Linear Response Theory of Scale-Dependent Viscoelasticity for Overdamped Brownian Particle Systems

Takashi Uneyama

JST-PRESTO, and Department of Materials Physics, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan

Abstract

We show the linear response theory of spatial-scale-dependent relaxation moduli for overdamped Brownian particle systems. We employ the Irving-Kirkwood stress tensor field as the microscopic stress tensor field. We show that the scale-dependent relaxation modulus tensor, which characterizes the response of the stress tensor field to the applied velocity gradient field, can be expressed by using the correlation function of the Irving-Kirkwood stress tensor field. The spatial Fourier transform of the relaxation modulus tensor gives the wavenumber-dependent relaxation modulus. For isotropic and homogeneous systems, the relaxation modulus tensor has only two independent components. The transverse and longitudinal deformation modes give the wavenumber-dependent shear relaxation modulus and the wavenumber-dependent bulk relaxation modulus. As simple examples, we derive the explicit expressions for the relaxation moduli for two simple models the non-interacting Brownian particles and the harmonic dumbbell model.

1 INTRODUCTION

To measure rheological properties, (macroscopic) rheometers are widely employed. We apply the macroscopic strain (or stress) to the sample, and measure the macroscopic stress (or the strain) as the response. Then we obtain rheological properties such as the linear viscoelasticity. In some cases, measurements by rheometers become difficult. The typical amount of a sample required for the measurements is about 1 ml. If the amount of a sample is limited, the measurements become difficult. The microrheology measurements have been proposed to obtain rheological properties with small amount of samples.

In the microrheology, small spherical colloidal particles are dispersed in the sample and then the dynamics of the colloidal particles is measured[1, 2]. The dynamics of the colloidal particle is assumed to obey the generalized Langevin equation:

\[ 0 = -\int_{-\infty}^{t} dt' \Gamma(t-t') \frac{dR(t')}{{dt'}} + \Xi(t), \]  

where \( R(t) \) is the center of mass position of the colloid particle in a three dimensional space, \( \Gamma(t) \) is the friction kernel, and \( \Xi(t) \) is the Gaussian colored noise. (In eq (1), the inertia term is dropped by assuming that the momentum relaxation is sufficiently fast.) From the fluctuation-dissipation relation, the noise \( \Xi(t) \) satisfies

\[ \langle \Xi(t) \rangle = 0, \quad \langle \Xi(t)\Xi(t') \rangle = k_B T \Gamma(|t-t'|)1. \]  

Here, \( \langle \ldots \rangle \) represents the statistical average, \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( 1 \) is the unit tensor. If we assume that the sample around the particle behaves as viscoelastic
fluid which has the same linear viscoelasticity at the macroscopic scale, the friction kernel $\Gamma(t)$ can be related to the linear viscoelasticity of the sample (the generalized Stokes relation):

$$\Gamma(t) = 6\pi a G(t).$$

(3)

$a$ is the radius of the particle and $G(t)$ is the macroscopic shear relaxation modulus. The mean squared displacement (MSD) of the particle can be related to the friction kernel. By combining the MSD and eq (3), we have the so-called the generalized Stokes-Einstein relation:

$$\langle [R(t) - R(0)]^2 \rangle = \frac{k_B T}{\pi a} J(t),$$

(4)

where $J(t)$ is the macroscopic shear creep compliance. Therefore, we can estimate the linear viscoelasticity of the sample by measuring the MSD of a colloidal particle.

The microrheological methods explained above sounds interesting. However, we should point that its validity is not fully guaranteed. The assumption that the sample around the particle has the same linear viscoelasticity as the macroscopic one is generally not correct. The fact that the viscoelasticity depends on the length scale (or the wavenumber scale) is well known. Therefore, the generalized Stokes-Einstein relation does not hold in general. What we obtain from the microrheology measurements is rather the spatial-scale-dependent linear viscoelasticity than the macroscopic linear viscoelasticity. (In what follows, we call the spatial-scale-dependent linear viscoelasticity as the spatial-dependent linear viscoelasticity.) We will need a relation between the MSD and the scale-dependent linear viscoelasticity, instead of eq (4). However, the flow field around a colloidal particle is not simple and the relation between the MSD and the scale-dependent linear viscoelasticity will not be simple. The scale-dependent linear viscoelasticity itself is not well understood compared with the macroscopic linear viscoelasticity. Therefore, to correctly understand the microrheology measurements and utilize them to study various rheological properties, we need the microscopic theory of scale-dependent linear viscoelasticity as a first step.

The scale-dependent linear viscoelasticity will be also useful to study spatially inhomogeneous systems. The macroscopic linear viscoelasticity reflects the relaxation dynamics of molecules in the sample. Naively, we expect that the relaxation depends both on the temporal and spatial scales. The temporal scale of the relaxation can be evaluated by the macroscopic linear viscoelasticity. However, the information on the spatial scale of the relaxation cannot be obtained from the macroscopic linear viscoelasticity. The use of the scale-dependent linear viscoelasticity will enable us to extract the characteristic spatial scale of the relaxation dynamics.

Some researchers studied the scale-dependent linear viscoelasticity by molecular dynamics simulations and calculated several quantities such as the wavenumber-dependent shear viscosity. As far as the author knows, however, most of studies are based on the Hamiltonian dynamics. In the field of rheology, the overdamped Langevin dynamics is widely utilized as the microscopic model. For example, polymer dynamics models such as the Rouse model and the reptation model are based on the overdamped Langevin equation. These models can reasonably explain the rheological properties which are measured by the (macroscopic) rheometers. The theory of scale-dependent linear viscoelasticity based on the overdamped Langevin equation will be required to study the microrheology or the spatial scale of the relaxation.

To theoretically analyze the scale-dependent linear viscoelasticity, we need the expression of the position-dependent stress tensor field. As a position-dependent stress tensor field, so-called the Irving-Kirkwood stress is widely utilized. The Irving-Kirkwood stress tensor field is derived on the basis of the conservation equation for the momentum field. In the linear response theory, the stress field should be defined as the thermodynamic conjugate to the applied strain field. Therefore, whether the linear response is actually described by the auto correlation function of the Irving-Kirkwood stress tensor field or not is not fully clear.

In this work, we consider the linear response theory for the microscopic stress field to the applied microscopic strain field. We consider the interacting Brownian particle systems, which obey the overdamped Langevin equations, as the target system. We assume that the microscopic deformation field and the microscopic velocity field for the target system can be controlled. This is consistent with the Langevin equation with the external flow field, which is often employed.
to analyze and simulate the dynamics of soft matters such as polymers and colloids. We define the microscopic stress tensor field and the velocity gradient tensor field, and construct the linear response theory. We show that the Irving-Kirkwood stress tensor field can be successfully employed as the microscopic stress tensor field, and the relaxation modulus tensor is given as the equilibrium correlation function of the microscopic stress tensor field. As simple examples, we analytically calculate relaxation moduli for the non-interacting Brownian particles and the harmonic dumbbell model.

