Self-consistency of Vuks equations for liquid-crystal refractive indices

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Vuks equations correlate the microscopic molecular polarizabilities to the macroscopic refractive indices of anisotropic crystalline materials. For anisotropic liquid crystals, the molecular polarizabilities are difficult to measure directly due to the short- and long-range interactions. We have converted Vuks equations into different forms. By measuring the refractive indices at different temperatures and wavelengths, the Vuks equations can be validated. Five liquid-crystal materials with refractive index ranging from \( \sim 1.46 \) to \( \sim 1.86 \) are used to validate the modified Vuks equations. The experimental results agree with the theory very well. Based on the Vuks equations, the molecular polarizabilities of 4-cyano-4-n-pentylbiphenyl are calculated.

\[ \frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3N} \alpha. \]  
\[ \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3N} \alpha. \]

For an anisotropic LC, there are two principal refractive indices, \( n_e \) and \( n_o \), where \( n_e \) and \( n_o \) are refractive indices for the extraordinary ray and ordinary ray, respectively. In principle, each refractive index should be related to the corresponding molecular polarizabilities, \( \alpha_e \) and \( \alpha_o \). An early approach replaces both \( n^2 \) in Eq. (2) by \( n^2_e \) and \( \alpha \) by \( \alpha_e \). However, this model does not fit the experimental results well. Vuks made a bold assumption that the internal field in a crystal is the same in all directions, and

\[ E_i = \frac{(n_e^2) + 2}{3} E, \]

where \( E_i \) is the internal field, the average field that acts on a molecule, and \( E \) is the macroscopic electric field. This assumption is later validated experimentally. With this assumption, Vuks derived the following equation for anisotropic media:

\[ \frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3N} \alpha. \]
Equation (4) is different from Eq. (2) in two aspects: (1) the \( n^2 \) term in the denominator of Eq. (2) is replaced by \( \langle n^2 \rangle = (n_e^2 + 2n_o^2)/3 \), while the \( n^2 \) term in the numerator is replaced by \( n_{e,o}^2 \) and (2) the \( \alpha \) is replaced by \( \alpha_{e,o} \).

In Eq. (4), the macroscopic LC refractive indices \( n_e \) and \( n_o \) can be measured easily, however, the microscopic molecular polarizabilities \( \alpha_e \) and \( \alpha_o \) are difficult to determine directly. To validate Vuks equations, we rewrite Eq. (4) as follows:

\[
\frac{n_{e,o}^2 - 1}{\langle n^2 \rangle + 2} = \frac{4\pi}{3} N\alpha_{e,o}.
\]

Multiplying both sides of Eq. (5b) by 2 and then add the corresponding terms with Eq. (5a), we obtain the following equation:

\[
\frac{(n_{e,o}^2 + 2n_{e,o}^2) - 3}{\langle n^2 \rangle + 2} = \frac{4\pi}{3} N\left(\alpha_e + 2\alpha_o\right).
\]

Equation (6) can be rewritten as

\[
\frac{\langle n^2 \rangle - 1}{\langle n^2 \rangle + 2} = \frac{4\pi}{3} N\langle \alpha \rangle,
\]

where the average molecular polarizability is defined as \( \langle \alpha \rangle = (\alpha_e + 2\alpha_o)/3 \). To evaluate Eq. (7) experimentally, we need to correlate \( N\langle \alpha \rangle \) with another measurable macroscopic parameter, such as the average refractive index.

From Eq. (4), we can express \( n_e \) and \( n_o \) as follows:

\[
n_e = \sqrt{2.5 \left[ 1 + \frac{(x_o - 1.5)}{2.5} \right]^{1/2}},
\]

\[
n_o = \sqrt{2.5 \left[ 1 + \frac{(x_o - 1.5)}{2.5} \right]^{1/2}},
\]

\[
\alpha_e = \langle \alpha \rangle + \frac{2\delta}{3}(\gamma_e - \gamma_o),
\]

\[
\alpha_o = \langle \alpha \rangle - \frac{\delta}{3}(\gamma_e - \gamma_o).
\]

