Cahn-Hilliard-type phase-transition dynamics

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Context

- Stand-alone lecture on **conserved (Cahn-Hilliard-type) dynamics** for a single order parameter field
- Follow up of lecture on *nonconserved (Allen-Cahn-type) dynamics* (some knowledge assumed here)
- Given in the context of a lecture course *Introduction to the Theory of Phase Transitions* (ITPT)
- **Introductory lecture** tailored for Bachelor/Master students, possibly also useful for beginning PhD
- Background information on gradient dynamics may be obtained in the lecture *Introduction to Non-equilibrium Thermodynamics & Onsager's variational principle*

Aims

- **Understand**: Basic (conserved) dynamics as modelled by a continuum model
- **Analyse**: Linear stability of homogeneous states
- **Consider**: Nonlinear behaviour in spinodal/binodal region
- **Discuss**: Shape of phase transition fronts, coarsening behaviour
- **Expand:** towards more complicated energies (crystallisation fronts)

Bibliography and Further Reading

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[7] H. Emmerich, H. Löwen, R. Wittkowski, T. Gruhn, G. I. Tóth, G. Tegze, and L. Gránásy. Phase-field-crystal models for condensed matter

Introduction

- Consider **gradient dynamics** on underlying energy functional as obtained, e.g., via Onsager's variational principle
- Nonconserved order parameter field (Allen-Cahn-type dynamics); *see corresponding lecture*

$$\partial_t \psi = -Q_{\rm nc} \frac{\delta F[\psi]}{\delta \psi} \tag{1}$$

- Conserved order parameter field (Cahn-Hilliard-type dynamics); **our present focus**

$$\partial_t \psi = \nabla \cdot \left\{ Q_{\rm c}(\psi) \nabla \frac{\delta F[\psi]}{\delta \psi} \right\} \tag{2}$$

Mixed conserved and nonconserved dynamics

- One scalar field

$$\partial_t \psi = \nabla \cdot \left(Q_{\rm c}(\psi) \nabla \frac{\delta F[\psi]}{\delta \psi} \right) - Q_{\rm nc} \frac{\delta F[\psi]}{\delta \psi} \tag{3}$$

- n scalar fields $\psi_1, \ldots, \psi_n$

$$\partial_t \psi_\alpha = \sum_\beta \nabla \cdot \left[Q^{\rm c}_{\alpha\beta}(\psi_1, \ldots, \psi_n) \nabla \frac{\delta F}{\delta \psi_\beta} \right] - \sum_\beta Q^{\rm nc}_{\alpha\beta}(\psi_1, \ldots, \psi_n) \frac{\delta F}{\delta \psi_\beta} \tag{4}$$

Energy consideration for CH-type dynamics

- Does energy decrease in time for CH-type dynamics?
- Take Eq. (2), multiply by $\delta F/\delta\psi$, and integrate

$$\int_V \frac{\delta F[\psi]}{\delta \psi} \partial_t \psi \, d^3 r = \int_V \frac{\delta F[\psi]}{\delta \psi} \nabla \cdot \left(Q_{\rm c}(\psi) \nabla \frac{\delta F[\psi]}{\delta \psi} \right) d^3 r$$

- Integrate r.h.s. by parts

$$\frac{dF[\psi]}{dt} = -\int_V Q_{\rm c}(\psi) \left(\nabla \frac{\delta F[\psi]}{\delta \psi} \right)^2 d^3 r \leq 0 \tag{5}$$

i.e., F decreases monotonically **for any** F, i.e., mathematically F is Lyapunov functional

Proper Cahn-Hilliard equation

Specific free energy functional

- Order parameter field ψ can be: (scaled shifted) density in liquid-gas phase transition; concentration in phase separation
- Specific free energy functional that accounts for interfaces (same as for Allen-Cahn equation)

$$F[\psi(\mathbf{r})] = \int_V \left[\frac{\kappa}{2}(\nabla\psi)^2 + f(\psi)\right] d^3r \qquad (6)$$

- First term captures energetic cost of interfaces ($\kappa \geq 0$)
- Local energy density is double-well potential

$$f(\psi) = -\frac{a}{2}\psi^2 + \frac{b}{4}\psi^4 \qquad (7)$$

- With energy (6) and (7) in (2) and mobility $Q_c(\psi)$ =constant → proper **Cahn-Hilliard equation**[5]

$$\begin{aligned}\partial_t \psi &= -Q_c\Delta\left[\kappa\Delta\psi - \partial_\psi f\right] \\ &= -Q_c\Delta\left[\kappa\Delta\psi + a\psi - b\psi^3\right] \qquad (8)\end{aligned}$$

