

# Models in Phase Transitions

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# Outline

1. The Van der Waals-Cahn-Hilliard model
2. Second order materials
3. Surfactant

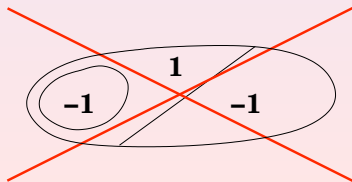
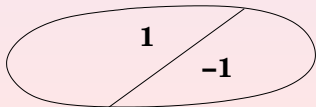
## The Van der Waals-Cahn-Hilliard model

Let  $\Omega \subset \mathbb{R}^N$  be a bounded open set (container) and  $u: \Omega \rightarrow [-1, 1]$  be phase function. We consider the singularly-perturbed energy

$$\mathcal{E}_\varepsilon(u) := \int_{\Omega} \left[ \frac{1}{\varepsilon} W(u) + \varepsilon |\nabla u|^2 \right] dx,$$

where  $W(s) := (s^2 - 1)^2$ .

### Van der Waals-Cahn-Hilliard energy



## Main Tool: $\Gamma$ -convergence

Equilibrium configurations of a physical system are described by the minimizers of a suitable energy  $F_\varepsilon$ :

$$(P_\varepsilon) \quad \min\{F_\varepsilon(u) : u \in X_\varepsilon\} \quad (\varepsilon > 0).$$

$$\downarrow \quad \varepsilon \rightarrow 0^+$$

$$(P) \quad \min\{F(u) : u \in X\} \quad (\text{effective problem})$$

Variational convergence [**Ennio De Giorgi, 1975**]: convergence of minimizers  $u_\varepsilon$  of  $(P_\varepsilon)$  to those of  $(P)$ .

## The Van der Waals-Cahn-Hilliard model

$$\mathcal{E}_\varepsilon(u) := \int_{\Omega} \left[ \frac{1}{\varepsilon} W(u) + \varepsilon |\nabla u|^2 \right] dx$$

Modica-Mortola '77:  $W(s) := \sin^2(\pi s)$ ;

Gurtin '85: **Conjecture**  $\mathcal{E}_\varepsilon \xrightarrow{\Gamma} \text{Per}$ , with  $W(s) := (s^2 - 1)^2$ ;

Modica '87: **Proof of the conjecture**,  $W(s) := (s^2 - 1)^2$ ;

Sternberg '87: **Proof of the conjecture**,  $W(s) := (s^2 - 1)^2$ .

# The Van der Waals-Cahn-Hilliard model

The sequence of energies

$$\mathcal{E}_\varepsilon(u) := \int_{\Omega} \left[ \frac{1}{\varepsilon} W(u) + \varepsilon |\nabla u|^2 \right] dx \quad \text{if } u \in H^1(\Omega).$$

$\Gamma(L^1)$ -converges as  $\varepsilon \rightarrow 0^+$  to

$$\mathcal{E}(u) := \begin{cases} c_W \text{Per}_{\Omega}(\{u = 1\}) & \text{if } u \in BV(\Omega, \{\pm 1\}) \\ +\infty & \text{if } u \in L^1(\Omega) \setminus BV(\Omega, \{\pm 1\}), \end{cases}$$

where

$$c_W := \min \left\{ \int_{\mathbb{R}} [W(u) + |u'|^2] dx : u(-\infty) = -1, u(\infty) = 1 \right\}.$$

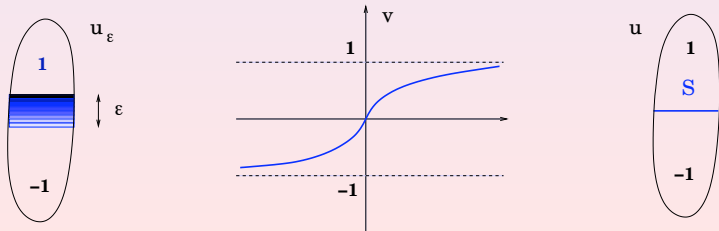
# The Van der Waals-Cahn-Hilliard model

**Theorem.** *Minimizers of  $\mathcal{E}_\varepsilon$  converge to a minimizers of  $\mathcal{E}$ .*

Van der Waals-Cahn-Hilliard energy  $\longleftrightarrow$  minimal surfaces

If  $u_\varepsilon$  is a smooth minimizer of  $\mathcal{E}_\varepsilon$ , then  $2\varepsilon^2 \Delta u_\varepsilon = \nabla_u W(u_\varepsilon)$ .

Shape of the minimizers of  $\mathcal{E}_\varepsilon$ :  $u_\varepsilon(x) \cong v\left(\frac{\text{dist}(x,S)}{\varepsilon}\right)$



## Second order materials

Andelman, Kawakatsu, Kawasaki, and Taniguchi (1993-94):  
variational model to study the shape deformations of a mixed  $A/B$   
unilamellar membrane undergoing an inplane phase separation.  
Precisely, the free energy takes the form

$$\mathcal{E}_1 = \int \left[ W(u) + b |\nabla u|^2 + b^* |\nabla^2 u|^2 \right] dx,$$

In  $A/B$  mixtures with different spontaneous curvatures, curved morphologies are preferred

$$\mathcal{E}_2 = \Lambda \int (u\kappa).$$



## 3.1. Second order materials: Motivation

Andelman and Seul have approximated this complex nonlocal problem by the free energy

$$\int_{\Omega} \left[ W(u) - q |\nabla u|^2 + b^* |\nabla^2 u|^2 \right] dx,$$

where  $q := \Lambda^2 - b$ .

When  $q > 0$ , one expects a **curvature instability** of the membrane generating **pattern of domains** that differ in composition as well as in local curvature.

