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Microstructures and Phase Transitions (*)

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Abstract. – *This is a short survey on some recent developments in the theory of phase transitions and microstructures in a mathematically rigorous context. The issue is discussed at the microscopic, mesoscopic and macroscopic levels recalling the most used mathematical techniques, mainly from probability theory and variational calculus.*

1. – Introduction

I have been working in the last years on some problems related to phase transitions and microstructures and I will try in these notes to give an idea of the state of the art in this field at least from my very personal perspective.

Maybe the best way to introduce the issues is by discussing some simple examples. The "microstructures" mentioned in the title refer to phenomena where the competition between forces acting on very different scales gives rise to "fast oscillations", microstructures. The following example is borrowed from lectures by Stefan Müller on elasticity, it explains the issue very nicely. The problem is to minimize the functional

$$F(u) = \int_0^1 \left\{ \left(\left(\frac{du}{dx} \right)^2 - 1 \right)^2 + u^2 \right\} dx \tag{1.1}$$

$F(u)$ describes a competition between $\dfrac{du}{dx}$ which wants to be equal to ± 1 and u^2 which instead wants $u = 0$. The two requests are obviously incompatible but a good compromise can be reached because the two "act on very different scales", the integral of u^2 is on "scale 1" the derivative instead depends on the "infinitesimal variations" of u. This can be exploited by taking functions u which are always close to 0 but have derivative equal to ± 1, as for instance a function u which oscillates between $-\varepsilon$ and $+\varepsilon$ with slopes ± 1. The inf of $F(u)$ on such functions is 0 (by letting $\varepsilon \to 0$), thus F has infimum equal to 0 and no minimum.

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The infimum is described by minimizing sequences as those introduced above which are examples of microstructures, in this case the oscillations do not have a definite scale as they become infinitely fast (as $\varepsilon \to 0$).

The other main issue in these lectures is about phase transitions. This is one of the most significant achievements of modern science which settles an old philosophical dispute: gas, liquid and solid are only accidental attributes of matter, a same substance (same atoms and molecules) may appear in the solid liquid or vapor phase by changing the external conditions; you may change dress but you are still the same person.

I will restrict to a very special class of phase transitions, technically "phase transitions of first order with order parameter the [mass] density". This simply means that there is a "forbidden interval" of densities, say (ρ', ρ''), so that if we put a mass $\rho|\Lambda|$ of fluid in the region Λ ($|\Lambda|$ the volume of Λ) with $\rho \in (\rho', \rho'')$, ("canonical constraint"), then the fluid separates into a part with density ρ' and another one with density ρ''. It does not exist an equilibrium state with homogeneous density ρ. (ρ' and ρ'' play the role of the slopes ± 1 in the Müller example). Thus if we "move in Λ" we go from one phase (with density ρ') to another phase (with density ρ''), hence we see a "phase transition".

How fragmented are the phases? In most cases, due to surface tension, the fragmentation is minimal (compatibly with the canonical constraint of a given mass), with many results on the optimal shape of the interface, the so called Wulff shape problems. However there are cases where other forces than surface tension enter into play and it may then happen that the interface "disintegrates" into very many small pieces, this is the microstructures regime.

The existence of a forbidden interval is related to a lack of convexity (at least in all the cases that we shall consider here). Let us examine a simple example which, as before, involves a functional, the Ginzburg-Landau functional. Let Λ be a torus in $\mathbb{R}^d$, u a non negative, smooth function on Λ and

$$F^{\rm gl}_\Lambda(u) = \int_\Lambda \{W(u(r)) + |\nabla u(r)|^2\} dr \tag{1.2}$$

$F^{\rm gl}_\Lambda(u)$, the Ginzburg-Landau functional, is interpreted as the free energy of the density profile u. We suppose W a double well, more precisely that W is smooth and that there is an interval (ρ', ρ'') where the convexification W^{**} of W is strictly smaller than W, while elsewhere they are equal to each other. As we shall see (ρ', ρ'') is the forbidden interval in a phase transition.

By thermodynamic principles the equilibrium free energy density is obtained by minimizing the free energy functional in regions so large that surface effects are negligible. We thus postulate that the free energy density $\Phi(\rho)$ when the mass density is $\rho \in \mathbb{R}_+$ is

$$\Phi(\rho) = \liminf_{|\Lambda| \to \infty} \Phi_\Lambda(\rho), \quad \Phi_\Lambda(\rho) = \inf \left\{ \frac{F^{\mathrm{gl}}_\Lambda(u)}{|\Lambda|} \;\middle|\; \int_\Lambda u = \rho|\Lambda| \right\} \tag{1.3}$$

The free energy $f_\Lambda(s)$ of a homogeneous density profile with density s is

$$f_\Lambda(s) = F^{\mathrm{gl}}_\Lambda(s\mathbf{1}_\Lambda) = |\Lambda| W(s)$$

which is not a convex function of s. If in (1.3) $\rho \in (\rho', \rho'')$ the phase transition picture suggests that the true free energy density is $W(\rho')p + W(\rho'')(1-p)$, p such that $\rho = p\rho' + (1-p)\rho''$, because the parts of the fluid with density ρ' and ρ'' carry a free energy density equal to $W(\rho')$ and respectively $W(\rho'')$, and their volume fractions are p and $1-p$ (as imposed by the mass constraint). Since $W^{**}(\rho) = W(\rho')p + W(\rho'')(1-p)$, consistency of the above requires that:

THEOREM. – $\Phi(\rho) = W^{**}(\rho)$.

PROOF. – See for instance [7], here we just give a sketch.

Lower bound: $F^{\mathrm{gl}}_\Lambda(u) \geq \int_\Lambda W^{**}(u) \geq |\Lambda| W^{*}(\rho)$. where ρ: $\int_\Lambda u = \rho|\Lambda|$ (to derive the first inequality the gradient term in (1.2) has been dropped and W bounded from below by W^{**}; the last inequality follows from the Jensen inequality as W^{**} is convex).

Upper bound. If $\rho \notin (\rho', \rho'')$ take $u = \rho\mathbf{1}_\Lambda$. If instead $\rho = p\rho' + (1-p)\rho''$, $p \in (0,1)$, construct a minimizing sequence by taking a regularization (with the required mass $\rho|\Lambda|$) of the function $\rho'\mathbf{1}_{\Lambda'} + \rho''\mathbf{1}_{\Lambda''}$ where Λ' is (for instance) a rectangle in Λ and Λ'' its complement (such that $|\Lambda'|/|\Lambda| = p$). ☐

This suggests that the appearance of a forbidden density interval is caused by the "homogeneous profiles free energy density" developing a concavity, so that free energy decreases by fragmentation. While this is exactly what we have seen in the above example, much less clear is how it translates in atomistic models of fluids. I will try to do that starting in the next section from the analysis of phase transitions at 0 temperature, where the theory is supported by mathematical proofs.

From Section 3 on we study positive temperatures. I will first recall the definition of Gibbs measures (which are postulated to be the equilibrium states in the statistical mechanics theory) and then see what phase transitions should look like in such a context, the conditional tense because a mathematical proof is still lacking and is, in my view, among the most important open problems in statistical mechanics.

A deep insight on phase transitions came from the van der Waals theory of the liquid-vapor transition, and many of its ideas are still actual today. The van der Waals theory, outlined in Section 3, does not fit into the Gibbs formalism and in the 60's there have been works to derive it from statistical mechanics models. Kac introduced his famous Kac potentials and the analysis was then extended by Lebowitz and Penrose with coarse graining and renormalization group ideas. All that is sketched in Section 4 where it is shown that non local versions of the Ginzburg-Landau functional describe (approximately) the Gibbs measures after coarse graining. This is an important step as it establishes a bridge with continuum theories and opens the way to the use of variational techniques.

In this way the van der Waals theory has been derived from statistical mechanics, but the derivation involves a scaling limit where the range of the interparticles interaction diverges while its strength vanishes (keeping fixed the interaction energy per particle). By taking first the thermodynamic limit (i.e. the domain where the system is confined invades the whole space) and then the above scaling limit, it was proved that the equation of state of the fluid is like in the van der Waals theory. However such an equation of state does not refer to any particle system, it is only the limit of equations of state of particle models and it is not clear whether it is of van der Waals type even before the limit. This has been proved for some special versions of Kac potentials as discussed in Section 5. Variants of the model and conjectures on their behavior are presented in Section 6. In Section 7 we shall briefly discuss interfaces, their optimal shape (the Wulff problem) and the case of microstructures when the interface breaks into many small pieces.

2. – Zero Temperature

We shall consider a system of point particles in $\mathbb{R}^d$, restricting to $d = 2$ because it is significantly simpler than $d = 3$ and yet rich of interesting features. Our analysis will be in the framework of classical mechanics neglecting all quantum effects: they are indeed very relevant at low temperatures and hence we are far from realistic in this section which deals with systems at 0 temperature. Reason is twofold, this is an introductory chapter to phase transitions at higher temperatures and, secondly, we want to keep the analysis as simple as possible.

As mentioned our systems are made of identical point particles which interact pairwise via a potential repulsive at the origin and with an attractive tail at large distances, the prototype is the Lennard-Jones potential

$$V(R) = aR^{-12} - bR^{-6}, \quad a, b > 0 \tag{2.1}$$

so that the energy of the particles configuration $q = (q_1, \dots, q_n)$, $n \in \mathbb{N}$, $q_i \in \mathbb{R}^d$, is

$$H(q) = \frac{1}{2}\sum_{i \neq j} V(|q_i - q_j|) \tag{2.2}$$

$H(q)$ is invariant under permutations of q, i.e. it does not depend on the labels of the particles which are considered as undistinguishable.

The positive divergence of V at the origin ensures stability of matter (i.e. the energy per particle is bounded from below). If on the contrary the interaction was negative and bounded away from zero in a neighborhood of the origin then by putting all the particles of q in that set we would get $H(q) \leq -c|q|^2$ so that the energy per particle $H(q)/|q|$ would diverge to $-\infty$ and matter would not be stable. The attractive tail of the Lennard-Jones potential is instead responsible for the occurrence of a phase transition, as we shall see.

The basic axiom of equilibrium statistical mechanics at 0 temperature is that the equilibrium states are "ground states" namely configurations which minimize the energy (velocities are thus set equal to 0 and particles configurations will be described only by the positions of the particles). Our aim in this section is to prove that the ground state energy density, defined next, has a phase transition in the sense discussed in the introduction.

