Transients in phase kinetics

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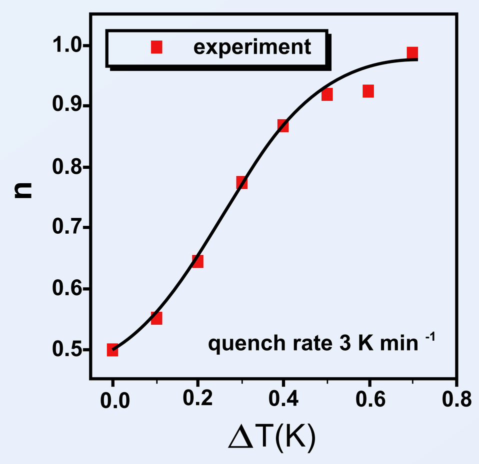
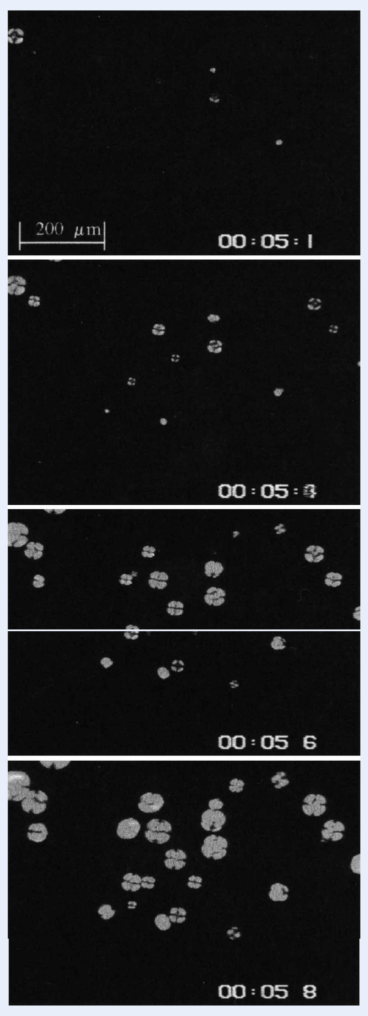
Motivation

- In the isotropic to nematic transition of liquid Crystals (LC's) the power of domain growth $R \propto t^{\,n}$ has been found[1,2] to depend on the amount of undercooling $\Delta T{=}T\text{-}T_0$
- The radius of a nematic domain grows as $R \propto t^{\,1/2}$ into the undercooled isotropic phase for low undercooling.
- Growth $R \propto t$ for high undercooling.





RIGHT: Nematic germs of PCH5 growing out of the isotropic phase. In the lower right corner of each picture the time after the temperature quench is given. The quench depth $\Delta T = T_{start} - T_{end}$ is 0.15K.
Figure and caption taken from ref. 1

LEFT: Experimentally determined growth exponent n as a function of quench depth ΔT. Errors are in the order of the size of
the symbols. The data confirm the theoretically predicted change of n=1/2 for ΔT=0 K to n→1 for large quench depths.
Figure and caption adapted from ref. 2

Phase field approach[3]

Expand local free energy f as a function of an order parameter m and temperature $u{=}c_p(T\text{-}T_0)/L$: $f(m,u) = m^2(m-1)^2 + \frac{1}{2}\delta u m$

Order parameter m evolves to minimize total free energy: $\frac{\partial m}{\partial t} = -\Gamma \frac{\delta F[m(\vec{r}), u(\vec{r})]}{\delta m}$ (1)

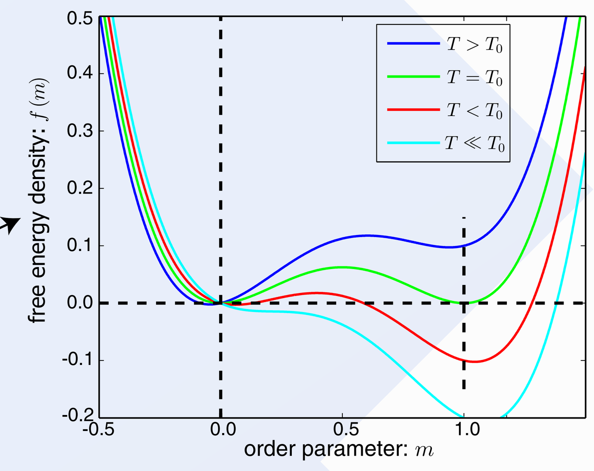
where F is given by the local f and a surface energy part

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

functional derivation of (1) gives a p.d.e. for order parameter evolution:

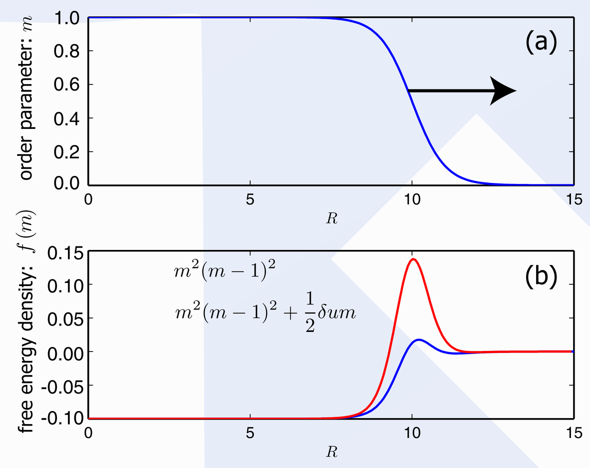
$$\frac{\partial m}{\partial t} = \frac{\xi^2}{2}\nabla^2 m - 2m(m-1)(2m-1) - \frac{1}{2}\delta u$$

The solution $m(r{,}t)$ for spherical symmetry is a moving $\tanh$ profile centered at $R(t)$, with an approximately fixed width.



TOP: Landau expansion of the free energy density for a first order phase transition, depicted for different temperatures.

BOTTOM: Typical order parameter profile $m(r)$ (a) and corresponding free energy density (b) for a system with $T{<}T_0$



Latent heat[3]

A first order change of phase generates latent heat:

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

Latent heat increases temperature $u(R)$, slowing down growth. L enters the p.d.e. for thermal diffusion as a source term:

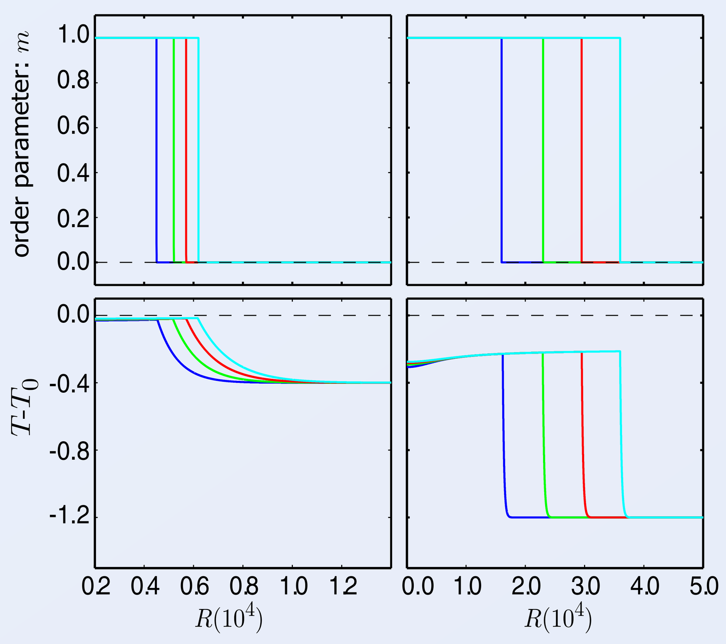
$$\frac{\partial u}{\partial t} = D_T\frac{\partial^2 u}{\partial x^2} + \frac{\partial m}{\partial t}$$

Hence we have two coupled, nonlinear p.d.e.'s:

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

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

Where the equations are scaled so that a change of phase $\Delta m{=}1$ increases the temperature by $\Delta u{=}1$.



LEFT: For undercooling $-1{<}\Delta u{<}0$ the latent heat warms the interface up to near the coexistence temperature $u{=}0$. The growth is limited by thermal diffusion, and therefore R will eventually grow as $R \propto t^{1/2}$

RIGHT: for undercooling $\Delta u{<}{-1}$ the temperature at the front approaches a finite value $u{=}\Delta u{+}1$, and domains will grow as $R \propto t^1$

Usually one integrates the two coupled p.d.e.'s numerically. This can become very expensive. We have devised a different scheme.