2 THEORY

2.1 Microscopic Strain Tensor and Microscopic Stress Tensor

We consider overdamped Brownian particle systems where we do not have the degrees of freedom of momenta. For simplicity, we assume that our system is statistically isotropic and homogeneous. (The statistical properties of the system is not changed under the rotation and the translation.) We assume that the particles interact by pairwise potentials. We describe the position of the \(i\)-th particle as \(R_i\). The potential energy of the system is

\[
\mathcal{U}({\{R_i\}}) = \sum_{i>j} \phi_{ij}(R_{ij}),
\]

where \(R_{ij} \equiv |R_{ij}|\) and \(R_{ij} \equiv R_i - R_j\), and \(\phi_{ij}(r)\) is the interaction potential between particles \(i\) and \(j\). We assume that the interaction potential depends only on the distance between two particles.

First we consider to impose a deformation to the system. The deformation is characterized by the displacement field \(u(r)\). The particle positions after the deformation is

\[
R'_i \equiv R_i + u(R_i).
\]

We assume that the displacement field is smooth. Then the change of the potential energy by the deformation can be expanded into the series

\[
\mathcal{U}({\{R'_i\}}) - \mathcal{U}({\{R_i\}}) = \sum_{i>j} \frac{\partial \mathcal{U}({\{R_i\}})}{\partial R_{ij}} \cdot [u(R_i) - u(R_j)] + \text{(higher order terms)}.
\]

The higher order terms in eq (7) can be safely neglected when the relative displacements of particles are small. This situation can be realized when \(\nabla u(r)\) is small. We assume that \(\nabla u(r)\) is sufficiently small, and simply drop higher order terms in eq (7) in what follows. From the operational point of view, we may interpret that the system is deformed by the externally applied strain field \(\epsilon(r)\).

Then the change of the potential energy should be expressed by using the strain field and the stress field which is conjugate to the strain field as

\[
\mathcal{U}({\{R'_i\}}) - \mathcal{U}({\{R_i\}}) = \int dr \, \hat{\sigma}^{(p)}(r) : \epsilon(r),
\]

where \(\hat{\sigma}^{(p)}(r)\) is the microscopic stress tensor field which is related to the potential (the potential part). We assume that the strain field can be simply related to the displacement field \(u(r)\) as

\[
\epsilon(r) = \frac{1}{2} \left[ \nabla u(r) + [\nabla u(r)]^T \right].
\]

Then our problem is to find the explicit expression of the stress tensor \(\hat{\sigma}^{(p)}(r)\) which gives the potential energy change by eq (7) correctly. Eq (7) can be rewritten as

\[
\mathcal{U}({\{R'_i\}}) - \mathcal{U}({\{R_i\}}) = \sum_{i>j} \frac{\partial \phi_{ij}(R_{ij})}{\partial R_{ij}} \frac{R_{ij}}{R_{ij}} [u(R_i) - u(R_j)]
\]

\[
= \sum_{i>j} \frac{\partial \phi_{ij}(R_{ij})}{\partial R_{ij}} \frac{R_{ij}}{R_{ij}} \int_{C_{ij}} dl \, \frac{\partial}{\partial l} u(l),
\]

3
The total stress tensor field is then given as the sum of eqs (13) and (14): 

\[ \sigma(r) = \hat{\sigma}^{(p)}(r) + \hat{\sigma}^{(k)}(r). \]  

The macroscopic stress tensor corresponds to the spatial average of eq (15).
2.2 Linear Response Theory

To consider the scale-dependent linear viscoelasticity, we consider the Langevin equation with the external flow field. We assume that the dynamics is described by the following overdamped Langevin equation:

\[
\frac{dR_i(t)}{dt} = \mathbf{v}(R_i(t), t) - \sum_{j \neq i} L_{ij}(\{ R_i \}) \frac{\partial U(\{ R_i \})}{\partial R_j} + k_B T \sum_j \frac{\partial}{\partial R_j} \cdot L_{ij}(\{ R_i \}) + \sqrt{2k_B T} B_{ij}(\{ R_i \}) \cdot \mathbf{w}_j(t),
\]

(16)

where \( \mathbf{v}(r, t) \) is the flow field, \( L_{ij}(\{ R_i \}) \) is the mobility tensor, \( B_{ij}(\{ R_i \}) \) is the noise coefficient tensor, and \( \mathbf{w}_i(t) \) is the Gaussian white noise. We interpret the Gaussian white noise in eq (16) in the Itô manner. The fluctuation-dissipation relation requires that the following relations hold:

\[
B_{ij}(\{ R_i \}) \cdot B_{kj}^T(\{ R_i \}) = L_{ik}(\{ R_i \}),
\]

(17)

\[
\langle \mathbf{w}_i(t) \rangle = 0, \quad \langle \mathbf{w}_i(t) \mathbf{w}_j(t') \rangle = \delta(t - t').
\]

(18)

The dynamic equation for the time-dependent probability distribution would be convenient when we consider the linear response. We describe the time-dependent probability distribution for particle positions as \( P(\{ R_i \}, t) \). From the Langevin equation (16), \( P(\{ R_i \}, t) \) obeys the following Fokker-Planck equation (14):

\[
\frac{\partial P(\{ R_i \}, t)}{\partial t} = \mathcal{L}_0 P(\{ R_i \}, t) - \sum_i \frac{\partial}{\partial R_i} \cdot [v(R_i, t)P(\{ R_i \}, t)],
\]

(19)

where we have defined the equilibrium Fokker-Planck operator as

\[
\mathcal{L}_0 P(\{ R_i \}) \equiv \sum_{i,j} \frac{\partial}{\partial R_i} \cdot \left[ L_{ij}(\{ R_i \}) \cdot \left[ \frac{\partial U(\{ R_i \})}{\partial R_j} P(\{ R_i \}) + k_B T \frac{\partial P(\{ R_i \})}{\partial R_j} \right] \right].
\]

(20)

In absence of the flow field, \( \mathbf{v}(r, t) = 0 \), the stationary solution of the Fokker-Planck equation becomes the equilibrium distribution

\[
P_{\text{eq}}(\{ R_i \}) \equiv \frac{1}{Z} \exp \left[ -\frac{U(\{ R_i \})}{k_B T} \right],
\]

(21)

with the partition function defined as

\[
Z \equiv \int d\{ R_i \} \exp \left[ -\frac{U(\{ R_i \})}{k_B T} \right].
\]

(22)

It is straightforward to show \( \mathcal{L}_0 P_{\text{eq}}(\{ R_i \}) = 0 \). We define the equilibrium statistical average by using eq (21) as \( \langle \cdots \rangle_{\text{eq}} \equiv \int d\{ R_i \} \cdots P_{\text{eq}}(\{ R_i \}) \). In equilibrium, from the symmetry, the average stress tensor should be isotropic and homogeneous. Thus the average stress tensor can be characterized only by the pressure \( p_{\text{eq}} \):

\[
\langle \mathbf{\sigma}(r) \rangle_{\text{eq}} = -p_{\text{eq}} \mathbf{1}.
\]

(23)

If a weak time-dependent flow field is applied, the distribution function is slightly deviated from the equilibrium distribution. Following the standard procedure [6], we express the distribution function as the sum of the equilibrium part and the time-dependent perturbation part:

\[
P(\{ R_i \}, t) = P_{\text{eq}}(\{ R_i \}) + \Delta P(\{ R_i \}, t).
\]

