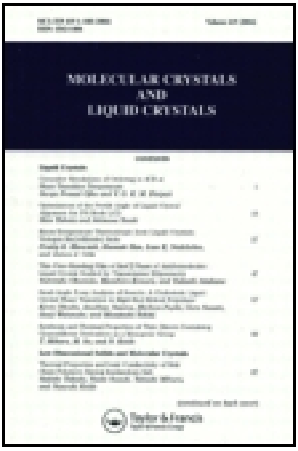

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On the Signs of the Leslie Viscosities α_2 and α_3 for Nematics and Discotic Nematics

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On the Signs of the Leslie Viscosities α_2 and α_3 for Nematics and Discotic Nematics

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The signs of the Leslie viscosities α_2 and α_3 for rod-like and disc-like molecules in the uniaxial nematic phase are discussed using a dynamic molecular mean field theory based upon a Fokker-Planck equation. The viscosities are shown to depend on the particle geometry and alignment order parameters. In particular, for positive degree of alignment S_2, the calculations tend to confirm Carlsson's conjecture relating the signs of the two viscosities to the particle geometry. Furthermore, a transition in the signs of α_2 for discotics and α_3 for nematics is predicted with increasing order parameter S_2 in accord with recent experiments. For small degree of alignment S_2, the results reproduce previous calculations obtained by Hess in a truncation approximation. The qualitative flow behaviour depends upon the signs of these viscosities.

Keywords: Liquid crystals; Leslie viscosities; mean-field theory; particle geometry

1. INTRODUCTION

The Ericksen-Leslie theory [1,2] for uniaxial nematic liquid crystals introduces for the stress tensor six viscosity coefficients α_i (called the Leslie viscosities). Only two of these Leslie coefficients appear in the director equation:

$$\mathbf{0} = (\mathbf{1} - \mathbf{nn}) \cdot [\mathbf{h} + (\alpha_2 - \alpha_3)\mathbf{N} - (\alpha_2 + \alpha_3)\,\mathbf{D}\cdot\mathbf{n}] \tag{1.1}$$

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where **n** is the director, **D** the symmetric strain rate tensor, **W** the skew symmetric spin tensor, $\mathbf{N} := \dot{\mathbf{n}} - \mathbf{W}\cdot\mathbf{n}$ the corotational time derivative of the director, and **h** the molecular field. Commonly, the sum and difference of α_2 and α_3 are called rotational viscosities and are denoted by

$$\gamma_1 := \alpha_3 - \alpha_2 \quad \gamma_2 := \alpha_2 + \alpha_3.$$

Carlsson [3,4] has discussed how the qualitative flow behavior (e.g., tumbling in shear flow) is determined primarily by the signs of the two Leslie coefficients α_2 and α_3. Since dissipation arguments [1] require that

$$\alpha_3 \geqslant \alpha_2, \tag{1.2}$$

there are thus three possibilities for the signs of α_2 and α_3:

(i) $0 \geqslant \alpha_3 \geqslant \alpha_2$, hence $\lambda > 1$ (i.e., aligned);
(ii) $\alpha_3 \geqslant 0 \geqslant \alpha_2$, hence $-1 < \lambda < 1$ (i.e., tumbling);
(iii) $\alpha_3 \geqslant \alpha_2 \geqslant 0$, hence $\lambda < -1$ (i.e., aligned),

where

$$\lambda := (\alpha_2 + \alpha_3)/(\alpha_2 - \alpha_3).$$

Whereas most known nematics belong to group i, Carlsson pointed out that there are some examples belonging to group ii. However, Carlsson also pointed out that no known nematics with rod-like molecules satisfy the third case where α_2 is positive. Based on calculations by Volovik [5], who obtained $\lambda \approx 1$ for ideal rod-like molecules and $\lambda \approx -1$ for infinitely thin disc-like molecules, Carlsson proposed that for *rod-like molecules*:

$\alpha_2 < 0$, α_3 positive or negative;

and that for *disc-like molecules:*

α_2 positive or negative, $\alpha_3 > 0$.

