

# Variational principle for the Kirkwood theory for the dynamics of polymer solutions and suspensions

Masao Doi

Department of Physics, Faculty of Science, Tokyo Metropolitan University, Setagaya, Tokyo, Japan  
(Received 3 December 1982; accepted 25 April 1983)

The general theory of Kirkwood for the dynamics of polymer solutions and suspensions is reformulated in the form of a variational principle. This formulation is analogous to Lagrangian mechanics and the time evolution equation is derived from a certain scalar functional. The advantage of this formulation is that: (i) it states the essential physics of the Kirkwood theory without using the Riemannian geometry; and (ii) it suggests various new schemes of approximation. Two examples are given to illustrate the usefulness of the formulation, i.e., the dynamics of rodlike polymers and the deformation of an elastic particle in elongational flow.

## I. INTRODUCTION

In 1949,<sup>1,2</sup> Kirkwood gave a general theory for the dynamics of polymer solutions and suspensions. Based on the earlier work of Burgers,<sup>3</sup> Kuhn,<sup>4</sup> and Kramers,<sup>5</sup> he established how to take into account the Brownian motion, how to include the effects of the macroscopic flow and the hydrodynamic interaction, and how to calculate the stress tensor. After a correction<sup>6,7</sup> of an error included in the original theory, his theory has been regarded as a very general foundation for the kinetic theory of polymer solutions and suspensions.

Unfortunately, the original Kirkwood theory was written in the language of the Riemannian geometry, which has formidable appearance of mathematics. For example, his general diffusion equation for flexible polymers appeared almost impossible to solve even with the aid of computer. Thus for some time, the Kirkwood theory was regarded as being formally correct, but not useful for practical calculations.

A new evolution of the Kirkwood theory was brought by Fixman,<sup>8-10</sup> who rewrote the theory in terms of the usual Cartesian coordinate. In the case of flexible polymers, Fixman's representation was much more transparent than Kirkwood's, and indeed enabled him to calculate the intrinsic viscosity of polymers in a reasonable approximation.<sup>8,9</sup>

The present work was motivated by the success of Fixman's work. In this paper, we shall give a new formulation of the Kirkwood theory. The formulation is analogous to the variational principle proposed by Onsager<sup>11</sup> for the general irreversible process. In this formulation, as in the Lagrangian mechanics, the time evolution equation is obtained from a variation of a certain scalar functional. (Similar variational principle based on Rayleigh's work has been successfully applied to polymer systems by Edwards and Freed.<sup>12</sup>) Though the present formulation is merely a mathematical re-writing of the Kirkwood theory, it has various merits:

(i) The formulation states the physical content of the Kirkwood theory without using the sophisticated Riemannian geometry.

(ii) The formulation is independent of the coordinate system, and allows a great freedom in choosing the co-

ordinate. Both Kirkwood's representation and Fixman's representation are naturally derived from this formulation. A new representation which may be more convenient for practical calculation is also obtained. An example is given in Sec. V.

(iii) As a consequence of these advantages, the variational principle suggests various new methods of approximation. An example is given in Sec. VI. Further examples will be given in the future.

## II. THE KIRKWOOD THEORY

First we briefly review the Kirkwood theory. The Kirkwood theory considers a collection of Brownian particles, called beads, immersed in a Newtonian fluid of viscosity  $\eta_s$ , interacting via a certain interaction potential. All beads are assumed to be a sphere of radius  $a$ . Though this model was proposed for polymer solutions, it can be readily applied to suspensions with certain generalization.

If the Brownian motion is neglected, the dynamics of the beads is described by hydrodynamics. Since the relevant Reynolds number is very small, the Stokes approximation can be used. Let  $\{\mathbf{R}\} = (\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$  be the set of the position vectors of the beads, and  $\mathbf{F}_m$  be the nonhydrodynamic force acting on the  $m$ th bead. If the separation between beads is large compared to  $a$ , the velocity  $\dot{\mathbf{R}}_m$  of the  $m$ th beads is given by the Stokes-Oseen law:

$$\zeta \left( \dot{\mathbf{R}}_m - \kappa \cdot \mathbf{R}_m - \sum_{n \neq m} \mathbf{T}(\mathbf{R}_m - \mathbf{R}_n) \cdot \mathbf{F}_n \right) = \mathbf{F}_m, \quad (2.1)$$

where  $\zeta = 6\pi\eta_s a$  is the Stokes friction constant  $\kappa$  the macroscopic velocity gradient and  $\mathbf{T}(\mathbf{r})$ , the Oseen tensor

$$\mathbf{T}(\mathbf{r}) = \frac{1}{8\pi\eta_s |\mathbf{r}|} \left[ \mathbf{I} + \frac{\mathbf{r}\mathbf{r}}{|\mathbf{r}|^2} \right] \quad (2.2)$$

( $\mathbf{I}$  being the unit tensor). Defining the tensor  $\mathbf{H}_{nm}$  as

$$\mathbf{H}_{nm} \equiv \frac{\mathbf{I}}{\zeta}, \quad \mathbf{H}_{nm} \equiv \mathbf{T}(\mathbf{R}_n - \mathbf{R}_m), \quad (n \neq m), \quad (2.3)$$

we can rewrite Eq. (2.1) as

$$\dot{\mathbf{R}}_m - \kappa \cdot \mathbf{R}_m = \sum_n \mathbf{H}_{nm} \cdot \mathbf{F}_m. \quad (2.4)$$

If the force is given by a known interaction potential  $V(\{\mathbf{R}\})$  as

$$\mathbf{F}_m = - \frac{\partial V}{\partial \mathbf{R}_m}, \quad (2.5)$$

the motion of the beads is determined by Eqs. (2.4) and (2.5). In general, however, a complication arises since the beads are usually subject to certain constraints such as the constant bond lengths or constant bond angles. If the degree of freedom of the system is  $f$ , such constraints are generally expressed as  $3N - f$  functional relations:

$$C_p(\{\mathbf{R}\}) = 0, \quad (p = 1, 2, \dots, 3N - f). \quad (2.6)$$

These constraints can be handled by two methods:

(i) In the first method, which was adopted by Kirkwood, a set of independent variables  $\{Q\} = (Q_1, Q_2, \dots, Q_f)$  are used to specify the configuration of the beads under the constraints (2.6). The velocity  $\dot{\mathbf{R}}_m$  is given as

$$\dot{\mathbf{R}}_m = \sum_a \frac{\partial \mathbf{R}_m}{\partial Q_a} \dot{Q}_a. \quad (2.7)$$

(Note that the dots in  $\dot{\mathbf{R}}_m$  and  $\dot{Q}_a$  do not mean the time derivatives, but simply define new variables.)

The force  $\mathbf{F}_m$  now represents the potential force and the constraining force. Since the constraining force does no work, we have

$$\sum_m \mathbf{F}_m \cdot \frac{\partial \mathbf{R}_m}{\partial Q_a} = - \frac{\partial V}{\partial Q_a}. \quad (2.8)$$

Equations (2.4), (2.7), and (2.8) determine  $\dot{\mathbf{R}}_m$ ,  $\dot{Q}_a$ , and  $\mathbf{F}_m$ .

(ii) An alternative method used by Fixman<sup>8</sup> is to regard  $\mathbf{R}_m$  as an independent variable and to take into account the constraints by explicitly adding the constraining force to Eq. (2.1).

$$\mathbf{F}_m = - \frac{\partial V}{\partial \mathbf{R}_m} + \sum_p \lambda_p \frac{\partial C_p}{\partial \mathbf{R}_m}, \quad (2.9)$$

where  $\lambda_p$  are unknowns, which are determined by the condition that  $\dot{\mathbf{R}}_m$  given by Eqs. (2.4) and (2.9) satisfies

$$\sum_m \dot{\mathbf{R}}_m \cdot \frac{\partial C_p}{\partial \mathbf{R}_m} = 0, \quad (p = 1, 2, \dots, 3N - f). \quad (2.10)$$

[In Eq. (2.9), for the derivative  $\partial V(\{\mathbf{R}\})/\partial \mathbf{R}_m$  to be defined,  $V(\{\mathbf{R}\})$  must be defined over the entire  $3N$  dimensional phase space. If  $V(\{\mathbf{R}\})$  is known only in the  $f$ -dimensional constrained space, arbitrary generalization is allowed for  $V(\{\mathbf{R}\})$  outside the constrained space. Whatever the generalized potential is, the resulting force  $\mathbf{F}_m$  is independent of the way of generalization as long as Eq. (2.10) is satisfied.]

