On the Microscopic Stress Tensor for Anisotropic Molecules in Homogeneous Systems *

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The flowing nematic liquid crystal is considered in the small velocity gradient approximation. The molecular expression for the stress tensor is improved by use of the procedure of Doi. The symmetric and antisymmetric parts of the microscopic stress tensor are shown to differ by the formfactor in comparison to forms which have been used so far. The consequences for the molecular hydrodynamic theories are considered.

1. Introduction

The expression for the microscopic stress tensor σ^{micr} is fundamental in the molecular theories describing the rheological properties of nematics. It represents an internal friction among nematic molecules and corresponds to the moment of force acting on a given molecule in the mean field produced by the whole system. Application of it to the statistical kinetic theory accounts for the dependence of viscous properties on molecular parameters.

In 1981 [1] Doi introduced a new idea of obtaining the microscopic stress tensor for anisotropic molecules. The method is based on the expression of the free energy for a system consisting of ellipsoidal molecules. The system undergoes the influence of a small velocity gradient field. This field causes a molecule to move along a periodic Jefferey's orbit with a certain angular velocity [2]. As a consequence, the distribution function and the free energy are changed. According to the elasticity theory, the change in the free energy should be equal to the inner product of the stress and the deformation tensors. The stress tensor appears to have the form of an average of a microscopic expression which can be regarded as the microscopic stress tensor σ^{micr}. It depends on orientations of molecules and the mean potential which acts on a given molecule in the system. The crucial point in this method is the expression for the angular Jefferey's velocity which originally contains a formfactor dependent on the length to width ratio of a molecule. In [1] this formfactor is omitted and the obtained microscopic stress tensor is simplified. For very long molecules this formfactor is meaningless, but this is not the case of realistic systems. In [3] Kuzuu and Doi use the right expression for Jefferey's angular velocity but, probably having in mind a simplified form of the stress tensor, they make an error in their calculations which leads to the same form but multiplied by the formfactor. This is correct only for the symmetric part of σ^{micr}. In [3] Kuzuu and Doi treat the microscopic stress tensor as completely symmetric because of the wrong assumption that the direct correlation function is dependent on the product of the orientations of molecules. The asymmetric part of the microscopic stress tensor does not emerge from their calculations. So far we have discussed the part of σ^{micr} due to the potential field. Taking into account the free energy connected with the existence of a magnetic field (Kuzuu, Doi [3]) one gets a part of σ^{micr} which is not completely symmetric. This is a trick which allows one to obtain the macroscopic asymmetric viscous stress tensor. But on the other hand, such a trick means that without magnetic field there is no asymmetry in the viscosity which, of course, is not true.

The purpose of this paper is to present a systematical derivation of the microscopic stress tensor by use of the Doi idea without introducing a magnetic field.

2. The Microscopic Stress Tensor

Let us consider a spatially homogeneous system of anisotropic molecules under the influence of a small velocity gradient field. The molecule is characterized by the length L and the diameter d; its long axis is parallel to the unit vector $\boldsymbol{a}$.

According to Onsager [4] the free energy A of the system per unit volume is expressed as

$$A = c\,k\,T \int f(\boldsymbol{a}, t)\,[\ln f(\boldsymbol{a}, t)]\,\mathrm{d}\boldsymbol{a} \qquad (2.1)$$
$$- c/2 \int K(\boldsymbol{a}_1, \boldsymbol{a}_2)\,f(\boldsymbol{a}_1, t)\,f(\boldsymbol{a}_2, t)\,\mathrm{d}\boldsymbol{a}_1\,\mathrm{d}\boldsymbol{a}_2,$$

where the orientational distribution function $f(\boldsymbol{a}, t)$ is the probability that the axis of an arbitrary molecule points into the direction of $\boldsymbol{a}$ at a time t.

Since a viscoelastic liquid behaves as elastic material for instantaneous deformation, we will analyze the change in the free energy caused by the small velocity gradient field.

