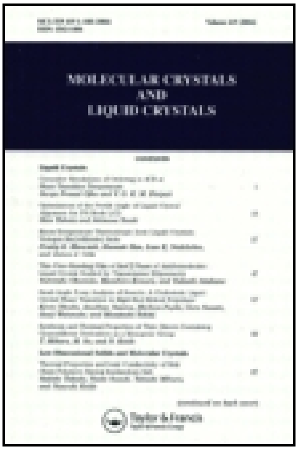

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Surface Anchoring of Nematic Liquid Crystals

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Version of record first published: 03 Jan 2007.

To cite this article: H. Yokoyama (1988): Surface Anchoring of Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 165:1, 265-316

To link to this article: http://dx.doi.org/10.1080/00268948808082204

Mol. Cryst. Liq. Cryst., 1988, Vol. 165, pp. 265–316
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Printed in the United States of America

Surface Anchoring of Nematic Liquid Crystals

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(*Received November 20, 1987; in final form April 19, 1988*)

Existing experimental techniques for measuring the orientational anchoring strength at a substrate-nematic interface are critically analyzed with a particular emphasis on their macroscopic basis and on the range of applicability and precision. Conceptual basis of the anchoring strength is first clarified by making a distinction between the macroscopic and the microscopic approaches toward the substrate-nematic interface, and the significance of the Gibbs' dividing surface is emphasized together with some thermodynamic properties of the anchoring strength and pretilt angle. The principles of some typical experimental techniques are next reviewed from a fundamental viewpoint, and possible complications and sources of error in these methods, when applied to an interface with strong anchoring, are discussed. Drawing upon the result of the "high-electric-field technique" which yields an anchoring energy apparently larger than 10^{-3} J/m^2, the greatest value ever observed, for a planar-aligned nematic on rubbed polymer surface, it is argued through the consideration of the dividing surface that the observed anchoring strength, though still meaningful as a thermodynamic parameter, does not necessarily imply the existence of strong substrate-nematic orientational coupling on the microscopic scale.

I. INTRODUCTION

The alignment of nematic liquid crystals at their boundary with other distinct media has been a constant scientific and technical issue through the history of liquid crystal. From the very early days, indeed, the ability of some solid substrates to uniformly orient liquid crystal molecules has fascinated such great figures as Lehmann,[1] Mauguin,[2] Grandjean,[3] Zocher,[4] and Chatelain,[5] and helped them facilitate precise measurements of the anisotropic properties of liquid crystals. In

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particular, the advent of liquid crystal displays in the late 1960s sparked a great deal of practical interest into this phenomenon, resulting in an extensive pursuit and elaboration of alignment know-hows[6-8] including such well-known surface-treatment methods as rubbing and mechanical scribing, vacuum deposition of metals and oxides, application of polymer coatings, and physical or chemical adsorption of surface active agents. Recently, furthermore, stimulated by the emergence of supertwisted nematic[9] and ferroelectric[10] liquid crystal displays, the list of these techniques has been steadily expanding,[11] even outside the realm of nematics.[12] Despite the eminent developments of alignment techniques, however, a detailed characterization of the nematic-substrate interface has long remained formidably difficult due to the lack of appropriate experimental techniques. Nevertheless, some progress has been made in recent years, which would hopefully be a first step to a more profound understanding of the physicochemical basis of the alignment. The purpose of this article is to critically review the existing characterization methods from a fundamental standpoint with a view to founding a basis for future development. Those who are interested in the details of alignment techniques are advised to consult an extensive review by Congnard.[7]

The surface alignment of nematics is one of the few macroscopic phenomena in which the boundary effect plays an essential role in determining the behavior of the bulk phase. In fact, the preferential (microscopic) molecular orientation induced at the surface propagates far into the bulk nematic by way of the curvature elasticity and leads to an overall alignment of the nematic director. Put differently, the director is "anchored" along an easy axis produced by the nematic surface. For a given nematic and a substrate, the easy axis assumes either perpendicular, parallel, or slanted orientation with respect to the substrate. These configurations are referred to as homeotropic, planar, and pretilted alignments, respectively. From a technological viewpoint, a precise and reliable control of the easy axis is indispensable. Indeed, in twisted nematic displays, a slightly pretilted alignment is playing an important role to eliminate orientational defects which significantly deteriorates the device performance. At preset, the supertwisted nematic display,[9] which essentially requires a pretilt angle as large as 30° for its operation, is posing a new challenge for alignment techniques.[11] Though some substrates are conventionally known to yield a pretilted alignment,[7] it has been found in several occasions[13-17] that the easy axis undergoes a marked temperature-induced variation, especially at temperatures near the clearing point.

In order to microscopically explain the behavior of the easy axis at various types of nematic surfaces, a number of theoretical efforts have so far been made from a continuum,[18-22] statistical mechanical,[23-32] phenomenological,[33-37] and elastic[38,39] standpoints. Although they gave a good deal of information on the surface alignment phenomenon, a first-principle description of the anchoring process in real systems is still an overwhelmingly complicated matter, because of the variety of intermolecular interactions involved and the presence of an interfacial inhomogeneous layer whose properties are little understood.

For the purpose of accounting for the surface effects on bulk nematics, therefore, the surface anchoring has been most commonly treated and understood on the basis of a phenomenological formalism due to Rapini and Papoular.[40] Therein, the interfacial tension between the nematic and the substrate γ is regarded as a function of the director at the interface $\mathbf{n}_0$:

$$\gamma(\mathbf{n}_0) = \gamma_0 + \frac{1}{2} E_a[1 - (\mathbf{n}_0 \cdot \mathbf{n}_e)^2], \tag{1}$$

where $\mathbf{n}_e$ is a unit vector along the easy axis, and γ_0 is the interfacial tension when $\mathbf{n}_0$ is parallel to the easy axis. And E_a is a phenomenological coefficient expressing the anchoring strength, usually referred to as the anchoring energy. Then, it is generally understood that $\gamma(\mathbf{n}_0)$ supplies a boundary condition for the director configuration in the bulk nematic. For simplicity, the anchoring energy is here assumed to be isotropic with respect to the direction to which $\mathbf{n}_0$ is deviated from $\mathbf{n}_e$. In general, however, the anchoring energy depends on the direction; that associated with the rotation of the director within the plane spanned by $\mathbf{n}_e$ and the substrate normal is referred to as the "polar" or "out-of-polar" anchoring energy and that corresponding to the rotation perpendicular to it is called the "azimuthal," "torsional," or "in-plane" anchoring energy. The surface anchoring is further classified, sometimes loosely though, into "strong" or "weak" anchoring according to whether or not $\mathbf{n}_0$ can be assumed to stay approximately parallel to $\mathbf{n}_e$. Several years ago, de Gennes[41] noted on the basis of a heuristic argument that, if the anisotropic interaction at a nematic-substrate interface is as large as that acting between nematic molecules, the anchoring energy can be roughly estimated by $E_a \sim K/a$, where K is the Frank elastic constant and a the molecular dimension; so that, by taking $K \sim 5 \times 10^{-12}$ N and $a \sim 5 \times 10^{-10}$ m, one finds $E_a \sim 10^{-2}$ J/m^2, which corresponds to the strong anchoring in virtually all practical cases. By later experiments,[42-74] however, the values of the anchoring energy have been found to be scattered over $10^{-7} \sim 10^{-3}$ J/m^2, reflecting the variety of interfacial conditions in real systems. In addition, although the reports on the azimuthal anchoring energy are relatively scarce,[49,50,64,71] their values tend to be one or two orders smaller than the corresponding polar anchoring energy.[75]

In the Rapini-Papoular formalism, the property of the nematic surface is expressed in terms of a couple of parameters, the easy axis and the anchoring energy. However, there exists a fundamental conceptual difference between these two parameters. First of all, the easy axis always has an unambiguous physical meaning, independent of a model of interface as Equation 1. In fact, it represents the director in the *bulk* nematic in the absence of deformations; so that, as a macroscopic variable, it can now be routinely measured with considerable accuracy by means of, for example, the magneto-capacitance or magneto-optical null method.[76] The anchoring energy, on the other hand, is essentially an interfacial parameter that embodies the anisotropic interactions operating at the nematic-substrate interface, and, as often the case with other surface-specific properties,[77] it is a rather abstract concept which is accessible only through an appropriate theoretical framework. As will be mentioned in the next section, it is possible to give a thermodynamic definition to it; but we must emphasize that, strictly speaking, the anchoring energies which could be measured by conventional methods do not always coincide with the thermodynamic definition and could also in general be very different from each other. Although this subtlety might appear to play only a minor role unless the anchoring is very strong, it does become important once we attempt to facilitate a unified treatment of anchoring process or to infer the alignment mechanism from the knowledge of anchoring strength. This, I believe, is partly the reason why, despite numerous attempts so far devoted to measure the anchoring energy for various nematic-substrate combinations,[42-74] its measurement and interpretation still remain highly problematic and even controversial.

In the present paper, I would like to emphasize the thermodynamic aspect of the anchoring strength and show its consequences on various methods so far developed for measuring the anchoring strength. For this purpose, I shall clarify in Section II the conceptual basis of the anchoring energy by outlining the distinction between macroscopic (thermodynamic) and microscopic approaches toward the substrate-nematic interface, the point which has been largely overlooked in the literature, and also derive some thermodynamic relationships for the easy axis and the anchoring strength. In Section III, the principles of some typical experimental methods will be analyzed from a thermodynamic standpoint, and their precision and potential problems in applying these methods will be discussed. Finally, drawing upon the results of the application of the "high-electric-field technique,"[69,70] I will point out, through a qualitative examination of the role of dividing surface, that the strong macroscopic anchorage does not necessarily imply the existence of strong substrate-nematic orientational coupling on the microscopic level.

II. CONCEPTUAL BASIS OF THE ANCHORING ENERGY

As mentioned above, the anchoring energy is defined as a phenomenological parameter appearing in the expression of the interfacial tension. However, depending on one's recognition of the physical status of the phenomenological theory itself, *i.e.*, whether one views it as a purely macroscopic (thermodynamic) representation of the nematic interface or a type of microscopic model, the meaning of the anchoring energy does experience a significant conceptual change. Since the phenomenological descriptions such as the Rapini-Papoular formalism have been naively understood in the literature, this intricacy has been largely overlooked and still seems to be causing an unnecessary confusion among workers.

In the most generalized form, those phenomenological theories assume that the free energy of the system Ω be written as a sum of the surface and the bulk contributions.[78] For simplicity, let us suppose a semi-infinite slab of nematic liquid crystal in contact with a substrate of area A. Then, phenomenological theories demand that

$$\Omega = A\gamma + \Omega_{\text{bulk}}, \tag{2}$$

where the first and the second terms on the right-hand side represent the surface and the bulk contributions, respectively. In the case of the Rapini-Papoular formalism, the interfacial tension γ is given by Equation 1, and Ω_{bulk} is identified with the Frank curvature elastic energy supplemented with the interaction energy with external fields.

The role of the phenomenological expression as Equation 2 is two fold: Firstly, when γ and Ω_{bulk}[23,34-39,79-82] are assigned with appropriate functions of the director, the order parameter, or the like, it serves as a theoretical model of the interface and yields information on the interface structures on the basis of the minimum property of Ω; Secondly, if we restrict the attention to thermal equilibrium, Equation 2 can be regarded as a thermodynamical decomposition of the free energy in Gibbs' sense.[83] These two standpoints, which we shall hereafter refer to as the *structure-model perspective* and the *thermodynamic perspective* respectively, should be clearly distinguished from each other. In the former perspective, the choice of function for γ is somewhat arbitrary as far as it can be expected to represent some reality of the nematic interface, and its consequence on bulk behavior and so forth is studied afterwards. In the latter, however, we are first given the thermodynamic state of the bulk phase, and γ is then automatically defined as the difference between Ω and Ω_{bulk} according to Equation 2; and only in this perspective, we can define the anchoring strength as a macroscopically meaningful parameter just like the easy axis.