Previously, Hess [6] had calculated the γ_i's based on a truncation approximation to a Fokker-Planck equation, obtaining

$$\gamma_1 \propto S_2^2(1 - aS_2^2), \quad \gamma_2 \propto -\left(\frac{r^2-1}{r^2+1}\right) S_2(1 + bS_2 - cS_2^2), \tag{1.3}$$

where a,b,c are temperature dependent constants, r is the axis ratio, and S_2 is the degree of alignment order parameter. Note that (1.3) is also consistent with Carlsson's conjecture on the signs of α_2 and α_3 provided that S_2 is positive. A tensorial model of Farhoudi and Rey [7] for uniaxial, spatially homogeneous and monodomain nematics under shear flow indicated the appearance of tumbling, oscillating, and stationary flow regimes as the strength of shear increases even for disc-like particles.

The purpose of this paper is to calculate α_2 and α_3 (and hence, γ_i and λ) for rod-like and disc-like molecules. We use a mean field theory based on a Fokker-Planck equation to obtain expressions in terms of particle axis ratio r and the alignment order parameters S_2 and S_4. The procedure is direct and makes no use of an decoupling approximation between the moments of the uniaxial orientational distribution function. Our results support Carlsson's conjecture provided that the order parameter S_2 is positive. In the unusual case of negative S_2, the roles of rod-like and disc-like are reversed. Furthermore, transitions in the signs of α_2 for discotics and α_3 for nematics are predicted by varying S_2. Such a transition for discotics has in fact been recently observed. The result (1.3) of Hess is reproduced in the case of small order parameter S_2.

2. MEAN FIELD THEORY FOR NEMATICS

In mean field theory [6,8,9], we consider a single molecule having symmetry axis $\mathbf{u}$ ($|\mathbf{u}| = 1$) subject to a macroscopic flow $\nabla\mathbf{v} = \mathbf{D} + \mathbf{W}$. The time evolution of the alignment $\mathbf{u}$ is determined by a balance of torques: hydrodynamic, brownian, external, and mean field. It is given by

$$\dot{\mathbf{u}} = \mathbf{W}\cdot\mathbf{u} + B(1 - \mathbf{u}\mathbf{u})\cdot\mathbf{D}\cdot\mathbf{u} - D_r\nabla_{\mathbf{u}}(\log f + V/k_B T) \tag{2.1}$$

where D_r is the effective rotary diffusion coefficient, $f(\mathbf{u})$ is the orientation distribution function, $V(\mathbf{u})$ is the potential, and B is a function of the molecular axis ratio r:

$$B = \frac{(r^2 - 1)}{(r^2 + 1)}. \tag{2.2}$$

Rod-like molecules correspond to $0 < B < 1$, disc-like molecules to $-1 < B < 0$. Commonly the potential $V(\mathbf{u})$ is taken as

$$V(\mathbf{u}) = V_{mf}(\mathbf{u}) + V_{ext}(\mathbf{u}), \tag{2.3}$$

where

$$V_{\rm ext}(\mathbf{u}) = -\frac{1}{2}\chi_a(\mathbf{H}\cdot\mathbf{u})^2,$$

$$V_{\rm mf}(\mathbf{u}) = -\frac{3}{2}U_{\rm mf}k_B T\langle\mathbf{u}\,\mathbf{u}\rangle:\mathbf{u}\,\mathbf{u}.$$

$V_{\rm ext}$ denotes the contribution due to an induced dipole by an external field $\mathbf{H}$, χ_a being the anisotropic susceptibility, and $V_{\rm mf}$ denotes the mean-field contribution, $U_{\rm mf}$ being a constant reflecting the energy intensity of the mean field.

The orientation distribution function $f(\mathbf{u})$ thus obeys the Fokker-Planck equation:

$$\frac{\partial f}{\partial t} = \nabla_{\mathbf{u}}\cdot[fD_r\nabla_{\mathbf{u}}(\log f + V/k_B T)] - \nabla_{\mathbf{u}}\cdot[f\mathbf{W}\cdot\mathbf{u} + fB(\mathbf{1}-\mathbf{u}\mathbf{u})\cdot\mathbf{D}\cdot\mathbf{u}]. \quad (2.4)$$