The velocity gradient field rotates the molecule with a certain angular velocity $\boldsymbol{\Omega}$ which is given by [2]

$$\boldsymbol{\Omega} = \frac{p^2 - 1}{p^2 + 1}\,\boldsymbol{a} \times (\mathbf{A} \cdot \boldsymbol{a}) - \boldsymbol{a} \times (\mathbf{g} \cdot \boldsymbol{a}), \qquad (2.2)$$

where $p = L/d$, and $\mathbf{A}$ and $\mathbf{g}$ are the symmetric and asymmetric parts of the velocity gradient tensor $\mathbf{k} = (\Delta v)^+$, respectively:

$$A_{\alpha\beta} = 1/2\,(\partial_\alpha v_\beta + \partial_\beta v_\alpha),$$
$$g_{\alpha\beta} = 1/2\,(\partial_\alpha v_\beta - \partial_\beta v_\alpha). \qquad (2.3)$$

In the infinitesimal time δt the molecule will change its orientation by a small angle $\delta\boldsymbol{\theta}$:

$$\delta\boldsymbol{\theta} \doteq \boldsymbol{\Omega}\,\delta t = \boldsymbol{a} \times \frac{(p^2 \boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}^+) \cdot \boldsymbol{a}}{p^2 + 1}, \qquad (2.4)$$

where $\boldsymbol{\varepsilon} = \mathbf{k}\,\delta t$ can be regarded as a hypothetical small deformation tensor which moves a point from r_α to $r'_\alpha = r_\alpha + \varepsilon_{\alpha\beta}\,r_\beta$. The direction $\boldsymbol{a}$ of the individual molecule is then changed to $\boldsymbol{a}' = \boldsymbol{a} + \delta\boldsymbol{a}$, where $\delta\boldsymbol{a} = \boldsymbol{a} \times \delta\boldsymbol{\theta}$. Accordingly, the distribution function $f(\boldsymbol{a}, t)$ is changed from f_0 to f':

$$f' = f_0 + \delta f = f_0(\boldsymbol{a}) - \boldsymbol{\nabla}_a [\delta\boldsymbol{a}\,f_0(\boldsymbol{a})], \qquad (2.5)$$

where f_0 is the equilibrium distribution function, and the perturbation δf depends linearly on the time δt. The change in the free energy has the form

$$\delta(A) = c\,k\,T \int \delta f(\boldsymbol{a}, t)\,\mathrm{d}\boldsymbol{a} \qquad (2.6)$$
$$+ c\,k\,T \int \delta f \left(\ln f_0 - \frac{1}{k\,T} \int K(\boldsymbol{a}_1, \boldsymbol{a}_2)\,f_0(\boldsymbol{a}_2, t)\,\mathrm{d}\boldsymbol{a}_2 \right) \mathrm{d}\boldsymbol{a}_1.$$

On the other hand it can be expressed as

$$\delta(A) = \langle \boldsymbol{\sigma}^{\mathrm{micr}} \rangle : \varepsilon^+ + O(\varepsilon^2). \qquad (2.7)$$

Since the evaluation is performed near the equilibrium point, the director of the system is not changed as far as the first order terms of ε are concerned and we still deal with the uniform nematic. So the value of the free energy should not be changed. This is apparent from (2.6) because the term in the brackets is constant thanks to the condition of the free energy minimum in the equilibrium point and the vanishing of the integral of δf (see Appendix). The only benefit in analyzing the vanishing $\delta(\beta A)$ is that we can come up with information about the microscopic stress tensor, and that is what we are looking for. It should be remarked here that the microscopic stress tensor is not a kinetic term. It can be treated as a response of the viscoelastic material undergoing the influence of a small velocity gradient field.

The above evaluation of the free energy differs from that introduced by Kuzuu and Doi [3] by replacing the kinetic nonequilibrium distribution function f with the equilibrium function f_0. This was done on purpose to show that the microscopic stress tensor $\boldsymbol{\sigma}^{\mathrm{micr}}$ has nothing in common with the nonequilibrium problem. It is the macroscopic viscous stress tensor which is the result of the viscoelastic response of the system and the nonequilibrium kinetic distribution function.

Let us express the direction $\boldsymbol{a}$ of the long molecular axis in respect to the director $\boldsymbol{n}$ as

$$\boldsymbol{a} = \boldsymbol{n}\cos\theta + \boldsymbol{e}\sin\theta, \qquad (2.8)$$

where components of $\boldsymbol{e}$ are: $e_x = \cos\phi$, $e_y = \sin\phi$, $e_z = 0$ and $n_z = 1$, $n_x = n_y = 0$. The derivative $\partial/\partial\boldsymbol{a}$ reads

$$\frac{\partial}{\partial\boldsymbol{a}} = (\boldsymbol{e}\cos\theta + \boldsymbol{n}\sin\theta)\frac{\partial}{\partial\theta} + \frac{\boldsymbol{n} \times \boldsymbol{e}}{\sin\theta}\frac{\partial}{\partial\phi}. \qquad (2.9)$$

