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Multiple discrete energy levels and the bistable state of weak anchoring NLC cells

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The weak anchoring nematic liquid crystal (NLC) cell is investigated with regard to energy. Because the Gibbs free energy of liquid crystal system used in theory does not include temperature and entropy, and because the equations and boundary conditions for $\delta G=0$ are also the mechanical equilibrium conditions of the continuum, the Gibbs free energy G is equivalent to the energy E of the liquid crystal continuum. There are multiple solutions which satisfy these equations and boundary conditions, each solution corresponding to a certain energy value. We call these discrete energy values and energy levels. Adopting a simple liquid crystal cell model, the energy levels are calculated in detail by means of analytical and numerical methods. The results show that there are three energy levels (or more in certain cases). The values and sequence of the energy levels are related to the external field and anchoring parameters. The relationships between the energy level structure and the bistable. Fréedericksz transition are disussed, together with their influence on the response time. The physical condition for the existence of more than three energy levels is also given.

1. Introduction

Recent experiments have shown that the first order Fréedericksz transition and bistable state exist in the nematic liquid crystal (NLC) cell under the action of an external field [1–5]. Theoretical investigations of these phenomena have also been made [6–8]. In these theoretical works the Gibbs free energy of the NLC is a very important quantity.

However, temperature and entropy are not contained in the Gibbs free energy G used in the theory. The differential equation and boundary conditions of angular deflection of the director (angular deflection is φ in this paper, and is a function of z) obtained from the first order variations $\delta G=0$, are also the mechanical equilibrium conditions for LC bulk and surface [9]; thus G is also the energy E of the liquid crystal continuum. G consists of three parts, of which (i) Frank elastic free energy [10] can be considered as the elastic energy of the continuum, (ii) surface anchoring energy can be considered as interface potential energy of the continuum, (iii) diamagnetic or dielectric free energy can be considered as the potential energy of the continuum in an external field, originating from the magnetic or electric moment of molecules in the external field. Therefore, the investigation of the Gibbs free energy G of a liquid crystal cell is equivalent to a study of the energy E of the liquid crystal continuum.

We note that the differential equation with boundary conditions for the angular deflection of the director obtained from $\delta G=0$ has three or more solutions. Each solution corresponds to a mechanical equilibrium state and a certain energy value E, so E may have multiple values. One can make a comparison with the solution of the stationary Schrödinger equation of a *microcosmic* particle in quantum mechanics [11]. The director angular deflection $\varphi(z)$ is equivalent to the stationary wave function of a particle. The differential equation and boundary condition of $\varphi(z)$ are equivalent to those of a stationary Schrödinger equation. The energy E of a liquid crystal continuum satisfying mechanical equilibrium conditions is equivalent to the energy eigen value of a particle. In quantum mechanics theory, the eigen energy is also called the energy level. Accordingly, the energy of a liquid crystal continuum satisfying mechanical equilibrium conditions is also called an energy level. Similarly, we call the mechanical equilibrium state of the lowest energy level the ground state; the others are excited states.

In this paper, we study the energy levels of weak anchoring NLC cells under an external field. The main contents are: (i) the energy levels and corresponding director distribution, i.e. angular deflection function $\varphi(z)$; (ii) the relationship between the energy levels and

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the external field as well as the parameters of anchoring energy; (iii) the relationship between energy levels and the Fréedericksz transition and the bistable state. We prove that there may be more than three discrete energy levels in weak anchoring NLC cells under certain conditions. The value and sequence of energy levels relate to the external field. As a result, the first order Fréedericksz transitions occurs and the bistable state is formed.

The significance of the investigation of energy levels is as follows. First, energy level is diectly related to the Fréedericksz transition and the existence of a bistable state. Second, the energy level structure affects the calculation of response and relaxation times. Finally, it is a new physical phenomenon for the NLC cell, as a classical macroscopic object, to have multiple discrete energy levels. Certainly, the importance of this phenomenon is related to the physical meaning of 'excited state' mentioned above. In the mechanics view, an excited state is the mechanical equilibrium state, but the energy E in an excited state is not the smallest. From the viewpoint of thermodynamics, we shall point out that Gibbs free energy in an excited state is minimal, but is not the smallest, so it is a metastable state.

The arrangement of this paper is as follows. In § 2, a simple liquid crystal cell model is adopted in order to simplify the mathematical process and numerical calculation; but this does not influence the main physical conclusion. In § 3, a series of equations to determine energy levels are derived, and numerical results of the reduced Gibbs free energy are obtained and described in some figures. In § 4, diagrams of reduced energy levels and the corresponding mechanical equilibrium state $\varphi(z)$ are given for some typical cases; we also describe some application examples. In § 5, the condition for more than three energy levels in a weak anchoring NCL cell is given. In § 6 the states obtained by $\delta G=0$ are discussed. The mathematical proof for the metastable state is presented in the appendix.

