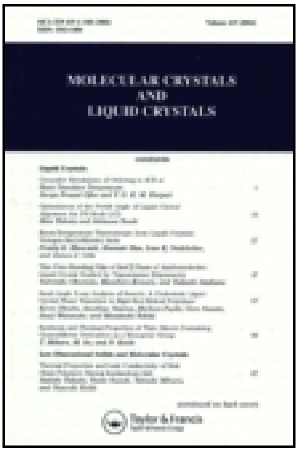

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 14 Jun 2011

To cite this article: A. N. Zakhlevnykh & O. R. Semenova (2011): First Order Orientational Transitions in Ferronematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 540:1, 219-226

To link to this article: http://dx.doi.org/10.1080/15421406.2011.568887

Mol. Cryst. Liq. Cryst., Vol. 540: pp. 219–226, 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.568887

First Order Orientational Transitions in Ferronematic Liquid Crystals

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The influence of external magnetic field on the orientational structure of a ferronematic liquid crystal is analyzed. We use modified Rapini potential for the anisotropic part of coupling energy between the ferronematic and the limiting surfaces. We show that under magnetic field action one of three ferronematics phases is possible: the uniform state, the disturbed state and the saturation state. We find that the transition between these ferronematic phases can be either the first- or the second order transition depending on the surface anchoring anisotropy and segregation parameter. We show the influence of the segregation effect on the orientational transitions in ferronematics.

Keywords Ferronematic; magnetic suspension; phase transitions; segregation effect

1. Introduction

Ferronematics are suspensions of needle-like ferromagnetic particles in nematic liquid crystals. For the first time the idea of creation of such a magnetic suspension on the base of liquid crystal has been proposed by Brochard and de Gennes in their classical work [1] from which the continuum theory of a ferronematic has begun. Nowadays these soft magnetic materials are intensively investigated both theoretically and experimentally [2–5]. The characteristic property of such a suspension is large magnetic susceptibility and the presence of strong orientational coupling between anisometric magnetic particles and liquid-crystalline matrix [1,3].

It is known, that the orientation of a liquid crystal molecules near the boundary of a layer can be described phenomenologically with the help of anchoring energy, which depends on the mutual orientation of the director $\boldsymbol{n}$ (i.e., the unit vector in the direction of average orientation of a liquid crystal molecules) and easy orientation axis $\boldsymbol{e}$. Usually for study of orientational behavior of liquid crystal cells in the external fields the surface anchoring energy write down in the form of Rapini potential [6]. This potential gives sufficient description of many effects observed in liquid crystal layers in the presence of limiting surface [7–9], but is not satisfactory for strong external fields, when essential deviations of the director from the easy

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orientation axis take place [8,10,11]. In that case the Rapini potential [6] must contain next order expansion terms which take into account the anchoring anisotropy of higher order. Such modification of the Rapini surface potential was already used for the analysis of phase transitions in pure nematic liquid crystals [10–13].

In the present paper we consider the influence of modified surface potential on the magnetic field induced orientational transitions in ferronematic layer.

2. Equilibrium Equations

We consider plane-parallel ferronematic cell of thickness L. We assume, that the limiting surfaces are identical to each other, the axis of easy orientation $\boldsymbol{e}$ is parallel to these surfaces and is directed along the x axis: $\boldsymbol{e} = (1, 0, 0)$. We choose the z axis perpendicularly to the boundaries of a layer so $z = 0$ corresponds to lower boundary, and $z = L$ corresponds to top boundary, an external magnetic field we direct along the limiting surfaces in the direction of the y axis: $\boldsymbol{H} = (0, H, 0)$ (see Fig. 1).