(24)

We assume that the flow field is sufficiently small, and thus the perturbation part is also sufficiently small. Then, the higher order perturbation terms than the second order can be neglected. We have the following equation for the perturbation part:

\[
\frac{\partial \Delta P(\{ R_i \}, t)}{\partial t} = \mathcal{L}_0 \Delta P(\{ R_i \}, t) - \sum_i \frac{\partial}{\partial R_i} \cdot [v(R_i, t)P_{\text{eq}}(\{ R_i \})].
\]

(25)
Eq (25) can be formally solved as follows:

\[
\Delta P\{\{R_i\}, t\} = -\int_{-\infty}^{t} dt' e^{(t-t')L_0} \sum_i \frac{\partial}{\partial R_i} \cdot [v(R_i, t')P_{eq}\{\{R_i\}\}] \\
= -\int_{-\infty}^{t} dt' e^{(t-t')L_0} \left[ \sum_i \left[ \frac{\partial}{\partial R_i} \cdot v(R_i, t') \right] P_{eq}\{\{R_i\}\} \right. \\
\left. - \frac{1}{k_BT} \sum_i \frac{\partial u(\{R_i\})}{\partial R_i} \cdot v(R_i, t') P_{eq}\{\{R_i\}\} \right].
\]  

(26)

The first term in the last line of eq (26) can be rewritten as follows:

\[
\sum_i \left[ \frac{\partial}{\partial R_i} \cdot v(R_i, t') \right] P_{eq}\{\{R_i\}\} \\
= \frac{1}{k_BT} \int dr' k_BT \sum_i \delta(r' - R_i)1 : \nabla' v(r', t') P_{eq}\{\{R_i\}\} \\
= -\frac{1}{k_BT} \int dr' \sigma^{(v)}(r') : \kappa(r', t') P_{eq}\{\{R_i\}\},
\]

(27)

where \(\nabla' \equiv \partial/\partial r'\), and \(\kappa(r, t) \equiv [\nabla v(r, t)]^T\) can be interpreted as the velocity gradient tensor field. The second term in the last line of eq (26) has a similar form to eq (7). Actually, it can be rewritten in terms of the potential part stress tensor field and the velocity gradient field:

\[
-\frac{1}{k_BT} \sum_i \frac{\partial u(\{R_i\})}{\partial R_i} \cdot v(R_i, t') P_{eq}\{\{R_i\}\} \\
= -\frac{1}{k_BT} \int dr' \sigma^{(v)}(r') : \kappa(r', t') P_{eq}\{\{R_i\}\}.
\]

(28)

By substituting eqs (27) and (28) into eq (26), finally the perturbation part of the distribution function can be rewritten by using the Irving-Kirkwood stress tensor field:

\[
\Delta P\{\{R_i\}, t\} = \frac{1}{k_BT} \int dr' \int_{-\infty}^{t} dt' e^{(t-t')L_0} [\tilde{\sigma}(r') : \kappa(r', t') P_{eq}\{\{R_i\}\}].
\]

(29)

When we monitor the average stress tensor field under flow, we will observe a time-dependent tensor field \(\bar{\sigma}(r, t)\). From eq (29), it can be expressed as

\[
\bar{\sigma}(r, t) + p_{eq}1 = \int d\{R_i\} \tilde{\sigma}(r) \Delta P\{\{R_i\}, t\} \\
= \frac{1}{k_BT} \int dr' \int_{-\infty}^{t} dt' \int d\{R_i\} [\delta(t-t')L_0 \tilde{\sigma}(r)] [\tilde{\sigma}(r') : \kappa(r', t') P_{eq}\{\{R_i\}\}] \\
= \frac{1}{k_BT} \int dr' \int_{-\infty}^{t} dt' \langle \tilde{\sigma}(r, t-t') \tilde{\sigma}(r') \rangle_{eq} : \kappa(r', t').
\]

(30)

Here, \(L_0^\dagger\) is the adjoint Fokker-Planck operator, and \(\tilde{\sigma}(r, t) \equiv e^{tL_0^\dagger} \tilde{\sigma}(r)\) is the time-shifted stress tensor field. From eq (30), we find that the response of the stress tensor field to the applied velocity gradient field \(\kappa(r, t)\) is characterized by the following relaxation modulus tensor:

\[
\Lambda(r, t) = \frac{1}{k_BT} \langle \tilde{\sigma}(r, t) \tilde{\sigma}(0, 0) \rangle_{eq}.
\]

(31)

Eq (31) can be interpreted as the distance-dependent relaxation modulus. \(\Lambda(r, t)\) represents the response of the stress tensor field at position \(r\) and time \(t\), to the perturbation of the velocity gradient tensor field at position 0 and time 0.
The (spatial) Fourier transform of eq \((31)\) would be convenient. We introduce the Fourier-transformed relaxation modulus:

\[
\Lambda(k, t) \equiv \int d\mathbf{r} e^{-i \mathbf{k} \cdot \mathbf{r}} \Lambda(\mathbf{r}, t).
\]  

(32)

Eq \((32)\) can be interpreted as the wavenumber-dependent relaxation modulus. The Fourier transform of eq \((31)\) is

\[
\sigma(\mathbf{k}, t) + p_{\text{eq}} \delta(\mathbf{k}) \mathbf{1} = \int_{-\infty}^{t} dt' \Lambda(\mathbf{k}, t - t') : \kappa(\mathbf{k}, t'),
\]

(33)

where \(\sigma(\mathbf{k}, t)\) and \(\kappa(\mathbf{k}, t)\) are the Fourier transforms of \(\sigma(\mathbf{r}, t)\) and \(\kappa(\mathbf{r}, t)\).

Eq \((31)\) has almost the same form as the Green-Kubo formula for macroscopic relaxation modulus. Thus we interpret eq \((31)\) as the scale-dependent version of the Green-Kubo formula. Here it should be pointed that Evans\(^4\) derived a similar but different linear response formula. Evans derived the linear response based on the generalized hydrodynamics and claimed that the correlation function of the the transverse momentum current field gives the relaxation modulus. Thus the dynamics of individual particles is not explicitly considered. In contrast, our derivation is based on the Langevin equation. Our system does not have the degrees of freedom of momenta, and thus we cannot directly apply Evans’s approach to our system. For particle-based systems, our approach seems to be physically natural.