DEFINITION. – The ground state energy $e(\rho)$. *Let Λ be a torus in $\mathbb{R}^d$ (eventually $d = 2$), $|\Lambda|$ its volume, $\mathcal{X}_\Lambda$ the space of configurations q with all particles in Λ and $\mathcal{X}_{\Lambda,n}$ the subset of $q \in \mathcal{X}_\Lambda$ such that $|q| = n$, $|q|$ the number of particles in q. Set*

$$e\left(\frac{n}{|\Lambda|}; \Lambda\right) = \inf_{q \in \mathcal{X}_{\Lambda,n}} \frac{H(q)}{|\Lambda|} \tag{2.3}$$

and, for any $\rho > 0$ and any increasing sequence of tori Λ,

$$e(\rho) := \liminf_{\Lambda \to \mathbb{R}^d; n/|\Lambda| \to \rho} e\left(\frac{n}{|\Lambda|}; \Lambda\right) \tag{2.4}$$

THEOREM. – *$e(\rho)$ is a continuous, convex function of $\rho \in \mathbb{R}_+$ and the liminf in* (2.4) *is actually a limit.*

The proof of the theorem is omitted, see [46] for the proof of an analogous statement at positive temperatures.

Equilibrium states are minimizers of the energy (at given density and in a given region Λ) and, for what said in the introduction, a phase transition should correspond to minimizers of $e(\rho; \Lambda)$ which are not spatially "homogeneous". It is not obvious what "homogeneous" means for a particles configuration, in general the notion requires the use of "coarse graining" with a transition to a continuum description. In the particular case of zero temperature we can make the ansatz that the relevant homogeneous configurations are lattice configurations; moreover, supposing that lattice ground states want to maximize the number of nearest neighbors (n.n.) of a site, and recalling that we are in $d = 2$ dimensions, we restrict to triangular lattice configurations, denoted by $\mathbb{T}_R$, R the lattice mesh.

Define

$$e_T(\rho) := \lim_{\Lambda \to \mathbb{R}^d} \frac{H(\mathbb{T}_{R(\rho)} \cap \Lambda)}{|\Lambda|}, \quad R(\rho) := \lim_{\Lambda \to \mathbb{R}^d} \frac{|\mathbb{T}_{R(\rho)} \cap \Lambda|}{|\Lambda|} = \rho \tag{2.5}$$

THEOREM. – *There are a' and b' both strictly positive so that*

$$e_T(\rho) = a'\rho^7 - b'\rho^4 \tag{2.6}$$

PROOF. – It is readily seen from (2.5) that, supposing $0 \in \mathbb{T}_R$,

$$e_T(\rho) = \frac{\rho}{2} \sum_{x \in \mathbb{T}_{R(\rho)}} V(|x|) \tag{2.7}$$

In fact the r.h.s. is the product of the density ρ times the energy per particle, i.e. $1/2$ the interaction energy of the particle at the origin with all the others. The factor $1/2$, also present in (2.2) is to avoid counting twice a same pair of particles.

To compute the r.h.s. of (2.7) we use a scaling argument:

$$\sum_{x \in \mathbb{T}_R} V(|x|) = \frac{aR^{-12}}{2} \sum_{x \in \mathbb{T}_1} |x|^{-12} - \frac{bR^{-6}}{2} \sum_{x \in \mathbb{T}_1} |x|^{-6} \tag{2.8}$$

hence (2.6) after observing that $R(\rho) = c'\rho^{-1/2}$, $c' > 0$. □

$e_T(\rho)$ is not convex, its graph and the graph of its convexification $e_T^{**}(\rho)$ are as in Figure 1.

Fig. 1. – $e_T(\rho)$ and $e_T^{**}(\rho)$ (dashed line) differ in $(0, \rho_c)$.

In the interval $(0,\rho_c)$ (where $e_T^{**}(\rho)<e_T(\rho)$)

$$e_T^{**}(\rho) = e_T(\rho_c)\frac{\rho}{\rho_c} < e_T(\rho) \tag{2.9}$$

ρ_c is the point where $e_T(\rho)$ and $e_T^{**}(\rho)$ are equal and have the same derivative:

$$\frac{e_T(\rho_c)}{\rho_c} = e'_T(\rho_c) \tag{2.10}$$

Since $e(\rho)$ (defined in (2.4)) is convex and $e(\rho) \le e_T(\rho)$ then $e(\rho) \le e_T^{**}(\rho)$, so that by (2.9) $e_T(\rho) > e(\rho)$ in $(0,\rho_c)$ which proves that $\mathbb{T}_R(\rho)$ is not a ground state when $\rho \in (0,\rho_c)$. Let $\Delta = \Delta(\Lambda,\rho)$ be a cube such that $|\Delta|/|\Lambda| = \rho/\rho_c$, then by (2.9)

$$e_T^{**}(\rho) = \lim_{|\Lambda|\to\infty} \frac{H\big(\mathbb{T}_{R(\rho_c)} \cap \Delta(\Lambda,\rho)\big)}{|\Lambda|}, \quad \rho \in (0,\rho_c) \tag{2.11}$$

where $\Delta = \Delta(\Lambda,\rho)$ is a cube such that $|\Delta|/|\Lambda| = \rho/\rho_c$. Namely $e_T^{**}(\rho)$ can be approximated in a large box Λ by putting a triangular lattice configuration with mesh $R(\rho_c)$ in a fraction $\frac{\rho}{\rho_c}|\Lambda|$ of the box and nothing else in the complement. To prove (2.11) we observe that the error in energy goes like the surface, i.e. as $|\Lambda|^{(d-1)/d}$, and since in (2.11) we divide by $|\Lambda|$, the error goes like $|\Lambda|^{-1/d}$ and thus vanishes in the limit.

The above would prove that the system has a phase transition if we knew that $e_T^{**}(\rho)$ is indeed equal to the ground state energy $e(\rho)$. In principle the true ground state energy could be attained at completely different configurations than the triangular ones considered so far. That this is not the case has been proved by Theil, [49], as we are going to discuss. Theil studies the energy per particle rather than the energy per volume:

$$E := \liminf_{n\to\infty} E_n, \quad E_n := \inf_{q:|q|=n} \frac{H(q)}{|q|} \tag{2.12}$$

and he has proved that:

THEOREM 2.1. – *For a class of potentials (of Lennard-Jones type)* $E = \dfrac{e_T(\rho_c)}{\rho_c}$, ρ_c *as in* (2.10).

REMARK. – By (2.10) the inf of $\dfrac{e_T(\rho)}{\rho}$ is attained at ρ_c so that $E = \inf\left\{\dfrac{e_T(\rho)}{\rho}\right\}$.

COROLLARY. – $e(\rho) = e_T^{**}(\rho)$, $\rho \in (0,\rho_c)$, so that $e(\rho)$ is the limit as $|\Lambda| \to \infty$ of energies of triangular lattice configurations with density ρ_c in suitable subsets of Λ as in the r.h.s. of (2.11).

PROOF. – We have already seen (after (2.10)) that $e(\rho) \le e_T^{**}(\rho)$. Suppose by contradiction that there is $\rho' \in (0, \rho_c)$ such that

$$e(\rho') < e_T^{**}(\rho') = e_T(\rho_c)\frac{\rho'}{\rho_c}$$

Then $E' = \dfrac{e(\rho')}{\rho'} < E$ while by Theil's theorem $E' \ge E$ because if $q^{(i)}$ is a minimizing sequence for (2.4) then

$$\lim_{i\to\infty} \frac{H(q^{(i)})}{|q^{(i)}|} = E' \qquad \square$$

A physical interpretation of the above is as follows. Suppose we have a region Λ which contains exactly a subset of the triangular configuration with density $\rho > \rho_c$. To decrease the density we may dilate Λ by pulling outwards its boundaries. The triangular lattice in Λ then stretches uniformly to a larger mesh. However when we are past the critical density ρ_c the triangular configuration becomes unstable and eventually it "breaks" by shrinking to a triangular configuration with the smaller mesh $R(\rho_c)$ and a fraction of Λ is left empty.

Earlier results, [45], [27], refer to more special interactions; a more recent paper, [50], studies the optimal shape, Wulff shape, of the crystal with a finite number of particles, see also the notes by G. Friesecke available at
http://www.acmac.uoc.gr//CKM2011/talks/Friesecke.pdf

3. – Gibbs measures and the van der Waals theory

The idea behind the theory of equilibrium states at positive temperatures is that energy levels higher than the ground state energy may be favored by the larger number of configurations where they are attained. Following Boltzmann, volumes in phase space are related to thermodynamic entropy which leads to the well known competition between energy and entropy with the minimization of the free energy $f = e - Ts$. All these ideas are contained in the Gibbs formula on which modern equilibrium statistical mechanics is based, as the main postulate of the theory is that the equilibrium states are described by Gibbs measures.

DEFINITION. – *The canonical Gibbs measure for a system of N particles in the torus Λ is the probability on Λ^N defined by the formula*

$$\mu_{\Lambda,\beta,N}(dq) = Z^{-1}_{\Lambda,\beta,N} e^{-\beta H(q)} \mathbf{1}_{q\in\Lambda^N} \frac{dq}{N!}, \quad \beta = \frac{1}{kT} \tag{3.1}$$

where $dq = dq_1 \cdots dq_N$ is the Lebesgue measure on $\mathbb{R}^N$ and $Z_{\Lambda,\beta,N}$, the canonical *partition function, is the normalizing factor; k is the Boltzmann constant and (by an abuse of language)* β *is the inverse temperature.*

The $N!$ in (3.1) is redundant as it simplifies with the one in $Z_{\Lambda,\beta,N}$. It is added to remind that particles are identical so that the $N!$ configurations which differ from each other by a permutation of the labels are counted only once. The $N!$ becomes important when identifying the thermodynamic potentials which is the content of the second postulate in the theory:

DEFINITION. – *The thermodynamic free energy density* $f_\beta(\rho)$ *is identified to*

$$f_\beta(\rho) = - \lim_{\Lambda \to \mathbb{R}^d, N/|\Lambda| \to \rho} \frac{1}{\beta|\Lambda|} \log Z_{\Lambda,\beta,N} \tag{3.2}$$

where $Z_{\Lambda,\beta,N} = \int_{\Lambda^N} e^{-\beta H(q)} \frac{dq}{N!}$.

(3.2) establishes a bridge between intermolecular forces and thermodynamic potentials which is by now well established and accepted. It is a theorem (among the most significant in statistical mechanics) that the thermodynamic potentials defined in this way do satisfy the thermodynamic principles, see for instance the Ruelle's basic book, [46].

