Equilibrium Statistical Mechanics

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1. Foundations: atoms and molecules

Classical Statistical Mechanics studies properties of macroscopic aggregates of particles, atoms and molecules, based on the assumption that they are point masses subject to the laws of classical mechanics. Distinction between macroscopic and microscopic is evanescent and in fact the foundations of statistical mechanics have been laid on properties, proved or assumed, of few particles systems.

Macroscopic systems are often considered in stationary states: which means that their microscopic configurations follow each other as time evolves while looking the same macroscopically. Observing time evolution is the same as sampling ("not too closely" time-wise) independent copies of the system prepared in the same way.

A basic distinction is necessary: a stationary state can be either in equilibrium or not. The first case arises when the particles are enclosed in a container Ω and are subject only to their mutual conservative interactions and, possibly, to external conservative forces: typical example is a gas in a container subject forces due to the walls of Ω and to gravity, besides the internal interactions. This is a very restricted class of systems and states.

A more general case is when the system is in a stationary state but it is also subject to non conservative forces: a typical example is a gas or fluid in which a wheel rotates, as in the Joule experiment, with some device acting to keep the temperature constant. The device is called a thermostat and in statistical mechanics it has to be modeled by forces, non conservative as well, which prevent an indefinite energy transfer from the external forcing to the system: such transfer would impede reaching stationary states. For instance the thermostat could be simply a constant friction force (as in stirred incompressible liquids or as in electric wires in which current circulates because of an electromotive force).

A more fundamental approach would be to imagine that the thermostatting device is not a phenomenologically introduced non conservative force (like a friction force) but is due to the interaction with an external infinite system which is in "equilibrium at infinity".

In any event non equilibrium stationary states are intrinsically more complex than equilibrium states. Here attention will be confined to equilibrium statistical mechanics of systems of N identical point particles $\mathbf{Q} = (\mathbf{q}_1, \ldots, \mathbf{q}_N)$ enclosed in a cubic box Ω, with volume V and side L, usually supposed with perfectly reflecting walls.

Particles of mass m located at $\mathbf{q}, \mathbf{q}'$ will be supposed to interact via a pair potential $\varphi(\mathbf{q} - \mathbf{q}')$. Microscopic motion will follow the equations

$$m\ddot{\mathbf{q}}_i = -\sum_{j=1}^{N} \boldsymbol{\partial}_{\mathbf{q}_i} \varphi(\mathbf{q}_i - \mathbf{q}_j) + \sum_i W_{wall}(\mathbf{q}_i) \stackrel{def}{=} -\boldsymbol{\partial}_{\mathbf{q}_i} \Phi(\mathbf{Q}) \tag{1.1}$$

where the potential φ will be supposed smooth except, possibly, for $|\mathbf{q} - \mathbf{q}'| \le r_0$ where it could be $+\infty$ meaning the particles cannot come closer than r_0 and at r_0 (1.1) is interpreted by imagining that they undergo elastic collisions; the potential W_{wall} models the container and it will be replaced, unless explicitly stated, by an elastic collision rule.

The time evolution $(\mathbf{Q},\dot{\mathbf{Q}}) \to S_t(\mathbf{Q},\dot{\mathbf{Q}})$ will, therefore, be described on the space $\widehat{\mathcal{F}}(N)$ of the pairs position-velocity of the N particles or, more conveniently, on *phase space*: *i.e.* by a time evolution S_t on the space $\mathcal{F}(N)$ of the pairs $(\mathbf{P},\mathbf{Q})$ momentum–position with $\mathbf{P} = m\dot{\mathbf{Q}}$. The motion being conservative, the energy $U \stackrel{def}{=} \sum_i \frac{1}{2m}\mathbf{p}_i^2 + \sum_{i<j}\varphi(\mathbf{q}_i - \mathbf{q}_j) + \sum_i W_{wall}(\mathbf{q}_i) \stackrel{def}{=} K(\mathbf{P}) + \Phi(\mathbf{Q})$ will be a constant of motion; the last term in Φ is missing if walls are perfect. This makes it convenient to regard the dynamics as associated with two dynamical systems $(\mathcal{F}(N), S_t)$ on the $6N$ dimensional phase space, and $(\mathcal{F}_U(N), S_t)$ on the $6N-1$ dimensional surface of energy U. Since the dynamics (1.1) is Hamiltonian on phase space, with Hamiltonian $H(\mathbf{P},\mathbf{Q}) \stackrel{def}{=} \sum_i \frac{1}{2m}\mathbf{p}_i^2 + \Phi(\mathbf{Q}) \stackrel{def}{=} K + \Phi$, it follows that the volume $d^{3N}\mathbf{P}d^{3N}\mathbf{Q}$ is conserved (*i.e.* a region E has the same volume as S_tE) and also the area $\delta(H(\mathbf{P},\mathbf{Q}) - U)d^{3N}\mathbf{P}d^{3N}\mathbf{Q}$ is conserved.

The above dynamical systems are well defined, *i.e.* S_t is a map on phase space globally defined for all $t \in (-\infty,\infty)$, when the interaction potential is bounded below: this is implied by the *a priori* bounds due to energy conservation. For gravitational or Coulomb interactions a lot more has to be said, assumed and done in order to even define the key quantities needed for a statistical theory of motion.

Although our world is 3–dimensional (or *at least was* so believed to be until recent revolutionary theories) it will be useful to consider also systems of particles in dimension $d \neq 3$: in this case the above $6N$ and $3N$ become, respectively, $2dN$ and dN. Systems with dimension $d = 1, 2$ are in fact sometimes very good models for thin filaments or thin films. For the same reason it is often useful to imagine that space is discrete and particles can only be located on a lattice, *e.g.* on $\mathbb{Z}^d$, see Sect.15.

Bibliography: [Ga99].

2. Pressure, temperature and kinetic energy

The beginning was BERNOULLI's derivation of the perfect gas law via the identification of the *pressure* at numerical *density* ρ with the average momentum transferred per unit time to a surface element of area dS on the walls: *i.e.* the average of the observable $2mv\,\rho v\, dS$ with v the normal component of the velocity of the particles which undergo collisions with dS. If $f(v)dv$ is the distribution of the normal component velocity and $f(\mathbf{v})d^3\mathbf{v} \equiv \prod_i f(v_i)\, d^3\mathbf{v}$, $\mathbf{v} = (v_1, v_2, v_3)$, is the total velocity distribution the average of $\frac{K}{N}$ is pdS given by

$$dS \int_{v>0} 2mv^2 \rho f(v)dv = dS \int mv^2\rho f(v)dv = \rho\frac{2}{3}dS\int \frac{1}{2}\mathbf{v}^2 f(\mathbf{v})d^3\mathbf{v} = \rho\frac{2}{3}\langle\frac{K}{N}\rangle dS \qquad (2.1)$$

Furthermore $\frac{2}{3}\langle\frac{K}{N}\rangle$ was identified as proportional to the *absolute temperature* $\langle\frac{K}{N}\rangle \stackrel{def}{=}$

$const\frac{3}{2}T$ which, with present day notations, is written $\frac{2}{3}\langle\frac{K}{N}\rangle = k_B T$. The constant k_B was (later) called *Boltzmann's constant* and it is the same constant for all perfect gases at least. Its independence on the particular nature of the gas is a consequence of *Avogadro's law* stating that equal volumes of gases at the same conditions of temperature and pressure contain equal number of molecules.

Proportionality between average kinetic energy and temperature via the universal constant k_B became, since, a fundamental assumption extending to all aggregates of particles gaseous or not, never challenged in all later works (until quantum mechanics, where this is no longer true, see Sect. 26).

Bibliography: [Ga99].

3. Heat and entropy

After Clausius' discovery of entropy and to explain it mechanically, Boltzmann introduced the *heat theorem*, which he developed to full generality between 1866 and 1884. Identification of absolute temperature with average kinetic energy and the heat theorem can be considered the founding elements of statistical mechanics.

The theorem makes precise the notion of time average and then states in great generality that given *any* mechanical system one can associate with its dynamics four quantities U, V, p, T, defined as time averages of suitable mechanical observables (*i.e.* functions on phase space) so that when the external conditions are infinitesimally varied and the quantities U, V change by dU, dV respectively, the ratio $\frac{dU+p\,dV}{T}$ is exact, *i.e.* there is a function $S(U,V)$ whose corresponding variation equals the ratio. It will be better, for the purpose of considering very large boxes ($V\to\infty$) to write this relation in terms of intensive quantities $u\stackrel{def}{=}\frac{U}{N}$ and $v=\frac{V}{N}$ as

$$\frac{du+p\,dv}{T}\ \text{is exact} \tag{3.1}$$

i.e. the ratio equals the variation ds of $s(\frac{U}{N},\frac{V}{N})\equiv\frac{1}{N}S(U,V)$.

The proof originally dealt with *monocyclic systems*, *i.e.* systems in which all motions are periodic. The assumption is clearly much too restrictive and justification for it developed from the early "*non periodic motions can be regarded as periodic with infinite period*" (1866), to the later *ergodic hypothesis* and finally to the realization that, after all, the heat theorem does not really depend on the ergodic hypothesis (1884).

Although for a one dimensional system the proof of the heat theorem is a simple check it was a real breakthrough because it led to answering the general question of under which conditions one could define mechanical quantities whose variations were constrained to satisfy (3.1) and therefore could be interpreted as mechanical model of Clausius' macroscopic thermodynamics. It is reproduced in the next few lines.

Consider a one-dimensional system subject to forces with a confining potential $\varphi(x)$ such that $|\varphi'(x)|>0$ for $|x|>0$, $\varphi''(0)>0$ and $\varphi(x)\xrightarrow[x\to\infty]{}+\infty$. All motions are periodic so that the system is *monocyclic*. Suppose that the potential $\varphi(x)$ depends on a parameter V and define *a state* to be a motion with given energy U and given V; let

$$\begin{aligned}
U &= \text{total energy of the system} \equiv K+\Phi\\
T &= \text{time average of the kinetic energy } K,\ \langle K\rangle\\
V &= \text{the parameter on which } \varphi \text{ is supposed to depend}\\
p &= -\text{ time average of } \partial_V\varphi,\ -\langle\partial_V\varphi\rangle.
\end{aligned}\tag{3.2}$$

A state is thus parameterized by U, V; if such parameters change by dU, dV, respectively, let: $dL \stackrel{def}{=} -pdV, dQ \stackrel{def}{=} dU+pdV$. Then (3.1) holds. In fact let $x_\pm(U,V)$ be the extremes of the oscillations of the motion with given U,V and define S as:

$$S = 2\log\int_{x_-(U,V)}^{x_+(U,V)}\sqrt{(U-\varphi(x))}dx \ \Rightarrow\ dS = \frac{\int\big(dU-\partial_V\varphi(x)dV\big)\frac{dx}{\sqrt{K}}}{\int K\frac{dx}{\sqrt{K}}}\tag{3.3}$$

Noting that $\frac{dx}{\sqrt{K}} = \sqrt{\frac{2}{m}}dt$, (3.1) follows because time averages are given by integrating with respect to $\frac{dx}{\sqrt{K}}$ and dividing by the integral of $\frac{1}{\sqrt{K}}$.

Bibliography: [Bo84], [Ga99].

4. Heat theorem and ergodic hypothesis

Boltzmann tried to extend the result beyond the one dimensional systems: for instance to Keplerian motions: which are not monocyclic unless only motions with a fixed eccentricity are considered. However the early statement that "aperiodic motions can be regarded as periodic with infinite period" is really the heart of the application of the heat theorem for monocyclic systems to the far more complex gas in a box.

Imagine that the gas container Ω is closed by a piston of section A located to the right of the origin at distance L and acting as a lid, so that the volume is $V = AL$. The microscopic model for the piston will be a potential $\overline{\varphi}(L-\xi)$ if $x = (\xi,\eta,\zeta)$ are the coordinates of a particle. The function $\overline{\varphi}(r)$ will vanish for $r > r_0$, for some $r_0 \ll L$, and diverge to $+\infty$ at $r = 0$. Thus r_0 is the width of the layer near the piston where the force of the wall is felt by the particles that happen to be roaming there.

The contribution to the total potential energy Φ due to the walls is $W_{wall} = \sum_j \overline{\varphi}(L-\xi_j)$ and $\partial_V\overline{\varphi} = A^{-1}\partial_L\overline{\varphi}$; assuming monocyclicity it is necessary to evaluate the time average of $\partial_L\Phi(x) = \partial_L W_{wall} \equiv -\sum_j \overline{\varphi}'(L-\xi_j)$. As time evolves the particles x_j with ξ_j in the layer within r_0 of the wall will feel the force exercised by the wall and bounce back. One particle in the layer will contribute to the average of $\partial_L\Phi(x)$ the amount

$$\frac{1}{\text{total time}}2\int_{t_0}^{t_1} -\overline{\varphi}'(L-\xi_j)dt\tag{4.1}$$

if t_0 is the first instant when the point j enters the layer and t_1 is the instant when the ξ-component of the velocity vanishes "against the wall". Since $-\overline{\varphi}'(L-\xi_j)$ is the

ξ-component of the force, the integral is $2m|\dot\xi_j|$ (by Newton's law), provided $\dot\xi_j > 0$ of course.

Suppose that no collisions between particles occur while the particles travel within the range of the potential of the wall: *i.e.* the mean free path is much greater than the range of the potential $\overline{\varphi}$ defining the wall. The collisions contributions to the average momentum transfer to the wall per unit time is therefore given by, see (2.1), $\int_{v>0} 2mv\, f(v)\, \rho_{wall}\, A\, v\, dv$ if $\rho_{wall}, f(v)$ are the average density near the wall and, respectively, the average fraction of particles with a velocity component normal to the wall between v and $v+dv$. Here p, f are supposed to be independent of the point on the wall: this should be true up to corrections of size $o(A)$.

Thus writing the average kinetic energy per particle and per velocity component, $\int \frac{m}{2}v^2 f(v)dv$, as $\frac12\beta^{-1}$ (*c.f.* (2.1)) it follows that

$$p \stackrel{def}{=} -\langle\partial_V\Phi\rangle = \rho_{wall}\beta^{-1} \tag{4.2}$$

has the physical interpretation of pressure. The $\frac12\beta^{-1}$ is the average kinetic energy per degree of freedom: hence it is proportional to the absolute temperature T (*c.f.* Sect.2).

On the other hand if motion on the energy surface takes place on a single periodic orbit the quantity p in (4.2) is the right quantity that would make the heat theorem work, see (3.2). Hence regarding the trajectory on each energy surface as periodic (*i.e.* the system as monocyclic) leads to the heat theorem with p, U, V, T having the *right physical interpretation* corresponding to their appellations. This shows that monocyclic systems provide natural models of thermodynamic behavior.

Assuming that a chaotic system like a gas in a container of volume V will satisfy "for practical purposes" the above property a quantity p can be defined such that $dU + p\,dV$ admits the inverse of the average kinetic energy $\langle K\rangle$ as an integrating factor and furthermore $p, U, V, \langle K\rangle$ have the physical interpretations of pressure, energy, volume and (up to a proportionality factor) absolute temperature.

Boltzmann's conception of space (and time) as discrete allowed him to conceive the property that the energy surface is constituted by "points" all of which belong to a single trajectory: a property that would be impossible if phase space was really a continuum. Regarding phase space as consisting of a finite number of "cells" of finite volume h^{dN}, for some $h > 0$ (rather than of a continuum of points) allowed him to think, without logical contradiction, that the energy surface consisted of a single trajectory and, hence, that motion was a cyclic permutation of its points (actually cells).

Furthermore it implied that the time average of an observable $F(\mathbf{P},\mathbf{Q})$ *had to be* identified with its average on the energy surface computed via the Liouville distribution $C^{-1}\int F(\mathbf{P},\mathbf{Q})\delta(H(\mathbf{P},\mathbf{Q})-U)\,d\mathbf{P}d\mathbf{Q}$ with $C = \int \delta(H(\mathbf{P},\mathbf{Q})-U)\,d\mathbf{P}d\mathbf{Q}$ (the appropriate normalization factor): a property that was written symbolically $\frac{dt}{T} = \frac{d\mathbf{P}d\mathbf{Q}}{\int d\mathbf{P}d\mathbf{Q}}$ or

$$\lim_{T\to\infty}\frac1T\int_0^T F(S_t(\mathbf{P},\mathbf{Q}))dt = \frac{\int F(\mathbf{P}',\mathbf{Q}')\delta(H(\mathbf{P}',\mathbf{Q}')-U)\,d\mathbf{P}'d\mathbf{Q}'}{\int \delta(H(\mathbf{P}',\mathbf{Q}')-U)\,d\mathbf{P}'d\mathbf{Q}'} \tag{4.3}$$

The validity of (4.3) for all (piecewise smooth) observables F and for all points of the energy surface, with the exception of a set of zero area, is called the *ergodic hypothesis*

Bibliography: [Bo84], [Ga99].

5. Ensembles

Eventually (1884) Boltzmann realized that the validity of the heat theorem for averages computed via the *r.h.s.* of (4.3) held *independently* of the ergodic hypothesis, *i.e.* the (4.3) was not necessary because the heat theorem (*i.e.* (3.1)) could also be derived under the only assumption that the averages involved in its formulation were computed as averages over phase space with respect to the probability distribution in the *r.h.s.* of (4.3).

Furthermore, if T was identified with the average kinetic energy, U with the average energy, p with the average force per unit surface on the walls of the container Ω with volume V, the relation (3.1) held *for a variety of families of probability distributions on phase space* besides the (4.3). Among which

(a) the *microcanonical ensemble*, which is the collection of probability distributions in the *r.h.s.* of (4.3) parameterized by $u = \frac{U}{N}, v = \frac{V}{N}$ (energy and volume per particle)

$$\mu^{mc}_{u,v}(d\mathbf{P}d\mathbf{Q}) = \frac{1}{Z_{mc}(U,N,V)}\delta(H(\mathbf{P},\mathbf{Q}) - U)\,\frac{d\mathbf{P}d\mathbf{Q}}{N!\,h^{dN}}, \tag{5.1}$$

where h is a constant with the dimensions of an action which, in the discrete representation of phase space mentioned in Sect.4, can be taken such that h^{dN} equals the cells volume and, therefore, the integrals with respect to (5.1) can be interpreted as an (approximate) sum over the cells conceived as microscopic configurations of N *indistinguishable* particles (whence the $N!$).
(b) the *canonical ensemble* which is the collection of probability distributions parameterized by $\beta, v = \frac{V}{N}$

$$\mu^{c}_{\beta,v}(d\mathbf{P}d\mathbf{Q}) = \frac{1}{Z_{c}(\beta,N,V)}e^{-\beta H(\mathbf{P},\mathbf{Q})}\,\frac{d\mathbf{P}d\mathbf{Q}}{N!\,h^{dN}} \tag{5.2}$$

to which more ensembles can be added. For instance Gibbs introduced

(c) the *grand canonical ensemble* which is the collection of probability distributions parameterized by β, λ and defined over the space $\mathcal{F}_{gc} = \cup_{N=0}^{\infty}\mathcal{F}(N)$

$$\mu^{gc}_{\beta,\lambda}(d\mathbf{P}d\mathbf{Q}) = \frac{1}{Z_{gc}(\beta,\lambda,V)}e^{\beta\lambda N-\beta H(\mathbf{P},\mathbf{Q})}\,\frac{d\mathbf{P}d\mathbf{Q}}{N!\,h^{dN}} \tag{5.3}$$

Hence there are *several* different models of Thermodynamics: a key test for accepting them as real microscopic descriptions of macroscopic Thermodynamics is that
(1) a correspondence between the macroscopic states of thermodynamic equilibrium and the elements of a collection of probability distributions on phase space can be established

by identifying on one side macroscopic thermodynamic states with given values of the thermodynamic functions and, on the other side, probability distributions attributing the *same average values* to the corresponding microscopic observables (*i.e.* whose averages have the interpretation of thermodynamic functions).
(2) once the correct correspondence between the elements of the different ensembles is established, *i.e.* once the pairs (u,v), (β,v), (β,λ) are so related to produce the same values for the averages U, V, $k_BT \stackrel{def}{=} \beta^{-1}$, $p\,|\partial\Omega|$ of

$$H(\mathbf{P},\mathbf{Q}),\ V,\ \frac{2K(\mathbf{P})}{3N},\ \int \delta_{\partial\Omega}(\mathbf{q}_1)\,2m(\mathbf{v}_1\cdot\mathbf{n})^2\,d\mathbf{q}_1, \tag{5.4}$$

($\delta_{\partial\Omega}(\mathbf{q}_1)$ is a delta function pinning $\mathbf{q}_1$ to the surface $\partial\Omega$) then the averages of all physically interesting observables *should coincide at least in the thermodynamic limit*, $\Omega\to\infty$. In this way the elements μ of the considered collection of probability distributions can be identified with the states of macroscopic equilibrium of the system. The μ's depend on parameters and therefore they form an *ensemble*: each of them corresponds to a macroscopic equilibrium state whose thermodynamic functions are appropriate averages of microscopic observables and therefore are functions of the parameters identifying μ.

Remark: The word *ensemble* is often used to indicate the individual probability distributions of what is called here ensemble. The meaning used here seems closer to the original sense in the 1884 paper of Boltzmann (in other words often by "ensemble" one means that collection of the phase space points on which a given probability distribution is considered, and this does not seem to be the original sense).

For instance in the case of the microcanonical distributions this means interpreting energy, volume, temperature and pressure of the equilibrium state with specific energy u and specific volume v as proportional, through appropriate universal proportionality constants, to the integrals with respect to $\mu^{mc}_{u,v}(d\mathbf{P}\,d\mathbf{Q})$ of the mechanical quantities in (5.4); and the averages of other thermodynamic observables in the state with specific energy u and specific volume v should be given by their integrals with respect to $\mu^{mc}_{u,v}$.

Likewise one can interpret energy, volume, temperature and pressure of the equilibrium state with specific energy u and specific volume v as the averages of the mechanical quantities (5.4) with respect to the canonical distribution $\mu^{c}_{\beta,v}(d\mathbf{P}\,d\mathbf{Q})$ which has average specific energy precisely u; and the averages of other thermodynamic observables in the state with specific energy and volume u and v are given by their integrals with respect to $\mu^c_{\beta,v}$. And a similar definition can be given for the description of thermodynamic equilibria via the grand canonical distributions.

Bibliography: [Gi81], [Ga99].

6. Equivalence of ensembles

Boltzmann proved that, computing averages via the microcanonical or canonical distributions, the essential property (3.1) was satisfied when changes in their parameters (*i.e.* u, v or β, v respectively) induced changes du, dv on energy and volume. He also proved that the function s, whose existence is implied by (3.1), was *the same* function once expressed as a function of u, v (or of any pair of thermodynamic parameters, *e.g.* of T, v or of p, u). A close examination of Boltzmann's proof shows that the (3.1) holds *exactly* in the canonical ensemble and up to corrections tending to 0 as $\Omega \to \infty$ in the microcanonical ensemble. Identity of thermodynamic functions evaluated in the two ensembles holds, as a consequence, up to corrections of this order. And Gibbs added that the same held for the grand canonical ensemble.

