Stress Tensor of Single Rigid Dumbbell by Virtual Work Method

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Abstract

We derive the stress tensor of a rigid dumbbell by using the virtual work method. In the virtual work method, we virtually apply a small deformation to the system, and relate the change of the energy to the work done by the stress tensor. A rigid dumbbell consists of two particles connected by a rigid bond of which length is constant (the rigid constraint). The energy of the rigid dumbbell consists only on the kinetic energy. Also, only the deformations which do not violate the rigid constraint are allowed. Thus we need the dynamic equations which is consistent with the rigid constraint to apply the virtual deformation. We rewrite the dynamic equations for the underdamped SLLOD-type dynamic equations into the forms which are consistent with the rigid constraint. Then we apply the virtual deformation to a rigid dumbbell based on the obtained dynamic equations. We derive the stress tensor for the rigid dumbbell model from the change of the kinetic energy. Finally, we take the overdamped limit and derive the stress tensor and the dynamic equation for the overdamped rigid dumbbell. We show that the Green-Kubo type linear response formula can be reproduced by combining the stress tensor and the dynamic equation at the overdamped limit.

1 INTRODUCTION

The stress tensor is one of the most important quantities in rheology. A macroscopic material consists of molecules, and thus the stress tensor can be related to the microscopic state of molecules. For example, the stress tensor of a polymer melt can be related to the conformation of polymer chains. By combining the molecular-level expression of the stress tensor and the linear response theory, we can study the microscopic molecular dynamics from the macroscopic rheological quantities.

There are several methods to calculate the stress tensor of a molecular system. A simple yet useful method is so-called the method of the virtual work[1, 2]. We virtually apply small deformation to the system, and relate the change of the energy to the work done by the stress. Here we briefly review the virtual work method. For simplicity, we consider a dilute dumbbell suspension in which individual dumbbell molecules do not interact each other. In many cases, we can safely assume that the momentum relaxation is much faster than the characteristic time scale of the bond vector (typically the orientation relaxation time), and thus we can take the overdamped limit. We model a dumbbell molecule by two particles of which positions are expressed as $\mathbf{R}_1$ and $\mathbf{R}_2$. In this work, we consider two types of dumbbell models: the rigid dumbbell and the flexible dumbbell. In the rigid dumbbell model, two particles are connected by a rigid bond. In the flexible dumbbell model, two particles are connected by the tethering potential $\phi(\mathbf{r})$ with $\mathbf{r} \equiv \mathbf{R}_2 - \mathbf{R}_1$ being the bond vector.

We consider to virtually change the particle positions from $\mathbf{R}_j$ to $\mathbf{R}'_j = \mathbf{R}_j + \mathbf{E} \cdot \mathbf{R}_j$, where $\mathbf{E}$ is the displacement gradient tensor. Then the bond vector is changed to $\mathbf{r}' = \mathbf{r} + \mathbf{E} \cdot \mathbf{r}$. If the
deformation is sufficiently small, the change of the potential energy can be expressed as

\[ \phi(r') - \phi(r) = \frac{\partial \phi(r)}{\partial r} : E + O(\|E\|^2), \]

(1)

where \( : \) represents the dyadic product (for two second order tensors \( A \) and \( B \), \( A : B = \sum_{\alpha\beta} A_{\alpha\beta} B_{\alpha\beta} \)) and \( \|E\| \) represents the norm of \( E \). (Although there are several different definitions for the norm, we employ the 2-norm in this work.) The change of the energy can be interpreted as the work done by the stress, \( V \hat{\sigma}_{bond}^{(OD)}(r) : E \) with \( V \) being the volume of the system and \( \hat{\sigma}_{bond}^{(OD)}(r) \) being the stress tensor by a single bond. (The superscript “(OD)” means the overdamped limit where the momenta are assumed to be fully equilibrated.) Then we have the single bond stress tensor as

\[ \hat{\sigma}_{bond}^{(OD)}(r) = \frac{1}{V} \frac{\partial \phi(r)}{\partial r} r. \]

(2)

Although we can utilize the virtual work method in most cases, it is not clear whether it is still applicable to systems with rigid constraints. In the rigid dumbbell model, the bond length \( |r| \) is set to be constant and there is no tethering potential. We cannot consider the change of the potential energy by the virtual deformation. In addition, we cannot apply a deformation which violates the rigid constraint. (One may consider that the rigid dumbbell can be handled as the limit of the stiff tethering potential. We will discuss the dumbbell model with the stiff tethering potential in Appendix A.)

In this work, we show that we can derive the stress tensor for a rigid dumbbell by the virtual work method. To apply the virtual work method to the rigid dumbbell, we first derive the dynamic equations for the rigid dumbbell under flow. We employ the SLLOD-type dynamic equations for the bond vector and the bond momentum, and rewrite the dynamic equations which are consistent with the rigid constraint. Second, we apply the virtual deformation to the system by using the obtained dynamic equations. This procedure gives the explicit expression for the stress tensor of the rigid dumbbell. Finally we calculate the shear relaxation modulus of a dilute rigid dumbbell suspension. The stress tensor at the overdamped limit together with the dynamic equation at the overdamped limit can reproduce the shear relaxation modulus calculated by the kinetic theory, except the instantaneous delta function type term.

2 MODEL

2.1 Flexible Dumbbell with Tethering Potential

The energy of a single rigid dumbbell consists only on the kinetic energy. Then, it would be reasonable for us to consider the contribution of the kinetic energy to the stress tensor. Before we consider the rigid dumbbell, here we consider the flexible dumbbell model with the tethering potential. We consider the underdamped dynamics[3] and introduce the momenta of two particles as \( P_1 \) and \( P_2 \). The Hamiltonian of a single dumbbell is

\[ \mathcal{H}(R_1, R_2, P_1, P_2) = \frac{P_1^2 + P_2^2}{2M} + \phi(R_2 - R_1), \]

(3)

where \( M \) is the mass of a particle. To apply the virtual deformation to the system, we consider the dynamic equations under an externally imposed flow. We employ the SLLOD dynamic equations which describe the dynamics of particles under a flow[4, 5]. By combining the SLLOD dynamic equations and the Langevin thermostat, the dynamic equations become:

\[ \frac{dR_j(t)}{dt} = \frac{1}{M} P_j(t) + \kappa(t) \cdot R_j(t), \]

