Chapter 6

Breakdown of classical nucleation theory in nucleation kinetics

In this chapter we present results of a study of nucleation of nematic droplets from the metastable isotropic phase. To the best of our knowledge, this is the first study of the kinetics of nematic nucleation which is based on a Ginzburg-Landau description. We use the stochastic equations of motion for the nematic director presented earlier, together with a method of lines integration scheme, to study this problem. As in the studies of the previous chapters, all five tensorial degrees of freedom of the nematic director are allowed to fluctuate. This allows for novel kinetic pathways, absent in liquid-gas or liquid-liquid nucleation, through which nematic droplets can form. The few previous studies of this problem where full director fluctuations are included were particle-based Monte-Carlo simulations of hard spherocylinders (HSC), whose kinetic interpretation can be ambiguous.

Our principal results are the following. In both two and three dimensions, the overall shape of the nematic droplet is generally ellipsoidal, and not spherical as assumed in classical nucleation theory. In two dimensions, depending on the signs of the elastic constants and the anchoring conditions they enforce on the director, we find that nematic nuclei contain defects within them. In three dimensions, we are not able to clearly discern their presence in the droplet, but we do find a non-uniform director distribution in the nuclei. Our study thus reveals pathways that involve states with non-trivial spatial distributions of the nematic director, which are not accounted for in classical nucleation theory. Our study shows that classical nucleation theory, with its assumption of spherical, spatially uniform nuclei, is insufficient to account for the complexity of nematic droplet nucleation.

6.1 Introduction

As the transition from isotropic to nematic phase is weakly first order, there exists a regime of parameters where the kinetics proceeds through nucleation of the stable phase in the unstable medium. This regime is bounded by the binodal and spinodal lines as indicated in the phase diagram Fig. (1.5). Classical homogeneous nucleation theory, with a non-conserved order parameter, studies the critical droplet size, the energy of the barrier height and the nucleation rate of a single droplet, all with an inherent assumption of nucleation that proceeds
through the free energy of spherical droplets of radius R.

The free energy of a droplet consists of contributions from the energy of the bulk (which is the volume energy of the nucleating stable phase) and the surface energy required to create the interface between the stable and the metastable medium. This can be defined as

$$\mathcal{F}(R) = -V \rho_N \Delta \mu + \mathcal{A} \sigma,$$  \hspace{1cm} (6.1)

where $V = \frac{4}{3} \pi R^3$ is the volume and $\mathcal{A} = 4 \pi R^2$ is the surface area of the spherical droplet, $\rho_N$ is the density of the nucleating stable phase and $\Delta \mu = L \Delta T / T^*$ is the change in the chemical potential of the unstable to stable phase. $L$ is the latent heat emitted due to the change in temperature $\Delta T$, critical temperature is denoted by $T^*$ and $\sigma$ is the surface tension.

A droplet of stable phase in an unstable background shrinks if it is smaller than a critical size $R_c$. Droplets which are larger than $R_c$ grow in size till they expand to the size of the system. A droplet of size $R_c$ is thus metastable. The critical shape of the droplet is obtained by maximizing $\mathcal{F}(R)$ with respect to R, resulting into $R_c = \frac{2\sigma}{\rho_N |\Delta \mu|}$.

The barrier height can also be calculated by using this form of $R_c$ as $\mathcal{F}_c = 16\pi \sigma^3 / 3\rho_N^2 (\Delta \mu)^2$. From this, the nucleation rate can be calculated which is defined as, $I = Z \rho_I f_c^+ \exp \left[ -\mathcal{F}_c / k_B T \right]$. Here, $Z = \sqrt{|\Delta \mu| / 6\pi k_B T n_c}$ is the Zeldovich factor, $n_c$ is the number of monomers in the critical nucleus, $\rho_I$ is the density of the unstable phase and $f_c^+$ is the rate of attachment to the critical nucleus [5]. Typically, in classical nucleation theory (CNT), the calculation of the rate is a formidable problem as the quantities $f_c^+$ and $\sigma$ are outside the scope of experimental measurements which can be matched with theoretical predictions.

The development in time of a fluctuation-induced nematic droplet is a key factor in determining the nucleation rate in nematics [22]. Unlike conventional isotropic fluids, as the nucleation of crystalline phases does not proceed through formation of a spherical nucleus due to the anisotropic surface tension, the nucleus in a nematic is also not expected to be spherical [9]. Allowing the shape to deviate from perfect sphericity reduces the total energy, which is a sum of the elastic energy associated with the director deformation in the bulk and a surface energy associated with the anchoring condition at the interface of the droplet. Thus, determining the droplet shape of least energy involves a minimization over the strength of ordering as well as the director degrees of freedom [33, 16, 73].

