

Atomistic and continuum descriptions of fluids:  
some examples of their inter-relations.

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Contents.

## **Part I: A short survey on ferromagnetic systems**

Macroscopic–Mesoscopic–Microscopic theories.

Will recall classical notions as:

Free energy, Ginzburg-Landau functional, Gibbs measures.

Kawasaki dynamics, Gradient flows, Cahn Hilliard, Stefan problem.

Goal:

*underline role of scalings to connect the different levels.*

## **Part II: Stationary non equilibrium states.**

Example: Heat flow from hot to cold plates; stationary state with non zero heat current.

Goal: (non equilibrium) thermodynamic theory of such phenomena. An open problem at least at the microscopic level.

Recent progresses have been obtained which I will elaborate at the macroscopic level.

## References for Part II.

E.G.D. Cohen, G. Gallavotti: Note on two theorems in non equilibrium statistical mechanics. *J. Stat. Phys.*, **96**, 1343–1349 (1999).

B. Derrida, J.L. Lebowitz, E. Speer: Large deviations of the density profile in the steady state of the open symmetric simple exclusion process. *J. Stat. Phys.* **107** 599–634 (2002).

L. Bertini, A. De Sole, D. Gabrielli, G. Jona-Lasinio, C. Landim: Non equilibrium current fluctuations in stochastic lattice gases. *J. Stat. Phys.* **123**, 237–276 (2006).

T. Bodineau, B. Derrida: Cumulants and large deviations of the current through non-equilibrium steady states. *C.R. Physique* **8**, 540–555 (2007).

## I.1. Macroscopic Theory

Starts with a primitive notion of thermodynamic equilibrium. We thus suppose to have:

The free energy as a function of the order parameters (which characterize the thermodynamic states).

**Postulate 1.** The system is a continuum body:

*Each macroscopic point is a large system of molecules in equilibrium*

*the equilibrium is specified by the order parameter and the corresponding free energy*

*States: order parameter valued functions on  $\Omega$*

$\Omega$ : region occupied by the system

Specific example.

Ferromagnetic crystal where relevant order parameters are: temperature and magnetization  $m$  along a characteristic axis.

Free energy density  $f_\beta(m)$  of the inverse temperature  $\beta$  and of the the magnetization density  $m$ .

$\beta$  is kept fixed (in space and time), only order parameter is  $m$ .

**Postulate 1.** *Barometric formula.*

The free energy of a state  $m(\cdot)$  is:

$$F(m) = \int_{\Omega} f_{\beta}(m(r)) dr$$

**Postulate 2.** *Gradient dynamics.*

Conservative dynamics:

$$\frac{dm}{dt} = -\nabla J$$

Gradient flow assumption:

$$J(x) = -\chi(m(x)) \frac{\delta F(m)}{\delta m(x)}$$

$\chi(\cdot) > 0$  “mobility coefficient”.

$$\frac{dm}{dt} = \nabla \left( \chi \nabla f'_\beta(m) \right)$$

Diffusion equation with coefficient  $D := \chi f''_\beta(m)$ .

The Curie-Weiss free energy is the convex envelope of

$$-\frac{m^2}{2} + \frac{1}{\beta} \left( \frac{1+m}{2} \log \frac{1+m}{2} + \frac{1-m}{2} \log \frac{1-m}{2} \right)$$

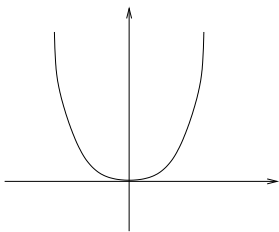


Figure: Curie-Weiss free energy at  $\beta < 1$

$D > 0$ . Strictly parabolic

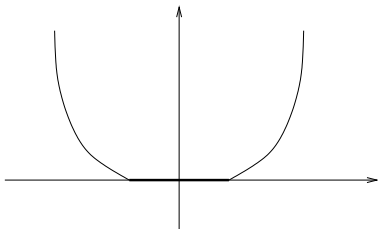


Figure: Curie-Weiss free energy at  $\beta > 1$ , linear for  $|m| \leq m_\beta$ .

$D = 0$  when  $|m| \leq m_\beta$ . Free boundary problem, Stefan problem.

## Shortcomings of macroscopic theory

The theory does not distinguish magnetization values in  $[-m_\beta, m_\beta]$ ;  
any profile  $m(r)$ ,  $|m(r)| \leq m_\beta$ , is invariant.

Instead we observe as time grows:

Microstructures, mushy regions, interfaces, Wulff shape.

Blow ups needed to catch such phenomena.

## I.2 Mesoscopic Theory

Free energy  $f_\beta(m)$  no longer a primitive notion.