(4)

\[ \frac{dP_j(t)}{dt} = -\frac{\partial \phi(R_1(t) - R_2(t))}{\partial R_j(t)} - \kappa(t) \cdot P_j(t) - Z M P_j(t) + \sqrt{2\beta k_B T} W_j(t). \]

(5)
Here, \( \kappa(t) \equiv (\nabla \mathbf{v}(t))^T \) is the velocity gradient tensor with \( \mathbf{v}(t) \) being the imposed flow field, \( Z \) is the friction coefficient of a particle, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. \( W_j(t) \) is the Gaussian white noise which satisfies the following relations:

\[
\langle W_j(t) \rangle = 0, \quad \langle W_j(t) W_k(t') \rangle = \delta_{jk} \delta(t - t'), \quad (6)
\]

where \( \langle \ldots \rangle \) represents the statistical average and \( \mathbf{1} \) is the unit tensor. The dynamic equations (4) and (5) can be decomposed into two set of statistically independent equations. We introduce the center of mass position \( \mathbf{R}(t) \equiv [\mathbf{R}_1(t) + \mathbf{R}_2(t)]/2 \) and the bond vector \( \mathbf{r}(t) \equiv \mathbf{R}_2(t) - \mathbf{R}_1(t) \). We also introduce the momentum of the center of mass and the bond vector, \( \mathbf{P}(t) \equiv \mathbf{P}_1(t) + \mathbf{P}_2(t) \) and \( \mathbf{p}(t) \equiv [\mathbf{P}_2(t) - \mathbf{P}_1(t)]/2 \). Then the Hamiltonian (5) can be rewritten as a function of \( \mathbf{R}, \mathbf{P}, \mathbf{r}, \) and \( \mathbf{p} \):

\[
\mathcal{H}(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p}) = \frac{\mathbf{P}^2}{2M} + \frac{\mathbf{p}^2}{2m} + \phi(\mathbf{r}), \quad (7)
\]

where \( M \equiv 2M \) and \( m \equiv M/2 \) are masses. Eqs (8) and (9) can be rewritten as

\[
\frac{d\mathbf{R}(t)}{dt} = \frac{1}{M} \mathbf{P}(t) + \kappa(t) \cdot \mathbf{R}(t), \quad (8)
\]

\[
\frac{d\mathbf{P}(t)}{dt} = -\kappa(t) \cdot \mathbf{P}(t) - \frac{\dot{Z}}{M} \mathbf{P}(t) + \sqrt{2Zk_BT} \mathbf{W}(t), \quad (9)
\]

\[
\frac{d\mathbf{r}(t)}{dt} = \frac{1}{m} \mathbf{p}(t) + \kappa(t) \cdot \mathbf{r}(t), \quad (10)
\]

\[
\frac{d\mathbf{p}(t)}{dt} = -\frac{\partial \phi(\mathbf{r}(t))}{\partial \mathbf{r}(t)} - \kappa(t) \cdot \mathbf{p}(t) - \frac{\zeta}{m} \mathbf{p}(t) + \sqrt{2\zeta k_BT} \mathbf{w}(t). \quad (11)
\]

Here, \( \dot{Z} = 2Z \) and \( \zeta = Z/2 \) are the friction coefficients, and \( \mathbf{W}(t) \equiv [\mathbf{W}_1(t) + \mathbf{W}_2(t)]/\sqrt{2} \) and \( \mathbf{w}(t) \equiv [\mathbf{W}_2(t) - \mathbf{W}_1(t)]/\sqrt{2} \) are Gaussian white noises. It is straightforward to show that two Gaussian noises \( \mathbf{W}(t) \) and \( \mathbf{w}(t) \) are statistically independent. From eqs (8)-(11), we find that the dynamics of the center of mass \( \mathbf{R}(t) \) and the bond vector \( \mathbf{r}(t) \) are statistically independent.

### 2.2 Virtual Work Method

We consider to apply the impulsive small strain to the system. This can be done by setting the velocity gradient tensor in eqs (8)-(11) as an impulse at \( t = 0 \): \( \kappa(t) = E \delta(t) \). As before, we assume that \( E \) is sufficiently small. The positions and momenta change instantaneously around \( t = 0 \).

We express the center of mass positions and momenta just before and just after the impulse as \( \mathbf{R} = \mathbf{R}(-0), \mathbf{P} = \mathbf{P}(-0), \mathbf{r} = \mathbf{r}(-0), \mathbf{p} = \mathbf{p}(-0) \), and \( \mathbf{r}' = \mathbf{r}(+0), \mathbf{p}' = \mathbf{p}(+0) \). By integrating the dynamic equations (8)-(11) from \( t = -0 \) to \( t = +0 \), we have

\[
\mathbf{R}' = \mathbf{R} + E \cdot \mathbf{r}, \quad \mathbf{P}' = \mathbf{P} - E \cdot \mathbf{P}, \quad (12)
\]

\[
\mathbf{r}' = \mathbf{r} + E \cdot \mathbf{r}, \quad \mathbf{p}' = \mathbf{p} - E \cdot \mathbf{p}. \quad (13)
\]

With the virtual deformation described by eqs (12) and (13), the total energy of the dumbbell is changed from \( \mathcal{H}(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p}) \) to \( \mathcal{H}(\mathbf{R}', \mathbf{P}', \mathbf{r}', \mathbf{p}') \). The change of the energy can be related to the single dumbbell stress tensor as:

\[
\mathcal{H}(\mathbf{R}', \mathbf{P}', \mathbf{r}', \mathbf{p}') - \mathcal{H}(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p}) = V \hat{\sigma}^{(UD)}(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p}) : \mathbf{E} + O(\|\mathbf{E}\|^2), \quad (14)
\]

where \( \hat{\sigma}^{(UD)}(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p}) \) is the stress tensor of a single dumbbell in the underdamped system. (The superscript “(UD)” means the underdamped system.) The single dumbbell stress tensor can be decomposed into the contributions of the center of mass and the bond vector as:

\[
\hat{\sigma}^{(UD)}(\mathbf{R}, \mathbf{P}, \mathbf{r}, \mathbf{p}) = \hat{\sigma}^{(UD)}_{CM}(\mathbf{R}, \mathbf{P}) + \hat{\sigma}^{(UD)}_{bond}(\mathbf{r}, \mathbf{p}), \quad (15)
\]

