In Silico Measurement of Elastic Moduli of Nematic Liquid Crystals

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Experiments on confined droplets of the nematic liquid crystal 5CB have questioned long-established bounds imposed on the elastic free energy of nematic systems. This elasticity, which derives from molecular alignment within nematic systems, is quantified through a set of moduli which can be difficult to measure experimentally and, in some cases, can only be probed indirectly. This is particularly true of the surfacelike saddle-splay elastic term, for which the available experimental data indicate values on the cusp of stability, often with large uncertainties. Here, we demonstrate that all nematic elastic moduli, including the saddle-splay elastic constant k_{24}, may be calculated directly from atomistic molecular simulations. Importantly, results obtained through *in silico* measurements of the 5CB elastic properties demonstrate unambiguously that saddle-splay elasticity alone is unable to describe the observed confined morphologies.

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Though liquid crystals (LCs) [1] have long been central components of display technologies [2], their optically responsive and highly controllable nature has lead to a host of emerging applications in nanoscale and colloidal templating [3], organic electronics [4], biosensing [5,6], compact lenses [7], and switchable diffraction gratings [8]. These applications rely on their ordering elasticity, which through competition with applied fields and surface interactions can lead to topological defects whose nature and structure is governed by a precise interplay [9–11]. The balance between these different contributions to the free energy is apparent in the morphologies adopted by confined liquid crystals [12–14], where it is possible to manipulate different variables to develop exquisitely sensitive systems for sensing applications [6,15]; a properly chosen liquid crystal can in fact be balanced on a knife's edge, ready for a vanishingly small concentration of analyte to induce a mesoscopic transformation, visible under standard crossed-polarizer optics. Precision engineering of such new devices requires an in-depth understanding of the elastic behavior of the underlying liquid crystalline phases.

The resistance of a nematic phase to orientational deformations can be described through a set of quadratic-order terms and the corresponding response coefficients [1]. Though this energy is relatively simple to phrase, elastic properties are difficult to measure experimentally. The saddle-splay constant k_{24}, in particular, which penalizes bidirectional deformations [16], is only accessible through indirect measurements that rely on morphological instability thresholds [9,10,17–19]. Past experimental studies have reported conflicting measurements, and some of the published values of k_{24} have in fact been found to lie outside stability criteria established by Ericksen [20], hinting at new physics that may be used to purposely engineer instability into nematic materials. Here, we demonstrate that it is possible to rely on detailed molecular simulations to predict the elastic moduli of nematic liquid crystals. By extending methods that rely on real-space free-energy perturbations [21,22] to utilize an accurate atomistic force field [23], we are able to characterize the elastic coefficients and their temperature dependence, including the elusive k_{24}. Our results lead to values consistent with Ericksen's bounds and in agreement with a subset of the experimental literature, implying that previously observed morphological instabilities in confined 5CB [18,24] could have been due to inappropriate *Ansätze*, surface effects, or higher-order elastic moduli.

For the common case of apolar, achiral, and uniaxial nematic liquid crystals, the phase may be described by a local orientation vector $\hat{\mathbf{n}}$. In the absence of boundaries and external fields, this is a global vector. The local order, however, can be perturbed, leading to small distortions that incur a free energy penalty and a corresponding elastic restoring force. To order $(\nabla\hat{\mathbf{n}})^2$, the elastic free energy can be written as [1]

$$f = \frac{1}{2}k_{11}(\nabla\cdot\hat{\mathbf{n}})^2 + \frac{1}{2}k_{22}(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2 + \frac{1}{2}k_{33}(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2 + \frac{1}{2}(k_{22}+k_{24})[\mathrm{Tr}(\nabla\hat{\mathbf{n}})^2 - (\nabla\cdot\hat{\mathbf{n}})^2] \qquad (1)$$