Of course *not every collection of stationary probability distributions on phase space* would provide a model for Thermodynamics: Boltzmann called *orthodic* the collections of stationary distributions which generated models of Thermodynamics through the above mentioned identification of its elements with macroscopic equilibrium states. The microcanonical, canonical and the later grand canonical ensembles are the chief examples of orthodic ensembles: which Boltzmann and Gibbs *proved to be not only orthodic but to generate the same thermodynamic functions*, *i.e.* to generate the same Thermodynamics

This freed from the analysis of the truth of the doubtful ergodic hypothesis (still unproved in any generality) or of the monocyclicity (manifestly false if understood literally rather than regarding phase space as consisting of finitely many small, discrete, cells), and allowed Gibbs to formulate the problem of Statistical Mechanics of equilibrium as

Problem: study the properties of the collection of probability distributions constituting (any) one of the above ensembles.

However by no means the three ensembles just introduces exhaust the class of orthodic ensembles producing the same models of Thermodynamics in the limit of infinitely large systems. The wealth of ensembles with the orthodicity property, hence leading to equivalent mechanical models of Thermodynamics, can be naturally interpreted in connection with the phase transitions phenomenon, see Sect.9.

Clearly the quoted results do not "prove" that thermodynamic equilibria "are" described by the microcanonical or canonical or grand canonical ensembles. However they certainly show that for most systems, independently of the number of degrees of freedom, one can define *quite unambiguously a mechanical model of Thermodynamics* establishing *parameter free, system independent, physically important* relations between Thermodynamic quantities (*e.g.* $\partial_u \frac{p(u,v)}{T(u,v)} \equiv \partial_v \frac{1}{T(u,v)}$, from (3.1)).

The ergodic hypothesis which was at the root of the mechanical theorems on heat and entropy cannot be taken as a justification of their validity. *Naively* one would expect that the time scale necessary to see an equilibrium attained, called *recurrence time scale*, would have to be at least the time that a phase space point takes to visit all possible microscopic states of given energy: hence an explanation of why the necessarily enormous size of the recurrence time is not a problem becomes necessary..

In fact the recurrence time can be estimated once the phase space is regarded as discrete: for the purpose of countering mounting criticism Boltzmann assumed that momentum was discretized in units of $(2mk_BT)^{\frac{1}{2}}$ (*i.e.* the average momentum size) and space was discretized in units of $\rho^{-\frac{1}{3}}$ (*i.e.* the average spacing), implying a volume of cells h^{3N} with $h \stackrel{def}{=} \rho^{-\frac{1}{3}}(2mk_BT)^{\frac{1}{2}}$; then he calculated that, even with such a *gross* discretization, a cell representing a microscopic state of $1cm^3$ of hydrogen at normal condition would require a time (called "recurrence time") of the order of $\sim 10^{10^{19}}$ times the age of the Universe (!) to visit the entire energy surface. [In fact the phase space volume is $\Gamma = (\rho^{-3}N(2mk_BT)^{\frac{3}{2}})^N \equiv h^{3N}$ and the number of cells of volume h^{3N} is $\Gamma/(N!h^{3N}) \simeq e^{3N}$: and the time to visit all will be $e^{3N}\tau_0$ with τ_0 a typical atomic unit, *e.g.* $10^{-12}sec$: but $N = 10^{19}$]. In this sense the statement boldly made by the young Boltzmann that "aperiodic motions can be regarded as periodic with infinite period" was even made quantitative.

The time is clearly so long to be *irrelevant for all purposes*: nevertheless the correctness of the microscopic theory of Thermodynamics can still rely on microscopic dynamics once it is understood, as stressed by Boltzmann, that the reason why we observe approach to equilibrium, and equilibrium itself, over "human" time scales, *far shorter than the recurrence times*, is due to the property that on most of the energy surface the (very few) observables whose averages yield macroscopic thermodynamic functions (namely pressure, temperature, energy ...) *assume the same value* even if N is only very moderately large (of the order of 10^3 rather than 10^{19}). This implies that this value coincides with the average and therefore satisfies the *heat theorem* without any contradiction with the length of the recurrence time. The latter rather concerns the time needed to the *generic observable* to *thermalize*, *i.e.* to reach its time average: the generic observable will indeed take a very long time to "thermalize" *but no one will ever notice because the generic observable* (*e.g.* the position of a pre-identified particle) *is not relevant for Thermodynamics*.

The word "proof" used so far in this paper is not in the mathematical sense: the relevance of a *mathematically rigorous* analysis was widely realized only around the 1960's at the same time when the first numerical studies of the thermodynamic functions became possible and rigorous results became needed to check the correctness of various numerical simulations.

Bibliography: [Bo66], [Bo84], [Ga99].

7. Thermodynamic limit

Adopting Gibbs axiomatic point of view it is interesting to see the path to be followed to achieve an equivalence proof of three ensembles introduced in Sect 4.

A preliminary step is to consider, given a cubic box Ω of volume $V = L^d$, the normalization factors $Z^{gc}(\beta,\lambda,V), Z^c(\beta,N,V), Z^{mc}(U,N,V)$ in (5.1),(5.2),(5.3), and to check that the following *thermodynamic limits* exist:

$$\begin{aligned}
\beta p_{gc}(\beta,\lambda) &\stackrel{def}{=} \lim_{V\to\infty} \frac{1}{V}\log Z_{gc}(\beta,\lambda,V)\\
-\beta f_c(\beta,\rho) &\stackrel{def}{=} \lim_{V\to\infty,\,\frac{N}{V}=\rho} \frac{1}{N}\log Z^c(\beta,N,V)\\
k_B^{-1}s_{mc}(u,\rho) &\stackrel{def}{=} \lim_{V\to\infty,\,\frac{N}{V}=\rho,\,\frac{U}{N}=u} \frac{1}{N}\log Z^{mc}(U,N,V)
\end{aligned}\tag{7.1}$$

where the density $\rho \stackrel{def}{=} v^{-1} \equiv \frac{N}{V}$ is used instead of v for later reference. The normalization factors play an important role because they have simple thermodynamic interpretation, see Sect. 8: they are called grand canonical, canonical and microcanonical *partition functions*, respectively.

Not surprisingly assumptions on the interparticle potential $\varphi(\mathbf{q}-\mathbf{q}')$ are necessary to achieve an existence proof of the limits in (7.1). The assumptions on φ are not only quite general but also have a clear physical meaning. They are

(1) *stability*: *i.e.* existence of a constant $B \ge 0$ such that $\sum_{i<j}^N \varphi(\mathbf{q}_i - \mathbf{q}_j) \ge -BN$ for all $N \ge 0, \mathbf{q}_1, \ldots, \mathbf{q}_N \in \mathbb{R}^d$, and

(2) *temperedness*: *i.e.* existence of constants $\varepsilon_0, R > 0$ such that $|\varphi(\mathbf{q}-\mathbf{q}')| < B|\mathbf{q}-\mathbf{q}'|^{-d-\varepsilon_0}$ for $|\mathbf{q}-\mathbf{q}'| > R$.

The assumptions are satisfied by essentially all microscopic interactions *with the notable exceptions of the gravitational and Coulombic interactions*, which require a separate treatment (and lead to somewhat different results on the Thermodynamic behavior).

For instance the (1), (2) are satisfied if $\varphi(\mathbf{q})$ is $+\infty$ for $|\mathbf{q}| < r_0$ and smooth for $|\mathbf{q}| > r_0$, for some $r_0 \ge 0$, and furthermore $\varphi(\mathbf{q}) > B_0|\mathbf{q}|^{-(d+\varepsilon_0)}$ if $r_0 < |\mathbf{q}| \le R$, while for $|\mathbf{q}| > R$ it is $|\varphi(\mathbf{q})| < B_1|\mathbf{q}|^{-(d+\varepsilon_0)}$ with $B_0, B_1, \varepsilon_0 > 0, R > r_0$ suitably chosen. Briefly *φ is fast diverging at contact and fast approaching 0 at large distance.* This is called a (generalized) *Lennard–Jones potential.* If $r_0 > 0$ the φ is called a *hard core potential.* If $B_1 = 0$ the potential is said to have *finite range.* See Appendix A1 for physical implications of violations of the above stability and temperedness properties. *However* in the following it will necessary, both for simplicity and to contain the length of the exposition, to restrict consideration to the case $B_1 = 0$, *i.e.* to

$$\varphi(\mathbf{q}) > B_0|\mathbf{q}|^{-(d+\varepsilon_0)}, \quad r_0 < |\mathbf{q}| \le R \quad \text{and} \quad |\varphi(\mathbf{q})| \equiv 0, \quad |\mathbf{q}| > R \tag{7.2}$$

unless explicitly stated.

Assuming (1) and (2) the existence of the limits in (7.1) can be mathematically proved: in Appendix A2 the proof of the first is analyzed to provide the simplest example of the technique. A remarkable property of the functions $\beta p_{gc}(\beta,\lambda), -\beta\rho f_c(\beta,\rho), \rho s_{mc}(u,\rho)$ is that they are *convex* functions: hence they are continuous in the interior of their domains of definition and at one variable fixed are, with at most countably many exceptions, differentiable in the other.

In the case of a potential without hard core ($\rho_{\max} = \infty$) the $-\rho f_c(\beta,\rho)$ can be checked to tend to 0 slower than ρ as $\rho \to 0$ and to $-\infty$ faster than $-\rho$ as $\rho \to \infty$ (essentially proportionally to $-\rho\log\rho$ in both cases). Likewise in the same case $s_{mc}(u,\rho)$ can be shown to tend to 0 slower than $u - u_{min}$ as $u \to u_{min}$ and to $-\infty$ faster than $-u$ as $u \to \infty$. The latter asymptotic properties can be exploited to derive from the relations between the partition functions in (7.1)

$$\begin{aligned} Z^{gc}(\beta,\lambda,V) &= \textstyle\sum_{N=0}^\infty e^{\beta\lambda N} Z^c(\beta,N,V) \quad \text{and} \\ Z^c(\beta,N,V) &= \textstyle\int_{-B}^\infty e^{-\beta U} Z^{mc}(U,N,V)\, dU \end{aligned} \tag{7.3}$$

and from the mentioned convexity the consequences

$$\begin{aligned} \beta p_{mc}(\beta,\lambda) =& \max_v (\beta\lambda v^{-1} - \beta v^{-1} f_c(\beta, v^{-1})) \\ -\beta f_c(\beta, v^{-1}) =& \max_u (-\beta u + k_B^{-1} s_{mc}(u, v^{-1})) \end{aligned} \tag{7.4}$$

and that the maxima are attained in points, *or intervals*, internal to the intervals of definition. Let v_{gc}, u_c be points where the maxima are respectively attained in (7.4).

Remark that the quantity $\frac{e^{\beta\lambda N} Z^c(\beta,N,V)}{Z^{gc}(\beta,\lambda,V)}$ has the interpretation of probability of a density $v^{-1} = N/V$ evaluated in the grand canonical distribution. It follows that *if the maximum in the first of (7.4) is strict*, *i.e.* it is reached at a single point, the values of v^{-1} in closed intervals *not containing* the maximum point v_{gc}^{-1} have a probability behaving as $< e^{-cV}, c > 0$, as $V \to \infty$, compared to the probability of v^{-1}'s *in any interval containing* v_{gc}^{-1}. Hence v_{gc} has the interpretation of average value of v in the grand canonical distribution, in the limit $V \to \infty$.

Likewise the interpretation of $\frac{e^{-\beta u N} Z^{mc}(uN,N,V)}{Z^c(\beta,N,V)}$ as probability in the canonical distribution of an energy density u shows that if the maximum in the second of (7.4) is strict the values of u in closed intervals *not containing* the maximum point u_c have a probability behaving as $< e^{-cV}, c > 0$, as $V \to \infty$, compared to the probability of u's in any interval containing u_c. Hence in the limit $\Omega \to \infty$ the average value of u in the canonical distribution is u_c.

If the maxima are *strict* the (7.4) also establishes a relation between the grand canonical density, the canonical free energy and the grand canonical parameter λ, or between the canonical energy, the microcanonical entropy and the canonical parameter β:

$$\lambda = \partial_{v^{-1}}(v_{gc}^{-1} f_c(\beta, v_{gc}^{-1})), \qquad k_B\beta = \partial_u s_{mc}(u_c, v^{-1}) \tag{7.5}$$

where convexity and strictness of the maxima imply the derivatives existence.

Remark: Therefore in the equivalence between canonical and microcanonical ensembles the canonical distribution with parameters (β, v) should correspond with the microcanonical with parameters (u_c, v). And the grand canonical distribution with parameters (β, λ) should correspond with the canonical with parameters (β, v_{gc}) .

Bibliography: [Ru69], [Ga99].

8. Physical interpretation of thermodynamic functions

The existence of the limits (7.1) implies several properties of interest. The first is the possibility of finding the physical meaning of the functions p_{gc}, f_c, s_{mc} and of the parameters λ, β

Note first that, for all V the grand canonical average $\langle K\rangle_{\beta,\lambda}$ is $\frac{d}{2}\beta^{-1}\langle N\rangle_{\beta,\lambda}$ so that β^{-1} is proportional to the temperature $T_{gc} = T(\beta,\lambda)$ in the gand canonical distribution: $\beta^{-1} = k_B T(\beta,\lambda)$. Proceeding *heuristically* the physical meaning of $p(\beta,\lambda)$ and of λ can be found by the following remarks.

Consider the microcanonical distribution $\mu^{mc}_{u,v}$ and denote by $\int^*$ the integral over $(\mathbf{P},\mathbf{Q})$ extended to the domain of the $(\mathbf{P},\mathbf{Q})$ such that $H(\mathbf{P},\mathbf{Q})=U$ *and*, at the same time, $\mathbf{q}_1\in dV$ where dV is an infinitesimal volume surrounding the region Ω. Then by the microscopic definition of the pressure p, see Sect. 1, it is

$$pdV=\frac{N}{Z(U,N,V)}\int^*\delta\,\frac{2}{3}\frac{p_1^2}{2m}\frac{d\mathbf{P}\,d\mathbf{Q}}{N!h^{dN}}\equiv\frac{2}{3Z(U,N,V)}\int^*\delta\,K(\mathbf{P})\frac{d\mathbf{P}\,d\mathbf{Q}}{N!h^{dN}}\tag{8.1}$$

where $\delta\equiv\delta(H(\mathbf{P},\mathbf{Q})-U)$. The *r.h.s.* of (8.1) can be compared with $\frac{\partial_V Z(U,N,V)dV}{Z(U,N,V)}=\frac{N}{Z(U,N,V)}\int^*\frac{d\mathbf{P}\,d\mathbf{Q}}{N!h^{dN}}$ to give $\frac{\partial_V Z\,dV}{Z}=N\frac{p\,dV}{\frac{2}{3}\langle K\rangle^*}=\beta pdV$ because $\langle K\rangle^*$, which denotes the average $\int^*K/\int^*1$, *should be essentially the same as the microcanonical average* $\langle K\rangle_{mc}$ (*i.e.* insensitive to the fact that one particle is constrained to the volume dV) if N is large. In the limit $V\to\infty$, $\frac{V}{N}=v$ the latter remark together with the second of (7.5) yields

$$k_B^{-1}\partial_v s_{mc}(u,v^{-1})=\beta\,p(u,v),\qquad k_B^{-1}\partial_u s_{mc}(u,v)=\beta\tag{8.2}$$

respectively. Note that $p\ge0$ and it is *not increasing in* v because $s_{mc}(\rho)$ is *concave* as a function of $v=\rho^{-1}$ (in fact by the remark following (7.2) $\rho s_{mc}(u,\rho)$ is convex in ρ and, in general, if $\rho g(\rho)$ is convex in ρ then $g(v^{-1})$ is, always, concave in $v=\rho^{-1}$).

Hence $ds_{mc}(u,v)=\frac{du+pdv}{T}$ so that taking into account the physical meaning of p,T (as pressure and temperature, see Sec. 2), s_{mc} is, in Thermodynamics, the *entropy*. Therefore, see the second of (7.4), $-\beta f_c(\beta,\rho)=-\beta u_c+k_B^{-1}s_{mc}(u_c,\rho)$ becomes

$$f_c(\beta,\rho)=u_c-T_c s_{mc}(u_c,\rho),\qquad df_c=-p\,dv-s_{mc}\,dT\tag{8.3}$$

and since u_c has the interpretation, as mentioned in Sect. 7, of average energy in the canonical distribution $\mu^c_{\beta,v}$ it follows that f_c has the thermodynamic interpretation of *free energy* (once compared with the free energy definition $F=U-TS$ in Thermodynamics).

By (7.5), (8.3) $\lambda=\partial_{v^{-1}}(v_{gc}^{-1}f_c(\beta,v_{gc}^{-1}))\equiv u_c-T_c s_{mc}+p\,v_{gc}$ and v_{gc} has the meaning of specific volume v. Hence, after comparison with the chemical potential definition $\lambda V=U-TS+pV$ in Thermodynamics, it follows that the thermodynamic interpretation of λ is the *chemical potential* and, see (7.4),(7.5), the grand canonical relation $\beta p(\beta,\lambda)=\beta\lambda v_{gc}^{-1}-\beta v_{gc}^{-1}(-\beta u_c+k_B^{-1}s_{mc}(u_c,v^{-1}))$ shows that $p(\beta,\lambda)\equiv p$ implying that $p(\beta,\lambda)$ is the pressure expressed, however, as a function of temperature and chemical potential.

To go beyond the heuristic derivations above it should be remarked that convexity and the property that the maxima in (7.4),(7.5) are reached in the interior of the intervals of variability of v or u are sufficient to turn the above arguments into rigorous mathematical deductions: this means that given (8.2) as definitions of $p(u,v),\beta(u,v)$ the second of (8.3) follows as well as $p(\beta,\lambda)\equiv p(u_v,v_{gc}^{-1})$. But the values v_{gc} and u_c in (7.4) *are not necessarily unique*: convex functions can contain horizontal segments and therefore the general conclusion is that the maxima may possibly be attained in intervals. Hence instead of a single v_{gc} there might be a whole interval $[v_-,v_+]$ where the *r.h.s.* of (7.4) reaches the maximum and instead of a single u_c there might be a whole interval $[u_-,u_+]$ where the *r.h.s.* of (7.5) reaches the maximum.

Convexity implies that the values of λ or of β for which the maxima in (7.4) or (7.5) are attained in intervals rather than in single points are *rare* (*i.e.* at most denumerably many): the interpretation is, in such cases, that the thermodynamic functions show discontinuities: and the corresponding phenomena are called *phase transitions*, see Sect.9.

Bibliography: [Ru69], [Ga99].

9. Phase transitions and boundary conditions

The analysis in Sect.7,8 of the relations between elements of ensembles of distributions describing macroscopic equilibrium states not only allows us to obtain mechanical models of Thermodynamics but it also shows that the models, for a given system, coincide at least as $\Omega \to \infty$. Furthermore the equivalence between the thermodynamic functions computed via corresponding distributions in different ensembles can be extended to a full equivalence of the distributions.

If the maxima in (7.4) are attained in single points v_{gc} or u_c the equivalence should take place in the sense that a correspondence between $\mu^{gc}_{\beta,\lambda}, \mu^{c}_{\beta,v}, \mu^{mc}_{u,v}$ can be established so that given *any local observable* $F(\mathbf{P},\mathbf{Q})$, defined as an observable *depending on* $(\mathbf{P},\mathbf{Q})$ *only through the* $\mathbf{p}_i, \mathbf{q}_i$ *with* $\mathbf{q}_i \in \Lambda$ where $\Lambda \subset \Omega$ is a finite region, has the *same average* with respect to corresponding distributions in the limit $\Omega \to \infty$.

The correspondence is established by considering $(\lambda,\beta) \longleftrightarrow (\beta, v_{gc}) \longleftrightarrow (u_{mc}, v)$ where v_{gc} is where the maximum in (7.4) is attained, $u_{mc} \equiv u_c$ is where the maximum in (7.5) is attained and $v_{gc} \equiv v$, (*c.f.* also (8.2),(8.3)). This means that the limits

$$\lim_{V\to\infty} \int F(\mathbf{P},\mathbf{Q})\mu^a(d\mathbf{P}\, d\mathbf{Q}) \stackrel{def}{=} \langle F \rangle_a = a - \text{independent}, \qquad a = gc, c, mc \tag{9.1}$$

coincide if the averages are evaluated by the distributions $\mu^{gc}_{\beta,\lambda}, \mu^{c}_{\beta,v_c}, \mu^{mc}_{u_{mc},v_{mc}}$

Exceptions to the (9.1) are possible: and are certainly likely to occur at values of u, v where the maxima in (7.4) or (7.5) are attained in intervals rather than in isolated points; but this does not exhaust, in general, the cases in which (9.1) may not hold.

However no case in which (9.1) fails *has to be regarded as an exception.* It rather signals that an interesting and important phenomenon occurs. To understand it properly it is necessary to realize that the grand canonical, canonical and microcanonical families of probability distributions are *by far* not the only ensembles of probability distributions whose elements can be considered to generate models of Thermodynamics, *i.e.* which are orthodic in the sense of Sect. 6. More general families of orthodic statistical ensembles of probability distributions can be very easily conceived. In particular

Definition: *consider the grand canonical, canonical and microcanonical distributions associated with an energy function in which the potential energy contains, besides the interaction* Φ *between particles located inside the container, also the interaction energy* $\Phi_{in,out}$ *between particles inside the container and external particles, identical to the ones in the container but not allowed to move and fixed in positions such that in every unit cube* Δ

external to Ω there is a finite number of them bounded independently of Δ. Such configurations of external particles will be called "boundary conditions of fixed external particles".

The thermodynamic limit with such boundary conditions is obtained by considering the grand canonical, canonical and microcanonical distributions constructed with potential energy function $\Phi + \Phi_{in,out}$ in containers Ω of increasing size taking care that, while the size increases, the fixed particles that would become internal to Ω are eliminated. The argument used in Sec.7 to show that the three models of thermodynamics, considered there, did define the same thermodynamic functions can be repeated to reach the conclusion that the also the (infinitely many) "new" models of Thermodynamics in fact give rise to the same thermodynamic functions and averages of local observables. Furthermore the values of the limits corresponding to (7.1) can be computed using the new partition functions and *coincide* with the ones in (7.1) (*i.e.* are boundary conditions independent).

However it may happen, and in general it really happens, for many models and for particular values of the state parameters, that the limits in (9.1) do not coincide with the analogous limits computed in the new ensembles: *i.e.* the averages of some local observables are *unstable* with respect to changes of fixed particles boundary conditions.

There is a very natural interpretation of such apparent ambiguity of the various models of Thermodynamics: namely at the values of the parameters that are selected to describe the macroscopic states under consideration *there may correspond different equilibrium states with the same parameters*. When the maximum in (7.4) is reached on an interval of densities one should not think of any failure of the microscopic models for Thermodynamics: rather one has to think that there are several states possible with the same β, λ and that they can be identified with the probability distributions obtained by forming the grand canonical, canonical or microcanonical distributions with *different kinds of boundary conditions*.

