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Liquid Crystals

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 11 November 2010

To cite this Article Guochen, Yang and Suhua, Zhang(2002) 'The first order Freedericksz transition at saturation point for weak anchoring NLC cells', Liquid Crystals, 29: 5, 641 — 646 To link to this Article: DOI: 10.1080/02678290110120605 URL: http://dx.doi.org/10.1080/02678290110120605

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The first order Fréedericksz transition at saturation point for weak anchoring NLC cells

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(Received 16 July 2001; in final form 10 November 2001; accepted 12 November 2001)

On the basis of the modified Rapini–Papoular expression for the anchoring energy, the properties of the transition at saturation point for weak anchoring NLC cells has been studied analytically. We find that this transition may be of second order, as is usually predicted by many authors; however, it may also be first order. Whether it is first or second order is determined by the material, anchoring energy and thickness of the cell. The conditions for first order transition are deduced by an analytical method, and the results of calculation are shown by graph for $\kappa (= K_{11}/K_{33})$ values 0.8, 0.6 and 0.4. The saturation field strengths for the first order transition case are calculated and shown in the table.

1. Introduction

The first order liquid crystal (LC) texture transition has received a great deal of attention [1, 2]. Several devices using weak anchoring have been proposed, and the transition properties for this weak anchoring case constitute an important subject from both academic and applications viewpoints. Dozov and Martinot-Lagarde [3] have presented experimental evidence for a first order transition in the case of tilted weak anchoring of 5CB on substrates with evaporated SiO. Recently, Yang Guochen *et al.* [4] have proposed that a first order Fréedericksz transition at the threshold point may be possible for weak anchoring NLC cells. In this paper, we now propose that a first order transition at saturation point may also be possible.

In fact, the LC texture in NLC cells may undergo two transitions as the external field increases. The director **n** and its uniform distribution do not change when the field is small; when the field increases to a definite value, the director **n** and its distribution start to change. This value is called the threshold field strength. If we use a number axis showing the value of the field, the point corresponding with the threshold field is called the threshold point. If the field continues to increase, the deviation of the director and its distribution change continuously, until the field reaches another definite value, with the director **n** parallel to the direction of the external field and its distribution again uniform. This higher value is called the saturation field strength; the corresponding axis point is called the saturation point.

Rapini and Papoular have proposed a simple phenomenological expression for the anchoring energy per unit area [5]:

$$g_s = \frac{1}{2}A\sin^2\theta \qquad (1a)$$

where θ is the angle between the easy direction **e** and the direction **n** of the NLC at the nematic–wall interface, and A is the anchoring strength. This is the so-called RP formula; it describes many effects successfully in the presence of a surface. However, the results calculated from the RP formula do not agree well with experimental observations in some cases (for instance, the distortions of the director in strong external fields) [6]. Many authors have introduced new anchoring energy forms to replace the RP formula (1 a) [7–13]. If we assume that the primary approximation of g_s is the RP formula (1 a), we can suppose that g_s can be expressed by a power series of $\sin^2 \theta$ and that only the lower order is included. Then the modified g_s can be expressed as

$$g_{\rm s} = A \, \sin^2 \theta (1 + \zeta \, \sin^2 \theta), \tag{1b}$$

where ζ is a modification parameter. $\zeta > 0$ means the $g_s - \sin^2 \theta$ curve is steeper than that for $\zeta = 0$; $\zeta < 0$ means this curve is flatter than that for $\zeta = 0$. $\zeta = 0$ expresses well the RP formula. By now the anchoring energy form (1 *b*) has been accepted by most authors [14].

For transition at the saturation point, many authors [15] hold that it must be a second order transition, so that the director \mathbf{n} and its distribution change continuously at the transition point, and the formula of the saturation field is obtained from this view. Now we will prove that a first order transition may occur under certain conditions at the saturation point; the director \mathbf{n} and its distribution then change discontinuously at the transition point.

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On the basis of the modified Rapini-Papoular expression for the anchoring energy, we study analytically the transition properties at saturation point for the weak anchoring NLC cell. In §2, we obtain fundamental equations and discuss their solutions. In §3, we give the numerical calculation results, showing that the transition at saturation point may be second order, as usually predicted, but may also be first order. In §4, we study the saturation field strength for the second order transition. Whether the transition is first or second order is determined by material parameters, and the anchoring energy and thickness of the cell. The conditions for first order transition are deduced by means of an analytical method. In §5 the calculation results are shown graphically for $\kappa (= K_{11}/K_{33})$ values 0.8, 0.6 and 0.4. In §6, the saturation field strength for the first order transition is calculated and shown in the table.