This expression contains the three most commonly used terms and their corresponding coefficients, or elastic moduli: splay (k_{11}), twist (k_{22}), and bend (k_{33}). The additional, divergencelike term ($\propto k_{22}+k_{24}$) is referred to as “saddle splay.” It penalizes bidirectional deformations, and can be defined so that the free energy is positive definite to quadratic order as outlined by Ericksen [20]. An illustration of these elastic modes is presented in Fig. 1. While originating from bulk interactions [16], the saddle splay may be transformed into a surfacelike term in a global free energy integral by invoking Gauss’s law. For that reason, it has generally been overlooked in elastic studies [1,25], and it is only recently that studies of confined nematic LCs have unearthed its relevance. It likely contributes far more than initially believed, to the point where under some conditions it is suggested to lie outside the Ericksen bounds [19,24], a feature that hints at an incomplete understanding of elasticity within the framework of a Frank-Oseen description. One implication of this is a spontaneous twisting of toroidal [18] or cylindrical [21] geometries, as depicted in Figs. 1(d) and 1(e). It should be noted that for k_{24}, all published measurements have been indirect, and have relied either on elastic instability thresholds in various geometries or a fit to a continuum model that matches polarized microscope measurements [9,10,17–19]. This has lead to disagreements in the values of k_{24} reported in the literature.

The goal of this work is to present a direct method for calculation of the elastic moduli of nematic materials from molecular simulations of atomistically detailed models, so that predictions can be quantitatively compared to experimental measurements. In such systems, the average orientation $\hat{\mathbf{n}}$ and degree of nematic alignment S are known and, as shown in this work, one can apply nanoscopic deformations to the material in order to excite distinct modes with extraordinary precision, thereby leading to direct, unambiguous characterization of all elastic moduli, including k_{24} (see Supplemental Material [26]). We hasten to note that past efforts to determine elastic coefficients of liquid crystals have focused on coarse-grained models [31,32]. Certain features underlying liquid crystalline ordering [33–35], however, are inaccessible without molecular specificity. Thus, a set of experimentally tuned atomistic force fields have been developed for, in particular, the widely studied cyanobiphenyls [23], as well as more general systems [36]. With such force fields, it has been possible to describe liquid crystal ordering with an extraordinary degree of precision, as revealed by comparison to x-ray reflectivity [34,35] and NMR data [37], and by studies of the molecular structure within nematic disclinations [33].

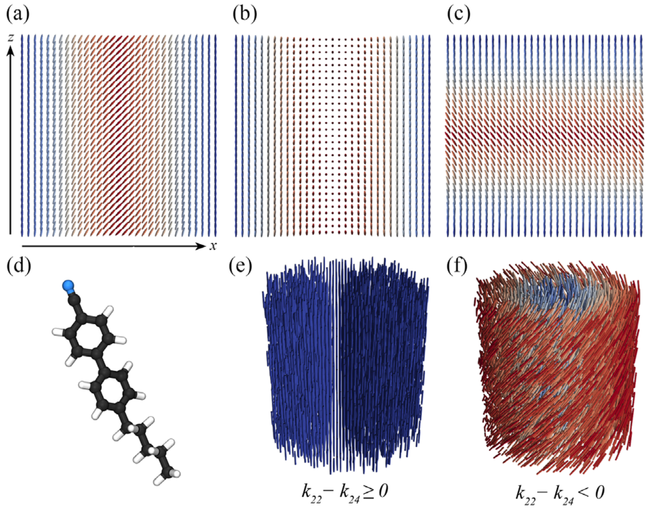

FIG. 1. The top row shows idealized bulk elastic modes (a) splay, (b) twist, and (c) bend, which can be directly probed in the experiment. The bottom row shows the 5CB molecule (d) and cylindrical twist deformations, which rely on the saddle-splay elastic constant k_{24}, in stable (e) and unstable (f) configurations under conditions of degenerate planar anchoring representative of the commonly studied 5CB-water interface. Saddle splay is not directly measurable through experiment but can be inferred indirectly. The positive definiteness of the elastic free energy expressed through the Ericksen bound $k_{22} - k_{24} \geq 0$ is thought to be violated for 5CB, though experiments are not conclusive.

