Fluctuating Nematodynamics using the Stochastic Method of Lines

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We construct Langevin equations describing the fluctuations of the tensor order parameter \( Q_{\alpha\beta} \) in nematic liquid crystals by adding noise terms to time-dependent variational equations that follow from the Ginzburg-Landau-de Gennes free energy. The noise is required to preserve the symmetry and tracelessness of the tensor order parameter and must satisfy a fluctuation-dissipation relation at thermal equilibrium. We construct a noise with these properties in a basis of symmetric traceless matrices and show that the Langevin equations can be solved numerically in this basis using a stochastic version of the method of lines. The numerical method is validated by comparing equilibrium probability distributions, structure factors and dynamic correlations obtained from these numerical solutions with analytic predictions. We demonstrate excellent agreement between numerics and theory. This methodology can be applied to the study of phenomena where fluctuations in both the magnitude and direction of nematic order are important, as for instance in the nematic swarms which produce enhanced opalescence near the isotropic-nematic transition or the problem of nucleation of the nematic from the isotropic phase.

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I. INTRODUCTION

Fluctuation phenomena in nematic liquid crystals are typically studied within Ericksen-Leslie theory, which assumes that the orientation of the normalized nematic director is the only fluctuating variable. This approximation is adequate deep within the nematic phase, where the strength of nematic order is not significantly affected by thermal fluctuations. However, in the vicinity of the weakly first-order isotropic-nematic transition, significant fluctuations in the nematic order are observed, suggesting that the phase-only approximation embodied in Leslie-Ericksen theory is inadequate. The study of nucleation in quenches from the isotropic to the nematic phase is inadequate for both isotropic and nematic phases on the same footing. In these and similar situations, a tensorial description of nematic order which uses the symmetric, traceless quadrupole moment tensor \( Q_{\alpha\beta} \), is appropriate, as first clarified by de Gennes in his Ginzburg-Landau theory of the isotropic-nematic transition. The Ginzburg-Landau-de Gennes (GLdG) approach provides a simple, but accurate phenomenological description of nematic fluctuations in the static case.

The description of the fluctuating dynamics of the orientation tensor within GLdG theory has received considerably less attention. Understanding the results of inelastic scattering experiments on nematic systems, the description of the rate of nucleation into the nematic phase, the modeling of nontrivial stresses arising from Casimir interactions and the calculation of the spectrum of capillary waves on the isotropic-nematic interface are all problems which require a dynamical theory of fluctuations in the orientation tensor. This problem is addressed in this paper, in which we present and solve the Langevin equations for dynamical fluctuations at equilibrium for the nematic orientation tensor. These are stochastic non-linear partial differential equations for the five components of the orientation tensor. Analytical solutions can be obtained when these equations are linearized. For the solution of the general non-linear equations, we propose an efficient numerical method, based on a stochastic generalization of the method of lines. We compare our results with analytic results where such calculations are possible, finding excellent agreement.

II. FLUCTUATING NEMATODYNAMICS

Orientational order in the nematic phase is described by a second-rank, symmetric traceless tensor \( Q_{\alpha\beta}(x,t) \). This is the second moment of the microscopic orientational distribution function. The tensor can be expanded as

\[
Q_{\alpha\beta} = \frac{3}{2} S(n_\alpha n_\beta - \frac{1}{3} \delta_{\alpha\beta}) + \frac{1}{2} T(l_\alpha l_\beta - m_\alpha m_\beta). \tag{1}
\]

The three principal axes of this tensor, obtained by diagonalizing \( Q_{\alpha\beta} \) in a local frame, specify the direction of nematic ordering \( \mathbf{n} \), the codirector \( \mathbf{l} \) and the joint normal to these, labeled by \( \mathbf{m} \). The principal values \( S \) and \( T \) represent the strength of ordering in the direction of \( \mathbf{n} \) and \( \mathbf{m} \), quantifying, respectively, the degree of uniaxial and biaxial nematic order.