2. Theoretical model of the weak anchoring NLC cell

In order to study the energy level structure of the weak anchoring NLC cell, we consider a very simple model of thickness l. An external magnetic field **H** is applied parallel to the substrates. The Oz Cartesian axis is perpendicular to the substrates lying in the $z=0$ and $z=l$ planes. Assuming that the easy direction **e**, both at the top and bottom substrates, is along the Ox axis, **e** and **H** can be written as:

$$\mathbf{e}=(1,\,0,\,0)$$

$$\mathbf{H}=(0,\,H,\,0)$$

and the director **n** can be written as:

$$\mathbf{n}=(\cos\varphi,\,sin\varphi,\,0)$$

where φ is the angle between **n** and the Ox axis, and is a function of z. The anchoring free energies at the $z=0$ and $z=l$ planes are equal, and can be expressed by [6]:

$$\begin{aligned} g_{\mathrm{s}}\big|_{z=l}&=\tfrac{1}{2}A\sin^2\varphi_l\left(1+\zeta\sin^2\varphi_l\right) \quad \text{for } z=l\\ g_{\mathrm{s}}\big|_{z=0}&=\tfrac{1}{2}A\sin^2\varphi_0\left(1+\zeta\sin^2\varphi_0\right) \quad \text{for } z=0 \end{aligned} \tag{1}$$

where φ_0 and φ_l are the azimuthal angles at $z=0$ and $z=l$, respectively, and ζ is an anchoring parameter. The Gibbs free energy of system can be written as

$$\begin{aligned} G=S\int_0^l\left[\frac{1}{2}k_{22}\left(\frac{\mathrm{d}\varphi}{\mathrm{d}z}\right)^2-\frac{1}{2}\chi_{\mathrm{a}}H^2\sin^2\varphi\right]\mathrm{d}z\\ +\frac{1}{2}SA\sin^2\varphi_0\left(1+\zeta\sin^2\varphi_0\right)\\ +\frac{1}{2}SA\sin^2\varphi_l\left(1+\zeta\sin^2\varphi_l\right) \end{aligned} \tag{2}$$

where S is the area of the substrates, k_{22} is the twist elastic constant and χ_{a} is the magnetic anisotropy of the liquid crystal medium.

From the first order variation $\delta G=0$, we obtain the equation of φ:

$$k_{22}\frac{\mathrm{d}^2\varphi}{\mathrm{d}z^2}+\chi_{\mathrm{a}}H^2\sin\varphi\cos\varphi=0 \tag{3}$$

and boundary condition:

$$\begin{aligned} A\sin\varphi_0\cos\varphi_0\left(1+2\zeta\sin^2\varphi_0\right)&=k_{22}\frac{\mathrm{d}\varphi}{\mathrm{d}z}\big|_{z=0}\\ A\sin\varphi_l\cos\varphi_l\left(1+2\zeta\sin^2\varphi_l\right)&=-k_{22}\frac{\mathrm{d}\varphi}{\mathrm{d}z}\big|_{z=l}. \end{aligned} \tag{4}$$

It should be pointed out that equations (3) and (4) are also the mechanical equilibrium conditions for the LC bulk and surface, respectively. Obviously, there are two trivial solutions: (i) $\varphi\equiv 0$, the uniform solution (the corresponding state is called the uniform state); (ii) $\varphi\equiv\frac{\pi}{2}$, the saturation solution (the corresponding state is called the saturation state). In addition, there is a non-trivial solution $\varphi=\varphi(z)$, the disturbed solution (the corresponding state is called the disturbed state).

From equation (3) we obtain

$$\frac{\mathrm{d}\varphi}{\mathrm{d}z}=\pm H\left[\frac{\chi_{\mathrm{a}}}{k_{22}}\left(\sin^2\varphi_{\mathrm{m}}-\sin^2\varphi\right)\right]^{\frac{1}{2}}, \tag{5}$$

where φ_{m} is the value of φ at the $z=l/2$ plane. Then the boundary condition (4) can be expressed as:

$$\begin{aligned} &\mathbf{H}\left[\frac{\chi_{\mathrm{a}}}{k_{22}}\left(\sin^2\varphi_{\mathrm{m}}-\sin^2\varphi\right)\right]^{\frac{1}{2}}\\ &=A\sin\varphi_0\cos\varphi_0\left(1+2\zeta\sin^2\varphi_0\right). \end{aligned} \tag{6}$$

From equation (5), one has

$$dz = \frac{1}{\mathbf{H}}\left(\frac{k_{22}}{\chi_a}\right)^{\frac{1}{2}} \frac{1}{\left(\sin^2\varphi_m - \sin^2\varphi\right)^{\frac{1}{2}}} d\varphi \tag{7}$$

then

$$z = \frac{1}{\mathbf{H}}\left(\frac{k_{22}}{\chi_a}\right)^{\frac{1}{2}} \int_{\varphi_0}^{\varphi(z)} \frac{1}{\left(\sin^2\varphi_m - \sin^2\varphi\right)^{\frac{1}{2}}} d\varphi \tag{8}$$

and

$$\mathbf{H} = \frac{2}{l}\left(\frac{k_{22}}{\chi_a}\right)^{\frac{1}{2}} \int_{\varphi_0}^{\varphi_m} \frac{1}{\left(\sin^2\varphi_m - \sin^2\varphi\right)^{\frac{1}{2}}} d\varphi. \tag{9}$$

Equations (9), (6), (8) determine the disturbed state $\varphi(z)$ completely.

Gibbs free energy corresponding to the uniform, saturation and disturbed states, G_U, G_S and G_D, respectively, are

$$G_U = 0 \tag{10}$$

$$G_S = S\left[-\frac{1}{2}\chi_a \mathbf{H}^2 l + A(1+\zeta)\right] \tag{11}$$

$$G_D = S\left[\frac{1}{2}\chi_a \mathbf{H}^2 \sin^2\varphi_m - \chi_a \mathbf{H}^2 \int_{\varphi_0}^{\varphi_m} \frac{\sin^2\varphi}{\left(\sin^2\varphi_m - \sin^2\varphi\right)^{\frac{1}{2}}} d\varphi\right] + SA\sin^2\varphi_0\left(1+\zeta\sin^2\varphi_0\right). \tag{12}$$

We conclude that equation (3) with boundary condition (4) has three kinds of solution corresponding to uniform, saturation and disturbed states. Note that there may be more than one disturbed state solution in certain condition.