It readily follows from (3.1) that if $T \to 0$ (hence $\beta \to \infty$) the Gibbs measure in the limit is supported by configurations with minimal energy, hence:

CONJECTURE. – If $d \geq 2$ then for all β large enough there is a "forbidden interval" $(\rho'_\beta, \rho''_\beta)$ with $(\rho'_\beta, \rho''_\beta) \to (0, \rho_c)$ as $\beta \to \infty$, ρ_c as in Theorem 2.1.

Of course the conjecture remains empty till we specify the meaning of a forbidden interval of densities. The definition involves a coarse graining and it is given next.

Let $\pi^{(\ell)}$, $\ell > 0$, be a partition of $\mathbb{R}^d$ into cubes of side ℓ. We then associate to a configuration q the function

$$\rho^{(\ell)}(r; q) = \frac{|q \cap C_r^{(\ell)}|}{\ell^d} \tag{3.3}$$

where $|q \cap C_r^{(\ell)}|$ is the number of particles of the configuration q which are in the cube of the partition $\pi^{(\ell)}$ which contains the point r, this cube denoted by $C_r^{(\ell)}$. $\rho^{(\ell)}(r; q)$ is evidently constant on the cubes of $\pi^{(\ell)}$ and is therefore "$\pi^{(\ell)}$-measurable". It is the local density in the configuration q measured with mesh ℓ.

$(\rho'_\beta, \rho''_\beta)$ is called a forbidden interval if for any $\rho \in (\rho'_\beta, \rho''_\beta)$ the following happens. For any $\varepsilon > 0$ there is ℓ_ε and for any $\ell > \ell_\varepsilon$ the following picture holds whenever Λ is large enough. Let N be the integer part of $\rho|\Lambda|$ and $\mu \equiv \mu_{\Lambda,\beta,N}$. Then there is a "nice set" $G \subset \mathcal{X}_{\Lambda,N}$, $\mu[G] > 1 - \varepsilon$, so that if $q \in G$ then $\rho^{(\ell)}(r; q)$,

$r \in \Lambda$, has either values in $[\rho'_\beta - \varepsilon, \rho'_\beta + \varepsilon]$ or $[\rho''_\beta - \varepsilon, \rho''_\beta + \varepsilon]$ except for r in a set which has Lebesgue measure $\le \varepsilon|\Lambda|$.

In $d = 1$ there is no phase transition for a large class of systems (see for instance [43] for a proof in the Ising system). It is also known that in all dimensions forbidden intervals must be away from 0 ($\rho'_\beta > 0$), see for instance [46], but there is no proof that for Lennard-Jones or Lennard-Jones type of potentials that a forbidden interval actually esists. This is in my view one of the most important open problems in statistical mechanics.

There are however proofs of existence of forbidden intervals for the lattice gas (if particles are constrained to be on a lattice with at most one particle per site) and for more general lattice spin systems (in particular for the the Ising model) the key words being Peierls estimates and Pirogov-Sinai theory, see for instance [47], [51] and [39].

By integrating $\mu = \mu_{\Lambda,\beta,N}$ in (3.1) over the region

$$\bigcup_{E \in dE} \{q \in \mathcal{X}_{\Lambda,N} : H(q) = E\}$$

we obtain the probability $\mu(dE)$ of having energy values in the interval dE. Under some regularity properties on H this measure has a density:

$$\mu(dE) = Z^{-1} e^{-\beta E} D(E) dE \tag{3.4}$$

$D(E)dE$ is the Lebesgue volume of phase space where the energy is dE. Boltzmann's famous formula states that the thermodynamic entropy $S(E)$ is equal to

$$S(E) = k \log D(E) \tag{3.5}$$

(3.4) then reads as:

$$\mu(dE) = Z^{-1} e^{-\beta(E - TS(E))} dE = Z^{-1} e^{-\beta|\Lambda|(e - Ts(E))} |\Lambda| de \tag{3.6}$$

$e = E/|\Lambda|$ $s(E) = S(E)/|\Lambda|$ the energy and entropy densities. We are thus reduced to the analysis of the free energy $e - Ts(E)$ and due to the presence of the large factor $|\Lambda|$ the relevant part of the measure will be concentrated around its minimizers. In particular this suggests that

$$\lim_{|\Lambda| \to \infty} \frac{\log Z_{\Lambda,\beta,N}}{|\Lambda|} = \sup_e \{-\beta(e - Ts(E))\} \tag{3.7}$$

(3.7) is indeed theorem (valid for a large class of interactions, see [46]) known as "equivalence of ensemble" (here the equivalence is between "the microcanonical and canonical ensembles"). By the second postulate which relates the l.h.s. of (3.7) to the free energy density, see (3.2), (3.7) shows that entropy and free energy are related via a Legendre transform in agreement with the laws of thermodynamics.

Thus the second postulate which identifies the free energy is equivalent to the Boltzmann formula for the entropy. While theoretically important this representation of the Gibbs measure has little practical consequences, the major difficulty is to handle surfaces of constant energy, which enter in the computation of the entropy $S(E)$, a task which has so far eluded all attempts due to the complexity of the interactions among all the particles.

The problem drastically simplifies if we change hamiltonians. Let us start from mean field.

3.1 – *The mean field theory*

In mean field the Lennard-Jones interaction is replaced by a constant potential where the constant depends on the region where the system is confined:

$$V(q_i, q_j) = -\frac{J}{|\Lambda|}, \; J > 0; \quad H(q) = -\frac{J}{2|\Lambda|}|q|\big(|q|-1\big) \tag{3.8}$$

Since the energy depends only on the particle numbers the sets of phase space with constant energy are the same as those with given number of particles and thus easy to compute. Before doing that a few remarks on (3.8).

To explain the prefactor $|\Lambda|$ observe that the interaction of a particle with all the others is $-J(N-1)/|\Lambda| \approx -J\rho$ and thus bounded as desired. With (3.8) we are considering only the contribution of the long, slowly varying attractive tail of the interaction, which justifies neglecting the actual position of the particles so that each one interacts almost equally with any other one.

The mean field partition function is:

$$Z^{\mathrm{mf}}_{\Lambda,\beta,N} = e^{\beta JN(N-1)/(2|\Lambda|)}\,\frac{|\Lambda|^N}{N!} \tag{3.9}$$

Hence, after using the Stirling formula for $N!$, we get from (3.2) and (3.9)

$$f^{\mathrm{mf}}_\beta(\rho) = -\frac{J}{2}\,\rho^2 + \frac{\rho}{\beta}\Big(\log\rho - 1\Big) \tag{3.10}$$

which is physically a nonsense ! In fact $f^{\mathrm{mf}}_\beta(\rho)$ is not a convex function of ρ, as it should in a theory compatible with thermodynamic principles, and moreover it is not even possible to convexify it, as $\inf f^{\mathrm{mf}}_\beta(\rho)/\rho = -\infty$: matter is unstable if the energy per particle is unbounded from below, the entropy term $\rho\log\rho$ cannot contrast the $-\rho^2$ energy as $\rho \to \infty$.

The origin of the problem goes back to the initial assumption (3.8) where the energy keeps only the attractive part of the Lennard-Jones interaction and drops the short range repulsive part, which is in fact essential to ensure stability. A way to take it into account in a simple way (but not so simple in the end) is to suppose that particles are not points but small hard spheres (of radius R) which cannot overlap with each other. Then (3.9) is replaced by

$$Z^{\mathrm{mf,R}}_{\Lambda,\beta,N} = e^{\beta JN(N-1)/(2|\Lambda|)} \int_{\Lambda^N} \Big\{ \prod_{i\neq j} \mathbf{1}_{|q_i-q_j|>2R} \Big\} \frac{dq}{N!} \tag{3.11}$$

The problems we had in (3.10) are now absent because the density is bounded but the analysis of the integral in (3.11) is far from trivial.

3.2 – *The van der Waals theory.*

Van der Waal proposed a theory for the liquid-vapor transition which is mean field with an approximation to (3.11), thus it is based on the following two assumptions:

- *Energy.* The energy $H(q)$, $q \in \mathcal{X}_\Lambda$, is only a function of the number of particles $|q|$ in q and of the volume $|\Lambda|$, in particular $H(q) = -J\frac{|q|^2}{2|\Lambda|}$, $J > 0$
- *Phase space volumes.* The Lebesgue phase space volume of a system with N particles is $(|\Lambda| - Na)^N$, $a > 0$.

Van der Waals explains the parameter a as the volume "occupied" by a particle, thus if there are N particles the volume they occupy is Na, hence $Na < |\Lambda|$. The volume "left free" is $|\Lambda| - Na$ and the second assumption argues that the system behaves as if each particle is free to move (independently of the others) in the free volume. $(|\Lambda| - Na)^N$ is a crude approximation of the integral in (3.11) (yet it is correct in $d = 1$ dimensions). It has the advantage of providing an explicit expression to the entropy which is

$$S(\rho) = k \log \Big\{ \frac{1}{N!} (|\Lambda| - Na)^N \Big\}, \quad \rho = \frac{N}{|\Lambda|} \tag{3.12}$$

Writing $E - TS = |\Lambda| f(\rho)$ and using the Stirling formula we get in the limit $|\Lambda| \to \infty$

$$f(\rho) = -\frac{J}{2}\rho^2 - \frac{1}{\beta}\Big(-\rho(\log\rho - 1) + \rho\log(1 - \rho a)\Big) \tag{3.13}$$

which like in (3.10) is not convex but instead is stable, i.e. it has a well defined convexified, as we are going to discuss.

In thermodynamics the chemical potential λ is defined as $\lambda = \frac{df(\rho)}{d\rho}$ and by the second principle of thermodynamics it should be a non decreasing function of ρ. Instead its graph is as in Figure 2.

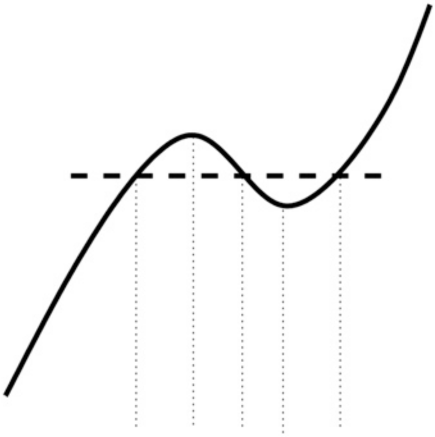

Fig. 2. – λ as a function of ρ.

As a remedy Maxwell proposed to modify this graph by cutting along the dashed line so that the parts above and below the dashed line have the same area. This is the famous "Maxwell equal area rule" which is equivalent to replace $f(\rho)$ by $f^{**}(\rho)$, the convexification of $f(\rho)$.