A. Thermodynamic perspective

Let us consider that a nematic liquid crystal is put into contact with a uniform substrate, and is in complete thermodynamic equilibrium in the absence of an external field. So, if we assume that ξ_i is the thickness of the interfacial inhomogeneous region and that the interface lies somewhere around $z = 0$, the nematic at a point $z \gg \xi_i$ can be well regarded bulklike. Imagine that the nematic is subject to a small director distortion along the z-axis (by means of some orientational agent at infinity). Since, as well known, the configuration of the director within bulk region can be described by the Frank theory of curvature elasticity as long as the distortion is sufficiently weak,[41] it immediately follows that, if a couple of directors $\mathbf{n}_1$ and $\mathbf{n}_2$ are known at two points z_1 and z_2 ($\gg \xi_i$) in the bulk region, the equilibrium configuration of the director in question can be completely reproduced all through the bulk nematic.[84] The presence of the substrate-nematic interface, however, makes not all the choices of $\mathbf{n}_1$ and $\mathbf{n}_2$ correspond to the equilibrium states of the system in question. Indeed, in this situation, we have to regard[83] $\mathbf{n}_2$ as a function of $\mathbf{n}_1$, or vice versa. As a consequence, by giving a director at an arbitrary point in the bulk nematic, we can fully specify the equilibrium state of the nematic in contact with a substrate. Equation 2 can then be more specifically written as

$$\Omega = A\gamma(\mathbf{n}_1) + \Omega_{\mathrm{bulk}}(\mathbf{n}_1). \tag{3}$$

In the Gibbs surface thermodynamics,[77] a hypothetical *dividing surface* is first taken at an arbitrary point, and both phases in contact with each other are then assumed to remain bulklike right up to the dividing surface so as to define various superficial quantities. At present, by adopting the dividing surface at z_d, we may write the hypothetical bulk contribution as follows:

$$\Omega_{\text{bulk}} = \Omega_0 + A\int_{z_d}^{\infty} f_d(\mathbf{n}[z;\mathbf{n}_1], d\mathbf{n}[z;\mathbf{n}_1]/dz)\, dz. \tag{4}$$

Here, Ω_0 is the free energy in the absence of deformation, $\mathbf{n}[z;\mathbf{n}_1]$ is the director at z for the equilibrium director profile specified by $\mathbf{n}_1$, and f_d denotes the Frank elastic energy density. In Equation 4, when such points where $z >> \xi_i$ no longer holds are involved, the director configuration is understood to be analytically continued from the bulk profile in accordance with Gibbs' spirit. Therefore, although the position where $\mathbf{n}_1$ is taken is originally assumed to be well inside the bulk region, it is now essentially arbitrary and conveniently located on the dividing surface. Then, we can rewrite Equation 3 as[85]

$$(\Omega - \Omega_0)/A = \gamma(z_d,\mathbf{n}_d) + \int_{z_d}^{\infty} f_d(\mathbf{n}[z;\mathbf{n}_d], d\mathbf{n}[z;\mathbf{n}_d]/dz)\, dz. \tag{5}$$

In this case, there is also an important thermodynamic relation, valid at constant temperature and chemical potentials:

$$d\gamma(z_d,\mathbf{n}_d) = \sum_{j=x,y,z} \frac{\partial f_d}{\partial(dn_{d_j}/dz)}\, dn_{d_j}, \tag{6}$$

which allows us to find the interfacial tension from the knowledge of the equilibrium director configuration in the bulk nematic. In particular, though the functional dependence of $\gamma(z_d,\mathbf{n}_d)$ on $\mathbf{n}_d$ may differ with the choice of z_d, it can be shown[83] that when the elastic distortion is infinitesimally small ($\mathbf{n}(z)\approx\mathbf{n}_e$), the interfacial tension can be generally written as

$$\gamma(z_d,\mathbf{n}_d) \approx \gamma_0 + \frac{1}{2} E_a(z_d)\, [1 - (\mathbf{n}_d\cdot\mathbf{n}_e)^2]. \tag{7}$$

where $E_a(z_d)$ is a function of z_d and also of the mode of deformation, bend, twist, or splay, existing in the bulk phase. Accordingly, once z_d is specified, $E_a(z_d)$ becomes a well-defined thermodynamic parameter which takes care of the response of the substrate-nematic interface to an *infinitesimal* external curvature stress. All the existing experimental methods for macroscopically measuring the anchoring strength can be viewed as aiming, in one way or another, at the determination of the parameter $E_a(z_d)$.

Equations 5–7, when z_d is identified with the *position of the interface*, look very much like the Rapini-Papoular formalism. However, there exist some fundamental differences that must be clearly noted: (1) $\gamma(z_d,\mathbf{n}_d)$ is defined with respect to an arbitrarily taken dividing surface, and hence the corresponding anchoring energy and director are meaningful only in relation to the dividing surface; (2) Since the director $\mathbf{n}_d$ is essentially a variable to specify the *bulk* director configuration, it does not necessarily coincide with the *actual local* director at z_d (particularly when z_d is taken inside the interfacial region); (3) When $z_d >> \xi_i$ holds, however, $\mathbf{n}_d$ is equal to the actual director at z_d and $\gamma(z_d,\mathbf{n}_d)-\gamma(z_d,\mathbf{n}_e)$ is just the free energy stored in the region $z<z_d$ during the course of director rotation from $\mathbf{n}_e$ to $\mathbf{n}_d$. Unfortunately, however, no serious care has ever been taken to the meaning of z_d and of the infinitesimal criterion of the applied curvature stress in each specific experimental situation. To show up the contrast with the Rapini-Papoular formalism, it should also be worth pointing out that when an electric or magnetic field F_{ext} exists, the thermodynamic anchoring energy should in general become a function of F_{ext},

$$E_a = E_a(z_d,F_{ext}). \tag{8}$$

As Equation 7 suggests, the anchoring energy $E_a(z_d)$ is a notion concerned with the energetics of the substrate-nematic interface. As first shown by de Gennes,[41] it is also possible to define a geometrical measure of the anchoring strength, *i.e.*, the extrapolation length d_e: The distance between the *substrate-nematic interface* and the fictitious point where the director would be always parallel to $\mathbf{n}_e$, when the bulk profile is extrapolated to that point. In the thermodynamic perspective,[83] however, this definition is not generally valid, and we need to revise it as a distance between the dividing surface and the hypothetical surface across which no orientational work is performed in response to the deformation of the bulk director profile; we shall call this surface as the "surface of extrapolation." Since no orientational work can evidently be done across a plane where the director is fixed (at $\mathbf{n}_e$), it should be clear that the revised definition contains the usual one as a special case. In this revised sense, the extrapolation length is a more universal concept than the anchoring energy, and we can talk about it even when a finite director distortion with an arbitrary mode exists in the bulk nematic.

For a change of the dividing surface ($z_d \to z_d'$), the extrapolation length by definition satisfies

$$d_d(z_d') = d_e(z_d) + z_d' - z_d. \tag{9}$$

Furthermore, at an infinitesimal distortion with a pure splay-bend or a pure twist-bend mode, the extrapolation length can be related to the corresponding anchoring energy by

$$d_e(z_d) = [K_1 + (K_3 - K_1)(\mathbf{n}_e \cdot \mathbf{k})^2]/E_a(z_d), \tag{10}$$

$$d_e(z_d) = [K_2 + (K_3 - K_2)(\mathbf{n}_e \cdot \mathbf{k})^2]/E_a(z_d), \tag{11}$$

where **k** is the unit normal of the substrate, and K_1, K_2, and K_3 are the Frank elastic constants for splay, twist, and bend deformations, respectively.[41] From Equations 9–11, the anchoring energies for different dividing surfaces satisfy

$$1/E_a(z_d') = 1/E_a(z_d) + (z_d' - z_d)/K, \tag{12}$$

with K being the appropriate elastic constant for splay-bend or twist-bend mode. It is worth noting that, in the thermodynamic perspective, E_a can assume even a negative value depending on the location of the dividing surface.

As thermodynamic parameters, $\mathbf{n}_e$ and E_a satisfy some thermodynamic relations[70,83] which serve as a good source of information as to the alignment mechanism. For simplicity, let us assume that the nematic in question is of single component. Then, as well-known in surface thermodynamics,[77] the surface-excess entropy S^s is obtained from the temperature derivative of the interfacial tension with the dividing surface taken at the plane of zero adsorption z_0. By writing the orientational part as $\Delta S^s(\mathbf{n}_0)$, we find from Equation 7 that

$$\Delta S^s(\mathbf{n}_0) = -\left[\frac{\partial[\gamma(\mathbf{n}_0, z_0) - \gamma_0]}{\partial T}\right]_{\mathbf{n}_d}$$

$$\approx -\frac{1}{2}\frac{\partial E_a(z_0)}{\partial T}[1 - (\mathbf{n}_0 \cdot \mathbf{n}_e)^2] + E_a(z_0)(\mathbf{n}_0 \cdot \mathbf{n}_e)\mathbf{n}_0 \cdot \frac{\partial \mathbf{n}_e}{\partial T}. \tag{13}$$

Similarly, the surface-excess energy becomes

$$\Delta U^s(\mathbf{n}_0) \approx \frac{1}{2}\left[E_a(z_0) - T\frac{\partial E_a(z_0)}{\partial T}\right] [1 - (\mathbf{n}_0\cdot\mathbf{n}_e)^2] + TE_a(z_0)(\mathbf{n}_0\cdot\mathbf{n}_e)\mathbf{n}_0\cdot\frac{\partial \mathbf{n}_e}{\partial T}. \qquad (14)$$

When the easy axis changes with temperatures as found for cyanobiphenyls in contact with SiO films deposited at a glancing angle,[14-16] the second term dominates on the right-hand side of Equations 13 and 14 as long as $\mathbf{n}_0$ is sufficiently close to $\mathbf{n}_e$. In this case, it follows that, when $\mathbf{n}_0$ is forced to rotate from $\mathbf{n}_e$ in the same direction as $\mathbf{n}_e$ moves with the increase in temperature, we have $\Delta U^s \approx T\Delta S^s > 0$, but when $\mathbf{n}_0$ is rotated in the opposite direction, $T\Delta S^s \approx \Delta U^s < 0$; for brevity, E_a is here assumed to be positive. This shows that the stability of the alignment along $\mathbf{n}_e$ is realized by the balance between energetic and entropic forces, say, van der Waals[23,24] and the surface excluded volume[28] interactions, and that $\mathbf{n}_e$ changes its direction in such a way that the entropic force tends to dominate as the temperature is raised.

At the free surface of MBBA, Bouchiat and Langevin,[13] and Chiarelli, *et al.*[17] found that the alignment direction continuously transforms from pretilted to homeotropic as the temperature is increased, while the angle θ_e between the easy axis and the surface normal satisfies the relation, $\theta_e \propto (T_0 - T)^{1/2}$, where T_0 is a temperature about 1 K below the clearing point. In conformity with the above, Kimura and Nakano[29] interpreted this behavior via mean-field theory in terms of the competition between the intermolecular van der Waals attraction and steric repulsion, which respectively favor the planar and the homeotropic alignments at a nematic free surface. Upon substituting the above θ_e in Equation 13, we readily find that E_a has to change as $(T_0 - T)^\eta$ with $\eta \geq 1$ in order for the entropy to remain finite at T_0. The experimental observation by Chiarelli *et al.*,[64] that the anchoring energy vanishes at T_0 as $(T_0 - T)$ is indeed consistent with this condition. Finally, when the easy axis is invariant with respect to temperature, the temperature dependence of the anchoring energy gives the information on the entropic and the energetic contributions. This time, however, the dominance between these two parts does not depend on the direction to which the director is deviated from the easy axis.

B. Structure-model perspective

In the structure-model perspective, the *director at the interface* and so forth are expected, in contrast to the above, to have directly something to do with the averaged orientation of actual molecules present near the interface. A classic paper by Dubois-Violette and de Gennes[23] provides a good example of this approach; they studied the effect of long range van der Waals interaction between an anisotropic substrate and a nematic by using the local director as a sole variable to express the orientational structure of the nematic even within the interfacial transition layer. Although they didn't show explicitly, their model amounts to chose the interfacial tension as

$$\gamma = \frac{1}{2}\, U[\mathbf{n}(0)\cdot\mathbf{n}_e]^2 + \int_0^{\infty} \frac{1}{2}\, \Gamma_{VW}(z)\, [\mathbf{n}(z)\cdot\mathbf{n}_e]^2\, dz. \tag{15}$$

Here, U denotes the strength of the localized interaction at $z = 0$ (the position of the substrate surface), and $\Gamma_{VW}(z)$ gives the density of van der Waals interaction energy between the substrate and the nematic with the local director $\mathbf{n}(z)$. They adopted the Frank elastic energy for Ω_{bulk}, and obtained the extrapolation length $d_e(0)$ for the model interfacial tension Equation 15.

In the structure-model perspective, the choices of the variables to express the microstructure and of the functional form of the interfacial tension are essentially dependent on one's interest and the degree of approximation required. And they are expected to eventually yield the thermodynamic interfacial tension $\gamma(z_d,\mathbf{n}_d)$ and hence $E_a(z_d)$ and $d_e(z_d)$ for the model to compare with experimental results. In this respect, there still seem to remain some confusions between the structure-model and the thermodynamic perspectives even in the current literature. Barbero *et al.*,[81] for example, *analyzed* various functional forms of the thermodynamic interfacial tension on the basis of the data from *their* macroscopic experiment; and they *generally* rejected the existing functional forms reported by other workers as being inadequate for explaining their experiment, and proposed a new mathematical scheme for the representation of the interfacial tension. Here, however, we need to recall the fact that there is no thermodynamic restriction on the form of $\gamma(z_d,\mathbf{n}_d)$ except at around some special points where a uniform director alignment is stable or mestastable, *i.e.* $\mathbf{n}_d = \mathbf{n}_e$, etc., [cf. Equation 7]. This means that $\gamma(z_d,\mathbf{n}_d)$ is something that must be experimentally determined, case by case, via Equation 6 [for an example of this procedure, see Reference (69)]. So, mathematical representation of $\gamma(z_d,\mathbf{n}_d)$ itself is not so important a matter as long as it can satisfactorily reproduce the individual experimental result while satisfying a minimum condition as Equation 7; in this sense, the functional forms discarded by Barbero *et al.* are as good as their own. Considerations of the general functional form of the thermodynamic interfacial tension make sense only when they are based on some model of microstructure.

Finally, I would like to quote another example from the literature which clearly signifies the nature of the structure-model perspective. In the theory of curvature elasticity due to Oseen[86] and Nehring and Saupe,[87] there appears a surface contribution as

$$K_{13}\mathrm{div}(\mathbf{n}\ \mathrm{div}\ \mathbf{n}), \tag{16}$$

along with the usual volumetric terms found in the Frank theory. This contribution apparently gives rise to a surface energy which contains the spatial derivative of the director.[88] Similar terms have also been introduced through phenomenological consideration of the interfacial free energy by Dubois-Violette and Parodi,[79] and Mada.[34] And the treatment of these terms has posed a somewhat long lasting problem in the surface physics of nematics.[80,81,89] As clear from the earlier discussion, it is absolutely nonsense to ask whether the thermodynamic interfacial tension should include such terms or not, as long as the orientational state of the bulk nematic is assumed to obey the Frank theory. In the structure-model perspective, however, such a question does deserve a serious consideration, although the presence of these terms makes the configurational problem ill-defined in the ordinary context, as explicitly indicated by Oldano and Barbero.[81] As also pointed out by these authors, since the derivative-dependent term comes from the nonlocal nature of the nematic-nematic and substrate-nematic interactions,[88] what one needs to do, if it is truly necessary, is to take this point more explicitly into account, as done by Dubois-Violette and de Gennes,[23] not to simply discard it as intractable. In any event, it should be strictly noted that the existence of derivative-dependent terms in the structure model never jeopardize the validity of thermodynamic interfacial tension $\gamma(z_d,\mathbf{n}_d)$, which depends only on the director. Similarly, a surface term proportional to $\mathbf{n}\cdot\mathbf{k}$ is meaningful in a structure model which attempts to account for a "polar order" at a nematic interface,[45,90] but not permissible in the thermodynamic interfacial tension, since the latter should always be invariant for $\mathbf{n}_d \rightarrow -\mathbf{n}_d$.

