem. Let us consider colloidal suspensions. In the previous sections, dynamics of suspensions was discussed with particle positions used as slow variables. Here the dynamics is considered at a higher level of coarse graining. Let us focus on the evolution of the particle concentration. Let $n(x;t)$ be the number density of particles at position x and time t. This is a proper set of slow variables since, given $n(x;t)$ at time t, $n(x,t+\Delta t)$ is uniquely determined.

The free energy of the system is written as a functional of $n(x;t)$:

$$A[n(x;t)] = \int dx f(n) \tag{22}$$

where $f(n)$ the free energy density of the solution at concentration n. In dilute solution, $f(n)$ is given by

$$f(n) = nk_BT \ln n. \tag{23}$$

In concentrated solutions, $f(n)$ includes other terms arising from the interaction between particles.

To construct the dissipation function, we consider how much energy is dissipated in the fluid when $n(x,t)$ is changing at rate $\dot{n}(x,t)$. Energy dissipation takes place because the change of concentration is associated with the motion of particles in fluids. Let $v(x,t)$ is the average velocity of particles at position x. It is related to $\dot{n}$ by the conservation equation

$$\dot{n} = -\frac{\partial(nv)}{\partial x}\cdot \tag{24}$$

The dissipation function is a quadratic function of v, and can be written as

$$\Phi = \frac{1}{2}\int dx \xi(n) v^2 \tag{25}$$

where $\xi(n)$ is the friction coefficient of particles per unit volume: the total hydrodynamic drag exerted on the particles moving with velocity v in unit volume is given by $-\xi(n)v$. In dilute solution, $\xi(n)$ can be written as

$$\xi(n) = n\zeta \tag{26}$$

where $\zeta = 6\pi\eta a$ is the Stokes friction constant of a particle. $\xi(n)$ in concentrated suspensions has been discussed extensively in Stokesian hydrodynamics [15].

The evolution of the system is given by v which minimizes the Rayleighian $R = \Phi + \dot{A}$. By Eqs. (22) and (24) $\dot{A}$ is calculated as

$$\dot{A} = \int dx \frac{\partial f}{\partial n}\dot{n} = -\int dx \frac{\partial f}{\partial n}\frac{\partial nv}{\partial x} = \int dx \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial n}\right) nv. \tag{27}$$

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

$$v = -\frac{n}{\xi}\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial n}\right)\cdot \tag{28}$$

Equations (24) and (28) give the diffusion equation

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x}\left[\frac{n^2}{\xi}\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial n}\right)\right] = \frac{\partial}{\partial x}\left[D\frac{\partial n}{\partial x}\right] \tag{29}$$

where D is given by

$$D = \frac{n^2}{\xi}\frac{\partial^2 f}{\partial n^2}\cdot \tag{30}$$

In dilute solutions, Eqs. (23) and (26) can be used for $f(n)$ and $\xi(n)$, and Eq. (29) gives the usual diffusion equation.

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}, \qquad \text{with} \quad D = \frac{k_BT}{\zeta}\cdot \tag{31}$$

The above derivation of the diffusion equation shows an advantage of using the variational principle. The slow variable in this case is a function $n(x,t)$, and therefore Φ has to be written as a function (or rather a functional) of $\dot{n}(x,t)$. It is difficult to write down such a functional, but by introducing a new variable $v(x,t)$, it is easy to write down Φ (see Eq. (25)). Notice that, in our present definition, $v(x,t)$ is not the slow variables since $v(x,t)$ does not appear in the expression of the free energy A. (The slow variables are the set of variables appearing in the free energy of the system.) $v(x,t)$ is an auxiliary variable introduced to write down the dissipation function.

Such flexibility in choosing variables or introducing new variables is the advantage of the variational formulation. This is similar to Lagrangian mechanics [16] where, as long as one can write down the kinetic energy as a function of certain set of variables, one can eventually get correct set of equations of motion independently of the choice of the variables.