Building on the pioneering work of Cleaver and Allen [38], several methods have been proposed to calculate the elastic constants of coarse-grained LC systems from molecular simulations. As useful as they have been, past methods have been hampered by limited accuracy, numerical complexity, or significant finite-size effects [38–40]. These limitations have prevented applications to atomistic systems without invoking theoretical assumptions that limit the reliability of the calculations. Indeed, in one of the few studies that considered a bulk model of 5CB, elastic constants were obtained using three different approaches, leading to significantly different elastic coefficients [41]. Though one set of predictions was found to be in good agreement with experimental measurements, it was regarded as “fortuitous” by the authors due to the crudeness of the underlying assumptions [41]. Another notable effort utilized a hybrid molecular field theory [42] to account for molecular flexibility from structures predicted by density functional theory (DFT) and geometry optimizations. Good agreement with experiment was reported for the k_{ii} elastic constants of several 4-*n*-alkyl-4’-cyanobiphenyls (*n*CBs) and *para*-azoxyanisole. Unfortunately, that method cannot capture all molecular conformations and, in particular, the mutual arrangements that nearby molecules adopt in response to bidirectional deformations, which are essential to capturing k_{24}.

Recently, we proposed a new method [21] in which orientational perturbations and free energy sampling techniques are coupled to obtain elastic constants by exciting distinct modes within the Frank free energy formulation [Eq. (1)]. The proposed method was shown to exhibit minimal sensitivity to finite-size effects [21,22], and was successfully applied to a broad range of Gay-Berne ellipsoids [22] and Lebwohl-Lasher lattice models [43,44]. In this work, we demonstrate the ability to directly predict *in silico* the elastic constants of an atomistic model of 5CB. This molecule is among the most widely studied and well characterized LCs. Despite its individual asymmetry, 5CB behaves largely as a uniaxial nematic. For the following investigations, we employ the force field of Tiberio and co-workers [23,26], which has been validated against experimental data in a variety of situations [33–35,37]. From our elastic measurements, we aim to gain additional insight into the relationship between molecular geometry and elasticity. More generally, we outline a computational methodology that in the future may be used for reliable screening of the elasticity of liquid crystalline materials for specific applications.

We recount the general approach here; the reader is referred to the Methods section and Ref. [21] for further algorithmic details. The free energy perturbation approach requires an order parameter ξ to select for deformations that excite a particular elastic mode. We take ξ to be $\partial n_x/\partial x$ for splay, $\partial n_y/\partial x$ for twist, and $\partial n_x/\partial z$ for bend in a system that is constrained to orient along the $\hat{\mathbf{z}}$ axis at the periodic boundary. The director at the center of the box is then tilted using a bias applied to the chosen order parameter to produce chevronlike patterns, resulting in a uniform-magnitude gradient between the restriction and bias regions. Figures 2(a)–2(c) illustrate this approach in practice. A stiff harmonic potential is used to maintain alignment to the $\hat{\mathbf{z}}$ direction at the periodic boundaries of the box. A second region in the box center is actively biased along a chosen deformation ξ using an adaptive sampling method. Here, we choose basis function sampling [43], which is constructed in a way such that material properties are easily extracted from the converged parabolic simulation bias. A similar approach is adopted for k_{24} by imposing a cylindrical geometry with degenerate planar anchoring and selecting ξ as $\partial n_\theta/\partial r$ [21].

The elastic constants are measured by implementing the order parameter in the advanced sampling software suite, SSAGES [47]. Basis function sampling [43] is used with $N = 14$ Legendre polynomials to measure the free energy of director deformation over the interval $[-0.5, 0.5]$. Using the final decorrelated trajectories from the previous simulations, four walkers contribute to the overall free energy estimate. Simulations are carried out at *NVT* conditions for 1 μs, at which point the polynomial coefficients converge to within $O(10^{-6})$. The elastic constants are computed from the final free energy surface as previously described.