III. TECHNIQUES FOR MEASURING THE ANCHORING STRENGTH

As noted in the previous section, the concept of the anchoring strength has double facets; one is concerned with the energetics of the nematic interface and the other with its geometrical property with respect to the director configuration. In principle, therefore, the measurement of the anchoring strength can be accomplished from both directions. In Figure 1, various techniques reported in the literature are classified according to their measurement principles. First, we distinguish between *indirect*[42-49] and *direct*[50-74] techniques. The indirect technique refers to a method which passes the energetics route, and in reality, consists in the physico-chemical measurements of the work of adhesion (between the nematic and the substrate) by means of, for example, the traditional contact angle experiments. The direct technique, on the other hand, goes the geometrical path, and stands for such methods that rely, literally, on directly observing the change of the director configuration when the nematic in contact with the substrate is subjected to an external curvature stress. The direct techniques are further categorized into several sub-groups according to how the orientational torque is introduced. For example, the high-

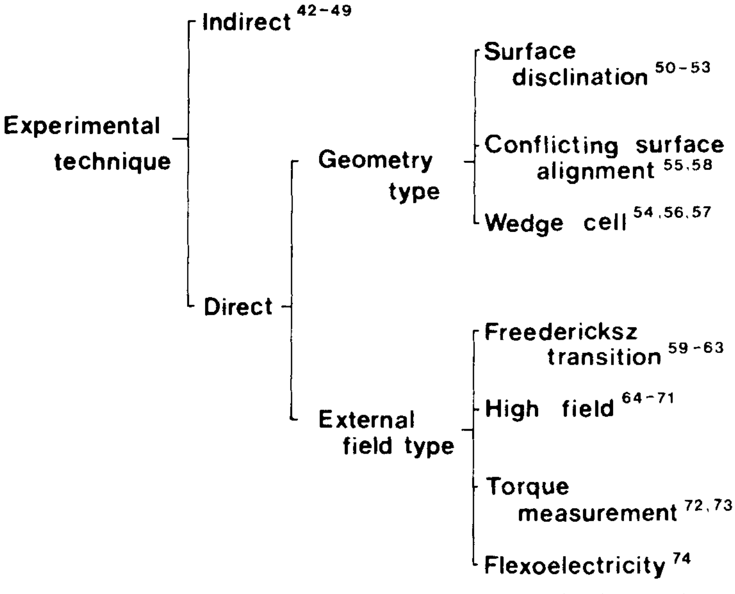

FIGURE 1. Classification of various macroscopic experimental techniques for measuring the anchoring strength. Numbers denote the references.

electric-field technique, which we will discuss in detail later, belongs to the class of *direct*, *external-field type*, and *high-field* techniques.

A. Indirect technique

This type of technique consists in the comparison of the interfacial tensions when the director is set parallel or perpendicular to the easy axis. Based on the Rapini-Papoular interfacial tension, Equation 1, we readily find a formal expression of the anchoring energy as

$$E_a = 2[\gamma(\pi/2) - \gamma_0], \tag{17}$$

where $\gamma(\pi/2)$ and γ_0 denote the interfacial tensions when $\mathbf{n}_0$ is perpendicular and parallel to $\mathbf{n}_e$, respectively. Hence, if $\gamma(\pi/2)$ and γ_0 are known, the anchoring energy can be automatically obtained via Equation 17. It should, however, be emphasized that the above E_a can be identical with the thermodynamic anchoring energy (which depends on z_d), only if the Rapini-Papoular form applies even for large distortions; but this can at best be true for a special choice of z_d.

To proceed, the well-known Girifalco-Good-Fowkes semi-empirical relation[91-93] has been utilized so as to evaluate the relevant interfacial tensions. According to this relation, the work of adhesion W_{ab} between two media, a and b, can be written as

$$W_{ab} = 2\Phi(\gamma_a\gamma_b)^{1/2}, \tag{18}$$

in terms only of the surface tensions of each separate phase, γ_a and γ_b. Here, Φ is a system parameter that is apt to be set unity in most applications. Hence, the interfacial tension between a and b becomes

$$\gamma_{ab} = \gamma_a + \gamma_b - 2(\gamma_a\gamma_b)^{1/2}. \tag{19}$$

Fowkes,[93] furthermore, postulated that the contributions to γ_{ab} from various types of intermolecular interactions, *i.e.* polar, dispersion, hydrogen-bonding, etc., are additive, and Equation 19 is valid for each component of interaction.

In order to simplify the argument, let us here consider the case in which only the dispersion force is in action between the solid and the nematic. In the literature,[42-49] it is tacitly assumed that the director-dependent interfacial tension $\gamma(\mathbf{n}_0)$ can also be written in the Girifalco-Good-Fowkes form:

$$\gamma(\mathbf{n}_0) = \gamma_S + \gamma_L(\mathbf{n}_0) - 2[\gamma_S\gamma_L(\mathbf{n}_0)]^{1/2}, \tag{20}$$

even when the director $\mathbf{n}_0$ differs from the easy axis $\mathbf{n}_e$, where γ_S and $\gamma_L(\mathbf{n}_0)$ are the surface tensions of the substrate and the nematic.[94] Then, from Equations (20) and (17), we find

$$E_a = 2[\gamma_S^{1/2} - \gamma_L(\pi/2)^{1/2}]^2 - 2[\gamma_S^{1/2} - \gamma_L(0)^{1/2}]^2. \tag{21}$$

Equation 21 is the fundamental formula for the indirect physico-chemical technique for estimating the anchoring energy at a solid-nematic interface. The remarkable feature of this technique is that the ingredients of the theory are only the surface tensions of the solid and the nematic phases, when they exist separately. When, in particular, the anisotropy of the nematic surface tension, $\Delta\gamma_L = \gamma_L(\pi/2) - \gamma_L(0)$, is small, Equation 21 can be approximated by

$$E_a \approx 2\frac{\gamma_L^{1/2} - \gamma_S^{1/2}}{\gamma_L^{1/2}}\Delta\gamma_L. \tag{22}$$

This equation shows that when $\gamma_L > \gamma_S$, the nematic tends to align at the solid surface in the same direction as at the nematic free surface, and when $\gamma_L < \gamma_S$, in the perpendicular direction. If we admit that the alignment at the free surface is homeotropic (although this is not necessarily true in reality), this agrees with the Creagh-Kmetz empirical rule.[52,95] Naemura[44,45] applied these formulas to a wide variety of surfactant-coated substrates in contact with a homeotropically aligned nematic, and favorably compared the resultant anchoring energies (on the order of 10^{-5} J/m^2) with those directly measured with the Freedericksz transition technique (see below). Mada,[49] on the other hand, estimated the azimuthal anchoring energy of a planar-aligned cyanobiphenyl by introducing the anisotropic surface tensions of the substrate and of the liquid crystal, and found the values around 10^{-4} J/m^2, which are substantially larger than that directly obtained by the torque-measurement method[73] for a similar system.

Let us now shortly consider the basic problems and the validity of this physico-chemical technique as a method for quantitatively measuring the anchoring strength. Of central importance to the present framework is clearly the use of Girifalco-Good-Fowkes relation. Although the utility of this relation is now well established for ordinary liquid systems, this formula can be used with certain confidence, as admitted by Girifalco and Good,[91] only when an error of a few 10^{-3} J/m^2 is permissible. However, since the anchoring energies are at most 10^{-3} J/m^2, it might appear quite senseless to use this semi-empirical formula to calculate the anchoring energy. Although it might be expected that a favorable cancellation between these errors would occur in Equation 21, it is therefore important to note that this relation is based on several assumptions whose validity is not necessarily clear with regard to anisotropic systems as follows: (1) When two media are put into contact, the change of their structures near the contact plane has only a negligible effect on the interfacial tension; (2) The intermolecular interaction acting between the two media is pairwise additive and isotropic. Even in the case of ordinary liquids, it is hardly possible in each specific case to assess how good these assumptions are.[96] With regard to the first assumption, an exact statistical mechanical theory of solid-liquid interface[96] shows that the work of adhesion can be formally written as a sum of (1) solid-liquid interaction term and (2) relaxation term, and that in many cases, these terms make comparable contributions. Qualitatively speaking, the Girifalco-Good-Fowkes theory takes account only of the former term while neglecting the latter which corresponds to the free energy change when the liquid is relaxed from the structure assumed near the substrate to that at a free surface. The commonest structural change at a nematic interface is the spatial variation of the orientational order parameter induced by the substrate.[36,97-100] Indeed, it is experimentally known that the orientational order near the interface drastically changes from one substrate to the other; the order parameter is generally high at the surface of rubbed polymer, but it is low at an inorganic surface such as evaporated SiO. As clear evidence showing that these structural changes do have a significant effect on the anchoring energy, it has been demonstrated in recent experiments (using direct methods with which we will be concerned later) that the anchoring strength at obliquely evaporated SiO reduced ten times only in 1 K just below the clearing temperature,[70,73] while at a rubbed polymer surface, the anchoring remains strong as will be shown in the next section [see also Reference 68]. On the basis of the physico-chemical formula Equation (22), it seems hopelessly difficult to consistently explain such behaviors.

In order, next, to appreciate the effect of the second assumption listed above, it will suffice to consider the following thought-experiment. Let us imagine that the substrate is such as to align the nematic director in the same direction as at the free surface, i.e. $\gamma_L > \gamma_S$. Then, according to Equation 21, it is readily shown that

$$E_a < 2\,\Delta\gamma_L. \qquad (23)$$

This indicates that the anchoring energy at this solid surface can never exceed the value at the free surface. In other words, as far as the alignment in the direction same as that at the free surface is concerned, any solid is only to disturb the alignment. This is obviously physically unreasonable, for it is in principle possible to conveive a substrate which exerts a torque of whatever strength in such a way as to enhance the strength of the alignment. This paradox arises from the neglect of the anisotropic interaction between the substrate and the nematic in the Girifalco-Good-Fowkes theory. Similarly, since γ_L should obviously be invariant for rotations of the director about the surface normal, the neglect of anisotropic interaction leads again to an unphysical prediction that the azimuthal anchoring energy be always zero; to overcome this difficulty, however, Mada[49] took into account the anisotropy of surface tensions in a rather *ad hoc* manner.

In view of all these shortcomings, the indirect physico-chemical technique appears to be only of qualitative or heuristic significance, as drawing an easy picture of the surface alignment in terms of a language familiar to surface scientists. As a quantitative method for measuring the anchoring energy, it is almost fatal that we cannot estimate the uncertainty involved in the resulting anchoring energies and cannot infer its origins. This type of technique would be useful only after the physico-chemical basis of the substrate-nematic interfacial tension is fully understood.

B. Direct technique

The direct techniques measure, in one way or another, the effect of solid substrate on the director profile near the interface. In this context, the wall effect manifests itself only when the director is deformed from its equilibrium configurations. Since the nematic liquid crystal can be made to deform in many different ways and no liquid crystal is free from its boundary, every possible deformed configuration of nematic director contains more or less information as to the nature of the substrate-nematic interface. Thus, corresponding to all these configurations, there can in principle be innumerable methods for estimating the anchoring strength. The most important characteristic of a good measurement method is that it allows for accurate, unambiguous, and easy determination of the quantity in question, preferably in wide variety of different systems. The development of experimental techniques for measuring the anchoring strength is actually a history of selecting a director configuration that meets these requirements. We have now a rather large stock of such attempts as shown in Figure 1.

The earliest direct measurement of the anchoring energy was performed by measuring the width of a surface disclination line,[50–52] which is an intersection between the substrate and a wall singularity of director orientation (like a Neel wall in ferromagnets) running between the opposing substrates. Its width is determined by the compromise between the bulk and the surface elastic energies, and by an approximate analysis of the essentially two-dimensional problem, the optimum width of the wall h has been expressed as[50-53]

$$h \approx \pi(dK/E_a)^{1/2} \approx \pi(d\, d_e)^{1/2}, \qquad (24)$$

where d is the cell thickness, and K the Frank elastic constant; in the case of Neel wall, E_a and d_e are the azimuthal anchoring energy and the extrapolation length, and in the case of a Bloch wall, they correspond to those of the polar anchorage. Because the director is not limited in the vicinity of the easy axis inside the disclinations, E_a and d_e appearing in Equation 4 should be understood as some averaged anchoring strength not as that in the thermodynamic sense. The disclination wall is shown[51,53] to be stable only when the cell thickness d is smaller than d_e. Hence, h can not be not greater than the extrapolation length. Since the resolution of a polarizing microscope is at best a few micrometers, quantitatively meaningful measurements can therefore be made by this method only when the anchoring energies are smaller than 10^{-6} J/m^2. As the anchoring energies of solid-nematic systems of practical significance are mostly around 10^{-5} J/m^2, this presents a severe restriction on the applicability of this technique. Furthermore, since the production of surface disclination cannot be satisfactorily controlled, this technique has not gained popularity as a practical method for measuring the anchoring strength.

Other direct techniques quoted in Figure 1 have been developed more systematically to allow measurements in uniformly aligned samples with wider range of anchoring conditions. Presumably, the measurement of anchoring strength becomes increasingly difficult as anchorage becomes stronger. And each method has its own limiting anchoring strength that it can reliably measure. Below, I would like to analyze the experimental techniques with a focus on its allowable maximum anchoring strength, so that the factors affecting the measurement of anchoring strength can be clearly shown up. As discussed below, the treatment of the anchoring strength can be consistent only when it is sufficiently weak so that the inherent ambiguity in the dividing surface can be neglected. When it is strong, however, we are forced to take direct account of the microstructure of the substrate-nematic interface, and here the distinction between the thermodynamic and the structure-model perspectives becomes truly important.