Using (2.9), one can derive the following rules for the operator $\partial/\partial\boldsymbol{a}$:

$$\frac{\partial}{\partial\boldsymbol{a}}(X\,Y) = Y\frac{\partial}{\partial\boldsymbol{a}}X + X\frac{\partial}{\partial\boldsymbol{a}}Y, \qquad (2.10)$$

$$\frac{\partial}{\partial a_\beta}a_\alpha = \delta_{\alpha\beta} - a_\alpha a_\beta, \qquad (2.11)$$

$$\int X\frac{\partial}{\partial\boldsymbol{a}}Y\,\mathrm{d}\boldsymbol{a} = \mathrm{surf} - \int Y\frac{\partial}{\partial\boldsymbol{a}}X\,\mathrm{d}\boldsymbol{a}$$
$$- 2\int(\boldsymbol{i}_\alpha \cdot \boldsymbol{a})\,X\,Y\,\mathrm{d}\boldsymbol{a}, \qquad (2.12)$$

where X and Y are some functions of θ, ϕ.

The rule (2.12) shows the way of the integration by parts, where surf denotes the surface term. The derivation of these rules one can find in [1]. For the purpose of handy calculation it is quoted in the Appendix. The rule of the integration by parts differs from that in the paper of Doi by the term

$$- 2 \int (i_x \cdot a) \, X \, Y \, da. \qquad (2.13)$$

In the particular case we are considering here, (2.13) vanishes because all contributions to it are proportional to

$$\varepsilon_{ijk} \, a_j \, a_i \, (a \times a)_k, \qquad (2.14)$$

which is zero. So, omitting the term (2.13) in the rule of the integration by parts is meaningless in that case.

The change in the orientation can be explicitly written as

$$\delta a_j = \frac{p^2 - 1}{p^2 + 1} (a_a \, a_b \, a_j \, \varepsilon_{ab}^+ - a_b \, \varepsilon_{jb}^+) - \frac{p^2}{p^2 + 1} a_b (\varepsilon_{jb} - \varepsilon_{jb}^+). \qquad (2.15)$$

Applying (2.10)–(2.12) and (2.15) to (2.6) we obtain

$$\langle \sigma^{\text{micr}} \rangle = \left\langle 3 \, c \, k \, T \frac{p^2 - 1}{p^2 + 1} \left(a_\alpha \, a_\beta - \frac{1}{3} \delta_{\alpha\beta} \right) \right. \qquad (2.16)$$
$$\left. + \left(\frac{p^2}{p^2 + 1} a_\alpha \frac{\partial U_{\min}}{\partial a_\beta} - \frac{1}{p^2 + 1} a_\beta \frac{\partial U_{\min}}{a_\alpha} \right) \right\rangle.$$

The expression within the brackets defines the microscopic stress tensor. It differs from the form which has been used so far [1, 3, 5, 6] by different factors containing the ratio p. Splitting (2.16) into the symmetrical and asymmetrical parts we eventually come up with the expressions

$$\sigma_{\alpha\beta}^{\text{asym}} = \frac{1}{2} \left(a_\alpha \frac{\partial U_{\min}}{\partial a_\beta} - a_\beta \frac{\partial U_{\min}}{\partial a_\alpha} \right), \qquad (2.17)$$

$$\sigma_{\alpha\beta}^{\text{sym}} = \frac{p^2 - 1}{p^2 + 1} \left(3 \, c \, k \, T \left(a_\alpha \, \alpha_\beta - \frac{1}{3} \delta_{\alpha\beta} \right) \right. \qquad (2.18)$$
$$\left. + \frac{1}{2} \left(a_\alpha \frac{\partial U_{\min}}{\partial a_\beta} - a_\beta \frac{\partial U_{\min}}{\partial a_\alpha} \right) \right).$$

Now we have the forms which are almost the same as those used so far but improved by the fact that only the symmetric part must be enriched by the formfactor $f(p) = (p^2 - 1)/(p^2 + 1)$.

3. Conclusions

In [3] the asymmetric part of the potential microscopic stress tensor is not taken into account at all. This is a result of the assumption that the correlation function $K(a_1, a_2)$ is dependent on the product $a_1 \cdot a_2$, which is not true. Kuzuu and Doi try to compensate the lack of the asymmetric part by introducing a magnetic field, suggesting that only the appearance of that field allows a symmetry break in the stress tensor. In the molecular theory by Osipov and Terentjev [5, 6] this mistake is improved and the asymmetric character of the microscopic stress tensor is taken into account. But the formfactor $f(p)$ is missing in the symmetric part. The main discrepancy which arises as a consequence of this ommision of the formfactor, is that the Parodi relation would not be fulfilled, and viscosity coefficients would be larger. For example, when the molecules have a ratio $p = 2$, the emerging mistake is about 40%.