Substituting Eqs. (8a) and (8b) back to Eqs. (11a) and (11b), respectively, we can express \( n_e \) and \( n_o \) in terms of \( N \), \( \langle \alpha \rangle \), and \( \alpha_e - \alpha_o \) [which is equal to \( S(\gamma_e - \gamma_o) \)] by power expansions,

\[
n_e \approx \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\langle \alpha \rangle}{1 - \frac{4}{3}\pi N\langle \alpha \rangle} + \frac{(4\sqrt{10}/15)\pi NS(\gamma_e - \gamma_o)}{1 - \frac{4}{3}\pi N\langle \alpha \rangle},
\]

\[
n_o \approx \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10}/5)\pi N\langle \alpha \rangle}{1 - \frac{4}{3}\pi N\langle \alpha \rangle} - \frac{(4\sqrt{10}/15)\pi NS(\gamma_e - \gamma_o)}{1 - \frac{4}{3}\pi N\langle \alpha \rangle}.
\]

Here, \( \gamma_e - \gamma_o \) is the differential molecular polarizability in the crystalline state,

\[
S = (1 - T/T_c)^\beta.
\]

In Eq. (14), the exponent \( \beta \) is a material constant. For many LC compounds, \( \beta = 0.2 \) is not too sensitive to the LC molecular structures.
Based on Eqs. (13a) and (13b), we can calculate the average refractive index, which is defined as \( \langle n \rangle = (n_e + 2n_o)/3 \), and obtain the following equation:

\[
\langle n \rangle = \frac{7}{2\sqrt{10}} + \frac{(2\sqrt{10/5})\pi N(a)}{1 - \frac{3}{\pi} n(a)}. \tag{15}
\]

Equation (15) can be rearranged as follows:

\[
1 - \frac{3}{\sqrt{10}(n) - 0.5} = \frac{4}{3} n(a). \tag{16}
\]

Equation (16) correlates \( N(a) \) to the average refractive index \( \langle n \rangle \). This is an important step as the microscopic quantity \( N(a) \) can be determined experimentally by measuring the LC refractive indices. In order to compare with Eq. (16), we rewrite Eq. (7) as

\[
1 - \frac{3}{(n^2) + 2} = \frac{4}{3} \pi N(a). \tag{17}
\]

By comparing Eq. (16) with Eq. (17), we find

\[
\langle n^2 \rangle + 2 = \sqrt{10}(n) - 0.5. \tag{18}
\]

The significance of Eq. (18) is that the sophisticated microscopic Vuks equation can now be validated by two simple macroscopic parameters \( \langle n^2 \rangle \) and \( \langle n \rangle \). These two parameters can be obtained by measuring the individual refractive indices \( n_e \) and \( n_o \) of the liquid crystal. In Sec. IV, we will use the experimental data of five LC materials with birefringence ranging from 0.08 to 0.35 to validate Eq. (18).

### III. EXPERIMENT

We measured the refractive indices of UCF-35 (a high birefringence LC mixture), 5CB, 4-cyan-4-n-pentylecyclohexane-phenyl (5PCH), MLC-6241-000 (a commercial low birefringence LC mixture), and UCF-280 (\( \Delta \varepsilon < 0 \)) using a multiwavelength Abbe refractometer (Atago DR-M4) at \( \lambda = 450, 486, 546, 589, 633 \), and 656 nm. The accuracy of the Abbe refractometer is up to the fourth decimal. For a given wavelength, we measured the refractive indices of these five LCs from 10 to 60 °C. The temperature of the Abbe refractometer is controlled by a circulating constant-temperature bath (Atago Model 60-C3). The LC molecules are aligned perpendicular to the main prism surface of the Abbe refractometer by coating a surfactant comprising of 0.294 wt % hexadecyltri-methyl-ammonium bromide in methanol solution. Both \( n_e \) and \( n_o \) are obtained through a polarizing eyepiece. From our measurements, the clearing points of UCF-35, 5CB, 5PCH, MLC-6241-000, and UCF-280 are 368.3, 306.6, 325.9, 373.7, and 339.2 K, respectively.