For instance a boundary condition with high density may produce an equilibrium state with parameters β, λ which has high density, *i.e.* the density v_+^{-1} at the right extreme of the interval in which the maximum in (7.4) is attained, while using a low density boundary condition the limit in (9.1) may describe the averages taken in a state with density v_-^{-1} at the left extreme of the interval or, perhaps, with a density intermediate between the two extremes. Therefore the following definition emerges.

Definition: *If the grand canonical distributions with parameters (β, λ) and different choices of fixed external particles boundary conditions generate for some local observable F average values which are different by more than a quantity $\delta > 0$ for all large enough volumes Ω then one says that the system has a phase transition at (β, λ). This implies that the limits in (9.1), when existing, will depend on the boundary condition and their values will represent averages of the observables in "different phases". A corresponding definition is given in the case of the canonical and microcanonical distributions when, given (β, v) or (u, v), the limit in (9.1) depends on the boundary conditions for some F.*

Remarks: (1) The idea is that by fixing one of the thermodynamic ensembles and by varying the boundary conditions one can realize all possible states of equilibrium of the system that can exist with the given values of the parameters determining the state in the chosen ensemble (*i.e.* (β,λ), (β,v) or (u,v) in the grand canonical, canonical or microcanonical cases respectively).

(2) The impression that in order to define a phase transition the thermodynamic limit is necessary is *incorrect*: the definition *does not require* considering the limit $\Omega\to\infty$. The phenomenon is that by changing boundary conditions the average of a local observable can change *at least by amounts independent of the system size*. Hence occurrence of a phase transition is perfectly observable in finite volume: it suffices to check that by changing boundary conditions the average of some observable changes by an amount whose minimal size is volume *independent*. It is a manifestation of an instability of the averages with respect to boundary conditions changes: an instability which does not fade away when the boundary recedes to infinity, *i.e.* boundary perturbations produce bulk effects and at a phase transitions the averages of the local observable, if existing at all, will exhibit a nontrivial boundary conditions dependence. This is also called "*long range order*".

(3) It is possible to show that when this happens then some thermodynamic function whose value is boundary condition independent (like the free energy in the canonical distributions) has discontinuous derivatives in terms of the parameters of the ensemble defining them. This is in fact one of the frequently used alternative definitions of phase transitions: the latter two natural definitions of first order phase transition are equivalent. However it is very difficult to prove that a given system shows a phase transition. For instance existence of a liquid-gas phase transition is still an open problem in systems of the type considered until Sect.15.

(4) A remarkable unification of the theory of the equilibrium ensembles emerges: all distributions of any ensemble describe equilibrium states. If a boundary condition is fixed once and for all then some equilibrium states might fail to be described by an element of an ensemble. However if all boundary conditions are allowed then all equilibrium states should be realizable in a given ensemble by varying the boundary conditions.

(5) The analysis leads us to consider as completely equivalent *without exceptions* grand canonical, canonical or microcanonical ensembles enlarged by adding to them the distributions with potential energy augmented by the interaction with fixed external particles.

(6) The above picture is *really proved* only for special classes of models (typically in models in which particles are constrained to occupy points of a lattice and in systems with hard core interactions, $r_0>0$ in (7.2)) but it is believed to be correct in general: at least it is consistent with all what is so far known in classical statistical mechanics. The difficulty is that conceivably one might even need boundary conditions more complicated than the fixed particles boundary conditions (like putting different particles outside interaction with the system with an arbitrary potential, rather than via φ).

The discussion of the equivalence of the ensembles and the question of boundary conditions importance has already imposed the consideration of several limits as $\Omega\to\infty$. Occasionally it will again come up. For conciseness purposes it is useful to set up a formal definition of equilibrium states of an "infinite volume" system: although infinite volume is an idealization void of physical reality it is nevertheless useful to define such states because certain notions, like that of *pure state* can be sharply defined, with few words and avoiding wide circumvolutions, in terms of them. Therefore let:

Definition: *An infinite volume state with parameters (β,λ), or (β,v) is a collection of* *average values $F \to \langle F\rangle$ obtained, respectively, as limits of finite volume averages $\langle F\rangle_{\Omega_n}$ defined from canonical, microcanonical or grand canonical distributions in Ω_n with fixed parameters (β,λ), (β, v), or (u,v) and with general boundary condition of fixed external particles, on sequences $\Omega_n \to \infty$ for which such limits exist simultaneously for all local observables F.*

Having set the definition of infinite volume state consider a local observable $G(X)$ and let $\tau_\xi G(X) = G(X+\xi)$, $\xi \in \mathbb{R}^d$, with $X+\xi$ denoting the configuration X in which all particles are translated by ξ: then an infinite volume state is a *pure state* if for any pair of local observables F, G it is

$$\langle F\tau_\xi G\rangle - \langle F\rangle\langle \tau_\xi G\rangle \xrightarrow[\xi\to\infty]{} 0 \tag{9.2}$$

which is called a *cluster property* of the pair F, G.

The result alluded to in remark (6) is that at least in the case of hard core systems (or of the simple lattice systems discussed in Sect.15) the infinite volume equilibrium states in the above sense exhaust at least the totality of the infinite volume *pure states*. And furthermore the other states that can be obtained in the same way are convex combinations of the pure states, *i.e.* they are "statistical mixtures" of pure phases. Note that $\langle\tau_\xi G\rangle$ cannot be replaced, in general, by $\langle G\rangle$ because not all infinite volume states are necessarily translation invariant and in simple cases (crystals) it is even possible that no translations invariant state is a pure state.

Remarks: (1) This means that, in the latter models, generalizing the boundary conditions, *e.g.* considering external particles not identical to the ones in the system, or using periodic or partially periodic boundary conditions or *the widely used alternative device of introducing a small auxiliary potential and first taking the infinite volume states in presence of it and then letting the potential vanish* does not enlarge further the set of states (but may sometimes be useful: an example of a study of a phase transition by using the latter method of small fields will be given in Sect.13).
(2) If χ is the indicator function of a local event it will make sense to consider the probability of occurrence of the event in a infinite volume state defining it as $\langle\chi\rangle$. In particular the probability density for finding p particles in $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_p$, called the *p-point correlation function*, will thus be defined in an infinite volume state. For instance if the state is obtained as a limit of canonical states $\langle\cdot\rangle_{\Omega_n}$ with parameters β, ρ, $\rho = \frac{N_n}{V_n}$, in a sequence of containers Ω_n, then $\rho(\mathbf{x}) = \lim_n \langle\sum_{j=1}^{N_n}\delta(\mathbf{x}-\mathbf{q}_j)\rangle_{\Omega_n}$, and $\rho(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_p) = \lim_n \langle\sum_{i_1,\ldots,i_p}^{N_n}\prod_{j=1}^p \delta(\mathbf{x}_j-\mathbf{q}_{i_j})\rangle_{\Omega_n}$, where the sum is over the *ordered* p-ples $(j_1,\ldots,j_p)$. Thus the pair correlation $\rho(\mathbf{q},\mathbf{q}')$ and its possible cluster property are

$$\begin{aligned}&\rho(\mathbf{q},\mathbf{q}') \stackrel{def}{=} \lim_n \frac{\int_{\Omega_n} e^{-\beta U(\mathbf{q},\mathbf{q}',\mathbf{q}_1,\ldots,\mathbf{q}_{N_n-2})}d\mathbf{q}_1\ldots d\mathbf{q}_{N_n-2}}{(N_n-2)!\,Z_0^c(\beta,\rho,V_n)}\\ &\rho(\mathbf{q},(\mathbf{q}'+\boldsymbol{\xi})) - \rho(\mathbf{q})\rho(\mathbf{q}'+\boldsymbol{\xi}) \xrightarrow[\boldsymbol{\xi}\to\infty]{} 0\end{aligned} \tag{9.3}$$

where $Z_0^c \stackrel{def}{=} \int e^{-\beta U(\mathbf{Q})} d\mathbf{Q}$ is the "configurational" partition function.

Bibliography: [Ru69], [Do68], [LR69], [Ga99].

10. Virial theorem and atomic dimensions

For a long time it has been doubted that "just changing boundary conditions" could produce such dramatic changes as macroscopically different states (*i.e.* phase transitions in the sense of the definition in Sect.9). The first evidence that by taking the thermodynamic limit very regular analytic functions like $N^{-1} \log Z^c(\beta, N, V)$ as a function of $\beta, v = \frac{V}{N}$ could develop in the limit $\Omega \to \infty$ singularities like discontinuous derivatives (corresponding to the maximum in (7.4) being reached on a plateau and to a *consequent* existence of several pure phases) arose in the *van der Waals' theory* of liquid gas transition.

Consider a real gas with N identical particles with mass m in a container Ω with volume V. Let the force acting on the i-th particle be $\mathbf{f}_i$; multiplying both sides of the equations of motion $m\ddot{\mathbf{q}}_i = \mathbf{f}_i$ by $-\frac{1}{2}\mathbf{q}_i$ and summing over i it follows $-\frac{1}{2}\sum_{i=1}^N m\mathbf{q}_i \cdot \ddot{\mathbf{q}}_i = -\frac{1}{2}\sum_{i=1}^N \mathbf{q}_i \cdot \mathbf{f}_i \stackrel{def}{=} \frac{1}{2}C(\mathbf{q})$ and the quantity $C(\mathbf{q})$ defines the *virial of the forces* in the configuration $\mathbf{q}$; note that $C(\mathbf{q})$ is *not* translation invariant because of the presence of the forces due to the walls.

Writing the force $\mathbf{f}_i$ as a sum of the internal and of the external forces (due to the walls) the virial C can be expressed naturally as sum of the virial C_{int} of the internal forces (translation invariant) and of the virial C_{ext} of the external forces.

By dividing both sides of the definition of the virial by τ and integrating over the time interval $[0, \tau]$ one finds in the limit $\tau \to +\infty$, *i.e.* up to quantities relatively infinitesimal as $\tau \to \infty$, that $\langle K \rangle = \frac{1}{2}\langle C \rangle$, *and* $\langle C_{ext} \rangle = 3pV$ where p is the pressure and V the volume. Hence $\langle K \rangle = \frac{3}{2}pV + \frac{1}{2}\langle C_{int} \rangle$ or

$$\frac{1}{\beta} = pv + \frac{\langle C_{int} \rangle}{3N} \tag{10.1}$$

Equation (10.1) is the *Clausius' virial theorem*: in the case of no internal forces it yields $\beta pv = 1$, the ideal gas equation.

The internal virial C_{int} can be written, if $\mathbf{f}_{j\to i} = -\partial_{\mathbf{q}_i}\varphi(\mathbf{q}_i - \mathbf{q}_j)$, as $C_{int} = -\sum_{i=1}^N \sum_{i\neq j} \mathbf{f}_{j\to i} \cdot \mathbf{q}_i \equiv -\sum_{i<j} \partial_{q_i}\varphi(\mathbf{q}_i - \mathbf{q}_j) \cdot (\mathbf{q}_i - \mathbf{q}_j)$ which shows that the contribution to the virial by the internal repulsive forces is *negative* while that of the attractive forces is *positive*. The average of C_{int} can be computed by the canonical distribution, which is convenient for the purpose. van der Waals first used the virial theorem to perform an actual computation of the corrections to the perfect gas laws. Simply neglect the third order term in the density and use the approximation $\rho(\mathbf{q}_1, \mathbf{q}_2) = \rho^2 e^{-\beta\varphi(\mathbf{q}_1 - \mathbf{q}_2)}$ for the pair correlation function, (9.3), then

$$\frac{1}{2}\langle C_{int} \rangle = V\frac{3}{2\beta}\rho^2 I(\beta) + VO(\rho^3) \tag{10.2}$$

where $I(\beta) = \frac{1}{2}\int \left(e^{-\beta\varphi(\mathbf{q})} - 1\right) d^3\mathbf{q}$ and the equation of state (10.1) becomes $pv + \frac{I(\beta)}{\beta v} + O(v^{-2}) = \beta^{-1}$.

For the purpose of illustration the calculation of I can be performed approximately at "high temperature" (β small) in the case $\varphi(r)=4\varepsilon\big((\frac{r_0}{r})^{12}-(\frac{r_0}{r})^6\big)$ (the classical Lennard–Jones potential), $\varepsilon, r_0>0$. The result is $I\cong-(b-\beta a)$, $b=4v_0,\ a=\frac{32}{3}\varepsilon v_0,\ v_0=\frac{4\pi}{3}(\frac{r_0}{2})^3,$: hence $pv+\frac{a}{v}-\frac{b}{\beta v}=\frac{1}{\beta}+O(\frac{1}{\beta v^2})$, $(p+\frac{a}{v^2})\,v=(1+\frac{b}{v})\frac{1}{\beta}=\frac{1}{1-\frac{b}{v}}\frac{1}{\beta}+O(\frac{1}{\beta v^2})$ or:

$$(p+\frac{a}{v^2})(v-b)\beta=1+O(v^{-2}),\tag{10.3}$$

which gives the equation of state for $\beta\varepsilon\ll1$. Equation (10.3) can be compared with the well-known empirical *van der Waals equation* of state:

$$\beta(p+a/v^2)(v-b)=1\quad\text{or}\quad(p+An^2/V^2)(V-nB)=nRT\tag{10.4}$$

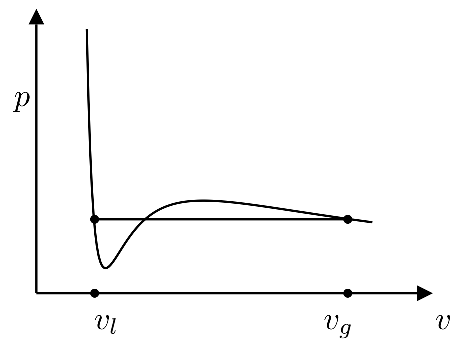
where, if N_A is Avogadro's number, $A=aN_A^2$, $B=bN_A$, $R=k_BN_A$, $n=N/N_A$. It shows the possibility of accessing the microscopic parameters ε and r_0 of the potential φ via measurements detecting deviations from the Boyle-Mariotte law $\beta pv=1$ of the rarefied gases: $\varepsilon=3a/8b=3A/8BN_A$, $\quad r_0=(3b/2\pi)^{1/3}=(3B/2\pi N_A)^{1/3}$.

As a final comment it is worth stressing that *the virial theorem gives in principle the exact corrections to the equation of state, in a rather direct and simple form, as time averages of the virial of the internal forces.* Since the virial of the internal forces is easy to calculate from the positions of the particles as a function of time the theorem *provides a method for computing the equation of state* in numerical simulations. In fact this idea has been exploited in many numerical experiments, in which the (10.1) plays a key role.

Bibliography: [Ga99].

11. van der Waals theory

Equation (10.4) is empirically used *beyond* its validity region (small density and small β) by regarding A,B as phenomenological parameters to be experimentally determined by measuring them near generic values of p,V,T. The measured values of A,B do not "usually vary too much" as functions of v,T and, apart from this small variability, the predictions of (10.4) have reasonably agreed with experience until, as experimental precision increased over the years, serious inadequacies eventually emerged.



(1)

The van der Waals equation of state at a temperature $T<T_c$ where the pressure is not monotonic. The horizontal line illustrates the "Maxwell rule".

Certain consequences of (10.4) are appealing: *e.g.* Fig.1 shows that it does not give a p monotonic non increasing in v if the temperature is small enough. A *critical temperature* can be defined as the largest value T_c of the temperature below which the graph of p as a function of v is not monotonic decreasing; the critical volume V_c is the value of v at the horizontal inflection point occurring for $T = T_c$.

For $T < T_c$ the van der Waals interpretation of the equation of state is that the function $p(v)$ may describe *metastable states* while the actual equilibrium states would follow an equation with a monotonic dependence on v and $p(v)$ becoming horizontal in the coexistence region of specific volumes. The precise value of p where to draw the plateau (see Fig.1) would then be fixed by experiment or theoretically predicted via the simple rule that the plateau associated with the represented isotherm is drawn at a height such that the area of the two cycles in the resulting loop are equal.

This is *Maxwell's rule*: obtained by assuming that the isotherm curve joining the extreme points of the plateau and the plateau itself defines a cycle, see Fig.1, representing a sequence of possible macroscopic equilibrium states (the ones corresponding to the plateau) or states with extremely long time of stability ("metastable") represented by the curved part. This would be an isothermal Carnot cycle which therefore could not produce work: since the work produced in the cycle (*i.e.* $\oint p dv$) is the signed area enclosed by the cycle the rule just means that the area is zero. The argument is doubtful at least because it is not clear that the *intermediate* states with p increasing with v could be realized experimentally or could even be theoretically possible.

A striking prediction of (10.4), taken literally, is that the gas undergoes a "gas-liquid" phase transition with a critical point at a temperature T_c, volume v_c and pressure p_c that can be computed via (10.4) and are given by $RT_c = 8A/27B, V_c = 3B,\ (n = 1)$.

At the same time this is interesting as it shows that there are simple relations between the critical parameters and the microscopic interaction constants ($\varepsilon \simeq k_B T_c$ and $r_0 \simeq (V_c/N_A))^{1/3}$: $\varepsilon = 81 k_B T_c/64,\ r_0 = (V_c/2\pi N_A)^{1/3}$ if a classical Lennard–Jones potential (*i.e.* $\varphi = 4\varepsilon\big((\frac{r_0}{|\mathbf{q}|})^{12} - (\frac{r_0}{|\mathbf{q}|})^6\big)$, see Sect.10) is used for the interaction potential φ.

However (10.4) *cannot be accepted acritically* not only because of the approximations (essentially the neglecting of $O(v^{-1})$ in the equation of state), but mainly because, as remarked above, for $T < T_c$ the function p is *no longer monotonic* in v as it *must be*, see comment following (8.2).

The van der Waals' equation, refined and complemented by Maxwell's rule, predicts the following behavior:

$$\begin{aligned} (p - p_c) &\propto (v - v_c)^\delta \qquad && \delta = 3,\ T = T_c \\ (v_g - v_l) &\propto (T_c - T)^\beta \qquad && \beta = 1/2, \text{ for } T \to T_c^- \end{aligned} \tag{11.1}$$

which are in sharp contrast with the experimental data gathered in the twentieth century. For the simplest substances one finds *instead* $\delta \cong 5$, $\beta \cong 1/3$.

Finally blind faith in the equation of state (10.4) is untenable, last but not least, also because nothing in the analysis would change if the space dimension was $d = 2$ or $d = 1$: but in the last case, $d = 1$, it is easily *proved* that the system, if the interaction decays rapidly at infinity, does not undergo *phase transitions*, see Sect. 12.

In fact it is now understood that van der Waals' equation *represents rigorously only a limiting situation*, in which particles have a hard core interaction (or a strongly repulsive one at close distance) and a further smooth interaction φ with very long range. More precisely suppose that the part of the potential outside a hard core radius $r_0 > 0$ is attractive (*i.e.* non negative) and has the form $\gamma^d \varphi_1(\gamma^{-1}|\mathbf{q}|) \le 0$ and call $P_0(v)$ the (β-independent) product of β times the pressure of the hard core system *without any attractive tail* ($P_0(v)$ is not explicitly known except if $d = 1$ in which case it is $P_0(v)(v - b) = 1$, $b = r_0$), and let $a = -\frac{1}{2}\int_{|\mathbf{q}|>r_0} |\varphi_1(\mathbf{q})| d\mathbf{q}$. If $p(\beta, v; \gamma)$ is the pressure when $\gamma > 0$ then it can be proved

$$\beta\, p(\beta, v) \stackrel{def}{=} \lim_{\gamma\to 0} \beta\, p(\beta, v; \gamma) = \Big[-\frac{\beta\, a}{v^2} + P_0(v) \Big]_{Maxwell\ rule} \tag{11.2}$$

where the subscript means that the graph of $p(\beta, v)$ as a function of v is obtained from the function in square bracket by applying to it Maxwell's rule, described above in the case of the van der Waals' equation. The (11.2) reduces exactly to the van der Waals equation in dimension $d = 1$ and for $d > 1$ it leads to an equations with identical critical behavior (even though $P_0(v)$ cannot be explicitly computed).

Bibliography: [LP79], [Ga99].

12. Absence of Phase Transitions: $d = 1$

One of the most quoted "no go" theorems in Statistical Mechanics is that 1–dimensional systems of particles interacting via short range forces do not exhibit phase transitions (*c.f.* Sect. 13) unless the somewhat unphysical situation of having zero absolute temperature is considered. This is particularly easy to check in the case of "nearest neighbor hard core interactions": call r_0 the hard core size, so that the interaction potential $\varphi(r) = +\infty$ if $r \le r_0$, and suppose also that $\varphi(r) \equiv 0$ if $f \ge 2r_0$. In this case the thermodynamic functions can be exactly computed and checked to be analytic: hence the equation of state cannot have any phase transition plateau. This is a special case of *van Hove's theorem* establishing smoothness of the equation of state for interactions extending beyond the nearest neighbor and rapidly decreasing at infinity.

If the definition of phase transition based on sensitivity of the thermodynamic limit to variations of boundary conditions is adopted then a more general, conceptually simple, argument can be given to show that in one-dimensional systems there cannot be any phase transition if the potential energy of mutual interaction between a configuration $\mathbf{Q}$ of particles to the left of a reference particle (located at the origin O, say) and a configuration $\mathbf{Q}'$ to the right of the particle (with $\mathbf{Q} \cup O \cup \mathbf{Q}'$ compatible with the hard cores) is *uniformly bounded below*. Then a mathematical proof can be devised showing that boundary conditions influence disappears as the boundaries recede to infinity. One also says that *no long-range order can be established in* 1*-dimensional*, in the sense that one loses .

The analysis fails if the space dimension is ≥ 2: in this case, *even if the interaction is* *short ranged*, the energy of interaction between two regions of space separated by a boundary is *of the order of the boundary area.* Hence one cannot bound above and below the probability of any two configurations in two half-spaces by the product of the probabilities of the two configurations, each computed as if the other was not there: because such bound would be proportional to the exponential of the surface of separation, which tends to ∞ when the surface grows large. This means that we cannot consider, at least not in general, the configurations in the two half spaces as independently distributed.

Analytically a condition on the potential sufficient to imply that the energy between a configuration to the left and one to the right of the origin is bounded below, if the dimension d is $d = 1$, is simply expressed by $\int_{r'}^{\infty} r \mid \varphi(r) \mid dr < +\infty$ for $r' > r_0$.

Therefore *in order to have phase transitions in $d = 1$ a potential is needed that is "so long range" that it has a divergent first moment.* It can be shown by counterexamples that if the latter condition fails there can be phase transitions even in $d = 1$ systems.

The results just quoted apply also to discrete models like *lattice gases* or *lattice spin* models that will be considered later, see Sect. 15.

Bibliography: [LL67], [Dy69], [Ga99], [GBG04].