Prinsen and Schoot studied the shape and director field conformation of nematic tactoids within a Frank description of the elastic free energy [59]. In their formulation, a planar anchoring condition of the director to the interface is enforced through a plausible surface free energy term proposed by Rapini and Papoular [61]. By minimization of the free energy, different morphology of ellipsoidal nematic droplets has been proposed as a function of the elastic stiffness and the anchoring strength. No kinetic description is available of the nucleation and the growth of nematic tactoids.

The only study of kinetic pathways of growth of nematic droplet is addressed by Cuetos and Dijkstra through a Monte Carlo study of HSC [22]. They studied the pressure controlled supersaturation of colloidal fluid with two different aspect ratios of the HSC, as well as the nucleation and growth from an isotropic to nematic transition below the critical temperature. Their principal findings are that for a high aspect ratio, an ellipsoidal nematic cluster with a homogeneous director field forms and grows in time to span the system size. However the
6.2 Structure of nucleated nematic droplets in two dimensions

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Table 6.1: Numerical parameters in the Landau-de Gennes theory used for the computer experiments in nucleation kinetics presented in this chapter.

The GLdG parameters used for the calculations are highlighted in Table 6.1.

kinetic description is not well-defined in a Monte Carlo technique as it samples only the most probable states. Although in Monte Carlo technique, the local moves can faithfully reproduce the Brownian dynamics trajectories for rod-like particles, but a true kinetic pathway is outside the scope of such studies. We mention that a truly kinetic scenario can only be captured through the dynamical study of the tensorial order parameter $Q$ defined in Eq.(2.2). The GLdG parameters used for the calculations are highlighted in Table 6.1.

6.2 Structure of nucleated nematic droplets in two dimensions

We consider the nucleation of a nematic droplet in an isotropic background, in the presence of the fluctuations in the orientation due to temperature. We prepare an isotropic phase with the mean of $S$ and $T$ set to zero but with finite variance. We construct the $n,l,m$ triad such that the direction is completely random in the three Cartesian directions. We evolve the nematodynamic equation (2.2) and study the phase behaviour in the early and late stage of the kinetics. The nematic droplets nucleate in the isotropic phase due to the external thermal noise $\xi$, which serves as the driving force that drives the isotropic state to overcome the nucleation barrier. We incorporate the anisotropic contribution to elasticity of both positive and negative signs of elastic constant while ensuring the positivity of the Frank elastic constants. We systematically discuss different cases while comparing the results with
6.2.1 Circular droplets with uniform director at $\kappa = 0$

In the absence of the anisotropic elastic term in the equation of motion, several spherical droplets of uniaxial nematic phase nucleate in the fluctuating isotropic medium with homogeneous director anchoring inside the droplet. The direction of orientation of the director is local to the droplets, and is different from droplet to droplet. These droplets grow in size by reducing the isotropic region significantly and coalesce with each other while evolving in time, smoothing out the director field throughout the system to reduce the elastic energy. In this process, topological defects form due to the coalescence of droplets, which annihilate at the late stage of the dynamics satisfying topological constraints. Finally, the stable uniaxial nematic phase fluctuates in equilibrium.

Fig. (6.1) shows the scalar order parameter $S$ in false colours and the director field $\mathbf{n}$ as needles superimposed on top of that. To avoid clumsiness in the description, the director is plotted on each and every fourth lattice point in all of the directions. The formation of several nematic droplets\(^1\) are shown in Fig. [6.1(a)]. The nematic phase with defects at a late stage is shown in Fig. [6.1(b)], where the defect-anti defect pair eventually annihilates. Fig. [6.1(c)] and Fig. [6.1(d)] show the schlieren textures at the time of formation of droplets and a later time of fully developed defects at the fluctuating nematic phase. We notice that our previous assumption of uniform director field inside the immersed nematic droplet as discussed in the previous section, holds well with a spherical shape of the droplet.