1. ***Nature of the experimental determination of anchoring strength.*** As emphasized in Section II, the anchoring energy $E_a(z_d)$ and the extrapolation length $d_e(z_d)$, which we attempt to determine via macroscopic experiments, are thermodynamic quantities, which are meaningful only in combination with the dividing surface z_d. In conventional experiments, however, the dividing surface has rarely been treated explicitly, and has been loosely identified with the *position of the interface*, a quantity only definable in the structure-model perspective. In fact, any macroscopic experiment involves a definite procedure, be it explicit or not, to specify the dividing surface. In direct techniques, the substrate-nematic system is, as schematically shown in Figure 2, first subject to an orientational stimulus of known quality, and then the response is observed and analyzed based on the Rapini-Papoular type formalism. Actually, the response, $U_{\rm exp}$, is observed through the optical retardation, the threshold field of the Freedericksz transition, etc., corresponding to the stimulus, s, such as the change of cell thickness, the electric or magnetic field, and so on. To analyze this result, we usually assume that the system is *ideal* in the sense that the property of the nematic is bulklike, optically, mechanically, dielectrically, etc., right up to the interface (the dividing surface, in fact) and calculate the theoretical response $U_{\rm ideal}$ for the given stimulus s. Hence, the result of an experiment can generally be expressed as,

$$U_{\rm exp} = U_{\rm ideal}(E_a, z_d, \mathrm{s}). \tag{25}$$

This equation indicates that E_a and z_d must be given so that we obtain $U_{\rm exp} = U_{\rm ideal}$.

On the one hand, when the stimulus involves the cell thickness, as in the wedge-cell or the Freedericksz transition technique, the measurement of the thickness itself fixes the dividing surface. On the other hand, when the cell thickness is not involved, as in the high-electric-

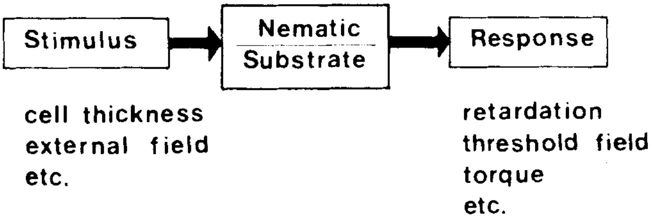

FIGURE 2. General scheme of the experimental determination of the anchoring strength.

field or the torque measurement technique, the observation of U_{exp} itself provides a way to fix z_d. For example, in case U_{exp} is the optical retardation R, Equation 25 implies that z_d must be taken to let $U_{\text{exp}} = U_{\text{ideal}}$ and E_a is determined afterwards. In other words, the dividing surface is here located at the zero-adsorption plane for the retardation, which in general changes with s. Similarly, if U_{exp} is the magnetic torque,[72,73] the dividing surface is automatically located at the zero-adsorption plane for the torque. Clearly from these examples, the position of the dividing surface is in general different from one experimental technique to the other, and does not necessarily coincide with the position of interface in the structure-model perspective. Because of the presence of interfacial transition layer, which may extend a few tens of nanometers in nematics,[36] the awareness about the possible differences of the dividing surface becomes quite important under the strong anchoring condition.

2. *Characteristic lengths in the surface-aligned nematics.* For the sake of unified treatment of various experimental techniques, it is helpful to first define the characteristic lengths governing the director configuration in a surface-aligned nematic layer. We consider one-dimensional deformations occurring within a sandwich cell of thickness d placed in a uniform external field. To simplify the argument, we restrict our attention to the polar anchorage. The case of the azimuthal anchorage can be treated in completely the same manner. Furthermore, we consider only the case of an electric field applied along the cell normal; as well known, the results for an electric field are readily convertible to those for a magnetic field.[41]

Let us now write down the free energy of the cell in the thermodynamic form:

$$\Omega/A = \gamma_1(z_1,D,\theta_1) + \gamma_2(z_2,D,\theta_2) + \int_{z_1}^{z_2} \frac{1}{2}K(\theta)\left[\frac{d\theta}{dz}\right]^2 + \frac{1}{2}\kappa(\theta)D^2 dz, \tag{26}$$

where

$$K(\theta) = K_1\sin^2\theta + K_3\cos^2\theta, \quad \text{and} \quad \kappa(\theta) = 1/(\epsilon_1\cos^2\theta + \epsilon_2\sin^2\theta).$$

Here, θ is the angle between the director and the cell normal, D the electric displacement, and ϵ_1 and ϵ_2 are the dielectric constants parallel and perpendicular to the director, respectively; we assume a positive dielectric anisotropy $\Delta\epsilon = \epsilon_1 - \epsilon_2 > 0$. And, z_1 and z_2 denote the dividing surfaces taken at an arbitrary point while satisfying

$$z_2 - z_1 = d, \tag{27}$$

with the cell thickness d. $\gamma_1(z_1,D,\theta_1)$ and $\gamma_2(z_2,D,\theta_2)$ are the thermodynamic interfacial tensions corresponding to these dividing surfaces, and are now dependent on the field strength D as well as on the director. We denote the angles of the easy axes at the respective interfaces by θ_{e_1} and θ_{e_2}.

For the purpose of qualitative discussion, it is convenient to assume the one-constant approximation ($K_1 = K_2 = K_3 = K$) and a small dielectric anisotropy ($\Delta\epsilon << \epsilon_1$). In this case, the torque balance in the bulk nematic demands

$$K\frac{d^2\theta}{dz^2} = \frac{D^2\Delta\epsilon}{2\epsilon^2}\sin 2\theta. \tag{28}$$

This equation clearly shows that in an electric field with D, the director tends to reorient along the field direction over the distance d_c given by

$$d_c = \frac{\epsilon}{D}\left[\frac{K}{\Delta\epsilon}\right]^{1/2}. \tag{29}$$

In other words, the region where the director is appreciably different from the field direction is practically localized within a layer of thickness d_c from the substrate-nematic interface. This may be called the "electric coherence length" in analogy with the magnetic coherence length[41] which is defined by

$$d_c = \frac{1}{H}\left[\frac{K}{\Delta\chi}\right]^{1/2}, \tag{30}$$

where H is the magnetic field and $\Delta\chi$ is the anisotropy of the diamagnetic susceptibility. The electric or magnetic coherence length is a characteristic length of the system which describes the response of the nematic to these external fields.

Including this coherence length, we now have four parameters, ξ_i, d_e, d, and d_c, which exhaust all the characteristic lengths in the present system. Depending on their relative magnitudes, the behavior of the director is essentiallly determined. In terms of these parameters, connections among various techniques can be clearly visualized, thereby enabling us to appreciate the validity condition of each method. Among these parameters, only ξ_i is of microscopic nature, and only if the condition, $\xi_i \ll d_c$, d, d_e, holds, the director configuration can be consistently treated on the macroscopic level. On the other hand, if this condition is not met, microscopic considerations are definitely needed. In particular, when $d_e(z_1) - z_1 \sim \xi_i$, i.e. when the surface of extrapolation is inside the interfacial transition layer, meaningful measurements of the anchoring strength can be made only on the basis of an appropriate microscopic model of the interface. In the present paper, we understand this condition as a criterion of the strong anchoring.

3. *Wedge-cell technique.*

This is a typical example of the geometry-type methods which introduce a necessary director deformation by means of geometry of the cell configuration or such, without the aid of an external field. In the wedge-cell technique, which was originally proposed by Riviere *et al.*,[54] and later refined by Barbero *et al.*,[57] a couple of planar substrates are put together to form a wedge-shape cell so that the thickness of the nematic layer may be continuously changed from one side of the cell to the other; the angle subtended by the wedge is made very small something around 10^{-3} rad so that the director configuration at each point can be well approximated by that in a parallel plate cell. The surfaces of the substrates are so treated in advance as to give the easy axes in distinct directions. The conflicting boundary conditions at the upper and the lower interfaces amount to a so-called hybrid alignment, in which a spontaneous deformation of the director exists. As we shall see below, the effect of finite anchoring strength becomes visible only when the condition, $d \sim d_e$, is satisfied. Here, we shall formulate the wedge-cell technique, completely within the thermodynamic perspective, so as to illuminate the macroscopic basis and limitations of this technique; we will *never* assume a prescribed functional form for the interfacial tension as in the Rapini-Papoular formalism.

As a matter of course in thermodynamics, we have to begin with specifying the bulk equilibrium. Since no external field exists at present, the equilibrium director profile in the bulk nematic is determined only by the balance of the curvature stress, which is expressed by[45]

$$\frac{d}{dz} K(\theta) \frac{d\theta}{dz} - \frac{1}{2} \frac{dK(\theta)}{d\theta} \left[\frac{d\theta}{dz}\right]^2 = 0. \tag{31}$$

As this equation is invariant with respect to the transformation of variable as $z \to k_1 z + k_2$, any solution of Equation 31 can always be written in the following form,

$$\theta = \Theta\left(\frac{z - z^*}{d^*}\right), \tag{32}$$

by using appropriate constants, z^* and d^*, in conjunction with $\Theta(\zeta)$ which is a special solution of Equation 31 satisfying $\Theta(0) = \theta_{e_1}$ and $\Theta(1) = \theta_{e_2}$. Actually, we can write $\Theta(\zeta)$ as an implicit function of ζ as

$$\int_{\theta_{e1}}^{\Theta} K(\theta)^{1/2}\, d\theta = \zeta \int_{\theta_{e1}}^{\theta_{e2}} K(\theta)^{1/2}\, d\theta. \tag{33}$$

According to the boundary condition of $\Theta(\zeta)$, it is clear that z^* can be identified with the position of the surface of extrapolation for the lower interface, and d^* with the distance between such surfaces at lower and upper interfaces. In terms of the dividing surface and the extrapolation length, therefore, we can rewrite them as

$$\begin{aligned} z^* &= z_1 - d_{e_1}(z_1,d^*) = z_2 + d_{e_2}(z_2,d^*) - d^*, \\ d^* &= d + d_{e_1}(z_1,d^*) + d_{e_2}(z_2,d^*). \end{aligned} \tag{34}$$

Note here that the extrapolation lengths, $d_{e_1}(z_1,d^*)$ and $d_{e_2}(z_2,d^*)$, are written as functions dependent on the *effective* cell thickness d^*, to take account of the presence of a finite curvature deformation. Finally, setting $z = z_1$ and $z = z_2$ in Equation 32, we obtain

$$\theta_1 = \Theta\left[\frac{d_{e1}(z_1,d^*)}{d^*}\right], \quad \text{and} \quad \theta_2 = \Theta\left[\frac{d^* - d_{e2}(z_2,d^*)}{d^*}\right]. \tag{35}$$

These equations show that when θ_1 and θ_2 are known for a given d, we can deduce the extrapolation lengths at both interfaces. It must be strictly noted that we have so far made no use of the specific functional form of the interfacial tension, so the above results are completely general regardless of the model of interface used.

To measure the director angles, Riviere *et al.*[54] observed the light reflection from the substrate-nematic interface. Although Riviere's method is complete in the sense that it can measure both θ_1 and θ_2, it requires a tedious numerical calculations, whose validity is limited to rather thick cells. Barbero *et al.*[57] eliminated this process by observing the overall configuration of the director via the optical retardation. The retardation R is the optical phase difference between the ordinary and the extraordinary rays after passing through a nematic cell, and is expressed as

$$R = \frac{2\pi}{\lambda} \int_{-\infty}^{\infty} \Delta n_{eff}(z)\, dz, \tag{36}$$

where λ is the wavelength of light and $\Delta n_{eff}(z)$ is the effective birefringence, which is in the bulk nematic given by

$$\Delta n_{eff}(\theta) = \frac{n_e n_o}{(n_o^2 \sin^2\theta + n_e^2 \cos^2\theta)^{1/2}} - n_o, \tag{37}$$

with n_e and n_o being the refractive indices for the extraordinary and the ordinary rays, respectively [for the validity of Equations 36 and 37, see Appendix]. Therefore, by using Equations 32 and 36, we obtain, for the ideal nematic in between z_1 and z_2,

$$R_{\text{ideal}} = \frac{2\pi d^*}{\lambda} \int_{\theta_1}^{\theta_2} \Delta n_{eff}(\theta) \frac{d\Theta^{-1}(\theta)}{d\theta}\, d\theta = \frac{2\pi d^*}{\lambda} \frac{\int_{\theta_1}^{\theta_2} \Delta n_{eff}(\theta) K(\theta)^{1/2}\, d\theta}{\int_{\theta_{e1}}^{\theta_{e2}} K(\theta)^{1/2}\, d\theta}. \tag{38}$$

This is the basic equation of the wedge-cell technique developed by Barbero *et al.*[57] Since this equation involves two unknowns θ_1 and

θ_2, an auxiliary condition is needed between them to invert the retardation to the respective anchoring strength. It has usually been provided by choosing one of the substrates in such a way that the induced anchorage is much stronger than that at the other substrate. If we, for example, conceive that the upper substrate is so treated, we can, to a good approximation, set $\theta_2 = \theta_{e2}$ in Equation 38; hence θ_1 can be uniquely found for a given R_{ideal}. Indeed, Barbero *et al.* applied the silane coating to the upper substrate, which is known to induce a strong homeotropic alignment, and measured the anchoring strength of MBBA to a rubbed silane-coated glass, which gave rise to a tilted alignment with a rather weak anchorage. They found the extrapolation length ranging from 1 μm to 15 μm depending on the rubbing condition with a relative error of about ± 10%.