### 2.3 Transverse and Longitudinal Modes

At the linear response regime, a deformation field can be decomposed into deformation fields with different wavenumber vectors. Here we consider a deformation field with a single wavenumber vector \(\mathbf{k}\). Without loss of generality, we can set the wavenumber vector \(\mathbf{k} = k \mathbf{e}_x\) with \(\mathbf{e}_x\) with being the unit vector in the \(x\)-direction, to analyze the relaxation modulus. The wavenumber-dependent fields such as \(\sigma(\mathbf{k}, t)\) can be interpreted as a function of \(k\) such as \(\sigma(k, t)\). From the symmetry, we need to consider only two types of velocity gradient fields: the transverse mode and the longitudinal mode. Figure 2 illustrates the transverse and longitudinal deformation modes. The velocity fields of the transverse and longitudinal modes are given as, for example,

\[
v^{(t)}(\mathbf{r}, t) = v(t) \sin(kr_x) \mathbf{e}_y,
\]

(34)

\[
v^{(l)}(\mathbf{r}, t) = v(t) \sin(kr_x) \mathbf{e}_x,
\]

(35)

where the superscripts “\((t)\)” and “\((l)\)” represent the transverse and longitudinal modes, respectively. \(v(t)\) is the time-dependent velocity amplitude, and \(\mathbf{e}_y\) is the unit vector in the \(y\)-direction. The velocity gradient tensor fields which corresponds to eqs \((34)\) and \((35)\) are

\[
\kappa^{(t)}(\mathbf{r}, t) = \kappa(t) \cos(kr_x) \mathbf{e}_y \mathbf{e}_x,
\]

(36)

\[
\kappa^{(l)}(\mathbf{r}, t) = \kappa(t) \cos(kr_x) \mathbf{e}_x \mathbf{e}_x,
\]

(37)

where \(\kappa(t) \equiv kv(t)\) can be interpreted as the amplitude of the velocity gradient.

We have only two independent components for the relaxation modulus tensor for an isotropic material\(^{12}\). For the transverse mode, the response of the shear stress field would be useful. From eq \((32)\) we have \(\sigma_{yz}(k, t) = \Lambda_{yzx}(k, t) \kappa(t) \cos(kr_x)\). We define the wavenumber-dependent shear relaxation modulus as

\[
G(k, t) \equiv \Lambda_{yzx}(k, t).
\]

(38)

For the longitudinal mode, the response of the normal stress fields would be useful. From eq \((32)\), \(\sigma_{xx}(k, t) = \Lambda_{xxx}(k, t) \kappa \cos(kr_x)\). \(\Lambda_{xxx}(k, t)\) can be interpreted as the wavenumber-dependent longitudinal modulus. Then we can define the wavenumber-dependent bulk relaxation modulus as

\[
K(k, t) \equiv \Lambda_{xxx}(k, t) - \frac{4}{3} G(k, t),
\]

(39)
Figure 2: The deformation modes with a finite wavenumber. Gray circles represent particles. Grids are shown as the guide for eye. (a) The reference state without any deformations. The $x$-, $y$-, and $z$-directions are shown with arrows. (b) The transverse deformation mode. The wavenumber vector $k$ is parallel to the $x$-axis whereas the velocity vector $v$ is parallel to the $y$-axis. $k$ and $v$ are orthogonal. (c) The longitudinal deformation mode. Both the wavenumber vector $k$ and the velocity vector $v$ are parallel to the $x$-axis.

With $G(k,t)$ given by eq (38). Alternatively, we can utilize the sum of all the normal components to calculate the bulk modulus:

$$K(k, t) = \frac{1}{3} \sum_{\alpha=x,y,z} \Lambda_{\alpha \alpha \alpha}(k, t). \quad (40)$$

The storage and loss moduli are defined as the (temporal) Fourier transforms of eqs (38) and (39):

$$G'(k, \omega) + iG''(k, \omega) \equiv i\omega \int_0^\infty dt e^{-i\omega t} G(k, t), \quad (41)$$

$$K'(k, \omega) + iK''(k, \omega) \equiv i\omega \int_0^\infty dt e^{-i\omega t} K(k, t). \quad (42)$$

Eqs (41) and (42) describe the responses of the wavenumber-dependent stress to the temporarily oscillating wavenumber-dependent velocity fields. The macroscopic moduli are recovered at $k = 0$. For example, the macroscopic shear relaxation modulus is given as $G(t) = G(0, t)$.
3 EXAMPLES

3.1 Non-Interacting Brownian Particles

As a simple example, we consider non-interacting Brownian particles. We express the number of Brownian particles as \(M\) and the system size as \(V\). The number density of particles is \(\nu = M/V\).

There is no interaction potential in this system and thus we have only the kinetic part for the stress tensor field. Also, due to the non-interacting nature, the contributions of individual particles are statistically independent. Then what we need to consider is the kinetic part stress tensor for just a single particle:

\[
\hat{\sigma}(r, t) = \hat{\sigma}^{(k)}(r, t) = -k_B T \delta(r - R(t)),
\]

where \(R\) is the position of the Brownian particle.

The dynamic equation for the particle position \(R\) is

\[
\frac{dR(t)}{dt} = \sqrt{\frac{2k_B T}{\zeta}} w(t),
\]

where \(\zeta\) is the friction coefficient and \(w(t)\) is the Gaussian white noise. The propagator for the position is calculated to be

\[
W(r, t|r', 0) = \langle \delta(r - R(t))\delta(r' - R(0)) \rangle = \left( \frac{1}{4\pi D t} \right)^{3/2} \exp \left[ -\frac{(r - r')^2}{4Dt} \right],
\]

where \(D \equiv k_B T/\zeta\) is the diffusion coefficient. The equilibrium distribution for \(R\) is trivial: \(P_{eq}(R) = 1/V\).

The relaxation modulus of a single particle can be calculated by using eqs (45) and (43):

\[
\Lambda^{(\text{single})}(r, t) = \frac{1}{k_B T} (\hat{\sigma}(r, t)\hat{\sigma}(0, 0))_{eq} = \frac{k_B T}{V} \int dR dR' W(R, t|R', 0) P_{eq}(R') \delta(r - R) \delta(R')
\]

By collecting the contributions of \(M\) particles, the relaxation modulus of the non-interacting Brownian particles becomes

\[
\Lambda(r, t) = M \Lambda^{(\text{single})}(r, t) = \nu k_B T \left( \frac{1}{4\pi D t} \right)^{3/2} \exp \left[ -\frac{r^2}{4Dt} \right].
\]

Then the Fourier transform of eq (47) with \(k = ke_x\) is

\[
\Lambda(k, t) = \int d^3r e^{-ikr} \Lambda(r, t) = \nu k_B T \left( \frac{\omega}{Dk^2} \right) \exp(-Dk^2 t).
\]

From eq (48), the shear relaxation modulus is zero: \(G(k, t) = 0\). The bulk relaxation modulus is

\[
K(k, t) = \nu k_B T \exp(-Dk^2 t).
\]

The (temporal) Fourier-transform of eq (49) gives the wavenumber-dependent bulk storage and loss moduli:

\[
K'(k, \omega) = \nu k_B T \frac{(\omega/Dk^2)^2}{1 + (\omega/Dk^2)^2}, \quad K''(k, \omega) = \nu k_B T \frac{\omega/Dk^2}{1 + (\omega/Dk^2)^2}.
\]
From eq (49), we find that the bulk relaxation modulus at a finite wavenumber decays exponentially. The relaxation time becomes a function of the wavenumber \( k \), as \( \tau(k) \equiv 1/Dk^2 \). This relation is physically reasonable because the relaxation at the finite wavenumber should be governed by the diffusion of Brownian particles, and the large wavenumber modes generally decay faster than the low wavenumber modes in the diffusion dynamics. By setting \( k = 0 \), we have the macroscopic bulk relaxation modulus: \( K(t) = K(0, t) = \nu k_B T \). This simply means that the bulk modulus is constant and does not relax. Macroscopically, non-interacting Brownian particles simply behave as an ideal gas. There is essentially no macroscopic relaxation. However, at the finite wavenumber, they exhibit the relaxation by the diffusion.