\[
\hat{\sigma}^{(UD)}_{CM}(\mathbf{R}, \mathbf{P}) = -\frac{1}{V} \frac{\mathbf{P} \mathbf{P}}{M}, \quad (16)
\]

\[
\hat{\sigma}^{(UD)}_{bond}(\mathbf{r}, \mathbf{p}) = \frac{1}{V} \left[ \frac{\partial \phi(\mathbf{r})}{\partial \mathbf{r}} \mathbf{r} - \frac{\mathbf{p} \mathbf{p}}{m} \right]. \quad (17)
\]
If the momentum relaxation process is sufficiently fast, we can take the local equilibrium average over $P$ and $p$. This gives the stress tensor at the overdamped limit. The local equilibrium distribution functions for momenta $P$ and $p$ are independent of $\bar{R}$ and $r$:

$$\Psi_{eq}(\bar{P}|\bar{R}) = \left(\frac{1}{2\pi M k_B T}\right)^{3/2} \exp \left(-\frac{\bar{P}^2}{2M k_B T}\right), \quad (18)$$

$$\psi_{eq}(p|r) = \left(\frac{1}{2\pi mk_B T}\right)^{3/2} \exp \left(-\frac{p^2}{2mk_B T}\right). \quad (19)$$

Then the stress tensor at the overdamped limit becomes

$$\sigma^{(OD)}(\bar{R}, r) = \sigma_{CM}^{(OD)}(\bar{R}) + \sigma_{\text{bond}}^{(OD)}(r), \quad (20)$$

$$\sigma_{CM}^{(OD)}(\bar{R}) \equiv \int d\bar{P} \psi_{eq}(\bar{P}|\bar{R}) \sigma^{(UD)}_{CM}(\bar{R}, P) = -k_B T \frac{V}{\bar{R}^3} \bar{R}, \quad (21)$$

$$\sigma_{\text{bond}}^{(OD)}(r) \equiv \int dp \psi_{eq}(p|r) \sigma^{(UD)}_{\text{bond}}(r, p) = \frac{1}{V} \left[ \frac{\partial \phi(r)}{\partial r} r - k_B T \right]. \quad (22)$$

Except the trivial isotropic component, eq (22) coincides to eq (2).

### 2.3 Rigid Dumbbell

We consider the rigid dumbbell model. In the rigid dumbbell model, two particles are connected by a rigid bond instead of a tethering potential. Since the dynamics of the center of mass is independent of the bond, it is common for the flexible and rigid dumbbells. What we need to consider is the dynamics of the bond and the stress tensor by the bond.

If we naively employ eqs (20)-(22) for the stress tensor of the rigid dumbbell at the overdamped limit, we cannot calculate the stress tensor. The center of mass is independent of the bond vector and thus eq (21) can be utilized without any modifications. However, we cannot directly utilize eq (22) because it contains the tethering potential $\phi(r)$. If we employ a very stiff tethering potential with which the bond length becomes almost constant, we can calculate the stress tensor as shown in Appendix A. But the stiff limit is not physically reasonable and the validity is not clear. If we simply set $\phi(r) = 0$ in eq (22), we are led to conclude that the rigid dumbbell exhibits only the isotropic stress. Clearly this is wrong. It is known that an anisotropic rigid body immersed in a fluid generally exhibits an anisotropic stress tensor. The origin of the anisotropic stress tensor is attributed to so-called the Brownian potential or the stress of the surrounding fluid. However, in our coarse-grained description, we can not employ the Brownian potential nor the effect of the surrounding fluid.

One way to avoid this difficulty is to go back to the underdamped system and replace the potential force $-\partial \phi(r)/\partial r$ in eq (17) by the constraint force acting on the bond. If we replace the potential force by the constraint force $F_{\text{constraint}}$, we can construct the stress tensor at the underdamped system. Under the rigid constraint, the local equilibrium distribution of the bond momentum can deviate from eq (19). Thus we should be careful when we take the overdamped limit.

We employ the expression for the centrifugal force to keep $r = |r|$ constant as the constraint force: $F_{\text{constraint}} = -\left(\bar{p}^2/mr^2\right) r$. With this phenomenological replacement, we have

$$\sigma_{\text{bond}}^{(UD)}(r, p) = \frac{1}{V} \left( \frac{\bar{p}^2}{mr^2} rr - \frac{pp}{m} \right). \quad (23)$$

From the fact that the bond momentum $p$ is perpendicular to $r$ if $r$ is fixed, $p$ should be distributed on a plane which is perpendicular to $r$. Thus the local equilibrium distribution function for the bond momentum $p$ depends on the bond vector unlike eq (19). The explicit form of the distribution function is:

$$\psi_{eq}(p|r) = \delta \left( \frac{rr}{r^2} \cdot p \right) \frac{1}{2\pi mk_B T} \exp \left(-\frac{p^2}{2mk_B T}\right). \quad (24)$$
\( r r / r^2 \) works as the projection tensor which extracts the parallel component to \( r \) from a vector. From eqs (23) and (24), we have the following expression for the bond stress tensor at the overdamped limit:

\[
\hat{\sigma}^{(\text{OD})}_{\text{bond}}(r) = \frac{k_B T}{V} \left( \frac{3rr}{r^2} - 1 \right).
\]  

(The detailed calculation is shown in Appendix B.) Eq (25) states that the anisotropic part of the stress tensor is proportional to \( rr \). This is consistent with the intuitive expectation, and thus we expect that eq (25) is reasonable.

Here we recall that the stress tensor (17) is originally constructed based on the energy change for the instantaneous deformation by eq (13). For the rigid dumbbell, such a deformation is generally not allowed since the bond length can be changed by eq (13). Also, the validity of the simple centrifugal force to the instantaneous deformation is not clear. Therefore, the validity of eqs (23) and (25) is questionable from the viewpoint of the virtual work. To be fair, we should mention that the same stress tensor can be obtained without applying the virtual deformation\[8, 9\]. For example, the Irving-Kirkwood formalism\[10\] can give the same result without considering a virtual deformation. But the Irving-Kirkwood formalism is not simple compared with the virtual work method. The virtual work method would be preferred in some cases, if it gives the correct stress tensor without a heuristic replacement.