5.2 Onsager principle as a tool for approximation

The variational principle has other advantages. It provides us a new way of getting approximate solution of the problem [17]. This advantage has been demonstrated by many examples [18–21]. The base of the approximation is as follows.

The Onsager principle states that, given the state x of the system at time t, the state at the next time step $t + \Delta t$ is given by $x + \Delta x$ that minimizes the Rayleighian $R(x, \Delta x/\Delta t)$. Now instead of searching the minimum in the entire parameter space, we search the minimum in a limited space where x_i is expressed as a function of other parameter set $\alpha = (\alpha_1, \alpha_2, ...\alpha_p)$ as $x_i(t) = x_i(\alpha(t))$. The evolution of $\alpha(t)$ is then determined by the Onsager principle.

For example, let us consider to solve the diffusion Eq. (31) in an infinite space ($-\infty < x < \infty$) under the initial condition $n(x,0) = \delta(x)$. The exact solution of this problem is

$$n^{exact}(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \cdot \tag{32}$$

Let us assume that the solution is approximated by the following piece-wise linear function

$$n(x,t) = \begin{cases} \frac{1}{a(t)} \left|1 - \frac{x}{a(t)}\right| & |x| < a(t) \\ 0 & |x| > a(t) \end{cases} \tag{33}$$

where $a(t)$ is a parameter representing the width of the function $n(x,t)$. Equation (33) is exact at time $t = 0$ if we impose $a(0) = 0$. To determine the evolution of $a(t)$, we use the Onsager principle.

If $a(t)$ changes at rate $\dot{a}(t)$, $n(x,t)$ changes as

$$\dot{n} = \begin{cases} -\frac{\dot{a}}{a^2}\left(1 - \frac{2x}{a}\right) & 0 < x < a(t) \\ 0 & a(t) < x. \end{cases} \tag{34}$$

Here only the region of $x > 0$ is considered since the solution is symmetric with respect to $x = 0$. Now we calculate the dissipation function Φ and the free energy change rate $\dot{A}$ associated with this change. The particle velocity v is obtained from Eq. (24) and Eq. (34)

$$-\frac{\dot{a}}{a^2}\left(1 - \frac{2x}{a}\right) = -\frac{\partial nv}{\partial x} \tag{35}$$

which gives

$$v = \begin{cases} \frac{\dot{a}}{a}x & 0 < x < a(t) \\ 0 & a(t) < x. \end{cases} \tag{36}$$

Hence Φ and $\dot{A}$ are calculated straightforwardly by Eqs. (25) and (27). The result is:

$$\Phi = \frac{1}{6}\zeta a^2 \qquad \text{and} \qquad \dot{A} = -\frac{2k_BT}{a}\dot{a}. \tag{37}$$

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

$$a\dot{a} = 6\frac{k_BT}{\zeta} = 6D \tag{38}$$

which is solved as

$$a(t) = \sqrt{12Dt}. \tag{39}$$

The peak position of the distribution function is

$$n(0,t) = \frac{1}{\sqrt{12Dt}}\cdot \tag{40}$$

This is close to the exact value $n^{exact}(0,t) = 1/\sqrt{4\pi Dt}$. The variance $\langle x^2\rangle$ calculated for the distribution function (33) is $\langle x^2\rangle = 2Dt$, which agrees with that of the exact solution. Therefore the approximate solution obtained here is a fairly good solution.

6 Conclusion

In this paper, I reviewed the classical theory of Brownian motion, and showed that the essential structure of the theory can be applied to general non-equilibrium systems in which the state of the system is specified by a certain set of slow variables. The kinetic equations for such a system have a general form, and the evolution law of such a system can be stated in a form of variational principle. I have demonstrated this for a simple problem of diffusion, but the method can be applied to many other problems [17–21]. The variational principle will also gives us a new simulation scheme for dynamical systems.

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