One may consider that the wavenumber dependence of eq (49) is similar to that of a dynamic structure factor in scattering experiments [15]. This is rather natural because both the dynamic structure factor and the bulk relaxation modulus reflect the diffusion dynamics. The kinetic part of the stress tensor field is localized at the particle positions, and the relaxation modulus becomes the two-point correlation function for the particle position, as observed in eq (48).

### 3.2 Harmonic Dumbbell Model

As another simple example, we consider the harmonic dumbbell model. We consider a system which consists of non-interacting harmonic dumbbells [16, 17]. We express the system size as \( M \), and assume that \( M \) dumbbells are uniformly dispersed in the system. The number density of dumbbells is \( \nu = M/V \).

Due to the non-interacting nature, the information on the dynamics of a single dumbbell is sufficient for us to calculate the linear response, in the same way as Sec. 3.1. We express the two-point correlation function for the particle position, as observed in eq (46). We need the explicit expression of the stress correlation function to calculate the relaxation modulus. It can be calculated by using the equilibrium distribution function and the propagators. The equilibrium distribution is simply given as

\[
P_{eq}(\mathbf{R}, Q) = \frac{1}{V} \left( \frac{3}{2\pi b^2} \right)^{3/2} \exp \left( -\frac{3Q^2}{2b^2} \right). \tag{55}\]

The dynamics of the harmonic dumbbell model can be solved analytically. We introduce the center of mass position and the bond vector \( \mathbf{R}(t) \equiv [\mathbf{R}_1(t) + \mathbf{R}_2(t)]/2 \) and \( Q(t) \equiv \mathbf{R}_1(t) - \mathbf{R}_2(t) \). Then, we can rewrite the Langevin equation (51) into the Langevin equations for the center of mass position and the bond vector:

\[
\frac{d\mathbf{R}(t)}{dt} = -\frac{1}{\zeta} \frac{\partial \phi(\mathbf{R}_1(t) - \mathbf{R}_2(t))}{\partial \mathbf{R}_1(t)} + \sqrt{2k_B T \over \zeta} \mathbf{w}_1(t), \tag{51}\]

where \( \zeta \) is the friction coefficient, and \( \mathbf{w}_1(t) \) is the Gaussian white noise. The noise \( \mathbf{w}_1(t) \) satisfies the fluctuation-dissipation relation:

\[
\langle \mathbf{w}_1(t) \rangle = 0, \quad \langle \mathbf{w}_1(t)\mathbf{w}_j(t') \rangle = \delta_{ij} \delta(t - t'). \tag{52}\]

The dynamics of the harmonic dumbbell model can be solved analytically. We introduce the center of mass position and the bond vector \( \mathbf{R}(t) \equiv [\mathbf{R}_1(t) + \mathbf{R}_2(t)]/2 \) and \( Q(t) \equiv \mathbf{R}_1(t) - \mathbf{R}_2(t) \). Then, we can rewrite the Langevin equation (51) into the Langevin equations for the center of mass position and the bond vector:

\[
\frac{d\mathbf{R}(t)}{dt} = \sqrt{\frac{k_B T \over \zeta} \mathbf{w}_+(t), \tag{53}\]

\[
\frac{dQ(t)}{dt} = -\frac{6k_B T}{\zeta b^2} Q(t) + \sqrt{\frac{4k_B T}{\zeta} \mathbf{w}_-(t)}, \tag{54}\]

with \( \mathbf{w}_\pm(t) \equiv [\mathbf{w}_1(t) \pm \mathbf{w}_2(t)]/\sqrt{2} \).

We need the explicit expression of the stress correlation function to calculate the relaxation modulus. It can be calculated by using the equilibrium distribution function and the propagators.

The equilibrium distribution is simply given as

\[
P_{eq}(\mathbf{R}, Q) = \frac{1}{V} \left( \frac{3}{2\pi b^2} \right)^{3/2} \exp \left( -\frac{3Q^2}{2b^2} \right). \tag{55}\]
The propagators for the center of mass and the bond are statistically independent. Eq (54) describes the Ornstein-Uhlenbeck process. The solution is

\[ Q(t) = e^{-t/\tau}Q(0) + \sqrt{\frac{4k_BT}{\zeta}} \int_0^t dt' e^{-(t-t')/\tau} w_-(t'), \]

(56)

where \( \tau \equiv \zeta b^2/6k_BT \) is the relaxation time. The propagator for \( Q \) is given as

\[ W_Q(q, t|q', 0) = \langle \delta(q - Q(t))\delta(q' - Q(0)) \rangle = \left[ \frac{3}{2\pi b^2(1 - e^{-2t/\tau})} \right]^{3/2} \exp \left[ -\frac{3(q - e^{-t/\tau}q')^2}{2b^2(1 - e^{-2t/\tau})} \right]. \]

(57)

The propagator for \( R \) is essentially the same as that calculated in Sec. 3.1. By replacing \( D \) in (45) by \( k_BT/2\zeta = b^2/12\tau \), the propagator for \( R \) becomes

\[ W_R(r, t|r', 0) = \left( \frac{3\tau}{\pi b^2t} \right)^{3/2} \exp \left[ -\frac{3(r - r'\prime)^2}{b^2t} \right]. \]

(58)

We calculate the stress correlation functions by using eqs (54), (57), and (58). The kinetic and potential parts of the stress tensor field for a single dumbbell are

\[ \sigma^{(k)}(r, t) = -k_BT \sum_{\mu = \pm 1/2} \delta(r - R(t) - \mu Q(t)), \]

(59)

\[ \sigma^{(p)}(r, t) = \frac{3k_BT}{b^2} Q(t) Q(t) \int_{-1/2}^{1/2} \mu \delta(r - R(t) - \mu Q(t)). \]

(60)

The kinetic part does not have the shear component. We can ignore the kinetic part when we calculate the shear relaxation modulus. For the bulk relaxation modulus, however, we need the contribution of the kinetic part stress tensor. This makes the calculations for the bulk relaxation modulus very lengthy and complicated. In this work, therefore, we limit ourselves to the shear relaxation modulus and do not go into detail about the bulk relaxation modulus.