To apply the virtual work method to the rigid dumbbell, we should consider the dynamic equations for the rigid dumbbell carefully. Without the flow field, the dynamic equations are well known. The constraint force \( F_{\text{constraint}}(t) \) should be added to the dynamic equations, instead of the potential force\[4\]. The constraint force is parallel to the bond vector, and thus we express it as \( F_{\text{constraint}}(t) = \lambda(t) r(t) \) with \( \lambda(t) \) being a time-depending scalar quantity. By combining the effect of the SLLOD-type flow and the rigid constraint, we have the following dynamic equations:

\[
\frac{dr(t)}{dt} = \frac{1}{m} p(t) + \kappa(t) \cdot r(t),
\]

\[
\frac{dp(t)}{dt} = \lambda(t) r(t) - \kappa(t) \cdot p(t) - \frac{\zeta}{m} p(t) + \sqrt{2\zeta k_B T w(t)}.
\]

Here, \( \lambda(t) \) can be interpreted as the Lagrange multiplier which is determined to satisfy the constraint \( |r(t)| = b \) with \( b \) being the bond length. Similar dynamic equations have been employed to study the dynamics for more complex systems such as alkanes\[11, 12\]. In numerical simulations, the dynamic equations are discretized and the Lagrange multiplier \( \lambda(t) \) is numerically determined at every time step. In this work, we will calculate \( \lambda(t) \) analytically.

3 RESULTS

3.1 Dynamic Equations

Although we expect that the dynamics of the rigid dumbbell under flow can be described by eqs (26) and (27), it is apparently not clear how the rigid constraint \( r(t) = |r(t)| = b \) is satisfied in eqs (26) and (27). To apply the virtual deformation, eqs (26) and (27) do not seem to be convenient. Therefore, first we attempt to rewrite eqs (26) and (27) and obtain dynamic equations which are suitable for our purpose.

From the rigid constraint, we have

\[
\frac{d}{dt} r^2(t) = 2r(t) \cdot \frac{dr(t)}{dt} = 0.
\]

By combining eqs (26) and (28), we find that the right hand side of eq (26) cannot contain the component which is parallel to \( r(t) \):

\[
0 = \frac{1}{m} r(t) \cdot p(t) + r(t) \cdot \kappa(t) \cdot r(t).
\]
For convenience, we decompose the bond momentum $p(t)$ into two components which are parallel and perpendicular to $r(t)$: $p(t) = p_\parallel(t) + p_\perp(t)$ with $p_\parallel(t) \equiv [r(t)r(t)/r^2(t)] \cdot p(t)$ and $p_\perp(t) \equiv [1 - r(t)r(t)/r^2(t)] \cdot p(t)$. Then we have

$$p_\parallel(t) = -m\kappa_\parallel(t) \cdot r(t),$$

with $\kappa_\parallel(t) \equiv [r(t)r(t)/r^2(t)] \cdot \kappa(t)$. Now we can rewrite eq (30) as

$$\frac{dr(t)}{dt} = \frac{1}{m}p_\perp(t) + \kappa_\perp(t) \cdot r(t).$$

Here, $\kappa_\perp(t) \equiv [1 - r(t)r(t)/r^2(t)] \cdot \kappa(t)$ can be interpreted as the perpendicular component of the velocity gradient tensor. The simple manipulation shown above tells us that the parallel component of the momentum $p_\parallel(t)$ is not an internal degree of freedom of the rigid dumbbell. This is not surprising because the bond length $|r(t)| = b$ is not an internal degree of freedom, neither. We have only 4 internal degrees of freedom for a rigid bond (2 for the bond orientation and 2 for the perpendicular bond momentum). Eq (31) means that the bond vector effectively feels the flow field which is perpendicular to $r(t)$.

We want to rewrite the dynamic equation for the bond momentum $p_\perp(t)$ (eq (27)) in an explicit form. However, it is not that clear how we should manipulate eq (27). We go back to the derivation of the SLLOD dynamic equation. The SLLOD dynamic equation is designed to reproduce the following dynamic equation with the external flow[5, 13]:

$$\frac{d^2r(t)}{dt^2} = \frac{1}{m}F(t) + \frac{d\kappa(t)}{dt} \cdot r(t) + O(\|\kappa(t)\|^2),$$

where $F(t)$ is the force acting on the bond. (In general, we have the second order term which is expressed as $O(\|\kappa(t)\|^2)$ in eq (52). We can remove the second order term by employing so-called the p-SLLOD dynamic equations[13]. In this work, we simply ignore higher order terms.) The force $F(t)$ in eq (52) can be decomposed to the parallel and perpendicular component: $F(t) = F_\parallel(t) + F_\perp(t)$. The parallel component can be interpreted as the Lagrange multiplier $F_\parallel(t) = \lambda(t)r(t)$. The perpendicular component contain the friction and noise terms: $F_\perp(t) = -\zeta/m\kappa_\perp(t) + \sqrt{2\zeta k_B T}w_\perp(t)$, where $w_\perp(t)$ is the Gaussian white noise which is perpendicular to $r(t)$. (The parallel component of the friction and noise terms can be absorbed into $\lambda(t)$.) We can rewrite eq (52) as

$$\frac{d^2r(t)}{dt^2} = \frac{1}{m}[\lambda(t)r(t) + F_\perp(t)] + \frac{d[\kappa_\perp(t) + \kappa_\parallel(t)]}{dt} \cdot r(t) + O(\|\kappa(t)\|^2)$$

$$= \frac{1}{m}[\lambda'(t)r(t) + F_\perp(t)] + \frac{\kappa_\perp(t)}{m} \cdot r(t) + \frac{\text{Tr} \kappa_\parallel(t)}{m} p_\perp(t) + O(\|\kappa(t)\|^2).$$

See Appendix[13] for the detailed calculations of eq (33). Here, Tr represents the trace (for a second order tensor $A$, $\text{Tr} A \equiv \sum_\alpha A_{\alpha\alpha}$). We have absorbed all the terms which are proportional to $r(t)$ into $\lambda'(t)$. ($\lambda'(t)$ contains the contribution from $[d\kappa(t)/dt] \cdot r(t)$ and is generally different from $\lambda(t)$.) On the other hand, by taking the time derivative of eq (31), we have the following equation:

$$\frac{d^2r(t)}{dt^2} = \frac{1}{m}\frac{dp_\perp(t)}{dt} + \frac{d\kappa_\perp(t)}{dt} \cdot r(t) + \frac{1}{m} \kappa_\perp(t) \cdot p_\perp(t) + \kappa_\perp(t) \cdot \kappa_\perp(t) \cdot r(t).$$