The static fluctuations of \( Q_{\alpha\beta} \) can be calculated from a Ginzburg-Landau functional, first proposed by de Gennes, based on an expansion in rotationally invariant combinations of \( Q_{\alpha\beta} \) and its gradients. The Ginzburg-Landau-de Gennes functional \( F \) is

\[
F = \frac{1}{2} \int d^3x \left[ \frac{1}{2} A Tr Q^2 + \frac{1}{3} B Tr Q^3 + \frac{1}{4} C (Tr Q^2)^2 \right] + \frac{1}{2} L_1 (\partial_\alpha Q_{\beta\gamma})(\partial_\alpha Q_{\beta\gamma}) \tag{2}
\]

where \( A \), \( B \), and \( C \) are the Ginzburg-Landau coefficients representative of the energy of the system.
Here, $A = A_0(1 - T/T^*)T^*$ denoting the supercooling transition temperature, $A_0$ a constant, $L_1$ is an elastic constant and $\alpha, \beta, \gamma$ denote the Cartesian directions. From the inequality $\frac{1}{6}(TrQ)^3 \geq (TrQ^3)^{\frac{2}{3}}$, higher powers of $TrQ^3$ can be excluded for the description of the uniaxial phase. Uniaxial phases are described by $E' = 0$ while biaxial phases require $E' \neq 0$. For the nematic phase (rod-like molecules) $B < 0$ whereas for the dis- cotic phase (plate-like molecules) $B > 0$. The quantities $C$ and $E'$ must always be positive to ensure boundedness and stability of the free energy in all phases. We omit other symmetry-allowed gradient terms in this paper, thus working in the limit where all three Frank constants are assumed to be equal. Such symmetry-allowed terms, as also total derivative surface terms, can be accounted for without essential change, using the numerical method described below.

In the limit that hydrodynamic interactions may be neglected, i.e. the Rouse or free-draining limit, the dynamical fluctuations of $Q_{\alpha \beta}$ are not coupled to other hydrodynamic variables. The Langevin equations are those appropriate to a non-conserved order parameter with an overdamped, relaxational dynamics of the form

$$\partial_t Q_{\alpha \beta} = -\Gamma_{\alpha \beta \mu \nu} \frac{\delta F}{\delta Q_{\mu \nu}} + \xi_{\alpha \beta},$$

(3)

Here the kinetic coefficients $\Gamma_{\alpha \beta \mu \nu}$, defined as $\Gamma_{\alpha \beta \mu \nu} = \Gamma(\delta_{\alpha \mu} \delta_{\beta \nu} + \delta_{\alpha \nu} \delta_{\beta \mu} - \frac{2}{3} \delta_{\alpha \beta} \delta_{\mu \nu})$, ensure that the dynamics preserves the symmetry and tracelessness property of the order parameter. In the absence of long-range forces, a local approximation for the kinetic coefficients is adequate and $\Gamma$ can be taken as constant. The $\xi_{\alpha \beta}$ are symmetric, traceless Gaussian white noises, which satisfy a fluctuation-dissipation relation at equilibrium of the form

$$\langle \xi_{\alpha \beta}(x, t)\rangle = 0,$$

(4)

$$\langle \xi_{\alpha \beta}(x, t)\xi_{\alpha \nu}(x', t') \rangle = 2k_B T \Gamma_{\alpha \beta \mu \nu} \delta(x - x')\delta(t - t').$$

(5)

Here $k_B$ is the Boltzmann constant, $T$ the temperature and $\langle \rangle$ denotes the average over the probability distribution of the noise. These Langevin equations, together with the fluctuation-dissipation relation for the noise, ensure that the stationary one-point probability distribution of $Q_{\alpha \beta}$, $P[Q_{\alpha \beta}]$, converges to Boltzmann equilibrium with $P[Q_{\alpha \beta}] \sim \exp(-F/k_B T)$.

The equations above are five coupled, non-linear stochastic partial differential equations, with a noise term which has a tensorial structure. A numerical method of solution must maintain the symmetry and tracelessness of $Q_{\alpha \beta}$. To ensure equilibrium dynamics, it must also maintain the balance between fluctuation and dissipation. These two stringent requirements may be satisfied by transforming to a basis in which $Q_{\alpha \beta}$ is traceless and symmetric by construction. Symmetry and tracelessness of $Q_{\alpha \beta}$ is automatic. As we show below, the noise can be constructed out of independent Gaussian noises.

We expand the orientational tensor in a basis of symmetric traceless matrices $T'_{\alpha \beta}$ as

$$Q_{\alpha \beta}(x, t) = \sum_{i=1}^{5} a_i(x, t)T'_{\alpha \beta}$$

(6)

with $T^1 = \sqrt{3/2} \hat{x}z$, $T^2 = \sqrt{1/2}(\hat{x} \hat{x} - \hat{y} \hat{y})$, $T^3 = \sqrt{2} \hat{x} \hat{y}$, $T^4 = \sqrt{2} \hat{x} \hat{z}$ and $T^5 = \sqrt{2} \hat{y} \hat{z}$. The complete basis of matrices is orthogonal in the sense that $T'_{\alpha \beta} T'_{\alpha \gamma} = \delta_{\beta \gamma}$. In previous work we have presented explicitly the equations for the basis coefficients $a_i(x, t)$ that follow from the deterministic part of the relaxational kinetics $\partial_t a_i = -\Gamma_{\alpha \beta \mu \nu} \frac{\delta F}{\delta Q_{\mu \nu}} [11]$. (These differ from the equations derived by others in that we include all non-linearities as well as an additional symmetry-allowed gradient ($L_2$) term.) Here we focus on how an explicit construction of the noise can be implemented by expanding in the same basis.