The equilibrium configurations of the director and magnetization are determined from the condition of minimum of full free energy of a ferronematic, including both bulk, and surface contributions:

$$F = \int F_b dV + \oint F_{sur} dS. \tag{1}$$

The bulk free energy density of a ferronematic is defined by the expression [1,14]

$$\begin{aligned} F_b =& \frac{1}{2}\left[K_{11}(\nabla \cdot \boldsymbol{n})^2 + K_{22}(\boldsymbol{n} \cdot \nabla \times \boldsymbol{n})^2 + K_{33}(\boldsymbol{n} \times \nabla \times \boldsymbol{n})^2\right] \\ & - \frac{1}{2}\chi_a(\boldsymbol{nH})^2 - M_s f \boldsymbol{mH} + \frac{W_p}{d} f(\boldsymbol{mn})^2 + \frac{k_B T}{\nu} f \ln f. \end{aligned} \tag{2}$$

Here K_{ii} are elastic constants, $\chi_a > 0$ is the anisotropy of the magnetic susceptibility, $\boldsymbol{H}$ is the external magnetic field strength, M_s is the saturation magnetization of a particle substance, ν is the volume of a particle, f is the local volume fraction of magnetic particles in a suspension, $\boldsymbol{m}$ is the unit vector in the direction of the magnetization $\boldsymbol{M} = M_s f \boldsymbol{m}$, d is the transverse diameter of a particle, T is the temperature, k_B is the Boltzmann constant, and W_p is the surface energy density of coupling between

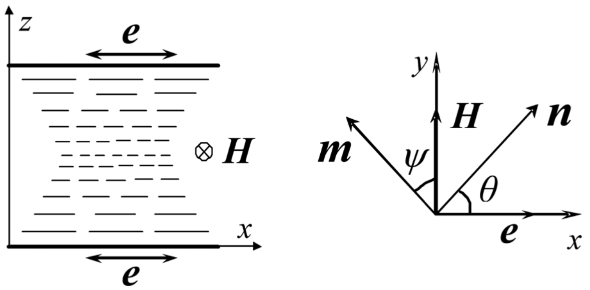

Figure 1. Orientation of the director $\boldsymbol{n}$ and the unit magnetization vector $\boldsymbol{m}$ under magnetic field $\boldsymbol{H} = (0, H, 0)$.

magnetic particles and nematic matrix. We suppose $W_p > 0$, in this case in the absence of a magnetic field the free energy is minimal at $\boldsymbol{m} \perp \boldsymbol{n}$ that corresponds to soft homeotropic coupling between the director and ferroparticles.

We assume that the surface potential on the boundaries of a layer has the following form [10–12]

$$F_{sur} = \frac{1}{2} W_0 (\boldsymbol{n} \times \boldsymbol{e})^2 \left[1 - \zeta (\boldsymbol{n} \times \boldsymbol{e})^2 \right], \tag{3}$$

where $W_0 > 0$ is the surface density of the anchoring energy, $\zeta \in [0,\ 1]$ is the additional parameter of surface anchoring anisotropy. For $\zeta = 0$ the potential F_{sur} coincides with the Rapini potential [6] and has one minima at $\boldsymbol{n} \| \boldsymbol{e}$, and in the case $\zeta = 1$ it has two minima's of equal depths at $\boldsymbol{n} \| \boldsymbol{e}$ and $\boldsymbol{n} \perp \boldsymbol{e}$. The first of them corresponds to the planar coupling between the director and the boundaries of the layer, the second one corresponds to homeotropic coupling.

The components of the director $\boldsymbol{n}$ and magnetization $\boldsymbol{m}$ can be written as (see Fig. 1)

$$\boldsymbol{n} = [\cos\theta(z),\ \sin\theta(z),\ 0], \quad \boldsymbol{m} = [-\sin\psi(z),\ \cos\psi(z), 0]. \tag{4}$$