With the van der Waals plus thre Maxwell equal area rule theory we have recovered what found at 0 temperature with the energy replaced by the free energy. There are however three main drawbacks in the theory:

- The interaction between two particles depends on the region Λ where the system is and moreover it vanishes as $|\Lambda| \to \infty$.
- The phase space volume in the second van der Waals assumption is only an approximation, the correct expression is the one in (3.11)
- The Maxwell equal area rule is an ad hoc prescription, it should instead be derived from within the theory, as in the zero temperature case

4. – Kac potentials and free energy functionals

The problem of deriving the van der Waals theory in a statistical mechanics framework was solved in the 60's with the works of Kac, Uhlenbeck and Hemmer, [29], [30], [31], followed by those of Lebowitz and Penrose, [35], and Gates and Penrose, [17], [18], [19], see also the more recent [32].

A very short summary of these results is presented here, in a form useful for the sequel but not always historically accurate. With this in mind we may say that Kac basic idea is to relax the mean field assumption to a local condition. Write the hamiltonian in the form $H(q) = \int e(r;q)dr$ thus interpreting $e(r;q)$ as the energy density at r when the particles configuration is q.

- *Local mean field.* Kac shifts the assumption from the total energy H to the local energy density $e(r;q)$ by assuming that the latter depends only on the "local particles density $\rho(r;q)$" at r (which will be defined next). By an abuse of notation we write $e(\rho(r;q))$ for $e(r;q)$.

- *Local particles density.* A choice (others, more convenient, will be discussed later on) is

$$\rho(r;q) := \frac{|q \cap B_{\gamma^{-1}}(r)|}{|B_{\gamma^{-1}}(r)|} \tag{4.1}$$

$B_{\gamma^{-1}}(r)$ the ball of radius γ^{-1} and center r; $|B_{\gamma^{-1}}(r)| = \gamma^{-d}|B_1|$ its volume ($|B_1|$ the volume of the unit ball). Observe that if we replace $B_{\gamma^{-1}}(r)$ by Λ we are back to mean field.

- *The hamiltonian $H_\gamma(q)$.* Being the integral of the energy density is:

$$H_\gamma(q) = \int e\big(\rho(r,q)\big)dr \tag{4.2}$$

By taking the Kac scaling parameter γ small the system looks like mean field and since mean field has a phase transition we may hope to prove in this way that there is a phase transition as well for the system with $\gamma > 0$ sufficiently small, or in the limit $\gamma \to 0$.

- *Choice of the energy density.* Kac choice is $e(\rho) = -\dfrac{\rho^2}{2} - \lambda\rho$ (we are here including the chemical potential in the energy). The energy per particle $e(\rho)/\rho$ is in this way unbounded from below, same problem as in the van der Waals theory which Kac solves in the same way:

- *Hard cores.* To ensure stability, the phase space is restricted to configurations q such that for all pairs q_i, q_j of particles in q, $|q_i - q_j| > 2R$, $R > 0$ the "hard core radius". We may as well say that we have added a pair interaction which is $= \infty$ if $|q_i - q_j| \le 2R$ and $= 0$ otherwise. A system of particles with such an interaction is called the "gas of hard spheres".

Before proceeding with the theory it is convenient to generalize the definition of the local particle density $\rho(r;q)$ as

$$\rho(r;q) = J_\gamma * q(r) := \sum_{q_i \in q} J_\gamma(r, q_i), \quad r \in \mathbb{R}^d \tag{4.3}$$

(4.1) is a particular case of (4.3) with $J_\gamma(r,r') = \dfrac{\mathbf{1}_{|r-r'|\le\gamma^{-1}}}{|B_{\gamma^{-1}}(r)|}$. It is in fact convenient to have $J_\gamma(r, r')$ smooth rather than discontinuous as in (4.1). We keep however the same scaling dependence on γ and set

$$J_\gamma(r, r') = \gamma^d J(\gamma r, \gamma r') \tag{4.4}$$

where $J(r, r')$ is a symmetric, translation invariant ($J(r, r') = J(0, r' - r)$) smooth probability kernel which vanishes when $|r - r'| \geq 1$. Observe that by definition

$$\int J_\gamma(r, r') dr' = \int J(r, r') dr' = 1 \tag{4.5}$$

so that the sum in (4.3) is the empirical density of q around a point r, weighted with the probability kernel J_γ (which therefore involves the particles of q which are in a ball of radius γ^{-1} and center r).

Reduction to pair interactions. The definition of the model is now complete. It can however be reformulated in the more familiar context of pair interactions. We get in fact from (4.2)

$$H_\gamma(q) = -\frac{1}{2} \sum_{i \neq j} V_\gamma(q_i, q_j) - \lambda' |q| \tag{4.6}$$

where $\lambda' = \lambda + \sum_{q_i} V_\gamma(q_i, q_i)$ and

$$V_\gamma(q_i, q_j) = \int J_\gamma(r, q_i) J_\gamma(r, q_j) dr = (J_\gamma * J_\gamma)(q_i, q_j) \tag{4.7}$$

Thus $V_\gamma = J_\gamma * J_\gamma$, the convolution of J_γ with itself: it then follows that the interactions V_γ in the theory we have presented are positive operators (while in the original Kac formulation they could be arbitrary). Observe that the the interaction range is $2\gamma^{-1}$ and that $\lambda' \to \lambda$ as $\gamma \to 0$.

The Lebowitz-Penrose approach to Kac potentials uses ideas from renormalization group. The basic step of renormalization group is to coarse grain the Gibbs measure with a given hamiltonian on some scale and find the corresponding effective hamiltonian. This defines a map from hamiltonians to hamiltonians and its iterations define the renormalization group. The scheme is the following.

- Introduce a family of partitions $\pi^{(\ell)}$ of $\mathbb{R}^d$ into cubes of side $\ell = 2^k$, $C_r^{(\ell)}$ being the element of the partition containing a point $r \in \mathbb{R}^d$. The partitions are chosen so that each one refines the next one, in the sense that each cube in $\pi^{(2\ell)}$ is union of cubes of $\pi^{(\ell)}$.
- Given ℓ denote by N_r, $r \in \mathbb{R}^d$, a non negative integer valued function measurable on $\pi^{(\ell)}$, i.e. constant on each cube of $\pi^{(\ell)}$.
- The effective hamiltonian $H_{\text{eff}}^{(\ell)}$ on the scale ℓ is (modulo an additive con-

stant) $H_{\text{eff}} = -\beta^{-1}\log\mu(\{N_r\})$, $\mu(\{N_r\})$ the Gibbs probability that in each $C_r^{(\ell)}$ there are N_r particles.

The computation of $H_{\text{eff}}^{(\ell)}$ is usually very hard, but it becomes easy for Kac potentials, at least on scales $1 \ll \ell \ll \gamma^{-1}$. By the smoothness of J_γ the Kac energy is quite insensitive to variations of the positions of the particles inside a cube $C_r^{(\ell)}$ (as J_γ varies in the cube at most by $c\gamma\ell$) and to a first approximation we can replace q by $\rho^{(\ell)}(r) = \ell^{-d}|q \cap C_r^{(\ell)}|$ in the convolution $J_\gamma * q$. Indeed, for any configuration $q \in \mathcal{X}_\Lambda$ satisfying the hard core condition,

$$\left|H_\gamma(q) - \int e\big(J_\gamma * \rho^{(\ell)}(r)\big)dr\right| \le c(\ell\gamma)\,|\Lambda| \tag{4.8}$$

where $\rho^{(\ell)}(r) \equiv \rho^{(\ell)}(r,q) = \dfrac{|q \cap C_r^{(\ell)}|}{\ell^d} = \dfrac{N_r}{\ell^d}$ is the particles density in the cube $C_r^{(\ell)}$.

The energy $\int e\big(J_\gamma * \rho^{(\ell)}(r)\big)dr$ is not yet the effective hamiltonian because we still have to integrate over all the configurations yielding the assigned occupation numbers $\{N_r\}$: the effective hamiltonian has also an entropy contribution (the log of the above phase space volume). This would be easy to compute if particles were points, it is instead pretty hard because of the hard core constraint (an issue overcome in the van der Waals theory by ad hoc assumptions on the entropy). It is not hard to prove that we make a "small error" if we assume factorization, namely if we take the entropy, i.e. the log of the volume of phase space of configurations in $\{N_r\}$, as the sum of the entropies in each cube, which, modulo a minus sign, is

$$f_C^{\text{hc}}\Big(\frac{N}{|C|}\Big) = -\frac{1}{\beta|C|}\log\Big\{\int_{C^N} \mathbf{1}_{|q_i-q_j|>2R}\,\frac{dq}{N!}\Big\} \tag{4.9}$$

(Factorization increases the entropy, as we disregard the hard core constraint among particles of different cubes; a lower bound is obtained by restricting particles in each cube to be away from the boundaries of the cube by R, for such integrals the factorization is correct and the error in restricting to such volumes will become negligible in the limit).

Even with the simplification (4.9) the computation of the integral remains difficult for the presence of the hard cores constraints $\mathbf{1}_{|q_i-q_j|>2R}$. From general results in statistical mechanics it follows that there is a convex function $f^{\text{hc}}(\rho)$ (the free energy of the hard cores gas) so that

$$\lim_{|\Lambda|\to\infty}\lim_{N/|\Lambda|\to\rho} f_\Lambda^{\text{hc}}\Big(\frac{N}{|\Lambda|}\Big) = f^{\text{hc}}(\rho) \tag{4.10}$$

In the next section we shall describe in more details what is known about f^{hc}, which is not much. There are in the literature several formulas for $f^{\text{hc}}(\rho)$ elaborated via numerical simulations and heuristic considerations, [48], [26], [28], we refer to [32] for their analysis. We state below some properties which we are going to use (which strictly speaking should be regarded as conjectures).