In the case of disclike molecules, this formfactor may have a significant meaning because of its negative value, and omitting it can cause a change in sign for some viscosity coefficients.

Appendix

The infinitesimal change in the orientation a due to the small deformation $\varepsilon_{\alpha\beta}$ can be obtained from: $\delta a = a \times \delta \theta$:

$$\delta a_j = \frac{1}{p^2 + 1} \varepsilon_{klj} a_k [a_s (p^2 \varepsilon_{ab} - \varepsilon_{ab}^+) a_b \varepsilon_{\text{asl}}$$
$$= \frac{p^2 - 1}{p^2 + 1} [a_a \, a_j \, a_b \, \varepsilon_{ab}^+ - a_b \, \varepsilon_{jb}^+] \qquad (A-1)$$
$$+ \frac{p^2}{p^2 + 1} [a_a \, a_j \, a_b (\varepsilon_{ab} - \varepsilon_{ab}^+) - a_b (\varepsilon_{jb} - \varepsilon_{jb}^+)].$$

Because $\varepsilon_{jb} = \varepsilon_{bj}^+$, the variation δa_j reads

$$\delta a_j = \frac{p^2 - 1}{p^2 + 1} (a_a \, a_b \, a_j \, \varepsilon_{ab}^+ - a_b \, \varepsilon_{jb}^+) - \frac{p^2}{p^2 + 1} a_b (\varepsilon_{jb} - \varepsilon_{jb}^+). \qquad (A-2)$$

$a = n \cos \theta + e \sin \theta$, where the components of e are: $e_x = \cos \phi$, $e_y = \sin \phi$, $e_z = 0$ and $n_z = 1$, $n_x = n_y = 0$. The derivative $\partial / \partial a$ reads

$$\frac{\partial}{\partial a} = i_\theta \frac{\partial}{\partial \theta} + \frac{i_\phi}{\sin \theta} \frac{\partial}{\partial \phi}, \qquad (A-3)$$

where

$$i_\theta = \frac{\partial a}{\partial \theta} = \cos \theta \cos \phi \, i_x + \cos \theta \sin \phi \, i_y - \sin \theta \, i_z$$
$$= e \cos \theta - n \sin \theta \qquad (A-4)$$

and

$$i_\phi = \frac{1}{\sin\theta} \frac{\partial a}{\partial \phi} = -\sin\phi\, i_x + \cos\phi\, i_y = n \times e. \quad (A\text{-}5)$$

So we can write

$$\frac{\partial}{\partial a} = (e\cos\theta - n\sin\theta)\frac{\partial}{\partial\theta} + \frac{n \times e}{\sin\theta}\frac{\partial}{\partial\phi}. \quad (A\text{-}6)$$

Regarding that $\partial_\alpha = i_\alpha \cdot \partial/\partial a$, the following differential formulas are easily shown:

$$\partial_\alpha(X\,Y) = Y\,\partial_\alpha X + X\,\partial_\alpha Y, \quad (A\text{-}7)$$

where X, Y are some functions of θ, ϕ, and

$$\partial_\alpha a_\beta = \delta_{\alpha\beta} - a_\alpha a_\beta. \quad (A\text{-}8)$$

Integration with respect to $\mathrm{d}a$ gives:

$$\int X\,\mathrm{d}a = \int_0^\pi \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \sin\theta\, X,$$

$$\int X\,\partial_\alpha Y\,\mathrm{d}a = \int_0^\pi \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \sin\theta\, X \left(i_\alpha \cdot i_\theta \frac{\partial Y}{\partial\theta} + \frac{i_\alpha \cdot i_\phi}{\sin\theta}\frac{\partial Y}{\partial\phi} \right)$$

$$= \int_0^\pi \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi \left(\frac{\partial}{\partial\theta}(\sin\theta\, i_\alpha \cdot i_\theta X Y) + \frac{\partial}{\partial\phi}(i_\alpha \cdot i_\phi X Y) \right)$$

$$- \int_0^\pi \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi\, Y \left(\frac{\partial}{\partial\theta}(\sin\theta\, i_\alpha \cdot i_\theta X) + \frac{\partial}{\partial\phi}(i_\alpha \cdot i_\phi X) \right)$$

$$= -\int_0^\pi \mathrm{d}\theta \int_0^2 \mathrm{d}\phi\, Y \left(\cos\theta\, i_\alpha \cdot i_\theta X + \sin\theta \left(i_\alpha \cdot \frac{\partial}{\partial\theta} i_\theta \right) X \right.$$

$$\left. + \sin\theta\, i_\alpha \cdot i_\theta \frac{\partial X}{\partial\theta} + \left(i_\alpha \cdot \frac{\partial}{\partial\phi} i_\phi \right) X + i_\alpha \cdot i_\phi \frac{\partial X}{\partial\phi} \right)$$

$$= -\int Y\,\partial_\alpha X\,\mathrm{d}a - 2\int i_\alpha \cdot a\, X Y\,\mathrm{d}a, \quad (A\text{-}9)$$

where we have used

$$\frac{\partial}{\partial\theta} i_\theta = -a \quad \text{and} \quad \frac{\partial}{\partial\phi} i_\phi = -a\sin\theta - i_\theta\cos\theta.$$