3. The reduced Gibbs free energy

We now consider the Gibbs free energy further. We adopt the parameter u

$$u = \sin^2\varphi_m \tag{13}$$

to characterize the state of texture of the liquid crystal, as in [6, 7], and make a transformation of φ to a new variable denoted by v [12]

$$v = \frac{\tan^2\varphi}{\tan^2\varphi_m},\quad v_0 = \frac{\tan^2\varphi_0}{\tan^2\varphi_m} \tag{14}$$

We also introduce the reduced anchoring strength α, the reduced field strength h and the reduced Gibbs free energy g as

$$\alpha = \frac{Al}{2k_{22}},\quad h = \frac{\mathbf{H}}{\mathbf{H}_c^0}\left[\mathbf{H}_c^0 = \frac{\pi}{l}\left(\frac{k_{22}}{\chi_a}\right)^{\frac{1}{2}}\right],\quad g = G\frac{l}{2k_{22}S}. \tag{15}$$

Equations (6)–(12) can then be expressed as

$$\frac{\pi}{2}h = \alpha\left[\frac{v_0}{(1-v_0)(1-u+uv_0)}\right]^{\frac{1}{2}}\left(1+2\zeta\frac{uv_0}{1-u+uv_0}\right) \tag{16}$$

$$\frac{\pi}{2}h = I_1 \tag{17}$$

$$g_U = 0 \tag{18}$$

$$g_S = -\left(\frac{\pi}{2}h\right)^2 + \alpha(1+\zeta) \tag{19}$$

$$g_D = u\left[\left(\frac{\pi^2}{4}h^2 - \pi h I_2\right) + \alpha\frac{v_0}{1-u+uv_0}\left(1+\zeta\frac{uv_0}{1-u+uv_0}\right)\right] \tag{20}$$

where

$$I_1 = \int_{v_0}^{1} \frac{1}{2[v(1-v)(1-u+uv)]^{\frac{1}{2}}} dv \tag{21}$$

$$I_2 = \int_{v_0}^{1} \frac{v}{2[v(1-v)(1-u+uv)]^{\frac{1}{2}}} \frac{1}{1-u+uv} dv \tag{22}$$

By means of equations (16)–(20), the reduced Gibbs free energy g_U, g_S and g_D can be solved for given h.

Now we discuss the reduced free energy obtained by numerical calculation. Combining equations (16) and (17) results in

$$\int_{v_0}^{1} \frac{1}{2[v(1-v)(1-u+uv)]^{\frac{1}{2}}} dv = \alpha\left[\frac{v_0}{(1-v_0)(1-u+uv_0)}\right]^{\frac{1}{2}}\left(1+2\zeta\frac{uv_0}{1-u+uv_0}\right). \tag{23}$$

When u is given, the corresponding v_0 can be calculated from equation (23). Then h can be obtained from equation (17) via (21); the reduced free energy g_U, g_S and g_D can then be obtained from equations (18)–(20). Hence the values of the reduced Gibbs free energy g versus h are obtained. The results calculated depend on the values of the anchoring parameters α and ζ. Here we take three typical sets of parameters as examples: (*a*) $\alpha = 1.0$, $\zeta = 0.0$; (*b*) $\alpha = 1.0$, $\zeta = -0.2$; (*c*) $\alpha = 0.1$, $\zeta = -0.2$. The results are illustrated in figures 1, 2 and 3 respectively.

From many calculations and from the three typical

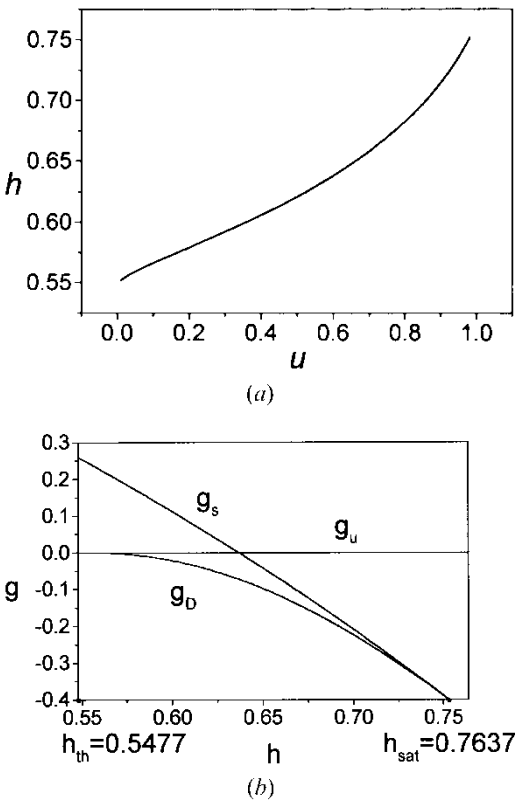


Figure 1. (*a*) The reduced external field h as a function of state parameter u; (*b*) the reduced free energy g as a function of the reduced external field h. The anchoring energy parameters used in the calculation are $\alpha=1.0$, $\zeta=0.0$. We see that h is the monotonous function of u ($dh/du>0$), and there are three values of g (g_U, g_S and g_D) for a given value of h.