We choose the thickness L of a cell as the unit of length, then $\tilde{z} = z/L$ is the dimensionless coordinate. We define the dimensionless parameters $\xi = M_s f_0 L / \sqrt{K_{22}\chi_a}$, $\kappa = L^2 k_B T f_0 / (\nu K_{22})$, $w_p = L^2 f_0 W_p / (K_{22} d)$, $w_0 = W_0 L / K_{22}$, the average concentration of magnetic particles in a suspension $f_0 = N\nu / V$ (N is the number of particles, V is the volume of a ferronematic) and dimensionless magnetic field $h = LH\sqrt{\chi_a / K_{22}}$. The parameters ξ and κ has been earlier discussed in Refs. [15–17]. The parameter ξ is the ratio of two characteristic fields [15]: $\xi = H_q / H_d$. Here $H_d = K_{22} / (M_s f_0 L^2)$ is the field at which the distortion of the director causes by the dipolar (ferromagnetic) mechanism; $H_q = L^{-1}\sqrt{K_{22}/\chi_a}$ is the characteristic field causing the distortion of the director under the action of the quadrupolar (diamagnetic) mechanism. For $\xi >> 1$ the orientational deformations are realized due to dipolar mechanism, and in the case $\xi << 1$ they are caused preferentially due to quadrupolar interactions. Therefore, the parameter ξ characterizes the modes of external field influence on a ferronematic. Parameter $\kappa = (L/\lambda)^2$, where $\lambda = \sqrt{\nu K_{22} / f_0 k_B T}$ is the so-called segregation length [1], gives the characteristic scale of concentration redistribution. Parameter κ is responsible for the segregation effect; for $\kappa >> 1$ this effect is negligible.

The equations of orientational equilibrium can be obtained from the conditions of minimum of total free energy (1)–(3):

$$\xi h \sin\psi = w_p \sin 2(\theta - \psi), \tag{5}$$

$$f = f_0 Q \exp\left\{ \frac{\xi h}{\kappa} \cos\psi - \frac{w_p}{\kappa} \sin^2(\theta - \psi) \right\}, \tag{6}$$

$$\tilde{z} = \int_{\theta_0}^{\theta(\tilde{z})} A^{-1/2}(\theta,\ \psi(\theta)) d\theta, \tag{7}$$

$$\int_{\theta_0}^{\theta_m} A^{-1/2}(\theta,\psi(\theta))d\theta = \frac{1}{2}, \tag{8}$$

$$A^{1/2}(\theta_0,\psi(\theta_0)) = \frac{1}{2} w_0 \sin 2\theta_0 \left[1 - 2\zeta \sin^2 \theta_0\right], \tag{9}$$

where $A(\theta,\ \psi(\theta)) = h^2(\sin^2\theta_m - \sin^2\theta) + 2\kappa(f_m - f)/f_0$; $\theta_0 = \theta(\tilde{z})|_{\tilde{z}=0}$; $\theta_m = \theta(\tilde{z})|_{\tilde{z}=1/2}$; $f_m = f(\tilde{z})|_{\tilde{z}=1/2}$. The parameter Q is determined from the condition of conservation of particles number in a suspension $\int f dV = N\nu$.

The set of equilibrium Equations (4–9) has three types of solutions which correspond to three kinds of orientational states:

1. *The uniform state* $\theta = \psi = 0$ of a ferronematic for which $\boldsymbol{n}||\boldsymbol{e}$ and $\boldsymbol{m}\perp\boldsymbol{n}$ (the so-called ferronematic phase with homeotropic type of coupling between the director and magnetization [18]). This state can exist at $h \le h_F$, where h_F is the Freedericksz field determined by the equations

$$\lambda \tan\frac{\lambda}{2} = w_0, \quad \lambda = \sqrt{h_F^2 - \frac{2w_p\xi h_F}{2w_p + \xi h_F}}. \tag{10}$$

2. The disturbed state of a ferronematic is described by non-uniform solution $0 < \theta(\tilde{z}) < \pi/2$. Here the director and magnetization are no longer perpendicular; the angle between them decreases with the field increasing. Such a phase is known [18] as angular ferronematic phase. This state is possible for $h_F < h < h_S$, where the saturation field h_S can be determined from the equations

$$\alpha \tanh\frac{\alpha}{2} = w_0(1 - 2\zeta), \quad \alpha = \sqrt{h_S^2 + \frac{2w_p\xi h_S}{2w_p - \xi h_S}}. \tag{11}$$

3. The saturation state $\theta = \pi/2$, $\psi = 0$ for which $\boldsymbol{n}||\boldsymbol{m}||\boldsymbol{H}$ (the so-called ferronematic phase with planar type of coupling between the director and magnetization [18]), which is possible at $h \ge h_S$.