To compare the obtained result with the mean field calculation, we have also studied the time evolution of a single nematic droplet immersed in an isotropic background working at the zero temperature limit of the problem. To study any conformational changes to the droplet, our initial condition was chosen so as the uniaxial order was set to the equilibrium value ($S = S_c$) with the director anchored at an angle of $\pi/4$ with the nematic-isotropic interface inside the droplet. We took $S = 0$ in the isotropic region, while randomly orienting the direction of the triad and relaxed the system at a temperature intermediate between the binodal and spinodal temperatures in the absence of fluctuation.

For droplets larger than the critical radius, the nematic region was observed to grow in size, finally evolving into the nematic state spanning the system size. For the parameters used, the alignment of the director did not change significantly during the evolution of the droplet. Fig. (6.2) shows the evolution of a single, initially circular droplet, illustrating how the droplet shape evolves in a circular fashion in the absence of elastic anisotropy $\kappa = 0$.

6.2.2 Complex droplet geometry with integer defect at $\kappa > 0$

With a positive contribution of the elastic anisotropy to the free energy, in the droplet growth regime, we notice a change in the geometry of the nucleated nematic droplet, satisfying earlier

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\(^1\) The formation of a single nematic droplet is outside the scope of computational time and resources, since to observe a single droplet nucleation event, the free energy must be deep inside the nucleation regime (not close to the spinodal lines as in the cases studied here). This increases the first passage time considerably, making droplet nucleation a rare event.
6.2. Structure of nucleated nematic droplets in two dimensions

Figure 6.1: The first two frames designate the degree of uniaxial order and director conformation of the nucleating droplets. The last two show the corresponding schlieren textures. Panel (a) shows the circular droplets with uniform director at an early stage. The full grown defects at a late stage is been shown in panel (b). Panel (c) shows differently oriented, uniform nematic domains while the half integer defects (two brushes) are shown in panel (d). The SRK4 numerical integration is performed upto $1.2 \times 10^4$ iterations with unit time increment.
Figure 6.2: Time evolution of the uniaxial order in the relaxation of a nematic droplet. Fig.(a) shows the circular droplet at time \( t = 0 \). The time evolution with \( \kappa = 0 \) of the circular droplet at a later time \( t = 3 \times 10^3 \) is shown in fig.(b).

Theoretical predictions and numerical estimates. The initial elliptic nuclei, however, change shape to complex geometries before coalescence. Also, we observe the existence of topological defects with integer charge, a hedgehog conformation of the director, formed inside each and every droplet. This result has not been reported in the literature. A plausible reasoning for the formation of the defects could be the small ratio of the volume to surface free energy, which results into a deformation of the bulk nematic director inside the droplet to a hedgehog structure due to the strong anchoring of the director at the surface of the droplet. At late stages of the dynamics, the bubbles coalesce and the fluctuating uniaxial nematic phase spans the system size as discussed in the previous subsection. Unlike the previous case, we never observe half integer defects forming due to coalescence of the nematic droplets.

Fig.(6.3) shows the scalar order parameter \( S \) in false colors and the director field as needles superimposed on tops. For visualization purposes, the director is shown at every fourth lattice point. Fig.[6.3(a)] shows the formation of droplets with an ellipsoidal shape with an integer defect inside the droplets at an early stage. Fig.[6.3(b)] shows the evolution of the ellipsoidal droplets to complex structures at a late stage of the kinetics. The schlieren textures at these particular times are shown in Fig.[6.3(c)-6.3(d)]. The interesting fact we note is even at the late stage of the kinetics, while the droplets completely coalesce to form the fluctuating nematic phase, integer defects persist till the end of the kinetics with a relaxation time much larger than that of the computational time. Qualitatively, this matches the experimental predictions reported in the reference [60].

In our mean field calculation without incorporating fluctuation in temperature but in the presence of elastic anisotropy, the droplet orients along the direction of nematic order for planar anchoring (\( \kappa > 0 \)). In our numerics, we quantify the geometrical change through measurements of the change in the aspect ratio. The aspect ratio, defined as the ratio of the...
Figure 6.3: The first two frames show the degree of uniaxial order and director conformation of the nucleating droplets, while the last two show the corresponding schlieren textures. Panel (a) shows the nucleated ellipsoidal droplets at an early stage of the kinetics. Panel (b) shows complex droplet structures at a late stage (before coalescence of domains). Panel (c) shows the integer defect with four brushes while panel (d) shows the grown brushes of the defects. The SRK4 numerical integration is performed up to $1.2 \times 10^4$ iterations with unit time increment.
major to minor axis of the ellipse, are indicated in Fig.(6.4). This is calculated by extracting a contour at a fixed value of $S$ (say $S_c/2$) and fitting it with an ellipse. The aspect ratio in $\kappa > 0$ changes from 1 as 1.1191, 1.3046 and 1.5037 from time $t = 0$ to 300, 600 and 900 respectively.