To calculate the shear relaxation modulus \( G(k, t) \), we first calculate \( \Lambda_{xyxy}(r, t) \):

\[ \Lambda_{xyxy}(r, t) = \frac{M}{k_BT} \int dR dR' \delta Q dQ' W_R(R, t|R', 0) W_Q(Q, t|Q', 0) P_{eq}(R, Q) \]

\[ \times \frac{9k_BT^2}{b^4} Q_y Q_x Q'_y Q'_x \int_{-1/2}^{1/2} \mu \int_{-1/2}^{1/2} \mu' \delta(r - R - \mu Q)(-R' - \mu Q') \]

\[ = \frac{9\nu k_BT}{b^4} \left[ \frac{27\tau}{4\pi b^6t(1 - e^{-2t/\tau})} \right]^{3/2} \int_{-1/2}^{1/2} \mu \int_{-1/2}^{1/2} \mu' \int dQ dQ' Q_x Q_y Q'_x Q'_y \]

\[ \times \exp \left[ -\frac{3}{b^2} \left( \frac{\tau(r - \mu Q + \mu' Q')^2}{t} + \frac{Q^2 - 2e^{-t/\tau} Q \cdot Q' + Q'^2}{2(1 - e^{-2t/\tau})} \right) \right]. \]

(61)

The Fourier transform of eq (61) with \( k = ke_x \) becomes

\[ G(k, t) = \int dr e^{-ikr} \Lambda_{xyxy}(r, t) \]

\[ = \nu k_BT \int_{-1/2}^{1/2} \mu \int_{-1/2}^{1/2} \mu' \left[ e^{-t/\tau} + (\mu - \mu' e^{-t/\tau})(\mu' - \mu e^{-t/\tau}) b^2 k^2 \right] \]

\[ \times \exp \left[ -\frac{t}{\tau} - \left( \frac{t}{2\tau} + \mu^2 - 2\mu\mu' e^{-t/\tau} + \mu'^2 \right) \frac{b^2 k^2}{6} \right]. \]

(62)

After long calculations, we have the following simple form as the wavenumber-dependent shear relaxation modulus:

\[ G(k, t) = \nu k_BT \exp \left[ -\left( 1 + \frac{b^2 k^2}{12} \right) \frac{t}{\tau} - \frac{b^2 k^2}{12} \right] \frac{12}{b^2 k^2} \sinh \left( \frac{b^2 k^2}{12} e^{-t/\tau} \right). \]

(63)
The detailed calculations for eqs (62) and (63) are summarized in Appendix A. We show the shear relaxation modulus $G(k, t)$ with several different wavenumber values in Figure 3. If the wavenumber $k$ is sufficiently small compared with the inverse of the dumbbell size ($b^2 k^2/12 \ll 1$), $G(k, t)$ can be well approximated by the macroscopic shear relaxation modulus. Actually, by taking the limit of $k \to 0$, we recover the macroscopic shear relaxation modulus for the dumbbell model: $G(t) = G(0, t) = \nu k_B T e^{-2t/\tau}$. However, if the wavenumber is not sufficiently small, we find that $G(k, t)$ depends on the wavenumber rather strongly. As the wavenumber increases, the shear relaxation modulus decreases and the relaxation time becomes short. The shape of $G(k, t)$ seems to be close to the single exponential for any wavenumbers.

The decrease of the shear relaxation modulus as increasing the wavenumber can be shown analytically. From eq (63), we find that the shear relaxation modulus at the short-time limit simply becomes

$$G(k, 0) = \nu k_B T \frac{6(1 - e^{-b^2 k^2/6})}{b^2 k^2}.$$  

(64)

Eq (64) is a monotonically decreasing function of $k$, and thus the shear modulus decreases as the wavenumber increases. For sufficiently large wavenumber ($b^2 k^2/12 \gg 1$) and relatively short-time scale ($t/\tau \ll 1$), $G(k, t)$ can be well approximated by a single exponential decay:

$$G(k, t) \approx \nu k_B T \frac{6}{b^2 k^2} \exp \left[-\left(1 + \frac{b^2 k^2}{6}\right) \frac{t}{\tau}\right].$$  

(65)

Thus the relaxation is accelerated as the wavenumber increases. The wavenumber-dependent effective relaxation time is estimated as $\tau_{\text{eff}}(k) \approx \tau/(1 + b^2 k^2/6)$. This is consistent with Figure 3. At the long-time scale, $G(k, t)$ switches to another single exponential decay form. But the value of $G(k, t)$ at such a long-time scale is very small and the deviation at the long-time region is practically negligible.

The wavenumber-dependent shear storage and loss moduli, $G'(k, \omega)$ and $G''(k, \omega)$, can be calculated by combining eqs (41) and (63). The Fourier transform of eq (63) cannot be evaluated analytically, and thus we calculate $G'(k, \omega)$ and $G''(k, \omega)$ numerically. We use the double exponential formula[19] to accurately calculate the integral over $\omega$ in eq (41). We show the shear storage and loss moduli, $G'(k, \omega)$ and $G''(k, \omega)$, in Figure 4. As expected from the $G(k, t)$ data in Figure 3, the shapes of $G'(k, \omega)$ and $G''(k, \omega)$ seem to be similar to those of the single Maxwell model.
Figure 4: The wavenumber-dependent shear storage and loss moduli \( G'(k, \omega) \) and \( G''(k, \omega) \) for non-interacting harmonic dumbbells. \( G'(k, \omega) \) and \( G''(k, \omega) \) are numerically calculated from \( G(k, t) \). \( G'(0, \omega) \) and \( G''(0, \omega) \) correspond to the macroscopic shear storage and loss moduli, respectively.

4 CONCLUSIONS

We derived the linear response theory for scale-dependent linear viscoelasticity of overdamped Brownian particle systems. The dynamics of the system is assumed to be governed by the overdamped Langevin equation, and there is no degree of freedom for the momenta. We showed that the Irving-Kirkwood stress tensor field can be employed as the microscopic stress tensor field for Brownian particle systems. Following the standard procedure, we obtained the expression for the scale-dependent relaxation modulus tensor. It can be interpreted as the scale-dependent version of the Green-Kubo formula.

From the symmetry, for isotropic and homogeneous systems, there are only two independent components for the relaxation modulus tensor field. The transverse deformation mode gives the wavenumber-dependent shear relaxation modulus \( G(k, t) \), and the longitudinal deformation gives the wavenumber-dependent bulk modulus \( K(k, t) \). The macroscopic relaxation modulus is recovered at \( k = 0 \).

As simple examples, we calculated the wavenumber-dependent relaxation moduli for the non-interacting Brownian particles and the harmonic dumbbell model. For the non-interacting Brownian particles, we obtained the single exponential type bulk relaxation modulus \( K(k, t) \). The relaxation time depends on the diffusion coefficient and the wavenumber. For the harmonic dumbbell model, we obtained the wavenumber-dependent shear relaxation modulus \( G(k, t) \). \( G(k, t) \) has non-exponential form except \( k = 0 \) (eq (63)), but can be well approximated by a single exponential form. The relaxation time and the modulus decrease as the wavenumber increases. The fact that even these simple models exhibit nontrivial scale-dependent linear viscoelasticity implies that more complex models and real systems exhibit much more complex scale-dependent linear viscoelasticity. Molecular dynamics simulations of scale-dependent relaxation moduli for well-known systems such as polymer melts would be interesting works. Theoretical analyses for the relation between the MSD of a colloidal particle and the scale-dependent relaxation moduli would be also interesting.