By comparing eqs (33) and (34), we find that the dynamic equation for $p_\perp(t)$ should be given as

$$\frac{dp_\perp(t)}{dt} = \lambda'(t)r(t) + F_\perp(t) - [\kappa_\perp(t) - 1 \text{Tr} \kappa_\parallel(t)] \cdot p_\perp(t).$$

The Lagrange multiplier $\lambda'(t)$ can be determined from the constraint $r(t) \cdot p_\perp(t) = 0$. By taking the time derivative of this constraint, we have

$$0 = r(t) \frac{dp_\perp(t)}{dt} + p_\perp(t) \frac{dr(t)}{dt}$$

$$= \lambda'(t)r^2(t) + \frac{1}{m}p_\perp^2(t) + p_\perp(t) \cdot \kappa_\perp(t) \cdot r(t),$$









and the explicit form of \( \lambda'(t) \) is given as

\[
\lambda'(t) = -\frac{p_{\perp}^2(t)}{mr^2(t)} - \frac{r(t) \cdot \kappa^T(t) \cdot p_{\perp}(t)}{r^2(t)},
\]

Finally we have the explicit form of the dynamic equation for the bond momentum \( p_{\perp}(t) \):

\[
\frac{dp_{\perp}(t)}{dt} = -\frac{p_{\perp}^2(t)}{mr^2(t)}r(t) - \frac{\zeta}{m} p_{\perp}(t) + \frac{\sqrt{2\zeta k_B T}}{m} w_{\perp}(t)
\]

\[
- [\kappa_{\perp}(t) + (\kappa^T)_{\parallel}(t) - \text{Tr} \kappa_{\parallel}(t)] \cdot p_{\perp}(t),
\]

with \((\kappa^T)_{\parallel}(t) \equiv [r(t)r(t)/r^2(t)] \cdot \kappa^T(t)\). The noise \( w_{\perp}(t) \) satisfies the following relations:

\[
\langle w_{\perp}(t) \rangle = 0, \quad \langle w_{\perp}(t)w_{\perp}(t') \rangle = \left[ 1 - \frac{r(t)r(t)}{r^2(t)} \right] \delta(t - t').
\]

Eqs (31) and (38) are the dynamic equations for the bond vector of the rigid dumbbell under flow.

### 3.2 Virtual Work Method

We can apply the instantaneous virtual deformation to the system by utilizing eqs (31) and (38). As before, we set \( \kappa(t) = E \delta(t) \) and integrate the dynamic equations from \( t = -0 \) to \( t = +0 \). The contribution of the center of mass is common for the flexible and rigid dumbbells. The stress tensor by the center of mass is given as eq (10) (for the underdamped system) or eq (21) (for the overdamped system). Thus we consider only the contribution of the bond vector in what follows.

The parallel component of the bond momentum is zero: \( p'_{||} = p_{||} = 0 \). By integrating eqs (31) and (38), the bond vector and the perpendicular component of the bond moment change as

\[
r' = r + \left( 1 - \frac{rr}{r^2} \right) \cdot E \cdot r + O(\|E\|^2),
\]

\[
p'_{\perp} = p_{\perp} - \left( 1 - \frac{rr}{r^2} \right) \cdot E \cdot p_{\perp} + \frac{r \cdot E \cdot r}{r^2} p_{\perp} - \frac{p_{\perp} \cdot E \cdot r}{r^2} r + O(\|E\|^2).
\]

Here, we have utilized the identity \((E^T)_{\parallel} \cdot p_{\perp} = r(r \cdot E^T \cdot p_{\perp})/r^2 \) to derive eq (31). In eqs (30) and (31), the higher order terms in \( E \) are not explicitly shown because their contribution to the energy change is negligibly small. (For our purpose, only the first order terms are required.) The kinetic energy of the bond is changed as

\[
\frac{(p'_{\perp})^2}{2m} - \frac{p_{\perp}^2}{2m} = \left[ - \frac{p_{\perp}p_{\perp}}{m} + \frac{p_{\perp}^2}{m} \frac{rr}{r^2} \right] \cdot E + O(\|E\|^2).
\]

Then we have the stress tensor for the single bond as

\[
\sigma_{\text{bond}}^{(UD)}(r, p_{\perp}) = \frac{1}{V} \left[ - \frac{p_{\perp}p_{\perp}}{m} + \frac{p_{\perp}^2}{m} \frac{rr}{r^2} \right].
\]

Eq (43) coincides to eq (23). If we take the local equilibrium average over the bond momentum, we have eq (25).

Therefore, our method gives the same result with the simple heuristic method in which the potential force is replaced by the constraint force. Here we emphasize that we did not employ such a heuristic replacement. What we did is just to rewrite the SLLOD dynamic equations and applied the virtual deformation to the system which does not violate the rigid constraint. According to our derivation, the stress tensor by the bond (eq (43)) purely comes from the kinetic energy.

We expect that our method can be applied to other systems with different thermostats. For example, we will be able to construct the stress tensor of a rigid dumbbell driven by the SLLOD dynamic equations with the Nose-Hoover thermostat, in the same way as this work. What important in our formalism is the explicit expressions for the advection terms in the dynamic equations.
3.3 Relaxation Modulus at Overdamped Limit

We consider the situation where the momentum relaxation is sufficiently fast. Under such a situation, we take the overdamped limit and eliminate the degree of freedom of the momenta. By setting \( dp(t)/dt = 0 \) and \( \kappa(t) = 0 \) in eq (27), we can eliminate \( p_\perp(t) \) from eq (26). We can rewrite eq (26) as

\[
\frac{dr(t)}{dt} = -\lambda''(t)r(t) + \sqrt{\frac{2k_BT}{\zeta}}w_\perp(t) + \kappa_\perp(t) \cdot r(t),
\]

where \( \lambda''(t) \) is the Lagrange multiplier, and all the terms which are parallel to \( r(t) \) are absorbed into the Lagrange multiplier. \( \lambda'(t) \) can be determined from the constraint \( dr(t)/dt = 0 \). By using the Ito formula\[15, 16\] together with eqs (39), (44) and \( \partial^2(r^2)/\partial r \partial r = 21 \), we have

\[
0 = 2r(t) \frac{dr(t)}{dt} + \frac{1}{2} \frac{k_BT}{\zeta} \left[ 1 - \frac{r(t)r(t)}{r^2(t)} \right] : 21
\]

\[
= 2r(t) \cdot \left[ \lambda''(t)r(t) + \sqrt{\frac{2k_BT}{\zeta}}w_\perp(t) + \kappa_\perp(t) \cdot r(t) \right] + \frac{k_BT}{\zeta} Tr \left[ 1 - \frac{r(t)r(t)}{r^2(t)} \right]
\]

\[
= -2\lambda''(t)r^2(t) + \frac{2k_BT}{\zeta}.
\]