Equations (2.4), (2.7), and (2.8), or (2.4), (2.9), and (2.10) determine the motion of beads for given velocity gradient. Now when the Brownian motion is involved, one cannot determine the position of beads precisely. Instead one can determine the probability density  $\Psi(\{\mathbf{R}\}; t)$  that the beads are in the configuration  $\{\mathbf{R}\}$  at time  $t$ . The conservation equation for the probability is

$$\frac{\partial \Psi}{\partial t} = - \sum_m \frac{\partial}{\partial \mathbf{R}_m} \cdot [\dot{\mathbf{R}}_m \Psi]. \quad (2.11)$$

Now the essential point of the Kirkwood theory is the proposal that due to the Brownian motion a new term  $k_B T \ln \Psi$ , called the Brownian potential, must be added to the potential. Hence, Eqs. (2.8) or (2.9) are now replaced by

$$\text{Eq. (2.8): } \sum_m \mathbf{F}_m \cdot \frac{\partial \mathbf{R}_m}{\partial Q_a} = - \frac{\partial}{\partial Q_a} (V + k_B T \ln \Psi), \quad (2.12)$$

$$\text{Eq. (2.9): } \mathbf{F}_m = - \frac{\partial}{\partial \mathbf{R}_m} (V + k_B T \ln \Psi) + \sum_p \lambda_p \frac{\partial C_p}{\partial \mathbf{R}_m}. \quad (2.13)$$

The set of equations [(2.4), (2.7), (2.11), and (2.12)] gives Kirkwood's representation for the diffusion equation, and the set of equations [(2.4), (2.10), (2.11), and (2.13)] leads to Fixman's representation. The explicit form for the diffusion equation is complicated and given in Appendix A.

To discuss rheological properties, we need to know the microscopic expression for the stress tensor. According to Kirkwood, the excess stress due to the presence of the polymers is given as

$$\sigma_{\alpha\beta} = - \frac{1}{\Omega} \sum_m \langle R_{m\alpha} F_{m\beta} \rangle + \text{isotropic term}, \quad (2.14)$$

where  $\alpha, \beta (= x, y, z)$  denote the component of the vectors or tensors,  $\Omega$  is the volume of the solution, and  $\langle \dots \rangle$  represents the average over the distribution function  $\Psi(\{\mathbf{R}\}; t)$ :

$$\langle \dots \rangle \equiv \int d\{\mathbf{R}\} \Psi(\{\mathbf{R}\}; t) \dots \quad (2.15)$$

The total stress of the system is thus

$$\sigma_{\alpha\beta}^{\text{tot}} = \eta_s (\kappa_{\alpha\beta} + \kappa_{\beta\alpha}) + p \delta_{\alpha\beta} + \sigma_{\alpha\beta}. \quad (2.16)$$

Equation (2.14) agrees with the formula given by Batchelor.<sup>13</sup>

Since Eqs. (2.4), (2.7), and (2.12) [or Eqs. (2.4), (2.10), and (2.13)] determine  $\mathbf{F}_m$  as a linear function of  $\kappa(t)$  as

$$F_{m\alpha} = F_{m\alpha}^{(E)}(\{\mathbf{R}\}; \Psi) + \Xi_{m\alpha\mu\nu}^{(V)}(\{\mathbf{R}\}) \kappa_{\nu\mu}(t) \quad (2.17)$$

(where summation convention is used for the repeated Greek indices), the excess stress is generally written as

$$\sigma_{\alpha\beta} = \sigma_{\alpha\beta}^{(E)} + \sigma_{\alpha\beta}^{(V)} \quad (2.18)$$

with

$$\sigma_{\alpha\beta}^{(E)} = - \frac{1}{\Omega} \left\langle \sum_m R_{m\alpha} F_{m\beta}^{(E)}(\{\mathbf{R}\}; \Psi) \right\rangle, \quad (2.19)$$

$$\begin{aligned} \sigma_{\alpha\beta}^{(V)} &= - \frac{1}{\Omega} \left\langle \sum_m R_{m\alpha} \Xi_{m\beta\mu\nu}^{(V)}(\{\mathbf{R}\}) \kappa_{\nu\mu}(t) \right\rangle \\ &\equiv \eta_{\alpha\beta\mu\nu}^{(V)} \kappa_{\nu\mu}(t). \end{aligned} \quad (2.20)$$

We call  $\sigma^{(E)}$  the elastic stress and  $\sigma^{(V)}$  the viscous stress. The viscous stress  $\sigma^{(V)}(t)$  at time  $t$  is proportional to the velocity gradient  $\kappa(t)$  at the same time, while the elastic stress  $\sigma^{(E)}(t)$  is independent of it. The distinction between  $\sigma^{(E)}$  and  $\sigma^{(V)}$  is important and will be discussed in Sec. IV.

Before ending this section, a comment is made about the tensor  $\mathbf{H}_{nm}$ . The formula (2.1) is correct only if the distance between beads is large enough, otherwise, Eq. (2.4) poses some problems.<sup>14,15</sup> For example, although the mobility tensor  $H_{nm}$  must be positive definite, i. e.,

$$\sum_{n,m} \mathbf{F}_n \cdot \mathbf{H}_{nm} \cdot \mathbf{F}_m \geq 0. \quad (2.21)$$

$\mathbf{H}_{nm}$ , defined by Eq. (2.3), does not always satisfy this condition. One way of avoiding this difficulty is to use an improved expression for  $\mathbf{H}_{nm}$ .<sup>16,17</sup> Another way, which is formally very simple, but not so in practice is to introduce the "subbeads" which have infinitesimal size and cover the surface of the beads continuously. If  $\mathbf{R}_n$  and  $\mathbf{F}_n$  are understood as representing the quantities of the subbeads, then Eq. (2.1) reduces to Green's function method known in zero Reynolds number hydrodynamics.<sup>17</sup> In this case, Eq. (2.21) is guaranteed. With this understanding, the Kirkwood theory can be applied for suspensions of solid particles since any particle can be regarded as made up of infinite subparticles of infinitesimal size.

### III. THE VARIATIONAL FORMULATION

Now we translate the above equations into a variational principle. For that purpose we regard  $\dot{\mathbf{R}}_m$  as a function of  $\{\mathbf{R}\}$  and introduce the following functionals:

$$\mathcal{W}[\{\dot{\mathbf{R}}\}] \equiv \int d\{\mathbf{R}\} \Psi \sum_{n,m} (\dot{\mathbf{R}}_n - \boldsymbol{\kappa} \cdot \mathbf{R}_n) \cdot (\mathbf{H}^{-1})_{nm} \cdot (\dot{\mathbf{R}}_m - \boldsymbol{\kappa} \cdot \mathbf{R}_m), \quad (3.1)$$

$$\mathcal{A}[\{\dot{\mathbf{R}}\}] \equiv \int d\{\mathbf{R}\} [k_B T \dot{\Psi} \ln \Psi + k_B T \dot{\Psi} + \dot{\Psi} V], \quad (3.2)$$

where  $(\mathbf{H}^{-1})_{nm}$  is the inverse of  $\mathbf{H}_{nm}$ :

$$\sum_m \mathbf{H}_{nm} \cdot (\mathbf{H}^{-1})_{mk} = \mathbf{I} \delta_{nk} \quad (3.3)$$

and the function  $\dot{\Psi}$  is defined by

$$\dot{\Psi} = - \sum_m \frac{\partial}{\partial \mathbf{R}_m} \cdot [\dot{\mathbf{R}}_m \Psi]. \quad (3.4)$$