For magnetic suspension of $\gamma-\mathrm{Fe_2O_3}$ particles on the base of nematic MBBA [19,20] with the magnetization of saturation $M_s \approx 370\,\mathrm{G}$, the particle diameter $d \approx 7\cdot 10^{-6}\,\mathrm{cm}$, the particle volume $\nu \approx 2\cdot 10^{-15}\,\mathrm{cm}^3$, the average concentration of magnetic particles $f_0 \approx 10^{-6}$, with $K_{22} \approx 3\cdot 10^{-7}\,\mathrm{dyn}$, $\chi_a \approx 1\cdot 10^{-7}$ SGSE units, and for the cell thickness $L = 10^{-2}\,\mathrm{cm}$, the dimensionless parameters ξ and κ have the values $\xi \approx 20$ and $\kappa \approx 10^{-2}$.

3. Orientational Structure of a Ferronematic in a Magnetic Field

The set of orientational state Equations (5–9) has been solved numerically; some results we demonstrate below. In Figure 2 the dependence $\theta_m(h)$ is shown for ferronematic with $\xi = 5$, $\kappa = 4\cdot 10^{-4}$, $w_p = 0.05$, $w_0 = 10$, and different values of surface energy anisotropy ζ.

As is seen from Figure 2, in the case $\zeta = 0$ corresponding to Rapini potential, the uniform state $\theta_m = 0$ [see *ab* part of the curve $\theta_m(h)$] is stable for $h \le h_F = 2.64$. At $h = h_F$ [see Eq. (10)] the second order Freedericksz transition takes place between the uniform state $\theta_m = 0$ and the disturbed state $\theta_m \neq 0$ (see *bc* part of the curve).

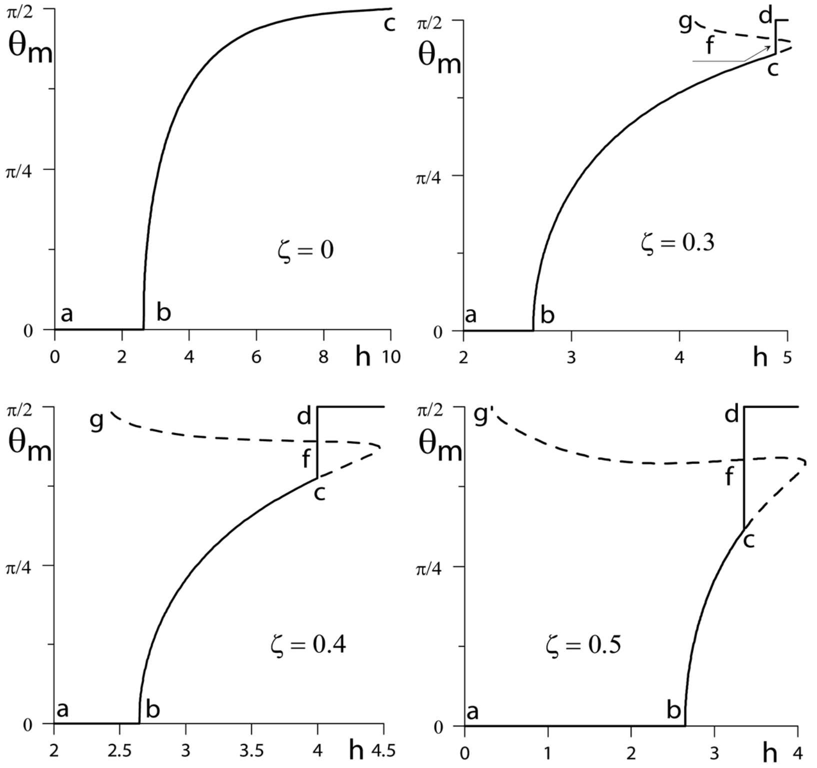

Figure 2. The dependences $\theta_m(h)$ at $\xi = 5$, $\kappa = 4 \cdot 10^{-4}$, $w_p = 0.05$, $w_0 = 10$ and different values of parameter of surface coupling anisotropy ζ.