Thermodynamically speaking, the procedure to set $\theta_2 = \theta_{e_2}$ is equivalent to locating the upper dividing surface at the position of the surface of extrapolation so that $d_{e_2} = 0$. Consequently, the variable d, referred to as the *cell thickness*, means in this respect a distance of the lower dividing surface measured from the upper surface-of-extrapolation. Since the cell thickness is usually measured by a separate experiment, not given as a distance between the dividing surfaces predetermined in relation to some physical properties of the nematic interfaces, there always remain certain ambiguities in the actual locations of the dividing surface, thereby obscuring the status of the measured extrapolation lengths. This is a common characteristic of experimental techniques which rely on the knowledge of cell thickness. The requirement of strong anchoring at a reference substrate is nothing but a condition to make sure that the upper surface of extrapolation lies somewhere *very* near the substrate surface. Although the cell thickness measured by, say, the optical interference method, may in principle be accurate to molecular scale, there is no way to confirm that the thickness is compatible with the macroscopic description of the substrate-nematic system envisaged in the formulation of the specific experimental technique. The following example may be enough to clarify this point. Suppose an equilibrium layer of nematic in a wedge-cell, and that the retardation of the cell is measured to be R_{exp}. Since the bulk director profile is already given in equilibrium, the retardation for an ideal nematic should also be completely specified as a function of the positions of the dividing surfaces z_1 and z_2. Furthermore, if we locate as above the upper dividing surface at the surface of extrapolation, which is also a fixed point in equilibrium, the ideal retardation becomes a function only of z_1. As already noted, we generally require

$$R_{\text{exp}} = R_{\text{ideal}}(z_1). \tag{39}$$

Hence, z_1 is automatically determined once R_{exp} is supplied. The angle at the dividing surface θ_1 and the extrapolation length d_{e_1} follow immediately. Obviously, the separation between those dividing surfaces does not necessarily equal to the *cell thickness* which is obtained by an independent experiment; hence we in general have $R_{\text{exp}} \neq R_{\text{ideal}}(d)$. In this sense, such a cell thickness is incompatible with the thermodynamic description. What one actually does in the wedge-cell technique is that, by first giving the cell thickness, then, the angle θ_1 is determined to make $R_{\text{exp}} = R_{\text{ideal}}$. Since this is in general possible only when θ_1 is different from the true equilibrium value, this process amounts to deviate the bulk profile itself from the true equilibrium configuration. As Equation (9) shows, the true thermodynamic extrapolation length has to shift, upon the change of the dividing surface, by the same amount in the opposite direction. This means at present that, although the extrapolation lengths do change with the choice of the dividing surface, the effective cell thickness d^* should be immune to such changes and reamin always constant, *i.e.*

$$d^* = d + d_{e_1}(z_1,d^*) + d_{e_2}(z_2,d^*) = \text{const}. \tag{40}$$

We shall call those techniques that satisfy this condition as a thermodynamically consistent technique. The wedge-cell technique is not in general thermodynamically consistent, as we will see below.

At large cell thicknesses, R_{ideal} exhibits a linear dependence on d, which provides an easy and convincing method for deducing the anchoring strength. In order to expand Equation 38 in powers of d_{e_1}/d^* and d_{e_2}/d^*, let us first expand Equation 35 up to second order with the help of Equation 33:

$$\theta_1 \approx \theta_{e_1} + \frac{\int_{\theta_{e_1}}^{\theta_{e_2}} K(\theta)^{1/2}\, d\theta}{K(\theta_{e_1})^{1/2}} \frac{d_{e_1}(z_1,d^*)}{d^*}$$

$$- \frac{K'(\theta_{e_1})}{4K(\theta_{e_1})^2} \left[\int_{\theta_{e_1}}^{\theta_{e_2}} K(\theta)^{1/2}\, d\theta \right]^2 \left[\frac{d_{e_1}(z_1,d^*)}{d^*} \right]^2, \tag{41}$$

where the prime denotes the differentiation with respect to its argument; a similar expression can also be derived for θ_2. Clearly, an appreciable change of the angle θ_1 occurs, only when the cell is thin enough to meet $d \sim d_{e_1}$. Substituting Equation 41 into the expansion of Equation 38, we get

$$R_{\text{ideal}} \approx \frac{2\pi}{\lambda} A \Bigg[d + (1 - B_1)\, d_{e_1}(z_1,d^*) + (1 - B_2)\, d_{e_2}(z_2,d^*) - C_1 \frac{d_{e_1}(z_1,d^*)^2}{d^*} + C_2 \frac{d_{e_2}(z_2,d^*)^2}{d^*} \Bigg], \quad (42)$$

where A, B_i, and C_i (i = 1,2) are the coefficients of expansion given by

$$A = \frac{\int_{\theta_{e1}}^{\theta_{e2}} \Delta n_{eff}(\theta)\, K(\theta)^{1/2}\, d\theta}{\int_{\theta_{e1}}^{\theta_{e2}} K(\theta)^{1/2}\, d\theta}, \quad B_i = \frac{\Delta n_{eff}(\theta_{e_i})}{A},$$
$$C_i = \frac{\Delta n'_{eff}(\theta_{e_i}) \int_{\theta_{e1}}^{\theta_{e2}} K(\theta)^{1/2}\, d\theta}{2A\, K(\theta_{e_i})^{1/2}}. \quad (43)$$

Equation 42 indeed shows that, for sufficiently large cell thicknesses, R_{ideal} is linearly dependent on d, and its apparent intercept is proportional to the extrapolation lengths. This type of relation has an advantage over the direct use of Equation 38 that it can help us appreciate the validity of experiments. Indeed, in the wedge-cell technique, the uniformity of the substrates is a decisive factor in real experiments, and the linearity at large cell thickness gives certain measure of the uniformity.

In conformity with the usual experimental setting, let us asume that the upper substrate is so treated as to produce a homeotropic alignment (θ_{e_2} = 0). In this case, it readily follows from Equations

37 and 43 that

$$B_2 = C_2 = 0. \tag{44}$$

Furthermore, if we assume the alignment at the lower substrate is planar ($\theta_{e_1} = \pi/2$), we obtain $C_1 = 0$ and Equation 42 can be simplified to

$$R_{\mathrm{ideal}} = \frac{2\pi}{\lambda} A[d + (1 - B_1)\, d_{e_1}(z_1,d^*) + d_{e_2}(z_2,d^*)]. \tag{45}$$

Because $\Delta n_{eff}(\theta)$ (> 0) is an increasing function, $B_1 > 1$. Hence, the coefficient of d_{e_1} is always negative. This means that the anchoring strengths at the upper and the lower substrates essentially make an opposite contribution to the retardation, which is one of the important features of the wedge-cell technique. Based on the consideration of the higher order corrections, we can show that Equation 45 is valid as long as

$$d_{e_1}(z_1,d^*),\ d_{e_2}(z_2,d^*) < 0.3d, \tag{46}$$

which, according to Equation 41, is equivalent to

$$|\theta_1 - \theta_{e_1}|,\ |\theta_2 - \theta_{e_2}| < 0.3 \tag{47}$$

On the other hand, when a pretilted alignment prevails at the lower surface, the term with C_1 survives, and Equation 45 can be expected to remain valid only for $|\theta - \theta_e| < 0.1$. So that, to obtain the extrapolation length from the intercept with an accuracy of ±10% relative error, the cell thickness must be measured with a relative error of at most a few percent. In the conventional wedge-cell experiments,[54,57] the thickness has been interpolated from the thickness of the spacer used and the distance from it. However, because of the ambiguity as to the thickness of the contact region and also of the possible deformation of the substrates, it seems hardly possible to determine the cell thickness smaller than 1 μm with the desired accuracy. Therefore, in the conventional type of the wedge-cell technique, the measurable anchoring strength may be limited to

$$d_e > 0.1\ \mu\mathrm{m}. \tag{48}$$

Nevertheless, by employing some other direct method to measure the point-wise thickness, the wedge-cell technique would be applicable to stronger anchorages.

For a measured retardation R_{exp}, Equation 45 gives the effective cell thickness as

$$d^* = \frac{R_{\mathrm{exp}}\lambda}{2\pi A} + B_1 d_{e_1}(z_1, d^*). \tag{49}$$

Since the extrapolation length $d_{e_1}(z_1, d^*)$ in general changes with the choice of d, the effective thickness also undergoes some variation with the dividing surface, and does not satisfy the condition of thermodynamic consistency [Equation 40]; though it may seem to satisfy the condition, when $d_{e_1} = 0$, it is an artifact resulting from the homeotropic alignment at the upper surface. As already mentioned, this comes phenomenally from the fact that we set $R_{\mathrm{exp}} = R_{\mathrm{ideal}}$ while using an incompatible cell thickness, but essentially originates from the fact that d is not an appropriate variable to specify the bulk equilibrium of the nematic. From a rigorous point of view, in order to retain the thermodynamic consistency, we need to subtract the surface excess retardation $R_s(z_1, z_2, d^*)$ from R_{exp}. Therefore, we should formally write

$$R_{\mathrm{exp}} - R_s(z_1, z_2, d^*) = R_{\mathrm{ideal}}. \tag{50}$$

The usual "wedge-cell technique," thus, amounts to neglect R_s as being small compared to $R_{\mathrm{exp}} - R_{\mathrm{bulk}}$, where R_{bulk} is the retardation when the anchorage is infinitely strong. To R_s does contribute the interfacial transition layer as well as the mere uncertainty in the cell thickness. So, we may qualitatively write

$$R_s \sim \frac{2\pi\Delta n}{\lambda}(g\xi_i + \delta d) \tag{51}$$

where g is a parameter to express the degree of inhomogeneity in the interfacial transition layer, and $\Delta n = n_e - n_o$. Hence, by using Equation 45, we find

$$\frac{R_s}{R_{\mathrm{exp}} - R_{\mathrm{bulk}}} \sim \frac{g\xi_i + \delta d}{(1 - B_1)d_{e_1} + d_{e_2}} \tag{52}$$

We can, therefore, roughly understand that when d_e is comparable to ξ_i, we cannot expect for the wedge-cell technique to yield a meaningful result for the anchoring strength. It should also be noted that when $d_{e_1} \sim d_{e_2}$, the effect of R_s can be significant, even if d_{e1}, $d_{e2} >> \xi_i$ holds. In these cases, a microscopic framework to take account of R_s is entailed.

Finally, I would like to give some comments on the d^*-dependence of the anchoring strength. Although we have not explicitly discussed, the validity of the linear relation between R_{ideal} and d is heavily dependent on how the extrapolation length changes with d^*. Indeed, as clear from the course of derivation, $d_e(z_d,d^*)$ is a thermodynamic state function, like the gas equation, which describes the state of the interface in relation to the bulk equilibria. Hence, it is expected to more or less change with d^* (the variable taking care of the bulk state). Since the surface alignment should be thermodynamically stable at undeformed state, $d_e(z_d,d^*)$ has to remain finite as $d^* \rightarrow \infty$. So, we may be able to perform a virial expansion of d_e as

$$d_e(z_d,d^*) = d_e(z_d) + \sum_{n=1}^{\infty} \frac{b_n}{d^{*n}}. \tag{53}$$

The virial coefficients $b_n(z_d)$ are all thermodynamically meaningful, and may be reflecting some subtleties of the substrate-nematic interface. For instance, if the anchoring strength tends to be different depending on the sign of $(\theta_1 - \theta_{e1})$, the first coefficient b_1 should be finite and is expected to give some information on the asymmetry of the substrate-nematic interaction, which would eventually lead to the temperature- or composition-induced change of the pretilt angle. Putting Equation 53 in Equation 45, it is clear that if $d_e(z_d)$ is small compared to the higher order terms, the relation between R_{ideal} and d is by no means linear even though d_e/d^* is sufficiently small. Consequently, the careful check of the linearity is quite important not only for determining the primary extrapolation length $d_e(z_1)$, but for studying the higher order contributions to the extrapolation length.

4. *Freedericksz transition technique*

Another important variation of the experimental technique for anchoring measurement comes from the use of an external field as an agent to induce desired director deformations. As well known, when the initial alignment is uniform within a parallel cell and an external electric or magnetic field is applied strictly perpendicular or parallel to the alignment direction (depending on the sign of $\Delta\epsilon$ or $\Delta\chi$), the initial alignment remains stable up to a well defined threshold field. And, above this threshold, the director begins to rotate. This phenomenon called the Freedericksz transition originates from the competition between the torque exerted by the applied field and that due to the cell boundary. So, it could soon be suspected that the anchoring strength would have significant effect on this transition. This is indeed the point studied by Rapini and Papoular[40] in relation to the wall-effect on the magnetic field-induced Freedericksz transition. Obviously, this technique can in principle be applied to both polar and azimuthal anchorages.