Now we analyze the change in the free energy

$$\delta A = c\,k\,T \int \delta f(a,t)\,\mathrm{d}a \quad (A\text{-}10)$$

$$+ c\,k\,T \int \delta f \left(\ln f - \frac{1}{kT}\int K(a_1, a_2) f(a_2, t)\,\mathrm{d}a_2 \right)\mathrm{d}a_1.$$

Applying the rule of integration by parts to (A-10) one can derive the following expressions:

1) The first term:

$$\int \delta f(a,t)\,\mathrm{d}a = -\int a \times \frac{\partial}{\partial a}\cdot(\partial\theta f)\,\mathrm{d}a$$

$$= -\int \varepsilon_{ijk} a_i \partial_j(\delta\theta_k f)\,\mathrm{d}a \quad (A\text{-}11)$$

$$= \int \varepsilon_{ijk} \delta\theta_k f\, \partial_j a_i\,\mathrm{d}a + 2\int (i_j \cdot a)\varepsilon_{ijk} \delta\theta_k f\, a_i\,\mathrm{d}a$$

$$= \int \varepsilon_{ijk} \delta\theta_k f\,(\delta_{ij} - a_i a_j + 2 a_i a_j)\,\mathrm{d}a = 0.$$

2) The second term:

$$\int \delta f \ln f\,\mathrm{d}a = -\int a \times \frac{\partial}{\partial a}\cdot(\delta\theta f)\ln f\,\mathrm{d}a$$

$$= -\varepsilon_{ijk} \int a_i \partial_j(\delta\theta_k f)\ln f\,\mathrm{d}a$$

$$= \varepsilon_{ijk} \int \delta\theta_k f\, \partial_j(a_i \ln f)\,\mathrm{d}a + 2\varepsilon_{ijk}\int (i_j \cdot a)\delta\theta_k f\, a_i \ln f\,\mathrm{d}a$$

$$= \varepsilon_{ijk} \int \delta\theta_k f\,(\partial_j a_i \ln f + a_i \partial_j \ln f)\,\mathrm{d}a$$

$$= \varepsilon_{ijk} \int \delta\theta_k f\,[(\delta_{ij} - a_i a_j)\ln f + a_i\, 1/f\, \partial_j f]\,\mathrm{d}a$$

$$= \varepsilon_{ijk} \int \delta\theta_k a_i \partial_j f\,\mathrm{d}a = -\varepsilon_{ijk}\int f\, \partial_j(\delta\theta_k a_i)\,\mathrm{d}a$$

$$- 2\varepsilon_{ijk}\int f\, a_j \delta\theta_k a_i\,\mathrm{d}a = \langle \partial_j(\partial a_j) \rangle. \quad (A\text{-}12)$$

3) The third term:

$$\int \delta f\, K(a_1, a_2) f(a_2, t)\,\mathrm{d}a_2\,\mathrm{d}a_1$$

$$= \int U_{\min} \delta f\,\mathrm{d}a_1 = -\varepsilon_{ijk}\int U_{\min} a_i \partial_j(\delta\theta_k f)\,\mathrm{d}a_1$$

$$= \varepsilon_{ijk}\int \delta\theta_k f\, \partial_j(a_i U_{\min})\,\mathrm{d}a + 2\varepsilon_{ijk}\int \delta\theta_k f\, a_j a_i U_{\min}\,\mathrm{d}a$$

$$= \varepsilon_{ijk}\int \delta\theta_k f\,(U_{\min} \partial_j a_i + a_i \partial_j U_{\min})\,\mathrm{d}a$$

$$= \varepsilon_{ijk}\int \delta\theta_k f\,(a_i \partial_j U_{\min})\,\mathrm{d}a = -\langle \delta a_j \partial_j U_{\min} \rangle, \quad (A\text{-}13)$$

where we have used $\partial_j a_i = \delta_{ij} - a_i a_j$ and the antisymmetrical character of the tensor of ε_{ijk}: $\varepsilon_{ijk} a_j \delta\theta_k a_1 = 0$.

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