- $f^{\mathrm{hc}}(\rho)$ is a continuous convex function in $(0, \rho_c)$, $\rho_c > 0$
- $f^{\mathrm{hc}}(\rho)$ is asymptotic to $-\rho(\log \rho - 1)$ as $\rho \to 0$ together with its first and second derivatives
- $f^{\mathrm{hc}}(\rho) \to +\infty$ as $\rho \to \rho_c$ and its second derivative is strictly positive in a neighborhood of ρ_c

Neglecting the error in (4.8) and replacing $f_C^{\mathrm{hc}}\left(\frac{N}{|C|}\right)$ by its limit we then have

$$\mu(\{N_r\}) \approx Z^{-1} e^{-\beta F_\gamma(\rho)}, \quad \rho(r) = \frac{N_r}{|C^{(\ell)}|} \tag{4.11}$$

where the free energy functional $F_\gamma(\rho)$ is

$$F_\gamma(\rho) = \int \left\{ e\big(J_\gamma * \rho(r)\big) + \frac{1}{\beta} f^{\mathrm{hc}}(\rho(r)) \right\} dr \tag{4.12}$$

By scaling $r \to \gamma r$ we get, calling $\rho^*(r) = \rho(\gamma^{-1} r)$ and $F = F_1$,

$$F_\gamma(\rho) = \gamma^{-d} F(\rho^*) \tag{4.13}$$

which replaced in (4.11) shows that for small γ the Gibbs measures should concentrate around the minimizers of F, the conditional tense because (4.11) is only an approximation.

However the above arguments can be made rigorous even though in a weaker sense:

THEOREM 4.1. – *Let $\{\Lambda\}$ be an increasing sequence of tori in $\mathbb{R}^d$. Let $s \in (0, \rho_c)$,*

$$f_{\gamma,\beta}(s) = \lim_{|\Lambda| \to \infty,\, N/|\Lambda| \to s} \frac{1}{\beta |\Lambda|} \log Z_{\gamma,\Lambda,\beta,N} \tag{4.14}$$

the free energy density (notation are explained after the theorem). Then

$$\lim_{\gamma \to 0} f_{\gamma,\beta}(s) = \lim_{|\Lambda| \to \infty,\, N/|\Lambda| \to s} \frac{1}{|\Lambda|} \inf \left\{ F_{\Lambda,\beta}(\rho) \mid \rho : \int_\Lambda \rho = N \right\} \tag{4.15}$$

In the above theorem $Z_{\gamma,\Lambda,\beta,N}$ is the canonical partition function defined in (3.2) with $H = H_\gamma$ as in (4.2), $e(\rho) = -\frac{\rho^2}{2} - \lambda \rho$ and there is a hard core repulsion among particles; (the existence of the limit (4.14) is true in general); $F_{\Lambda,\beta}$ is the corresponding functional defined in (4.13) on $L^\infty(\Lambda; \mathbb{R}_+)$ (with the convolution defined in the torus Λ). The proof of the theorem is omitted.

THEOREM 4.2. – *In the same context as in Theorem* 4.1, *the limit in* (4.15) *is equal to* $\phi^{**}(s)$, *i.e. the convexification of*

$$\phi(s) = -\frac{\alpha s^2}{2} - \lambda s + \frac{1}{\beta} f^{\text{hc}}(s) \tag{4.16}$$

PROOF. – We need to prove that

$$\lim_{|\Lambda|\to\infty} \frac{1}{\beta|\Lambda|} \inf\Big\{F_{\Lambda,\beta}(\rho) \mid \rho : \int_\Lambda \rho = s|\Lambda|\Big\} = \phi^*(s) \tag{4.17}$$

The proof of (4.17) is obtained by rewriting first $F_{\Lambda,\beta}$ in a more convenient way, see (4.20) below; exploiting this we will then show that $\phi^{**}(s)$ is a lower bound for the liminf of the l.h.s. of (4.17) and complete the proof by exhibiting a recovering sequence which realizes the bound $\phi^{**}(s)$.

Recall that $F_{\Lambda,\beta}$ is defined on $L^\infty(\Lambda;\mathbb{R}_+)$ with periodic conditions, meaning that $J * \rho$ is computed by repeating periodically ρ on the whole $\mathbb{R}^d$: this is what we mean when we say that we take Λ to be a torus in $\mathbb{R}^d$. We then have

$$\int_\Lambda (J * \rho(r))^2 dr = \int_\Lambda\int_\Lambda V(r',r'')\rho(r')\rho(r'')dr'dr'' \tag{4.18}$$

$V(r',r'') = (J * J)(r',r'') = \int_{\mathbb{R}^d} J(r,r')J(r,r'')dr$. Thus

$$-\frac{1}{2}\int_\Lambda (J * \rho(r))^2 dr = -\frac{1}{2}\int_\Lambda \rho(r)^2 dr + \frac{1}{4}\int_\Lambda\int_\Lambda V(r,r')\{\rho(r)-\rho(r')\}^2 dr dr' \tag{4.19}$$

hence

$$F_{\Lambda,\beta}(\rho) = \int_\Lambda \phi(\rho(r))dr + \frac{1}{4}\int\int V(r,r')\{\rho(r)-\rho(r')\}^2 dr dr' \tag{4.20}$$

In this form the functional looks very much like the Ginzburg-Landau functional of (1.2) with the gradient term replaced by the non local expression in (4.20) and indeed the proof is now a repetition of the one sketched in the introduction for the minimization of the Ginzburg-Landau functional.

Lower bound. We shall prove that

$$\liminf_{|\Lambda|\to\infty} \frac{1}{\beta|\Lambda|} \inf\{F_{\Lambda,\beta}(\rho) \mid \rho : \int_\Lambda \rho = s|\Lambda|\} \ge \phi^*(s) \tag{4.21}$$

Define $F^*_{\Lambda,\beta}$ by replacing ϕ by ϕ^{**} in (4.20). By definition $\phi \ge \phi^{**}$ so that

$F_{\Lambda,\beta} \ge F^*_{\Lambda,\beta}$. Since $V(r,r') \ge 0$,

$$F^*_{\Lambda,\beta}(\rho) \ge \int_\Lambda \phi^{**}(\rho(r))dr \ge |\Lambda|\phi^{**}\Big(\frac{1}{|\Lambda|}\int_\Lambda \rho(r)dr\Big) \tag{4.22}$$

having used Jensen in the last inequality (as ϕ^{**} is convex by definition). The lower bound (4.21) is then proved.

Recovering sequences. If s is such that $\phi^{**}(s) = \phi(s)$, for each Λ we take $\rho(r) \equiv s$ and for such ρ, $F_\Lambda(\rho) = \phi^{**}(s)$. Suppose next that $\phi^{**}(s) < \phi(s)$, there are then $s' < s < s''$ so that

$$\phi^{**}(s) = p\phi(s') + (1-p)\phi(s''), \quad p \in (0,1) \tag{4.23}$$

Let Λ' a coordinate rectangle in Λ with $|\Lambda'| = p|\Lambda$. Define $u_\Lambda(r) = \rho'$ in Λ' and $= \rho''$ elsewhere in Λ, so that $\int u_\Lambda = s|\Lambda|$. The last term in (4.20) is bounded proportionally to L^{d-1} (L the length of the side of the cube Λ) hence

$$\lim_{|\Lambda|\to\infty} \frac{F_\Lambda(u_\Lambda)}{|\Lambda|} = p\phi(\rho') + (1-p)\phi(\rho'') = \phi^{**}(s) \tag{4.24}$$

which shows that u_Λ is indeed a recovering sequence. □

Phase transitions. By a continuity argument, $\phi(s)$ is concave in any given interval strictly contained in $(0,\rho_c)$ once β is large enough, so that there are indeed forbidden density intervals and Theorem 4.1 together with Theorem 4.2 show that the particle system has a phase transition at least in the limit $\gamma \to 0$. We shall come back later on the meaning of such a statement.

A function which satisfies the same properties as $f^{\rm hc}(\rho)$ is the van der Waals free energy $\rho(\log\rho - 1) - \rho(\log(1-\rho/\rho_c)$, see (3.13): with such a replacement we have obtained the van der Waals phase transition without using the Maxwell equal area rule, as the limit free energy is $\phi^{**}(s)$.

The functional $F_{\Lambda,\beta}(\rho)$ hides the existence of microstructures. The replacement in (4.10) of the finite volume free energy $f^{\rm hc}_C\left(\frac{N}{|C|}\right)$ by its thermodynamic limit $f^{\rm hc}(\rho)$ turns out to be [partially] incorrect when the hard spheres gas undergoes a phase transition (as it is believed to occur in $d=3$, see Section 6). Indeed if there is a phase transition then a density ρ in the forbidden interval is realized by a non homogeneous profile which alternates regions with density ρ_1 and with density ρ_2. The grains of such fragmentation are believed to be "slightly" smaller than γ^{-1} and in such a case the typical configurations will have in the cubes C (whose side is $\ll \gamma^{-1}$) one of the above two densities. The predictions of the functional will however be correct on scales larger than γ^{-1}. In conclusion if when studying the functional we read a density value ρ inside the forbidden interval we should always remember that it is in fact describing a hidden finer structure with oscillations between the two extremal values ρ_1 and ρ_2, such microstructures are also called in the literature "mushy regions".

5. – The LMP model

The weak point in the theory of the previous section is that phase transitions are proved only in the limit $\gamma \to 0$. The graph of the free energy density $f_{\gamma,\beta}$ (see Theorem 4.1) has (for β large enough) a linear segment, but the statement is proved only in the limit $\gamma \to 0$. When $\gamma > 0$, no matter how small it is, $f_{\gamma,\beta}$ may very well be a strictly convex function.

On the other hand J_γ and hence the hamiltonian H_γ have no well defined limit as $\gamma \to 0$ so that we cannot attribute the phase transition observed in the limit to any statistical mechanics particles model.

All that is not a mathematical subtlety, for instance we know that in $d = 1$ there is no phase transition, while in the Kac theory phase transitions occur independently of the dimensions, hence also in $d = 1$.

It seems that we are back to the same problem we had with the mean field and van der Waals theories, but already at the times when the Kac and the Lebowitz-Penrose papers appeared the feeling was that much more could in fact be done with Kac potentials. The two main technical obstacles are:

- The basic step in the theory is to reduce to variational problems with free energy functionals, which requires a proof that the effective hamiltonians are well approximated by such functionals. Their difference however grows as $|\Lambda|$ multiplied by a small factor vanishing with γ. Thus if γ is kept fixed as we want, the approximation becomes useless when studying the Gibbs measure in large volumes.
- There is a poor control of the hard cores interaction. Even without the Kac potential we do not know how the hard spheres gas behaves. It may very well be that the hard spheres gas alone has a phase transition without the help of Kac potentials, as shown in $d = 3$ by numerical computations.

Let us start from the second point, namely the poor knowledge of the hard spheres system. As we shall discuss later this is not totally true, we have in fact a very good control of the hard spheres gas for small densities (i.e. when the typical inter-particles distance is much larger than the hard core radius). In this case the entropy of the hard spheres is to leading orders the same as in the ideal gas.