As understandable from its origin, the Freedericksz transition is expected to occur, when the electric or magnetic coherence length becomes almost comparable with the cell thickness (provided the surface anchoring is strong):

$$d_c \approx d. \tag{54}$$

Actually, based on Equation 26 with fixed boundary conditions, $\theta_1 = \theta_2 = \pi/2$ (planar alignment), it is easy to show that the threshold field is given by,[41]

$$D_{th0} = \frac{\pi\epsilon}{d}\left[\frac{K}{\Delta\epsilon}\right]^{1/2}. \tag{55}$$

Taking into account the finite strength of the surface anchoring, Rapini and papoular[40] derived the threshold field. We now assume that both substrates are identical and take the dividing surfaces at symmetrical points so that we have

$$E_{a1}(z_1,D) = E_{a2}(z_2,D) \equiv E_a(z_1,D). \tag{56}$$

Then, according to Rapini and Papoular, the threshold field D_{th} is given by the following implicit equation:

$$\cot\left[\frac{\pi}{2}\frac{D_{th}}{D_{th0}}\right] = \pi\frac{d_e^*(z_1,D_{th})}{d}\frac{D_{th}}{D_{th0}}, \tag{57}$$

where we have defined the *energetistic* extrapolation length $d_e^*(z_1,D_{th})$ by

$$d_e^*(z_1,D_{th}) \equiv \frac{K_1}{E_a(z_1,D_{th})}.$$

The same equation as Equation 57 holds for magnetic field and for other configuration if D_{th} is replaced by H_{th} and K_1 by an appropriate elastic constant. This equation enables us to determine the anchoring energy from the measurement of the threshold field. In particular, when $d_e^*(z_1,D_{th})/d$ is much smaller than unity, or equivalently, when D_{th}/D_{th_0} is close to unity, we can expand Equation 57 to give

$$D_{th} = \frac{D_{th_0}}{1 + 2\, d_e^*(z_1,D_{th})/d}. \tag{58}$$

This equation shows, as intuitively expected, that the threshold field decreases as the anchoring strength and/or the cell thickness decreases. As in the case of wedge-cell technique, substantial reduction of the threshold field is observable only when d is comparable to $d_e^*(z_1,D_{th})$. Thus, the reliability criterion of the Freedericksz transition technique can be expressed as

$$d \sim d_c \sim d_e^*. \tag{59}$$

Naemura[59,61] observed the threshold field of the magnetic field-induced Freedericksz transition for layers of MBBA, which had been homeotropically aligned between substrates treated by various surfactants. He obtained anchoring energies on the order of $10^{-6} \sim 10^{-5}$ J/m^2 (the corresponding extrapolation lengths range from 10 μm to 1 μm) by using sample layers with a thickness of 100 ~ 10 μm. More recently, Yang and Rosenblatt,[62] and Rosenblatt[63] conducted careful experiments using a very thin cell in conjunction with a high magnetic field to meet the above condition. They applied a magnetic field of up to 100 kG to a few micrometers-thick layer of MBBA, homeotropically aligned between surfactant-treated substrates, and found values of the anchoring energy more than one order of magnitude larger than the value obtained by Naemura for the same surfactant-liquid crystal system.

As Equations 57 and 58 indicate, the accuracy of the cell thickness plays a decisive role in determining the precision of measurement. However, in contrast to the wedge-cell technique, the cell thickness acts here only to specify the dividing surface; so that, it is not an orientational stimulus in the sense of Figure 2. To further clarify this point, it may be instructive to rewrite Equation 58 in the following form:

$$d + 2d_e^*(z_1,D_{th}) = \frac{\pi\epsilon}{D_{th}}\left[\frac{K}{\Delta\epsilon}\right]^{1/2} \equiv d^*. \tag{60}$$

The right-hand side of this equation consists only of the quantities which can be experimentally determined regardless of the cell thickness *d*. And, it is giving the *effective* cell thickness d^* for which $D_{th_0} = D_{th}$, and absolutely fixes the surface of extrapolation in space; namely, d^* denotes the thickness of a hypothetical cell with rigid boundary condition, yet undergoing a Freedericksz transition at the same threshold as D_{th}. Equation 60 shows that, next by specifying the cell thickness, d_e^* can be determined. Therefore, an increase in *d* always results in the decrease in d_e^*, indicating a contrast with the wedge-cell technique in which the opposite is normally the case [cf. Equation 45]. Since the geometrical extrapolation length $d_e(z_1,D_{th})$ is by definition given by

$$d_e(z_1,D_{th}) \equiv \frac{d^* - d}{2,} \tag{61}$$

Equation 60 furthermore shows that, when the extrapolation length is small compared to *d*, the geometrical and energetistic extrapolation lengths are approximately equal, i.e., $d_e \approx d_e^*$. However, if d^* is appreciably different from *d*, this simple property no longer holds. Indeed, from the general expression Equation 57, it readily follows that

$$\frac{d}{dz_1} d_e^*(z_1,D_{th}) = 1/\sin^2\left[\frac{\pi}{2}\frac{d}{d^*}\right] \tag{62}$$

Hence, with the change of the dividing surface, $d_e^*(z_1,D_{th})$ does not satisfy a simple geometrical relation as expected from Equation 9 or 61, but it changes more rapidly as a result of the rotational effect of the external field. In any case, as d^* is constant regardless of *d*, the Freedericksz transition technique is thermodynamically consistent.

Due to the above mentioned two-step nature of the Freedericksz transition technique, it is convenient to separately consider the errors resulting from the measurements of the threshold field and the cell thickness. We first note that the actual experimental procedure consists in the comparison of threshold field values for different cell thicknesses, at least one of which is much larger than the extrapolation length. Thus, by writing the threshold field for such a very thick cell with thickness d_∞ as D_{th_∞}, we can express d^* as

$$d^* = d_\infty \frac{D_{th_\infty}}{D_{th}}. \tag{63}$$

Hence, the relative error in d^* is given by

$$\frac{\delta d^*}{d^*} = \frac{\delta d_\infty}{d_\infty} + \frac{\delta D_{th_\infty}}{D_{th_\infty}} - \frac{\delta D_{th}}{D_{th}}. \tag{64}$$

Accordingly, in order that the extrapolation length can be determined within an accuracy of 10 %, the cell thickness must be so chosen that

$$d^* < 6\ d_e, \tag{65}$$

even if we assume that the right-hand side of Equation 64 is at most 3%. This in turn implies that the cell has to be thin enough to satisfy

$$d < 4\ d_e, \tag{66}$$

even when the error in d is disregarded. As the cell thickness increases, the measured anchoring strength is likely to suffer from larger uncertainties. In particular, since these experimental errors tend to give an apparently weaker anchoring strength, the final error in the extrapolation length is apt to be underestimated, thereby making an *a posteriori* judgement of the reliability rather difficult. Therefore, it is highly recommended to employ progressively thin cells until a good convergence of the anchoring strength is reached.

As noted above, the cell thickness d is needed in the present technique only to locate the dividing surface. And, as long as the condition as Equation 66 is satisfied, the requirement for the relative error in d is not so stringent as in the wedge-cell technique [unless the cell is extremely thin compared to the extrapolation length, cf. Equation 62]. So, in this respect, there is no limit on the strength of anchoring to be dealt with by this technique. Obviously, however, the strength of field to induce a Freedericksz transition increases roughly proportional to d^{-1}. Actually, for MBBA with a thickness of about 3 μm, the threshold magnetic field is about 26 kG [Reference 62]; so that, measurements below 0.3 μm appears at present impractical.

Although a Freedericksz transition can also be induced by means of an electric field, the measurement of an absolute electric field strength becomes quite inconclusive in thin cells because of the presence of various insulating layers between the conductive surface and the liquid crystal and the ionic shielding. Consequently, the practical limit of this technique may well be given by

$$d_e > 0.1\ \mu\mathrm{m}, \tag{67}$$

just as in the case of the wedge-cell technique.

Aside from these technical limitations, I also would like to point out that it becomes increasingly important to consider the *intrinsic* field dependence of the anchoring strength as d approaches ξ_i. This is not the apparent field dependence resulting from the choice of the dividing surface [cf. Equation 62], but the intrinsic property of the interface connected with the different response of the interfacial region to an external field compared to the bulk nematic. And it is essentially the question how the Freedericksz transition be modified when the layer thickness is as small as the nematic correlation length. This is obviously a kind of problem that can be properly tackled only in the structure-model perspective.

5. ***High-electric-field technique.***

The Freedericksz technique is characterized by the condition $d \sim d_c \sim d_e$. However, the first condition, $d \sim d_c$, is an auxiliary one resulting from the use of the Freedericksz transition; so that, as long as one uses this technique, it is automatically satisfied. On the other hand, the latter condition denotes the true criterion which assures the validity of this technique. Thus, it is expected that by relaxing the condition $d \sim d_c$, we can devise a more versatile method for measuring the anchoring strength. There have actually appeared several attempts[64-73] to obtain the anchoring energy from the analysis of field-induced director deformations under such a condition that the thickness of the nematic layer no longer plays a significant role. This is the idea of the high-field technique. The precision of these techniques, *i.e.* how closely the condition $d_c \sim d_e$ should be met, depends on the method to probe the director deformations. In the case of volumetric method such as the retardation[68-70] and the torque[72,73] measurements, this condition is very critical; but in such methods as optical reflection,[65-67] which is sensitive only to interfacial properties, this condition could be substantially relaxed. Indeed, Ohide, *et al.*[71] recently devised a novel magnetic-field-based technique for azimuthal anchorage by adopting a surface-sensitive optical scheme, and applied it rather successfully to rubbed polyimide even though $d_c/d_e >> 1$. In these techniques, however, the director deformation is in general expressed by a complicated function of the field strength which implicitly contains the anchoring strength, and the calculation of the ideal response is also rather involved. Consequently, a laborious and often opaque multivariate numerical fitting procedures have to be performed to extract the anchoring strength, which is making the analysis of precision quite difficult.

The high-electric-field technique[69] bypasses these difficulties, and allows a straightforward determination of anchoring strength; the same is true for torque-measurement technique.[101] This technique is based on a general scaling property existing in the semi-infinite nematic system in an external field,[70] just as in the case of the wedge-cell technique. So, the principle is valid for any functions of $K(\theta)$ and $\kappa(\theta)$, as long as they are not explicitly dependent on z and D. For a semi-infinite case, Equation 26 reads

$$\Omega/A = \gamma(z_1,D,\theta_1) + \int_{z_1}^{\infty} \frac{1}{2} K(\theta) \left[\frac{d\theta}{dz}\right]^2 + \frac{1}{2} \kappa(\theta) D^2 \, dz, \tag{68}$$

By using a scaled variable $\zeta = Dz$, we can rewrite Equation 68 as

$$\Omega/A = \gamma(\zeta_1,D,\theta_1) + D \int_{\zeta_1}^{\infty} \frac{1}{2} K(\theta) \left[\frac{d\theta}{d\zeta}\right]^2 + \frac{1}{2} \kappa(\theta) \, d\zeta. \tag{69}$$

Since the integrand on the right-hand side does not explicitly involve D, $\theta(\zeta)$ can generally be written in the form,

$$\theta = \Theta[\zeta - \zeta_1 + \Theta^{-1}(\theta_1)], \tag{70}$$

where $\Theta(\zeta)$ is an arbitrary special solution of the variational equation,

$$\frac{d}{d\zeta} K(\theta) \frac{d\theta}{d\zeta} - \frac{1}{2} \frac{dK(\theta)}{d\theta} \left[\frac{d\theta}{d\zeta}\right]^2 - \frac{1}{2} \frac{d\kappa(\theta)}{d\theta} = 0. \tag{71}$$

Then, in terms of the original variable, we get

$$\theta(z) = \Theta[D(z - z_1) + \Theta^{-1}(\theta_1)], \tag{72}$$

In particular, by adopting such a solution that satisfies $\Theta(0) = \theta_{e1}$, we reach

$$\theta_1 = \Theta[Dd_e(z_1,D)]. \tag{73}$$

where $d_e(z_1,D)$ is the geometrical extrapolation length, *i.e.* the distance between the surface of extrapolation and z_1. It is easily shown from Equation 71 that $\Theta(\zeta)$ is now specifically given by

$$\int_{\Theta}^{\theta_{e1}} \left[\frac{K(\theta)}{\kappa(0) - \kappa(\theta)}\right]^{1/2} d\theta = \zeta. \tag{74}$$

Since the function $\Theta(\zeta)$ is completely known once the bulk properties are specified, Equation 73 shows that when θ_1 is experimentally measured for a given D, the extrapolation length can be readily determined. For this purpose, the optical phase retardation is utilized in the high-electric-field technique. Using Equations 36 and 72, we can write the retardation for the ideal system beyond z_1 as follows:

$$R_{\text{ideal}} = \frac{2\pi}{\lambda}\frac{1}{D}\int_{\theta_1}^{0} \Delta n_{eff}(\theta)\,\frac{d\Theta^{-1}(\theta)}{d\theta}\,d\theta. \tag{75}$$

This equation determines the angle θ_1 as a function of R_{ideal}. An important feature of this result can be readily seen, if we assume the rigid boundary condition at z_1 so that θ_1 is always θ_{e1}. Because the integral in Equation 75 is now a constant, R_{ideal} should be inversely proportional to the field strength D. This is essentially equivalent to the fact that d_c is inversely proportional D and the retardation is coming only from the region of thickness d_c from the interface.

Before discussing the detailed consequences of Equation 75, a comment on the dividing surface in the high-electric-field technique is in order. The important point here is that the bulk equilibrium of a nematic is completely determined once the field strength D is specified, so that D is now a good macroscopic variable in contrast to the cell thickness wedge-cell technique. Due to this property, there is no fear to disturb the bulk profile, even when we equate the experimentally measured retardation and that for an ideal system:

$$R_{\text{exp}} = R_{\text{ideal}}[\theta_1(z_1)]. \tag{76}$$

This equation now simply states that z_1 should be located at a point where the actual and the ideal (neglecting the interfacial inhomogeneity) retardations are equal; hence, z_1 is, apart from an experimental error, the position of the *zero-adsorption surface* for the retardation. Note that, in contrast to the wedge-cell and the Freedericksz transition techniques, the dividing surface is here unambiguously fixed in connection with a physical property of the nematic interface. Clearly, the dividing surface can be moved by adding an arbitrary constant to R_{exp}. However, since $d_e(z_1,D) = z_1$, the extrapolation length satisfies

$$\frac{d}{dz_1} d_e(z_1,D) = 1. \tag{77}$$

This shows that the high-electric-field technique is thermodynamically consistent.