We expand the noise as

$$\xi_{\alpha \beta}(x, t) = \sum_{i=1}^{5} \xi_i(x, t) T'^i_{\alpha \beta},$$

(7)

where each $\xi_i(x, t)$ is a zero-mean Gaussian white noise. From the orthogonality of the basis the inverse relation is

$$\xi_i(x, t) = \sum_{\alpha \beta} \xi_{\alpha \beta}(x, t) T'^i_{\alpha \beta}.$$

(8)

From this, and the fluctuation-dissipation relation it follows that

$$\langle \xi_i(x, t)\xi_j(x', t') \rangle = \sum_{\alpha \beta} \langle \xi_{\alpha \beta}(x, t)\xi_{\mu \nu}(x', t') \rangle T'^i_{\alpha \beta} T'^j_{\mu \nu}$$

(9)

$$= \sum_{\alpha \beta} 2k_B T \Gamma_{\alpha \beta \mu \nu} T'^i_{\alpha \beta} T'^j_{\mu \nu} \delta(x - x') \delta(t - t'),$$

(10)

This shows that the non-trivially correlated noise $\xi_{\alpha \beta}$ can be constructed from uncorrelated noises $\xi_i$. Thus, by construction, the noise $\xi_{\alpha \beta}$ is symmetric, traceless and satisfies the fluctuation-dissipation relation.

When anharmonic terms are ignored in the Ginzburg-Landau-de Gennes functional, the Langevin equations are linear and correlation functions can be calculated explicitly in the $T$ basis. Then, the Langevin equations of motion in terms of

$$a_i(q, t) = \int d^3 x \exp(-i q \cdot x) a_i(x, t),$$

(10)

are

$$\partial_t a_i(q, t) = -\Gamma(A + L_1 q^2) a_i(q, t) + \xi_i(q, t).$$

(11)

From this, the static and dynamic correlations follow immediately,

$$C_{ij}(q) = \langle a_i(q)a_j(-q) \rangle = \frac{k_B T}{A + L_1 q^2} \delta_{ij}.$$  

(12)
The average is taken over 10 independent realizations while the integration is performed for 10 lines approach was used to solve the deterministic time-dependent Ginzburg-Landau equations numerically. The methodology here can thus be thought of as a generalization of the method of lines to stochastic partial differential equations.

The method of lines is based on the idea of semidiscretisation, where an initial-value partial differential equation in space and time is discretised only in the spatial variable. This yields a (possibly large) system of ordinary differential equations which is then solved by standard numerical integrators. To apply this method to stochastic partial differential equations, we must account for the fact that integrators for ordinary differential equations do not automatically provide efficient and accurate solutions of stochastic differential equations. Qualitatively, the noise term in a stochastic differential equation is a rapidly varying function and hence must be integrated with some care. At a more technical level, the noise is a Wiener process and the theory of stochastic integration must be used to evaluate it correctly.

Common stochastic integrators include those due to Maryama and Milstein. In this work, we use an integrator proposed recently by Wilkie, based on a multi-step Runge-Kutta strategy. The integrator is accurate and easy to implement by making small changes to a deterministic Runge-Kutta integrator. Further, since it is an explicit integrator, no matrix inversions are involved. This makes it attractive when the method of lines discretisation produces a large system of ordinary differential equations, as in our case.

