Kinetics of liquid crystal phase transitions: A phase field approach

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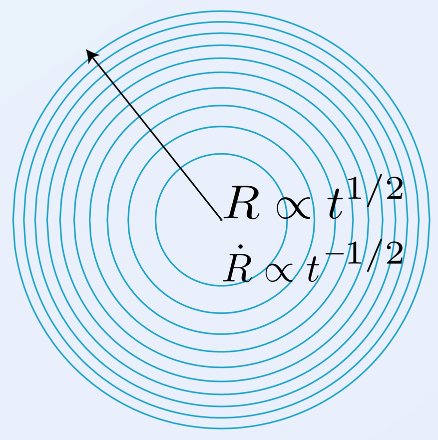
Motivation

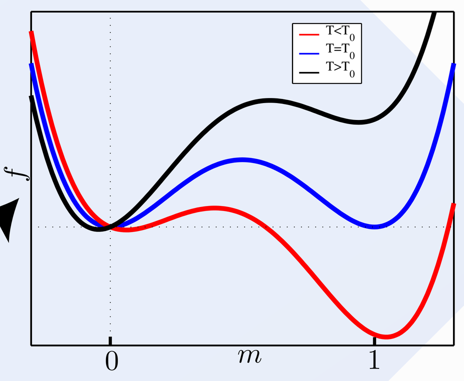


▪ Liquid Crystals (LC's) isotropic to nematic phase transition: Nematic domains experimentally[1,2] found to grow as $R \propto t^{1/2}$ into undercooled isotropic phase.
▪ Diamagnetic LC's found[1,2] to grow faster in high magnetic fields. Possibly with different, higher power.
▪ Reason for faster growth unknown.

▪ Isotropic to nematic phase transition is weakly first order.
▪ Time scales of thermal diffusion and order parameter kinetics are 5 orders apart[3].

Phase field approach

Order parameter m evolves to minimize free energy: $\frac{\partial m}{\partial t} = -\Gamma \frac{\delta F[m(\vec{r}), u(\vec{r})]}{\delta m}$



where F is given by a local (see figure) and a surface energy part[3]

$$F[m(\vec{r}), u(\vec{r})] = \int \left\{ f[m(\vec{r}), u(\vec{r})] + \frac{\xi_m^2}{2} (\nabla m(\vec{r}))^2 \right\} dV$$

$$f(m,u) = m^2(m-1)^2 + \frac{1}{2}\delta u m \qquad u = \frac{c_p}{L}(T - T_0)$$

functional derivation gives:

$$\frac{\partial m}{\partial t} = \frac{\xi^2}{2}\nabla^2 m - 2m(m-1)(2m-1) - \frac{1}{2}\delta u$$

Phase change enters as heat source in heat equation: $\frac{\partial u}{\partial t} = D_T \frac{\partial^2 u}{\partial x^2} + \frac{\partial m}{\partial t}$

Such that the latent heat is:

$$L = T_0 \left(\frac{\partial F}{\partial T}\Big|_{m=0} - \frac{\partial F}{\partial T}\Big|_{m=1} \right)$$

Solving the equations

Equations discretized by finite differences. Time integration by series expansion.

$$\frac{\partial m}{\partial t} = g(m)$$

$$\frac{m(t_{i+1}) - m(t_i)}{\Delta t} \approx g(m(t_i)) + \frac{1}{2}\frac{\partial g}{\partial m}\Big|_{t_i} \Big(m(t_{i+1}) - m(t_i)\Big)$$

Two regimes

Low undercooling or slow thermal diffusion: latent heat increases interface temperature towards T_0. The dynamics of the order parameter front R is dominated by thermal diffusion: $R \propto t^{1/2}$

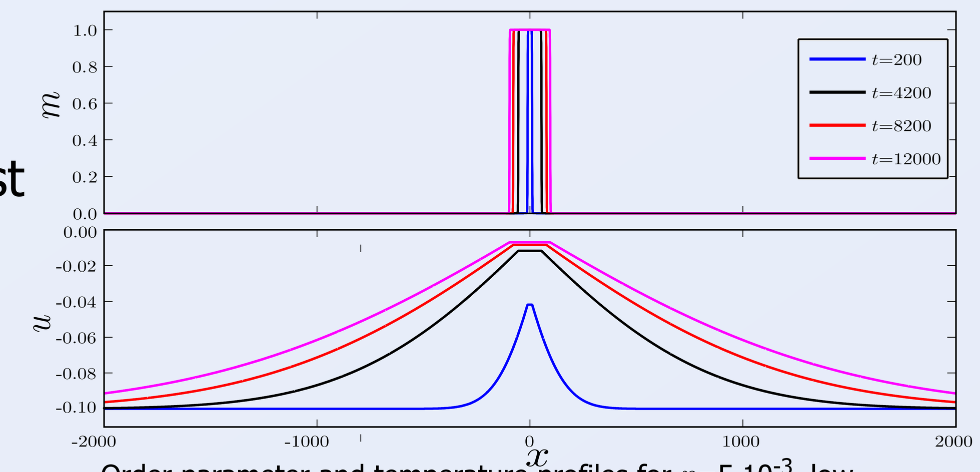
High undercooling or fast thermal diffusion: order parameter front propagates at constant velocity: $R \propto t$. Interface temperature approximately constant.