**Postulate 1.** The system is a continuum body:

*Each macroscopic point is (still) a large system of molecules  
but not necessarily in thermodynamic equilibrium*

Local state specified by magnetization density  $m \in \mathbb{R}$ .

States:

*Functions  $m(r)$ ,  $r \in \Lambda$*

$\Lambda$ : blow up of the macroscopic region  $\Omega$

Free energy of  $m(\cdot)$  is no longer “local” (points interact with each other)

*The Ginzburg-Landau free energy of the state  $m(\cdot)$  is:*

$$F(m) = \int_{\Lambda} W(m(r)) + |\nabla m|^2$$

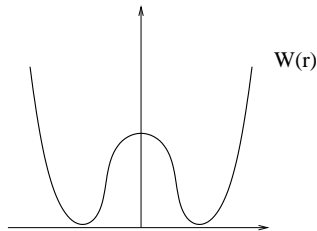


Figure:  $\beta > 1$ ,  $W$  is double well with minima at  $\pm 1$ .

Scale transformation:

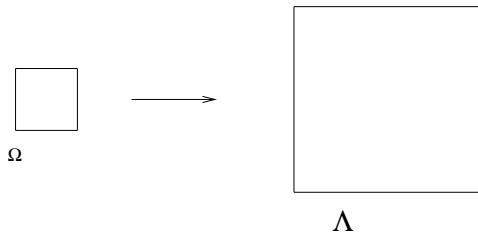


Figure:  $\Omega \rightarrow \Lambda = \varepsilon^{-1}\Omega$ , macro  $\rightarrow$  meso.

To any mesoscopic profile  $m \in L^1(\varepsilon^{-1}\Omega)$  we associate a macro profile

$$u(r) := m(\varepsilon^{-1}r), \quad r \in \Omega$$

Define free energy of  $u$  as  $F_\varepsilon^*(u) = F(m)$ , so that

$$F_\varepsilon^*(u) = \varepsilon^{-d} \int_{\Omega} \{W(u) + \varepsilon^2 |\nabla u|^2\}$$

and the free energy density of  $u$  as

$$F_\varepsilon(u) := \varepsilon^d F_\varepsilon^*(u) = \int_{\Omega} \{W(u) + \varepsilon^2 |\nabla u|^2\}$$

Macroscopic behavior in the limit  $\varepsilon \rightarrow 0$ :

*choice of topology essential*

In the macroscopic theory  $u(r)$ ,  $r \in \Omega$ , is the magnetization density of a macroscopically small yet mesoscopically large portion of the fluid. Thus:

*Two magnetization profiles  $v$  and  $u$  on  $\Omega$  are called close if, for  $\delta > 0$  and  $\zeta > 0$  small,*

$$\|K_\delta(v - u)\|_{L^1(\Omega)} := \int_{\Omega} |K_\delta(v - u)| < \zeta$$

where

$$(K_\delta f)(r) := \frac{1}{|B_\delta(r)|} \int_{B_\delta(r)} f(r') dr'$$

$B_\delta(r)$  the ball in the torus  $\Omega$  of radius  $\delta > 0$  and center  $r$ ,

**Theorem.**

The Gamma limit of  $F_\varepsilon$  exists and it is given by

$$F^{\text{macro}}(u) := \int_{\Omega} CE\{W\}(u(r))$$

namely:

$$F^{\text{macro}}(u) := \liminf_{\zeta, \delta \rightarrow 0} \liminf_{\varepsilon \rightarrow 0} \inf_{\|K_\delta(v-u)\|_{L^1(\Omega)} < \zeta} F_\varepsilon(v)$$

(same with limsup)

Gradient dynamics:

$$\frac{dm}{dt} = -\nabla J$$

$$J = -\chi \frac{\delta F(m)}{\delta m(r)} = -\chi (W' - 2\Delta m)$$

Supposing  $\chi \equiv 1$  we get the Cahn-Hilliard equation

$$\frac{dm}{dt} = \Delta (W' - 2\Delta m)$$

## Hydrodynamic limit.

By parabolic rescaling

$$u^{(\varepsilon)}(r, t) := m(\varepsilon^{-1}r, \varepsilon^{-2}t),$$

$m(r, t)$  solving Cahn-Hilliard. Explicitly:

$$\frac{du^{(\varepsilon)}}{dt} = \Delta \left( W' - 2\varepsilon^2 \Delta u^{(\varepsilon)} \right)$$

and if  $W$  is strictly convex,  $u^{(\varepsilon)} \rightarrow u$  where

$$\frac{du}{dt} = \Delta W'$$

( $W'' > 0$  the diffusion coefficient).

If  $W$  is a double well convergence to a free boundary problem.

## Shortcomings of mesoscopic theory

Fluctuations are not taken into account (in macro-theory as well).

Spinodal decomposition, metastability,....