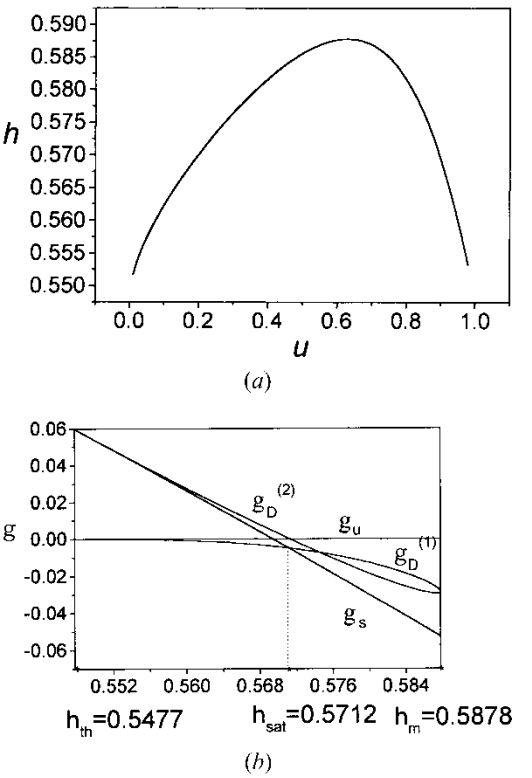


Figure 2. (*a*) The reduced external field h as a function of state parameter u; (*b*) the reduced free energy g as a function of the reduced external field h. The anchoring energy parameters used in the calculation are $\alpha=1.0$, $\zeta=-0.2$. We see that, with the increase of u, the curve h increases ($dh/du>0$) first, then reaches a maximum ($dh/du=0$) and finally decreases ($dh/du<0$). For a given value of h, there are two corresponding values of u (the smaller is $u_D^{(1)}$ and the larger $u_D^{(2)}$). Hence there are four values of the reduced free energy g $\left(g_U, g_S, g_D^{(1)} \text{ and } g_D^{(2)}\right)$ for a given value of h.

sets of figures shown, we know that there are three different cases: (1) for a certain value of α and $\zeta\geqslant 0$, there are three values of g (g_U, g_S and g_D) for a given value of h. The value of g_D is the smallest in a certain range of h (i.e. h_{th}, h_{sat}); (2) for a small value of α and $\zeta<0$ there are four values of g $\left(g_U, g_S, g_D^{(1)} \text{ and } g_D^{(2)}\right)$ for a given value of h. The value of $g_D^{(1)}$ is the smallest value in the certain range of h (i.e h_{th}, h_{sat}); (3) for a smaller value of α and $\zeta<0$, there are three values of g (g_U, g_S and g_D) for a given value of h. However the value of g_D is the largest for each value of h.

4. Diagram of the reduced energy levels

In order to explain the multiple discrete energy levels of the NLC cell we draw the diagram of the energy levels and corresponding mechanical equilibrium state $\varphi(z)$ for a given value of h. The Gibbs free energy G is equivalent to the energy E of the NLC cell, i.e. $E=G$. The reduced energy ε may be written as $\varepsilon=El/2k_{22}S$, and ε equals the reduced Gibbs free energy g. Hence figure 1 (*b*), 2 (*b*) and 3 (*b*) also represent the reduced energy ε versus h.

Denoting the reduced energy of the ground states by ε_0 and excited states by ε_1, ε_2 …, one can calculate the mechanical equilibrium state $\varphi(z)$ for each value of ε_i ($i=0, 1, 2$ …) from equation (8), which gives

$$\frac{z}{l}=\frac{2}{\pi h}\int_{\varphi_0}^{\varphi}\frac{1}{\left(u-\sin^2\varphi\right)^{\frac{1}{2}}}\mathrm{d}\varphi$$

where

$$\varphi_0=\tan^{-1}\left(\frac{uv_0}{1-u}\right)^{\frac{1}{2}}.$$

We can then draw the diagrams of reduced energy levels as well as the corresponding $\varphi(z)$ for a given value of h.

The results calculated for some typical case are shown in figures 4–6. The anchoring parameters used in

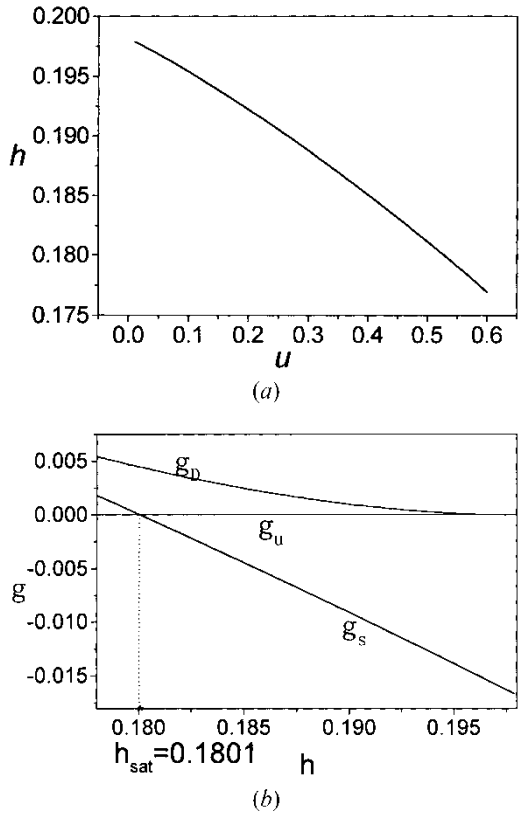


Figure 3. (*a*) The reduced external field h as a function of state parameter u; (*b*) the reduced free energy g as a function of the reduced external field h. The anchoring energy parameters used in the calculation are $\alpha=0.1$, $\zeta=-0.2$. We see that h is a monotonous function of u ($dh/du<0$), and there are three values of g (g_U, g_S and g_D) for a given value of h.

the calculation are the same as for figure 2, i.e. $\alpha=1.0$, $\zeta=-0.2$. The reduced field $h=0.5663$, 0.5712 and 0.5867 for figures 4, 5 and 6, respectively. The symbols φ_U, φ_S, $\varphi_D^{(1)}$, $\varphi_D^{(2)}$ denote the mechanical equilibrium states; i.e. uniform state, saturation state, disturbed state 1 (corresponding to $u_D^{(1)}$) and disturbed state 2 (corresponding to $u_D^{(2)}$), respectively. Because $\varphi_U\equiv 0$, $\varphi_S\equiv 90^\circ$ are well known, φ_U and φ_S are omitted from the diagrams.