Liquid crystals

$$\frac{\partial m}{\partial t} = \frac{1}{2}\nabla^2 m - 2m(m-1)(2m-1) - \frac{1}{2}\delta u$$

$$\frac{\partial u}{\partial t} = \frac{1}{2p}\nabla^2 u + \frac{\partial m}{\partial t} \qquad \delta = \frac{2}{\psi}\frac{L}{k_B T_0}\frac{L}{c_p T_0} \qquad p \equiv \frac{\xi_m^2/\tau_m}{D_T} = \frac{D_m}{D_T}$$

p: ratio thermal and order parameter diffusion constants. p extremely low in LC's -> Time and length scales of u and m very different at low undercooling.

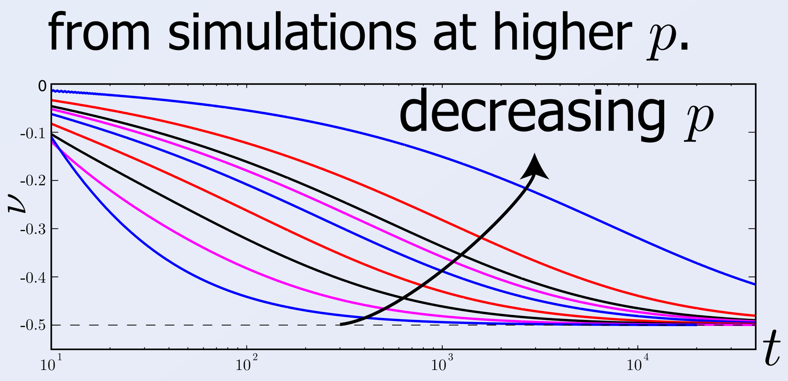


Order parameter and temperature profiles for $p=5\cdot 10^{-3}$, low undercooling. Order parameter interface width $2^{1/2}$ in adimensional units. Thermal profile much wider.

Determining Exponents

Assume: $\dot{R} \propto t^{\nu}$ then: $\frac{d \log(\dot{R})}{d \log(t)} = \nu$

At low undercooling: $\lim_{t\to\infty} \nu = -0.5$
Asymptotic behavior unreachable for p=10^{-5}, typical for the liquid crystal 8CB.
We estimate onset of powerlaw from simulations at higher p.



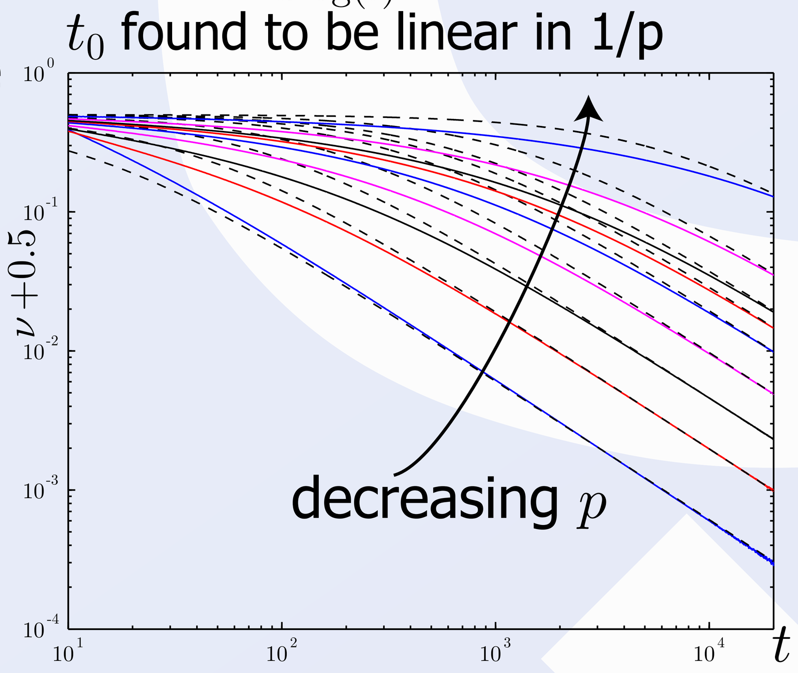
Growth exponent ν versus time for (exponentially) decreasing p. Asymptotic behavior reached at later times for lower p