Linear stability analysis of homogeneous state $\psi = \psi_0$

- Conserved dynamics → homogeneous state exists for any ψ_0
- **Linear stability** of ψ_0, use ansatz

$$\psi = \psi_0 + \epsilon\psi_1(x,t) \qquad \text{with} \qquad \epsilon \ll 1, \psi_1 = O(1) \qquad (9)$$

→ perturbation is $O(\epsilon)$

- Ansatz (9) in Eq. (8), gives

$$\begin{aligned}\epsilon\partial_t\psi_1 &= -Q_c\Delta\left[\kappa\epsilon\Delta\psi_1 + a(\psi_0+\epsilon\psi_1) - b(\psi_0+\epsilon\psi_1)^3\right] \\ &= -\epsilon Q_c\Delta\left[\kappa\Delta\psi_1 + a\psi_1 - 3b\psi_0^2\psi_1\right] + O(\epsilon^2)\end{aligned}$$

- Fourier/Laplace mode ansatz $\psi_1(x,t) = e^{\lambda t + iqx}$ gives $\partial_t \to \lambda$ and $\Delta \to -q^2$

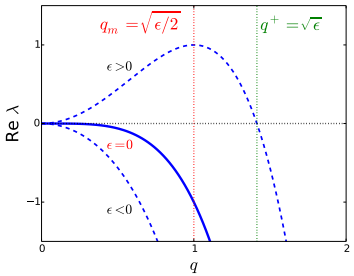
$$\lambda = Q_c(\psi_0)q^2\left[-\kappa q^2 + a - 3b\psi_0^2\right] \qquad (10)$$

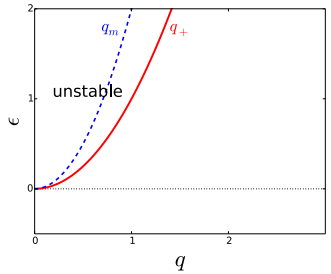
Dispersion relation

$$\lambda(q) = -Q_c\kappa q^2(q^2 - q_+^2)$$

$$\text{with} \qquad q_+ = \sqrt{-\frac{1}{\kappa}\frac{d^2f}{d\psi^2}\bigg|_{\psi_0}} = \sqrt{\frac{a-3b\psi_0^2}{\kappa}}$$

- q_+ **same as in Allen-Cahn case!**
- Minimal (scaled) form $\lambda(q;\epsilon) = q^2(\epsilon - q^2)$





Nonlinear behaviour in Cahn-Hilliard (CH) model

- At $q = q_+$, branch of steady heterogeneous (phase-separated) states emerges sub- or supercritically. Such states exist for $|\bar{\psi}| \leq \sqrt{a}$ (binodals)
- Eq. (8) with $\partial_t\psi = 0$ integrated twice:

$$0 = \kappa\Delta\psi - \partial_\psi f + \mu \qquad (11)$$

μ acts as Lagrange multiplier for mass conservation

- Eq. (11) identical to steady Allen-Cahn (AC) eq., however, following AC states one fixes μ ($\bar{\psi}$ changes) but when following CH states one fixes $\bar{\psi}$ (μ changes)

Results in different bifurcation diagrams (different stabilities of identical states) reflecting different perturbations allowed by AC and CH dynamics (at constant external field and at constant mass, respectively) *[see tutorial ACCH]*

Transition supercritical to subcritical primary bifurcation

- Obtained via **weakly nonlinear analysis** (projetion onto critical mode); also called **one-mode approximation** see lecture course *Nonlinear Physics*
- For Cahn-Hilliard type equations gives condition for transition

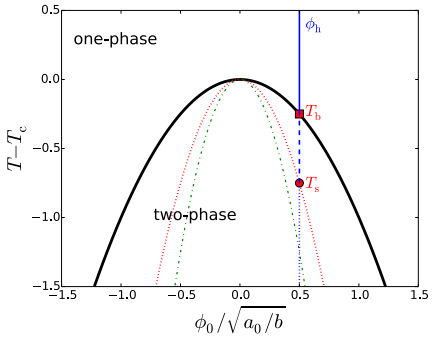
$$0 = 3\frac{d^2f}{d\psi^2}\frac{d^4f}{d\psi^4} + \left(\frac{d^3f}{d\psi^3}\right)^2 \qquad (12)$$