### 6.2.3 Ellipsoidal droplets with uniform director at $\kappa < 0$

In the presence of a negative contribution of the elastic anisotropy to the droplet surface energy, we notice formations of ellipsoidal droplets with homogeneous director anchoring. These droplets coalesce to form topological defects which eventually disappear from the system by the defect-antidefect annihilation process. Though we expect defects inside the droplets with a finite contribution from the anisotropic elasticity, a plausible explanation could be the higher volume to surface energy ratio. The surface anchoring of the nematic director is unable to deform elastically the director in the bulk significantly, thus resulting into a smooth director field inside the droplet.

Fig.(6.5) shows the scalar order parameter $S$ in false colors with the director field $\mathbf{n}$, plotted as needles superimposed on top. For visualization purposes, the director is strided at every fourth lattice point. Fig.[6.5(a)-6.5(b)] shows the formation and complex structures of the nematic droplet in the growth kinetics. The schlieren textures at these particular times are shown in Fig.[6.5(c)-6.5(d)].

In our mean field calculation without incorporating fluctuation in temperature but in the presence of elastic anisotropy, the droplet orients perpendicular to the direction of nematic
6.2. Structure of nucleated nematic droplets in two dimensions

Figure 6.5: The first two frames show the degree of uniaxial order and director conformation of the nucleating droplets, while the last two show the corresponding schlieren textures. Panel (a) shows the elliptical droplets with uniform director conformation, panel (b) shows the grown defects at a late stage. Panel (c) shows the uniformity of the droplets while panel (d) shows the half integer two-brush defects. The SRK4 numerical integration is performed up to $1.2 \times 10^4$ iterations with unit increment.
6.3 Structure of nucleated nematic droplets in three dimensions

We discuss the nucleation of nematic droplets in an isotropic environment in three space-spin dimensions with the three cases of $\kappa$ in the following subsections.

6.3.1 Spherical droplets with $\kappa = 0$

Fig.(6.7) depicts four snapshots of the nucleation process of uniaxial nematic droplets at the isotropic medium. Nucleation events are followed by a coarsening kinetics while the droplets coalesce amongst themselves to form defect-anti defect strings. These eventually annihilate from the system by segment intercommutation and the formation of loops which contract.

Our central result is, with a zero contribution to the surface free energy from the anisotropic gradients, the nucleation event proceeds with the formation of spherical droplets. Fig.(6.8) shows the the uniaxial scalar field and the vector field conformation of the director at a particular time. The uniformity of the director is noticeable from the first two confor-
Figure 6.7: Time evolution of uniaxial order in a three dimensional volume. Panel (a) shows the emergence of uniaxial nematic droplet in the fluctuating isotropic medium. The coalescence of droplets, as shown in panel (b), form line defects as shown in panel (c). The defects at a late stage of the kinetics is shown in panel (d). The isosurfaces are plotted for a fixed iso-value $S = 0.05$. The numerical integration is performed upto $3 \times 10^3$ SRK4 iterations with unit increment in time.
Figure 6.8: Panel (a) and (b) show the uniaxial order and director conformation on the surface of nucleated nematic droplets in three dimensions. Panel (c) shows the uniaxial order in a plane (say x-y) that slices the three dimensional volume at \( z = 20 \). The isosurface is plotted for a fixed isovalue \( S = 0.05 \). The numerics is performed upto \( 3 \times 10^3 \) SRK4 iterations with unit time increment.

mations. The spherical shape is been shown through a cut in the three dimensional volume at a fixed value of \( z \) in the \( z-\)axis.

6.3.2 Ellipsoidal droplets with \( \kappa > 0 \)

Fig. (6.9) depicts four frames of the nucleation event happening in the presence of elastic anisotropy in the free energy. The uniaxial nematic droplets nucleate in the isotropic background, which eventually coarsens through the coalescence of the droplets to form defects. These defects annihilate through the usual defect string dynamics.