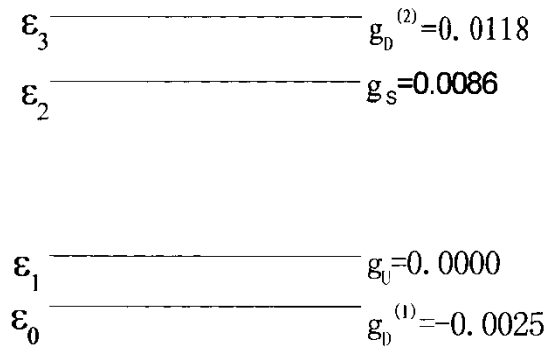
One can carry out similar calculations for many other cases. From many calculations we reach the conclusion that energy levels for the NLC cell have the following characteristics:

1. There is one reduced energy level ε_0 corresponding to the ground state (or states), and two or three levels ε_1, ε_2, ε_3 corresponding to excited states.
2. The ground state corresponding to the lowest energy level ε_0 is altered when the external field is changed. Moreover, when the external field is changed the corresponding mechanical equilibrium states are also altered.
3. The lowest energy level ε_0 may be degenerate, i.e. there are two corresponding mechanical equilibrium states, as shown in figure 5, for example.

Now we discuss some physical applications for the energy level diagrams.

4.1. *The Fréedericksz transition*

From the diagram of the energy levels, we can see that the ground state corresponding to the lowest energy level ε_0 is not fixed. Usually, for $h<h_{th}$, $h_{th}<h<h_{sat}$ and $h>h_{sat}$, the ground state is: a uniform state, a disturbed state and a saturation state (h_{th} and h_{sat} are the threshold field and saturation field), respectively. So the Fréedericksz transition can be considered as the transition of an excited state to the ground state when the value of h changes from 0 to large values. The



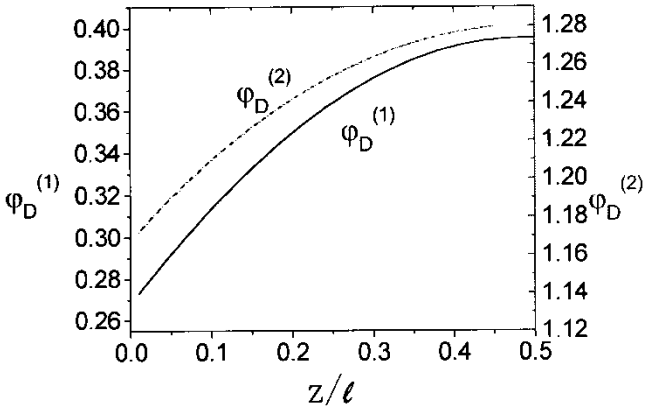


Figure 4. Reduced energy levels (left diagram) and corresponding mechanical equilibrium states $\varphi(z)$ (right diagram) for the reduced field $h=0.5663$. The anchoring parameters used in the calculation are $\alpha=1.0$, $\zeta=-0.2$. $\varphi_D^{(1)}$ and $\varphi_D^{(2)}$ correspond to the two mechanical equilibrium disturbed states with $u_D^{(1)}=0.1510$, $u_D^{(2)}=0.9110$, respectively. The unit of φ is the radian; $\varphi_D^{(1)}$ is the ground state.

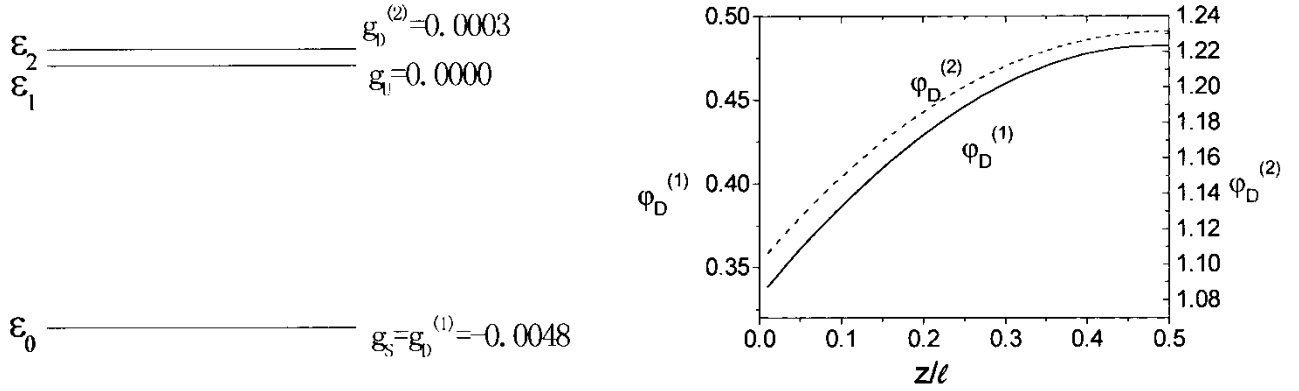


Figure 5. Reduced energy levels (left diagram) and corresponding mechanical equilibrium states $\varphi(z)$ (right diagram) for the reduced field $h=0.5712$. The anchoring parameters used in the calculation are $\alpha=1.0$, $\zeta=-0.2$. $\varphi_D^{(1)}$ and $\varphi_D^{(2)}$ correspond to the two mechanical equilibrium disturbed states with $u_D^{(1)}=0.2151$, $u_D^{(2)}=0.8831$, respectively. The unit of φ is the radian. The energy level ε_0 is degenerate, i.e. both saturation state and disturbed state 1 are the ground state.