13. Continuous symmetries: "no $d = 2$ crystal" theorem.

A second case in which it is possible to rule out existence of phase transitions or at least of certain kinds of transitions arises when the system under analysis enjoys large symmetry. *By symmetry it is meant a group of transformations acting on the configurations of a system and transforming each of them into a configuration which, at least for one boundary condition* (*e.g.* periodic or open), *has the same energy.*

A symmetry is said to be *continuous* if the group of transformations is a continuous group. For instance continuous systems have translational symmetry if considered in a container Ω with periodic boundary conditions. Systems with "too much symmetry" sometimes cannot show phase transitions. For instance the continuous translation symmetry of a gas in a container Ω with periodic boundary conditions is sufficient to exclude the possibility of crystallization in dimension $d = 2$.

To discuss this, which is a prototype of a proof which can be used to infer absence of many transitions in systems with continuous symmetries, consider the *translational symmetry* and a potential satisfying, besides the usual (7.2) and with the symbols used in (7.2), the further property that $|\mathbf{q}|^2|\partial^2_{ij}\varphi(\mathbf{q})| < \overline{B}|\mathbf{q}|^{-(d+\varepsilon_0)}$, with $\varepsilon_0 > 0$, for some $\overline{B}$ holds for $r_0 < |\mathbf{q}| \le R$. This is a very mild extra requirement (and it allows for a hard core interaction).

Consider an "ideal crystal" on a square lattice (for simplicity) of spacing a, *exactly fitting in its container Ω of side L* assumed with periodic boundary conditions: so that $N = (\frac{L}{a})^d$ is the number of particles and a^{-d} is the density, which is *supposed smaller than the close packing density* if the interaction φ has a hard core. The probability distribution of the particles is rather trivial: $\overline{\mu} = \sum_p \prod_{\mathbf{n}} \delta(\mathbf{q}_{p(\mathbf{n})} - a\,\mathbf{n})\frac{d\mathbf{Q}}{N!}$, the sum running over the permutations $\mathbf{m} \to p(\mathbf{m})$ of the sites $\mathbf{m} \in \Omega$, $\mathbf{m} \in \mathbb{Z}^d, 0 < m_i \le La^{-1}$. The density at $\mathbf{q}$

is $\widehat{\rho}(\mathbf{q}) = \sum_{\mathbf{n}} \delta(\mathbf{q} - a\,\mathbf{n}) \equiv \langle \sum_{j=1}^N \delta(\mathbf{q} - \mathbf{q}_j)\rangle$ and its Fourier transform is proportional to $\rho(\mathbf{k}) \stackrel{def}{=} \frac{1}{N}\langle \sum_j e^{-i\mathbf{k}\cdot\mathbf{q}_j}\rangle$ with $\mathbf{k} = \frac{2\pi}{L}\mathbf{n}$ with $\mathbf{n} \in \mathbb{Z}^d$. The $\rho(\mathbf{k})$ has value 1 for all $\mathbf{k}$ of the form $\mathbf{K} = \frac{2\pi}{a}\mathbf{n}$ and $\frac{1}{N}O(\max_{c=1,2}|e^{ik_c a} - 1|^{-2})$ otherwise. In presence of interaction it has to be expected that, in a crystal state, $\rho(\mathbf{k})$ has peaks near the values $\mathbf{K}$: but the value of $\rho(\mathbf{k})$ can depend on the boundary conditions.

Since the system is translation invariant a crystal state defined as a state with a distribution "close" to $\overline{\mu}$, *i.e.* with $\hat{\rho}(\mathbf{q})$ with peaks at the ideal lattice points $\mathbf{q} = \mathbf{n}a$, cannot be realized under periodic boundary conditions, even when the system state is crystalline. To realize such a state a symmetry breaking term in the interaction is needed.

This can be done in several ways: *e.g.* by changing the boundary condition. Such a choice implies a discussion of how much the boundary conditions influence the positions of the peaks of $\rho(\mathbf{k})$: for instance it is not obvious that a boundary condition will not generate a state with a period different from the one that *a priori* has been selected to disprove (a possibility which would imply a reciprocal lattice of $\mathbf{K}$'s different from the one considered to begin with). Therefore here the choice will be to imagine that an external weak force with potential $\varepsilon W(\mathbf{q})$ acts forcing a symmetry breaking that favors the occupation of regions around the points of the ideal lattice (which would mark the average positions of the particles in the crystal state that is being sought). The proof (*Mermin's theorem*) that no equilibrium state with particles distribution "close" to $\overline{\mu}$, *i.e.* with peaks in place of the delta functions (see below), is essentially reproduced below.

Take $W(\mathbf{q}) = \sum_{\mathbf{n}a\in\Omega} \chi(\mathbf{q} - \mathbf{n}a)$ where $\chi(\mathbf{q}) \le 0$ is smooth and 0 everywhere except in a small vicinity of the lattice points around which it decreases to some negative minimum keeping a rotation symmetry around them: the potential W is assumed invariant under the translations by the lattice steps. By the choice of the boundary condition and of εW the density $\widetilde{\rho}_\varepsilon(\mathbf{q})$ *will be periodic* with period a so that $\rho_\varepsilon(\mathbf{k})$ will, possibly, not have a vanishing limit as $N \to \infty$ only if $\mathbf{k}$ is a reciprocal vector $\mathbf{K} = \frac{2\pi}{a}\mathbf{n}$. If the potential is $\varphi + \varepsilon W$ and *if a crystal state in which particles have higher probability of being near the lattice points* $\mathbf{n}a$ *exists*, it should be expected that for $\varepsilon > 0$ small the system will be found in a state with Fourier transform $\rho_\varepsilon(\mathbf{k})$ of the density satisfying, for some vector $\mathbf{K} \ne \mathbf{0}$ in the reciprocal lattice,

$$\lim_{\varepsilon\to 0}\lim_{N\to\infty} |\rho_\varepsilon(\mathbf{K})| = r > 0, \tag{13.1}$$

i.e. the requirement is that uniformly in $\varepsilon \to 0$ *the Fourier transform of the density has a peak at some* $\mathbf{K} \ne \mathbf{0}$: note that if $\mathbf{k}$ is not in the reciprocal lattice $\rho_\varepsilon(\mathbf{k}) \xrightarrow[N\to\infty]{} 0$, being bounded above by $\frac{1}{N}O(\max_{c=1,2}|e^{ik_j a} - 1|^{-2})$ because $\frac{1}{N}\widetilde{\rho}_\varepsilon$ is periodic and has integral over $\mathbf{q}$ equal to 1. Hence excluding crystal existence will be identified with the impossibility of the (13.1). Other criteria can be imagined, *e.g.* considering crystals with a lattice different from simple cubic: they lead to the same result by following the same technique. Nevertheless it is not mathematically excluded (but unlikely) that with some weaker definition of crystal state existence could be possible even in 2 dimensions.

The following inequalities hold under the present assumptions on the potential and in the canonical distribution with periodic boundary conditions and parameters (β, ρ), $\rho = a^{-3}$ in a box Ω with side multiple of a (so that $N = (La^{-1})^d$) and potential of interaction

$\varphi + \varepsilon W$. The further assumption that the lattice $\mathbf{n}a$ is not a close packed lattice is (of course) necessary when the interaction potential has a hard core. Then for suitable $B_0, B, B_1, B_2 > 0$, independent of N, and ε and for $|\boldsymbol{\kappa}| < \frac{\pi}{a}$ and for all Ω (*if* $\mathbf{K} \neq \mathbf{0}$)

$$\begin{aligned} &\frac{1}{N}\langle|\sum_{j=1}^{N} e^{-i(\boldsymbol{\kappa}+\mathbf{K})\cdot\mathbf{q}_j}|^2\rangle \geq B\frac{(\rho_\varepsilon(\mathbf{K})+\rho_\varepsilon(\mathbf{K}+2\boldsymbol{\kappa}))^2}{B_1\,\boldsymbol{\kappa}^2+\varepsilon\,B_2} \\ &\frac{1}{N}\sum_{\boldsymbol{\kappa}}\gamma(\boldsymbol{\kappa})\,\frac{d\boldsymbol{\kappa}}{N}\,\langle|\sum_{j=1}^{N} e^{-i(\boldsymbol{\kappa}+\mathbf{K})\cdot\mathbf{q}_j}|^2\rangle \leq B_0 < \infty \end{aligned} \tag{13.2}$$

where the averages are in the canonical distribution (β, ρ) with periodic boundary conditions and a symmetry breaking potential $\varepsilon W(\mathbf{q})$; $\gamma(\mathbf{k}) \geq 0$ is an (arbitrary) smooth a function vanishing for $2|\boldsymbol{\kappa}| \geq \delta$ with $\delta < \frac{2\pi}{a}$. See Appendix A3 for the derivation of (13.2).

Multiplying both sides of the first in (13.2) by $N^{-1}\gamma(\boldsymbol{\kappa})$ and summing over $\boldsymbol{\kappa}$ the cristallinity condition in the form (13.1) implies that the *r.h.s.* is $\geq Br^2a^d \int_{|\boldsymbol{\kappa}|<\delta} \frac{\gamma(\boldsymbol{\kappa})\,d\boldsymbol{\kappa}}{\boldsymbol{\kappa}^2 B_1+\varepsilon\,B_2}$. For $d = 1, 2$ the integral diverges, as $\varepsilon^{-\frac{1}{2}}$ or $\log \varepsilon^{-1}$ respectively, implying $|\rho_\varepsilon(\mathbf{K})| \xrightarrow[\varepsilon\to 0]{} r = 0$: the criterion of crystallinity (13.1) *cannot be satisfied if* $d = 1, 2$.

The above inequality is an example of a general class of inequalities called *infrared inequalities* stemming from another inequality called *Bogoliubov's inequality*, see Appendix A3, which lead to the proof that certain kinds of ordered phases cannot exist *if the dimension of the ambient space is* $d = 2$ when a system in suitable boundary conditions (*e.g.* periodic) shows a *continuous symmetry*. The excluded phenomenon is, more precisely, the non existence of equilibrium states exhibiting, *in the thermodynamic limit*, a symmetry *lower* than the continuous symmetry holding in periodic boundary conditions.

In general existence of thermodynamic equilibrium states with symmetry lower than the symmetry enjoyed by the system in finite volume and under suitable boundary conditions is called a *spontaneous symmetry breaking*. It is yet another manifestation of instability with respect to changes in boundary conditions, hence its occurrence reveals a phase transition. There is a large class of systems for which an infrared inequality implies absence of spontaneous symmetry breaking: in most one or two dimensional systems a continuous symmetry cannot be *spontaneously broken*.

The limitation to dimension $d \leq 2$ is a strong limitation to the generality of the applicability of infrared theorems to exclude phase transitions. More precisely systems can be divided into classes each of which has a "critical dimension" below which too much symmetry implies absence of phase transitions (or of certain kinds of phase transitions).

It should be stressed that, at the critical dimension, the symmetry breaking is usually so weakly forbidden that one might need astronomically large containers to destroy small effects (due to boundary conditions or to very small fields) which break the symmetry: *e.g.* in the crystallization just discussed the Fourier transform peaks are only bounded by $O(\frac{1}{\sqrt{\log \varepsilon^{-1}}})$: hence from a practical point of view it might still be possible to have some kind of order even in large containers.

Bibliography: [Me68], [Ho67], [Ru69].

14. High Temperature and small density

There is *another* class of systems in which no phase transitions take place. These are the systems with stable and tempered interactions φ, *e.g.* satisfying (7.2), in the high temperature and low density region. The property is obtained by showing that the equation of state is analytic in the variables (β,ρ) near the origin $(0,0)$.

A simple algorithm (*Mayer's series*) yields the coefficients of the virial series $\beta p(\beta,\rho)=\rho+\sum_{k=2}^\infty c_k(\beta)\rho^k$. It has the drawback that the k-th order coefficient $c_k(\beta)$ is expressed as a sum of many terms (a number growing *more* than exponentially fast in the order k) and it is not so easy (but possible) to show combinatorially that their sum is bounded exponentially in k if β is small enough. A more common approach leads quickly to the desired solution. Denoting $\Phi(\mathbf{q}_1,\ldots,\mathbf{q}_n)\stackrel{def}{=}\sum_{i<j}\varphi(\mathbf{q}_i-\mathbf{q}_j)$ consider the ("spatial or configurational") correlation functions defined, in the grand canonical distribution with parameters β,λ (and empty boundary conditions), by

$$\rho_\Omega(\mathbf{q}_1,\ldots,\mathbf{q}_n)\stackrel{def}{=}\frac{1}{Z^{gc}(\beta,\lambda,V)}\sum_{m=0}^\infty z^{n+m}\int_\Omega e^{-\beta\Phi(\mathbf{q}_1,\ldots,\mathbf{q}_n,\mathbf{y}_1,\ldots,\mathbf{y}_m)}\frac{d\mathbf{y}_1\ldots d\mathbf{y}_m}{m!}\tag{14.1}$$

This is the probability density for finding particles with any momentum in the volume element $d\mathbf{q}_1\ldots d\mathbf{q}_n$ (irrespective of where other particles are), and $z=e^{\beta\lambda}(\sqrt{2\pi m\beta^{-1}h^{-2}})^d$ accounts for the integration over the momenta variables and is called the *activity*: it has the dimension of a density (*c.f.* (9.3)).

Assuming that the potential has a hard core (for simplicity) of radius R the interaction energy $\Phi_{\mathbf{q}_1}(\mathbf{q}_2,\ldots,\mathbf{q}_n)$ of a particle in $\mathbf{q}_1$ with any number of other particles in $\mathbf{q}_2,\ldots,\mathbf{q}_m$ with $|\mathbf{q}_i-\mathbf{q}_j|>R$ is bounded below by $-B$ for some $B\ge0$ (related but not equal to the B in (7.2)). The functions ρ_Ω will be regarded as a *sequence* of functions "of one, two,... particle positions": $\rho_\Omega=\{\rho_\Omega(\mathbf{q}_1,\ldots,\mathbf{q}_n)\}_{n=1}^\infty$ vanishing for $\mathbf{q}_j\not\in\Omega$. Then one checks that

$$\begin{aligned}&\rho_\Omega(\mathbf{q}_1,\ldots,\mathbf{q}_n)=z\delta_{n,1}\chi_\Omega(\mathbf{q}_1)+K\,\rho_\Omega(\mathbf{q}_1,\ldots,\mathbf{q}_n)\qquad\text{with}\\&K\,\rho_\Omega(\mathbf{q}_1,\ldots,\mathbf{q}_n)\stackrel{def}{=}e^{-\beta\Phi_{\mathbf{q}_1}(\mathbf{q}_2,\ldots,\mathbf{q}_n)}\Big(\rho_\Omega(\mathbf{q}_2,\ldots,\mathbf{q}_n)\,\delta_{n>1}+\\&+\sum_{s=1}^\infty\int_\Omega\frac{d\mathbf{y}_1\ldots d\mathbf{y}_s}{s!}\prod_{k=1}^s\big(e^{-\beta\varphi(\mathbf{q}_1-\mathbf{y}_k)}-1\big)\rho_\Omega(\mathbf{q}_2,\ldots,\mathbf{q}_n,\mathbf{y}_1,\ldots,\mathbf{y}_s)\Big)\end{aligned}\tag{14.2}$$

where $\delta_{n,1},\delta_{n>1}$ are Kronecker deltas and $\chi_\Omega(\mathbf{q})$ is the indicator function of Ω. The (14.2) is called the *Kirkwood-Salzburg equation* for the family of correlation functions in Ω. The kernel K of the equations is *independent of* Ω, but the domain of integration is Ω.

Calling α_Ω the sequence of functions $\alpha_\Omega(\mathbf{q}_1,\ldots,\mathbf{q}_n)\equiv0$ if $n\ne1$ and $\alpha_\Omega(\mathbf{q})=z\chi_\Omega(\mathbf{q})$, a recursive expansion arises, namely

$$\rho_\Omega=z\alpha_\Omega+z^2K\alpha_\Omega+z^3K^2\alpha_\Omega+z^4K^3\alpha_\Omega+\ldots\tag{14.3}$$

It gives the correlation functions, *provided the series converges.* The remark

$$|K^p\alpha_\Omega(q_1,\ldots,q_n)|\le e^{(2\beta B+1)p}\Big(\int|e^{-\beta\varphi(\mathbf{q})}-1|d\mathbf{q}\Big)^p\stackrel{def}{=}e^{(2\beta B+1)p}\,r(\beta)^{3p}\tag{14.4}$$

shows that the series (14.3), called *Mayer's series* converges if $|z| < e^{-(2\beta B+1)}r(\beta)^{-3}$. Convergence is uniform (as $\Omega \to \infty$) and $(K^p)\alpha_\Omega(\mathbf{q}_1,\ldots,\mathbf{q}_n)$ tends to a limit as $V \to \infty$ at fixed $\mathbf{q}_1,\ldots,\mathbf{q}_n$ and the limit is simply $(K^p\alpha)(\mathbf{q}_1,\ldots,\mathbf{q}_n)$, if $\alpha(\mathbf{q}_1,\ldots,\mathbf{q}_n) \equiv 0$ for $n \neq 1$, and $\alpha(\mathbf{q}_1) \equiv 1$. This is because the kernel K contains the factors $(e^{-\beta\varphi(\mathbf{q}_1-\mathbf{y})} - 1)$ which decay rapidly or will even be eventually 0, if φ has finite range. It is also clear that $(K^p\alpha)(q_1,\ldots,q_n)$ is translation invariant.

Hence if $|z|e^{2\beta B+1}\, r(\beta)^3 < 1$ the limits as $\Omega \to \infty$ of the correlation functions exist and can be computed by a convergent power series in z; the correlation functions will be translation invariant (in the thermodynamic limit).

In particular the one-point correlation function $\rho = \rho(q)$ is $\rho = z\big(1 + O(zr(\beta)^3)\big)$, which to lowest order in z just shows that activity and density essentially coincide when they are small enough. Furthermore $\beta\, p_\Omega \equiv \frac{1}{V}\log Z^{gc}(\beta,\lambda,V)$ is such that $z\,\partial_z\,\beta p_\Omega = \frac{1}{V}\int \rho_\Omega(q)dq$ (from the definition of ρ_Ω in (14.1)). Therefore

$$\beta p(\beta,z) = \lim_{V\to\infty}\frac{1}{V}\log Z^{gc}(\beta,\lambda,V) = \int_0^z \frac{dz'}{z'}\rho(\beta,z') \tag{14.5}$$

showing that the density ρ is analytic in z as well and $\rho \simeq z$ for z small: therefore the grand canonical *pressure is analytic in the density* and $\beta\, p = \rho\,(1 + O(\rho^2))$, at small density. In other words the equation of state is, to lowest order, essentially the equation of a perfect gas. All quantities that are conceivably of some interest turn out to be analytic functions of temperature and density. The system is essentially a free gas and it has no phase transitions in the sense of a *discontinuity or of a singularity* in the dependence of a thermodynamic function in terms of others. Furthermore the system cannot show phase transitions in the sense of sensitive dependence on boundary conditions of fixed external particles: this also follows, with some extra work, from the Kirkwood-Salzburg equations.

Bibliography: [Ru69], [Ga99].

15. Lattice models

The problem of proving existence of phase transitions in models of homogeneous gases with pair interactions is still open. Therefore it makes sense to study phase transitions problem in simpler models, tractable to some extent but nontrivial and which even have an interest in their own from the point of view of applications.

The simplest models are the so-called *lattice models* in which particles are constrained to points of a lattice: they cannot move in the ordinary sense of the word (but of course they could jump) and therefore their configurations do not contain momentum variables.

Interaction energy is just potential energy and ensembles are defined as collections of probability distributions on the position coordinates of the particle configurations. Usually the potential is a *pair potential* decaying fast at ∞ and, often, with a hard core forbidding double or higher occupancy of the same lattice site. For instance the *lattice gas with potential* φ, in a cubic box Ω with $|\Omega| = V = L^d$ sites of a square lattice with mesh $a > 0$, is defined by the potential energy attributed to the configuration X of occupied *distinct* sites, *i.e.* subsets $X \subset \Omega$:

$$H(X) = -\sum_{(x,y)\in X} \varphi(x-y). \tag{15.1}$$

where the sum is over pairs of distinct points in X. The *canonical ensemble* and the *grand canonical ensemble* are the collections of distributions, parameterized by (β,ρ) ($\rho = \frac{N}{V}$) or, respectively, by (β,λ), attributing to X the probability:

$$p_{\beta,\rho}(X) = \frac{e^{-\beta H(X)}}{Z^c_p(\beta,N,\Omega)}\delta_{|X|,N}, \qquad \text{or} \qquad p_{\beta,\lambda}(X) = \frac{e^{\beta\lambda|X|}e^{-\beta H(X)}}{Z^{gc}_p(\beta,\lambda,\Omega)}, \tag{15.2}$$

where the denominators are normalization factors that can be called, in analogy with the theory of continuous systems, *canonical* and *grand canonical* partition functions; the subscript p stands for particles.

A lattice gas in which in each site there can be at most one particle can be regarded as a model for the distribution of a family of *spins* on a lattice. Such models are quite common and useful: for instance they arise in studying systems with magnetic properties. Simply identify an "occupied" site with a "spin up" or $+$ and an "empty" site with a "spin down" or $-$ (say). If $\boldsymbol{\sigma} = \{\sigma_x\}_{x\in\Omega}$ is a spin configuration, the energy of the configuration "for potential φ and magnetic field h" will be

$$H(\boldsymbol{\sigma}) = -\sum_{(x,y)\in\Omega} \varphi(x-y)\sigma_x\sigma_y - h\sum_x \sigma_x \tag{15.3}$$

with the sum running over pairs $(x,y)\in\Omega$ of distinct sites. If $\varphi(x-y)\equiv J_{xy}\ge 0$ the model is called a *ferromagnetic Ising model.* As in the case of continuous systems it will assumed finite range for φ: *i.e.* $\varphi(x) = 0$ for $|x| > R$, for some R, unless explicitly stated otherwise.

The canonical and grand canonical ensembles in the box Ω with respective parameters (β,m) or (β,h) will be defined as the probability distributions on the spin configurations $\boldsymbol{\sigma} = \{\sigma_x\}_{x\in\Omega}$ with $\sum_{x\in\Omega}\sigma_x = M = mV$ or without constraint on M, respectively; hence

$$p_{\beta,m}(\boldsymbol{\sigma}) = \frac{e^{-\beta\sum_{(x,y)}\varphi(x-y)\sigma_x\sigma_y}}{Z^c_s(\beta,M,\Omega)}, \qquad p_{\beta,h}(\boldsymbol{\sigma}) = \frac{e^{-\beta h\sum\sigma_x-\beta\sum_{(x,y)}\varphi(x-y)\sigma_x\sigma_y}}{Z^{gc}_s(\beta,h,\Omega)} \tag{15.4}$$

where the denominators are normalization factors again called the *canonical* and *grand canonical* partition functions. As in the study of the previous continuous systems canonical and grand canonical ensembles with "external fixed particle configurations" can be defined together with the corresponding ensembles with "external fixed spin configurations"; the subscript s stands for spins.