2. Fundamental equations and solutions

For a typical NLC cell [4], two substrates lie in the Z = 0 and Z = 1 planes. Assuming the two substrates are identical, the easy direction **e** in both substrates is parallel to the direction of the X axis, and surface energy takes the form of equation (1 b). The applied field is parallel to the Z axis.

We use literature notation [4], but take θ as the polar angle; this is more convenient in discussing the transition at the saturation point. θ is a function of Z, written as $\theta(Z)$. The Gibbs free energy per unit volume in the cell can be written:

$$g_{\rm b} = \left(\frac{1}{2}K_{11}\sin^2\theta + \frac{1}{2}K_{33}\cos^2\theta\right) \left(\frac{\mathrm{d}\theta}{\mathrm{d}z}\right)^2 - \frac{1}{2}\chi_{\rm a}\mathbf{H}^2\cos^2\theta \qquad (2)$$

where K_{11} , K_{33} are Frank splay and bend elastic constants, respectively, and χ_a is the magnetic anisotropy of the NLC medium. The surface energy per unit area can be expressed as:

$$g_{s}|_{z=0} = \frac{A}{2} \cos^{2} \theta_{0} (1 + \zeta \cos^{2} \theta_{0})$$
(3)

$$g_{s}|_{z=1} = \frac{A}{2} \cos^{2} \theta_{1} (1 + \zeta \cos^{2} \theta_{1})$$
 (4)

where θ_0 is the value of θ at Z = 0; θ_1 is the value of θ at Z = 1. And the total energy of the system is:

$$G = S \int_{0}^{1} g_{b} dz + Sg_{s}|_{z=0} + Sg_{s}|_{z=1}$$
(5)

where S is the area of the substrate.

Applying the calculus of variations [16], we obtain the equation of θ :

$$(K_{11}\sin^2\theta + K_{33}\cos^2\theta)\frac{d^2\theta}{dz^2} - (K_{33} - K_{11})\cos\theta\sin\theta\left(\frac{d\theta}{dz}\right)^2 - \chi_a \mathbf{H}^2\sin\theta\cos\theta = 0$$
(6)

with the boundary condition:

$$(K_{11}\sin^2\theta_0 + K_{33}\cos^2\theta_0)\frac{\mathrm{d}\theta}{\mathrm{d}z}\Big|_{z=0}$$

= $-A\cos\theta_0\sin\theta_0(1+2\zeta\cos^2\theta_0).$ (7)

Equation (6) with the boundary condition (7) has three solutions. Two are trivial solutions. The solutions and corresponding Gibbs free energy are as follows:

(I) uniform solution: $\theta \equiv \pi/2$

$$G_{\rm u} = 0 \tag{8}$$

(II) saturation solution: $\theta \equiv 0$

$$G_{\rm s} = \left[-\frac{1}{2} \chi_{\rm a} \mathbf{H}^2 + A(1+2\zeta) \right] S \tag{9}$$

(III) disturbed solution: $\theta = \theta(z)$, where θ satisfies

$$\frac{\mathrm{d}\theta}{\mathrm{d}z} = -\mathbf{H} \left[\frac{\chi_{\mathrm{a}}(\cos^2\theta_{\mathrm{m}} - \cos^2\theta)}{K_{11}(1 + \gamma\cos^2\theta)} \right]^{1/2}, \quad \left(z < \frac{1}{2}\right)$$
(10)

and the boundary condition

$$(1 + \gamma \cos^2 \theta_0) \mathbf{H} \left[\frac{\chi_a K_{11} (\cos^2 \theta_m - \cos^2 \theta_0)}{1 + \gamma \cos^2 \theta_0} \right]$$
$$= A \cos \theta_0 \sin \theta_0 (1 + 2\zeta \cos^2 \theta_0)$$
(11)

$$G_{\theta} = \left[\frac{1}{2}\chi_{a}\mathbf{H}^{2}\cos^{2}\theta_{m} - 2\chi_{a}\mathbf{H}^{2}\int_{0}^{1}\cos^{2}\theta\,dz + A\cos^{2}\theta_{0}(1+\zeta\cos^{2}\theta_{0})\right]S$$
(12)

where $\theta_{\rm m}$ is the value at Z=1/2, and $\gamma=(K_{33}-K_{11})/K_{11}$.