We begin our studies by examining the standard bend, twist, and splay elastic constants of 5CB, for which multiple measurements exist in the literature. We choose, for comparison, the results of Madhusudana and Pratibha [45] and Chen and co-workers [46], which represent the span of available experimental elastic measurements for 5CB. After locating the nematic-isotropic transition temperature T_{NI}, we proceed to measure elastic coefficients at a range of temperatures down to 15 °C below T_{NI}. The 5CB model in question has been parametrized to accurately represent the thermodynamics of the nematic-isotropic transition, including appropriate densities and orientational order. Strikingly, though elastic behavior is not included in this parametrization, the measured coefficients we obtain [see Fig. 2(d)] lie directly on top of the experimental data range, intercalating the high and low estimates, when plotted as a function of $T - T_{\mathrm{NI}}$. It should be noted that the actual transition temperature predicted by this model is slightly higher (by two degrees) than the experimental value.

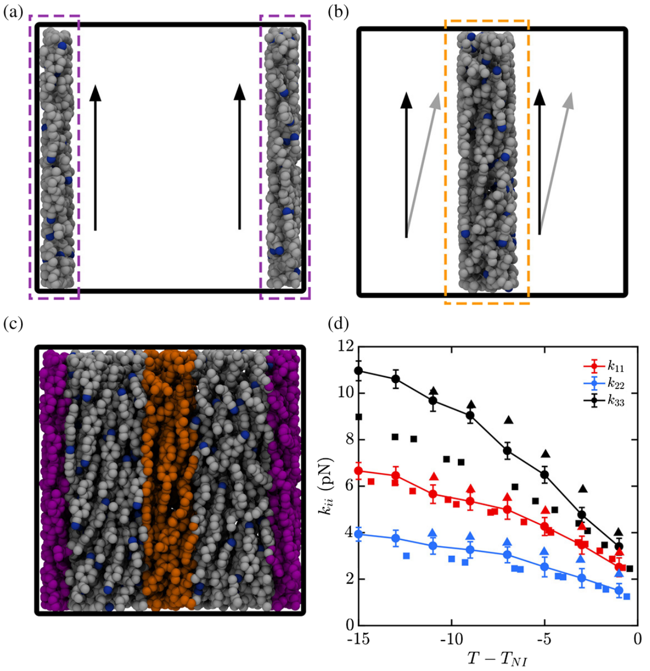

FIG. 2. (a) A harmonic restraint is applied to the periodic edges of a simulation box in order to align the molecules in the $\hat{\mathbf{z}}$ direction. (b) Molecule orientations in the central region of the simulation box are biased using basis function sampling [43] according to the appropriate order parameter to excite the desired elastic mode. Shown here are arrows representing splay deformations from the nonperturbed state. (c) Over the course of a simulation, molecules enter and exit the respective regions. Only those molecules which lie within the regions shown in purple (edges) and orange (center) are biased. A gradient is produced across the box dimension as a result of the sampling and the corresponding free energy is calculated. The resulting bulk elastic coefficients (k_{ii}) for 5CB (d) are compared to experimental data from Madhusudana and Pratibha [45] (squares) and Chen and co-workers [46] (triangles). Connected circles represent elastic constant calculations using the methodology outlined in this work. Uncertainties are calculated using 1500 bootstrap cycles on the collected decorrelated samples.

Having established the validity of the proposed method, we proceed to apply the free energy perturbation technique to obtain k_{24}. It is convenient to work in a cylindrical geometry to isolate the *normal* twist mode [16], which is directly analogous to double-twist arrangements observed in blue phases and toroidal geometries. Here, a larger system is required to achieve a stable cylinder with sufficient diameter to probe the normal twist mode. To ensure that only this mode is probed, one must remove the effects of surface interactions from the free energy profile. It is sufficient to choose a system that has degenerate planar anchoring, so that any preferred surface orientations are imposed only by the bulk nematic order. It is well known, and has been validated in simulations [34], that aqueous interfaces impose exactly this type of anchoring. Hence, we embed a periodic cylinder of liquid crystal within a solvent of extended simple point charge (SPC/E) water [48]. A typical configuration of this cylindrical geometry is given in Fig. 3(a). The presence of an interface, while not affecting orientation, nevertheless imposes order on the 5CB cylinder, effectively shifting T_{NI} by ≈5 K [see Fig 3(b)] while retaining similar ordering behavior [plotted as $S(T)$ in Fig. 3(b)] as a function of relative temperature. Hence, to relate these measurements to bulk elastic constants, we compare values at equivalent $T - T_{\mathrm{NI}}$.