Our central result is the change of shape in the droplet conformation in the early stages of nucleation. Fig. (6.10) depicts the local tilt angle \( \theta = \cos^{-1}(\mathbf{k} \cdot \mathbf{n}), (0 \leq \theta \leq \pi) \) on the surface of the droplets as well as a slice of the three dimensional volume at a particular value of \( z \) in the \( z-\)axis. As can be clearly noticeable, the change of colours on the surface of the uniaxial droplet clearly confirms the variation of the director. Thus CNT predictions for the nucleation rate will not estimate the droplet nucleation rate correctly. However, we are unable to locate any defect conformation inside or on the surface of the droplet. The ellipsoidal nature of the droplet can be visualized in Fig. [6.10(b)]. Like the two dimensional case, we also notice that the first passage time is slightly higher than the previous case.

6.3.3 Ellipsoidal droplets with \( \kappa < 0 \)

Fig. (6.11) depicts the nucleation of the uniaxial nematic droplets in an isotropic medium in the presence of a negative contribution of the elastic anisotropy to the free energy. Like
6.3. Structure of nucleated nematic droplets in three dimensions

Figure 6.9: Time evolution of uniaxial order in a three dimensional volume. Panel (a) shows the emergence of uniaxial nematic droplet in the fluctuating isotropic background. Panel (b) shows the coalescence of droplets, and the formation of line defects are shown in panel (c). The defects at a late of the kinetics is shown in panel (d). The isosurfaces are plotted for a fixed isovalue $S = 0.04$. The numerics is performed upto $6 \times 10^3$ SRK4 iterations with unit increment in time.
Figure 6.10: Panel (a) shows the uniaxial order and director field on the surface of a nucleated nematic droplet in the three dimensional volume at an early stage. The isosurface is plotted for a fixed isovalue $S = 0.04$. Panel (b) shows the uniaxial order in a $x$-$y$ plane that slices the three dimensional volume at $z = 20$. 
6.3. Structure of nucleated nematic droplets in three dimensions

Figure 6.11: Time evolution of uniaxial order in a three dimensional volume. Panel (a) shows the emergence of uniaxial nematic droplet in the fluctuating isotropic background. Panel (b) shows the coalescence of droplets to form line defects shown in panel (c). The defects at a late of the kinetics is shown in panel (d). The isosurfaces are plotted for the fixed iso-value $S = 0.05$. The numerics is performed upto $3.9 \times 10^3$ SRK4 iterations with unit time increment.
the other cases, we see the nucleation kinetics followed by a phase ordering kinetics with coalescence of droplets leading to defects which eventually annihilate from the system.

Our central result is the ellipsoidal shape of the droplet conformation in the early stage of nucleation. Fig.(6.12) depicts the local tilt angle $\theta$ on the surface of the droplets as well as a slice of the three dimensional volume at a particular value of $z$ in the $z-$axis. We notice defect ellipsoidal droplets with different conformation of the director at the surface of the droplet. We are unable to locate any defect conformation inside or on the surface of the droplet. The ellipsoidal nature of the droplet can be visualized in Fig.[6.12(b)]. Like the two dimensional case, we also notice the first passage time to be slightly higher than the previous case.

### 6.4 Conclusion

In this chapter we have studied various uniaxial nematic droplet conformation nucleated in an isotropic fluid medium, through a computational study of nucleation kinetics in nematics. We have shown, in the absence of temperature fluctuations, that a uniaxial nematic nuclei with uniform director conformation grows in size, preserving the circular symmetry, if the contribution from anisotropic gradient terms are not incorporated in the Landau-de Gennes
theory. This situation breaks down in the more general case, with the emergence of an elliptic nucleus with the long axis of the ellipse oriented along the direction of the director for $\kappa > 0$ while remaining perpendicular to this direction for $\kappa < 0$. We have verified that in the presence of moderate thermal fluctuations, the nucleating uniaxial nematic nuclei grows as in the case of $\kappa = 0$. The first signature of an anomaly in the director configuration is for the $\kappa > 0$ case, where ellipsoidal nuclei grow in size with an integer defect trapped inside. While the droplets coalesce among themselves, these defects last till the late stage of the kinetics until the annihilation process kicks in. We obtain ellipsoidal droplets with uniform director configuration for $\kappa < 0$.

We also present nematic droplet conformations in three dimensions for all three cases. Though we are unable to detect any integer defect inside the ellipsoidal droplet in the case of $\kappa > 0$, we notice an abrupt variation of the director on the surface of the droplet for both positive and negative values of $\kappa$. 