With this definition, the variational principle can be stated as follows: Let  $\mathcal{K}$  be defined by

$$\mathcal{K}[\{\dot{\mathbf{R}}\}] \equiv \frac{1}{2} \mathcal{W} + \mathcal{A} \quad (3.5)$$

then it follows:

(i) The functional  $\mathcal{K}$  becomes minimum for  $\dot{\mathbf{R}}_m$  which satisfies the equations of motion [Eqs. (2.4), (2.10), and (2.13)]. For this  $\{\dot{\mathbf{R}}\}$ ,  $\dot{\Psi}$  gives the time evolution of  $\Psi(\{\mathbf{R}\}; t)$ :

$$\frac{\partial \Psi}{\partial t} = \dot{\Psi}. \quad (3.6)$$

(ii) The minimum value of  $\mathcal{K}$  is quadratic in the velocity gradient tensor  $\boldsymbol{\kappa}$ , and the coefficients determine the viscous stress and the elastic stress as

$$\min \mathcal{K} = \left[ \frac{1}{2} \eta_{\alpha\beta\mu\nu}^{(V)} \kappa_{\beta\alpha} \kappa_{\nu\mu} + \sigma_{\alpha\beta}^{(E)} \kappa_{\beta\alpha} \right] \Omega + \text{terms independent of } \kappa_{\alpha\beta}. \quad (3.7)$$

The derivation of these results is straightforward and given in Appendix B.

We now discuss some physical implication of the variational principle.

Crudely speaking the variational principle states how to balance the "viscous" force which is included in  $\mathcal{W}$ , with the "elastic" force which is included in  $\mathcal{A}$ . This may be seen more clearly in the case that the Brownian motion is neglected. In this case we have the following variational principle: Regarding  $\dot{\mathbf{R}}_m$  as simple variables (not functions of  $\{\mathbf{R}\}$ ), we introduce

$$K(\{\dot{\mathbf{R}}\}) = \frac{1}{2} W(\{\dot{\mathbf{R}}\}) + \dot{A}(\{\dot{\mathbf{R}}\}), \quad (3.8)$$

where

$$W(\{\dot{\mathbf{R}}\}) = \sum_{n,m} (\dot{\mathbf{R}}_n - \boldsymbol{\kappa} \cdot \mathbf{R}_n) \cdot (\mathbf{H}^{-1})_{nm} \cdot (\dot{\mathbf{R}}_m - \boldsymbol{\kappa} \cdot \mathbf{R}_m), \quad (3.9)$$

$$\dot{A} = \sum_m \frac{\partial V}{\partial \mathbf{R}_m} \cdot \dot{\mathbf{R}}_m. \quad (3.10)$$

It is easy to show that the hydrodynamic equations of motion [Eqs. (2.4) and (2.9)] are obtained by minimizing  $K$  with respect to  $\{\dot{\mathbf{R}}\}$  under given constraints. In this case,  $W$  represents the hydrodynamic energy dissipation, and  $\dot{A}$  represents the rate of change of the potential energy. This variational principle is a special form of the "principle of minimum energy dissipation" proposed by Onsager, in which  $\mathbf{R}_m$  and  $V$  represent the general thermodynamic variables and the entropy, respectively.

In the general case of Eq. (3.5), the functional  $\mathcal{W}$  represents the mean energy dissipation caused by the hypothetical motion  $\dot{\mathbf{R}}_m$ . The functional  $\mathcal{A}$  represents the rate of change of the following quantity:

$$\mathcal{A}[\Psi] \equiv \int d\{\mathbf{R}\} [k_B T \dot{\Psi} \ln \Psi + \dot{\Psi} V]. \quad (3.11)$$

(Here  $V$  is assumed to be independent of time.) At equilibrium,  $\mathcal{A}[\Psi]$  reduces to the usual free energy:

$$\mathcal{A}[\Psi_{\text{eq}}] = -k_B T \ln \left[ \int d\{\mathbf{R}\} \exp(-V/k_B T) \right] \quad (3.12)$$

since

$$\Psi_{\text{eq}} = \exp(-V/k_B T) / \int d\{\mathbf{R}\} \exp(-V/k_B T). \quad (3.13)$$

The functional  $\mathcal{A}[\Psi]$  represents the free energy (in the sense of nonequilibrium thermodynamics) for the state described by the distribution function  $\Psi$ . We shall call  $\mathcal{A}[\Psi]$  the dynamic free energy.

The dynamic free energy has the following property of irreversibility (see Appendix B): If there is no velocity gradient, and if the potential  $V(\{\mathbf{R}\}; t)$  is independent of time, the dynamic free energy decreases monotonically with time, i. e.,

$$\frac{d\mathcal{A}}{dt} = \dot{\mathcal{A}} < 0. \quad (3.14)$$

Thus  $\mathcal{A}[\Psi]$  is always larger than  $\mathcal{A}[\Psi_{\text{eq}}]$  and can be a measure of how far the system is from the equilibrium state.

Now a few comments are made as to practical application of the variational principle:

(i) The advantage of the variational principle is that

the functional  $\mathcal{K}$  is independent of the coordinate system. If one expresses  $\mathcal{K}$  in terms of the generalized coordinates  $\{Q\}$ , he gets Kirkwood's representation. Alternatively, if he takes into account the constraints (2.6) by adding to  $\mathcal{K}$  a new term

$$\sum_p \lambda_p \frac{\partial C_p}{\partial \mathbf{R}_m} \cdot \dot{\mathbf{R}}_m \quad (3.15)$$

he gets Fixman's representation. Such flexibility in the choice of the coordinate is quite useful in actual calculation as will be demonstrated in Sec. V:

(ii) The variational principle determines the rate of change such as  $\mathbf{R}_m$  or  $\partial\Psi/\partial t$ , but not  $\Psi$  itself. Particularly, it does not determine the steady state directly: The steady state is obtained only by time integration of  $\partial\Psi/\partial t$ . In this sense, the present variational principle is different from the variational principle, recently proposed by Fixman<sup>19</sup> which directly determines the steady state and gives upper and lower bounds for transport coefficients (see also Refs. 20 and 21). However, the two formulations have apparent similarity. In fact, in the special case of steady state, weak flow, the form of the functional to be minimized becomes the same in the two formulations. The connection between the two formulations is not clear at present, but we hope to come back to that problem in the future.

#### IV. THE PRINCIPLE OF THE HYPOTHETICAL WORK

In this section, we discuss another interesting implication included in the Kirkwood theory. As is well known, in ideal elastic materials, the stress can be calculated from the variation in the free energy caused by a hypothetical strain. On the other hand, in purely viscous liquids, the stress is related to the energy dissipation. An interesting question is: How can we generalize these relations to viscoelastic materials? Although the general answer to this question may be delicate, there is a clear answer if the system is described by the Kirkwood theory.

Consider a small hypothetical deformation  $\delta\epsilon_{\alpha\beta}$  which displaces the material point  $r_\alpha$  to  $r_\alpha + \delta\epsilon_{\alpha\beta} r_\beta$ . If the deformation is done in a time  $\delta t$ , the velocity gradient is given by

$$\kappa_{\alpha\beta} = \delta\epsilon_{\alpha\beta}/\delta t. \quad (4.1)$$

We consider the limit of "instantaneous" deformation, i. e., the limit of  $\delta t \rightarrow 0$ . Since we keep  $\delta\epsilon_{\alpha\beta}$  small but finite,  $\kappa$  becomes very large in this limit.

In this limit,  $\dot{\mathcal{A}}$  can be neglected compared to  $\mathcal{W}$  and the real velocity  $\{\dot{\mathbf{R}}\}$  is given by those which minimize  $\mathcal{W}$  subject to the constraints (2.6). Thus, it follows:

(i) During the instantaneous deformation, the beads move with the velocity  $\{\dot{\mathbf{R}}\}$  which minimize  $\mathcal{W}$  subject to the constraints (2.6). The displacement  $\delta\mathbf{R}_m$  of the beads caused by the hypothetical deformation is given by  $\dot{\mathbf{R}}_m \delta t$ .