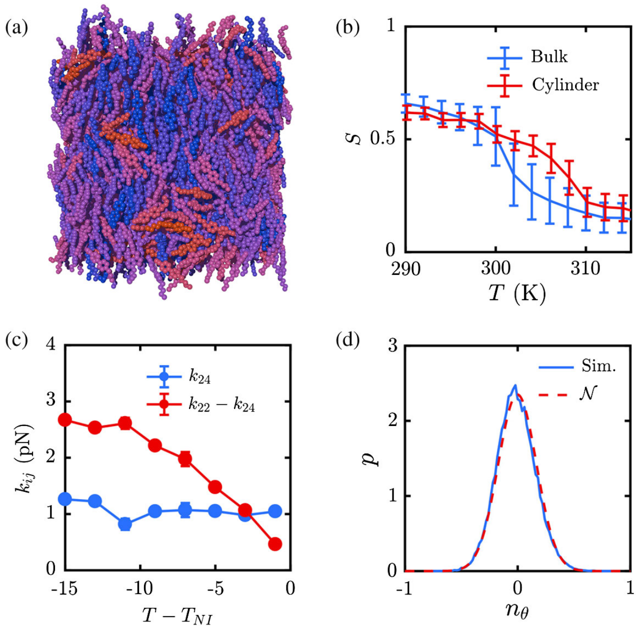

FIG. 3. Snapshot of 5CB cylindrical system (a) with solvent removed. Because of finite anchoring-induced ordering within the cylinder, the transition temperature T_{NI} is shifted slightly (b) by ≈5 K. The calculated saddle-splay surfacelike elastic constant (k_{24}) for 5CB (c) shows no violation of the Ericksen bound, delineated by $k_{22} - k_{24} \geq 0$. To validate k_{24} stability, we test the unbiased director probability distribution $p(n_\theta)$ against the normal distribution (d) using a Kolmogorov-Smirnov test (representative data at 296 K shown; distributions obtained at other temperatures are plotted in Fig. S2 of the Supplemental Material [26]). Uncertainties in the elastic measurements are estimated using 1500 bootstrap cycles on the collected decorrelated samples, yielding error bars comparable to the size of the points. Roughness in trendlines is not due to a statistical uncertainty of each measurement, but instead due to the underlying fluctuations in nematic order and volume that arise under *NPT* preparation.

The measured k_{24} elastic constants are shown in Fig. 3(c) [26]. It is apparent that the Ericksen bound $k_{22} - k_{24} \geq 0$ remains valid across the nematic range. This is a striking result, as indirect measurements in toroidal droplets [18], escaped radial morphologies [10], and aperiodic nematic films [17] yield a value for k_{24} for which the normal modes of deformation [16] are either nearly zero or in violation of the Ericksen bound. From our calculations, saddle splay retains a finite value throughout the nematic range that is, surprisingly, essentially constant. While this appears to be at odds with the behavior of most elastic coefficients near the nematic-isotropic transition, it is important to note that k_{24} never appears by itself within expressions for bidirectional modes [16], and that the cost of the bidirectional twist does trend toward zero, as one expects, when disorder is approached. Importantly, the approach of $k_{22} - k_{24}$ to zero may help explain some experimental observations, which are typically conducted at temperatures near T_{NI}. Our measurements also contradict the predictions made for 5CB using a hybrid molecular field theory (MFT) [42], which suggested that k_{24} varies significantly over the nematic range, and even predicted the value to switch sign at a crossover temperature of $T - T_{\mathrm{NI}} \approx -7$. Since that theory predicts k_{22} commensurate with experiments, this indicates *nonvanishing* normal twist as the transition temperature is approached. The differences in the present work and MFT predictions could be due to the underlying assumptions of MFT, which does not capture spatial dependencies and mutual deformations that play an important role in k_{24}. The k_{24} calculations reported here are significant in that saddle-splay contributions to the free energy play a critical role in stabilizing defects [11] and affect morphological transitions [12]. That we observe no lack of positive definiteness in our measurement suggests that the origin of spontaneous radial [24] and double-twist [18] morphologies observed in experiments on 5CB must be revisited.