For $h_F < h < h_S$ the disturbed phase is absolutely stable (*bc* part of the curve), and at $h = h_S = 10.01$ [see Eq. (11)] there is the second order transition between the distorted state and the saturation state $\theta_m = \pi/2$ ($\sin^2 \theta_m$ plays the role of the order parameter). As it is seen from Figure 2, in the case $\zeta \neq 0$, corresponding to the modified surface potential (3), the uniform state ($\theta_m = 0$) is absolutely stable [see parts *ab* of the curves $\theta_m(h)$] at $h < h_F$. At $h = h_F$ (point *b*) the uniform state is replaced by the disturbed state, similar to the case $\zeta = 0$. At $h_F < h < h_C$, where h_C is the field corresponding to the point *c*, the disturbed state (see part *bc* of the curve) is absolutely stable. At $h = h_C$ the first order transition between the distorted state and the saturation state ($\theta_m = \pi/2$) takes place, and the jump of the order parameter between the distorted state and the saturation state occurs (the jump is shown by vertical lines *cd*). The part *cfg* of the curve, shown in Figure 2 (at $\zeta \neq 0$) by dashed line, corresponds to unstable state and defines the area of multivaluedity of the function $\theta_m(h)$, which is typical for the first order transition. Stable branches of the curves $\theta_m(h)$, corresponding to the minimum of full free energy (1), are shown by solid lines in Figure 2.

As it is seen from Figure 2, the decrease in the parameter of surface energy anisotropy ζ leads to decrease in the jump of the order parameter at the transition point $h = h_C$ and for the chosen values of material parameters the jump diminishes at $\zeta^* = 0.17$. Thus, ζ^* is the tricritical value for the parameter of surface energy anisotropy at which the character of the phase transition changes: at $\zeta \leq \zeta^*$ the orientational transition between the disturbed phase and the saturation state is the second order transition, and at $\zeta > \zeta^*$ it is of the first order.

The calculations show that as ζ increases, the jump of the order parameter increases and culminates at maximal value for $\zeta = \zeta^{**} > \zeta^*$. This second threshold value of the parameter ζ can be found from the formula

$$\zeta^{**} = 1 - \frac{h_F^2 - 2w_p}{2w_0},$$

where h_F is the Freedericksz field determined by Eq. (10). At $\zeta \geq \zeta^{**}$ there is the first order transition from the uniform ferronematic state directly into the saturation state, escaping the disturbed state. Therefore in this case the jump of the angle θ_m is equal to $\pi/2$.

Figure 3 shows the threshold fields h_F, h_C and h_S as functions of surface energy anisotropy parameter ζ for ferronematic with $\xi = 5$, $\kappa = 4 \cdot 10^{-4}$, $w_p = 0.05$, and $w_0 = 10$. The tricritical value $\zeta^* = 0.17$ corresponds to the crossing point of the curves $h_S(\zeta)$ and $h_C(\zeta)$. The second threshold value $\zeta^{**} = 0.65$ corresponds to the crossing point of the curves $h_F(\zeta)$ and $h_C(\zeta)$. The curve $h_C(\zeta)$ is the bottom boundary of stability area for the saturation state, for $\zeta < \zeta^{**}$ the curves $h_C(\zeta)$ and $h_F(\zeta)$ limit the area where the disturbed state is stable, and the region between the abscises axis and the curve $h_F(\zeta)$ corresponds to the stable uniform state. For $\zeta \geq \zeta^{**}$ the uniform state is stable below the curve $h_C(\zeta)$, and above the curve $h_C(\zeta)$ the saturation state is stable. For $\zeta \geq \zeta^{**}$ the field h_C can be determined from the expression

$$h_C = \sqrt{2w_p + 2w_0(1 - \zeta)}.$$

Let us consider the influence of segregation effect on the orientational behavior of a ferronematic near the Freedericksz transition point. This effect follows from

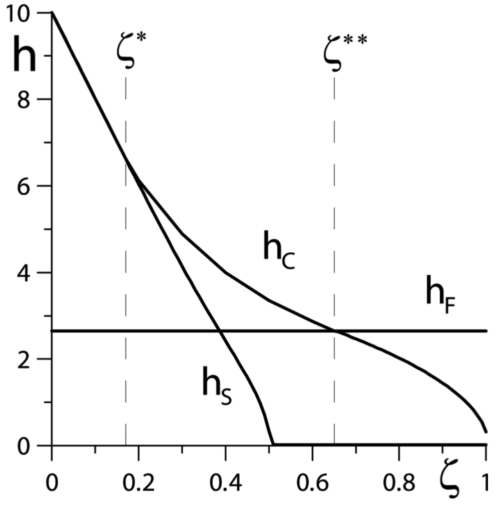

Figure 3. The threshold fields h_F, h_C and h_S as functions of surface coupling anisotropy parameter ζ for ferronematic with $\xi = 5$, $\kappa = 4 \cdot 10^{-4}$, $w_p = 0.05$ and $w_0 = 10$.