Approximations

If we write Eq. (2) in d-dimensional spherical coordinates, factor f in its roots m_1, m_2 and m_3, transform to $s{=}r\text{-}R(t)$, and assume a shape preserving interface, we can transform[4,5] Eq. (2) into two ordinary differential equations and solve these analytically, leading to a solution for the propagation of the front

$$\frac{\partial R(t)}{\partial t} = m_1 + m_2 - 2m_3 - \frac{d-1}{2R(t)}$$

with R_c the critical nucleus size, $R_c = \frac{d-1}{2m_1 + 2m_2 - 4m_3}$

and a solution for the m-profile

$$m(r,t) = m_2 + (m_1 - m_2)\{1 - \tanh\left[(m_1 - m_2)(r - R(t))\right]\}$$

So we can calculate $\partial m/\partial t$ analytically from $u(R)$ so that we only have to solve the thermal diffusion equation

$$\frac{\partial u}{\partial t} = D_T\frac{\partial^2 u}{\partial x^2} + \frac{\partial m(\mathrm{R}, \dot{\mathrm{R}}, u(R))}{\partial t}$$

And the front propagation equation

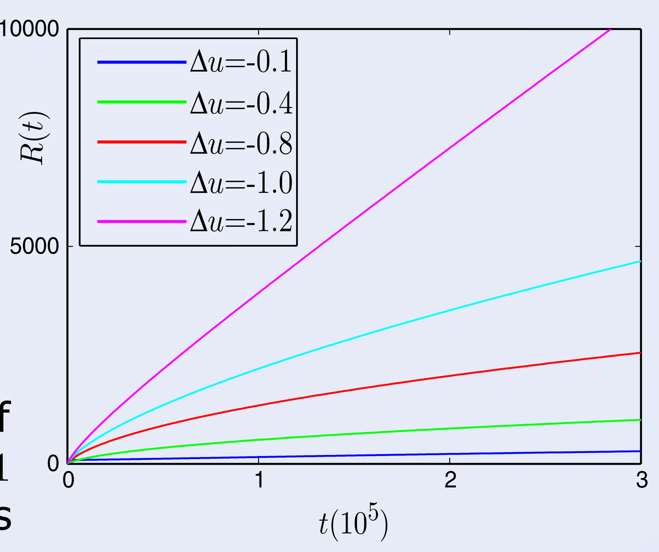
$$\frac{\partial R(t)}{\partial t} = m_1 + m_2 - 2m_3 - \frac{d-1}{2R(t)}$$

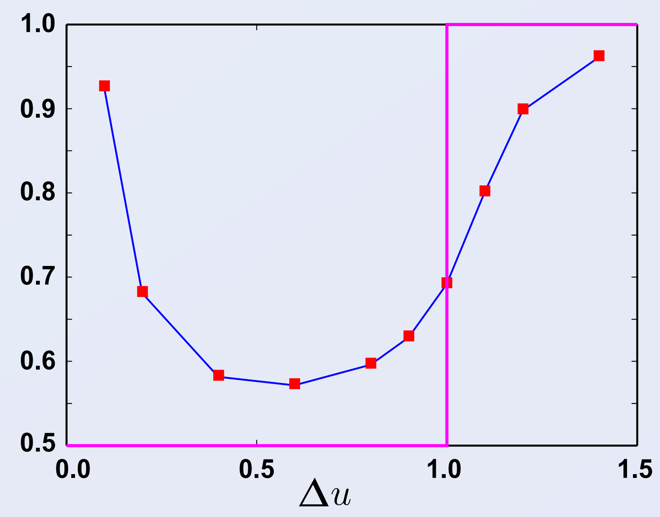
where m_1, m_2 and m_3, depend on $u(R)$.

This scheme is much faster to integrate and more stable, using the Crank-Nicholson method it only involves solving a tridiagonal equation each time step.

Results

- The order parameter goes through a transient before growth follows a power law $R \propto t^{\,n}$
- Two processes in the transient:
  - Heating up of the already converted part of the system to either near $u{=}0$ or to $u{=}\Delta u{+}1$
  - Growing to beyond where surface energy is of importance (most important for very low undercooling and >1D systems)





TOP: Position of order parameter front R as a function of time for different values of the undercooling Δu. Note that more undercooling means faster growth.

BOTTOM: Power of growth n as found from fitting $R \propto t^{\,n}$ to the data in the top figure. The thick purple line denotes the asymptotic value, $n{=}1$ for $\Delta u{<}{-1}$ and $n{=}1/2$ for $0{<}\Delta u{<}{-1}$. The high value of n for low undercoolings is due to the surface energy term dominating the transient in this regime. The measured curve will resemble the asymptotic curve more and more for longer experiment times.

Conclusions

- For low undercooling the asymptotic behavior is $R \propto t^{\,1/2}$, whereas for high undercooling the asymptotic behavior is $R \propto t^{\,1}$
- However for experimental conditions the asymptotic regime is often not obtainable, and a transient is measured.
- For very low undercooling the transient is dominated by the surface energy, and asymptotic behavior sets in much later.
  - This has not been found experimentally, and inspires further research.

Outlook

- We will use a more conventional form of the Landau free energy expansion.
- Study in a larger range of parameters describing different material properties.
- Study the effect of a small magnetic field to the transient behavior

References

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