Effects of fluctuations on interface dynamics ????

## I.3 Microscopic Theory

### The Ising model

$\Lambda$  a torus of  $\mathbb{Z}^d$  (periodic boundary conditions)

$\sigma_\Lambda$  spin configuration  $\in \{-1, 1\}^\Lambda = \textit{phase space}$

$\sigma_\Lambda(x)$  spin at  $x \in \Lambda$ ,  $\sigma_\Lambda(x) \in \{-1, 1\}$

## Energy

$$H_\Lambda(\sigma_\Lambda) = -\frac{1}{2} \sum_{x \neq y} J(x, y) \sigma_\Lambda(x) \sigma_\Lambda(y)$$

$J(x, y) \geq 0$  ferromagnetic interaction

$J(x, y) = J(0, y - x) = J(y, x)$  Translational invariance, symmetry

$J(0, x) = 0$  if  $|x| > R$ , finite range.

$R = 1$  nearest neighbor case, most studied.

Ground states:  $\sigma_{\Lambda}^{(+)}$  and  $\sigma_{\Lambda}^{(-)}$ ,

$$\sigma_{\Lambda}^{(+)}(x) = 1, \quad \sigma_{\Lambda}^{(-)}(x) = -1, \quad \text{for all } x \in \Lambda$$

$\sigma_{\Lambda}^{(\pm)}$  are not equilibrium states: minimize energy not free energy.

*Gibbs penalty.* Configurations  $\sigma_{\Lambda}$  have penalty  $e^{\beta H_{\Lambda}^{\text{per}}(\sigma_{\Lambda})}$

$\sigma_{\Lambda}$  has “weight”  $e^{-\beta H_{\Lambda}^{\text{per}}(\sigma_{\Lambda})}$ .

The energy  $E$  has then weight:

$$w(E) = \sum_{\sigma_{\Lambda}: H_{\Lambda}^{\text{per}}(\sigma_{\Lambda})=E} e^{-\beta E} =: e^{-\beta(E-S(E)/\beta)}$$

$S(E) = \log$  number of configs. with energy  $E$

Boltzmann hypothesis:  $S(E)$  entropy.

## Basic Postulate.

The thermodynamic pressure  $p_\beta$  is

$$p_\beta = \lim_{|\Lambda| \rightarrow \infty} \frac{\log Z_{\beta, \Lambda}}{\beta |\Lambda|}$$

where

$$Z_{\beta, \Lambda} = \sum_{\sigma_\Lambda} e^{-\beta H_\Lambda^{\text{per}}(\sigma_\Lambda)} = \textit{partition function}$$

Heuristic justification:

$$Z_{\beta, \Lambda} = \sum_E e^{-\beta(E - S(E)/\beta)} \approx \exp\{-\beta \inf_E [E - S(E)/\beta]\}$$

(since  $E$  and  $S(E)$  grow proportionally to  $|\Lambda|$ ).

Use thermodynamic relations.....

Definition. The fractional weight of  $\sigma_\Lambda$  is the Gibbs probability of  $\sigma_\Lambda$ :

$$G_{\beta,\Lambda}(\sigma_\Lambda) := \frac{e^{-\beta H_\Lambda^{\text{per}}(\sigma_\Lambda)}}{Z_{\beta,\Lambda}}$$

**Postulate 2.**  $\log G_{\beta,\Lambda}(\sigma_\Lambda)(\sigma_\Lambda \approx u)$  (i.e. the “Gibbs probability of the macrostate”  $u \in L^1(\Omega, [-1, 1])$ ) is minus the “excess free energy” of  $u$ .

$$\log G_{\beta,\Lambda}(\sigma_\Lambda \approx u) = \log Z_{\beta,\Lambda}(\sigma_\Lambda \approx u) - \log Z_{\beta,\Lambda}$$

$$Z_{\beta,\Lambda}(\sigma_\Lambda \approx u) = \sum_{\sigma_\Lambda \approx u} e^{-\beta H_\Lambda^{\text{per}}(\sigma_\Lambda)}$$

*Gibbs probability of a macrostate.*

$\Omega =$  unit torus in  $\mathbb{R}^d$ .

$\Lambda = \varepsilon^{-1}\Omega \cap \mathbb{Z}^d$ .