At low enough fields where the deviation of the director from the easy axis is small, the retardation and the field strength exhibit a linear relation (just as in the wedge-cell technique), from which the extrapolation length can be readily obtained. By first expanding Equation 73 up to second order in D, we obtain

$$\theta_1 \approx \theta_{e1} - \left[\frac{\kappa(0) - \kappa(\theta_{e1})}{K(\theta_{e1})}\right]^{1/2} Dd_e(z_1,D) + \frac{\kappa(0) - \kappa(\theta_{e1})}{4K(\theta_{e1})}\left[\frac{d}{d\theta}\ln\frac{K(\theta_{e1})}{\kappa(0) - \kappa(\theta_{e1})}\right] D^2 d_e(z_1,D)^2. \tag{78}$$

In view of the definition of the electric coherence length Equation 29, the above equation shows that the difference between θ_1, and θ_{e1} becomes substantial only when $d_c \sim d_e$. Then, expanding Equation 75 in powers of $(\theta_1 - \theta_{e1})$ and substituting Equation 78, we get

$$R_{\mathrm{ideal}} \approx \frac{2\pi}{\lambda}\frac{1}{D}\left[\int_{\theta_{e1}}^{0} \Delta n_{eff}(\theta)\frac{d\Theta^{-1}(\theta)}{d\theta}\,d\theta - \Delta n_{eff}(\theta_{e1})\,Dd_e(z_1,D) - \frac{1}{2}\Delta n'_{eff}(\theta_{e1})\left[\frac{\kappa(0) - \kappa(\theta_{e1})}{K(\theta_{e1})}\right]^{1/2} D^2 d_e(z_1,D)^2\right]. \tag{79}$$

Now we return from the semi-infinite case to the parallel cell, which consists of a couple of identical substrates separated by the distance d. We still assume that the field is sufficiently strong to assure $d_c \ll d$, but weak enough to satisfy $d_e \ll d_c$. Then, the total retardation is given by the sum of the contributions from the vicinity of the substrates, and is simply the twice of Equation 75 or Equation 79. In particular, when the second order term can be neglected in Equation 79, we obtain

$$\frac{R_{\text{ideal}}}{R_0} \approx \left[\frac{4\pi}{\lambda R_0} \int_{\theta_{e1}}^{0} \Delta n_{eff}(\theta) \, \frac{d\Theta^{-1}(\theta)}{d\theta} \, d\theta \right] \frac{1}{D} - 2 \, \frac{d_e(z_1,D)}{d}, \tag{80}$$

where $R_0 = 2\pi d \Delta \mathrm{n}_{eff}(\theta_{e1})/\lambda$ is the retardation of the uniformly aligned cell at $D = 0$. So, R_{ideal}/R_0 is linearly dependent on D^{-1} to zero-th order in D^{-1}, and the intercept with the ordinate directly gives $-2d_e(z_1,0)/d$. Although this formula very much looks like that in the wedge-cell technique [Equation 45], it is a great advantage of the high-electric-field technique that the extrapolation length can be obtained completely independent of bulk material parameters such as the Frank elastic constants, refractive indices, etc. Experimentally, the electric displacement can be derived from the capacitance of the cell C and the applied voltage V via $D \propto CV$. As pointed out in Reference 69, completely analogous formulae can also be obtained for a magnetic field; this is also true in the case of the torque-measurement technique.[101]

The validity of the above linear relation can be evaluated by comparing the first and the second terms in Equation 79. As clear from the form of $\Delta n_{eff}(\theta)$, its derivative vanishes at $\theta = \pi/2$, i.e. the planar alignment; so that, the coefficient of the second order term disappears. In this case, by considering the third order term, it is readily shown that the higher-order correction in Equation 80 can be neglected, when

$$d_e(z_1,D) < 0.3d_c, \tag{81}$$

which implies, on account of Equation 78, that $|\theta_1 - \theta_{e1}| < 0.3$. When the alignment is pretilted, however, we see from Equation 79 that Equation 80 is valid as long as

$$d_e(z_1,D) < 0.1d_c, \quad \text{and hence,} \quad |\theta_1 - \theta_{e1}| < 0.1. \tag{82}$$

The range of validity of Equation 80 is also limited by the condition to insure the semi-infinite approximation, $d_c \ll d$. By writing the director angle at the mid plane of the cell as θ_m, which has been assumed to be 0 in Equation 75, it is readily shown that the ratio between the error coming from the neglect of this finite θ_m and the anchoring strength term in Equation 79 is roughly given by $\theta_m^2 d_c/\sin^2\theta_{e1} d_e$. Therefore, if we, for instance, take $d = 1000\ d_e$, we see, for a planar cell, that the ratio is at worst $1000\ \theta_m^2$. According to the numerical calculation,[69] at such applied voltages $V > 6V_{th}$, where V_{th} is the threshold voltage of the Freedericksz transition, θ_m is smaller than 10^{-3}; hence, at these voltages, the error can be safely ignored. Finally, by using an approximate relation, $d_c \approx dV_{th}/\pi V$ in combination with Equations 81 and 82, we can estimate the range of voltages for which the linear relation applies as follows:

$$\begin{aligned} &6\ V_{th} < V < 0.3\,\frac{dV_{th}}{\pi d_e}, \quad \text{for planar alignment,} \\ &6\ V_{th} < V < 0.1\,\frac{dV_{th}}{\pi d_e}, \quad \text{for pretilted alignment.} \end{aligned} \tag{83}$$

As these inequalities indicate, it is crucially important to use a sufficiently thick cell (compared to d_e) to have a wide enough range of field in which the linear relation holds. For example, for a cell with thickness $d = 1000\ d_e$ and the threshold voltage $V_{th} = 1$ V, we can have the linear range which extends over a decade from 6 V to 100 V.

Analogous to the case of other techniques, the extrapolation length we are dealing with here is in general dependent on the field strength. As already emphasized, the position of the dividing surface in this technique is automatically determined in a real experimental context; so, we cannot arbitrarily choose the dividing surface as in the wedge-cell and the Freedericksz transition techniques. Consequently, we always need to consider z_1 as a function of D. By expanding $d_e(z_1,D)$ in powers of D, we obtain

$$d_e(z_1,D) = d_e + \sum_{n=1}^{\infty} c_n D^n, \tag{84}$$

where $d_e = d_e[z_1(0),0]$, and c_n's are thermodynamic expansion coefficients, which are not functions of the dividing surface as in Equation

53. We can then more precisely state that the linear relation between R_{ideal} and D holds, only when $d_e(z_1,D)$ can be well represented by d_e. Note that d_e is the extrapolation length for *infinitesimal* deformations; the extrapolation length measured in the Freedericksz transition technique $d_e(z_1,D_{th})$ exactly agrees with d_e only in the limit $D_{th} \rightarrow 0$.

If the field strength D is precisely given, the precision of the extrapolation length obtained from the intercept is primarily limited by the accuracy of the retardation measurement. From Equation 80, we have

$$\delta d_e(z_1,D) = -\delta R \frac{\lambda}{4\pi \Delta n_{eff}(\theta_{e1})}. \tag{85}$$

Since the uncertainty of the retardation measurement can be easily made below 10^{-4} rad, the above equation shows, by taking $\Delta n_{eff}(\theta_{e1}) = 0.1$ and $\lambda = 633$ nm, that the error in the extrapolation length is as small as 0.1 nm.

In contrast to the wedge-cell or the Freedericksz transition technique, the high-electric-field technique has no practical limit as to the measurable anchoring strength, owing to the use of an electric field. However, because of the ionic species more or less present in nematics, there might arise several complications, which have not been taken into account in the above formulation. Especially, in order to insure the uniformity of D and to be able to measure D in terms of the voltage and the capacitance, we need to use an alternating voltage with a period much smaller than the dielectric relaxation time $\tau = \epsilon\rho$, where ρ is the resistivity. And, obviously, we also need to work below the voltage of electrical breakdown. Indeed, by taking $d = 1000d_e$ as a typical value and also assuming that the voltage is up to 100 V, the highest field to be applied becomes $E_{\max} = 0.1/d_e$, and hence when $d_e = 10$ nm, we have $E_{\max} = 10^5$ V/cm. As the electrical properties of nematics are greatly varying from one material to another, it is difficult to draw a general conclusion on their influence on the anchoring strength measurement. Separate considerations are required in each experiment.

An example of the actual application of high-electric-field technique is shown in Figure 3 for 5CB (4-n-pentyl-4'-cyanobiphenyl) in contact with rubbed PVA (polyvinylalcohol) film. According to Equation 80, R/R_0 is plotted against $1/CV \propto 1/D$ for measurements done at 6.471 K and 0.437 K below the clearing point $T_c = 35.3°$ C; the cell thickness is 54.4 μm. In view of the fact that $V_{th} = 0.68$ V and 0.59 V at $T = T_c - 6.471$ K and $T_c - 0.437$ K, respectively, the plot is restricted in the range from V = 4.5 V to 100 V. As clear in the figure, each plot fits a straight line extremely well in accordance with Equation 80. Especially, the intercepts with the ordinate are almost 0, indicating that the anchoring at the rubbed PVA-5CB interface is very strong, irrespective of the temperature. Further, the good linearity shows that the higher order terms in the expansion of $d_e(D)$ are also negligible. By performing a least squares fitting, the extrapolation lengths are estimated as follows:

$$d_e = 0.0 \pm 2.7 \text{ nm}, \quad \text{at } T = T_c - 6.471 \text{ K},$$

$$d_e = -2.0 \pm 2.7 \text{ nm}, \text{ at } T = T_c - 0.437 \text{ K},$$

Then, using the splay elastic constants as obtained from the threshold voltage, we can give estimates of the anchoring energy as

$$E_a > 1.8 \times 10^{-3} \text{ J/m}^2, \text{ at } T = T_c - 6.471 \text{ K},$$

$$E_a > 2.8 \times 10^{-3} \text{ J/m}^2, \text{ at } T = T_c - 0.437 \text{ K},$$

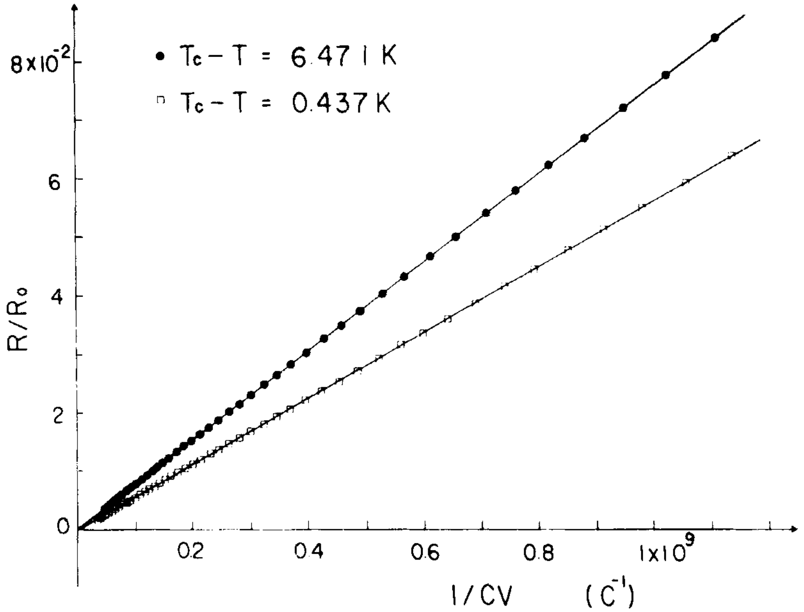

FIGURE 3. Plot of the normalized retardation R/R_0 versus $1/CV$ for a rubbed PVA-5CB interface, observed at two different temperatures close to and far from the clearing point. V is the applied voltage (7.43 kHz), and C is the capacitance of the cell. R_0 is the zero-field retardation of the cell: $R_0 = 2\pi \times 13.9108$ at $T = T_c - 6.471$ K, and $R_0 = 2\pi \times 9.4199$ at $T = T_c - 0.437$ K.

These are the largest values ever observed for the solid-nematic interface. Similar experiment has also been conducted by Ohide, *et al.*[71] for 5CB aligned by rubbed polyimide film, which is an alignment layer used almost unexceptionally in current displays. They reported, as above, the anchoring energy larger than 10^{-3} J/m^2 independent of the strength of rubbing action.

As discussed in the former section, the extrapolation length measured in a macroscopic experiment is a thermodynamic quantity which bears only an indirect relationship with the real structure of the interface. As a result, an observation of a strong anchoring, as above, does not necessarily imply the presence of a strong substrate-nematic coupling on the microscopic scale. This is because the dividing surface, from which the extrapolation length is measured, tends to move around depending on the nature of the interfacial inhomogeneity which has not been incorporated in the thermodynamic expression as Equation 68. In particular, it should be noticed that the observation that $d_e(D) \approx 0$ for the rubbed PVA-5CB does not necessarily mean that the anchoring strength is constant throughout the observed range of voltage, but merely that the changes of the surface of extrapolation and the dividing surface should almost cancel each other. The dividing surface at a substrate-nematic interface is determined by the contribution of several factors. Although these can be rigorously taken into account only starting from a microscopic consideration of the interface, we would like here to make a qualitative argument with a view to illustrating the importance of the dividing surface in treating a strong anchorage.