For each configuration $X\subset\Omega$ of a lattice gas let $\{n_x\}$ be $n_x = 1$ if $x\in X$ and $n_x = 0$ if $x\not\in X$. Then the transformation $\sigma_x = 2n_x - 1$ establishes a correspondence between lattice gas and spin distributions. In the correspondence the potential $\varphi(x-y)$ of the lattice gas generates a potential $\frac{1}{4}\varphi(x-y)$ for the corresponding spin system and the chemical potential λ for the lattice gas is associated with a magnetic field h for the spin system with $h=\frac{1}{2}(\lambda+\sum_{x\neq 0}\varphi(x))$.

The correspondence between boundary conditions is natural: for instance a boundary condition for the lattice gas in which all external sites are occupied becomes a boundary condition in which external sites contain a spin $+$. The relation between lattice gas and spin systems is so close to permit switching from one to the other with little discussion.

In the case of spin systems empty boundary conditions are often considered (no spins outside Ω). In lattice gases and spin systems (as well as in continuum systems) often periodic and semiperiodic boundary conditions are considered (*i.e.* periodic in one or more directions and with empty or fixed external particles or spins in the others).

Thermodynamic limits for the partition functions

$$\begin{aligned}
-\beta\, f(\beta,v)&=\lim_{\substack{\Omega\to\infty\\ \frac{V}{N}=v}}\frac{1}{N}\log Z^c_p(\beta,N,\Omega), &\qquad \beta\, p(\beta,\lambda)&=\lim_{\Omega\to\infty}\frac{1}{V}\log Z^{gc}_p(\beta,\lambda,\Omega)\\
-\beta\, g(\beta,m)&=\lim_{\substack{\Omega\to\infty,\\ \frac{M}{V}\to m}}\frac{1}{V}\log Z^c_s(\beta,M,\Omega), &\qquad \beta\, f(\beta,h)&=\lim_{\Omega\to\infty}\frac{1}{V}\log Z^{gc}_s(\beta,\lambda,\Omega)
\end{aligned}\tag{15.5}$$

can be shown to exist by a method similar to the one discussed in Appendix A2. They have convexity and continuity properties as in the cases of the continuum systems. In the lattice gas case the f,p functions are still interpreted as free energy and pressure. In the spin case $f(\beta,h)$ has the interpretation of *magnetic free energy* while $g(\beta,m)$ does not have a special name in the thermodynamics of magnetic systems. As in the continuum systems it is occasionally useful to define infinite volume equilibrium states:

Definition: *: An infinite volume state with parameters (β,h), or (β,m) is a collection of average values $F\to\langle F\rangle$ obtained, respectively, as limits of finite volume averages $\langle F\rangle_{\Omega_n}$ defined from canonical, or grand canonical distributions in Ω_n with fixed parameters (β,h) or (β,m), or (u,v) and with general boundary condition of fixed external spins or empty sites, on sequences $\Omega_n\to\infty$ for which such limits exist simultaneously for all local observables F.*

This is taken *verbatim* from the definition in Sect.9. In this way it makes sense to define the *spin correlation functions* for $X=(\boldsymbol{\xi}_1,\ldots,\boldsymbol{\xi}_n)$ as $\langle\sigma_X\rangle$ if $\sigma_X=\prod_j\sigma_{\boldsymbol{\xi}_j}$. For instance we shall call $\rho(\boldsymbol{\xi}_1,\boldsymbol{\xi}_2)\stackrel{def}{=}\langle\sigma_{\boldsymbol{\xi}_1}\sigma_{\boldsymbol{\xi}_2}\rangle$ and a pure phase can be defined as an infinite volume state such that

$$\langle\sigma_X\sigma_{Y+\boldsymbol{\xi}}\rangle-\langle\sigma_X\rangle\langle\sigma_{Y+\boldsymbol{\xi}}\rangle\xrightarrow[\boldsymbol{\xi}\to\infty]{}0\tag{15.6}$$

Bibliography: [Ru69], [Ga99].

16. Thermodynamic limits and inequalities

An interesting property of lattice systems is that it is possible to study delicate questions like existence of infinite volume states in some (moderate) generality. A typical tool is the use of *inequalities*. As the simplest example of a vast class of inequalities consider the *ferromagnetic Ising model* with some finite (but arbitrary) range interaction $J_{xy} \geq 0$ in a field $h_x \geq 0$: J, h may even be not translationally invariant. Then the average of $\sigma_X \stackrel{def}{=} \sigma_{x_1}\sigma_{x_2}\ldots\sigma_{x_n}$, $X = (x_1, \ldots, x_n)$, in a state with "empty boundary conditions" (*i.e.* no external spins) satisfies the inequalities $\langle\sigma_X\rangle$, $\partial_{h_x}\langle\sigma_X\rangle$, $\partial_{J_{xy}}\langle\sigma_X\rangle \geq 0$ $X = (x_1, \ldots, x_n)$. More generally let $H(\boldsymbol{\sigma})$ in (15.3) be replaced by $H(\boldsymbol{\sigma}) = -\sum_X J_X\sigma_X$ with $J_X \geq 0$ and X can be any finite set; then, if $Y = (y_1, \ldots, y_n), X = (x_1, \ldots, x_n)$, the following *Griffiths inequalities* hold

$$\langle\sigma_X\rangle \geq 0, \quad \partial_{J_Y}\langle\sigma_X\rangle \equiv \langle\sigma_X\sigma_Y\rangle - \langle\sigma_X\rangle\langle\sigma_Y\rangle \ \geq 0 \tag{16.1}$$

The inequalities can be used to check, in ferromagnetic Ising models, (15.3), existence of infinite volume states (*c.f.* Sect.9,15) obtained by fixing the boundary condition $\mathcal{B}$ to be either "all external spins +" or "all external sites empty". If $\langle F\rangle_{\mathcal{B},\Omega}$ denotes the grand canonical average with boundary condition $\mathcal{B}$ and any fixed $\beta, h > 0$, this means that *for all local observables* $F(\boldsymbol{\sigma}_\Lambda)$, *i.e.* for all F depending on the spin configuration in any fixed region Λ, *all* the following limits exist

$$\lim_{\Omega\to\infty}\langle F\rangle_{\mathcal{B},\Omega} = \langle F\rangle_{\mathcal{B}} \tag{16.2}$$

The reason is that the inequalities (16.1) imply that all averages $\langle\sigma_X\rangle_{\mathcal{B},\Omega}$ are monotonic in Ω for all fixed $X \subset \Omega$: so the limit (16.2) exists for $F(\boldsymbol{\sigma}) = \sigma_X$. Hence it exists for all F depending only on finitely many spins, because any local function F "measurable in Λ" can be expressed (uniquely) as a linear combination of functions σ_X with $X \subseteq \Lambda$.

Monotonicity with empty boundary conditions is seen by considering the sites outside Ω and in a region Ω' with side 1 unit larger than that of Ω and imagining that the couplings J_X with $X \subset \Omega'$ but $X \not\subset \Omega$ *vanish.* Then $\langle\sigma_X\rangle_{\Omega'} \geq \langle\sigma_X\rangle_\Omega$ because $\langle\sigma_X\rangle_{\Omega'}$ is an average computed with a distribution corresponding to an energy with the couplings J_X with $X \not\subset \Omega$ but $X \subset \Omega'$ changed from 0 to $J_X \geq 0$.

Likewise if the boundary condition is + then enlarging the box from Ω to Ω' corresponds to decreasing an external field acting h on the external spins from $+\infty$ (which would force all external spins to be +) to a finite value $h \geq 0$: so that increasing the box Ω causes $\langle\sigma_X\rangle_{+,\Omega}$ to decrease. Therefore as Ω increases Ising ferromagnets spin correlations increase if the boundary condition is empty and decrease if it is +.

The inequalities can be used in similar ways to prove that the infinite volume states obtained from + or empty boundary conditions are translation invariant; and that in zero external field, $h = 0$, the + and − boundary conditions generate pure states if the interaction potential is only a pair ferromagnetic interaction.

There are many other important inequalities which can be used to prove several existence theorems along very simple paths. Unfortunately their use is mostly restricted to lattice systems and requires very special assumptions on the energy (*e.g.* ferromagnetic interactions in the above example). The quoted examples were among the first discovered and provide a way to exhibit nontrivial thermodynamic limits and pure states.

Bibliography: [Ru69], [Le74], [Ga99], [LL01], [Li02].

17. Symmetry breaking phase transitions

The simplest phase transitions, see Sect. 9, are *symmetry breaking* transitions in lattice systems: they take place when the energy of the system in a container Ω and with some *special* boundary condition (*e.g.* periodic, or antiperiodic or empty) is invariant with respect to the action of a group $\mathcal{G}$ on phase space. This means that on the points x of phase space acts a group of transformations $\mathcal{G}$ so that with each $\gamma \in \mathcal{G}$ a map $x \to x\gamma$ is associated which transforms x into $x\gamma$ respecting the composition law in $\mathcal{G}$, *i.e.* $(x\gamma)\gamma' \equiv x(\gamma\gamma')$. If F is an observable the action of the group on phase space induces an action on the observable F changing $F(x)$ into $F_\gamma(x) \stackrel{def}{=} F(x\gamma^{-1})$.

A *symmetry breaking transition* occurs when by fixing suitable boundary conditions and taking the thermodynamic limit a state $F \to \langle F\rangle$ is obtained in which some local observable shows a non symmetric average $\langle F\rangle \neq \langle F_\gamma\rangle$ for some γ.

An example is provided by the "nearest neighbor ferromagnetic Ising model" on a d–dimensional lattice with energy function given by (15.2) with $\varphi(x-y) \equiv 0$ unless $|x-y| = 1$, *i.e.* unless x, y are nearest neighbors, in which case $\varphi(x-y) = J > 0$. With periodic or empty boundary conditions it exhibits a *discrete* "up-down" symmetry $\boldsymbol{\sigma} \to -\boldsymbol{\sigma}$.

Instability with respect to boundary conditions can be revealed by considering the two boundary conditions, denoted $+$ or $-$, in which the lattice sites outside the container Ω are either occupied by spins $+$ or by spins $-$. Consider also, for later reference, the boundary conditions in which the boundary spins in the upper half of the boundary are $+$ and the ones in the lower part are $-$: call this the $\pm$-boundary condition; see Fig.2. Or the boundary conditions in which some of the opposite sides of Ω are identified while $+$ or $-$ conditions are assigned on the remaining sides: call these "cylindrical or semiperiodic boundary conditions".

A new description of the spin configurations is useful: given $\boldsymbol{\sigma}$ draw a unit segment perpendicular to the center of each bond b having opposite spins at its extremes. An example of this construction is provided by Fig.2 for the boundary condition $\pm$.

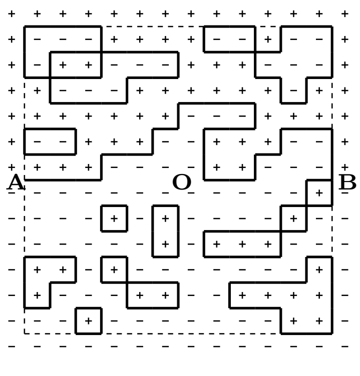


Fig.2: The dashed line is the boundary of Ω; the outer spins correspond to the $\pm$ boundary condition.

The points A, B are points where an open "line" λ ends.

The set of segments can be grouped into lines separating regions where the spins are positive from regions where they are negative. If the boundary condition is $+$ or $-$ the lines form "closed polygons" while if the condition is $\pm$ there is also a single polygon λ_1 which is not closed (as in Fig. 2). If the boundary condition is periodic or cylindrical all polygons are closed but some may "go around" Ω.

The correspondence $(\gamma_1, \gamma_2, \ldots, \gamma_n, \lambda_1) \longleftrightarrow \boldsymbol{\sigma}$, *for the boundary condition* $\pm$ or, *for the boundary condition $+$ (or $-$),* $\boldsymbol{\sigma} \longleftrightarrow (\gamma_1, \ldots, \gamma_n)$ is one-to-one and, if $h = 0$, the energy $H_\Omega(\boldsymbol{\sigma})$ of a configuration is higher than $-J \cdot$ (number of bonds in Ω) by an amount $2J(|\lambda_1| + \sum_i |\gamma_i|)$ or, respectively, $2J \sum_i |\gamma_i|$. The grand canonical probability of each spin configuration is therefore proportional, if $h = 0$, respectively to

$$e^{-2\beta J(|\lambda_1| + \sum_i |\gamma_i|)} \qquad \text{or} \qquad e^{-2\beta J \sum_i |\gamma_i|} \tag{17.1}$$

and the "up-down" symmetry is clearly reflected by (17.1).

The average $\langle \sigma_x \rangle_{\Omega,+}$ of σ_+ *with $+$ boundary conditions* is given by $\langle \sigma_x \rangle_{\Omega,+} = 1 - 2\, P_{\Omega,+}(-)$, where $P_{\Omega,+}(-)$ is the probability that the spin σ_x is -1. If the site x is occupied by a negative spin then the point x is *inside* some contour γ associated with the spin configuration $\boldsymbol{\sigma}$ under consideration. Hence if $\rho(\gamma)$ is the probability that a given contour belongs to the set of contours describing a configuration $\boldsymbol{\sigma}$, it is $P_{\Omega,+}(-) \le \sum_{\gamma o x} \rho(\gamma)$ where $\gamma o x$ means that γ "surrounds" x.

If $\Gamma = (\gamma_1, \ldots, \gamma_n)$ is a spin configuration and if the symbol $\Gamma\, comp\, \gamma$ means that the contour γ is "disjoint" from $\gamma_1, \ldots, \gamma_n$ (*i.e.* $\{\gamma \cup \Gamma\}$ is a new spin configuration), then

$$\rho(\gamma) = \frac{\sum_{\Gamma \ni \gamma} e^{-2\beta J \sum_{\gamma' \in \Gamma} |\gamma'|}}{\sum_{\Gamma} e^{-2\beta J \sum_{\gamma' \in \Gamma} |\gamma'|}} \equiv e^{-2\beta J |\gamma|} \frac{\sum_{\Gamma\, comp\, \gamma} e^{-2\beta J \sum_{\gamma' \in \Gamma} |\gamma'|}}{\sum_{\Gamma} e^{-2\beta J \sum_{\gamma' \in \Gamma} |\gamma'|}} \le e^{-2\beta J |\gamma|} \tag{17.2}$$

because the last ratio in (17.2) does not exceed 1. Remark that there are at most 3^p different shapes of γ with perimeter p and at most p^2 congruent γ's containing x; therefore the probability that the spin at x is $-$ when the boundary condition is $+$ satisfies the inequality $P_{\Omega,+}(-) \le \sum_{p=4}^{\infty} p^2 3^p e^{-2\beta J p} \xrightarrow[\beta \to \infty]{} 0$.

This probability can be made as small as wished so that $\langle \sigma_x \rangle_{\Omega,+}$ is estimated by a quantity which is as close to 1 as desired provided β is large enough and *the closeness of $\langle \sigma_x \rangle_{\Omega,+}$ to 1 is both x and Ω independent.*

A similar argument for the $(-)$-boundary condition, or the remark that for $h = 0$ it is $\langle \sigma_x \rangle_{\Omega,-} = -\langle \sigma_x \rangle_{\Omega,+}$, leads to conclude that, at large β, $\langle \sigma_x \rangle_{\Omega,-} \ne \langle \sigma_x \rangle_{\Omega,+}$ and the difference between the two quantities is positive uniformly in Ω. This is the proof (*Peierls' theorem*) of the fact that there is, if β is large, a strong instability with respect to the boundary conditions of the magnetization: *i.e.* the nearest neighbor Ising model in dimension 2 (or greater, by an identical argument) has a phase transition. If the dimension is 1 the argument clearly fails and no phase transition occurs, see Sect. 12.

Bibliography: [Ga99].

18. Finite volume effects

The description in Sect.17 of the phase transition in the nearest neighbor Ising model can be made more precise from the physical point of view as well as from the mathematical point of view giving insights into the nature of the phase transitions. Assume that the boundary condition is the (+)-boundary condition and describe a spin configuration $\boldsymbol{\sigma}$ by means of the associated closed disjoint polygons $(\gamma_1, \ldots, \gamma_n)$. Attribute to $\boldsymbol{\sigma} = (\gamma_1, \ldots, \gamma_n)$ a probability proportional to (17.1). Then the following *Minlos–Sinai's theorem* holds

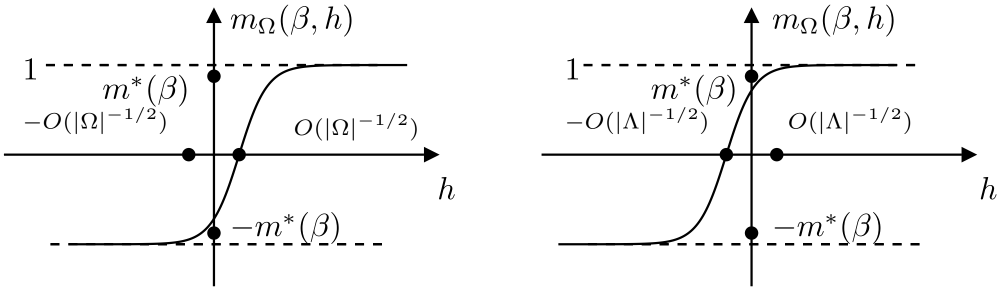
If β is large enough there exist $C > 0, \rho(\gamma) > 0$ with $\rho(\gamma) \le e^{-2\beta J|\gamma|}$ and such that a spin configuration $\boldsymbol{\sigma}$ randomly chosen out of the grand canonical distribution with $+$ boundary conditions and $h = 0$ will contain, with probability approaching 1 as $\Omega \to \infty$, a number $K_{(\gamma)}(\boldsymbol{\sigma})$ of contours congruent to γ such that

$$|K_{(\gamma)}(\boldsymbol{\sigma}) - \rho(\gamma)\,|\Omega|| \le C\sqrt{|\Omega|}\, e^{-\beta J|\gamma|} \tag{18.1}$$

and this relation holds simultaneously for all γ's.

Thus there are very few contours (and the larger they are the smaller is, in absolute and relative value, their number): a typical spin configuration in the grand canonical ensemble with (+)-boundary conditions is such that the large majority of the spins is "positive" and, in the "sea" of positive spins, there are a few negative spins distributed in *small and rare regions* (in a number, however, still of order of $|\Omega|$).

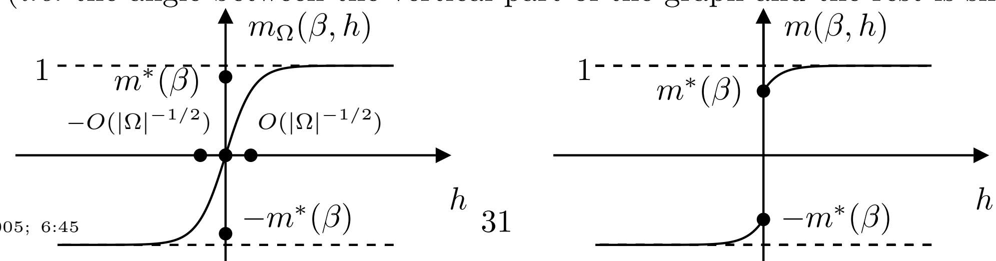
Another consequence of the analysis in Sect.17 concerns the the approximate equation of state near the phase transition region at low temperatures and finite Ω.



(3)

If Ω is finite the graph of $h \to m_\Omega(\beta, h)$ will have a rather different behavior depending on the possible boundary conditions; *e.g.* if the boundary condition is $(+)$ or $(-)$ one gets respectively, the results depicted in Fig.3, where $m^*(\beta)$ denotes the *spontaneous magnetization*, *i.e.* $m^*(\beta) \stackrel{def}{=} \lim_{h\to 0^+} \lim_{\Omega\to\infty} m_\Omega(\beta, h)$.

With periodic or empty boundary conditions the diagram changes as in the first of Fig.4: the thermodynamic limit $m(\beta, h) = \lim_{\Omega\to\infty} m_\Omega(\beta, h)$ exists for all $h \ne 0$ and the resulting graph is in the second of Fig.4, which shows that at $h = 0$ the limit is discontinuous. It can be proved, if β is large enough, that $\infty > \lim_{h\to 0^+} \partial_h m(\beta, h) = \chi(\beta) > 0$ (*i.e.* the angle between the vertical part of the graph and the rest is sharp).



(4)

Furthermore it can be proved that $m(\beta,h)$ is analytic in h for $h\neq 0$. If β is small enough analyticity holds at all h. For β large the function $f(\beta,h)$ has an *essential singularity at* $h=0$: a result that can be interpreted as excluding a naive theory of metastability as a description of states governed by an equation of state obtained from an analytic continuation to negative values of h of $f(\beta,h)$.

The above considerations and results further clarify what a phase transition for a finite system means.

Bibliography: [Ga99], [FP04].

19. Beyond low temperature (ferromagnetic Ising model)

A limitation of the results discussed above is the condition of low temperature ("β large enough"). A natural problem is to go beyond the low-temperature region and to describe fully the phenomena in the region where boundary condition instability takes place and first develops. A number of interesting partial results are known, which considerably improve the picture emerging from the previous analysis. A striking list, but far from exhaustive, of such results follows and focuses on *properties of ferromagnetic Ising spin systems*. The reason for restricting to such cases is that they are simple enough to allow a rather fine analysis which sheds considerable light on the structure of statistical mechanics suggesting precise formulation of the problems that it would be desirable to understand in more general systems.

(1) Let $z\stackrel{def}{=}e^{\beta h}$ and consider the the product of z^V (V is the number of sites $|\Omega|$ of Ω) times the partition function with periodic or perfect-wall boundary conditions with finite range feromagnetic interaction, not neceesarily nearest neighbor; a polynomial in z (of degree $2V$) is thus obtained. Its zeros *lie on the unit circle* $|z|=1$: this is *Lee-Yang's theorem.* It implies that the only singularities of $f(\beta,h)$ in the region $0<\beta<\infty$, $-\infty<h<+\infty$ can be found at $h=0$.

A singularity can appear only if the point $z=1$ is an accumulation point of the limiting distribution (as $\Omega\to\infty$) of the zeros on the unit circle: if the zeros are $z_1,\ldots,z_{2V}$ then $\frac{1}{V}\log z^V Z(\beta,h,\Omega,\text{periodic})=2\beta J+\beta h+\frac{1}{V}\sum_{i=1}^{2V}\log(z-z_i)$ and if $V^{-1}\cdot\big($number of zeros of the form $z_j=e^{i\theta_j}$ with $\theta\le\theta_j\le\theta+d\theta\big)\xrightarrow[\Omega\to\infty]{}\frac{d\rho_\beta(\theta)}{2\pi}$ it is

$$\beta f(\beta,h)=2\beta J+\frac{1}{2\pi}\int_{-\pi}^{\pi}\log(z-e^{i\theta})\,d\rho_\beta(\theta) \tag{19.1}$$

The existence of the measure $d\rho_\beta(\theta)$ follows from the existence of the thermodynamic limit: but $d\rho_\beta(\theta)$ is not necessarily $d\theta$-continuous, *i.e.* proportional to $d\theta$.