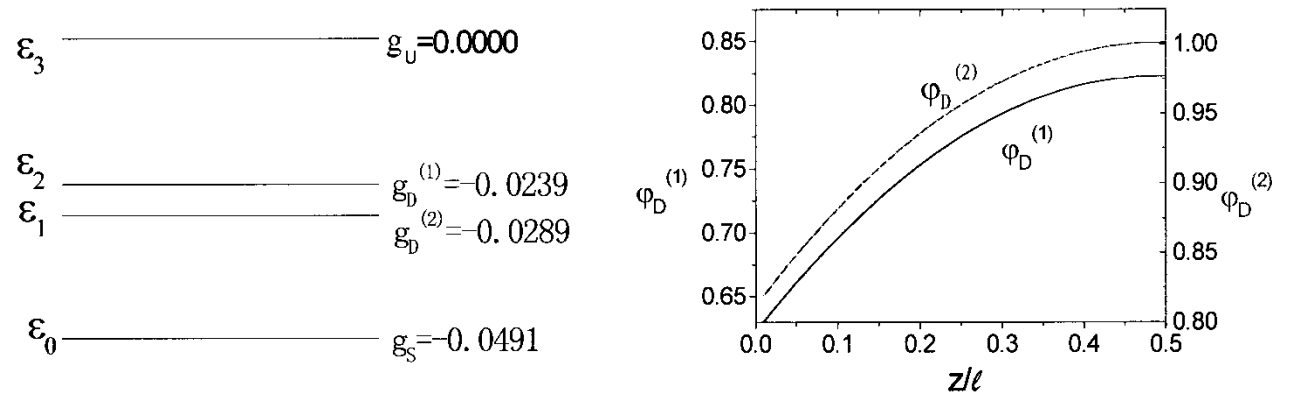


Figure 6. Reduced energy levels (left diagram) and corresponding mechanical equilibrium states $\varphi(z)$ (right diagram) for the reduced field $h=0.5867$. The anchoring parameters used in the calculation are $\alpha=1.0$, $\zeta=-0.2$. $\varphi_D^{(1)}$ and $\varphi_D^{(2)}$ correspond to the two mechanical equilibrium disturbed states with $u_D^{(1)}=0.5420$, $u_D^{(2)}=0.7052$, respectively. The unit of φ is the radian. There are two energy levels $\varepsilon_1=g_D^{(2)}$, $\varepsilon_2=g_D^{(1)}$ between ε_0 and ε_3 ($\varepsilon_0=g_S$, $\varepsilon_3=g_U$), so the transition from $\varphi_U\equiv 0$ to $\varphi_S\equiv 90^\circ$ should jump both $\varphi_D^{(2)}$ and $\varphi_D^{(1)}$.

mechanical equilibrium state will undergo two transitions; one is from a uniform state with $u=0$ to a disturbed state with $0<u<1$; the other is from a disturbed state to a saturation state with $u=1$. At the transition point, if the parameter u changes continuously, the transition is second order; otherwise it is first order.

In the cases of figure 2 where the anchoring parameters $\alpha=1.0$, $\zeta=-0.2$, and figure 3 where $\alpha=0.1$, $\zeta=-0.2$, we find first order transitions. In the former case of ($\alpha=1.0$, $\zeta=-0.2$), with increase of h, the reduced energy level diagram is changed from that depicted in figure 4 to figure 5 and finally to figure 6. The ground state is altered from disturbed state $\varphi_D^{(1)}$ with $u_D^{(1)}=0.2151$ to saturation state $\varphi_S\equiv 90^\circ$ with $u_s=1$ at transition point $h_S=0.5712$. It is first order because $u_D^{(1)}\neq u_S$. In the latter case ($\alpha=0.1$, $\zeta=-0.2$), the uniform state $\varphi_U\equiv 0$ with $u=0$ transforms directly to the saturation state $\varphi_S\equiv 90^\circ$ with $u_s=1$ at $h=0.1801$; it is also first order.

4.2. *The bistable state*

As we see from figure 5, $\varepsilon_0=g_S=g_D^{(1)}$, i.e. both the saturation state $\varphi_S=90^\circ$ with $u=1$ and the disturbed state 1 $g_D^{(1)}$ with $u_D^{(1)}=0.2151$ are the ground states; between the two states $u=1$ and $u_D^{(1)}=0.2151$ there is another state with $u_D^{(2)}=0.8831$ corresponding to the reduced energy ε_2. So the saturation state and the disturbed state 1 form a bistable state at $h=0.5712$.

Similarly, from figure 3, $\varepsilon_0=g_U=g_S$ at $h=h_{sat}=0.1801$. Between the two states $u=0$ and $u=1$, there is another state $u_D=0.531$, i.e. a disturbed state φ_D with $\varepsilon_1=g_D$. Thus the uniform and saturated states form a bistable state at $h=0.1801$.