Asymptotic behavior

Exponent fitted to

$$\nu(t) = \frac{d \log((t - t_0)^{\nu_f})}{d \log(t)} = \nu_f (1 - t_0/t)^{-1}$$

t_0 found to be linear in 1/p

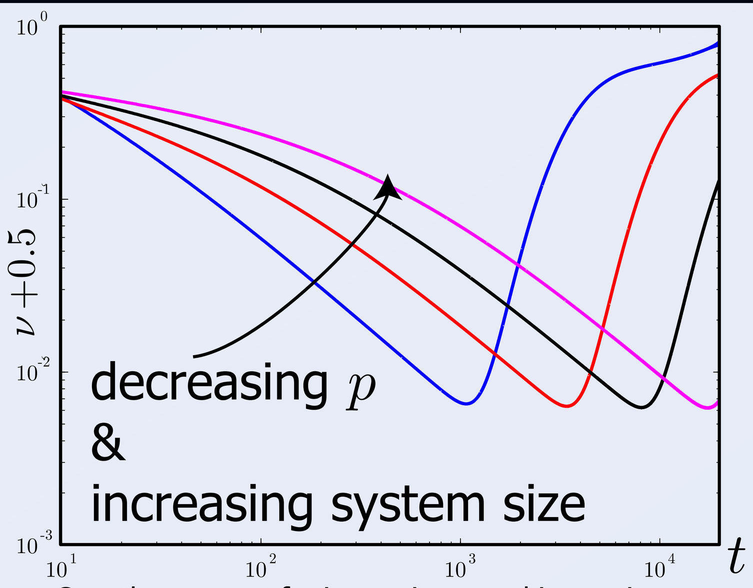


Growth exponent $\nu+0.5$ versus time for (exponentially) decreasing p. Dotted lines are fitted to $1/2(1+t_0/t)^{-1}$

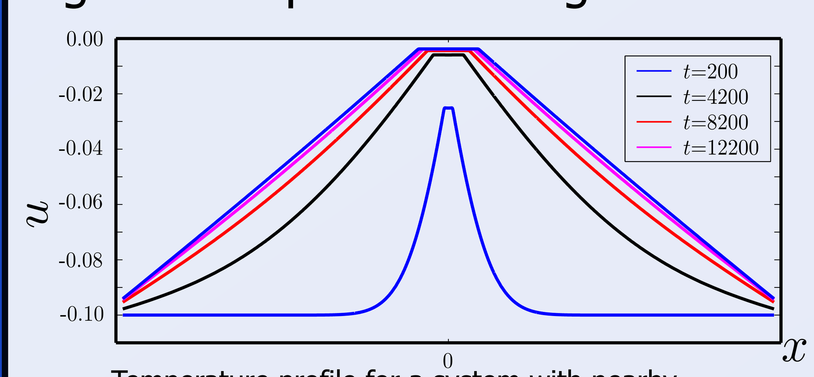
Boundaries

The boundary conditions act as a thermostat, keeping the systems boundaries at a fixed temperature.

Once the u-profile widenes beyond the system size, the growth exponent changes.



Growth exponent for increasing p and increasing system size. When temperature profile width exceeds the system size, the exponent grows.



Temperature profile for a system with nearby boundaries kept at the undercooling temperature. Note the difference before and after the field widened to the system size.

Liquid crystals

Temperature field width fitted for systems with far away boundaries. Extrapolated for parameters describing 8CB, found to be approx. 25 cm: much larger than experimental set up.

Conclusions

▪ Nematic domains experimentally found to grow into isotropic undercooled liquid as powerlaw $\dot{R} \propto t^{\nu}$ where $\nu = -0.5$.
▪ Phase field equations difficult to integrate in range of parameters suitable for liquid crystals. Extrapolation necessary.
▪ In the estimated time t_0 for the powerlaw behavior to set in, the thermal profile of liquid crystals is estimated to be around 25cm wide.
▪ Experimental set up much smaller: therefore exponent expected to be higher: $\nu > -0.5$

Remaining...

▪ Neighbouring domains. Can latent heat stall growth?
▪ Can we get $\dot{R} \propto t^{-0.5}$ without temperature field?
▪ The effect of dimensionality on the time t_0 (spherical coords.).
▪ Coupling to magnetic field.

References

[1] G. Tordini, P.C.M. Christianen, J.C. Maan. cond-mat/0408208 (2004).
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[3] H. Löwen, J. Bechhoefer, L.S. Tuckerman. Phys. Rev. Lett. **45**, 2399 (1992).

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