- For f double well potential transition at

$$\psi_{subsuper} = \pm\sqrt{\frac{a}{5b}} \qquad (13)$$

- Remember: Spinodal $\psi_s = \pm\sqrt{-\frac{d^2f}{d\psi^2}} = \pm\sqrt{\frac{a}{3b}}$
  Binodal $\psi_b = \pm\sqrt{-\frac{d^2f}{d\psi^2}} = \pm\sqrt{\frac{a}{b}}$
- To plot phase diagram $a = a_0(T - T_c)$

Phase diagram



- Binodal: black and spinodal: red line
- Super-/subcritical transition: green line
- Quench at fixed $\bar{\phi} = \phi_h$ into spinodal or binodal region
  → What happens?

- **Spinodal region:** linear instability (spinodal decomposition)
- **Binodal region:** homogeneous and heterogeneous nucleation
- **Outer spinodal region** (subcritical bif.): nucleation may dominate

Nonlinear behaviour - time evolution: instability in central spinodal region

Initial condition:
Homogeneous state $\psi = 0$ with weak noise

→ **Labyrinthine structure emerges**
→ **Coarsens into cluster or stripe state**
→ **Multistability; metastable state (stripes)**

Parameters: $\kappa = 1$, $a = 1$, $M = 1$

Nonlinear behaviour - time evolution: instability in spinodal region

$|\bar{\psi}| < 1/\sqrt{3} \approx 0.57$

Initial condition: Homogeneous state with weak noise

$\bar{\psi} = 0.2$ $\bar{\psi} = 0.3$ $\bar{\psi} = 0.5$

→ **Ensemble of clusters emerges (typical distance)**
→ **Slow coarsening into single cluster**

Parameters: $\kappa = 1$, $a = 1$, $M = 1$

Nonlinear behaviour - time evolution: nucleation in binodal region

$1/\sqrt{3} < |\bar{\psi}| < 1$

Initial condition: Homogeneous state with weak noise and gaussian depression of amplitude Δ

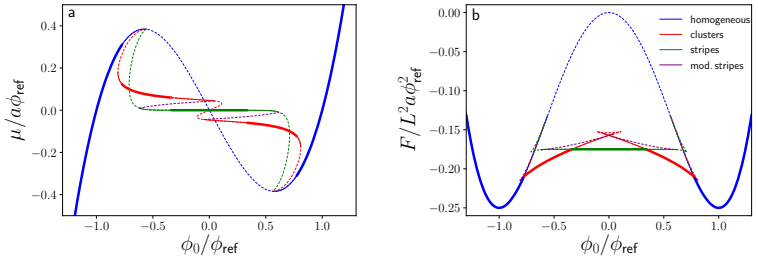
$\bar{\psi} = 0.6, \Delta = 0.05$ $\bar{\psi} = 0.6, \Delta = 0.15$

→ **Size of defect(s) determines outcome**

Parameters: $\kappa = 1$, $a = 1$, $M = 1$

Bifurcation diagrams for finite L (2D)

$L = 4L_c = \frac{8\pi}{q_+}$, **square domains** $L \times L$



(a) Chemical potential; (b) Mean free energy density as a function of $\bar{\phi}$

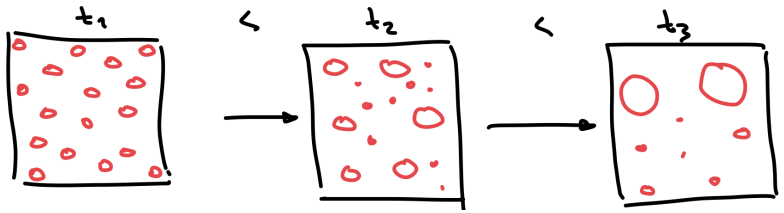
Explains multistability in central spinodal region!

Linearly stable (unstable) states are indicated by thin solid (dashed) lines. The thick solid lines denote the states of minimum free energy at each value of $\bar{\phi}$.