We emphasize again that, to our knowledge, published experimental measurements of k_{24} are indirect, and utilize an *Ansatz* to extract a result. In contrast, we directly simulate 5CB using a molecular model that has been parametrized to match experimental densities and orientational order, and report bulk (k_{ii}) elastic constants that are in full agreement with experiment. Hence, we were able to use the predictive power of molecular simulations to obtain a quantity that has proved elusive experimentally. As this prediction contradicts mechanisms hypothesized in experiment, it is important that we rigorously support the results of our simulations. To rule out the possibility that pretransitional ordering induced by anchoring or spatial inhomogeneity result in misleading measurements, we also plot the radial profiles of the nematic director within each cylinder at all studied temperatures in Fig. S1 in the Supplemental

Material [26] and show that they are linear. We also generate unbiased distributions of the director fluctuations in the outer annulus of each cylinder and perform a one-sample Kolmogorov-Smirnov test at a 1% significance level against a centered normal distribution. A representative data set at $T = 296$ K is shown in Fig. 3(d). All samples reject the null hypothesis, which indicates that there is no statistically detectable metastability at nonzero deflection. We include all director time profiles, resulting distributions, and parabolic free energy profiles with P_2 projections in the Supplemental Material [26].

One might also object to our k_{24} measurements on the basis of finite-size effects. The free energy perturbation approach adopted here has been shown [21,22] to be insensitive to finite-size effects, particularly in bulk measurements [22]. This is supported by the striking agreement of our k_{ii} measurements with experiment. However, k_{24} is measured in cylindrical confinement, which may exhibit different scaling behavior. While an explicit study of finite-size effects on k_{24} is currently intractable due to immense computational costs, we propose that it is not relevant for the broader observation that Ericksen's equalities are satisfied. Finite-size scaling may change the absolute magnitude of the reported values, but will not change the stable morphology—the cylinder either is or is not unstable to twisting. Unlike prior coarse-grained studies, which found no appreciable free energy penalty to twisting [21], and experiments and theory demonstrating twisting in toroidal geometries is similarly not penalized [18,49], these results demonstrate that k_{24}-containing modes have a positive-definite free energy for 5CB.

Our methods and calculations serve to shed light into some long-standing concerns about the experimental value of k_{24} and its role in driving morphology transitions in confined systems [10,14,17,18,24]. However, in doing so, we have opened up new questions about the true reason for such striking morphologies. If k_{24} is not responsible, then what is? Perhaps there are important third- or fourth-order terms that arise to stabilize spontaneous deformations. Perhaps anchoring and explicit solution chemistry play a larger role than previously appreciated. Regardless, our calculations represent a useful milestone in material property prediction. We demonstrate that it is possible to predict bulk elastic constants in agreement with experiment for a molecular system from simulation, and we provide the only direct measurements of saddle splay k_{24} for the otherwise extensively characterized 5CB. With these new developments, the tools are in place to begin unraveling the role of higher order elastic coefficients and subtle anchoring behaviors across the landscape of liquid-crystalline materials. A key challenge will be the calculation of the L_{ij} elastic coefficients utilized in the Landau–de Gennes $\mathbf{Q}$-tensor formalism, which are not directly accessible to experiment, and are not directly mappable onto the Frank elastic theory [50]. In each of these arenas, the methodology and framework employed here provide a foundation for computer-aided characterization and design of novel mesogenic compounds.

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