We now discuss the stable solution, with the external magnetic field **H** increasing from 0. If **H** is small, G_u is the smallest among G_u , G_s and G_{θ} , and the stable solution is the uniform solution (8). As **H** increases continuously and is equal to or bigger than \mathbf{H}_{th} (the threshold field strength), G_{θ} is equal to or smaller than G_u , but smaller than G_s ; the stable solution is then the

disturbed solution (12). When **H** is equal to or greater than \mathbf{H}_{sat} (the saturation field strength), G_s is equal to or smaller than G_{θ} , and if G_s is the smallest, the stable solution is the saturation solution (9).

We see that the saturation field strength may be decided by:

$$\mathbf{H} \ge \mathbf{H}_{\text{sat}}; \quad G_{\text{s}} - G_{\theta} \le 0. \tag{13}$$

From (13), the conditions for first order transition can also be obtained.

3. Numerical calculation

We now discuss the solution of equations (6) and (7) for both first and second order transitions by means of numerical calculation.

Defining parameters and variable:

$$u = \sin^2 \theta_{\rm m}, \quad v = \frac{\sin^2 \theta_{\rm m}}{\sin^2 \theta}, \quad v_0 \frac{\sin^2 \theta_{\rm m}}{\sin^2 \theta_0} \tag{14}$$

and the reduced field *h*, the reduced anchoring strength α :

$$h = \frac{\mathbf{H}}{\mathbf{H}_{c}^{0}}, \quad \mathbf{H}_{c}^{0} = \frac{\pi}{l} \left(\frac{K_{11}}{\chi_{a}} \right)^{1/2}$$
(15)

$$\alpha = \frac{Al}{2K_{11}}.$$
(16)

By means of these parameters and variable, equations (10) and (11) can be rewritten as

$$\frac{\pi}{2}h = \int_{v_0}^{t} \frac{1}{2v} \left[\frac{v + \gamma v - \gamma u}{(v - u)(1 - v)} \right]^{1/2} dv$$
(17)

$$\frac{\pi}{2}h = \frac{\alpha(v_0 + 2\zeta v_0 - 2\zeta u)(v_0 - u)^{1/2}}{v_0 [(v_0 + \gamma v_0 - \gamma u)(1 - v_0)]^{1/2}}.$$
 (18)

Defining the reduced free energy difference

$$g = \frac{l(G_{\theta} - G_{\rm s})}{2K_{11}S}.$$
 (19)

This can be expressed as:

$$g = 2I_1^2 - uI_1^2 - 2I_1I_2 + \alpha \frac{u}{v_0} \left(\zeta \frac{u}{v_0} - 2\zeta - 1\right) \quad (20)$$

where

$$I_{1} = \int_{v_{0}}^{l} \frac{(v + \gamma v - \gamma u)^{1/2}}{2v[(v - u)(1 - v)]^{1/2}} dv$$
(21)

and

$$I_{2} = \int_{v_{0}}^{1} \frac{\left[(v-u)(v+\gamma v-\gamma u) \right]^{1/2}}{2v^{2}(1-v)^{1/2}} \,\mathrm{d}v.$$
(22)

Based on the equations above, one can calculate g as a function of u. First, for a given u, we can solve v_0 and h from (17) and (18); second, from (21) and (22) we can obtain I_1 and I_2 ; lastly we can calculate g from (20). g is a function of u; if g > 0, the saturation solution is more stable; if g < 0, the disturbed solution is more stable. There exists $u = u_c$, such that when $u \le u_c$, $g \ge 0$, the transition point is u_c . If $u_c = 0$, the transition is of second order; otherwise it is of first order.

We may take compound MBBA as an example; its elastic constants are $K_{33} = 1.25K_{11}$, $K_{11} = 5.8 \times 10^{-12}$ N [13]. Taking two sets of values [a] $\alpha = 1.5$, $\zeta = 0.2$; and [b] $\alpha = 2.1$, $\zeta = -0.2$, we make numerical calculations and plot three figures to show the results: the v_0 as a function of *u*; *h* as a function of *u*; and *g* as function of *u*. These are shown respectively by figures 1, 2, and 3. From figure 3, we find the two curves expressing two differently typical situations for the transition at saturation point.