UT et al., NJP (2019)[10]

Domain coarsening in CH equation

- Coarsening differs from Allen-Cahn equation



- Small clusters are 'eaten' by large ones
- Two basic coarsening modes: by translation and by volume transfer
- One can show that at late stages

$$\frac{dR}{dt} \sim \frac{1}{R^2} \quad \rightarrow \quad R \sim t^{1/3}$$

Lifshitz-Slyozov-Wagner law (see Ref.[8] pg. 326-330)
Remember in AC equation: $R \sim t^{1/2}$

Possible extensions

- **Mixed conserved and non-conserved dynamics for one field**
- Other local energies and mobilities (e.g., dewetting, decomposition)
- Several fields with coupled dynamics (e.g., two-layer dewetting, phase separation in ternary mixtures)
- **More complicated energy functionals (e.g., crystallisation)**
- Breaking the gradient dynamics structure (e.g., driven systems, reaction-diffusion systems, biophysics, . . .)
  → entirely new phenomena, e.g., drifting and time-periodic states

MIXED CONSERVED AND NON-CONSERVED DYNAMICS

Mixed conserved and non-conserved dynamics

- Mixed dynamics for single order parameter field is (3)

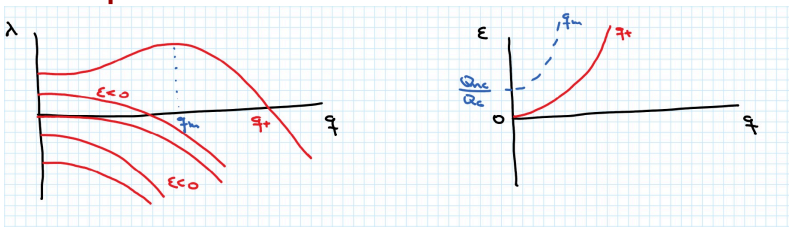
$$\partial_t \psi = \nabla \cdot \left(Q_c(\psi) \nabla \frac{\delta F[\psi]}{\delta \psi} \right) - Q_{nc} \frac{\delta F[\psi]}{\delta \psi} \qquad (14)$$

- Example: Evolution equation for height of thin film of volatile liquid with μ being imposed external vapour pressure (chem. potential)
- **Homogeneous steady states** solve $\frac{\delta F}{\delta \psi} = 0$
- **Linear stability** analysis gives dispersion relation

$$\lambda = -\kappa(Q_{nc} + Q_c q^2)(q^2 - q_+^2) \qquad (15)$$

with q_+ as before
First factor always > 0, i.e., no second root!

- **Dispersion relation**



- Always large-scale instability, i.e., no finite band of unstable wavenumbers about a critical $q_c \neq 0$
- Such a band only possible for broken gradient dynamics structure (or nonlocal energy)
- **Self-study:** Give conditions to distinguish different cases, calculate q_c from (14)

MORE COMPLICATED ENERGY FUNCTIONALS

→ COLLOIDAL CRYSTALLISATION IN PHASE-FIELD-CRYSTAL (PFC) MODEL

What is the phase-field-crystal (PFC) method?

from Review by Emmerich et al (2012)[7]

- *"one of the latest simulation methodologies in materials science for problems, where atomic and microscales are tightly coupled"*
- *"operates on atomic length and diffusive time scales, and thus constitutes a computationally efficient alternative to molecular simulation methods"*
- *"intense development in materials science started with the work by Elder et al."* [*Phys. Rev. Lett.* **88**, 245701 (2002)[6]]
- *"Dynamical density functional theory (DDFT) and thermodynamic concepts have been linked to the PFC approach"*

Basics of Dynamical Density Functional Theory (2d)

Evolution equation for conserved one-body density ρ

$$\partial_t \rho = \nabla \cdot \left\{ M\rho \nabla \frac{\delta F[\rho]}{\delta \rho} \right\}$$

with (equilibrium) energy functional ($r = |\mathbf{r} - \mathbf{r}'|$)

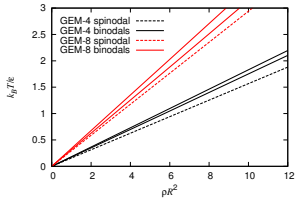
$$F[\rho] = k_B T \int \mathrm{d}\mathbf{r} \rho(\mathbf{r}) \left(\log[\rho(\mathbf{r})\Lambda^2] - 1 \right) + \frac{1}{2} \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{r}' \rho(\mathbf{r}) w(r) \rho(\mathbf{r}')$$

Example: soft penetrable particles

$$w(r) = \epsilon e^{-(r/R)^n}$$

$n = 2$ Gaussian core model (GCM)
$n > 2$ generalised exp. model (GEM)

Phase diagram (1d)



DDFT $\rightarrow$ PFC

From DDFT to Phase-Field-Crystal (PFC) model

Approximation DDFT *to* PFC

- Small deviations $\phi = \rho - \rho_0$
- Small gradients: cut-off Fourier series of $\int \rho w \rho' d\mathbf{r}'$ at k^6
- Integro-differential eqn. (DDFT) $\rightarrow$ Partial differential eqn. (PFC)