The time evolution equation for the second moment of the alignment follows directly from the Fokker-Planck equation:

$$\frac{\partial}{\partial t}\langle\mathbf{u}\,\mathbf{u}\rangle = \mathbf{W}\cdot\langle\mathbf{u}\,\mathbf{u}\rangle - \langle\mathbf{u}\,\mathbf{u}\rangle\cdot\mathbf{W} + B(\mathbf{D}\cdot\langle\mathbf{u}\,\mathbf{u}\rangle + \langle\mathbf{u}\,\mathbf{u}\rangle\cdot\mathbf{D}) - 2B\mathbf{D}:\langle\mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u}\rangle$$

$$- D_r[\langle\mathbf{u}\nabla_{\mathbf{u}}(\log f + V/k_B T)\rangle + \langle\nabla_{\mathbf{u}}(\log f + V/k_B T)\,\mathbf{u}\rangle]. \quad (2.5)$$

This equation will provide us with the values for the viscosities α_2 and α_3.

3. LESLIE VISCOSITIES

In the case of uniaxial alignment, we have the following explicit expressions [10] for the moments:

$$\langle u_i u_j\rangle_{\rm uni} = S_2 n_i n_j + \frac{1}{3}(1-S_2)\delta_{ij} \quad (3.1)$$

and

$$\langle u_i u_j u_k u_l \rangle_{\text{uni}} = S_4 n_i n_j n_k n_l + \frac{1}{7}(S_2 - S_4)(\delta_{ij} n_k n_l + \delta_{ik} n_j n_l + \delta_{kj} n_i n_l + \delta_{il} n_j n_k + \delta_{jl} n_i n_k + \delta_{kl} n_i n_j) + \frac{1}{105}(7 - 10S_2 + 3S_4)(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) \tag{3.2}$$

where $\mathbf{n}$ denotes the axis of symmetry, and S_2 and S_4 are scalar measures of alignment related to the Legendre polynomials:

$$S_2 := \langle P_2(\mathbf{u}\cdot\mathbf{n})\rangle, \qquad S_4 := \langle P_4(\mathbf{u}\cdot\mathbf{n})\rangle.$$

They are subject to the restrictions

$$-\frac{1}{2} \leqslant S_2 \leqslant 1, \qquad -\frac{3}{7} \leqslant S_4 \leqslant 1. \tag{3.3}$$

Perfect alignment corresponds to $S_2 = S_4 = 1$, random alignment to $S_2 = S_4 = 0$. Inserting these expressions into (2.5) and taking the dot product with $\mathbf{n}$, we obtain the director equation:

$$\mathbf{0} = (\mathbf{1} - \mathbf{n}\mathbf{n})\cdot\left[\mathbf{h} - \frac{35ck_B TS_2^2}{D_r(14 + 5S_2 + 16S_4)}\mathbf{N} + \frac{Bck_B TS_2}{D_r}\mathbf{D}\cdot\mathbf{n}\right]. \tag{3.4}$$

The molecular field $\mathbf{h}$ is defined by [11]

$$\mathbf{n} \times \mathbf{h} := -c\langle \mathbf{u} \times \nabla_{\mathbf{u}} V\rangle$$

with c the number density of molecules. Comparing (1.1) and (3.4), we immediately obtain

$$\gamma_1 = \alpha_3 - \alpha_2 = \frac{ck_B T}{D_r}\frac{35 S_2^2}{14 + 5S_2 + 16S_4}, \quad \gamma_2 = \alpha_2 + \alpha_3 = -\frac{ck_B T}{D_r} B S_2. \tag{3.5}$$

Note that from (3.3) we always have

$$14 + 5S_2 + 16S_4 > 0, \tag{3.6}$$

thus (1.2) is always satisfied in accord with dissipation requirements. Additionally, (3.5) shows that γ_1 does not depend on B, whereas γ_2 is proportional to BS_2. Thus in the case of positive S_2, γ_2 is negative for rod-like molecules and positive for disc-like molecules. Note also that (3.5) is in agreement with the results (1.3) of Hess for small S_2. Finally, we obtain

$$\alpha_2 = -\frac{Bck_B T}{2D_r}(1+\lambda^{-1})\, S_2,$$

$$\alpha_3 = -\frac{Bck_B T}{2D_r}(1-\lambda^{-1})\, S_2,$$

$$\lambda = \frac{(14+5\,S_2+16\,S_4)\,B}{35S_2}. \tag{3.7}$$

Eqs. (3.7a,b) have been given by Kuzuu and Doi [9], and Eq. (3.7c) was recently derived in Ref. [11]. In the two limiting cases of perfectly aligned, infinitely long rods and perfectly aligned, thin plates, (3.7c) yields $\lambda = 1$ and $\lambda = -1$, in accord with Volovik [5].