(1) The normal situation. Curve [a] is tangential to the horizontal axis of g = 0 at the point u = 0, and decrease monotonously as u increases. It indicates



Figure 1. The relation between u and v_0 .



Figure 2. The relation between u and h.



Figure 3. The relation between g and u.

that when u = 0, $G_{\theta} = G_s$; when u > 0, $G_{\theta} < G_s$; and the transition from the disturbed solution state to the saturation solution state occurs at the point u = 0; the director **n** and its distribution change continuously. Thus the transition is of second order.

(2) The anomalous situation. Curve [b] is also tangential to the horizontal axis of g = 0 at the point u = 0, but it first rises, then falls and finally intersects with the horizontal axis g = 0 at u = 0.19. When u > 0.19, the curve is below the horizontal axis of g = 0 and $G_{\theta} < G_{s}$. This indicates that the transition occurs at the point u = 0.20, and the changes of the director and its distribution are discontinuous. So the transition is of first order.

4. The saturation field strength of the second order transition

The saturation field can be obtained easily if we know that the transition must be second order; the transition point is at u = 0. From equation (17), when u approaches zero, we get:

$$\frac{\pi}{2}h_{\rm sat} = (1+\gamma)^{1/2}\ln\frac{1+(1-V_0)^{1/2}}{V_0^{1/2}}.$$
 (23)

Equation (18) can be rewritten as:

$$\frac{\pi}{2}h_{\rm sat} = \frac{\alpha(1+2\zeta)}{(1+\gamma)^{1/2}} \frac{1}{(1-V_0)^{1/2}}$$
(24)

and from equations (23) and (24), we obtain:

$$\frac{\pi}{2}h_{\rm sat} = \frac{\alpha(1+2\zeta)}{(1+\gamma)^{1/2}} \coth\left[\frac{1}{(1+\gamma)^{1/2}}\frac{\pi}{2}h_{\rm sat}\right].$$
 (25)

The saturation field may be obtained using this method, and the transition is seen as second order. The field satisfying the equation (25) is written as h_{sat}^0 .

We know [4] that the reduced threshold field satisfies $(\pi/2)h_{\rm th} = \alpha \coth[(\pi/2)h_{\rm th}]$; this leads to the determination of parameter ζ by means of equation (25) if $h_{\rm th}$ and $h_{\rm sat}$ are known.

5. The condition for the first order transition

As figure 3 curve [b] shows, the reduced free energy difference is greater than zero in the vicinity of u = 0 for a first order transition; but it is less than zero for a second order transition. From this, we can obtain the condition for a first order transition.

We can calculate the value of g and its first and second order derivative values at u = 0 from equations (17), (18), (20), (21), (22), etc. The results are as follows:

$$g|_{u=0} = 0 \tag{26}$$

$$\left. \frac{\mathrm{d}g}{\mathrm{d}u} \right|_{u=0} = 0 \tag{27}$$

$$\frac{d^2g}{du^2}\Big|_{u=0} = \frac{\kappa\alpha^2(1+2\zeta)^2 V_0^2 - 2\alpha\kappa(1+2\zeta)(1-V_0)}{-4\kappa V_0(1+2\zeta)(1-V_0)} + \alpha\kappa V_0(1+2\zeta)(1-V_0)}$$
(28)

where V_0 is the value of v_0 when u = 0. From equations (23) and (24) can we obtain

$$\ln \frac{1 - (1 - V_0)^{1/2}}{1 + (1 - V_0)^{1/2}} = -\frac{2\alpha\kappa(1 + 2\zeta)}{(1 - V_0)^{1/2}}$$
(29)

where $\kappa = K_{11}/K_{33}$.

Let us discuss the condition for the first order transition. When $d^2g/du^2|_{u=1} > 0$, g is greater than zero in the vicinity of u = 0 and the first order transition will appear. For a particular liquid crystal material and for a given substrate, κ , α and ζ are known. V_0 can be obtained from equation (29); we can then judge whether the transition is first or second order from (28).