From these statements, we can propose the condition

for existence of the bistable state. It is: if two states with the state parameter u_1 and u_2 ($u_1 < u_2$), are ground states, and between these two states there is another (excited) state with the state parameter u_3, and $u_1 < u_3 < u_2$; then these two states form a bistable state.

4.3. *Influence on response time*

As can be seen from figure 6, the ground state ε_0 is the saturation state $\varphi_S \equiv 90^\circ$. The uniform state $\varphi_U \equiv 0$ is the excited state corresponding to ε_3. Between the two states $u=0$ and $u=1$ there are two more states $\left(u_D^{(1)} \text{ and } u_D^{(2)}\right)$ corresponding to $\varphi_D^{(1)}$ and $\varphi_D^{(2)}$. So, when the transition from state $\varphi_U \equiv 0$ to state $\varphi_S \equiv 90^\circ$ occurs, the state parameter u must jump the two states $u = u_D^{(1)} = 0.5420$ and $u = u_D^{(2)} = 0.7052$. That is to say, both mechanical equilibrium states $\varphi_D^{(1)}$ and $\varphi_D^{(2)}$ may appear in the process of transition as intermediate states. As a result, the response time is affected.

5. The condition for the existence of four discrete energy levels

The case of four energy levels (two of them disturbed states) is more interesting, because it may be applied to some physical phenomena such as the first order transition and bistable state. We now discuss the situation where there are two disturbed solutions. From figure 2 (*a*) we see that this condition is equivalent to the extreme value of the curve $h(u)$ in the region (0, 1) of u, i.e. there is a value u in the region (0, 1), written as u_a, satisfying:

$$\frac{dh}{du}\Big|_{u=u_a} = 0. \tag{24}$$

Differentiating equations (16) and (17) with respect to u separately and substituting the results in (24), we obtain

$$\frac{dv_0}{du} = \frac{1}{2}[v_0(1-v_0)(1-u+uv_0)]^{\frac{1}{2}} \int_{v_0}^{1}\left[\frac{v}{(1-v)(1-u+uv)}\right]^{\frac{1}{2}}\frac{1}{1-u}dv - \frac{v_0(1-v_0)}{1-u} \tag{25}$$

$$\frac{dv_0}{du} = \frac{v_0(1-v_0)}{1-u}\left\{\frac{v_0(1-u+uv_0)[(1-u+uv_0)+2\zeta(uv_0+2u-2)]}{(1-u+uv_0)(1-u+uv_0^2)+2\zeta uv_0[(1-u)(3-2v_0)+uv_0^2)]} - 1\right\}. \tag{26}$$

Using equations (25), (26) and combining with boundary condition (23), we can solve for u. For a given α and ζ, if the value of u obtained is located in the region [0, 1], the condition (24) for two solutions is satisfied. Otherwise, the condition (24) is not satisfied. The result of numerical calculation is shown in Fig. 7. The area in figure 7 shows the region in which the two parameters satisfy the condition (24), i.e. the condition for which there are more than three energy levels. From the figure we can see that ζ must be negative and α is restricted to a certain range.

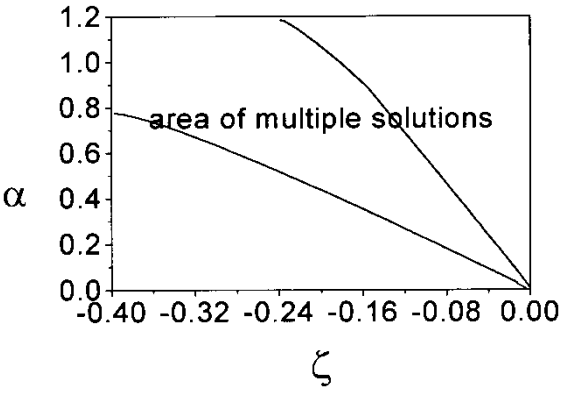


Figure 7. The area in which the two parameters α and ζ satisfy the conditions for having two solutions for the disturbed state.

6. Discussion

We have so far determined that the NLC cell may have three or more discrete energy levels, each corresponding to a certain mechanical equilibrium state, such as a uniform, saturation or disturbed state. We now discuss the thermodynamic properties of these states. According to statistical thermodynamic theory [13], the states with the minimal value of Gibbs free energy G are either stable or metastable states. If the value of G is not only the minimal but also the smallest, the state with the smallest G is stable. On the other hand, if the value of G is minimal only, then its state is metastable. The former is stable over a large interval of state variance, and the latter is stable only over a small interval of state variance.†

The condition for minimal G is [14]

$$\delta G = 0 \tag{27}$$

$$\delta^2 G > 0 \tag{28}$$

i.e if the states satisfy these two equations simultaneously, then they are stable or metastable.

We have proved that all the states φ_U, φ_S, $\varphi_D^{(1)}$ and $\varphi_D^{(2)}$ discussed in the previous section satisfy equations (27) and (28) simultaneously. Hence, all these states are

†Landau and Lifshitz stated that *if a body is in a metastable state, then after a sufficiently large deviation from it the body can not return to its initial state. Although a metastable state is stable within creation limits, sooner or later the body is bound to pass from it to another stable state.*

stable or metastable. The state corresponding to ε_0 is stable and the states corresponding to ε_1, ε_2 ... are metastable. The proof is given in the appendix.