As shown in Equation 76, the dividing surface in the high-electric-field technique is located so as to make the retardation R_{ideal} equal to the experimental value R_{exp}. Therefore, since the experimentally accessible retardation is an integral of the local effective birefringence [Equation 36, see also Appendix], it is clear that interfacial anomalies of refractive indices and of the molecular orientation are in general contributing to the shift of the dividing surface. In the absence of bulk deformations, however, it may be reasonable to conceive that the variation of the effective birefringence near the substrate is primarily effected by the local change of the orientational order.[36,97-100] Then, if we assume a simple model that the birefringence has an excess value $\Delta n_s(z)$ near the substrate surface ($z = 0$) over the bulk birefringence $\Delta n_{eff}(\theta_e)$, we get

$$R_{\text{exp}} = \frac{2\pi}{\lambda} \int_0^{\infty} \Delta n_{eff}(\theta_e) + \Delta n_s(z)\, dz. \tag{86}$$

Therefore, equating this to R_{ideal} with the dividing surface at z_1, we readily find

$$z_1 = -\frac{1}{\Delta n_{eff}(\theta_e)}\int_0^{\infty} \Delta n_s(z)\, dz. \tag{87}$$

Unfortunately, the surface excess retardation has never been experimentally measured in the nematic phase. In the isotropic phase, however, it has been measured by several authors,[97-100] and has been shown to have a value around $R_{\text{excess}} = 10^{-2}$ rad(λ = 633 nm) on rubbed polymer surfaces, even at several degrees above the clearing temperature. Hence, if we adopt the same value even in the nematic phase, we find from Equation 87 that the dividing surface is located at

$$z_1 = -10 \text{ nm}, \tag{88}$$

using $\Delta n_{eff}(\theta_e) = 0.1$. This shows (in the structure-model perspective) that the dividing surface is at the point 10 nm inside the substrate. Therefore, even when the extrapolation length is almost 0 as in the rubbed PVA-5CB case, the surface of extrapolation is not just at the substrate surface (the usual reminiscence of the "strong anchoring"), but is still well inside the substrate. As Equation 87 shows, when the surface excess retardation is positive, the real anchoring condition is somewhat weaker than that apparently suggested by the observed anchoring strength, and when it is negative, the surface anchoring should be stronger; the negative surface excess retardation has indeed been suggested for evaporated SiO substrate, based on a good deal of circumstantial evidence.[70,73,97,99,100,102,103] In particular, when an orientational wetting occurs in the nematic phase, *i.e.*, when the disordered phase precipitates in between the substrate and the nematic phase, it should have a tremendous effect on the location of the dividing surface, also affecting the apparent anchoring strength.

The surface order will also manifest itself in the elastic constants, the dielectric constants, *etc.*, thereby altering the manner in which the molecular orientation responds to an externally applied torque.[70] Furthermore, the range of the substrate-nematic interaction does also have a remarkable effect on the orientational behavior.[23] This time, let us neglect the interfacial variation of the order parameter, and assume a model that the angle $\theta(z)$ has a surface excess in such a way that $\theta(z) = \theta_{\text{ideal}}(z) + \theta_s(z)$, where θ_{ideal} denotes the angle at z when the bulk profile is extrapolated. Then, the experimentally accessible retardation may be written as

$$R_{\exp} \approx \int_0^{\infty} \Delta n_{eff}(\theta_{\text{ideal}}) + \Delta n'_{eff}(\theta_{\text{ideal}})\, \theta_s(z)\, dz. \tag{89}$$

Hence, the dividing surface is now at

$$z_1 \approx - \frac{1}{\Delta n_{eff}(\theta_e)} \int_0^{\infty} \Delta n'_{eff}(\theta_{\text{ideal}})\, \theta_s(z)\, dz. \tag{90}$$

Since $\Delta\theta_s$ would increase as the bulk deformation and/or the external field are increased, the above equation describes the movement of the dividing surface at finite deformation regime. When the interfacial region is more easily deformed than the bulk, *i.e.*, $\theta_s < 0$, the dividing surface tends to move into the nematic region. Obviously, the significance of this effect is dependent on the range and magnitude of θ_s. If we conceive that it is confined in the interfacial transition layer of thickness ξ_i, Equation 90 shows that $z_1 \approx \xi_i \langle\theta_s\rangle$, where $\langle\ \rangle$ denotes the average over ξ_i. Therefore, only when $\theta_s \sim 1$, z_1 could be as large as ξ_i. In the above experimental result, the electrical coherence length is at least 0.15 μm; so that, the dividing surface is expected not to be so much influenced by this mechanism. However, since the possibility cannot, in general, be ruled out that the electric field affects the interfacial orientation directly and/or indirectly through the buildup of space charge, it would not be easy to estimate the field effect in actual setting. In particular, it has recently been pointed out by Barbero and Durand[104] that the flexoelectric effect does have a significant influence on the director profile over sub-micron to micron range. If this effect is taking place in the above experiment, inducing a noticeable motion of the dividing surface, the observation that $d_e(z_1,D) \approx 0$ demands that the extrapolation length with respect to a fixed dividing surface $d_e(z_d,D)$ must also have a substantial D-dependence in such a way as to cancel the motion of the dividing surface.

IV. CONCLUSION

Surface anchoring of nematics is an important scientific and technical problem. However, the understanding of the phenomenon is highly premature. In particular, although it has long been known that the anchoring strength is an indispensable parameter for characterizing the substrate-nematic interface, its experimental determination has been greatly hindered due to its technical and conceptual difficulties. In this article, I emphasized the importance of making a clear distinction between the thermodynamic description of the interface and the microscopic structure model. In particular, it was pointed out that the anchoring energy and the extrapolation length, accessible in macroscopic experiments, are thermodynamic parameters which are meaningful only in combination with the dividing surface defined in the Gibbs' sense. We critically examined four existing experimental techniques for measuring the anchoring strenth: (1) Physico-chemical, (2) Wedge-cell, (3) Freedericksz transition, and (4) High-electric-field techniques. And it was argued that, although the last three methods are quantitatively reliable (when certain conditions are met), the first one is of only qualitative significance. Furthermore, only the last two techniques are thermodynamically consistent. In all of these techniques, there always exists certan ambiguity in the location of the dividing surface. In the wedge-cell and the Freedericksz transition technique, the cell thickness determines the dividing surface, usually without reference to any physical property of the substrate-nematic interface. In the high-electric-field technique, however, the dividing surface is located at the zero-adsorption plane of the optical phase retardation; but, because of the unknown interfacial structure, it suffers froom an uncertainty as large as a few 10 nm. The anchoring strength at rubbed PVA-5CB interface has been measured by the high-electric-field technique, giving the anchoring energy apparently larger than 10^{-3} J/m^2. However, the uncertainty in the dividing surface prevents us from saying something definite on the actual anchoring strength. A closed treatment of strong surface anchorage is possible only on the basis of some microscopic model of the substrate-nematic interface. This property can in a way be regarded as a defect of the thermodynamic description of the interface. However, this in turn implies that the measurement of strong anchoring would serve a bridge connecting the macroscopic and the microscopic worlds.

Acknowledgment

Part of this work has been performed during a visit by the author to AT&T Bell Laboratories. He wishes to thank Dr. M. P. Bohrer for his hospitality. He is also grateful to Prof. S. Kobayashi for helpful comments on the manuscript and preprints.

APPENDIX

Here, we derive a quantitative condition for Equations 36 and 37 to be sufficiently accurate. For propagation of electromagnetic wave along the z-axis, Maxwell's equations generally yield,[65]

$$\frac{d^2E_0}{dz^2} = -n_o^2k^2E_0, \quad \text{and} \quad \frac{d^2E_e}{dz^2} = -[\Delta n_{eff}(\theta) + n_o]^2k^2E_e. \tag{A.1}$$

where E_o and E_e are the ordinary and the extraordinary components of electric field, and $k = 2\pi/\lambda$ is the wave vector in vacuum. From the first equation, $E_o \propto e^{in_okz}$.

As we are interested in the phase difference between E_o and E_e, we set $E_e \propto \exp[i\phi(z) + in_okz]$. Then, substituting this expression in Equation A.1, we obtain

$$i\phi'' - \phi'^2 - 2n_ok\phi' = [n_o^2 - (\Delta n_{eff} + n_o)^2]k^2. \tag{A.2}$$

Based on the WKB method, we try to find an approximate solution in a power series in k. Substituting $\phi(z) = k\phi_0 + \phi_1 + k^{-1}\phi_2 + \cdots$ into the above, and comparing the terms of the same order in k, we readily find

$$\begin{aligned} \phi_0' &= \Delta n_{eff}, \qquad \phi_1' = \frac{i\Delta n'_{eff}}{2(\Delta n_{eff} + n_o)}, \\ \phi_2' &= \frac{3(\Delta n'_{eff})^2 - 2(\Delta n_{eff} + n_o)\Delta n''_{eff}}{8(\Delta n_{eff} + n_o)^3}. \end{aligned} \tag{A.3}$$

Therefore, since ϕ_1 is pure imaginary, the phase retardation R is, up to first order in k^{-1}, given by

$$R = \int_{-\infty}^{\infty} k\phi_0' + k^{-1}\phi_2'\, dz. \tag{A.4}$$

When the second term can be neglected, the above equation agrees with Equation 36. Hence, the validity criterion for Equation 36 can be written as

$$\frac{|\phi_2'|}{k^2|\phi_0'|} << 1. \tag{A.5}$$

Noting that $\Delta n_{eff} \sim 0.1$ and is hence much smaller than $n_o \sim 1.5$, we can rewrite Equation A.5 as

$$\frac{\lambda^2}{16\pi^2 n_o^{\,2}\xi^2} << 1, \tag{A.6}$$

where ξ is the characteristic length for the variation of Δn_{eff}. This shows that Equation 36 should be valid for

$$0.2\lambda < \xi. \tag{A.7}$$

Consequently, for $\lambda = 633$ nm, Equation 36 can be expected to hold, as long as the characteristic length over which the director orientation appreciably changes is larger than 0.1 μm. In the case of the high-electric-field technique, by using $d_c \approx dV_{th}/\pi V$, we see that the approximate expression remains valid for $V < 160V_{th}$ when $d = 50$ μm.

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75. Although it may not be a rigorous inequality, this trend is conceived to be connected with the fact that the azimuthal anchorage can appear only when the substrate is anisotropic in some way, while the polar anchorage is not [References 18–21, 24–33]. Some model calculations for meaningful cases are indeed consistent with these experimental observations. Based on Berreman's groove model [Reference 38], Faetti [Reference 39] recently derived a relation

$$E_a(az) < 2\pi^2\frac{A^2}{\lambda^2}E_a(p),$$

where $E_a(az)$ and $E_a(p)$ are the azimuthal and the polar anchoring energies, and A and λ are the amplitude and the wavelength of the surface groove, respectively. Hence, for realistic grooves that satisfy $A/\lambda << 1$, we see that $E_a(az)$ is always smaller than $E_a(p)$. For macroscopic van der Waals interfaction model, on the other hand, Okano, *et al.* [Reference 22] estimated the azimuthal anchoring energy on quartz with its optic axis lying parallel to the surface. The anchoring energy they obtained $E_a(az) \sim 10^{-5}$ J/m^2 is indeed fairly smaller than the polar anchoring energy calculated via the same approach [References 20 & 21].
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84. This result is, as repeatedly stressed in Reference 83, essentially dependent on the fact that the Frank theory is a linear elastic theory with respect to the director.
85. It is tacictly assumed that the thermodynamic state of the bulk region of the substrate is independent of the deformation state of the nematic. This assumption is expected to hold to a good approximation for such hard solids that are usually in use for liquid crystals experiments.
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rivative of the director is to some extent an artifact connected with the manner in which the mutual interaction energy between molecules is assigned to each molecule. The original statistical mechanical expression for the curvature strain energy is essentially nonlocal and the conventional elastic formula follows by applying the gradient expansion to the orientational distribution function or director.[51] Those second-order elasticity terms emerge, when the distribution functions are expanded about their local value in the orientationally deformed state [see, A. Poniewierski and J. Stecki, *Mol. Phys.*, **38**, 1931 (1979)]. But, if the expansion is made about the value in the uniform undeformed state, those terms can be totally avoided [H. Yokoyama, presented at *11th International Liquid Crystal Conference, Berkeley, California, July* (1986)]. At an interface between a solid substrate and a nematic, the distribution function should change very rapidly over several molecular dimensions; so that, the expansion about the local value, as if its initial distribution were uniform at this value, ceases to be a good approximation scheme. Indeed, the gradient expansion obtained this way may be poorly convergent in the interfacial region, and hence we need to take account of the elasticity terms involving much higher order derivatives to get a meaningful result. As clear from the above consideration, a proper account of the second-order elasticity is equivalent to solving the problem of alignment at nematic free surface; this time, however, the surface structure is modified by the solid substrate.

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94. Strictly speaking, it is not allowed to regard the work of adhesion for an arbitrary alignment as a work needed to reversibly separate the solid and the nematic in which the director is uniformly aligned. This follows from the very definition of the easy axis; that is, a uniform alignment is possible (except for some metastable orientation, if any), if and only if $\mathbf{n} \parallel \mathbf{n}_e$. So, the right-hand side of Equation 20 is *not* an equilibrium quantity, while the left-hand side should be. This pitfall results from the use of $\gamma(\mathbf{n}_0)$, treating it as a function which can be taken independently of the bulk state. This point is often overlooked in the literature, and is also an example of confusion between the thermodynamic and the structure-model quantities.
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101. In the case of the torque-measurement technique developed by Faetti *et al.* [Reference 73] for the azimuthal anchorage, the dividing surface is defined in practically the same manner as for the high-electric-field technique. In this technique, the torque τ exerted on the substrate immersed in a nematic liquid crystal under a uniform magnetic field H is measured as a function of the field strength. The torque for the ideal nematic is given by $\tau_{\text{ideal}} = (K_2\Delta\chi)^{1/2}HS\sin\phi_1(z_1)$, where K_2 is the twist constant, S the surface area of the substrate, and ϕ_1 is the azimuthal angle between the director at the dividing surface and the magnetic field applied parallel to the substrate. Then, for the measured torque τ_{exp}, the dividing surface z_1 is determined in such a way that $\tau_{\text{exp}} = \tau_{\text{ideal}}(z_1)$. Therefore, the dividing surface here has a meaning as the zero-adsorption plane for the magnetic torque. This property is also a result of the absence of cell thickness in this technique.

Similar to Equation 80, we can derive a linear relation between $1/\tau$ and $1/H$ as

$$\frac{1}{\tau} \approx \frac{1}{(K_2\Delta X)^{1/2} HS\sin\phi_e} + \frac{\cot\phi_e}{K_2 S} d_e,$$

where ϕ_e is the angle of the easy axis. Hence, the extrapolation length is straightforwardly obtained from the intercept with the ordinate.

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