In order to fully understand the condition, we have taken α and $1 + 2\zeta$ as variables and plotted their graphs for $\kappa = 0.8$, 0.6 and 0.4, respectively, in figures 4, 5, 6. In these figures, the curve of $d^2g/du^2|_{u=0} = 0$ divides the plane into two areas, one for first order, the other for second order transitions.

6. The saturation field for the first order transition

For the first order transition, $u_c \neq 0$, and the saturation field strength is not equal to h_{sat}^0 . However, one can calculate u_c and h_{sat} from equations (17)–(22). From



Figure 4. The areas of first order transition for $\kappa = 0.8$.



Figure 5. The areas of first order transition for $\kappa = 0.6$.



Figure 6. The areas of first order transition for $\kappa = 0.4$.

equation (19), we can obtain:

$$g = u \left[2I_1 I_3 - I_1^2 + \alpha \frac{1}{v_0} \left(\zeta \frac{u}{v_0} - 2\zeta - 1 \right) \right]$$
(30)

where

$$I_{3} = \frac{I_{1} - I_{2}}{u} = \int_{v_{0}}^{1} \frac{(v + \gamma v - \gamma u)^{1/2}}{2v^{2} [(v - u)(1 - v)]^{1/2}} \, \mathrm{d}v. \quad (31)$$

Because $u = u_c$ and g = 0, then u_c satisfies:

$$2I_1I_3 - I_1^2 + \alpha \frac{1}{v_0} \left(\zeta \frac{u_c}{v_0} - 2\zeta - 1 \right) = 0$$
 (32)

where I_1 , I_3 , v_0 have to be calculated at $u = u_c$. By means of equations (17), (18), (21), (30) and (32), u_c can be obtained and h_{sat} be calculated from equation (17).

The numerical results for h_{sat} and h_{sat}^0 for different values of α , κ and ζ are arranged in the table. From this table, we see that h_{sat} is larger than h_{sat}^0 ; $h_{sat} \approx 1.5 h_{sat}^0$. The physical effect of this is important.

Table. The value of h_{sat} .

k	а	<i>u</i> _c	$h_{\rm sat}$	$h_{\rm sat}^{\rm 0}$	$\frac{h_{\rm sat} - h_{\rm sat}^0}{h_{\rm sat}^0} \times 100\%$
0.8	2.1	0.193	1.399	0.859	62.9
0.8	2.6	0.082	1.641	1.001	64.0
0.6	3.5	0.133	1.923	1.165	65.1
0.6	3.2	0.088	1.819	1.090	66.9
0.4	3.0	0.087	1.511	0.971	55.6
0.4	2.0	0.088	1.028	0.758	35.6

Appendix

We may calculate the values of $dg/du|_{u=0}$ and $d^2g/du^2|_{u=0}$ from equations (17), (18), (20), (21) and (22). From (29) we obtain:

$$\frac{\mathrm{d}g}{\mathrm{d}u}\Big|_{u=0} = 4I_1\Big|_{u=0} \frac{\mathrm{d}I_1}{\mathrm{d}u}\Big|_{u=0} - I_1^2\Big|_{u=0} - 2I_1\Big|_{u=0} \frac{\mathrm{d}I_2}{\mathrm{d}u}\Big|_{u=0} - 2I_2\Big|_{u=0} \frac{\mathrm{d}I_1}{\mathrm{d}u}\Big|_{u=0} + \frac{\alpha}{V_0}(-2\zeta - 1)$$
(A1)

$$\frac{d^{2}g}{du^{2}}\Big|_{u=0} = 4\left(\frac{dI_{1}}{du}\right)^{2}\Big|_{u=0} + 2I_{1}\Big|_{u=0}\frac{d^{2}I_{1}}{du^{2}}\Big|_{u=0} -4I_{1}\Big|_{u=0}\frac{dI_{1}}{du}\Big|_{u=0} -4\frac{dI_{1}}{du}\Big|_{u=0}\frac{dI_{2}}{du}\Big|_{u=0} -2I_{1}\Big|_{u=0}\frac{d^{2}I_{2}}{du^{2}}\Big|_{u=0} + \frac{2\alpha(+2\zeta)}{V_{0}^{2}}\frac{dV_{0}}{du}\Big|_{u=0} + \frac{2\alpha\zeta}{V_{0}^{2}}.$$
(A2)