ACKNOWLEDGMENT

This work was supported by JST, PRESTO Grant Number JPMJPR1992, Japan, Grant-in-Aid (KAKENHI) for Scientific Research Grant B No. JP19H01861, and Grant-in-Aid (KAKENHI) for
APPENDIX

A Detailed Calculations

In this appendix, we show the detailed calculations for the wavenumber-dependent shear relaxation modulus \( G(k, t) \) for the harmonic dumbbell model. Although the wavenumber-dependent shear relaxation modulus \( G(k, t) \) for the harmonic dumbbell model can be calculated analytically, the calculations are very lengthy. We show calculations for eqs (62) and (63) in what follows.

First we show the calculations for eq (62), which is the Fourier transform of eq (61). In eq (61), the \( r \)-dependent part is only the Gaussian weight \((3\tau / \pi b^2 t)^{3/2} \exp[-3r(\mu Q + \mu' Q')/b^2 t]\). The Fourier transform of this factor is simple:

\[
\int dr e^{-ikr} \frac{3\tau}{\pi b^2 t}^{3/2} \exp \left[ -\frac{3\tau(r - \mu Q + \mu' Q')^2}{b^2 t} \right] = \left( \frac{3\tau}{\pi b^2 t} \right)^{1/2} \int dr_x \exp \left[ -\frac{3\tau(r_x - \mu Q_x + \mu' Q'_x)^2}{b^2 t} - i r_x k \right] = \exp \left[ -\frac{b^2 t}{12\tau} k^2 + i(-\mu Q_x + \mu' Q'_x)k \right].
\]

From eqs (61) and (66), we have

\[
G(k, t) = \frac{9\nu k_B T}{b^4} \left[ \frac{9}{4\pi^2 b^4 (1 - e^{-2t/\tau})} \right]^{3/2} \int_{-1/2}^{1/2} d\mu \int_{-1/2}^{1/2} d\mu' \int dQ dQ' Q_x Q_y Q'_x Q'_y \exp \left[ \frac{b^2 t}{12\tau} k^2 + i(-\mu Q_x + \mu' Q'_x)k - \frac{3(Q^2 - 2e^{-t/\tau} Q \cdot Q' + Q'^2)}{2b^2(1 - e^{-2t/\tau})} \right].
\]

The factor in the exponential function in eq (67) can be rearranged as follows:

\[
i(-\mu Q_x + \mu' Q'_x)k - \frac{3(Q^2 - 2e^{-t/\tau} Q \cdot Q' + Q'^2)}{2b^2(1 - e^{-2t/\tau})}
= -\frac{3}{2b^2(1 - e^{-2t/\tau})} \left[ Q - e^{-t/\tau} Q' + \frac{i\mu b^2(1 - e^{-2t/\tau})k e_x}{3} \right]^2 - \frac{b^2}{6} (\mu^2 - 2\mu \mu' e^{-t/\tau} + \mu'^2) k^2.
\]

With eq (68), we can straightforwardly calculate the integrals over \( Q \) and \( Q' \) in eq (67). We extract the part which depends on \( Q \) in eq (67) and calculate it:

\[
\left[ \frac{3}{2\pi b^2(1 - e^{-2t/\tau})} \right]^{3/2} \int dQ Q_x Q_y 
\times \exp \left[ -\frac{3}{2b^2(1 - e^{-2t/\tau})} \left[ Q - e^{-t/\tau} Q' + \frac{i\mu b^2(1 - e^{-2t/\tau})k e_x}{3} \right]^2 \right]
= e^{-t\tau} \left[ e^{-t\tau} Q'_x - \frac{i\mu b^2(1 - e^{-2t/\tau})k}{3} \right] Q'_y.
\]
Then we extract the part which depends on $Q'$ in eq (67) and calculate it in a similar way.

\[
\left(\frac{3}{2\pi b^2}\right)^{3/2} \int dQ' \frac{Q'}{Q_x^2} \left[ e^{-\tau/\xi}Q_x' - \frac{i\mu b^2(1 - e^{-2\tau/\xi})}{3} \right] Q_y^2 \\
\times \exp \left[ -\frac{3}{2b^2} \left( Q'^2 + \frac{i\mu b^2(\mu e^{-\tau/\xi} - \mu')k\epsilon_x}{3} \right)^2 \right] \\
= \frac{b^2}{3} \left(\frac{3}{2\pi b^2}\right)^{1/2} \int dQ' \left[ e^{-\tau/\xi}Q_x'^2 - \frac{i\mu b^2(1 - e^{-2\tau/\xi})k}{3} Q_x \right] \\
\times \exp \left[ -\frac{3}{2b^2} \left( Q'^2 + \frac{i\mu b^2(\mu e^{-\tau/\xi} - \mu')k}{3} \right)^2 \right] \\
= \frac{b^4}{9} \left[ e^{-\tau/\xi} + \mu e^{-\tau/\xi} \mu' \right] \left(\mu - \mu' \right) \left(\mu - \mu' \right) \left(\mu - \mu' \right) \left(\mu - \mu' \right)
\]

Finally we can rewrite eq (67) as eq (62) in the main text.

Next we show the calculations for eq (63). To calculate the integrals over $\mu$ and $\mu'$ in eq (62), we introduce the variable transform from $\mu$ and $\mu'$ to $\mu_\pm = \mu \pm \mu'$. The integrals over $\mu_+$ and $\mu_-$ is performed for a diamond-like region $\Omega$ which satisfies $|\mu_+ + \mu_-| \leq 1$ and $|\mu_+ - \mu_-| \leq 1$. $\mu$ and $\mu'$ can be expressed by $\mu_\pm$ as $\mu = (\mu_+ + \mu_-)/2$ and $\mu' = (\mu_+ - \mu_-)/2$. In eq (62), we have two factors which depend on $\mu$ and $\mu'$. Then cay be rewritten in terms of $\mu_\pm$ as follows:

\[
e^{-\tau/\xi} + \frac{b^2k^2}{3}
\]

\[
= \frac{1}{2} \left[ (1 + e^{-\tau/\xi})(1 - \xi + \mu_+^2) - (1 - e^{-\tau/\xi})(1 - \xi - \mu_-^2) \right] \\
- \left(\mu^2 - 2\mu\mu' e^{-\tau/\xi} + \mu'^2\right) \frac{b^2k^2}{6} \\
= - \left[ (1 - e^{-\tau/\xi})\mu_+^2 + (1 + e^{-\tau/\xi})\mu_-^2 \right] \frac{b^2k^2}{12} \\
\]

where we have defined $\xi_\pm \equiv b^2k^2(1 \pm e^{-\tau/\xi})/6$. By using eqs (71) and (72) together with $d\mu d\mu' = (1/2)d\mu_+ d\mu_-$, we can rewrite eq (62) as follows:

\[
G(k, t) = \frac{1}{4\nu k_B T} \exp \left[ - \left( 1 + \frac{b^2k^2}{12} \right) \frac{t}{\tau} \right] \\
\times \int_{\Omega} d\mu_+ d\mu_- \left[ (1 + e^{-\tau/\xi})(1 - \xi + \mu_+^2) - (1 - e^{-\tau/\xi})(1 - \xi - \mu_-^2) \right] \\
\times \exp \left( -\frac{1}{2} \xi_+ - \frac{1}{2} \xi_- \right) \\
= \frac{1}{4\nu k_B T} \exp \left[ - \left( 1 + \frac{b^2k^2}{12} \right) \frac{t}{\tau} \right] \left[ (1 + e^{-\tau/\xi})I_+ - (1 - e^{-\tau/\xi})I_- \right],
\]

with $I_\pm$ defined as

\[
I_\pm = \int_{\Omega} d\mu_+ d\mu_- (1 - \xi \mu_\pm^2) \exp \left( -\frac{1}{2} \xi_+ \mu_\pm^2 - \frac{1}{2} \xi_- \mu_\pm^2 \right).
\]