We have assumed that under flow the distribution remains uniaxial, thus neglecting flow-induced biaxiality [12]. Consequently the additional non-stationary regimes (e.g., wagging) as discussed by Larson and Öttinger [13] are neglected. Archer and Larson [14] have taken into account numerically the flow-induced biaxiality showing that there can be a modest but significant effect on the coefficient (3.7c).

It follows from (3.6) that the signs are related by

$$\operatorname{sign}\lambda = \operatorname{sign}(BS_2),$$

thus we have for the viscosities

$$\operatorname{sign}\alpha_2 = -\operatorname{sign}(\lambda+1), \quad \operatorname{sign}\alpha_3 = -\operatorname{sign}(\lambda-1).$$

We can summarize as follows in terms of B and S_2:

$$BS_2 > 0: \quad \alpha_2 < 0 \quad \text{(i.e., groups i–ii)}$$

$$BS_2 < 0: \quad \alpha_3 > 0 \quad \text{(i.e., groups ii–iii)} \tag{3.8}$$

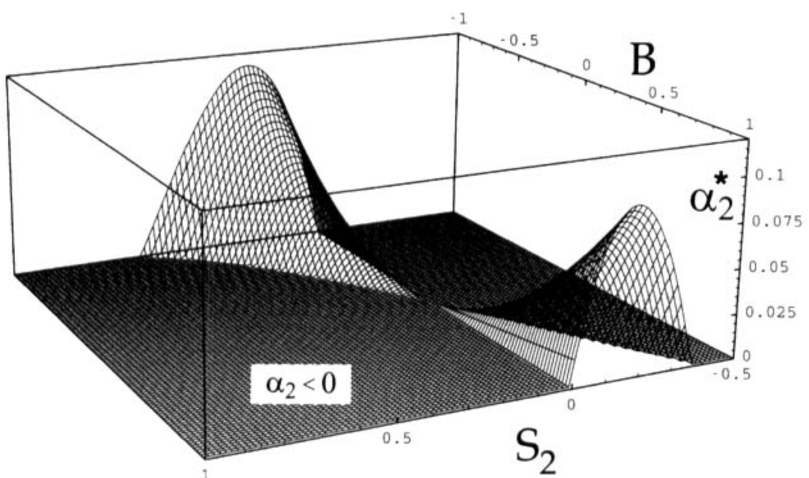
Provided that $S_2 > 0$, these results correspond exactly to the predictions of Carlsson. For $S_2 < 0$ the roles of rod-like and disc-like are reversed:

rod-like molecules: α_2 positive or negative, $\alpha_3 > 0$;
disc-like molecules: $\alpha_2 < 0$, α_3 positive or negative.

Further, for systems with $S_2 > 0$ Eq. (3.7) predicts a transition in sign of α_2 from positive to negative for discotics, and an opposite transition in sign of α_3 from negative to positive for nematics, with increasing degree of alignment order parameter S_2. These results are shown in Figures 1 and 2, where the closure relation [15] $S_4 = S_2 - S_2(1 - S_2)^\nu$ (with $\nu = 3/5$ according to a maximum entropy principle) has been used. Numerically, there is however no qualitative effect on the viscosities α_2 and α_3 in the choice of the exponent ν. (This closure relation however does not yield the negative values of S_4 that are commonly reported, e.g, Chandrasekhar [16].)