(2) It can be shown that, with a not necessarily nearest neighbor interaction, the zeros of the partition function do not move too much under small perturbations of the potential even if one perturbs the energy (at perfect-wall or periodic boundary conditions) into

$$H'_\Omega(\boldsymbol{\sigma})=H_\Omega(\boldsymbol{\sigma})+(\delta H_\Omega)(\boldsymbol{\sigma}),\qquad (\delta H_\Omega)(\boldsymbol{\sigma})=\sum_{X\subset\Omega}J'(X)\,\sigma_X \tag{19.2}$$

where $J'(X)$ is very general and defined on subsets $X = (x_1, \ldots, x_k) \subset \Omega$ such that the quantity $||J'|| = \sup_{y \in Z^d} \sum_{y \in X} |J'(X)|$ is small enough. More precisely fixed a ferromagnetic pair potential J suppose that one knows that, when $J' = 0$, the partition function zeros in the variable $z = e^{\beta h}$ lie in a certain closed set N (of the unit circle) in the z-plane. Then if $J' \neq 0$ they lie in a closed set N^1, Ω-independent and contained in a neighborhood of N of width shrinking to 0 when $||J'|| \to 0$. This leads to establish various relations between analyticity properties and boundary condition instability as described in (3) below.

(3) In the ferromagnetic Ising model, with a not necessarily nearest neighbor interaction, one says that there is a *gap* around 0 if $d\rho_\beta(\theta) = 0$ near $\theta = 0$. It can be shown that if β is small enough there is a gap for all h of width uniform in h.

(4) Another question is whether the boundary condition instability is always revealed by the one-spin correlation function (*i.e.* by the magnetization) or whether it might be shown only by some correlation functions of higher order. It can be proved that no boundary condition instability takes place for $h \neq 0$; at $h = 0$ it is possible only if

$$\lim_{h \to 0^-} m(\beta, h) \neq \lim_{h \to 0^+} m(\beta, h) \tag{19.3}$$

(5) A consequence of the Griffiths' inequalities, *c.f.* Sect.16, is that if (19.3) is true for a given β_0 then it is true for all $\beta > \beta_0$. Therefore item (4) leads to a natural definition of the *critical temperature* T_c as the least upper bound of the T's such that (19.3) holds ($k_B T = \beta^{-1}$).

(6) If $d = 2$ the free energy of the nearest neighbor ferromagnetic Ising model has a singularity at β_c and the value of β_c is known exactly from the exact solutions of the model: $m(\beta, 0) \stackrel{def}{=} m^*(\beta) \equiv (1 - \sinh^4 2\beta J)^{\frac{1}{8}}$. The location and nature of the singularities of $f(\beta, 0)$ as a function of β remains an open question for $d = 3$. In particular the question of whether there is a singularity of $f(\beta, 0)$ at $\beta = \beta_c$ is open.

(7) For $\beta < \beta_c$ there is instability with respect to boundary conditions (see (6) above) and a natural question is: how many "pure" phases can exist in the ferromagnetic Ising model? (*c.f.* (9.2) and Sect.9). Intuition suggests that there should be only two phases: the positively magnetized and the negatively magnetized ones.

One has to distinguish between translation invariant pure phases and non translation invariant ones. It can be proved that, in the case of the 2–dimensional nearest neighbor ferromagnetic Ising models, all infinite volume states (*c.f.* Sect.15) are translationally invariant. Furthermore they can be obtained by considering just the two boundary conditions $+$ and $-$: the latter states are pure states also for models with non nearest neighbor ferromagnetic interaction. The solution of this problem has led to the introduction of many new ideas and techniques in statistical mechanics and probability theory.

(8) In any dimension $d \geq 2$, for β large enough it can be proved that the nearest neigbor Ising model has only two translation invariant phases. If the dimension is ≥ 3 and β is large the $+$ and $-$ phases exhaust the set of translationally invariant pure phases but *there exist non translationally invariant phases.* For β close to β_c, however, the question is much

more difficult.

Bibliography: [On44], [LY52], [Ru71], [Si91], [Ga99], [Ai80], [Hi81], [FP04]

20. Geometry of phase coexistence.

Intuition about the phenomena connected with the classical phase transitions is usually based on the properties of the liquid-gas phase transition; this transition is experimentally investigated in situations in which the total number of particles is fixed (canonical ensemble) and in presence of an external field (gravity).

The importance of such experimental conditions is obvious; the external field produces a nontranslationally invariant situation and the corresponding separation of the two phases. The fact that the number of particles is fixed determines, on the other hand, the fraction of volume occupied by each of the two phases.

Once more consider the nearest neighbor ferromagnetic Ising model: the results available for it can be used to obtain a clear picture of the solution to problems that one would like to solve but which in most other models are intractable with present day techniques.

It will be convenient to discuss phase coexistence in the canonical ensemble distributions on configurations of fixed total magnetization $M = mV$, see Sect.15, (15.4). Let β be large enough to be in the two phases region and, for a fixed $\alpha \in (0,1)$, let

$$m = \alpha\, m^*(\beta) + (1-\alpha)\,(-m^*(\beta)) = \,(1-2\alpha)\, m^*(\beta) \tag{20.1}$$

i.e. m is in the vertical part of the diagram $m = m(\beta, h)$ at β fixed (see Fig.4).

Fixing m as in (20.1) does not yet determine the separation of the phases in two different regions; for this effect it will be necessary to introduce some external cause favoring the occupation of a part of the volume by a single phase. Such an asymmetry can be obtained in at least two ways: through a weak uniform external field (in complete analogy with the gravitational field in the liquid-vapor transition) or through an asymmetric field acting only on boundary spins. This second way should have the same qualitative effect as the former, because in a phase transition region a boundary perturbation produces volume effects: see Sect. 9,17. From a mathematical point of view it is simpler to use a boundary asymmetry to produce phase separations and the simplest geometry is obtained by considering $\pm$*-cylindrical or* $++$*-cylindrical boundary conditions*: this means $++$ or $\pm$ boundary conditions periodic in one direction (*e.g.* in Fig.2 imagine the right and left boundary identified after removing the boundary spins on them).

Spins adjacent to the bases of Ω act as symmetry-breaking external fields. The $++$-cylindrical boundary condition should favor the formation inside Ω of the positively magnetized phase; therefore it will be natural to consider, in the canonical distribution, this boundary condition only when the total magnetization is fixed to be the spontaneous magnetization $m^*(\beta)$.

On the other hand, the $\pm$-boundary condition favors the separation of phases (positively magnetized phase near the top of Ω and negatively magnetized phase near the bottom). Therefore it will be natural to consider the latter boundary condition in the case of a canonical distribution with magnetization $m=(1-2\alpha)\,m^*(\beta)$ with $0<\alpha<1$, (20.1). In the latter case the positive phase can be expected to adhere to the top of Ω and to extend, in some sense to be discussed, up to a distance $O(L)$ from it; and then to change into the negatively magnetized pure phase.

To make precise the phenomenological description consider the spin configurations $\boldsymbol{\sigma}$ through the associated sets of disjoint polygons (*c.f.* Sect.17). Fix the boundary conditions to be $++$ or $\pm$-cylindrical boundary conditions and note that polygons associated with a spin configuration $\boldsymbol{\sigma}$ are *all closed* and of two types: the ones of the first type, denoted $\gamma_1,\ldots,\gamma_n$, are polygons which do not encircle Ω, the second type of polygons, denoted by the symbols λ_α, are the ones which wind up, at least once, around Ω.

So a spin configuration $\boldsymbol{\sigma}$ will be described by a set of polygons the statistical weight of a configuration $\boldsymbol{\sigma}=(\gamma_1,\ldots,\gamma_n,\lambda_1,\ldots,\lambda_h)$ is (*c.f.* (17.1)):

$$e^{-2\beta J(\sum_i|\gamma_i|+\sum_j|\lambda_j|)}\,. \tag{20.2}$$

The reason why the contours λ that go around the cylinder Ω are denoted by λ (rather than by γ) is that they "look like" open contours, see Sect.17, if one forgets that the opposite sides of Ω have to be identified. In the case of the $\pm$-boundary conditions then the number of polygons of λ-type *must be odd* (hence $\neq 0$), while for the $++$-boundary condition the number of λ-type polygons *must be even* (hence it could be 0).

Bibliography: [Si91], [Ga99]

21. Separation and Coexistence of Phases

In the context of the geometric description of the spin configuration in Sect.20 consider the canonincal distributions with $++$-cylindrical or the $\pm$-cylindrical boundary conditions and zero field: they will be denoted briefly as $\mu_{\beta,++}$, $\mu_{\beta,\pm}$. The following theorem *Minlos-Sinai's theorem* provided the foundations of the microscopic theory of coexistence: it is formulated in dimension $d=2$ but, modulo obvious changes, it holds for $d\geq 2$.

For $0<\alpha<1$ fixed let $m=(1-2\alpha)\,m^*(\beta)$; then for β large enough a spin configuration $\boldsymbol{\sigma}=(\gamma_1,\ldots,\gamma_n,\lambda_1,\ldots,\lambda_{2h+1})$ randomly chosen with the distribution $\mu_{\beta,\pm}$ enjoys the properties (1)-(4) below with a $\mu_{\beta,\pm}$–probability approaching 1 as $\Omega\to\infty$:
(1) $\boldsymbol{\sigma}$ contains only one contour of λ-type and

$$|\,|\lambda|-(1+\varepsilon(\beta))L|<o(L) \tag{21.1}$$

where $\varepsilon(\beta)>0$ is a suitable (α-independent) function of β tending to zero exponentially fast as $\beta\to\infty$.
(2) If $\Omega^+_\lambda,\Omega^-_\lambda$ denote the regions above and below λ and $|\Omega|\equiv V,|\Omega^+|,|\Omega^-|$ are the volumes of Ω,Ω^+,Ω^- it is

$$|\,|\Omega^+_\lambda|-\alpha\,V\,|<\kappa(\beta)\,V^{3/4}\qquad |\Omega^-_\lambda|-(1-\alpha)V\,|<\kappa(\beta)\,V^{3/4} \tag{21.2}$$

where $\kappa(\beta) \xrightarrow[\beta\to\infty]{} 0$ *exponentially fast; the exponent* $\frac{3}{4}$*, here and below, is not optimal.*
(3) If $M_\lambda = \sum_{x\in\Omega_\lambda} \sigma_x$*, it is*

$$|M_\lambda - \alpha\, m^*(\beta)\, V| < \kappa(\beta) V^{3/4}, \qquad M'_\lambda - (1-\alpha)\, m^*(\beta)\, V| < \kappa(\beta) V^{3/4} \tag{21.3}$$

.

(4) If $K^\lambda_\gamma(\boldsymbol{\sigma})$ *denotes the number of contours congruent to a given* γ *and lying in* Ω^+_λ *then, simultaneously for all the shapes of* γ*:*

$$|\, K^\lambda_\gamma(\boldsymbol{\sigma}) - \rho(\gamma)\, \alpha\, V\,| \le C e^{-\beta J|\gamma|} V^{\frac{1}{2}} \qquad C > 0 \tag{21.4}$$

where $\rho(\gamma) \le e^{-2\beta J|\gamma|}$ *is the same quantity already mentioned in the text of the theorem of* §*(6.8). A similar result holds for the contours below* λ *(c.f. the comments on (18.1)).*

The theorem not only provides a detailed and rather satisfactory description of the phase separation phenomenon, but it also furnishes a precise microscopic definition of the line of separation between the two phases, which should be naturally identified with the (random) line λ.

A similar result holds in the canonical distribution $\mu_{\beta,++,m^*(\beta)}$ where (1) is replaced by: *no* λ-type polygon is present, while (2), (3) become superfluous and (4) is modified in the obvious way. In other words a typical configuration for the distribution the $\mu_{\beta,++,m^*(\beta)}$ has the same appearance as a typical configuration of the corresponding grand canonical ensemble with (+)-boundary condition (whose properties are described by the theorem of Sect.19).

Bibliography: [Si91], [Ga99].

22. Phase separation line and surface tension

Continuing to refer to the nearest neighbor Ising ferromagnet, the theorem of Sect.21 means that, if β is large enough, then the microscopic line λ, separating the two phases, is almost straight (since $\varepsilon(\beta)$ is small). The deviations of λ from a straight line are more conveniently studied in the grand canonical distributions $\mu^0_\pm$ with boundary condition set to +1 in the upper half of $\partial\Omega$, *vertical sites included*, and to −1 in the lower half: this is illustrated in Fig.2, Sect.17. The results can be converted into very similar results for grand canonical distributions with ±-cylindrical boundary conditions of Sect.21,22.

Define λ to be *rigid* if the probability that λ passes through the center of the box Ω (*i.e.* 0) *does not* tend to 0 as $\Omega \to \infty$; otherwise it is *not rigid*.

The notion of rigidity distinguishes between the possibilities for the line λ to be "straight": the "excess" length $\varepsilon(\beta)L$, see (21.1), can be obtained in two ways: either the line λ is essentially straight (in the geometric sense) with a few "bumps" distributed with a density of order $\varepsilon(\beta)$ or, otherwise, it is only locally straight and with an important part of the excess length being gained through a small bending on a large length scale. In three dimensions a similar phenomenon is possible. Rigidity of λ, or its failure, can in principle be investigated by optical means; there can be interference of coherent light scattered by macroscopically separated surface elements of λ only if λ is rigid in the above sense.

It has been rigorously proved that, the line λ is *not rigid* in dimension 2. And, at least at low temperature, the fluctuation of the middle point is of the order $O(\sqrt{L})$. In dimension 3 however it has been shown that the surface λ is rigid at low enough temperature.

A deeper analysis is needed to study the shape of the separation surface under otherconditions, *e.g.* with + boundary conditions and in a canonical distribution with magnetization intermediate between $\pm m^*(\beta)$. It involves, as a prerequisite, the definition and many properties of the *surface tension* between the two phases. Here only the definition of surface tension in the case of $\pm$-boundary conditions in the 2-dimensional case will be mentioned. If $Z^{++}(\Omega, m^*(\beta))$ and $Z^{+-}(\Omega, m)$ are the canonical partition functions for the $++$ and $\pm$-cylindrical boundary conditions the tension $\tau(\beta)$ is defined as $\beta\,\tau(\beta) = -\lim_{\Omega\to\infty} \frac{1}{L}\log\frac{Z^{+-}(\Omega,m)}{Z^{++}(\Omega,m^*(\beta))}$. The limit can be shown to be α-independent for β large enough: the definition motivation and justification is based on the microscopic geometric description in Sect.20. The definition can be naturally extended to higher dimension (and to more general non nearest neighbor models). If $d = 2$ the tension τ can be exactly computed at all temperature below criticality and is $\beta\,\tau(\beta) = +2\beta J + \log\tanh\beta J$.

More remarkably the definition can be extended to define the surface tension $\tau(\beta, \mathbf{n})$ in the "direction $\mathbf{n}$", *i.e.* when the boundary conditions are such that the line of separation is in the average orthogonal to the unit vector $\mathbf{n}$. In this way if $d = 2$ and $\alpha \in (0, 1)$ is fixed it can be proved that at low enough temperature the canonical distribution with + boundary conditions and intermediate magnetization $m = (1 - 2\alpha)m^*(\beta)$ has typical configurations containing a region of spins $-$ of area $\simeq \alpha V$; furthermore if the container is rescaled to size $L = 1$ the region will have a limiting shape filling an area α bounded by a *smooth* curve whose form is determined by the classical macroscopic *Wulff's theory* of the shape of crystals in terms of the surface tension $\tau(\mathbf{n})$.

An interesting question remains open in the three-dimensional case: it is conceivable that the surface, although rigid at low temperature, might become "loose" at a temperature $\widetilde{T}_c$ smaller than the critical temperature T_c (the latter being defined as the highest temperature below which there are at least two pure phases). The temperature $\widetilde{T}_c$, whose existence is rather well established in numerical experiments, would be called the "*roughening transition*" temperature. The rigidity of λ is connected with the existence of translationally noninvariant equilibrium states. The latter exist in dimension $d = 3$, but not in dimension $d = 2$ where the discussed nonrigidity of λ, established all the way to T_c, provides the intuitive reason for the absence of non translationally invariant states. It has been shown that in $d = 3$ the roughening temperature $\widetilde{T}_c(\beta)$ necessarily *cannot be smaller* than the critical temperature of the 2–dimensional Ising model with the same coupling.

Note that existence of translationally noninvariant equilibrium states is not necessary for the description of coexistence phenomena. The theory of the nearest neighbor two-dimensional Ising model is a clear proof of this statement.

Bibliography: [On44], [Be75], [Si91], [Mi95], [PV99], [Ga99],

23. Critical points

Correlation functions for a system with short range interactions and in an equilibrium state which is a pure phase have *cluster properties*, see (9.2): their physical meaning is that in a pure phase there is independence between fluctuations occurring in widely separated regions. The simplest cluster property concerns the "pair correlation function", *i.e.* the probability density $\rho(\mathbf{q}_1,\mathbf{q}_2)$ of finding particles in points $\mathbf{q}_1,\mathbf{q}_2$ independently of where the other particles may happen to be, see (9.3). In the case of spin systems the pair correlation $\rho(\mathbf{q}_1,\mathbf{q}_2)=\langle\sigma_{\mathbf{q}_1}\sigma_{\mathbf{q}_2}\rangle$ will be considered. The pair correlation of a translation invariant equilibrium state has a cluster property, (9.2),(15.6), if

$$|\rho(\mathbf{q}_1,\mathbf{q}_2)-\rho^2|\xrightarrow[|\mathbf{q}_1-\mathbf{q}_2|\to\infty]{}0 \tag{23.1}$$

where ρ is the probability density for finding a particle at $\mathbf{q}$ (*i.e.* the physical density of the state) or $\rho=\langle\sigma_\mathbf{q}\rangle$ is the average of the value of the spin at $\mathbf{q}$ (*i.e.* the magnetization of the state).

A general definition of *critical point* is a point c in the space of the parameters characterizing equilibrium states, *e.g.* β,λ in grand canonical distributions or β,v in canonical distributions or β,h in the case of lattice spin systems in a grand canonical distribution. In systems with short range interaction (*i.e.* with $\varphi(\mathbf{r})$ vanishing for $|\mathbf{r}|$ large enough) the point c is a critical point if the pair correlation tends to 0, see (23.1), slower than exponential, for instance as a power of the distance $|\mathbf{r}|=|\mathbf{q}_1-\mathbf{q}_2|$.

A typical example is the 2–dimensional Ising model on a square lattice and with nearest neighbor ferromagnetic interaction of size J. It has a single critical point at $\beta=\beta_c$, $h=0$ with $\sinh 2\beta_cJ=1$. The cluster property is that $\langle\sigma_x\sigma_y\rangle-\langle\sigma_x\rangle\langle\sigma_y\rangle\xrightarrow[|x-y|\to\infty]{}0$ as

$$A_+(\beta)\frac{e^{-\kappa(\beta)|x-y|}}{\sqrt{|x-y|}},\qquad A_-(\beta)\frac{e^{-\kappa(\beta)|x-y|}}{|x-y|^2},\qquad A_c\frac{1}{|x-y|^{\frac14}}\qquad \beta=\beta_c \tag{23.2}$$

for $\beta<\beta_c$, $\beta>\beta_c$ or $\beta=\beta_c$ respectively, where $A_\pm(\beta),A_c,\kappa(\beta)>0$. The properties (23.2) stem from the *exact solution* of the model.

At the critical point several interesting phenomena occurr: the lack of exponential decay indicates lack of a length scale over which really distinct phenomena can take place and properties of the system observed at different length scales are likely to be simply related by suitable scaling transformations. Many efforts have been dedicated at finding ways of understanding quantitatively the scaling properties which relate different observables. The result has been the development of the *renormalization group approach* to critical phenomena, *c.f.* Sect.25. The picture that emerges is that the closer the critical point is the larger becomes the maximal scale of length *below which scaling properties are observed.* For instance in a lattice spin system in 0 field the magnetization $M|\Lambda|^{-a}$ in a box $\Lambda\subset\Omega$ should have essentially the same distribution for all Λ's with side $<l_0(\beta)$ and $l_0(\beta)\to\infty$ as $\beta\to\beta_c$, *provided* a is suitably chosen. The number a is called a *critical exponent.*

There are several other "critical exponents" that can be defined near a critical point. They can be associated with singularities of the thermodynamic function or with the behavior of the correlation functions involving joint densities at two or more than two points. As an example consider a lattice spin system: then the "$2n$–spins correlation" $\langle\sigma_0\sigma_{\xi_1}\ldots\sigma_{\xi_{2n-1}}\rangle_c$ could behave proportionally to $\chi_{2n}(0,\xi_1,\ldots,\xi_{2n-1})$, $n=1,2,3,\ldots,$, for a suitable family of *homogeneous* functions χ_n, of some degree ω_{2n}, of the coordinates $(\xi_1,\ldots,\xi_{2n-1})$ at least when the reciprocal distances are large but $< l_0(\beta)$ and $l_0(\beta) = const\,(\beta-\beta_c)^{-\nu}\xrightarrow[\beta\to\beta_0]{}\infty$. This means that if ξ_i are regarded as points in $\mathbb{R}^d$ there are functions χ_{2n} such that:

$$\chi_{2n}(0,\frac{\xi_1}{\lambda},\ldots,\frac{\xi_{2n-1}}{\lambda}) = \lambda^{\omega_{2n}}\,\chi_{2n}(0,\xi_1,\ldots,\xi_{2n-1}) \qquad 0<\lambda\in\mathbb{R} \tag{23.3}$$

and $\langle\sigma_0\sigma_{\xi_1}\ldots\sigma_{\xi_{2n-1}}\rangle_c \propto \chi_{2n}(0,\xi_1,\ldots,\xi_{2n-1})$ if $1\ll|x_i-x_j|\ll l_0(\beta)$. The numbers ω_{2n} define a sequence of critical exponents.

Other critical exponents can be associated with approaching the critical point along other directions: for instance along $h\to0$ at $\beta=\beta_c$. In this case the length up to which there are scaling phenomena is $l_0(h)=\ell_o\,h^{-\overline{\nu}}$. And the magnetization $m(h)$ tends to 0 as $h\to0$ at fixed $\beta=\beta_c$ as $m(h)=m_0h^{\frac{1}{\delta}}$ for $\delta>0$.

None of the critical exponents is in any generality known rigorously, including its existence. An exception is the case of the 2–dimensional nearest neighbor Ising ferromagnet where some exponents are known exactly (*e.g.* $\omega_2=\frac{1}{4}$, $\omega_{2n}=n\omega_2$, or $\nu=1$ while $\delta,\overline{\nu}$ are not rigorously known). Nevertheless for Ising ferromagnets (even not nearest neighbor but, as always here, finite range) in all dimensions all mentioned exponents are conjectured to be the same as those of the nearest neighbor Ising ferromagnet. A further exception is the derivation of rigorous relations between critical exponents and, in some cases, even their values under the assumption that they exist.