Appendix

The proof of $\delta G=0$ and $\delta^2 G>0$ for all mechanical equilibrium states

Because the solutions of $\varphi(z)$ are obtained from $\delta G=0$, it is necessary to check whether they satisfy $\delta^2 G>0$ only. We adopt the method given in [14, 15], which can be described as follows:

Suppose that $\bar{\varphi}(z)$ is the solution of $\delta G=0$, let

$$\varphi(z)=\bar{\varphi}(z)+\varepsilon\eta(z) \tag{A1}$$

where $\eta(z)$ is an arbitrary function of z in principle and ε is a variable unrelated to z. Equation (A1) implies

$$\delta\varphi(z)=\varepsilon\eta(z). \tag{A2}$$

Substituting equation (A1) into equation (2), G will be a function of ε, denoted by $G(\varepsilon)$. $\delta^2 G>0$ is equivalent to

$$\frac{\mathrm{d}^2 G(\varepsilon)}{\mathrm{d}\varepsilon^2}|_{\varepsilon=0}>0. \tag{A3}$$

Equation (A3) can be used to judge whether $\bar{\varphi}(z)$ makes G minimal. Substituting equation (A1) into (2) and making the second order derivative with ε, we have

$$\begin{aligned}\frac{\mathrm{d}^2 G(\varepsilon)}{\mathrm{d}\varepsilon^2}|_{\varepsilon=0}=S\Bigg\{\int_0^l\Big[(-\chi_a H^2\cos 2\bar{\varphi})\eta^2+K_{22}\left(\frac{\mathrm{d}\eta}{\mathrm{d}z}\right)^2\Big]\mathrm{d}z\\ +A\left[\cos 2\bar{\varphi}_0+2\zeta\sin^2\bar{\varphi}_0\left(3\cos^2\bar{\varphi}_0-\sin^2\bar{\varphi}_0\right)\right]\eta^2(0)\\ +A\left[\cos 2\bar{\varphi}_l+2\zeta\sin^2\bar{\varphi}_l\left(3\cos^2\bar{\varphi}_l-\sin^2\bar{\varphi}_l\right)\right]\eta^2(l)\Bigg\}.\end{aligned} \tag{A4}$$

We adopt Jacobi's intensive condition in variational theory [11, 13] to prove $\delta^2 G>0$. Because we only check whether $\bar{\varphi}(z)$ makes G minimal in a particular region, we can put some restrictions on $\eta(z)$, for example, we adopt

$$\eta(z)=\sum_{n=n_0}^{\infty}C_n\sin\left(\frac{n\pi}{l}\right)z \tag{A5}$$

where C_n is an arbitrary constant quantity and n_0 is an arbitrary integer satisfying

$$n_0>\frac{l}{\pi}\left(\frac{\chi_a}{k_{22}}\right)^{\frac{1}{2}}\mathbf{H} \tag{A6}$$

Substituting equation (A5) into (A6) and taking note that $\cos 2\bar{\varphi}\leqslant 1$, we have

$$\frac{\mathrm{d}^2 G(\varepsilon)}{\mathrm{d}\varepsilon^2}|_{\varepsilon=0}>0.$$

Although some restrictions on $\eta(z)$ are made, this does not affect the property that $\bar{\varphi}(z)$ makes G minimal.† So we have proved that the solutions obtained by $\delta G=0$ make G minimal.

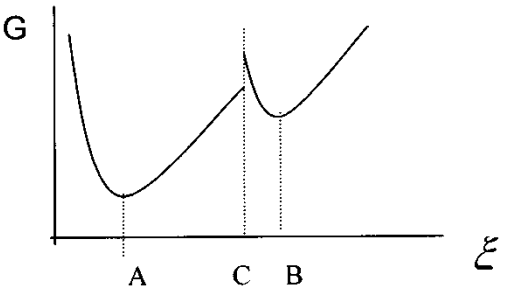


Figure 8. Gibbs free energy G versus state parameter ξ; points A and B correspond to minimal value of G, and C is a singularity.

Why are the values of G for all mechanical equilibrium states minimal? This is due to the existence of singularities in functional G. We can rewrite equation (2) of using the same method and symbols as in [16]:

$$\begin{aligned}G=S\int_{-\infty}^{\infty}\left[\frac{1}{2}k_{22}\left(\frac{\mathrm{d}\varphi}{\mathrm{d}z}\right)^2-\frac{1}{2}\chi_a\mathbf{H}^2\sin^2\varphi\right][\mu(z)-\mu(z-l)]\mathrm{d}z\\ +S\int_{-\infty}^{\infty}\frac{1}{2}A\sin^2\varphi\left(1+\zeta\sin^2\varphi\right)[\delta(z)-\delta(z-l)]\mathrm{d}z\end{aligned} \tag{A7}$$

where $\mu(z)$ is the unit step function and $\delta(z)$ is the Dirac function. Both $\mu(z)$ and $\delta(z)$ are singular function.

To explain the absence of maxima, we examine an ideal simple example, and assume that all states of the system can be expressed by ξ, and that the Gibbs free energy G is a function of ξ and can be described by the curve of figure 8. The two points A and B of this figure are both correspond to minimal values of G, and the point C is a singularity.

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†For a common function, suppose $f(x)$ has a minimal at point x, if we choose $\delta x=x-\bar{x}=\varepsilon$ (ε is small), we have $\delta f=0$, $\delta^2 f>0$; then, choose $\delta x=0.1\varepsilon$, then $\delta f=0$, $\delta^2 f>0$. We see that the property of $f(x)$ being minimal at the point x is not affected by the restriction of δx. The same restriction in discussion of the minimal of functional was in [14, 15].

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