One may then hope to be lucky so that the relevant densities which appear in the analysis are in the hard core low density regime, but unfortunately this does not seem likely. The attractive Kac interaction in fact goes like $-\rho^2$ and it thus wants ρ to grow to infinity; this can only be contrasted by the hard cores interaction which however in the above small density regime where it is close to the ideal gas has a free energy which grows only as $\rho \log \rho$. The argument then indicates that the hard core interaction can control the Kac energy only away from the ideal gas approximation.

To overcome the impasse, LMP (Lebowitz, Mazel and Presutti), [34] and [43], have proposed to change the Kac energy density $-\rho^2/2$ into

$$e(\rho) := -\frac{\rho^2}{2} + \frac{\rho^4}{4!} - \lambda\rho, \quad H_\gamma = \int e\big(J_\gamma * q(r))\big)dr \tag{5.1}$$

$e(\rho)$ is now stable, i.e. $e(\rho)/\rho$ is bounded from below, and with such a choice of the energy density there is no longer need to have a hard core interaction as well. The LMP model is indeed defined by the hamiltonian (5.1) with no hard-cores added. It should be said that

- the LMP analysis applies as well to other regularizing terms than ρ^4, (5.1) is just an example;
- the double well structure of $e(\rho)$ is misleading because $\rho \geq 0$: a double well will appear when adding (actually subtracting) the entropy.

The very first step of course is to check that also the LMP model has a phase transition in the limit $\gamma \to 0$. The coarse-graining estimates are mainly unchanged (actually simpler in the part regarding the entropy as here we have point particles) and Theorem 4.1 extends to the LMP model with $F_{\gamma,\beta,\Lambda}$ replaced by a new non local functional $F^{\rm LMP}_{\gamma,\beta,\Lambda}$ which has the scaling property (4.13), namely $F^{\rm LMP}_{\gamma,\beta,\Lambda}(\rho) = \gamma^{-d} F^{\rm LMP}_{\beta,\Lambda^*}(\rho^*)$, $\Lambda^* = \gamma\Lambda$ and $\rho^*(r) = \rho(\gamma^{-1}r)$, with $F^{\rm LMP}_{\beta,\Lambda}$ given by

$$F^{\rm LMP}_{\beta,\Lambda}(u) = \int_\Lambda \Big\{ e\big(J * u(r)\big) - \frac{1}{\beta} s(u(r)) \Big\} dr, \quad s(u) = -u(\log u - 1) \tag{5.2}$$

$s(u)$ the entropy of the ideal gas.

Minimizers of $F^{\rm LMP}_{\beta,\Lambda}$ are constant functions, as in the Ginzburg-Landau functional:

Lemma 5.1. – *Let Λ be a torus in $\mathbb{R}^d$, $d \geq 1$, then*

$$\inf_{u \in L^\infty(\Lambda, \mathbb{R}_+)} F^{\rm LMP}_{\beta,\Lambda}(u) = |\Lambda| \inf_{\rho \geq 0} \Big\{ e(\rho) - \frac{1}{\beta} s(\rho) \Big\} \tag{5.3}$$

Proof. – We rewrite $F^{\rm LMP}_{\beta,\Lambda}$ as

$$F^{\rm LMP}_{\beta,\Lambda}(u) = \int_\Lambda \bigg(\Big\{ e(J*u) - \frac{1}{\beta} s(J*u) \Big\} + \Big\{ \frac{1}{\beta} s(J*u) - \frac{1}{\beta} s(u) \Big\} \bigg)$$

We have $\int_\Lambda s(u) = \int_\Lambda J * s(u)$ and, by convexity ($-s$ is convex),

$$\frac{1}{\beta}s(J*u) - \frac{1}{\beta}J*s(u) \geq 0$$

so that

$$F^{\mathrm{LMP}}_{\beta,\Lambda}(u) \geq \int_\Lambda \left\{ e(J*u) - \frac{1}{\beta}s(J*u)\right\} \tag{5.4}$$
$$\geq |\Lambda| \inf_{\rho\geq 0} \phi_\beta(\rho), \quad \phi_\beta(\rho) := e(\rho) - \frac{1}{\beta}s(\rho)$$

□

The same ideas are used to prove the analogue of Theorem 4.2 (details omitted):

THEOREM 5.1. – *Let* $\phi^{**}_\beta(s)$ *be the convexification of* $\phi_\beta(s)$*, the latter defined in* (5.4), *then*

$$\lim_{|\Lambda|\to\infty} \frac{1}{\beta|\Lambda|} \inf\left\{ F^{\mathrm{LMP}}_\Lambda(\rho) \mid \rho : \int_\Lambda \rho = s|\Lambda| \right\} = \phi^{**}_\beta(s) \tag{5.5}$$

By a direct computation $\phi_{\beta,\lambda}$ (here the dependence on λ is made explicit) has the following properties:

- $\phi_{\beta,\lambda}(\,\cdot\,)$ is convex for $\beta \leq \beta_c = (3/2)^{3/2}$
- for $\beta > \beta_c$ there are $\rho_{-,\beta} < \rho_{+,\beta}$ so that $\phi_{\beta,\lambda}(s) > \phi^{**}_{\beta,\lambda}(s)$ in $(\rho_{-,\beta}, \rho_{+,\beta})$ while $\phi_{\beta,\lambda}(s) = \phi^{**}_{\beta,\lambda}(s)$ elsewhere
- for any $\beta > \beta_c$ there is $\lambda(\beta)$ so that the minimum of $\phi_{\beta,\lambda(\beta)}$ is attained at $\phi_{\beta,\lambda(\beta)}(\rho_{-,\beta}) = \phi_{\beta,\lambda(\beta)}(\rho_{+,\beta})$

The critical points of $\phi_{\beta,\lambda}(\rho)$ are the solutions of the mean field equation

$$\frac{d}{d\rho}\{e_\lambda(\rho) + \frac{1}{\beta}\,\rho(\log\rho - 1)\} = 0, \quad \rho = \exp\{-\beta e'_\lambda(\rho)\} =: K_{\beta,\lambda}(\rho) \tag{5.6}$$

which for $\beta > \beta_c$ and $\lambda = \lambda(\beta)$ looks as in Figure 3.

Let us go back to the problems raised in the beginning of this section where we have outlined the two main difficulties to realize the Kac program for phase transitions at fixed γ. The second one, which concerns the hard core interaction, has already been overcome by adopting the LMP model where hard spheres are replaced by point particles (stability being ensured by having changed the energy density).

The other main difficulty refers to the fact that the true effective hamiltonian differs from the functional by a term which grows as $|\Lambda|$ multiplied by a small factor $\varepsilon(\gamma)$ vanishing with γ. If γ is kept fixed, as we want, the error

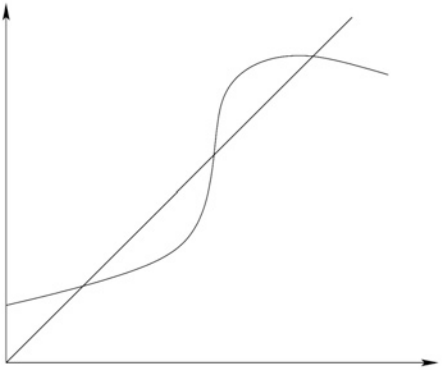

Fig. 3. – Graph of $K_{\beta,\lambda(\beta)}(\rho)$ with $\beta > \beta_c$.

explodes in the thermodynamic limit and Gibbs measure and free energy functional indeed give very different pictures for the relevant density profiles.

The conclusion is that we should not be so ambitious to pretend that the Gibbs measure is really well described by the functional: this may be true on large but not too large domains namely such that $\varepsilon(\gamma)|\Lambda|$ is small. On much larger scales the error between effective hamiltonian and functional becomes important.

Indeed the functional does not take into account fluctuations: rarely yet with finite frequency there are large deviations from the optimal behavior predicted by the functional. Such fluctuations have a macroscopic importance as the forbidden density interval turns out to depend on γ.

The typical configurations of a pure phase with density ρ have empirical local density close to ρ except in "small islands" where there are significant deviations from ρ and to prove phase transitions we need to control the probability of such deviations. To do that we use coarse graining but only in the region where such deviations occur. In this way the error grows only with the volume of this region (times the small factor $\varepsilon(\gamma)$). The excess free energy of the functional on the profiles describing excursions from the minimizers is large: the key point is to prove that it is proportional to the volume (of the region where the deviations occur) and so large to kill the error done in the coarse graining. This is just a rough sketch, many problems are hidden both technical and theoretical, and here I just refer to [34] and [43],

THEOREM 5.2. – *In the LMP model in dimensions* $d \geq 2$ *there is* $\beta^* > \beta_c$ *so that given any* $\beta \in (\beta_c, \beta^*)$ *for any* $\gamma > 0$ *small enough there is a "forbidden interval"* $(\rho_{-;\beta,\gamma}, \rho_{+;\beta,\gamma})$. $\rho_{\pm;\beta,\gamma} \to \rho_{\pm;\beta}$ *as* $\gamma \to 0$.

There are two senses in which the interval $(\rho_{-;\beta,\gamma}, \rho_{+;\beta,\gamma})$ is forbidden. There is a "thermodynamics sense" which simply means that the graph of the free energy density $f_{\beta,\gamma}(\rho)$ has a straight segment in $[\rho_{-;\beta,\gamma}, \rho_{+;\beta,\gamma}]$. The interval $(\rho_{-;\beta,\gamma}, \rho_{+;\beta,\gamma})$ is forbidden also in the sense outlined in the introduction and specified in Section 3, however a proof of the latter statement is not explicit in the literature (which states the existence of more than one DLR measures).

6. – LMP plus hard cores

While the Kac original hamiltonian (i.e. an attractive pair potential scaled with γ plus hard cores), may be regarded as a plausible schematization of the Lennard-Jones interaction, the LMP hamiltonian is certainly further away from a realistic model of interacting molecules. The LMP energy density $e(\,\cdot\,)$ should rather be seen as an effective energy due to the long tail of the interaction so that it is less sensitive to the actual position of the particles and depends only on their empirical density. The decreasing small density behavior ($\approx -\rho^2$) reflects the long range attractiveness of the interaction while repulsive forces take over at smaller distances where the density is higher ($\approx \rho^4$).

Energies at very large densities however become very sensitive to the actual position of the particles and the LMP approximation in terms of their empirical density is certainly quite rough. To improve the LMP model we can add a hard core interaction which then dominates the energy when the density grows towards the maximal, "close packing" density.