Remark: Naively it could be expected that in a pure state in 0 field with $\langle\sigma_x\rangle=0$ the quantity $s=|\Lambda|^{-\frac{1}{2}}\sum_{x\in\Lambda}\sigma_x$, if Λ is a cubic box of side ℓ, should have a probability distribution which is Gaussian with dispersion $\lim_{\Lambda\to\infty}\langle s^2\rangle$. This is "usually true": *but not always.* The (23.2) shows that in the $d=2$ ferromagnetic nearest neighbor Ising model $\langle s^2\rangle$ diverges proportionally to $\ell^{2-\frac{1}{4}}$ so that the variable s cannot have a Gaussian distribution. The variable $S=|\Lambda|^{-\frac{7}{8}}\sum_{x\in\Lambda}\sigma_x$ will have a finite dispersion: however there is no reason that it should be Gaussian. This makes clear the great interest of a fluctuation theory and its relevance for the critical point studies, see Sect.24,25.

Bibliography: [On44], [DG72], [MW73], [Ai82].

24. Fluctuations

As it appears from Sect.23 fluctuations of observabes around their averages have interesting properties particularly at critical points. Of particular interest are observables which are averages over large volumes Λ of local functions $F(x)$ on phase space: this is so because macroscopic observables often have this form. For instance given a region Λ inside the system container Ω, $\Lambda\subset\Omega$, consider a configuration $x=(\mathbf{P},\mathbf{Q})$ and the number of particles $N_\Lambda=\sum_{\mathbf{q}\in\Lambda}1$ in Λ, or the potential energy $\Phi_\Lambda=\sum_{(\mathbf{q},\mathbf{q}')\in\Lambda}\varphi(\mathbf{q}-\mathbf{q}')$ or the kinetic energy $K_\Lambda=\sum_{\mathbf{q}\in\Lambda}\frac{1}{2m}\mathbf{p}^2$. In the case of lattice spin systems consider a configuration $\boldsymbol{\sigma}$ and, for instance, the magnetization $M_\Lambda=\sum_{i\in\Lambda}\sigma_i$ in Λ. Label the above four examples by $\alpha=1,\ldots,4$.

Let μ_α be the probability distribution describing the equilibrium state in which the quantities X_Λ are considered; let $x_\Lambda=\langle\frac{X_\Lambda}{|\Lambda|}\rangle_{\mu_\alpha}$ and $p\stackrel{def}{=}\frac{X_\Lambda-x_\Lambda}{|\Lambda|}$. Then typical fluctuations properties to investigate are ($\alpha=1\ldots4$),

(1) *for all* $\delta>0$ *it is* $\lim_{\Lambda\to\infty}\mu_\alpha(|p|>\delta)=0$ *(law of large numbers)*
(2) *there is* $D_\alpha>0$ *such that* $\mu(p\sqrt{|\Lambda|}\in[a,b])\xrightarrow[\Lambda\to\infty]{}\int_a^b\frac{dz}{\sqrt{2\pi D_\alpha}}e^{-\frac{z^2}{2D_\alpha}}$ *(central limit law)*
(3) *there is an interval* $I_\alpha=(p^*_{\alpha,-},p^*_{\alpha,+})$ *and a concave function* $F_\alpha(p)$, $p\in I$, *such that if* $[a,b]\subset I$ *then* $\frac{1}{|\Lambda|}\log\mu\big(p\in[a,b]\big)\xrightarrow[\Lambda\to\infty]{}\max_{p\in[a,b]}F_\alpha(p)$ *(large deviations law)*

The law of large numbers provides the *certainty* of the macroscopic values; the central limit law controls the *small fluctuations* (of order $\sqrt{|\Lambda|}$) of X_Λ around its average; the large deviations law concerns the *fluctuations of order* $|\Lambda|$.

The relations (1),(2),(3) are not always true: they can be proved under further general assumptions if the potential φ satisfies (7.2) in the case of particle systems or if $\sum_{\mathbf{q}}|\varphi(\mathbf{q})|<\infty$ in the case of lattice spin systems. The function $F_\alpha(p)$ is defined in terms of the thermodynamic limits of suitable thermodynamic functions associated with the equilibrium state μ_α. The further assumption is, essentially in all cases, that a suitable thermodynamic function in terms of which the $F_\alpha(p)$ will be expressed is smooth and with a nonvanishing second derivative.

For the purpose of a simple concrete example consider a lattice spin system of Ising type with energy $-\sum_{x,y\in\Omega}\varphi(x-y)\sigma_x\sigma_y-\sum_x h\sigma_x$ and the fluctuations of the magnetization $M_\Lambda=\sum_{x\in\Lambda}\sigma_x$, $\Lambda\subset\Omega$, in the grand canonical equilibrium states $\mu_{h,\beta}$.

Let the free energy be $\beta f(\beta,h)$, see (15.5), let $m=m(h)\stackrel{def}{=}\langle\frac{M_\Lambda}{|\Lambda|}\rangle$ and let $h(m)$ the inverse function of $m(h)$. If $p=\frac{M_\Lambda}{|\Lambda|}$ the function $F(p)$ is

$$F(p)=\beta\big(f(\beta,h(p))-f(\beta,h)-\partial_h f(\beta,h)(h(p)-h)\big)\tag{24.1}$$

then a quite general result is

The relations (1),(2),(3) hold if the potential satisfies $\sum_x|\varphi(x)|<\infty$ *and if* $F(p)$, *(24.1), is smooth and* $F''(p)\neq0$ *in open intervals around those in which* p *is considered, i.e. around* $p=0$ *for the law of large numbers and for the central limit law or in an open interval containing* a,b *for the case of the large deviations law.*

In the envisaged cases the theory of equivalence of the ensembles implies that the function F can also be computed via thermodynamic functions naturally associated with other equilibrium ensembles. For instance instead of the grand canonical $f(\beta,h)$ one could consider the canonical $\beta g(\beta,m)$, see (15.5), then

$$F(p)=-\beta\big(g(\beta,p)-g(\beta,m)-\partial_m g(\beta,m)(p-m)\big) \tag{24.2}$$

It has to be remarked that there should a strong relation between the central limit law and the law of large deviations. Setting aside stating the conditions for a precise mathematical theorem, the statement can be rapidly illustrated in the case of a ferromagnetic lattice spin system and with $\Lambda\equiv\Omega$, by showing that the large deviations law in small intervals, around the average $m(h_0)$, at a value h_0 of the external field is implied by the validity of the central limit law for all values of h near h_0 and viceversa (here β is fixed). Taking $h_0=0$ (for simplicity) the heuristic reasons are the following. Let $\mu_{h,\Omega}$ be the grand canonical distribution in external field h. Then
(1) The probability $\mu_{h,\Omega}(p\in dp)$ is proportional, by definition, to $\mu_{0,\Omega}(p\in dp)e^{-\beta hm|\Omega|}$. Hence if the central limit law holds for all h near $h_0=0$ there will exist two functions $m(h)$ and $D(h)>0$, defined for h near $h_0=0$, with $m(0)=0$ and

$$\mu_0(p\in dp)e^{-\beta hp}=const\, e^{-|\Omega|\frac{(p-m(h))^2}{2D(h)}+o(\Omega)}\,dp \tag{24.3}$$

(2) there is a function $\zeta(m)$ such that $\partial_m\zeta(m(h))=\beta h$ and $\partial^2_m\zeta(m(h))=D(h)^{-1}$. [This is obtained by remarking that, given $D(h)$, the differential equation $\partial_m\beta h=D(h)^{-1}$ with the initial value $h(0)=0$ determines the function $h(m)$; therefore $\zeta(m)$ is determined by a second integration, from $\partial_m\zeta(m)=\beta h(m)$.

It then follows, heuristically, that the probability of p in zero field has the form $const\, e^{\zeta(p)|\Omega|}\,dp$ so that the probability that $p\in[a,b]$ will be $const\, e^{|\Omega|\max_{p\in[a,b]}\zeta(p)}$.]

Viceversa the large deviations law for p at $h=0$ implies the validity of the central limit law for the fluctuations of p in all small enough fields h: this simply arises from the function $F(p)$ having a negative second derivative.

This means that there is a ‘”duality” between central limit law and large deviation law or that the large deviations law is a “global version” of the central limit law. In the sense that
(a) if the central limit law holds for h in an interval around h_0 then the fluctuations of the magnetization at field h_0 satisfy a large deviation law in a small enough interval J around $m(h_0)$,
(b) if a large deviation law is satisfied in an interval around h_0 then the central limit law holds for the fluctuations of magnetization around its average in all fields h with $h-h_0$ small enough.

Going beyond the heuristic level in establishing the duality amounts to giving a precise meaning to “small enough” and to discuss which properties of $m(h)$ and $D(h)$ or of $F(p)$ are needed to derive properties (a),(b).

For illustration purposes consider the Ising model with ferromagnetic interaction φ: then the central limit law holds for all h if β is small enough and, under the same condition on β, the large deviations law holds for all h and all intervals $[a,b]\subset(-1,1)$. If β is not small then the condition $h \neq 0$ has to be added. Hence the conditions are fairly weak and the apparent exceptions concern the value $h = 0$ and β not small where the statements may become invalid because of possible phase transitions.

In presence of phase transitions the law of large numbers, the central limit law and law of large deviations should be reformulated. Basically one has to add the requirement that fluctuations are considered in *pure phases* and change in a natural way the formulation of the laws. For instance the large fluctuations of magnetization in a pure phase of the Ising model in zero field and large β (*i.e.* in a state obtained as limit of finite volume states with $+$ or $-$ boundary conditions) in intervals $[a,b]$ which *do not contain the average magnetization* m^* *are not necessarily exponentially small with the size of* $|\Lambda|$*: if* $[a,b] \subset [-m^*, m^*]$ *they are exponentially small but only with the size of the surface of* Λ (*i.e.* with $|\Lambda|^{\frac{d-1}{d}}$) while they are exponentially small with the volume if $[a,b] \cap [-m^*, m^*] = \emptyset$.

The discussion of Sect.23 shows that also at the critical point the nature of the large fluctuations is expected to change: no central limit law is expected to hold in general because of the example of (23.2) with the divergence of the average of the normal second moment of the magnetization in a box as the side tends to ∞.

Bibliography: [Ol87]

25. Renormalization group

The theory of fluctuations just discussed concerns only fluctuations of a single quantity. The problem of *joint fluctuations* of several quantities is also interesting and led to really new developments in the 1970's. It is necessary to restrict attention to rather special cases in order to illustrate some ideas and the philosophy behind the approach. Consider therefore the equilibrium distribution μ_0 associated with one of the classical equilibrium ensembles. For instance the equilibrium distribution of an Ising energy function βH_0, having included the temperature factor in the energy: the inclusion is done because the discussion will deal with the properties of μ_0 as a function of β. It will also be assumed that the average of each spin is zero ("no magnetic field", see (15.3) with $h = 0$). Wanting to keep in mind a concrete case imagine that βH_0 is the energy function of the nearest neighbor Ising ferromagnet in zero field.

Imagine that the volume Ω of the container has periodic boundary conditions and is very large, ideally infinite. Define the family of *blocks* $k\boldsymbol{\xi}$, parameterized by $\boldsymbol{\xi} \in \mathbb{Z}^d$ and k integer, consisting of the lattice sites $\mathbf{x} = \{k\xi_i \le x_i < (k+1)\xi_i\}$. This is a lattice of cubic blocks with side size k that will be called the "k-rescaled lattice". The quantities $m_{\boldsymbol{\xi}} = k^{-\alpha d} \sum_{\mathbf{x} \in k\boldsymbol{\xi}} \sigma_{\mathbf{x}}$ are called the *block spins.*

Given α define the map $R^*_{\alpha,k}\mu_0 = \mu_k$ transforming the initial distribution on the original spins into the distribution of the block spins. Note that if the initial spins have only two values $\sigma_{\mathbf{x}} = \pm 1$ the block spins take values between $-\frac{k^d}{k^{\alpha d}}$ and $\frac{k^d}{k^{\alpha d}}$ at steps of size $\frac{2}{k^{\alpha d}}$. Furthermore the map $R^*_{\alpha,k}$ makes sense independently of how many values the initial spins can assume, and even if they assume a continuum of values $S_{\mathbf{x}} \in \mathbb{R}$.

Taking $\alpha = 1$ means, for k large, looking at the probability distribution of the joint large fluctuations in the bloks $k\boldsymbol{\xi}$. Taking $\alpha=\frac{1}{2}$ corresponds to studying a joint central limit property for the block variables.

Considering a one parameter family of initial distributions μ_0 parameterized by a parameter β (that will be identified with the inverse temperature), *typically* there will be a *unique* value $\alpha(\beta)$ of α such that the joint fluctuations of the block variables admit a limiting distribution,

$$\mathrm{prob}_k(m_{\boldsymbol{\xi}}\in[a_{\boldsymbol{\xi}},b_{\boldsymbol{\xi}}],\,\boldsymbol{\sigma}\in\Lambda)\xrightarrow[k\to\infty]{}\int_{\{a_{\boldsymbol{\xi}}\}}^{\{b_{\boldsymbol{\xi}}\}} g_\Lambda((S_{\boldsymbol{\xi}})_{\boldsymbol{\xi}\in\Lambda})\prod_{\boldsymbol{\xi}\in\Lambda}dS_{\boldsymbol{\xi}} \tag{25.1}$$

for some distribution $g_\Lambda(\mathbf{z})$ on $\mathbb{R}^\Lambda$.

If $\alpha>\alpha(\beta)$ the limit will then be $\prod_{\boldsymbol{\xi}\in\Lambda}\delta(S_{\boldsymbol{\xi}})\,dS_{\boldsymbol{\xi}}$, or if $\alpha<\alpha(\beta)$ the limit will not exist (because the block variables will be too large, with a dispersion diverging as $k\to\infty$).

It is convenient to choose as sequence of $k\to\infty$ the sequence $k=2^n$ with $n=0,1,\ldots$ because in this way it is $R^*_{\alpha,k}\equiv R^{*n}_{\alpha,1}$ and the limit $k\to\infty$ along the sequence $k=2^n$ can be regarded as a sequence of iterations of a map $R^*_{\alpha,1}$ acting on the probability distributions of generic spins $S_{\mathbf{x}}$ on the lattice $\mathbb{Z}^d$ (the sequence 3^n would be equally suited).

It is even more convenient to consider probability distributions that are expressed in terms of energy functions H which generate, in the thermodynamic limit, a distribution μ: then $R^*_{\alpha,1}$ defines an action R_α on the energy functions so that $R_\alpha H=H'$ if H generates μ, H' generates μ' and $R^*_{\alpha,1}\,\mu=\mu'$. Of course the energy function will be more general than (15.3) and a form like δU in (19.2) has to be admitted, at least.

In other words R_α gives the result of the action of $R^*_{\alpha,1}$ expressed as a map acting on the energy functions. Its iterates define also a semigroup which is called the *block spin renormalization group.*

While the map $R^*_{\alpha,1}$ is certainly well defined as a map of probability distributions into probability distributions, it is by no means clear that R_α is well defined as a map on the energy functions. Because if μ is given by an energy function it is not clear that $R^*_{\alpha,1}\mu$ is such.

A remarkable theorem can be (easily) proved when $R^*_{\alpha,1}$ and its iterates act on initial μ_0's which are equilibrium states of a spin system with short range interactions and *at high temperature* (β small). In this case if $\alpha=\frac{1}{2}$ the sequence of distributions $R^{*n}_{\frac{1}{2},1}\mu_0(\beta)$ admits a limit which is given by a product of independent Gaussians

$$\mathrm{prob}_k(m_{\boldsymbol{\xi}}\in[a_{\boldsymbol{\xi}},b_{\boldsymbol{\xi}}],\,\boldsymbol{\sigma}\in\Lambda)\xrightarrow[k\to\infty]{}\int_{\{a_{\boldsymbol{\xi}}\}}^{\{b_{\boldsymbol{\xi}}\}}\prod_{\boldsymbol{\xi}\in\Lambda}e^{-\frac{1}{2D(\beta)}S^2_{\boldsymbol{\xi}}}\prod_{\boldsymbol{\xi}\in\Lambda}\frac{dS_{\boldsymbol{\xi}}}{\sqrt{2\pi D(\beta)}} \tag{25.2}$$

Note that this theorem is stated without even mentioning the renormalization maps $R^n_{\frac{1}{2}}$: it can nevertheless be interpreted as saying that

$$R^n_{\frac{1}{2}}\beta H_0\xrightarrow[n\to\infty]{}\sum_{\boldsymbol{\xi}\in\mathbb{Z}^d}\frac{1}{2D(\beta)}S^2_{\boldsymbol{\xi}} \tag{25.3}$$

but the interpretation is not rigorous because (25.2) does not even say that $R^n_{\frac12} H_0(\beta)$ makes sense for $n \ge 1$. The (25.2) says that at high temperature block spins have *normal independent fluctuations: it is therefore an extension of the central limit law.*

There are a few cases in which the map R_α can be rigorously shown to be well defined at least when acting on special equilibrium states like the high temperature lattice spin systems: but these are exceptional cases of relatively little interest.

Nevertheless there is a vast literature dealing with approximate representations of the map R_α. The reason is that assuming not only its existence but also assuming that it *has the properties that one would normally expect to hold for a map acting on a finite dimensional space* it follows that a number of consequences can be drawn, quite non trivial as they led to the first theory of the critical point that goes beyond the van der Waals theory of Sect.11.

The argument proceeds essentially as follows. At the critical point the fluctuations are expected to be *anomalous* (*c.f.* the last remark in Sect.23) in the sense that $\langle (\frac{\sum_{\mathbf{x}\in\Lambda}\sigma_{\boldsymbol{\xi}}}{\sqrt{|\Lambda|}})^2\rangle$ will tend to ∞, because $\alpha = \frac12$ does not correspond to the right fluctuation scale of $\sum_{\xi\in\Lambda}\sigma_\xi$, signaling that $R^{*n}_{\frac12,1}\mu(\beta_c)$ will *not have a limit* but, possibly, there is $\alpha_c > \frac12$ such that $R^{*n}_{\alpha_c,1}\mu_0(\beta_c)$ converges to a limit in the sense (25.1) ($\alpha_c = \frac78$ in the case of the critical nearest neighbor Ising ferromagnet, see ending remark in Sect.23).

Therefore if the map $R^*_{\alpha_c,1}$ is considered as acting on $\mu_0(\beta)$ it will happen that for all $\beta < \beta_c$, $R^{*n}_{\alpha_c,1}\mu_0(\beta_c)$ will converge to a trivial limit $\prod_{\boldsymbol{\xi}\in\Lambda}\delta(S_{\boldsymbol{\xi}})\,dS_{\boldsymbol{\xi}}$ because the value α_c is greater than $\frac12$ while normal fluctuations are expected.

If the map R_{α_c} can be considered as a map on the energy functions this says that $\prod_{\boldsymbol{\xi}\in\Lambda}\delta(S_{\boldsymbol{\xi}})\,dS_{\boldsymbol{\xi}}$ is a *"(trivial) fixed point of the renormalization group"* which "attracts" the energy functions βH_0 corresponding to the high temperature phases.

The existence of the critical β_c can be associated with the existence of a *non trivial fixed point* H^* for R_{α_c} which is hyperbolic with *just one* Lyapunov exponent $\lambda > 1$, hence it has a stable manifold of codimension 1. Call μ^* the probability distribution corresponding to H^*.

The migration towards the trivial fixed point for $\beta < \beta_c$ can be simply explained by the fact that for such values of β the initial energy function βH_0 is *outside the stable manifold of the non trivial fixed point* and under application of the renormalization transformation $R^n_{\alpha_c}\,\beta H_0$ migrates toward the trivial fxed point, which is *attractive in all directions.*

Increasing β it may happen that, for $\beta = \beta_c$, βH_0 *crosses* the stable manifold of the non trivial fixed point H^* for R_{α_c}. Then $R^n_{\alpha_c}\,\beta_c H_0$ will no longer tend to the trivial fixed point but it will tend to H^*: this means that the block spin variables will exhibit a completely different fluctuation behavior. If β is close to β_c the iterations of R_{α_c} will bring $R^n_{\alpha_c}\beta H_0$ close to H^*, *only to be eventually repelled along the unstable direction* reaching a distance from it increasing as $\lambda^n|\beta-\beta_c|$.

This means that up to a scale length $O(2^{n(\beta)})$ lattice units with $\lambda^{n(\beta)}|\beta-\beta_c| = 1$, *i.e.* up to a scale $O(|\beta-\beta_c|^{-\log_2\lambda})$ the fluctuations will be close to those of the fixed point distribution μ^*, but beyond that scale they will come close to those of the trivial fixed point: to see them the block spins would have to be normalized with index $\alpha = \frac12$ and they would appear as uncrorrelated Gaussian fluctuations, *c.f.* (25.2),(25.3).

The next question is "how to find the non trivial fixed points?" this means how to find the energy functions H^* and the corresponding α_c which are fixed points of R_{α_c}. If the above picture is correct the distributions μ^* corresponding to the H^* would describe the critical fluctuations and if there was only one choice, or a limited number of choices, of α_c and H^* this would open the way to a *universality theory* of the critical point hinted already by the "primitive" results of van der Waals' theory.

The initial hope was, perhaps, that there would be a very small number of critical values α_c and of H^* possible: but it rapidly faded away *leaving however the possibility* that the critical fluctuations could be classified into *universality classes*. Each class would contain many energy functions which upon iterated actions of R_{α_c} would evolve under the control of the trivial fixed point (always existing) for β small while for $\beta = \beta_c$ they would be controlled, instead, by a non trivial fixed point H^* for R_{α_c} with the same α_c and the same H^*. For $\beta < \beta_c$ a "resolution" of the approach to the trivial fixed point would be seen by considering the map $R_{\frac{1}{2}}$ rather than R_{α_c} whose iterates would, however, lead to a Gaussian distribution like (25.2) (and to a limit energy function like (25.3)).

The picture is highly hypothetical: but it is the first suggestion of a mechanism leading to critical points with character of universality and with exponents different from those of the van der Waals' theory or, for ferromagnets on a lattice, from those of its lattice version (the *Curie-Weiss' theory*): furthermore accepting the approximations, *e.g. Wilson–Fisher's ε–expansion*, that allow one to pass from the well defined $R^*_{\alpha,1}$ to the action of R_α on the energy functions it is possible to obtain quite unambiguously values for α_c and expressions for H^* which are associated with the action of R_{α_c} on various classes of models.

For instance it can lead to conclude that the critical behavior of *all* ferromagnetic finite range lattice spin systems (with energy functions given by (15.3)) have critical points controlled *by the same* α_c and *the same* non trivial fixed point: this property is far from being mathematically proved but it is considered a major success of the theory. One has to compare it with van der Waals critical point theory: for the first time an approximation scheme has led, even though under approximations not fully controllable, to computable critical exponents which are not equal to those of the van der Waals theory.