## Second order materials

Consider the family of singular perturbed energies  $F_\varepsilon: L^1(\Omega) \rightarrow \overline{\mathbb{R}}$  defined by

$$F_\varepsilon(u) := \begin{cases} \int_{\Omega} \left[ \frac{1}{\varepsilon} W(u) - q\varepsilon |\nabla u|^2 + \varepsilon^3 |\nabla^2 u|^2 \right] dx, & u \in H^2(\Omega) \\ +\infty & \text{else.} \end{cases}$$

Coleman-Mizel (80s), Coleman-Mizel-Marcus ('92):  $q > 0$ ;

Mizel-Peletier-Troy ('98):  $q > 0.9481$ , periodic minimizers;

Fonseca-Mantegazza ('00):  $q = 0$ ,  $F_\varepsilon \xrightarrow{\Gamma} \text{Per}$ ;

Hilhorst-Peletier-Schätzle ('02):  $q < 0$ ,  $F_\varepsilon \xrightarrow{\Gamma} \text{Per}$ .

## Second order materials

**Theorem (C.-Dal Maso-Fonseca-Leoni '09).** *Let  $q < q^*/N$  and  $\Omega \subset \mathbb{R}^d$  be bounded open with  $\partial\Omega \in C^1$ . Then  $\{F_\varepsilon\}$   $\Gamma(L^2)$ -converges to*

$$F(u) := \begin{cases} \mathbf{m}_{N,q} \operatorname{Per}_\Omega(\{u = 1\}) & u \in BV(\Omega, \{\pm 1\}) \\ +\infty & u \in L^2(\Omega) \setminus BV(\Omega, \{\pm 1\}), \end{cases}$$

where, letting  $Q := (-1/2, 1/2)^N$ ,

$$\mathbf{m}_{N,q} := \inf \left\{ \int_Q \left[ \frac{1}{\varepsilon} W(u) - q\varepsilon |\nabla u|^2 + \varepsilon^3 |\nabla^2 u|^2 \right] : \varepsilon > 0, u \in \mathcal{A} \right\},$$

$$\mathcal{A} := \left\{ u \in H_{\text{loc}}^2(\mathbb{R}^N) : u \text{ is } 1\text{-periodic in the first } N-1 \text{ directions,} \right. \\ \left. u(x) = -1 \text{ near } x \cdot e_N = -\frac{1}{2}, u(x) = 1 \text{ near } x \cdot e_N = \frac{1}{2} \right\}.$$

**Cicalese-Spadaro-Zeppieri '09:**  $N = 1$ ,  $\Gamma(L^1)$ -convergence.

## Surfactant

Consider the family of singular perturbed energies defined by

$$G_\varepsilon(u) := \frac{1}{\varepsilon} \int_{\Omega} f(u(x), \varepsilon \nabla u(x), \varepsilon \rho(x)) \, dx$$

where  $u \in H^1(\Omega; \mathbb{R}^N)$  is the concentration of a mixture of  $N$  fluids,  
 $\Omega \subset \mathbb{R}^d$  is open and bounded set with Lipschitz boundary  
 $\rho : \Omega \rightarrow [0, +\infty)$  is the density of the surfactant.

$$G_\varepsilon(u, \rho) := \frac{1}{\varepsilon} \int_{\Omega} W(u) \, dx + \varepsilon \int_{\Omega} |\nabla u|^2 \, dx + \varepsilon \int_{\Omega} (\rho - |\nabla u|^2)^2 \, dx$$

## Surfactant

**Theorem (C.-Fonseca '09).** *The sequence  $\{G_\varepsilon\}$   $\Gamma(L^2)$ -converges to  $G : L^1(\Omega; \mathbb{R}^N) \times \mathcal{M}^+(\bar{\Omega}) \rightarrow [0, +\infty]$  defined by*

$$G(u, \mu) := \int_{J_u} \sigma \left( \nu_u(x), \frac{d\mu}{d(\mathcal{H}^{d-1} \llcorner S_u)}(x) \right) d\mathcal{H}^{d-1}(x)$$

for  $u \in BV(\Omega; \{\alpha, \beta\})$ ,  $\mu = \rho dx$ , with  $\rho \in L^1(\Omega; [0, +\infty))$ ,

$$G(u, \rho) = +\infty \quad \text{otherwise,}$$

where  $J_u$  is the set of approximate jump points of  $u$  and  $\nu_u$  is the generalized unit inner normal to  $J_u$

## Surfactant

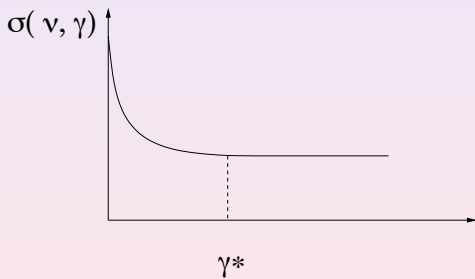
- the macroscopic energy  $G$  is only sensitive to the restriction of the surfactant density  $\mu$  to the interface  $J_u$ : **the surfactant segregates to the interface**;
- if we have a prescribed distribution of the surfactant  $\mu$  (say,  $\mu = \sum_{i=1}^L a_i \delta_{x_i}$ ) then the interfaces will be created exactly on the support of  $\mu$  (resp. at the concentration points  $x_i$ );
- the macroscopic energy  $G$  **will remain unchanged** if the density of the surfactant  $\mu$  on the interface  $J_u$ ,

$$\frac{d\mu}{d(\mathcal{H}^{d-1} \llcorner S_u)},$$

**exceeds a critical value.** The energy is impervious to adding more surfactant and the system reaches saturation;

- **below the saturation threshold** the addition of an arbitrarily small amount of **surfactant lowers the surface tension**, in agreement with experiments.

# Surfactant



THANKS FOR YOUR ATTENTION!