Issue hard $\rightarrow$ soft bumps
e.g. crystallisation fronts in van Teeffelen et al. (2009)[11]

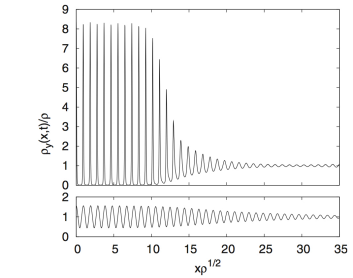


FIG. 4. The y-average density profile $\rho_y(x, t = \tau_B)$ obtained from the DDFT (top panel) and the PFC1 model (bottom panel) for the

see recent critique in Archer, Ratliff, Rucklidge, and Subramanian, *Phys. Rev. E* **100**, 22140 (2019)

Phase-field crystal model

Evolution equation for conserved order parameter ϕ

$$\partial_t \phi = \nabla \cdot \left\{ M \nabla \frac{\delta F[\phi]}{\delta \phi} \right\}$$

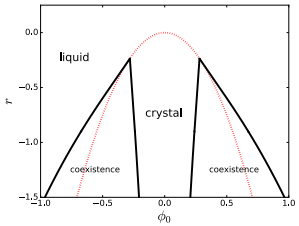
with energy

$$F[\phi] = \int_A \left[\frac{1}{2}(\Delta\phi)^2 - |\nabla\phi|^2 + (1+r)\frac{\phi^2}{2} + \frac{\phi^4}{4} \right] dA = \int_A f_{\mathrm{SH}}(\phi) dA$$

Identical to conserved Swift-Hohenberg equation

$$\partial_t \phi = \nabla \cdot \mathbf{j}$$
$$= M\Delta[r\phi + (\Delta+1)^2\phi + \phi^3]$$

Phase diagram (1d)



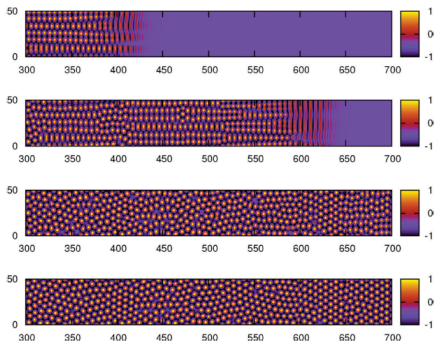
Relation between bifurcation and phase transition?

Advancing crystallisation front - PFC model

Does a crystallisation front create an equilibrium crystal?

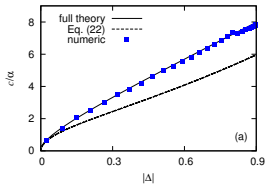
$\longrightarrow$ Front speed (undercooling) determines crystal spacing

Crystallisation front advances into an unstable liquid

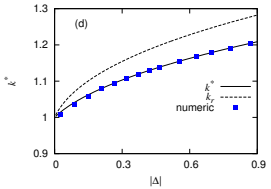


Archer, Robbins, UT and Knobloch, PRE 86, 031603 (2012)[1]

Front speed



Created structure length



$\longrightarrow$ Front speed (undercooling) determines 'non-equilibrium' transient crystal spacing

$\longrightarrow$ Approach to equilibrium: aging / defect creation

- Full DDFT results: *Archer, Walters, UT and Knobloch, PRE (2014)*[2]

Outlook

- DDFT/PFC active field of research
- Coarse graining of PFC model $\rightarrow$ phase-field models of crystallisation (Allen-Cahn-type or coupled Allen-Cahn & Cahn-Hilliard)
- Used to investigate dendrite formation in solidification (Mullins-Sekerka instability and beyond, see Materal Science)
- Similar models describe Bose-Einstein condensates, supraconductivity (vortex arrays)
- Nonequilibrium equivalents of all considered transitions and beyond

Summary & conclusion

- Analysed simple gradient dynamics model for conserved scalar field (proper Cahn-Hilliard)
- Linear behaviour: Dispersion relations gives fastest growing modes (typical length scale)
- Spinodal/binodal $\rightarrow$ phase diagram
- Fully nonlinear behaviour: time simulation & path continuation
- Spinodal decomposition vs. nucleation; cluster growth and coarsening
- Extension to mixed dynamics
- Extension to higher order energy functionals: crystallisation