Then we have \( \lambda''(t) = k_BT/\zeta r^2(t) \) and the overdamped dynamic equation for the bond becomes

\[
\frac{dr(t)}{dt} = -\frac{k_BT r(t)}{\zeta r^2(t)} + \sqrt{\frac{2k_BT}{\zeta}}w_\perp(t) + \kappa_\perp(t) \cdot r(t).
\]

As the case of the underdamped dynamics, only the perpendicular component of the velocity gradient tensor is applied to the bond vector.

We can calculate rheological properties of a rigid dumbbell model at the overdamped limit by combining eqs (25) and (16). To demonstrate that we can reasonably describe the rheological properties of a rigid dumbbell, here we derive the linear response formula and calculate the shear relaxation modulus. The probability distribution function for the bond vector \( \psi(r, t) \) obeys the following Fokker-Planck equation:

\[
\frac{\partial \psi(r, t)}{\partial t} = [L_{eq} + \Delta L(t)] \psi(r, t),
\]

with the Fokker-Planck operators defined as

\[
L_{eq} \psi(r) \equiv \frac{k_BT}{\zeta} \frac{\partial}{\partial r} \left[ (1 - \frac{rr}{r^2}) \cdot \frac{\partial \psi(r, t)}{\partial r} \right],
\]

\[
\Delta L(t) \psi(r) \equiv -\frac{\partial}{\partial r} \left[ (1 - \frac{rr}{r^2}) \cdot \kappa(t) \cdot r \psi(r, t) \right].
\]
$\mathcal{L}_\text{eq}$ describes the rotational diffusion in equilibrium whereas $\Delta \mathcal{L}(t)$ describes the advection by the applied flow.

We can construct the linear response theory by treating the applied velocity gradient as the perturbation. We split the distribution function into the equilibrium and perturbation parts as $\psi(r,t) = \psi_\text{eq}(r) + \Delta \psi(r,t)$, with $\psi_\text{eq}(r)$ being the equilibrium distribution function of the bond vector and $\Delta \psi(r,t)$ being the time-dependent perturbation part of the distribution function. In equilibrium, the bond vector is uniformly distributed on a sphere. The equilibrium distribution function depends only on $r = |r|$: 

$$
\psi_\text{eq}(r) = \psi(r) = \frac{1}{4\pi b^2} \delta(r - b). \tag{50}
$$

We interpret $\Delta \psi(r,t)$ and $\Delta \mathcal{L}(t)$ as perturbations. At the first order in the perturbation, the perturbation part of the distribution function satisfies the following equation:

$$
\frac{\partial \Delta \psi(r,t)}{\partial t} = \Delta \mathcal{L}(t) \psi_\text{eq}(r) + \mathcal{L}_\text{eq} \Delta \psi(r,t). \tag{51}
$$

The solution of eq (51) is

$$
\Delta \psi(r,t) = \int_{-\infty}^{t} dt' e^{(t-t')\mathcal{L}_\text{eq}} \Delta \mathcal{L}(t) \psi_\text{eq}(r)
= \frac{V}{k_B T} \int_{-\infty}^{t} dt' e^{-(t-t')\mathcal{L}_\text{eq}} \hat{\sigma}^{(OD)}(r) : \kappa(t) \psi_\text{eq}(r). \tag{52}
$$

In the calculation of eq (52), we have utilized the following relation:

$$
\Delta \mathcal{L}(t) \psi_\text{eq}(r) = \left[ \frac{2r}{r^2} \cdot \kappa(t) \cdot r - \text{Tr} \left[ \left( 1 - \frac{rr'}{r^2} \right) \cdot \kappa(t) \right] \right] \psi_\text{eq}(r)
= \frac{V}{k_B T} \sigma^{(OD)}(r) : \kappa(t) \psi_\text{eq}(r). \tag{53}
$$

The second order or higher order perturbation will be negligible if the applied flow is sufficiently weak. Then we can calculate the (ensemble) average stress tensor at time $t$ under the applied velocity gradient history with eq (52):

$$
\sigma^{(OD)}_{\text{bond}}(t) = \int dr \hat{\sigma}^{(OD)}_{\text{bond}}(r)[\psi_\text{eq}(r) + \Delta \psi(r,t)]
= \frac{V}{k_B T} \int_{-\infty}^{t} dt' \int dr \hat{\sigma}^{(OD)}(r) e^{(t-t')\mathcal{L}_\text{eq}} \hat{\sigma}^{(OD)}_{\text{bond}}(r) : \kappa(t) \psi_\text{eq}(r)
= \frac{V}{k_B T} \int_{-\infty}^{t} dt' \int dr \ \psi_\text{eq}(r) \left[ e^{(t-t')\mathcal{L}_\text{eq}} \hat{\sigma}^{(OD)}_{\text{bond}}(r) \right] \hat{\sigma}^{(OD)}_{\text{bond}}(r) : \kappa(t). \tag{54}
$$

Here, $\mathcal{L}_\text{eq}^\dagger$ is the adjoint Fokker-Planck operator of $\mathcal{L}_\text{eq}$, and $e^{(t-t')\mathcal{L}_\text{eq}}$ works as the time-shift operator.

If the perturbation is sufficiently weak, we can assume that the system behaves as the linear viscoelastic material. The average stress tensor can be related to the velocity gradient history by using the relaxation modulus tensor $\Lambda(t)$:

$$
\sigma^{(OD)}(t) = -P_{eq} \mathbf{1} + \int_{-\infty}^{t} dt' \Lambda(t - t') : \kappa(t'), \tag{55}
$$

with $P_{eq} \equiv k_B T / V$ being the equilibrium pressure. By comparing eqs (54) and (55), we have the linear response formula for the relaxation modulus tensor of a single rigid dumbbell:

$$
\Lambda(t) = \frac{V}{k_B T} \left< \hat{\sigma}^{(OD)}_{\text{bond}}(r,t) \hat{\sigma}^{(OD)}_{\text{bond}}(r) \right>_{\text{eq}}. \tag{56}
$$

9
where \( \langle \ldots \rangle_{eq} \) represents the equilibrium statistical average and \( \sigma^{(\text{OD})}_{\text{bond}}(r,t) \equiv e^{tC_f} \sigma(r) \) is the time-shifted stress tensor. Eq (54) is nothing but the Green-Kubo relation. Judging from the fact that eqs (26) and (46) reproduce the Green-Kubo relation, we conclude that they reasonably describe the dynamics and rheology of the rigid dumbbell.