In the LMP plus hard cores model there are two terms which fight against the growth of the density, one is the ρ^4 term present in the LMP energy, the other one is the hard core interaction. By adjusting the parameters we may well separate the two effects so that the hard core interaction is "very weak" in the density regime where the LMP phase transition appears and enters into play only later when the density is much larger.

In this section we shall discuss the phase diagram of the LMP plus hard cores model, none of the properties which will be stated have been actually proved so that this section should be regarded as merely conjectural, but research is going on and hopefully something will appear in the future.

Let us start with the pure hard spheres gas, the LMP energy will be added later on. As mentioned already several times, very little is known analytically on the hard spheres gas. The only results refer to low densities (i.e. when the typical interparticle distance is much larger than the hard core radius R: $\rho R^d \ll 1$). Asymptotically as $\rho \to 0$, the entropy $s^{\rm hc}(\rho)$ behaves as

$$s^{\rm hc}(\rho) \approx s^{\rm ideal}(\rho) = -\rho\Big(\log\rho - 1\Big) \tag{6.1}$$

$s^{\rm ideal}(\rho)$ the entropy of a gas of non interacting point particles.

The “imperfect gas” where the hard core length is not neglected as in (6.1) has been much studied starting from the famous Mayer virial expansion where the equation of state of the hard sphere gas is expressed as a convergent series in the density ρ, valid for ρR^d small enough. Many attempts have been made to improve the radius of convergence of the series, but nothing is known analytically on what happens when ρR^d is no longer small.

Numerical evidence, [26], [28], [48], shows that in $d = 3$ the hard core free energy density $f^{\mathrm{hc}}(\rho)$ is linear in an interval (ρ_1, ρ_2) (which scales as R^{-d}). Such a phase transition would mark the transition from disorder to order. When $\rho < \rho_1$ entropy wins and the hard spheres positions are random and thus quite disordered. We very well know (for instance when we play the game of who puts more non overlapping discs on a table) that in disordered configurations a lot of space gets lost and at some point it becomes very hard to find room for new spheres. When such a critical condition is reached, to increase the density we need to readjust (in some region of the space) the particles disposing them in some more ordered way which accommodates for a higher density. Such a phenomenon may explain the origin of the (ρ_1, ρ_2) phase transition.

There is no physical reason to expect the LMP phase transition to disappear if instead of points we take spheres, the proof however cannot be straightforward otherwise we would work directly with the Kac model (of attractive Kac interactions among spheres). However, since the analysis on the LMP model is “robust”, we may hope to be able to handle LMP plus hard cores if $\rho R^d \ll 1$, i.e. when the hard core radius R is much smaller than typical interparticle distance. We could then study the system as a perturbation of LMP because in the above regime the hard core constraint should be quite unimportant.

Coarse graining is about integrating over configurations with the “multi-canonical” constraint that the numbers N_i of particles in the cubes $C_i^{(\ell)}$ of a given partition $\pi^{(\ell)}$ are fixed. By choosing properly ℓ ($\ell \ll \gamma^{-1}$) we may consider to first order the Kac interaction independent of the actual positions of the particles in each cube and the integration within such an approximation is over particles which interact only via hard cores. If the relevant numbers N_i turn out to be such that the local densities N_i/ℓ^d are in the domain where the virial expansion applies, [37], [38], [46], [33], [42], [15], [16], we can then control the difference between entropies of hard spheres and point particles in terms of a convergent series in the particles density.

The fact that the numbers N_i cannot be dangerously large will be enforced by the repulsive ρ^4 part of the LMP energy. Such a term is absent in the Kac model where the growth of N_i is contrasted only by the hard cores interaction, for this reason in Kac the numbers N_i are typically large, while here they can be controlled by the LMP energy alone and by choosing R small we can then suppose to be in the virial expansion regime.

Recent works on cluster expansion, [44], have extended its validity to systems in the canonical ensemble (i.e. where the number of particles in a region is prescribed) and thus apply directly to the coarse graining procedure outlined above.

Conjectures on the phase diagram

We fix an inverse temperature $\beta \in (\beta_c, \beta^*)$ as in Theorem 5.2 and consider the LMP model with additional hard cores interaction with hard core length R. In agreement with the previous discussion we suppose $R^d \rho_{+,\beta} \ll 1$ ($\rho_{\pm,\beta}$ are the mean field pure phase densities in the LMP model) and the conjectures below are tacitly stated for values of γ sufficiently small.

Let us first discuss the phase diagram when we increase the chemical potential λ from $-\infty$ to $+\infty$ (with β fixed as above). We expect to see three phases, gas, liquid and solid, but while the transition gas-liquid will be sharp the liquid-solid one will be "diffuse". Let us start with λ increasing from $-\infty$. This is the gas phase regime where densities are very small and the typical interaction among particles is weak. This regime is very well understood even for general interactions and a fortiori here.

The system will stay in the gas phase till the chemical potential λ reaches a critical value $\lambda_{\beta,\gamma}$. Then a new phase appears and precisely at $\lambda_{\beta,\gamma}$ two phases exist, gas and liquid. As soon as the chemical potential increases past $\lambda_{\beta,\gamma}$ the gas phase is suppressed and only the liquid one survives. Due to the condition $R^d \rho_{+,\beta} \ll 1$ we expect that the gas and liquid densities at the transition are pretty close to those in LMP. The conjectures so far look quite solid, what follows is instead much more tentative.

If we further increase the chemical potential the liquid density will then increase with λ (but quite slowly due to the ρ^4 term in LMP). Once λ and the density become large the influence of the hard core interaction becomes more and more significant (and the analysis harder). At some large value of the chemical potential, say λ', the density will reach the value ρ_1, i.e. where the forbidden interval for the pure hard spheres system starts. A further increase of λ past λ' would cause a jump (from ρ_1 to ρ_2 in the pure hard sphere gas, but such a jump is not compatible with the LMP energy which (for large densities) is in its strongly convex region.

This is the competition between forces on very different scales discussed in the introduction, recall the Stefan Müller example. We thus expect to see microstructures, namely on scales smaller than γ^{-1} the hard core interaction wins and we locally see one or the other of the two allowed densities ρ_1 and ρ_2: they will be however spatially arranged in the right proportion so to have on a larger scale the uniform density ρ which the LMP energy demands. We thus observe as λ increases past λ' clusters of the solid phase (of density ρ_2) forming in some suitable pattern. The clusters size increases with λ till invading the whole space, i.e. at $\lambda = \lambda''$, namely when the total density is ρ_2: the competition between LMP and hard core interactions is at this point over. Further increases of λ past λ'' only cause an increase of density past ρ_2, with the solid being the only existing phase at all scales.

The corresponding picture in a canonical ensemble setting, where the order parameter is no longer the chemical potential λ but the particles density ρ, is as follows. Notation are as in Section 3, where we have introduced partitions $\pi^{(\ell)}$ into cubes $C_i^{(\ell)}$).

The gas phase exists when the density ρ is below a critical value $\rho'_{-,\beta,\gamma}$ close (for R small) to the LMP value $\rho_{-,\beta,\gamma}$. When $\rho \le \rho'_{-,\beta,\gamma}$, "typically" "most cubes" $C_i^{(\ell)}$ have density "essentially" equal to ρ. "Typically" "most" and "essentially" in the sense explained in Section 3.

In the forbidden density interval $(\rho'_{-,\beta,\gamma}, \rho'_{+,\beta,\gamma})$ ($\rho'_{+,\beta,\gamma}$ close for small R to the LMP value $\rho_{+,\beta,\gamma}$) typically most cubes $C_i^{(\ell)}$ are plus or minus cubes, namely they have density essentially equal to $\rho'_{\pm;\beta,\gamma}$. The minus and plus cubes are those where we see the gas or the liquid phases. ℓ can be arbitrarily large and we still see in most $C_i^{(\ell)}$ a pure phase (either the liquid or the gas phase), but the statement holds provided the region Λ is large enough (in terms of ℓ). This means that the clusters of each phase are large and not too dispersed, a statement which will be much strengthened in the next section.

As the density ρ increases past $\rho'_{+;\beta,\gamma}$, "typically" "most cubes" $C_i^{(\ell)}$ have density "essentially" equal to ρ, analogously to the picture we have seen for the gas phase.

However when ρ increases past ρ_1 we see two scales. For small ℓ (much smaller than the LMP interaction range γ^{-1}) typically most cubes $C_i^{(\ell)}$ have density essentially equal to ρ_1 or ρ_2, the phase in the cubes ρ_1 being liquid, in the others solid. For larger values of ℓ, $\ell \gg \gamma^{-1}$ instead typically most cubes $C_i^{(\ell)}$ have density essentially equal to ρ. These cubes, apparently "normal" have however microstructures, since when observed on smaller scales exhibit a different structure (droplets of density ρ_1 and ρ_2). When ρ is past ρ_2 only the solid phase is present and we see ρ at all scales.

7. – Wulff shape and microstructures

Phases may coexist with different geometries, the interface may be a single smooth surface or it may break into very many pieces. The former case arises when the surface tension is the dominant force, then, in the presence of a phase transition with a canonical constraint, the phases separate in such a way to minimize the integral of the surface tension over the interface (the Wulff problem) compatibly with the canonical constraint. Microstructures instead arise when other forces than surface tension enter into play: on some small scale surface tension wins and we see one phase or the other, but when averaging over larger scales other forces prevail and we see a constant density.

So far we have considered thermodynamic potentials like the free energy density and entropy, which are all bulk quantities (as they are obtained by computing the free energy or the entropy of the system in a large region Λ, then dividing by the volume $|\Lambda|$, and finally taking the thermodynamic limit $|\Lambda| \to \infty$). Surface tension instead is a thermodynamic potential of a different kind as it involves surface rather than volume properties, it thus belongs to a completely new and indeed much more complex chapter of statistical mechanics.

The primitive notion in the macroscopic theory of phase coexistence (with only two pure phases having density ρ' and $\rho'' > \rho'$) is that states are described by functions $u(r)$, $r \in \Omega$, Ω the macroscopic region where the system is confined (supposed to be the unit torus in $\mathbb{R}^d$), with values ρ' and ρ'' ("local equilibrium assumption"). The free energy of such states is

$$\Phi(u) = \int_{\Sigma} \sigma(\vec{n}) dr \tag{7.1}$$

where $\Sigma := \partial\{r : u(r) = \rho'\}$ (the boundary of the region where $u = \rho'$) is a smooth surface, $\vec{n}$ the unit normal on Σ and $\sigma(\vec{n}) \geq 0$ the surface tension that we suppose to be a strictly positive smooth function on the unit ball.