We calculate $I_\pm$. The integrals over $\mu_+$ and $\mu_-$ in the region $\Omega$ can be rewritten as

\[
\int_{\Omega} d\mu_+ d\mu_- = \int_{-1}^{1} d\mu_\pm \int_{-1 + |\mu_\pm|}^{1 - |\mu_\pm|} d\mu_\pm.
\]

(75)
Then $I_\pm$ can be integrated over $\mu_\mp$ as

$$I_\pm = \int_{-1}^{1} d\mu_\pm \exp\left(-\frac{1}{2} \xi_\mp \mu_\mp^2\right) \int_{-1+|\mu_\pm|}^{1-|\mu_\pm|} d\mu_\mp (1 - \xi_\mp \mu_\mp^2) \exp\left(-\frac{1}{2} \xi_\pm \mu_\pm^2\right)$$

$$= 2 \int_{-1}^{1} d\mu_\pm (1 - |\mu_\pm|) \exp\left(-\frac{1}{2} \xi_\mp \mu_\mp^2 - \frac{1}{2} \xi_\pm (1 - |\mu_\pm|)^2\right)$$

$$= 4 \int_{0}^{1} d\mu_\pm (1 - \mu_\pm) \exp\left[-\frac{1}{2} \xi_\mp \mu_\mp^2 - \frac{1}{2} \xi_\pm (1 - \mu_\pm)^2\right].$$

(76)

We calculate the integrals over $\mu_\pm$ in eq (76). By rearranging the exponent in eq (76), we have

$$I_\pm = 4 \exp\left[-\frac{(1 - e^{-2t/\tau}) b^2 k^2}{24}\right] \int_{0}^{1} d\mu_\pm (1 - \mu_\pm) \exp\left[-\frac{b^2 k^2}{6} \left(\mu_\pm - \frac{1}{2} e^{-t/\tau}\right)^2\right]$$

$$= 2 \exp\left[-\frac{(1 - e^{-2t/\tau}) b^2 k^2}{24}\right] \left[(1 + e^{-t/\tau}) I' - 2 I''_\pm\right],$$

(77)

with $I'$ and $I''_\pm$ defined as

$$I' = \int_{0}^{1} d\mu \exp\left[-\frac{b^2 k^2}{6} \left(\mu - \frac{1}{2} e^{-t/\tau}\right)^2\right],$$

(78)

$$I''_\pm = \int_{0}^{1} d\mu \left(\mu - \frac{1}{2} e^{-t/\tau}\right) \exp\left[-\frac{b^2 k^2}{6} \left(\mu - \frac{1}{2} e^{-t/\tau}\right)^2\right].$$

(79)

When we calculate $G(k, t)$, $I'$ cancels and thus we do not need to calculate it further. $I''_\pm$ can be calculated as

$$I''_\pm = \int_{0}^{1} d\mu \left(\mu - \frac{1}{2} e^{-t/\tau}\right) \exp\left[-\frac{b^2 k^2}{6} \left(\mu - \frac{1}{2} e^{-t/\tau}\right)^2\right]$$

$$= 3 \exp\left[-\frac{b^2 k^2}{24} (1 + e^{-t/\tau})^2\right] - \exp\left[-\frac{b^2 k^2}{24} (1 + e^{-t/\tau})^2\right]$$

$$= \frac{6}{b^2 k^2} \exp\left[-\frac{(1 + e^{-2t/\tau}) b^2 k^2}{24}\right] \sinh\left(\frac{b^2 k^2}{12} e^{-t/\tau}\right).$$

(80)

By combining eqs (78), (77), and (80), we have

$$G(k, t) = v k_B T \exp\left[-\left(1 + \frac{b^2 k^2}{12}\right) \frac{t}{\tau} - \frac{(1 - e^{-2t/\tau}) b^2 k^2}{24}\right]$$

$$\times \left[-(1 + e^{-t/\tau}) I''_+ + (1 - e^{-t/\tau}) I''_-\right]$$

$$= v k_B T \exp\left[-\left(1 + \frac{b^2 k^2}{12}\right) \frac{t}{\tau} - \frac{b^2 k^2}{12}\right] \frac{12}{b^2 k^2} \sinh\left(\frac{b^2 k^2}{12} e^{-t/\tau}\right).$$

(81)

Finally we have eq (63) in the main text.

References

[1] Waigh TA, Rep. Prog. Phys., 68, 685 (2005).
[2] Squires TM, Mason TG, Annu. Rev. Fluid Mech., 42, 413 (2009).
[3] Fox RF, J. Math. Phys., 18, 2331 (1977).
[4] Evans DJ, Phys. Rev. A, 23, 2622 (1981).
[5] Alley WE, Alder BJ, Phys. Rev. A, 27, 3158 (1983).

[6] Evans DJ, Morris GP, “Statistical Mechanics of Nonequilibrium Liquids”, 2nd ed., (2008), Cambridge University Press, Cambridge.

[7] Hansen JS, Daivis PJ, Travis KP, Todd BD, Phys. Rev. E, 76, 041121 (2007).

[8] Glavatskiy KS, Dalton BA, Daivis PJ, Todd BD, Phys. Rev. E, 91, 062132 (2015).

[9] Doi M, Edwards SF, “The Theory of Polymer Dynamics”, (1986), Oxford University Press, Oxford.

[10] Irving JH, Kirkwood JG, J. Chem. Phys., 18 (1950).

[11] Schofield P, Henderson JR, Proc. Roy. Soc. Lond. A: Math. Phys., 379 (1982).

[12] Landau LD, Lifshitz EM, “Theory of Elasticity”, 3rd ed., (1986), Butterworth-Heinemann, Oxford.

[13] Uneyama T, Nakai F, Masubuchi Y, Nihon Reoroji Gakkaishi (J. Soc. Rheol. Jpn.), 47, 143 (2019).

[14] Gardiner CW, “Handbook of Stochastic Methods”, 3rd ed., (2004), Springer, Berlin.

[15] Ewen B, Richter D, Adv. Polym. Sci., 134, 1 (1997).

[16] Öttinger HC, “Stochastic Processes in Polymeric Fluids: Tools and Examples for Developing Simulation Algorithms”, (1996), Springer, Berlin.

[17] Kröger M, Phys. Rep., 390, 453 (2004).

[18] van Kampen NG, “Stochastic Processes in Physics and Chemistry”, 3rd ed., (2007), Elsevier, Amsterdam.

[19] Ooura T, Mori M, J. Comp. Appl. Math., 38, 353 (1991), https://www.kurims.kyoto-u.ac.jp/~ooura/intde.html.