By straightforward calculation (see Appendix B) we can show:

(ii) The energy dissipation  $\mathcal{W}$  is related to the coef-

ficient in the viscous stress as

$$\eta_{\alpha\beta\mu\nu}^{(V)} \kappa_{\beta\alpha} \kappa_{\nu\mu} = \min \mathcal{W}; \quad (4.2)$$

(iii) The variation of the dynamic free energy  $\mathcal{A}$  is related to the elastic stress:

$$\delta\mathcal{A} = \sigma_{\alpha\beta}^{(E)} \delta\epsilon_{\beta\alpha}, \quad (4.3)$$

where

$$\delta\mathcal{A} = \int d\{\mathbf{R}\} [k_B T \delta\Psi \ln \Psi + k_B T \delta\Psi + \delta\Psi V] \quad (4.4)$$

and

$$\delta\Psi \equiv - \sum_m \frac{\partial}{\partial \mathbf{R}_m} \cdot [\delta\mathbf{R}_m \Psi]. \quad (4.5)$$

The meaning of Eqs. (4.2) and (4.3) is obvious: When a small strain  $\delta\epsilon_{\alpha\beta}$  is applied to the system in a very short time  $\delta t$ , part of the work done to the system is immediately dissipated due to the hydrodynamic friction, and the remainder is stored as an increase in the dynamic free energy. The former determines  $\eta_{\alpha\beta\mu\nu}^{(V)}$  and the latter  $\sigma_{\alpha\beta}^{(E)}$ . This result, though obvious, was useful for obtaining the microscopic expression for the stress tensor in concentrated suspensions.<sup>22</sup>

#### V. EXAMPLE 1: DYNAMICS OF RODLIKE POLYMER IN DILUTE SOLUTION

We now give examples of the application of the variational principle. In this section, we consider the dynamics of rodlike polymers in dilute solution. The primary purpose of this section is to demonstrate the neatness in the calculation based on the variational principle since the problem itself has been discussed by many authors.<sup>2,23</sup>

We consider a rodlike polymer of length  $L$  and diameter  $d$  immersed in a Newtonian fluid. The polymer is assumed to be made up of  $N \equiv L/d$  beads which are placed along a straight line with equal separation  $d$ . The beads are numbered from  $-N/2$  to  $N/2$ . Let  $\mathbf{R}$  be the position of the center of mass, and  $\mathbf{u}$  be the unit vector along the polymer, then the position, and the velocity of the  $n$ th bead is written as

$$\mathbf{R}_n = n d \mathbf{u} + \mathbf{R}, \quad \dot{\mathbf{R}}_n = n d \dot{\mathbf{u}} + \dot{\mathbf{R}}. \quad (5.1)$$

Since  $\mathbf{u}$  is a unit vector, the three components of  $\mathbf{u}$  and  $\dot{\mathbf{u}}$  must satisfy the relation

$$u_\alpha u_\alpha = 1, \quad (5.2a)$$

$$u_\alpha \dot{u}_\alpha = 0. \quad (5.2b)$$

Here we use the representation which is intermediate between Kirkwood's and Fixman's. We regard the six components of the two vectors  $\mathbf{R}$  and  $\mathbf{u}$  as independent variables and take into account the above constraint by Fixman's method.

Now from Eqs. (2.2) and (5.1),  $\mathbf{H}_{nm}$  is written as

$$\mathbf{H}_{nm} = h_{nm} (\mathbf{I} + \mathbf{u}\mathbf{u}), \quad (5.3)$$

where

$$h_{nm} = (1 - \delta_{nm}) / 8\pi\eta_s d |n - m| \quad (5.4)$$

and the term  $1\delta_{nm}/\xi$  is neglected since this term turns

out to be negligible for large  $N$ . The inverse of  $\mathbf{H}_{nm}$  is given as

$$(\mathbf{H}^{-1})_{nm} = (h^{-1})_{nm} \left( \mathbf{1} - \frac{\mathbf{u}\mathbf{u}}{2} \right), \quad (5.5)$$

where  $(h^{-1})_{nm}$  is the inverse matrix of  $h_{nm}$ .

Substituting Eqs. (5.1) and (5.5) into Eq. (3.1) we have

$$\begin{aligned} \mathcal{W} = & \int d\mathbf{u} \int d\mathbf{R} \Psi \left\{ \zeta_r [(\dot{\mathbf{u}} - \boldsymbol{\kappa} \cdot \mathbf{u})^2 - \frac{1}{2}(\mathbf{u} \cdot \boldsymbol{\kappa} \cdot \mathbf{u})^2] \right. \\ & \left. + \zeta_t [(\dot{\mathbf{R}} - \boldsymbol{\kappa} \cdot \mathbf{R})^2 - \frac{1}{2}(\mathbf{u} \cdot (\dot{\mathbf{R}} - \boldsymbol{\kappa} \cdot \mathbf{R}))^2] \right\}, \end{aligned} \quad (5.6)$$

where

$$\zeta_r = d^2 \sum_{n,m} (h^{-1})_{nm} nm, \quad \zeta_t = \sum_{n,m} (h^{-1})_{nm}. \quad (5.7)$$

Hence,

$$\begin{aligned} \mathcal{K} = & \int d\mathbf{u} \int d\mathbf{R} \left\{ \frac{1}{2} \zeta_r [(\dot{\mathbf{u}} - \boldsymbol{\kappa} \cdot \mathbf{u})^2 - \frac{1}{2}(\mathbf{u} \cdot \boldsymbol{\kappa} \cdot \mathbf{u})^2] \Psi \right. \\ & \left. + \zeta_t \left[ \frac{1}{2} (\dot{\mathbf{R}} - \boldsymbol{\kappa} \cdot \mathbf{R})^2 - \frac{1}{4} (\mathbf{u} \cdot (\dot{\mathbf{R}} - \boldsymbol{\kappa} \cdot \mathbf{R}))^2 \right] \Psi \right. \\ & \left. - \left( \frac{\partial}{\partial \mathbf{u}} \cdot \dot{\mathbf{u}} \Psi + \frac{\partial}{\partial \mathbf{R}} \cdot \dot{\mathbf{R}} \Psi \right) (k_B T \ln \Psi + V) - \lambda \mathbf{u} \cdot \dot{\mathbf{u}} \Psi \right\}, \end{aligned} \quad (5.8)$$

where  $V(\mathbf{u}; t)$  is the potential energy due to an external field. The last term of Eq. (5.8) comes from the constraints (5.2) with  $\lambda \Psi$  being the Lagrangian multiplier.

A cautionary remark is made here. Since  $\Psi(\mathbf{u})$  includes the factor  $\delta(|\mathbf{u}| - 1)$ , it follows that, for arbitrary function  $X(\mathbf{u})$ ,

$$X(\mathbf{u}) \Psi(\mathbf{u}) = [X(\mathbf{u})]_{|\mathbf{u}|=1} \Psi(\mathbf{u}). \quad (5.9)$$

Thus, in the expression of  $\mathcal{W}$ , we can use the relation (5.2a). On the other hand, since

$$X(\mathbf{u}) \frac{\partial \Psi}{\partial \mathbf{u}} \neq [X(\mathbf{u})]_{|\mathbf{u}|=1} \frac{\partial \Psi}{\partial \mathbf{u}}, \quad (5.10)$$

the relation (5.2a) cannot be used in the first term in  $\mathcal{A}$ . It must be remembered that the relation (5.2a) can be used only when the expression has the factor  $\Psi$ .