The shear relaxation modulus of a dilute suspension which consist of \( N \) rigid dumbbells is

\[
G(t) = G_{xyxy}(t) = \frac{9}{5} \nu k_B T \exp\left( -\frac{6k_B T}{\xi b^2} t \right) .
\]

Eq (58) coincides to the relaxation modulus calculated by the kinetic theory, except the instantaneous contribution which is proportional to \( \delta(t) \) [17, 18]. This result supports the validity of eq (56), and also the validity of eqs (25) and (46).

\section{CONCLUSIONS}

We calculated the stress tensor of the rigid dumbbell based on the virtual work method. To apply the virtual deformation and calculate the energy change, we considered the underdamped SLLOD-type dynamic equations for the bond vector. Due to the rigid constraint, the bond vector cannot affinely move following the applied velocity gradient tensor. We rewrote the dynamic equations in which the bond vector and the bond momentum are driven by the effective velocity gradient tensor (eqs (31) and (38)). We derived the explicit expression for the Lagrange multiplier in the dynamic equation, and the dynamic equations are expressed in an explicit form. With the thus derived dynamic equations, we applied the virtual deformation to the system. Then, from the change of the kinetic energy before and after the small impulsive deformation, we obtained the stress tensor of the single bond (eq (43)). Finally we considered the overdamped limit and derived the linear response formula for the single bond (eq (56)). We showed that the shear relaxation modulus calculated by the linear response formula is consistent with the modulus calculated by the kinetic theory, except the short-time scale delta function type contribution.

The results in this work will be informative to study other systems with rigid constraints. For example, stress of the freely jointed chain where the beads are connected by rigid bonds will be handled in a similar way to our method (although the analytic expressions will be too complicated). Our results suggest that the virtual work method can be applied to other systems with strong constraints. The hard sphere potentials can be interpreted as constraint rather than an interaction potential. It would be interesting to formulate the dynamic equations and the stress tensor of hard sphere systems in a similar way to this work.

\section{ACKNOWLEDGMENT}

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APPENDIX

A Dumbbell Model with Stiff Harmonic Potential

The rigid constraint may be approximated by a “stiff” tethering potential. In this appendix, we consider the case where the tethering potential is given as the following harmonic potential:

$$\phi(r) = \frac{1}{2}K(r - b)^2. \tag{59}$$

Here, $r = |r|$ is the bond length, $K$ is the spring constant and $b$ is the natural bond length. We consider the case where $K$ is sufficiently large: $K \gg k_B T$. Under such a condition, the bond length can only slightly fluctuate around the average value $b$. If we take the limit of $K \to \infty$, the bond length fluctuation will approach to zero and the bond length will be constant ($r \to b$).

If we naively assume the overdamped limit, from eqs (2) and (59), we have

$$\sigma^{(OD)}_{\text{bond}}(r) = \frac{1}{V}Kr(r - b) \frac{rr}{r^2}. \tag{60}$$

The equilibrium distribution of the bond length $r$ can be approximately expressed as

$$\psi_{\text{eq}}(r) \approx \sqrt{\frac{K}{2\pi k_B T}} \exp \left[- \frac{K}{2k_B T}(r - b)^2 \right]. \tag{61}$$

Then, by taking the partial average of eq (60) over the bond length, we have

$$\int dr \sigma^{(OD)}_{\text{bond}}(r) \psi_{\text{eq}}(r) = \frac{k_B T rr}{V}. \tag{62}$$

Eq (62) does not coincide to the correct expression (eq (25)).

The reason why we do not have the correct stress tensor with eqs (2) and (59) is rather simple. The characteristic relaxation time of the bond length becomes very short when $K \gg k_B T$. This means that we cannot simply take the overdamped limit. Thus we should consider the underdamped system as in the main text.

Even if we consider the underdamped system, the situation is not that clear. If the spring constant is very large, the quantum effect becomes non-negligible. This situation is similar to thermodynamic properties of the diatomic gases[19]. The specific heat of the diatomic gas consists of several different contributions. The vibrational motion of the bond contributes to the specific heat only at the relatively high temperature ($T \gg \hbar \omega$, with $\hbar$ being the reduced Planck constant and $\omega$ being the characteristic angular frequency of the vibration). If the temperature is relatively low ($T \ll \hbar \omega$), the specific heat coincides to that of rigid diatomic gases. This is because the vibration modes cannot take the excited states and the vibrational mode becomes essentially frozen.

The flexible dumbbell with a sufficiently stiff tethering potential has very large characteristic angular frequency ($\omega \to \infty$ at the limit of $K \to \infty$), and thus it will behave as the rigid dumbbell.

B Detailed Calculations

In this appendix, we show detailed calculations for some relations used in the main text. We show the calculations for the stress tensor of a single rigid dumbbell at the over damped limit, eq (25). To calculate the overdamped limit, we need to calculate the partial average over the bond momentum $p$. It is convenient to decompose the bond momentum into the parallel and perpendicular components: $p = p_\parallel + p_\perp$ with $p_\parallel = (rr/r^2) \cdot p$ and $p_\perp = (1 - rr/r^2) \cdot p$. Eq (24) can be rewritten as

$$\psi_{\text{eq}}(p|r) = \delta (p_\parallel) \frac{1}{2\pi mk_B T} \exp \left(- \frac{p_\parallel^2}{2mk_BT} \right). \tag{63}$$
Then stress tensor at the overdamped limit can be calculated as

$$\hat{\sigma}^{(\text{OD})}(r) = \int dp \psi_eq(p|r)\hat{\sigma}^{(\text{UD})}(r, p)$$

$$= \frac{1}{2\pi mk_B TV} \int dp_\parallel dp_\perp \delta(p_\parallel) \exp \left(-\frac{p_\parallel^2}{2mk_BT} \right) \times \left[ \frac{p_\perp^2}{mr^2} rr - \frac{(p_\parallel + p_\perp)(p_\parallel + p_\perp)}{m} \right]$$

$$(64)$$

$$= \frac{1}{2\pi mk_B TV} \int dp_\perp \exp \left(-\frac{p_\perp^2}{2mk_BT} \right) \left( \frac{p_\perp^2}{mr^2} rr - \frac{p_\perp p_\perp}{m} \right).$$