To test Wilkie’s algorithm for a stochastic Runge-Kutta integrator, henceforth denoted as SRK4, we first check that the fluctuation-dissipation is obeyed. We performed a simple benchmark test on the Ornstein-Uhlenbeck process, represented as the Ito differential equation,

\[ dv(t) = -\Gamma v(t)dt + dW(t), \]  

where \( dW(t) = \sqrt{2k_B T \Gamma} dt \mathcal{N}(0,1) \) is the increment of the stochastic variable in the interval \( dt \), and \( \mathcal{N}(0,1) \) is a zero-mean unit-variance normal deviate. By construction, the increments of this stochastic variable are independent and normally distributed with mean \( \langle dW(t) \rangle = 0 \). The particular choice of the variance ensures that the equilibrium distribution of \( v \) is a Gaussian with variance \( k_B T \). The stationary two-point autocorrelation of the velocity from Eqn. (13) is,

\[ \langle v(t)v(t+\tau) \rangle = k_B T \exp(-\Gamma \tau). \] 

Fig. 1 shows the autocorrelation as a function of time and the histogram of equal-time fluctuations of \( v \). The variance \( \langle v^2 \rangle = k_B T \) is correctly reproduced, as is the exponential decay of the autocorrelation function. We conclude that SRK4 is suitable as an integrator for problems where the fluctuation-dissipation relation must be maintained.

IV. NUMERICAL METHOD

We now apply the method of lines together with SRK4 to obtain a stochastic method lines discretisation (SMOL) for the equations of fluctuating nematodynamics. We benchmark our numerical results by comparing autocorrelations within a harmonic theory which
accurately describes fluctuations about the isotropic phase. We then consider expansions about the ordered state, comparing static correlations obtained analytically within the Frank approximation with our numerical results.

We use a finite-difference discretisation with nearest-neighbour stencils for gradients and the Laplacian. We implement periodic boundary conditions. Specifically, in three dimensions, we consider a box of dimension \( L_x, L_y \) and \( L_z \) along the Cartesian directions, and grid these lengths with equal grid spacing \( \Delta x = \Delta y = \Delta z = 1 \). The latter defines lattice units for the spatial coordinate. We define corresponding discrete time units for the temporal variables by choosing \( \Delta t = 1 \). Fourier modes are labelled by the wave-vector \( \mathbf{q} = (q_x, q_y, q_z) \), where each component is of the form \( q_\alpha = 2\pi n_\alpha/L_\alpha \), with \( n_\alpha = 0, 1, 2, \ldots, (L_\alpha - 1) \).

With this discretisation, the Laplacian in Fourier space is given by

\[
\mathcal{L}(\mathbf{q}) = 2[\cos(q_x) + \cos(q_y) + \cos(q_z) - 3].
\]

The nearest-neighbour finite difference stencil suffers from lack of isotropy at high wavenumbers. This can be improved through the use of higher-point stencils [17–19].

Applying the method of lines discretisation to Eq. (13) reduces it to a system of stochastic ordinary differential equations, whose Fourier representation in the harmonic approximation of Eq. (11) is

\[
\partial_t a_i(\mathbf{q},t) = -\Gamma D a_i(\mathbf{q},t) + \xi_i(\mathbf{q},t).
\]

The Fourier representation of the drift-diffusion dynamics is encoded in the linear operator \( \mathcal{D} \),

\[
\mathcal{D} = A - L_1 \mathcal{L}(\mathbf{q}).
\]

Fourier representations of the one and two-dimensional method of lines discretisations are obtained by setting the corresponding wavenumbers to zero. The static and dynamic autocorrelations in Fourier space follow in a straightforward manner though the replacement of \( \hat{q}^2 \) by its discrete Laplacian representation. The results are

\[
C_{ij}(\mathbf{q}) = \frac{k_B T}{D} \delta_{ij},
\]

\[
C_{ij}(\mathbf{q},\tau) = C_{ij}(\mathbf{q}) \exp(-\Gamma \mathcal{D} \tau).
\]

It is also useful to define an angle-averaged structure fac-

FIG. 2: (Color online) Histogram of the real part of \( a_i(\mathbf{q}) \) for \( n_x = n_y = 6 \) in a box of dimension \( L_x = L_y = 16 \), using a harmonic free energy, with \( k_B T = A = 0.05 \) and \( L_1 = 0.5 \), \( \Gamma = 1.0 \). The fluctuations are Gaussian with the expected variance. The histogram is obtained from 20 independent realizations, each realization contributing 4000 time steps.

FIG. 3: (Color online) (a) Contour plot of the structure factor \( C_{ij}(\mathbf{q}) \) and (b) angular average of \( C_{ij}(\mathbf{q}) \). The parameters are \( k_B T = A = 0.05 \), \( L_1 = 0.5 \), \( \Gamma = 1.0 \). The time averaging is over \( 5 \times 10^4 \) time steps and ensemble averaging is over 20 independent realizations in a box with \( L_x = L_y = 64 \). The relaxation time scale is \( \tau = (\Gamma A)^{-1} \approx 20 \), the diffusion time scale of the smallest Fourier mode is \( \tau_d = L_1^2/(4\pi^2 L_1 \Gamma) \approx 207.51 \) and the correlation length is \( \lambda = \sqrt{L_1/\lambda} = 3.16 \).
on a 64 × 64 grid. The time average is taken over 4τ 28.57, the diffusion time scale of the shortest Fourier mode is τ 13 and the correlation length is λ = √L1/A = 3.16.