"Geometric measure theory" shows that it is possible to extend Φ to functions u which are ρ', ρ'' valued and have "bounded variation". In fact, measure theoretically, the boundary of a BV set is almost everywhere C^1 relative to the Hausdorff measure of codimension 1, [9], [14], [4]. Thus modulo sets of zero measure we may regard the surface as C^1 and (7.1) naturally extends to such u. Any other state which is not BV has an infinite free energy cost: thus the cost of an interface controls its regularity (in the C^1 sense) but only modulo a region of the interface of zero measure.

In the mesoscopic theory states are described by functions $u(\,\cdot\,)$ with values in $\mathbb{R}_+$ (the local equilibrium assumption is dropped here) and their free energy is a functional $F(u)$, at the moment we restrict for simplicity to the Ginzburg-Landau functional (1.1), non local functionals will be considered later. Suppose that the potential W in (1.1) has value 0 at ρ' and ρ'' and it is everywhere else strictly positive. We call F_Λ the functional (1.1) defined on non negative functions u on the torus $\Lambda \subset \mathbb{R}^d$ such that $|\nabla u|^2$ is integrable. Our aim is to derive the macroscopic functional (7.1) from F_Λ in the thermodynamic limit $|\Lambda| \to \infty$. The first task is to relate macroscopic and mesoscopic states. Since they are functions on different spaces, Ω and Λ, we start by mapping Λ to Ω by $r \to r/L$, L the side of Λ. Then F_Λ becomes the functional

$$F^{(L)}(v) = F_\Lambda(u), \quad v(r) = u(Lr) \tag{7.2}$$

defined on non negative valued functions v on the torus Ω such that $|\nabla v|^2$ is integrable. Explicitly

$$F^{(L)}(v) = L^d \int_{\Omega} \{W(v) + L^{-2}|\nabla v|^2\} dr \tag{7.3}$$

In the meso-theory macroscopic states (recall that they are BV functions on Ω with values ρ' and ρ'') are not simply a subset of all the meso-states as they are not in the domain of $F^{(L)}$. To identify the macro-states u we use the L^1 distance and say that the meso-state v "recognizes" the macro-state u with accuracy $\varepsilon > 0$ if $|v - u|_{L^1} \leq \varepsilon$. Then the meso-free energy of u (with accuracy ε and meso/macro scale L) is

$$\Phi_{\varepsilon}^{(L)}(u) := \frac{1}{L^{d-1}} \inf_{|v-u|_{L^1} \leq \varepsilon} F^{(L)}(v) \tag{7.4}$$

The normalizing factor L^{d-1} foresees the fact that the mesoscopic free energy of a state with coexisting phases scales as the surface (if the interface is nice where nice means BV according to the macroscopic theory). Explicitly

$$\Phi_{\varepsilon}^{(L)}(u) := \inf_{|v-u|_{L^1} \leq \varepsilon} \int_{\Omega} \{LW(v) + L^{-1}|\nabla v|^2\} dr \tag{7.5}$$

We are thus led to conjecture that

$$\lim_{\varepsilon \to 0} \liminf_{L \to \infty} \Phi_{\varepsilon}^{(L)}(u) = \Phi(u) \tag{7.6}$$

with $\Phi(u)$ the functional defined in (7.1). This is indeed a theorem, [40], [7]. The surface tension in (7.1) is isotropic, its explicit value is

$$\sigma = 2 \int_{\rho'}^{\rho''} \sqrt{W(s)} ds \tag{7.7}$$

It is remarkable and in some sense surprising how the above considerations motivated by physical intuitions fit exactly in the scheme devised by De Giorgi in the calculus of variations which led to the introduction of the notion of Gamma convergence, see again [7] for details.

Analogous results have been proved for non local functional as those arising from particles or spins systems with Kac potentials. See [3], [5] and [43], for the case of Ising systems with Kac potentials where the limit free energy and the surface tension are explicitly computed. An extension to more general systems and a general definition of surface tension can be found in [1] and [2].

In the microscopic theory we follow the approach used in the mesoscopic theory and since in the previous considerations we had not fixed the total mass here as well we do not fix the number of particles in Λ. The equilibrium state in such a case is described by the gran canonical Gibbs measure $\mu_{\beta,\lambda,\Lambda}$ which is the probability on $\mathcal{X}_\Lambda := \bigcup_{n\ge 0} \Lambda^n$ defined so that its restriction to Λ^n is:

$$d\mu_{\beta,\lambda,\Lambda}(q) = \frac{1}{Z_{\beta,\lambda,\Lambda}} e^{-\beta(H(q)-\lambda n)} \frac{dq}{n!}, \quad q \in \Lambda^n \tag{7.8}$$

λ being the "chemical potential", $Z_{\beta,\lambda,\Lambda}$ the gran canonical partition function.

As in the mesoscopic theory we need to equilibrate the two phases: the existence of a forbidden interval translates in the language of the gran canonical Gibbs measures into the following statement. There is $\lambda = \lambda_\beta$ so that

$$\lim_{\varepsilon\to 0} \lim_{L\to\infty} \mu_{\beta,\lambda_\beta,\Lambda}\left[\left|\frac{|q|}{|\Lambda|} - s\right| < \varepsilon\right] = \frac{1}{2}, \quad s = \rho', \rho'' \tag{7.9}$$

Proceeding as in the mesoscopic theory and calling L the side of Λ, we set

$$\rho^{(L,\ell)}(r,q) := \frac{|q \cap C^{(\ell)}_{Lr}|}{\ell^d}, \quad q \in \mathcal{X}_\Lambda,\ r \in \Omega \tag{7.10}$$

the empirical density on scale ℓ (i.e. relative to the partition $\pi^{(\ell)}$) translated into a function on the torus Ω. Then, in analogy with (7.5) and recalling that the free energy is related to minus the log of the Gibbs measure we set

$$\Phi^{(L,\ell)}_\varepsilon(u) := -\frac{1}{\beta L^{d-1}} \log\left(\mu_{\beta,\Lambda,\lambda}\left[|\rho^{(L,\ell)}(\cdot,q) - u|_{L^1} \le \varepsilon\right]\right) \tag{7.11}$$

and define the free energy of the macro-state u as

$$\Phi(u) := \lim_{\varepsilon\to 0} \liminf_{\ell\to\infty} \liminf_{L\to\infty} \Phi^{(L,\ell)}_\varepsilon(u) \tag{7.12}$$

If $\Phi(u)$ has the form (7.1) we have then derived the macroscopic theory from the theory of Gibbs measures and identified the surface tension of the particle system. Results have been obtained so far only for Ising systems, we shall give some details after explaining the relation with the Wulff problem.

Macroscopic theory. The optimal shape for the coexistence of two phases with the total mass constraint is a minimizer of the functional (7.1) with the mass constraint. This problem has been solved by Wulff with an explicit construction of the minimizing surface, see for instance [25].

Since in the mesoscopic and microscopic theories the limit functional is (7.1) it is natural to conjecture that also the optimal state converges to the Wulf shape. This requires an inversion of limits as one should first minimize the functional and then take the thermodynamic limit. To interchange these operations a coercivity property is needed, we refer to [7] for an analysis of the mesoscopic theory.

The Wulff problem in a statistical mechanics context has been first studied by Dobrushin, Kotecký and Shlosman [13] for the n.n. ferromagnetic Ising model in

$d = 2$ at low temperatures. The proof uses sharp estimates on contours which are used to define the interface at the spin level. By such estimates it is possible to control the probability that the interface passes through a given set of points, defining a polygonal structure which approximates the Wulff shape. The result has then been extended to higher temperatures but the method is intrinsically two dimensional. The first paper where ideas of Gamma convergence have been used in a statistical mechanics context was the above paper [3] on the Ising model with Kac interactions. The result however was obtained in the spirit of the Lebowitz-Penrose theory that is in the thermodynamic limit followed by the scaling limit $\gamma \to 0$.

There were afterwards several generalization in this same context, but the first results on Wulff shape in general dimensions (obtained by using the ideas of Gamma convergence) are in [6] and [8] which have then been followed by many other papers with extensions and improvements.

We shall next briefly discuss the case where the interface breaks into many small pieces giving rise to microstructures. For brevity we shall discuss only the issue at the mesoscopic level, for particle models the analysis is still in fieri and rigorous proofs are lacking. For concreteness we consider a specific model, the Ginzburg-Landau functional $F^{\mathrm{gl}}_{\Lambda}(u)$ defined in (1.2) plus a non local term:

$$F_{\gamma;\Lambda}(u) := F^{\mathrm{gl}}_{\Lambda}(u) + \int_{\Lambda} (J_\gamma * u)^2 dr \tag{7.13}$$

where $u : \Lambda \to \mathbb{R}$ (which is interpreted as a magnetization density); the potential W in (1.2) is taken here equal to $W(s) = (s^2 - 1)^2$.

Without the non local term (i.e. setting $\gamma = 0$) there is a phase transition, the forbidden interval for the magnetization being $(-1, 1)$. Namely the graph of the limit free energy density is constantly 0 in $s \in (-1, 1)$

$$\lim_{|\Lambda|\to\infty} \inf \left\{ \frac{F^{\mathrm{gl}}_{\Lambda}(u)}{|\Lambda|} \;\middle|\; \int_{\Lambda} u = s|\Lambda| \right\} = 0 \tag{7.14}$$

and a recovering sequence is made by a regularization of profiles with $u = \pm 1$ (in the right proportion), as discussed in the introduction.

If we consider the problem with the non local term we have for $s \in (-1, 1)$:

$$\lim_{\gamma\to 0} \lim_{|\Lambda|\to\infty} \inf \left\{ \frac{F_{\gamma;\Lambda}(u)}{|\Lambda|} \;\middle|\; \int_{\Lambda} u = s|\Lambda| \right\} = \frac{s^2}{2} \tag{7.15}$$

In the double limit first $|\Lambda| \to \infty$ and then $\gamma \to 0$, the phase transition has disappeared and the limit free energy density is strictly convex. We conjecture that for $\gamma > 0$ small enough there is no phase transition and minimizers at finite Λ will be functions made by a regularization of profiles with $u = \pm 1$ (in the right proportion). The scale where the function varies is determined by the non local term and scale as ℓ with $\ell \ll \gamma^{-1}$. Thus if we look on scales smaller than ℓ we essentially see either 1 or -1, but on the average on scales much larger than ℓ, we see the imposed density s.

Proofs have been obtained when $J_\gamma * J_\gamma$ is "reflection positive", [20], and we conclude the discussion on these topics referring to the literature, in particular see [21], [22], [23], [24], [10], [12].

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