$r \in \Omega \mapsto$  window in  $\Lambda =$

$$\left\{ x \in \Lambda : |x - \varepsilon^{-1}r| \leq R \right\} = B_R(\varepsilon^{-1}r) \cap \mathbb{Z}^d$$

the *empirical magnetization profile* is the (random, i.e. it depends on  $\sigma_\Lambda$ ) function on  $\Omega$  :

$$u_{\varepsilon,R}(r; \sigma_\Lambda) := \frac{1}{|B_R|} \sum_{x \in B_R(\varepsilon^{-1}r) \cap \mathbb{Z}^d} \sigma_\Lambda(x)$$

*Gibbs probability of a macrostate  $u$  (with accuracy  $\zeta > 0$ ):*

$$G_{\beta, \Lambda} \left( \|u_{\varepsilon, R}(r; \cdot) - u\|_{L_1(\Omega)} < \zeta \right)$$

The excess free energy density of  $u$  is equal to

$$F^{\text{exc}}(u) := - \lim_{\zeta \rightarrow 0} \lim_{\varepsilon \rightarrow 0} \varepsilon^d \log G_{\beta, \Lambda} \left( \|u_{\varepsilon, R}(r; \cdot) - u\|_{L_1(\Omega)} < \zeta \right)$$

**Theorem.** There exists a convex function  $f_\beta(m)$  so that for any  $u \in L^1(\Omega)$ :

$$F^{\text{exc}}(u) := \int_{\Omega} \{f_\beta(u(r)) - \inf_{|m| \leq 1} f_\beta(m)\}$$

$\inf_{|m| \leq 1} f_\beta(m) = -p_\beta$ . The free energy density of  $u$  is

$$F(u) := \int_{\Omega} f_\beta(u(r))$$

*Phase transitions.*

In  $d \geq 2$  exists  $\beta_c > 0$  and  $m_\beta > 0$ ,  $\beta > \beta_c$ , so that  $f_\beta(m)$  is linear in the interval  $[-m_\beta, m_\beta]$ .

## Kawasaki dynamics

*Nearest neighbor sites  $x$  and  $y$  exchange their contents at rate*

$$c(x, y; \sigma_\Lambda) := e^{-\beta[H_\Lambda^{\text{per}}(\sigma_\Lambda^{x,y}) - H_\Lambda^{\text{per}}(\sigma_\Lambda)]/2}$$

$$\sigma_\Lambda^{x,y}(z) = \begin{cases} \sigma_\Lambda(z), & z \neq x, y \\ \sigma_\Lambda(x) & z = y \\ \sigma_\Lambda(y) & z = x \end{cases}$$

Gibbs measure invariant under Kawasaki dynamics.

$\beta = 0$ , infinite temperature, ideal gas.

*Stirring process: independently each pair of nearest neighbor sites exchange their contents at rate 1.*

Identify particles with spin 1 and absence of particles with spin  $-1$ .

*Isomorphic to Exclusion process: each particle independently of the others chooses at rate 1 a nearest neighbor site and jumps there if arrival site is empty.*

## Graphical Representation

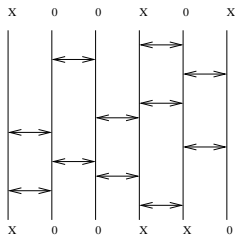


Figure: Time in vertical direction

Stirring process converges in “hydrodynamic limit” to:

$$\frac{dm}{dt} = \Delta m$$

Varadhan-Yau have proved convergence for  $\beta < \beta_c$  to

$$\frac{dm}{dt} = \nabla \left( D \nabla m \right)$$

Examples of convergence to free boundary problems for other models...

## Part II. Fluctuations.

Macroscopic fluctuations: prevent from being trapped in stationary non equilibrium states.

- Spinodal decomposition (escape from local maximum)
- Tunnelling and metastability (escape from local minimum)

Penalty functional to incorporate fluctuations in the macroscopic theory.

External magnetic field.  $f_\beta(m) \rightarrow f_{\beta,h}(m) := f_\beta(m) - hm$

$$F(m) \rightarrow F_h(m) := \int_{\Omega} f_{\beta,h}(m(r)), dr$$

$$\frac{dm}{dt} = -\nabla J, \quad J = -\chi(\nabla f'_\beta - \nabla h)$$

In general if  $E$  is an external field:

$$\frac{dm}{dt} = -\nabla J, \quad J := (-\chi \nabla f'_\beta + \chi E)$$

Environment can produce [random] forces on the system, their likelihood is ruled by a *Penalty functional*

$$\int_0^T \int_{\Omega} \chi E^2$$

Probability of a fluctuation  $m = m(r, t)$ ,  $r \in \Omega$ ,  $t \in [0, T]$  is:

$$P_T(m) := \inf_{E: E \rightarrow m} \int_0^T \int_{\Omega} \chi E^2$$

Current fluctuations. Recall:  $J = -\chi(\nabla f'_\beta - E)$

$$A_T(j) := \inf \left\{ P_T(m) \mid \int_0^T \int_\Omega J = jT|\Omega| \right\}$$

Existence of limit  $T \rightarrow \infty$ . “Dynamical phase transitions”, minimizers are not constant in time and/or space.