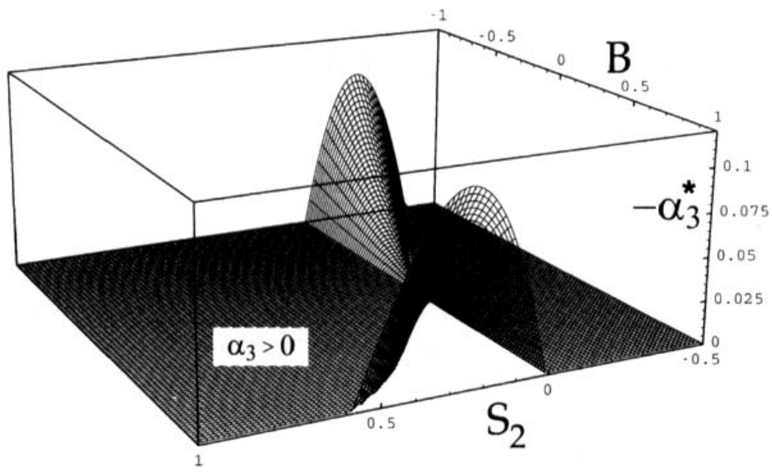
4. DISCUSSION

The Leslie coefficients α_2 and α_3 for nematics and discotic nematics have been calculated from a dynamic molecular mean field theory assuming only that the orientational distribution function f is uniaxial. This model yields all three



(a)

FIGURE 1 Plots of positive values of α_2^* (1a) and negative values of α_3^* (1b) versus B and S_2 The dimensionless viscosities are defined by $\alpha_i^* := \alpha_i D_r/(ck_B T)$.



(b)

FIGURE 1 (Continued).

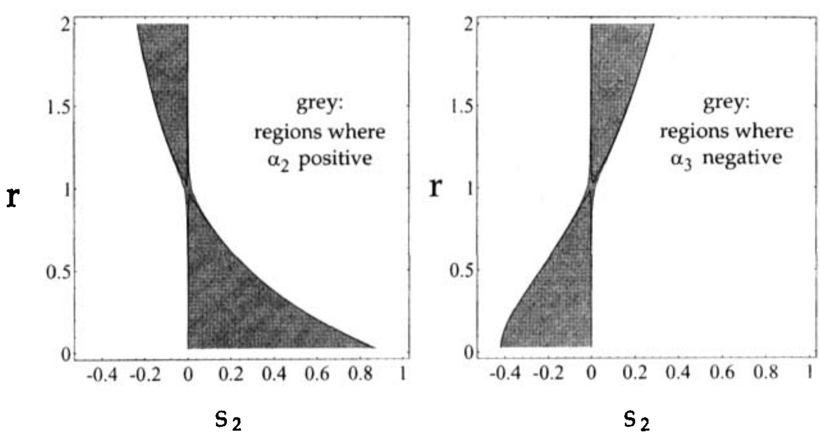


FIGURE 2 Signs of α_2^* and α_3^* as functions of axis ratio r and order parameter S_2. The dimensionless viscosities are defined by $\alpha_i^* := \alpha_i D_r/(ck_B T)$.

possible group ranges (i–iii) for the viscosities. In addition it is shown how the particle geometry and order parameters quantitatively affect the signs of α_2 and α_3, with BS_2 being the critical parameter. These results tend to confirm Carlsson's conjecture, provided that the degree of alignment S_2 is positive. Carlsson however did not consider the possibility of negative order parameters.

The coefficients α_2 and α_3 determine the type of flow via λ. For negative $\alpha_2 \alpha_3$ (i.e., $|\lambda| < 1$) there is no steady state solution in simple shearing. For positive $\alpha_2 \alpha_3$ the molecules will be aligned under shear flow, where the flow angle χ is given by $\cos 2\chi = \lambda^{-1}$. In Figure 3, we can see how the sign of $\alpha_2 \alpha_3$ varies with order parameter S_2 and geometry B (using the closure relation [15] $S_4 = S_2 - S_2 (1 - S_2)^{\nu}$ where $\nu = 3/5$, again there is no qualitative difference in the choice of the exponent ν).