Now from  $\partial \mathcal{K} / \partial \dot{\mathbf{u}} = 0$  and  $\partial \mathcal{K} / \partial \dot{\mathbf{R}} = 0$ , we have

$$\zeta_r (\dot{\mathbf{u}} - \boldsymbol{\kappa} \cdot \mathbf{u}) + \frac{\partial}{\partial \mathbf{u}} (k_B T \ln \Psi + V) - \lambda \mathbf{u} = 0, \quad (5.11a)$$

$$\zeta_t [(\dot{\mathbf{R}} - \boldsymbol{\kappa} \cdot \mathbf{R}) - \frac{1}{2} \mathbf{u} \cdot (\dot{\mathbf{R}} - \boldsymbol{\kappa} \cdot \mathbf{R}) \mathbf{u}] + \frac{\partial}{\partial \mathbf{R}} (k_B T \ln \Psi) = 0. \quad (5.11b)$$

From Eqs. (5.2b) and (5.11),  $\dot{\mathbf{u}}$  and  $\dot{\mathbf{R}}$  are solved as

$$\dot{\mathbf{u}} = -\frac{1}{\zeta_r} \nabla (k_B T \ln \Psi + V) + \boldsymbol{\kappa} \cdot \mathbf{u} - \frac{(\mathbf{u} \cdot \boldsymbol{\kappa} \cdot \mathbf{u})}{|\mathbf{u}|^2} \mathbf{u}, \quad (5.12)$$

$$\dot{\mathbf{R}} = -\frac{1}{\zeta_t} (\mathbf{1} + \mathbf{u}\mathbf{u}) \cdot \frac{\partial}{\partial \mathbf{R}} (k_B T \ln \Psi) + \boldsymbol{\kappa} \cdot \mathbf{R}, \quad (5.13)$$

where

$$\nabla \equiv \left( \mathbf{1} - \frac{\mathbf{u}\mathbf{u}}{|\mathbf{u}|^2} \right) \cdot \frac{\partial}{\partial \mathbf{u}}. \quad (5.14)$$

The minimum of  $\mathcal{K}$  is

$$\begin{aligned} \min \mathcal{K} = & \int d\mathbf{u} \int d\mathbf{R} \Psi \left[ \frac{1}{2} \zeta_r (\boldsymbol{\kappa} \cdot \mathbf{u})^2 + (\boldsymbol{\kappa} \cdot \mathbf{u}) \cdot \nabla (k_B T \ln \Psi + V) \right] \\ & + \text{terms independent of } \boldsymbol{\kappa}. \end{aligned} \quad (5.15)$$

Comparing this with Eq. (3.7), we get the expression for the stress tensor

$$\sigma_{\alpha\beta}^{(V)} = c \frac{\zeta_r}{2} \langle u_\alpha u_\beta u_\mu u_\nu \rangle \kappa_{\mu\nu}, \quad (5.16)$$

$$\begin{aligned} \sigma_{\alpha\beta}^{(E)} = & c \int d\mathbf{u} \int d\mathbf{R} u_\alpha \left( \delta_{\beta\mu} - \frac{u_\beta u_\mu}{|\mathbf{u}|^2} \right) \\ & \times \left( k_B T \frac{\partial \Psi}{\partial u_\mu} + \frac{\partial V}{\partial u_\mu} \Psi \right), \end{aligned} \quad (5.17)$$

where  $c \equiv 1/\Omega$  is the number of polymers per unit volume. By partial integration,  $\sigma_{\alpha\beta}^{(E)}$  is rewritten as

$$\begin{aligned} \sigma_{\alpha\beta}^{(E)} = & -c \int d\mathbf{u} \int d\mathbf{R} k_B T \Psi \frac{\partial}{\partial u_\mu} \left[ \left( \delta_{\beta\mu} - \frac{u_\beta u_\mu}{|\mathbf{u}|^2} \right) u_\alpha \right] + c \langle u_\alpha \nabla_\beta V \rangle \\ = & 3c k_B T \langle u_\alpha u_\beta - \frac{1}{3} \delta_{\alpha\beta} \rangle + c \langle u_\alpha \nabla_\beta V \rangle. \end{aligned} \quad (5.18)$$

Finally, using Eqs. (5.12) and (5.13) and the relation

$$\frac{\partial}{\partial \mathbf{u}} \cdot \dot{\mathbf{u}} \Psi = \nabla \cdot \dot{\mathbf{u}} \Psi, \quad (5.19)$$

we obtain the diffusion equation

$$\begin{aligned} \frac{\partial \Psi}{\partial t} = & D_r \nabla \cdot \left[ \nabla \Psi + \frac{\Psi}{k_B T} \nabla V \right] - \nabla \cdot [\boldsymbol{\kappa} \cdot \mathbf{u} - (\mathbf{u} \cdot \boldsymbol{\kappa} \cdot \mathbf{u}) \mathbf{u}] \\ & + D_t \frac{\partial}{\partial \mathbf{R}} \cdot (\mathbf{1} + \mathbf{u}\mathbf{u}) \cdot \frac{\partial \Psi}{\partial \mathbf{R}} - \frac{\partial}{\partial \mathbf{R}} \cdot \boldsymbol{\kappa} \cdot \mathbf{R} \Psi, \end{aligned} \quad (5.20)$$

where

$$D_r = k_B T / \zeta_r \quad \text{and} \quad D_t = k_B T / \zeta_t. \quad (5.21)$$

It is easy to show that Eq. (5.20) is rewritten in a more familiar form

$$\begin{aligned} \frac{\partial \Psi}{\partial t} = & D_r \mathfrak{R} \left[ \mathfrak{R} \Psi + \frac{\Psi}{k_B T} \mathfrak{R} V \right] - \mathfrak{R} \cdot [\mathbf{u} \times (\boldsymbol{\kappa} \cdot \mathbf{u}) \Psi] \\ & + D_t \frac{\partial}{\partial \mathbf{R}} \cdot (\mathbf{1} + \mathbf{u}\mathbf{u}) \cdot \frac{\partial \Psi}{\partial \mathbf{R}} - \frac{\partial}{\partial \mathbf{R}} \cdot \boldsymbol{\kappa} \cdot \mathbf{R} \Psi, \end{aligned} \quad (5.22)$$

where

$$\mathfrak{R} \equiv \mathbf{u} \times \frac{\partial}{\partial \mathbf{u}} \quad (5.23)$$

is the rotational operator. When rewritten in terms of the usual polar coordinates  $(\theta, \varphi)$ , Eqs. (5.16), (5.17), and (5.20) agree with those given in Refs. 2 and 19.

For completeness, the explicit expressions for  $D_r$  and  $D_t$  are now obtained. Since  $h_{nm}$  decreases quickly with  $|n-m|$ , we may approximate it as

$$h_{nm} \cong \bar{h} \delta_{nm} \quad (5.24)$$

with

$$\bar{h} = 2 \int_1^{N/2} dm h_{0m} = \frac{1}{4\pi\eta_s d} \ln(N/2). \quad (5.25)$$

Hence,

$$(h^{-1})_{nm} = \delta_{nm} / \bar{h} \quad (5.26)$$

and

$$\zeta_r = 2d^2 \int_0^{N/2} dm \frac{m^2}{h} = \frac{\pi\eta_s(Nd)^3}{3 \ln(N/2)} = \frac{\pi\eta_s L^3}{3 \ln(L/2d)}, \quad (5.27)$$

$$\zeta_t = N/h = 4\pi\eta_s L/\ln(L/2d). \quad (5.28)$$

These results agree with those of Kirkwood and his collaborators.<sup>2</sup>

### VI. EXAMPLE 2: DEFORMATION OF AN ELASTIC PARTICLE IN ELONGATIONAL FLOW

As the next example, we consider the following problem: Determine the deformation of an elastic particle of spherical shape placed in the elongational flow (see Fig. 1)

$$v_x = -\frac{\kappa x}{2}, \quad v_y = -\frac{\kappa y}{2}, \quad v_z = \kappa z. \quad (6.1)$$

Rigorous treatment for this problem becomes very complicated, particularly when the deformation becomes large. We shall now show that a simple approximate calculation is possible based on the variational principle.

Again we assume that the elastic particles are made up of beads, whose positions are denoted by  $R_m$ . Without loss of generality, we can assume that the center of particle is at the origin. An essential simplification can be made if we assume that the deformation of the particle is a homogeneous elongation represented by

$$R_n = E \cdot R_n^{(0)} \quad (6.2)$$

with

$$E = \begin{bmatrix} 1/\sqrt{\lambda} & 0 & 0 \\ 0 & 1/\sqrt{\lambda} & 0 \\ 0 & 0 & \lambda \end{bmatrix}, \quad (6.3)$$

where  $R_n^{(0)}$  is the position of the particle in the undeformed state. Mathematically, the parameter  $\lambda$  is regarded as a generalized coordinate characterizing the conformation of the particle.