The integration is performed for 4 × 103 time steps and an ensemble average is taken over 20 independent realizations. The relaxation time scale is τ = (ΓA)−1 = 20, the diffusion time scale of the shortest Fourier mode τ q = Lq 2/(4π 2L1Γ) ∼ 13 and the correlation length is λ = √L1/A = 3.16.

Thus, the present discretisation should be adequate in most cases, unless highly accurate isotropies are required from the simulation. From these results, we conclude that correlations in thermal equilibrium are accurately captured by the stochastic method of lines approach.

We next compare the dynamics of fluctuations at equilibrium, by comparing two-point autocorrelation functions calculated analytically and numerically. Fig. 4 shows C ij(q, τ) for three sets of Fourier modes. The exponential decay of the autocorrelation function is reproduced accurately within the numerics and fit the theoretical curve very closely. We conclude, therefore, that the stochastic method of lines accurately reproduces both static and dynamic fluctuations in a harmonic theory.

Finally, we compare theory and simulation in a situation where a linearization of the Q αβ equations about Q αβ = 0 is inapplicable, that of director fluctuations within the nematic phase. In the T basis, the equations of motion are

\[ \partial_t a_i = -\Gamma [(A + CT \text{Tr} Q^2) a_i - B + 6E' \text{Tr} Q^3] T_{\alpha\beta} Q_{\alpha\beta}^2 - L_1 \nabla^2 a_i + \xi_i. \]

where, Q αβ is the traceless symmetric projection of Q αβ. These equations of motion are anharmonic, and the analytical solutions obtained earlier within the harmonic expansion are no longer available for comparison. We therefore extract the fluctuations of the angular displacements from the uniform nematic ground state using an approach based on the Frank free energy.

Consider an uniform uniaxial nematic with director n 0 with small fluctuations δn(x). Decomposing the fluctuations into parts parallel and perpendicular to n 0 and imposing the normalization of the director, we find from the Frank free energy that,

\[ \langle |\delta n_\perp(q)|^2 \rangle = \frac{k_B T}{K q^2}, \]

where K = (9S^2/2)L 1 is a Frank constant [4]. Since fluctuations in the plane perpendicular to n 0 can be characterized through a single angle θ, an equivalent result is

\[ \langle \delta n_\perp(q) \rangle = \frac{k_B T}{K q^2}. \]
\[ \langle \theta(q)\theta(-q) \rangle = k_B T/Kq^2. \] In the semidiscrete representation, we obtain
\[ \langle \theta(q)\theta(-q) \rangle = -\frac{k_B T}{K L(q)}. \] (23)

Fig. (5) shows the angular average of the static correlations of director fluctuations\[\hat{C}_\theta(q) = \sum_{|q|=q} \langle \theta(q)\theta(-q) \rangle.\] The formally divergent \(q = 0\) mode is excluded both from the numerical data and analytical result. Given that the analytical result is obtained from a linearization about the aligned state whereas the numerical solution is calculated from the equations of motion arising from the full non-linear free energy, the agreement between theory and simulation is satisfactory. The stochastic method of lines thus accurately captures equilibrium fluctuations in the ordered state as well as in the disordered one.

V. DISCUSSION AND CONCLUSION

The numerical method of solution presented in this paper can be applied to a variety of problems in nematodynamics where accounting for fluctuations in nematic order are important. To the best of our knowledge, no systematic study of anharmonic fluctuations exists within the time-dependent Ginzburg-Landau framework. In previous work, Stratonovich\[5\] presented fluctuating equations of motion for harmonic fluctuations in terms of Langevin equations, analyzing these equations within the traceless symmetric basis described here in a straightforward manner\[6\]. Our equations of motion contain the necessary nonlinearities and our numerical methodology accounts for them in a computationally straightforward way.

We also present, to the best of our knowledge for the first time, a systematic stochastic integration scheme capable of yielding highly accurate solutions of the nonlinear equations of nematodynamics. These equations can be applied to study fluctuations of nematic order at the isotropic-nematic interface, pseudo-Casimir interactions close to the isotropic-nematic transition, as well as nucleation phenomena in nematogens. The study of these and similar problems is ongoing and will be reported elsewhere.

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