### IV. RESULTS AND DISCUSSIONS

We have measured the refractive indices of two LC compounds (5CB and 5PCH) and three eutectic mixtures [UCF-35, MLC-6241-000, and UCF-280 (\( \Delta \varepsilon < 0 \))] at various wavelengths and temperatures. Their raw data are listed in Tables I–V, respectively.

Figure 1 depicts the temperature-dependent birefringence of UCF-35, 5CB, 5PCH, MLC-6241-000, and UCF-280 measured at \( \lambda = 589 \) nm. The filled circles, squares, open circles, filled downward triangles, and open upward triangles are the measured birefringence of UCF-35, 5CB, 5PCH, and 280.
TABLE III. Measured refractive indices ($n_e$ and $n_o$) of UCF-280 at $\lambda = 589, 633,$ and $656$ nm at different temperatures. The five solid lines are the fitting curves using Eq. 20, which is a close approximation of Vuks equation.

<table>
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<tr>
<th>$T$ (°C)</th>
<th>$n_e$</th>
<th>$n_o$</th>
<th>$n_e$</th>
<th>$n_o$</th>
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<th>$n_o$</th>
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TABLE IV. Measured refractive indices ($n_e$ and $n_o$) of MLC-6241-000 at $\lambda = 589, 633,$ and $656$ nm at different temperatures.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$n_e$</th>
<th>$n_e$</th>
<th>$n_e$</th>
<th>$n_o$</th>
<th>$n_e$</th>
<th>$n_o$</th>
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<tbody>
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<td>633</td>
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<td>656</td>
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TABLE V. Measured refractive indices ($n_e$ and $n_o$) of UCF-280 at $\lambda = 589, 633,$ and $656$ nm at different temperatures.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
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<th>$n_o$</th>
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<td>633</td>
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<td>1.4877</td>
<td>1.5735</td>
<td>1.4853</td>
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its clearing temperature is much lower. As a result, its birefringence at room temperature is lower than that of MLC-6241-000 due to the order-parameter effect.

In Fig. 2, we plot the values of $\langle n^2 \rangle + 2$ and $\sqrt{10} \langle n \rangle - 0.5$ of 5CB and 5PCH in the same figure in order to validate Eq. (18) which is a close approximation of Vuks equation. The filled and open squares, circles, and upward triangles are the measured values of $\langle n^2 \rangle + 2$ and $\langle n \rangle - 0.5$ at $\lambda = 546, 589,$ and $633$ nm, respectively. From Fig. 2, we find that these data almost overlap each other. The difference is as small as $\sim 0.2\%$ for 5CB and $\sim 0.1\%$ for 5PCH. On the other hand, the average refractive index $\langle n \rangle$ decreases linearly as the temperature increases,

$$\langle n \rangle = A - BT.$$  \hspace{1cm} (20)

From Eq. (20), the right side of Eq. (18) can be written as
\[ \sqrt{10(n) - 0.5} = \sqrt{10(A - BT) - 0.5}. \]  

The solid lines shown in Fig. 2 are the fitting results using Eq. (21). From Fig. 2, the agreement between experiment and fitting results is excellent for 5CB and 5PCH. The experimental data measured at different wavelengths and temperatures of 5CB and 5PCH all satisfy Eq. (18) very well. Therefore, Vuks equation is proven to be self-consistent for describing the refractive indices of LC compounds (5CB and 5PCH), although the isotropic local field is assumed.

Figure 3 shows a similar plot for UCF-35, MLC-6241-000, and UCF-280. The filled squares, circles, and upward triangles are the measured values for \( \langle n^2 \rangle^2 + 2 \) at \( \lambda = 546 \text{ nm} \) for UCF-35, MLC-6241-000, and UCF-280, respectively. The open squares, circles, and upward triangles are the corresponding values of \( \sqrt{10(n) - 0.5} \) at \( \lambda = 656 \text{ nm} \). In Fig. 3, we plot the data at \( \lambda = 656 \text{ nm} \) because UCF-35 has more complete experimental data at this wavelength. The refractive indices of these three LC mixtures vary from \( \sim 1.46 \) to \( \sim 1.86 \), as listed in Tables I–V. Despite such variation, Eqs. (18) and (21) still hold very well.