We neglect the Brownian motion and use the variational principle of Eq. (3.8). Since the velocity of the beads is expressed as

$$\begin{aligned} \dot{R}_n &= \dot{E} \cdot R_n^{(0)} = \begin{bmatrix} -1/2\sqrt{\lambda} & 0 & 0 \\ 0 & -1/2\sqrt{\lambda} & 0 \\ 0 & 0 & 1 \end{bmatrix} \lambda R_n^{(0)} \\ &= \begin{bmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \frac{\dot{\lambda}}{\lambda} R_n \end{aligned} \quad (6.4)$$

the energy dissipation function is written as

$$W = \left(\frac{\dot{\lambda}}{\lambda} - \kappa\right)^2 X(\lambda), \quad (6.5)$$

where

$$\begin{aligned} X(\lambda) &= \sum_{m,n} \left[ \frac{1}{2} R_{mx}(H^{-1})_{mnyy} R_{ny} + R_{mz}(H^{-1})_{mnyy} R_{nz} \right] \\ &+ \frac{1}{2} R_{my}(H^{-1})_{mnyy} R_{ny} + R_{mz}(H^{-1})_{mnyy} R_{nz}. \end{aligned} \quad (6.6)$$

Though straightforward calculation of the summation in

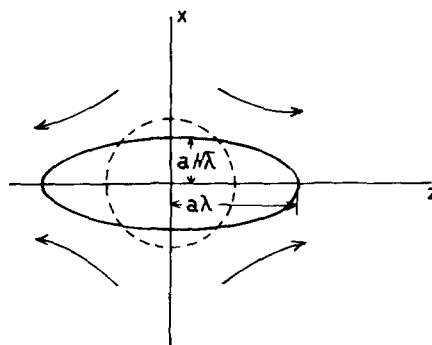


FIG. 1. Deformation of an elastic particle in an elongational flow.

Eq. (6.6) is difficult,  $X$  is easily obtained from the consideration of the special case: If the particle is a rigid ellipsoid, then  $\lambda = 0$  and the energy dissipation is given by  $\bar{\eta}(\lambda)\kappa^2$ , where  $\bar{\eta}(\lambda)$  is the excess elongational viscosity (per particle) of the solution of the rigid ellipsoid with principal axis  $\lambda a$ ,  $a/\sqrt{\lambda}$ , and  $a/\sqrt{\lambda}$ . Hence,  $X = \bar{\eta}(\lambda)$ . According to Jefferey,<sup>24</sup>

$$\bar{\eta}(\lambda) = \frac{4}{3} \pi a^3 \eta_s \frac{4e^5}{[(3 - e^2) \ln(1 + e)/(1 - e) - 6e](1 - e^2)}, \quad (6.7)$$

where  $e \equiv (1 - \lambda^{-3})^{1/2}$  is the ellipticity of the particle. Let  $U(\lambda)$  be the elastic energy of the deformed particle. Then  $K$  in Eq. (3.8) is given as

$$K = \frac{1}{2} \bar{\eta}(\lambda) \left(\frac{\dot{\lambda}}{\lambda} - \kappa\right)^2 + \dot{\lambda} \frac{\partial U}{\partial \lambda}. \quad (6.8)$$

Hence,  $\partial K / \partial \dot{\lambda} = 0$  gives,

$$\frac{d\lambda}{dt} = \dot{\lambda} = \lambda \left[ \kappa - \frac{\lambda}{\bar{\eta}(\lambda)} \frac{\partial U}{\partial \lambda} \right]. \quad (6.9)$$

Since

$$\min K = \lambda \kappa \frac{\partial U}{\partial \lambda} - \frac{\lambda^2}{2\bar{\eta}} \left(\frac{\partial U}{\partial \lambda}\right)^2, \quad (6.10)$$

the stress is obtained as

$$\sigma_{zz}^{(E)} - \sigma_{zz}^{(V)} = c\lambda \frac{\partial U}{\partial \lambda}; \quad \sigma_{zz}^{(V)} - \sigma_{xx}^{(V)} = 0, \quad (6.11)$$

where  $c = 1/\Omega$  is the number of particles in unit volume.

Further calculation requires the knowledge of  $U(\lambda)$ . As an example, we consider the case that the elastic energy  $U(\lambda)$  is proportional to the surface area  $S(\lambda)$  of the particle

$$U(\lambda) = \gamma S(\lambda). \quad (6.12)$$

For ellipsoidal particles, we have

$$S(\lambda) = 2\pi a^2 \left[ (1 - e^2)^{1/3} + \frac{(1 - e^2)^{-1/6}}{e} \arcsin(e) \right]. \quad (6.13)$$

Equation (6.9) determines the time evolution of  $\lambda$ . In the steady state, the deformation is determined by the following equation:

$$\kappa = \frac{\lambda}{\bar{\eta}(\lambda)} \frac{\partial U}{\partial \lambda}. \quad (6.14)$$

Thus, the intrinsic viscosity is obtained as

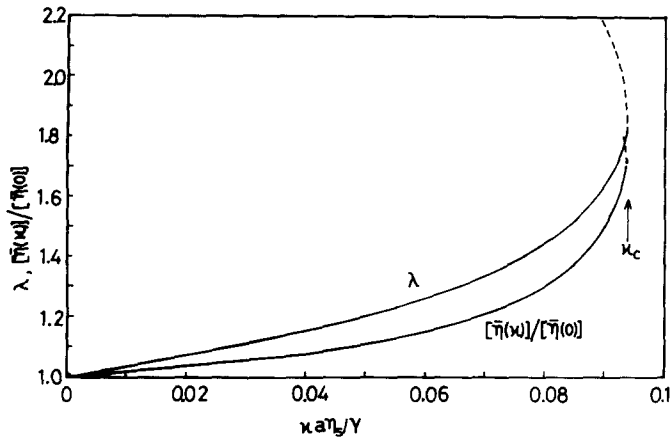


FIG. 2. The elongational ratio  $\lambda$  and the intrinsic elongational viscosity  $[\bar{\eta}(\kappa)]$  of an elastic particle is plotted against the elongational rate  $\kappa$ :  $a$ , the radius of the undeformed sphere;  $\eta_s$ , the solvent viscosity;  $\gamma$  the surface tension. For  $\kappa > \kappa_c$ , their particle will rupture.

$$[\eta] = \frac{1}{cK}(\sigma_{zz} - \sigma_{xx}) = \bar{\eta}(\lambda) \Big|_{\lambda=\lambda(\kappa)}. \quad (6.15)$$

Figure 2 shows the elongational ratio and the intrinsic viscosity as a function of the elongational rate  $\kappa$ . An interesting feature of this graph is that there is a critical elongational rate  $\kappa_c$  which corresponds to the maximum of the right-hand side of Eq. (6.14)

$$\kappa_c = \max_{\lambda} \frac{\lambda}{\eta(\lambda)} \frac{\partial U}{\partial \lambda} = 0.094 \frac{\gamma}{a\eta_s}. \quad (6.16)$$

According to Eq. (6.9), for  $\kappa < \kappa_c$ ,  $\lambda$  approaches monotonically to the steady state given by Eq. (6.14), while for  $\kappa > \kappa_c$ ,  $\lambda$  increases indefinitely, i. e., the droplet will rupture. This general feature agrees with the result of more sophisticated calculation. Ralison and Acrivos<sup>25</sup> carried out a numerical calculation for the large deformation of a droplet in an elongational flow of Newtonian liquid. Their result can be compared with the present calculation since, as far as the steady state is concerned, the deformation of the droplet of infinite viscosity is equal to the deformation of an elastic particle whose deformation energy is given by Eq. (6.12). According to Ralison and Acrivos, the rupture occurs at the critical elongational rate about  $0.105\gamma/a\eta_s$ , which is only 10% larger than Eq. (6.16). Furthermore, for small  $\kappa$  [Eq. (6.14)] gives the following magnitude of deformation<sup>25</sup>

$$r = \frac{L_1 - L_2}{L_1 + L_2} = \frac{75}{32} \frac{a\kappa\eta_s}{\gamma}, \quad (6.17)$$

where  $L_1$  and  $L_2$  are the length of the long axis and the short axis of the droplet, respectively. On the other hand, the rigorous perturbation calculation<sup>25</sup> gives the coefficient  $57/32$  instead of  $75/32$ . Thus, the present variational calculation gives reasonably good approximation.