Here, $p_\perp$ is distributed on the two dimensional plane which is perpendicular to $r$. We express it as $p_\perp = \xi e_1 + \eta e_2$ with $e_1$ and $e_2$ being two orthogonal unit vectors which are perpendicular to $r$. $(|e_1| = |e_2| = 1, e_1 \cdot e_2 = 0, \text{ and } e_1 \cdot r = e_2 \cdot r = 0)$. We have the following relation:

$$\frac{1}{2\pi mk_B T} \int dp_\perp \exp \left(-\frac{p_\perp^2}{2mk_BT} \right) p_\perp p_\perp = \frac{1}{2\pi mk_B T} \int d\xi d\eta \exp \left(-\frac{\xi^2 + \eta^2}{2mk_BT} \right) \times [\xi^2 e_1 e_1 + \eta(e_1 e_2 + e_2 e_1) + \eta^2 e_2 e_2] = e_1 e_1 + e_2 e_2 = 1 - \frac{rr}{r^2}.$$  

In the last line of eq (65), we utilized the fact that the second order tensor $e_1 e_1 + e_2 e_2$ is the unit tensor on the two dimensional plane which is perpendicular to $r$. By combining eqs (64) and (65), we have eq (55) in the main text.

We show the calculations for eq (57). The correlation function for the bond vector can be analytically evaluated with several different methods. Here we calculate $\langle r_x(t)r_y(t) r_x(0)r_y(0) \rangle_{eq}$ by using the Fokker-Planck equation (44). We consider the situation where the initial bond vector is given as $r(0) = r_0$ and the external flow field is absent $\kappa(t) = 0$. Then eq (47) can be rewritten as

$$\frac{d\kappa_\parallel(t)}{dt} \cdot r(t) = \text{Tr} \kappa_\parallel(t) \left[ \frac{1}{m} p_\perp(t) + \kappa_\perp(t) \cdot r(t) \right] + \text{terms parallel to } r(t)$$

$$= \frac{\text{Tr} \kappa_\parallel(t)}{m} p_\perp(t) + O(||\kappa(t)||) + \text{terms parallel to } r(t).$$

(67)

The terms which are parallel to $r$ can be absorbed into the Lagrange multiplier. Thus we have eq (33) in the main text.

We show the calculations for eq (57). The correlation function for the bond vector can be analytically evaluated with several different methods. Here we calculate $\langle r_x(t)r_y(t) r_x(0)r_y(0) \rangle_{eq}$ by using the Fokker-Planck equation (44). We consider the situation where the initial bond vector is given as $r(0) = r_0$ and the external flow field is absent $\kappa(t) = 0$. Then eq (47) can be rewritten as

$$\frac{\partial \psi(r, t)}{\partial t} = \frac{k_B T}{\zeta} \frac{\partial}{\partial r} \cdot \left( 1 - \frac{rr}{r^2} \right) \frac{\partial \psi(r, t)}{\partial r},$$

(68)

and the initial condition is given as

$$\psi(r, 0) = \delta(r - r_0).$$

(69)
The initial bond vector should obey the equilibrium distribution (50). Then the correlation function can be rewritten as follows:

\[ \langle r_x(t)r_y(t)r_x(0)r_y(0) \rangle_{eq} = \int dr_0 \left[ \int dr r_x r_y \psi(r, t) \right] r_0 x r_0 y \psi_{eq}(r_0). \]  

(70)

We calculate the integral over \( r \) in eq (70), \( C_{xy}(r_0, t) \equiv \int dr r_x r_y \psi(r, t) \). From eq (68), we have

\[ \frac{\partial C_{xy}(r_0, t)}{\partial t} = \frac{k_B T}{\zeta} \int dr r_x r_y \frac{\partial}{\partial r} \left[ \left( 1 - \frac{rr}{r^2} \right) \frac{\partial \psi(r, t)}{\partial r} \right] \]

(71)

\[ = - \frac{k_B T}{\zeta} \int dr \psi(r, t) \left[ \frac{rr}{r^2} \frac{\partial (r_x r_y)}{\partial r} \right] \]

\[ = - \frac{6k_B T}{\zeta} \int dr \frac{r_x r_y}{r^2} \psi(r, t). \]

\( r^2 \) is constant during the time-evolution by the Fokker-Planck equation \( (r^2 = |r_0|^2 = b^2) \), and thus we have

\[ \frac{\partial C_{xy}(r_0, t)}{\partial t} = - \frac{6k_B T}{\zeta b^2} C_{xy}(r_0, t). \]  

(72)

Also, from the initial condition, we have \( C_{xy}(r_0, t) = r_0 x r_0 y \). Therefore we have the explicit expression for \( C_{xy}(r_0, t) \) as

\[ C_{xy}(r_0, t) = r_0 x r_0 y \exp \left( - \frac{6k_B T}{\zeta b^2} \right). \]  

(73)

From eqs (70) and (73), finally we have

\[ \langle r_x(t)r_y(t)r_x(0)r_y(0) \rangle_{eq} = \exp \left( - \frac{6k_B T}{\zeta b^2} \right) \frac{1}{4\pi b^2} \int dr_0 r_0^2 r_0^2 \delta(|r_0| - b) \]

\[ = \frac{b^4}{4\pi} \exp \left( - \frac{6k_B T}{\zeta b^2} \right) 2\pi \int_0^\pi d\phi \cos^2 \theta \sin^2 \theta \sin^5 \phi \]

(74)

\[ = \frac{b^4}{15} \exp \left( - \frac{6k_B T}{\zeta b^2} \right). \]

In eq (74) we have utilized the variable transform from \( r_0 \) to \( \theta \) and \( \phi \) defined via \( r_0 = [b \cos \theta \sin \phi, b \sin \theta \sin \phi, b \cos \phi] \). By substituting eq (74) into eq (57), we have eq (58) in the main text.

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