From (21), we can obtain:

$$I_1|_{u=0} = -\frac{(1+\gamma)^{1/2}}{2} \ln \frac{1-(1-V_0)^{1/2}}{1+(1-V_0)^{1/2}}$$
(A3)

$$\frac{\mathrm{d}I_1}{\mathrm{d}u}\Big|_{u=0} = \frac{(1-V_0)^{1/2}}{4V_0(1+\gamma)^{1/2}} - \frac{1}{8(1+\gamma)^{1/2}} \ln\frac{1-(1-V_0)^{1/2}}{1+(1-V_0)^{1/2}}$$

$$-\frac{(1+\gamma)^{1/2}}{2V_0(1-V_0)^{1/2}}\frac{\mathrm{d}V_0}{\mathrm{d}u}\Big|_{u=0}$$
(A4)

$$\frac{\mathrm{d}^2 I_1}{\mathrm{d}u^2}\Big|_{u=0} = \frac{4\gamma + 3}{8(1+\gamma)^{3/2}} \left[\frac{(2+3V_0)(1-V_0)^{1/2}}{4V_0^2} \right]$$

$$-\frac{3}{8} \ln \frac{1 - (1 - V_0)^{1/2}}{1 + (1 - V_0)^{1/2}} \bigg] \\ + \bigg[\frac{(2 - 3V_0)(1 + \gamma)^{1/2}}{2V_0^2(1 - V_0)^{3/2}} \frac{dV_0}{du} \bigg|_{u=0} \\ - \frac{1}{2V_0^2(1 - V_0)^{1/2}(1 + \gamma)^{1/2}} \bigg] \frac{dV_0}{du} \bigg|_{u=0} \\ - \frac{(1 + \gamma)^{1/2}}{2V_0^2(1 - V_0)^{1/2}(1 + \gamma)^{1/2}} \bigg] \frac{dV_0}{du} \bigg|_{u=0}$$
(A5)

$$-\frac{(1+\gamma)^{1/2}}{2V_0(1-\gamma)^{1/2}} \frac{\mathrm{d}^2 V_0}{\mathrm{d}u^2}\Big|_{u=0}.$$
 (A5)

From (22), we calculate:

$$I_2|_{u=0} = I_1|_{u=0} \tag{A6}$$

$$\frac{\mathrm{d}I_2}{\mathrm{d}u}\Big|_{u=0} = \frac{(1+\gamma)^{1/2}(1-V_0)^{1/2}}{4V_0} + \frac{(1+\gamma)^{1/2}}{8}$$

$$\times \ln \frac{1 - (1 - V_0)^{1/2}}{1 + (1 - V_0)^{1/2}} - \frac{\gamma (1 - V_0)^{1/2}}{4V_0 (1 + \gamma)^{1/2}}$$

+
$$\frac{\gamma}{8(1+\gamma)^{1/2}} \ln \frac{1-(1-V_0)^{1/2}}{1+(1-V_0)^{1/2}}$$

$$-\frac{(1+\gamma)^{1/2}}{2V_0(1+\gamma)^{1/2}}\frac{\mathrm{d}V_0}{\mathrm{d}u}\Big|_{u=0}$$
(A7)

$$\frac{d^{2}I_{2}}{du^{2}}\Big|_{u=0} = \frac{-1}{8(1+\gamma)^{1/2}} \left[\frac{(2+3V_{0})(1-V_{0})^{1/2}}{4V_{0}^{2}} -\frac{3}{8} \ln \frac{1-(1-V_{0})^{1/2}}{1+(1-V_{0})^{1/2}} \right] + \left[\frac{(2-3V_{0})(1+\gamma)^{1/2}}{2V_{0}^{2}(1-V_{0})^{1/2}} \frac{dV_{0}}{du} \right]_{u=0} + \frac{(1+2\gamma)}{2V_{0}^{2}(1-V_{0})^{1/2}(1+\gamma)^{1/2}} \left] \frac{dV_{0}}{du} \Big|_{u=0} -\frac{(1+\gamma)^{1/2}}{2V_{0}(1-V_{0})^{1/2}} \frac{d^{2}V_{0}}{du^{2}} \Big|_{u=0}.$$
(A8)

From equations (18) and (21), we can obtain (29); with equations (A1–A8) and (20), we can easily obtain (27) and (28).

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