## ACKNOWLEDGMENT

This work was supported by the Grant-in-Aid for Scientific Research 56550631.

## APPENDIX A: EXPLICIT EXPRESSION FOR THE DIFFUSION EQUATION AND THE STRESS TENSOR

In this appendix, explicit expressions are given for the diffusion equation and the stress tensor in Kirkwood's and Fixman's representation.

### 1. Kirkwood's representation

Equation (2.4) is solved for  $\mathbf{F}_m$  as

$$\begin{aligned} \mathbf{F}_n &= (\mathbf{H}^{-1})_{nm} \cdot (\dot{\mathbf{R}}_m - \kappa \cdot \mathbf{R}_m) \\ &= (\mathbf{H}^{-1})_{nm} \left( \frac{\partial \mathbf{R}_m}{\partial Q_a} \dot{Q}_a - \kappa \cdot \mathbf{R}_m \right). \end{aligned} \quad (A1)$$

(In this appendix, summation is implied over the repeated indices.) Substituting Eq. (A1) into Eq. (2.12), we have

$$\frac{\partial \mathbf{R}_a}{\partial Q_a} \cdot (\mathbf{H}^{-1})_{nm} \cdot \left[ \frac{\partial \mathbf{R}_m}{\partial Q_b} \dot{Q}_b - \kappa \cdot \mathbf{R}_m \right] = - \frac{\partial}{\partial Q_a} (V + k_B T \ln \Psi).$$

This equation is solved as

$$\dot{Q}_a = \dot{Q}_a^{(v)} + h_{ab} F_b^{(E)}, \quad (A2)$$

where

$$(h^{-1})_{ab} = \frac{\partial \mathbf{R}_a}{\partial Q_a} \cdot (\mathbf{H}^{-1})_{nm} \cdot \frac{\partial \mathbf{R}_m}{\partial Q_b}, \quad (A3)$$

$$F_a^{(E)} = - \frac{\partial}{\partial Q_a} (V + k_B T \ln \Psi), \quad (A4)$$

$$\dot{Q}_a^{(v)} = h_{ab} \frac{\partial \mathbf{R}_a}{\partial Q_b} \cdot (\mathbf{H}^{-1})_{nm} \cdot \kappa \cdot \mathbf{R}_m. \quad (A5)$$

In the generalized coordinate system, the conservation of the probability is written as

$$\frac{\partial \Psi}{\partial t} = - \frac{1}{\sqrt{g}} \frac{\partial}{\partial Q_a} [\sqrt{g} \dot{Q}_a \Psi], \quad (A6)$$

where  $g$  is the determinant of the metric tensor  $g_{ab}$ , i. e.,

$$g = \det(g_{ab}); \quad g_{ab} = \frac{\partial \mathbf{R}_a}{\partial Q_a} \cdot \frac{\partial \mathbf{R}_m}{\partial Q_b}. \quad (A7)$$

Substituting Eq. (A3) into Eq. (A6), we have the diffusion equation

$$\frac{\partial \Psi}{\partial t} = \frac{1}{\sqrt{g}} \frac{\partial}{\partial Q_a} \sqrt{g} \left[ h_{ab} \left( k_B T \frac{\partial \Psi}{\partial Q_b} + \frac{\partial V}{\partial Q_b} \Psi \right) - \dot{Q}_a^{(v)} \Psi \right]. \quad (A8)$$

Since the force is obtained from Eqs. (A1) and (A2) as

$$\mathbf{F}_m = \mathbf{F}_m^{(E)} + \mathbf{F}_m^{(v)}, \quad (A9)$$

$$\mathbf{F}_n^{(E)} = (\mathbf{H}^{-1})_{nm} \cdot \frac{\partial \mathbf{R}_m}{\partial Q_a} h_{ab} F_b^{(E)}, \quad (A10)$$

$$\mathbf{F}_n^{(v)} = (\mathbf{H}^{-1})_{nm} \cdot \left( \frac{\partial \mathbf{R}_m}{\partial Q_a} \dot{Q}_a^{(v)} - \kappa \cdot \mathbf{R}_m \right), \quad (A11)$$

the stress is calculated as

$$\sigma^{(E)} = - \frac{1}{\Omega} \langle \mathbf{R}_m \mathbf{F}_m^{(E)} \rangle, \quad (A12)$$

$$\sigma^{(v)} = - \frac{1}{\Omega} \langle \mathbf{R}_m \mathbf{F}_m^{(v)} \rangle. \quad (A13)$$

### 2. Fixman's representation

Substituting Eqs. (2.4) and (2.13) into Eq. (2.10), we have an equation for  $\lambda_p$ .

$$h_{pa} \lambda_a = \frac{\partial C_p}{\partial \mathbf{R}_n} \cdot \mathbf{H}_{nm} \cdot \frac{\partial}{\partial \mathbf{R}_m} [k_B T \ln \Psi + V] - \frac{\partial C_p}{\partial \mathbf{R}_m} \cdot \boldsymbol{\kappa} \cdot \mathbf{R}_m, \quad (\text{A14})$$

where

$$h_{pa} = \frac{\partial C_p}{\partial \mathbf{R}_n} \cdot \mathbf{H}_{nm} \cdot \frac{\partial C_a}{\partial \mathbf{R}_m}. \quad (\text{A15})$$

Hence

$$\lambda_p = (h^{-1})_{pa} \frac{\partial C_a}{\partial \mathbf{R}_n} \cdot \mathbf{H}_{nm} \cdot \frac{\partial}{\partial \mathbf{R}_m} [k_B T \ln \Psi + V] + \lambda_p^{(v)}, \quad (\text{A16})$$

where

$$\lambda_p^{(v)} = - (h^{-1})_{pa} \frac{\partial C_a}{\partial \mathbf{R}_n} \cdot \boldsymbol{\kappa} \cdot \mathbf{R}_n. \quad (\text{A17})$$

The forces are thus obtained as

$$\mathbf{F}_n^{(E)} = - \left[ \frac{\partial}{\partial \mathbf{R}_n} - \frac{\partial C_p}{\partial \mathbf{R}_n} (h^{-1})_{pa} \times \frac{\partial C_a}{\partial \mathbf{R}_m} \cdot \mathbf{H}_{m1} \cdot \frac{\partial}{\partial \mathbf{R}_1} \right] (k_B T \ln \Psi + V), \quad (\text{A18})$$

$$\mathbf{F}_n^{(v)} = \lambda_p^{(v)} \frac{\partial C_p}{\partial \mathbf{R}_n}, \quad (\text{A19})$$

and the stress is given by Eqs. (A12) and (A13).