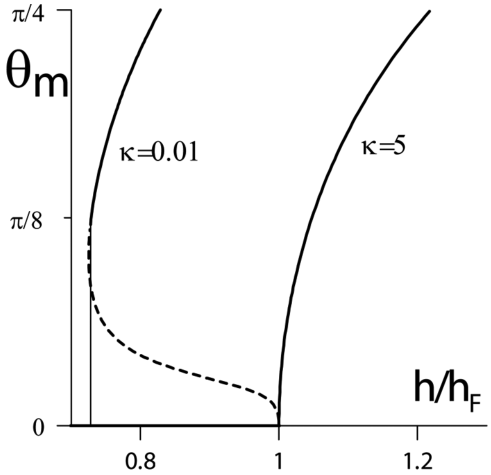

Figure 4. Dependence $\theta_m(h)$ for a ferronematic with $\xi = 5$, $w_p = 10$, $w_0 = 1$ and various values of the segregation parameter κ. Here h_F is the Freedericksz field.

Eq. (6) and corresponds to the tendency of magnetic particles to accumulate in those parts of a sample where the sum of their magnetic energy in the field ***H*** and orientational energy in the nematic matrix is minimal, migrating here from the regions with unfavorable orientation.

As it is seen from Eq. (10), the Freedericksz field h_F does not depend on the parameter of surface energy anisotropy ζ, therefore we consider the case $\zeta = 0$, corresponding to Rapini potential [10]. Results of numerical calculation of Eqs. (4)–(9) in the case of rather rigid coupling between the ferroparticles and nematic molecules ($w_p = 10$) near the Freedericksz transition are shown in Figure 4. It is seen that for weak magnetic segregation ($\kappa > \kappa^* = 0.511$) the Freedericksz transition between the uniform and disturbed phase is the second order transition, as well as the Freedericksz transition in pure liquid crystals [20]. In the case of strong segregation ($\kappa \le \kappa^*$) the Freedericksz transition in ferronematic becomes the first order transition and ferronematic observes the orientational bistability. Thus, κ^* determines the so-called tricritical point at which the character of the transition between the uniform state and disturbed state changes from the second to the first order. Such a tricritical behavior as a result of segregation phenomena in ferronematics has been recently found in Ref. [5]. in rather different geometry.

4. Conclusions

In the present work the influence of surface energy anisotropy on the magnetic field induced orientational transitions in a ferronematic layer is investigated. The surface potential has been chosen in the form (3). It is shown, that for fixed energy of surface coupling on the boundary of a layer the increase of external magnetic field leads to orientational transitions between the uniform state, the disturbed state, and the saturation state. The equations determining the critical fields of the transitions are received and dependences of critical fields on material parameters of a ferronematic and parameter of surface energy anisotropy are found.

It is shown, that in the dependence on the value of additional parameter ζ of surface energy anisotropy the transition between the disturbed and saturation states can be either the first, or the second order. The threshold values ζ^* and ζ^{**} of surface energy anisotropy parameter are found: at $\zeta > \zeta^*$ the first order transition between the disturbed state and the saturation state takes place, and at $\zeta \geq \zeta^{**}$ there is the first order transition from the uniform state directly in the saturation state. It is shown, that the growth of ζ leads to the increase in order parameter jump at the point of first order transition.

The influence of segregation effect on orientational properties of a ferronematic is also considered. We show that tricritical behavior of ferronematic near the Freedericksz transition takes place: for strong segregation the transition between the uniform and distorted states is the first order transition, and when the segregation is weak, the Freedericksz transition becomes the second order transition.

Acknowledgment

This work was supported by grant No. 10-02-96030 from Russian Foundation for Basic Research.

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