A typical relaxation time [17] for reorientations of the director is given by

$$\tau = \frac{1}{u' \sqrt{\lambda^2 - 1}}$$

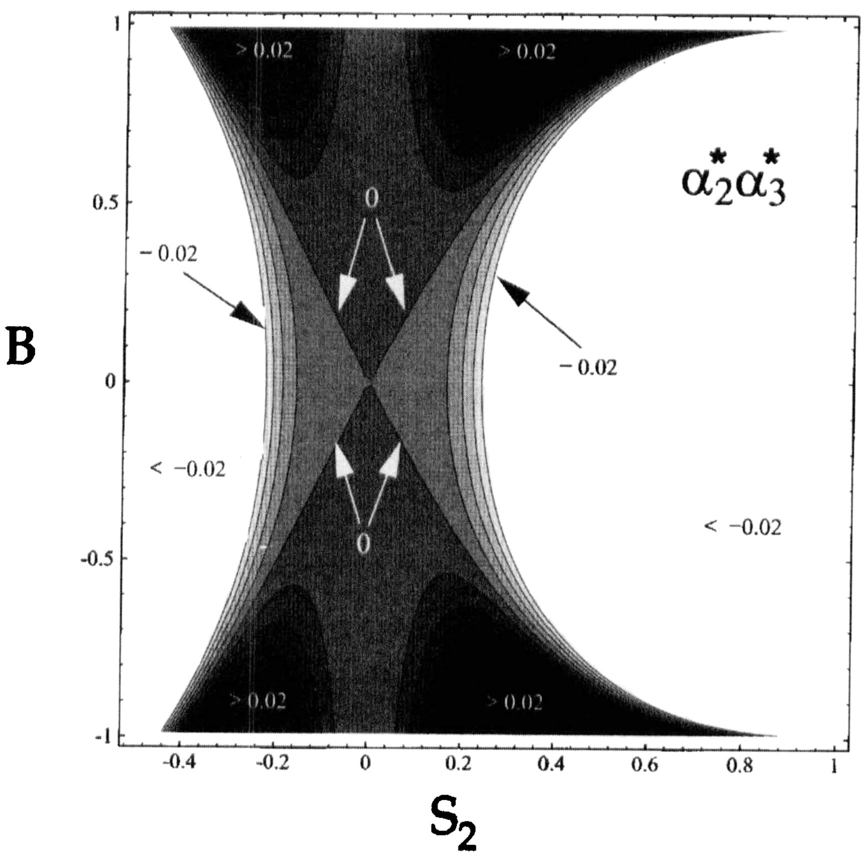


FIGURE 3 Contour plot of $\alpha_2 \alpha_3$ as a function of geometry B and order parameter S_2. Positive region corresponds to tumbling regimes, negative region to steady flow alignment. The dimensionless viscosities are defined by $\alpha_i^* := \alpha_i D_r / (c k_B T)$.

where u' is the shear rate. Thus from (3.7) τ is seen to be a function of the order parameters and the axis ratio.

We point out the Baals and Hess [18] proposed an alternative model for a fluid consisting of perfectly aligned ellipsoids. Their assumption was that the stress tensor of a perfectly aligned anisotropic fluid was related to that of an isotropic fluid by an affine, volume preserving variable transformation. This model also provides the viscosities in terms of the axis ratio. Recently this model has been extended to allow for partial alignment [15, 19]. In this case the viscosities are given by

$$\alpha_2 = \frac{\alpha_4}{2}\frac{4B}{B^2-1}(1+\lambda^{-1})\,S_2,$$

$$\alpha_3 = \frac{\alpha_4}{2}\frac{4B}{B^2-1}(1-\lambda^{-1})\,S_2,$$

$$\lambda = \frac{14+5\,S_2+16\,S_4}{35\,BS_2}. \tag{4.1}$$

Again, we have

$$\operatorname{sign}\lambda = \operatorname{sign} BS_2, \quad \operatorname{sign}\alpha_2 = -\operatorname{sign}(\lambda+1), \quad \operatorname{sign}\alpha_3 = -\operatorname{sign}(\lambda-1),$$

so that all three groups are predicted.

Although the affine model yields results for the viscosities that are quantitatively different from those obtained from the mean field model, the two models yield the same result for the signs of the two viscosities.

There is, as of yet, very few experimental data on discotics to make a detailed comparison with these theoretical predictions. However, a change in the sign of the viscosity α_2 for shear flows of discotics has been reported recently [20]. Such an effect could be attributed to a shear-dependent order parameter S_2, such that the alignment increases with increasing shear. As we have shown, at a certain critical alignment, α_2 should change sign.

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