### APPENDIX B: THE VARIATIONAL PRINCIPLE

The variational principle is proved in Kirkwood's representation. Substituting Eq. (2.7) into Eq. (3.1) and using the definitions (A3)–(A5), we have

$$\begin{aligned} \mathcal{W} = & \int d\{Q\} \sqrt{g} \Psi [h_{ab}^{-1} (\dot{Q}_a - \dot{Q}_a^{(v)}) (\dot{Q}_b - \dot{Q}_b^{(v)}) \\ & + (\boldsymbol{\kappa} \cdot \mathbf{R}_n) \cdot (\mathbf{H}^{-1})_{nm} \cdot (\boldsymbol{\kappa} \cdot \mathbf{R}_m) - (h^{-1})_{ab} \dot{Q}_a^{(v)} \dot{Q}_b^{(v)}]. \end{aligned} \quad (\text{A20})$$

Since the function  $\dot{\Psi}$  is given as

$$\dot{\Psi} = - \frac{1}{\sqrt{g}} \frac{\partial}{\partial Q_a} (\sqrt{g} \dot{Q}_a \Psi), \quad (\text{A21})$$

the functional  $\mathcal{A}$  is rewritten, by partial integration as

$$\begin{aligned} \dot{\mathcal{A}} = & \int d\{Q\} \sqrt{g} \dot{Q}_a \Psi \frac{\partial}{\partial Q_a} [k_B T \ln \Psi + k_B T + V] \\ = & - \int d\{Q\} \sqrt{g} \Psi \dot{Q}_a F_a^{(E)}. \end{aligned} \quad (\text{A22})$$

Hence,

$$\begin{aligned} \mathcal{K} = & \frac{1}{2} \int d\{Q\} \sqrt{g} \Psi [(h^{-1})_{ab} (\dot{Q}_a - \dot{Q}_a^{(v)}) (\dot{Q}_b - \dot{Q}_b^{(v)}) + (\boldsymbol{\kappa} \cdot \mathbf{R}_n) \\ & \cdot (\mathbf{H}^{-1})_{nm} \cdot (\boldsymbol{\kappa} \cdot \mathbf{R}_m) - (h^{-1})_{ab} \dot{Q}_a^{(v)} \dot{Q}_b^{(v)} - 2 \dot{Q}_a F_a^{(E)}]. \end{aligned} \quad (\text{A23})$$

Thus  $\partial \mathcal{K} / \partial \dot{Q}_a = 0$  gives Eq. (A2). The minimum of  $\mathcal{K}$  is obtained as

$$\begin{aligned} \min \mathcal{K} = & \frac{1}{2} \int d\{Q\} \sqrt{g} \Psi [-h_{ab} F_a^{(E)} F_b^{(E)} - 2 \dot{Q}_a^{(v)} F_a^{(E)} \\ & + (\boldsymbol{\kappa} \cdot \mathbf{R}_n) \cdot (\mathbf{H}^{-1})_{nm} \cdot (\boldsymbol{\kappa} \cdot \mathbf{R}_m) - (h^{-1})_{ab} \dot{Q}_a^{(v)} \dot{Q}_b^{(v)}]. \end{aligned} \quad (\text{A24})$$

Now using the symmetry,  $h_{ab} = h_{ba}$ , and Eq. (A10), we have

$$\dot{Q}_a^{(v)} F_a^{(E)} = \left[ (\boldsymbol{\kappa} \cdot \mathbf{R}_n) \cdot (\mathbf{H}^{-1})_{nm} \cdot \frac{\partial \mathbf{R}_m}{\partial Q_b} h_{ab} \right] F_a^{(E)}$$

$$= - \mathbf{F}_m^{(E)} \cdot \boldsymbol{\kappa} \cdot \mathbf{R}_m. \quad (\text{A25})$$

Also the third and the fourth terms in Eq. (A24) is rewritten, by use of Eq. (A5) as

$$\begin{aligned} & (\boldsymbol{\kappa} \cdot \mathbf{R}_n) \cdot (\mathbf{H}^{-1})_{nm} \cdot (\boldsymbol{\kappa} \cdot \mathbf{R}_m) - (h^{-1})_{ab} \dot{Q}_a^{(v)} \dot{Q}_b^{(v)} \\ & = \left[ \boldsymbol{\kappa} \cdot \mathbf{R}_n - \frac{\partial \mathbf{R}_n}{\partial Q_a} \dot{Q}_a^{(v)} \right] \cdot (\mathbf{H}^{-1})_{nm} \cdot \boldsymbol{\kappa} \cdot \mathbf{R}_m \\ & = - \mathbf{F}_m^{(v)} \cdot \boldsymbol{\kappa} \cdot \mathbf{R}_m. \end{aligned} \quad (\text{A26})$$

Thus,

$$\begin{aligned} \min \mathcal{K} = & \frac{1}{2} \int d\{Q\} \sqrt{g} [-h_{ab} F_a^{(E)} F_b^{(E)} \\ & - 2 \mathbf{F}_m^{(E)} \cdot \boldsymbol{\kappa} \cdot \mathbf{R}_m - \mathbf{F}_m^{(v)} \cdot \boldsymbol{\kappa} \cdot \mathbf{R}_m] \end{aligned} \quad (\text{A27})$$

from which Eq. (3.7) follows.

If there is no velocity gradient,

$$\dot{\mathcal{A}} = \min \mathcal{K} = - \frac{1}{2} \int d\{Q\} \sqrt{g} \Psi h_{ab} F_a^{(E)} F_b^{(E)}. \quad (\text{A28})$$

Since  $\mathbf{H}_{nm}$  is positive definite,  $h_{ab}$  is also positive definite. Thus, the right-hand side of Eq. (A28) is always negative. This proves Eq. (3.14).

<sup>1</sup>J. G. Kirkwood, *Rec. Trac. Chim.* **68**, 649 (1949).  
<sup>2</sup>J. G. Kirkwood, in *Documents on Modern Physics*, edited by P. L. Auer (Gordon and Breach, New York, 1967).  
<sup>3</sup>J. M. Burgers, *Second Report on Viscosity and Plasticity* (Amsterdam Academy of Science, Nordemann, 1938), Chap. 2.  
<sup>4</sup>W. Kuhn and H. Kuhn, *Helv. Chim. Acta* **28**, 97 (1945); **28**, 1533 (1945).  
<sup>5</sup>H. A. Kramers, *J. Chem. Phys.* **16**, 564 (1948).  
<sup>6</sup>Y. Ikeda, *Bull. Kobayashi Inst. Phys. Res.* **6**, 44 (1956).  
<sup>7</sup>J. J. Erpenbeck and J. G. Kirkwood, *J. Chem. Phys.* **29**, 909 (1958).  
<sup>8</sup>M. Fixman and J. Kovacs, *J. Chem. Phys.* **61**, 4939 (1974); **61**, 4950; **63**, 935 (1975).  
<sup>9</sup>M. Fixman and G. T. Evans, *J. Chem. Phys.* **64**, 3474 (1976); **68**, 195 (1978).  
<sup>10</sup>M. Fixman, *J. Chem. Phys.* **69**, 1527 (1978); **69**, 1538 (1978).  
<sup>11</sup>S. F. Edwards and K. F. Freed, *J. Chem. Phys.* **61**, 1189 (1974); **61**, 3236 (1974).  
<sup>12</sup>L. Onsager, *Phys. Rev.* **38**, 2265 (1931).  
<sup>13</sup>G. K. Batchelor, *J. Fluid Mech.* **41**, 545 (1970).  
<sup>14</sup>R. Zwanzig, J. Kiefer, and G. R. Weiss, *Proc. Natl. Acad. Sci.* **60**, 381 (1968).  
<sup>15</sup>H. Yamakawa, *J. Chem. Phys.* **53**, 436 (1970).  
<sup>16</sup>B. H. Zimm, *Macromolecules* **13**, 592 (1980).  
<sup>17</sup>M. Fixman, *J. Chem. Phys.* **76**, 6124 (1982).  
<sup>18</sup>O. A. Ladyzhenskaya, *The Mathematical Theory of Viscous Incompressible Flow*, 2nd ed. (Gordon and Breach, New York, 1969).  
<sup>19</sup>M. Fixman, *J. Chem. Phys.* **78**, 1588 (1983).  
<sup>20</sup>G. Wilemski and G. Tanaka, *Macromolecules* **14**, 1531 (1981).  
<sup>21</sup>J. Rotner and S. Prager, *J. Chem. Phys.* **50**, 4831 (1969).  
<sup>22</sup>M. Doi, in *Theory of Dispersed Multiphase Flow*, edited by R. E. Meyer (Academic, New York, 1983).  
<sup>23</sup>R. B. Bird, R. C. Armstrong, O. Hassager, and C. F. Curtiss, *Dynamics of Polymeric Liquids* (Wiley, New York, 1977), Vol. 2, and the references cited in p. 532.  
<sup>24</sup>G. B. Jefferey, *Proc. R. Soc. London Ser. A* **29**, 161 (1922).  
<sup>25</sup>J. M. Ralison and A. Acrivos, *J. Fluid Mech.* **89**, 191 (1978).