In Fig. 3, all the experimental data of the left and right terms of Eq. (18) overlap quite well for UCF-35, MLC-6241-000, and UCF-280 although UCF-35 has \( 4 \times \) higher birefringence than the other two mixtures. The difference between the right- and left-hand terms of Eq. (18) is as small as \( \sim 0.5\% \) for UCF-35 and \( \sim 0.1\% \) for MLC-6241-000 and UCF-280. Solid lines are the fitting results using Eq. (21). The fitting results agree very well with the experimental data. Therefore, Vuks equation is proven to be self-consistent for both high and low birefringence LC mixtures.

As shown in Figs. 2 and 3, the \( \langle n^2 \rangle^2 + 2 \) term is slightly larger than the \( \sqrt{10(n) - 0.5} \) term. This is because we have omitted the higher order terms while deriving Eqs. (11a) and (11b) which, in turn, lead to Eqs. (16) and (18). The five LC materials we selected have refractive index spanning from \( \sim 1.46 \) to \( \sim 1.86 \). All the experimental data satisfy Eq. (18) quite well. It implies that the Vuks equation is valid for describing LC refractive indices independent of their molecular structures and electron conjugation length.

Since Vuks equation correlates the macroscopic refractive index to the microscopic molecular polarizability, if we know refractive index, then we can calculate the molecular polarizability or vice versa. For instance, if we plug the measured \( n_e \) and \( n_o \) data listed in Tables I–V back to Eq. (4), we can calculate the \( \alpha_e \) and \( \alpha_o \) values of the five LC compounds and mixtures at different temperatures and wavelengths.

In Eq. (4), there is still an unknown parameter \( N \), the number of molecules per unit volume. However, \( N \) is equal to \( \rho N_A / M \), where \( \rho \) is the LC density, \( M \) is the molecular weight, and \( N_A \) is the Avogadro’s number. Rearranging Eq. (4), we find

\[
\alpha_e = \frac{3M}{4\pi\rho N_A} \frac{n_e^2 - 1}{\langle n^2 \rangle + 2},
\]

and

\[
\alpha_o = \frac{3M}{4\pi\rho N_A} \frac{n_o^2 - 1}{\langle n^2 \rangle + 2}.
\]

Let us use 5CB as an example to calculate the molecular polarizabilities, \( \alpha_e \) and \( \alpha_o \). For 5CB, the molecular weight is \( M = 249.3 \text{ g/mol} \) and the density \( \rho(T) \) is taken from that measured by Zeller. Using our measured refractive indices at \( \lambda = 589 \text{ nm} \), we can calculate the \( \alpha_e \) and \( \alpha_o \) of 5CB from Eq. (22).

Figure 4 plots the temperature-dependent \( \alpha_e \), \( \alpha_o \), and \( \langle n \rangle \) of 5CB at \( \lambda = 589 \text{ nm} \). The open and filled circles represent the calculated values for \( \alpha_e \) and \( \alpha_o \), respectively. In the isotropic state, \( \alpha_e \) and \( \alpha_o \) are equal. The open triangles represent...
the calculated average polarizability $k_{al}$ in the nematic phase. From Fig. 4, $\alpha_e$ decreases while $\alpha_o$ increases as the temperature increases. However, the average polarizability $k_{al}$ is quite insensitive to the temperature. The average polarizability for 5CB at $\lambda=589$ nm is found to be $k_{al}=3.3 \times 10^{-23}$ cm$^3$, which agrees very well with the calculated value $k_{al}=3.25 \times 10^{-23}$ cm$^3$ published by Sarkar et al.$^{21}$

V. CONCLUSIONS

We have developed a simple method for validating Vuks equations. By decoupling $n_e$ from $n_o$, we derived Vuks equations in a different form. We are able to correlate the molecular polarizabilities $\alpha_e, \alpha_o$ to another macroscopic term $\langle n \rangle$. Through the derivation process, we find another relationship between $\langle n^2 \rangle$ and $\langle n \rangle$, as described by Eq. (18). Using our experimental results, Vuks equation is validated despite that the isotropic local field is assumed. Based on Vuks equations, the molecular polarizabilities and average polarizability of 5CB at $\lambda=589$ nm are obtained in the nematic and isotropic phases.

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