The renormalization group approach to critical phenomena has many variants, depending on which kind of fluctuations are considered and on the models to which it is applied. In statistical mechanics there are a few mathematically complete applications: certain results in high dimension, theory of dipole gas in $d = 2$, hierarchical models, some problems in condensed matter and in statistical mechanics of lattice spins and a few others. Its main mathematical successes have been obtained in various related fields where not only the philosophy described above can be applied but it leads to renormalization transformations that can be defined precisely and studied in detail: *e.g.* constructive field theory, KAM theory of quasi periodic motions, various problems in dynamical systems.

However the applications always concern special cases and in each of them the general picture of the *trivial-nontrivial* fixed point dichotomy appears realized but without being accompanied except in rare cases (like the hierarchical models or the universality theory of maps of the interval) by the full description of stable manifold, unstable direction and action of the renormalization transformation on objects other than the one of immediate interest (a generality which looks often an intractable problem, but which also turns out to be not necessary),

In the renormalization group context mathematical physics has played an important role also by providing clear evidence that universality classes could not be too few: this was shown by the numerous exact solutions after Onsager's solution of the nearest neighbor Ising feromagnet: there are in fact several lattice models in $d = 2$ which exibit critical points with some critical exponents exactly computable and which depend *continuously* on the models parameters.

Bibliography: [MW73], [Ba82], [BS75], [WF72], [GK83], [GK85], [BG95], [Ma04].

26. Quantum statistics

Statistical mechanics is extended to assemblies of quantum particles rather straightforwardly. In the case of N identical particles the observables are operators O on the Hilbert space $\mathcal{H}_N = L_2(\Omega)^N_\alpha$, or $\mathcal{H}_N = (L_2(\Omega) \otimes \mathcal{C}^2)^N_\alpha$, where $\alpha = +, -$, of the symmetric ($\alpha = +$, bosonic particles) or antisymmetric ($\alpha = -$, fermionic particles) functions $\psi(\mathbf{Q})$, $\mathbf{Q} = (\mathbf{q}_1, \ldots, \mathbf{q}_N)$ of the position coordinates of the particles or of the positions-spin coordinates $\psi(\mathbf{Q}, \boldsymbol{\sigma})$, $\boldsymbol{\sigma} = (\sigma_1, \ldots, \sigma_N)$, normalized so that $\int |\psi(\mathbf{Q})|^2 d\mathbf{Q} = 1$ or $\sum_{\boldsymbol{\sigma}} \int |\psi(\mathbf{Q}, \boldsymbol{\sigma})|^2 d\mathbf{Q} = 1$, here only $\sigma_j = \pm 1$ is considered. As in classical mechanics a state is defined by the average values $\langle O \rangle$ that it attributes to the observables.

Microcanonical, canonical and grand canonical ensembles can be defined quite easily. For instance consider a system described by the Hamiltonian ($\hbar =$ Planck's constant)

$$H_N = -\frac{\hbar^2}{2m} \sum_{j=1}^{N} \Delta_{\mathbf{q}_j} + \sum_{j<j'} \varphi(\mathbf{q}_j - \mathbf{q}_{j'}) + \sum_j w(\mathbf{q}_j) \stackrel{def}{=} K + \Phi \tag{26.1}$$

where periodic boundary conditions are imagined on Ω and $w(\mathbf{q})$ is periodic smooth potential (the side of Ω is supposed a multiple of the periodic potential period if $w \neq 0$). Then a *canonical equilibrium state* with inverse temperature β and specific volume $v = \frac{V}{N}$ attributes to the observable O the average value

$$\langle O \rangle \stackrel{def}{=} \frac{\mathrm{Tr}\ e^{-\beta H_N} O}{\mathrm{Tr}\ e^{-\beta H_N}}. \tag{26.2}$$

Similar definitions can be given for the grand canonical equilibrium states.

Remarkably the ensembles are *orthodic* and a "heat theorem", see Sect. 4, can be proved. However "equipartition" *does not hold*: *i.e.* $\langle K \rangle \neq \frac{d}{2} N \beta^{-1}$ although β^{-1} is still the integrating factor of $dU + pdV$ in the heat theorem; hence β^{-1} keeps being proportional to temperature.

Lack of equipartition is important as it solves paradoxes that arise in classical statistical mechanics applied to systems with infinitely many degrees of freedom, like crystals (modeled by lattices of coupled oscillators) or fields like the electromagnetic field (black body radiation). However although this has been the first surprise of quantum statistics (and in fact responsible for the very discovery of quanta) it is by no means the last.

At low temperatures new unexpected (*i.e.* with no analogue in classical statistical mechanics) phenomena occurr: Bose-Einstein condensation (superfluidity), Fermi surface instability (superconductivity) and appearance of *off-diagonal long range order*, with the acronym *ODLRO*, will be selected to illustrate the deeply different kind of problems of quantum statistical mechanics. Largely not yet understood, such phenomena pose very interesting problems not only from the physical point of view but also from the mathematical point of view and may pose challenges even at a definitory level. However it should be kept in mind that in the interesting cases (*i.e.* 3-dimensional systems and even most 2 and 1 dimensional systems) there is no proof that the objects defined here really exist for the systems like (26.1), see however the final comment for an important exception.

(1) *Bose Einstein condensation:* In a canonical state with parameters β, v a definition of the occurrence of Bose condensation is in terms of the eigenvalues $\nu_j(\Omega, N)$ of the kernel $\rho(\mathbf{q}, \mathbf{q}')$ on $L_2(\Omega)$, called the 1-particle reduced density matrix, defined by

$$N\sum_{n=1}^{\infty}\frac{e^{-\beta E_n(\Omega,N)}}{\operatorname{Tr} e^{-\beta H_N}}\int\overline{\psi}_n(\mathbf{q},\mathbf{q}_1,\ldots,\mathbf{q}_{N-1})\psi_n(\mathbf{q}',\mathbf{q}_1,\ldots,\mathbf{q}_{N-1})d\mathbf{q}_1\ldots\mathbf{q}_{N-1} \tag{26.3}$$

where $E_n(\Omega, N)$ are the eigenvalues of H_N and $\psi_n(\mathbf{q}_1, \ldots, \mathbf{q}_N)$ are the corresponding eigenfunctions. If ν_j are ordered by increasing value the state with parameters β, v is said to contain a Bose-Einstein condensate if $\nu_1(\Omega, N) \geq b\,N > 0$ for all large Ω at $v = \frac{V}{N}, \beta$ fixed. This receives the interpretation that there are more than bN particles with equal momentum. The *free Bose gas* has a Bose condensation phenomenon at fixed density and small temperature.

(2) *Fermi surface*: the wave functions $\psi_n(\mathbf{q}_1, \sigma_1, \ldots, \mathbf{q}_N, \sigma_N) \equiv \psi_n(\mathbf{Q}, \boldsymbol{\sigma})$ are now antisymmetric in the permutations of the pairs $(\mathbf{q}_i, \sigma_i)$. Let $\psi(\mathbf{Q}, \boldsymbol{\sigma}; N, n)$ denote the n-th eigenfunction of the N particles energy H_N in (26.1) with eigenvalue $E(N, n)$ (labeled by $n = 0, 1, \ldots$ and nondecreasingly ordered). Setting $\mathbf{Q}'' = (\mathbf{q}''_1, \ldots, \mathbf{q}''_{N-p})$, $\boldsymbol{\sigma}'' = (\sigma''_1, \ldots, \sigma''_{N-p})$, introduce the kernels $\rho_p^{H_N}(\mathbf{Q}, \boldsymbol{\sigma}; \mathbf{Q}', \boldsymbol{\sigma}')$ by

$$\begin{aligned}\rho_p(\mathbf{Q},\boldsymbol{\sigma};\mathbf{Q}',\boldsymbol{\sigma}')\stackrel{def}{=}p!\binom{N}{p}\int\sum_{\boldsymbol{\sigma}''}d^{N-p}\mathbf{Q}''\sum_{n=0}^{\infty}\frac{e^{-\beta E(N,n)}}{\operatorname{Tr} e^{-\beta H_N}}\cdot\\ \cdot\overline{\psi}(\mathbf{Q},\boldsymbol{\sigma};\mathbf{Q}'',\boldsymbol{\sigma}'';N,n)\psi(\mathbf{Q}',\boldsymbol{\sigma}';\mathbf{Q}'',\boldsymbol{\sigma}'';N,n)\end{aligned} \tag{26.4}$$

which are called p-particles reduced density matrices (extending the corresponding one particle reduced density matrix (26.3)). Denote $\rho(\mathbf{q}_1 - \mathbf{q}_2) \stackrel{def}{=} \sum_\sigma \rho_1(\mathbf{q}_1, \sigma, \mathbf{q}_2, \sigma)$. It is also useful to consider spinless fermionic systems: the corresponding definitions are obtained simply by suppressing the spin labels and will not be repeated.

Let $r_1(\mathbf{k})$ be the Fourier transform of $\rho_1(\mathbf{q} - \mathbf{q}')$: the Fermi surface can be *defined* as the locus of the $\mathbf{k}$'s in the neighborhood of which $\partial_{\mathbf{k}} r_1(\mathbf{k})$ is *unbounded* as $\Omega \to \infty, \beta \to \infty$. The limit as $\beta \to \infty$ is important because the notion of a Fermi surface is, possibly, precise only at zero temperature, *i.e.* $\beta = \infty$.

So far existence of Fermi surface (*i.e.* the smoothness of $r_1(\mathbf{k})$ except on a smooth surface in $\mathbf{k}$ space) has been proved in free Fermi systems ($\varphi = 0$) and
(a) certain exactly soluble 1–dimensional *spinless* systems
(b) in rather general one dimensional *spinless* systems or systems with spin and repulsive pair interaction, possibly in an *external periodic potential*.

The spinning case in a periodic potential and dimension $d \ge 2$ is the most interesting case to study for its relevance in the theory of conduction in crystals. Essentially no mathematical results are available as the above mentioned ones do not concern any case in dimension > 1: this is a rather deceiving aspect of the theory and a challenge.

In dimension 2 or higher, for fermionic systems with Hamiltonian (26.1), not only there are no results available, *even without spin*, but it not even clear that a Fermi surface can exist in presence of interesting interactions.

(3) *Cooper pairs*: superconductivity theory has been phenomenologically related to the existence of *Cooper pairs.* Consider the Hamiltonian (26.1) and define, *c.f.* (26.4), $\rho(\mathbf{x}-\mathbf{y},\sigma;\mathbf{x}'-\mathbf{y}',\sigma';\mathbf{x}-\mathbf{x}') \stackrel{def}{=} \rho_2(\mathbf{x},\sigma,\mathbf{y},-\sigma;\mathbf{x}',\sigma',\mathbf{y}',-\sigma')$.

The system is said to contain Cooper pairs with spins $\sigma,-\sigma$ ($\sigma = +$ or $\sigma = -$) if there exist functions $g^\alpha(\mathbf{q},\sigma)\neq 0$ with $\int \overline{g^\alpha}(\mathbf{q},\sigma) g^{\alpha'}(\mathbf{q},\sigma)d\mathbf{q} = 0$ if $\alpha\neq\alpha'$, such that

$$\lim_{V\to\infty}\rho(\mathbf{x}-\mathbf{y},\sigma,\mathbf{x}'-\mathbf{y}',\sigma',\mathbf{x}-\mathbf{x}') \xrightarrow[\mathbf{x}-\mathbf{x}'\to\infty]{} \sum_\alpha g^\alpha(\mathbf{x}-\mathbf{y},\sigma)\overline{g^\alpha}(\mathbf{x}'-\mathbf{y}',\sigma') \tag{26.5}$$

In this case $g^\alpha(\mathbf{x}-\mathbf{y},\sigma)$ with largest norm can be called the *wave function* of the paired state of *lowest energy*: this is the analogue of the plane wave for a free particle (and, like it, it is manifestly not normalizable, *i.e.* it is not square integrable as a function of $\mathbf{x},\mathbf{y}$). If the system contains Cooper pairs and the non leading terms in the limit (26.5) vanish quickly enough the 2-particles reduced density matrix, (26.5), regarded as a kernel operator has an eigenvalue of order V as $V\to\infty$: *i.e.* the state of lowest energy is macroscopically occupied, quite like the free Bose condensation on the ground state.

Cooper pairs instability might destroy the Fermi surface in the sense that $r_1(\mathbf{k})$ becomes analytic in $\mathbf{k}$; but it is also possible that even in presence of the instability a surface remains which is the locus of the singularities of the function $r_1(\mathbf{k})$. In the first case there should remain a trace of it as a very steep gradient of $r_1(\mathbf{k})$ of the order of an exponential in the inverse of the coupling strength; this is what happens in the BCS model for superconductivity: the model is however a mean field model and this particular regularity aspect might be one of its peculiarities. In any event a smooth singularity surface is very likely to exist for some interesting density matrix (*e.g.* in the BCS model with "gap parameter γ" the wave function $g(\mathbf{x}-\mathbf{y},\sigma)\equiv\frac{1}{(2\pi)^d}\int_{\varepsilon(\mathbf{k})>0} e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{y})}\frac{\gamma}{\sqrt{\varepsilon(\mathbf{k})^2+\gamma^2}}\,d\mathbf{k}$ of the lowest energy level of the Cooper pairs is singular on a surface coinciding with the Fermi surface of the free system).

(4) *ODLRO:* Consider the k–fermions reduced density matrix $\rho_k(\mathbf{Q},\boldsymbol{\sigma};\mathbf{Q}',\boldsymbol{\sigma}')$ as kernel operators O_k on $L_2(\Omega\times\mathcal{C}^2)^k_-$. Suppose k even, then if O_k has a (generalized) eigenvalue of order $N^{\frac{k}{2}}$ as $N\to\infty$, $\frac{N}{V}=\rho$, the system is said to exhibit *off diagonal long range order*

of order k. For k odd ODLRO is defined to exist if O_k has an eigenvalue of order $N^{\frac{1}{2}(k-1)}$ and $k \geq 3$ (if $k=1$ the largest eigenvalue of O_1 is necessarily ≤ 1).

For bosons consider the reduced density matrix $\rho_k(\mathbf{Q};\mathbf{Q}')$ regarding it as a kernel operator O_k on $L_2(\Omega)^k_+$ and define ODLRO of order k to be present if $O(k)$ has a (generalized) eigenvalue of order N^k as $N \to \infty$, $\frac{N}{V} = \rho$.

The notion of ODLRO can be regarded as a unification of the phenomena of Bose condensation and of existence of Cooper pairs because Bose condensation could be said to correspond to the kernel operator $\rho_1(\mathbf{q}_1 - \mathbf{q}_2)$ in (26.3) having a (generalized) eigenvalue of order N, and to be a case of ODLRO of order 1. If the state is pure in the sense that it has a cluster property, see Sect.9,15, then ODLRO, Bose condensation and Cooper pairs existence imply that the system shows a *spontaneously broken symmetry*: conservation of particle number and clustering imply that the off-diagonal elements of (all) reduced density matrices vanish at infinite separation in states obtained as limits of states with periodic boundary conditions and Hamiltonian (26.1), and this is incompatible with ODLRO.

The free Fermi gas has no ODLRO, the BCS model of superconductivity has Cooper pairs and ODLRO with $k = 2$, but *no Fermi surface* in the above sense (possibly too strict). Fermionic systems cannot have ODLRO of order 1 (because the reduced density matrix of order 1 is bounded by 1).

The contribution of Mathematical Physics has been particularly effective by providing exactly soluble models: however the soluble models deal with 1–dimensional systems and it can be shown that in dimension $1,2$ no ODLRO can take place. A major advance is the recent proof of ODLRO and Bose condensation in the case of a *lattice* version of (26.1) at a special density value (and $d \geq 3$).

In no case, for the Hamiltonian (26.1) with $\varphi \neq 0$, existence of Cooper pairs has been proved nor existence of a Fermi surface for $d > 1$. Nevertheless both Bose condensation and Cooper pairs formation can be proved to occurr rigorously in certain limiting situations. There are also a variety of phenomena (*e.g.* simple spectral properties of the Hamiltonians) which are believed to occurr once some of the above mentioned four do occurr and several of them can be proved to exist in concrete models.

If $d = 1,2$ the ODLRO can be proved to be impossible at $T > 0$ through the use of Bogoliubov's inequality (used in the "no $d = 2$ crystal theorem", see Sect.13).

Bibliography: [PO56],[Ya62], [Ru69], [Ho67], [Ga99], [ALSSY].

Appendix A1. The Physical meaning of the stability conditions

It is therefore useful to see what would happen if the conditions of stability and temperedness (see (7.2)) are violated. The analysis also illustrates some of the typical methods of statistical mechanics.

(a) Coalescence catastrophe due to short distance attraction: the simplest violation of the first condition in (7.2) occurs when the potential φ is smooth and negative at the origin.

Let $\delta > 0$ be so small that the potential at distances $\le 2\delta$ is $\le -b < 0$. Consider the canonical distribution with parameters β, N in a (cubic) box Ω of volume V. The probability $P_{collapse}$ that *all* the N particles are located in a little sphere of radius δ around the center of the box (or around any pre-fixed point of the box) is estimated from below by remarking that $\Phi \le -b\binom{N}{2} \sim -\frac{b}{2}N^2$ so that

$$P_{collapse} = \frac{\int_{\mathcal{C}} \frac{d\mathbf{p}d\mathbf{q}}{h^{3N}N!} e^{-\beta(K(\mathbf{p})+\Phi(\mathbf{q}))}}{\int \frac{d\mathbf{p}d\mathbf{q}}{h^{3N}N!} e^{-\beta(K(\mathbf{p})+\Phi(\mathbf{q}))}} \ge \frac{\left(\frac{4\pi\sqrt{2m\beta^{-1}}^3}{3h^3}\right)^N \frac{\delta^{3N}}{N!} e^{\beta b \frac{1}{2} N(N-1)}}{\int \frac{d\mathbf{q}}{h^{3N}N!} e^{-\beta\Phi(\mathbf{q})}} \tag{A1.1}$$

Phase space is extremely small: nevertheless such configurations are *far* more probable than the configurations which "look macroscopically correct", *i.e.* configurations with particles more or less spaced by the average particle distance expected in a macroscopically homogeneous configuration, namely $(\frac{N}{V})^{-1/3} = \rho^{-\frac{1}{3}}$. Their energy $\Phi(\mathbf{q})$ is of the order of uN for some u, so that their probability will be bounded above by

$$P_{regular} \le \frac{\int \frac{d\mathbf{p}d\mathbf{q}}{h^{3N}N!} e^{-\beta(K(\mathbf{p})+uN)}}{\int \frac{d\mathbf{p}d\mathbf{q}}{h^{3N}N!} e^{-\beta(K(\mathbf{p})+\Phi(\mathbf{q}))}} = \frac{\frac{V^N\sqrt{2m\beta^{-1}}^3}{h^{3N}N!} e^{-\beta uN}}{\int \frac{d\mathbf{q}}{h^{3N}N!} e^{-\beta\Phi(\mathbf{q})}} \tag{A1.2}$$

However, no matter how small δ is, the ratio $\frac{P_{regular}}{P_{collapse}}$ will approach 0 as $V \to \infty$, $\frac{N}{V} \to v^{-1}$; extremely fast because $e^{\beta b N^2/2}$ eventually dominates over $V^N \sim e^{N\log N}$.

Thus it is far more probable to find the system in a microscopic volume of size δ rather than in a configuration in which the energy has some macroscopic value proportional to N. This catastrophe can be called an *ultraviolet catastrophe* (as it is due to the behavior at very short distances) and it causes the collapse of the particles into configurations concentrated in regions as small as we please as $V \to \infty$.

(b) Coalescence Catastrophe due to Long-Range Attraction. It occurs when the potential is too attractive near ∞. To simplify suppose that the potential has a *hard core*, *i.e.* it is $+\infty$ for $r < r_0$, so that the above discussed coalescence cannot occur and the system density bounded above by a certain quantity $\rho_{cp} < \infty$ (*close packing density*).

The catastrophe occurs if $\varphi(\mathbf{q}) \sim -g|\mathbf{q}|^{-3+\varepsilon}$, $g, \varepsilon > 0$, for $|\mathbf{q}|$ large. For instance this is the case of matter interacting gravitationally; if k is the gravitational constant, m is the particles mass then $g = km^2$ and $\varepsilon = 2$.

The probability $P_{regular}$ of "regular configurations", where particles are at distances of order $\rho^{-1/3}$ from their close neighbors, is compared with $P_{collapse}$ of "catastrophic configurations", with the particles at distances r_0 from their close neighbors to form a configuration of density $\rho_{cp}/(1+\delta)^3$ almost in close packing (so that r_0 is equal to the hard core radius times $1+\delta$). In the latter case the system *does not* fill the available volume and leaves empty a region whose volume is a fraction $\sim \frac{\rho_{cp}-\rho}{\rho_{cp}} V$ of V. And it can be checked thatthe ratio $P_{regular}/P_{collapse}$ tends to 0 at a rate $O(e^{g\frac{1}{2}N(\rho_{cp}(1+\delta)^{-3}-\rho)})$ if δ is small enough (and $\rho < \rho_{cp}$).

A system which is too attractive at infinity will not occupy the available volume but will stay confined in a close packed configuration even in empty space.

This is important in the theory of stars: stars cannot be expected to obey "regular thermodynamics" and in particular will not "evaporate" because their particles interact via the gravitational force at large distance. Stars do not occupy the whole volume given to them (*i.e.* the universe); they do not collapse to a point only because the interaction has a strongly repulsive core (even when they are burnt out and the radiation pressure is no longer able to keep them at a reasonable size, a reasonable size).

(c) Evaporation Catastrophe: this is a another *infrared* catastrophe, *i.e.* a catastrophe due to the long-range structure of the interactions like (b) above; it occurs when the potential is *too repulsive* at ∞: *i.e.* $\varphi(\mathbf{q}) \sim +g|\mathbf{q}|^{-3+\varepsilon}$ as $\mathbf{q} \to \infty$ so that the temperedness condition is again violated.

Also in this case the system does not occupy the whole volume: it will generate a layer of particles *sticking*, in close packed configuration, to the walls of the container. Therefore if the density is lower than the close packing density, $\rho < \rho_{cp}$, the system will leave a region *around the center of the container* Ω empty; and the volume of the empty region will still be of the order of the total volume of the box (*i.e.* its diameter will be a fraction of the box side L). The proof is completely analogous to the one of the previous case; except that now the configuration with lowest energy will be the one sticking to the wall and close packed there, rather than the one close packed at the center.

Also this catastrophe is important as it is realized in systems of charged particles bearing the *same* charge: the charges adhere to the boundary in close packing configuration, and dispose themselves so that the electrostatic potential energy is minimal. Therefore charges deposited on a metal will *not occupy* the whole volume: they will rather form a surface layer minimizing the potential energy (*i.e.* so that the Coulomb potential in the interior is constant). In general charges in excess of neutrality do not behave thermodynamically: for instance, besides not occupying the whole volume given to them, they will not contribute normally to the specific heat.

Neutral systems of charges behave thermodynamically if they have hard cores so that the ultraviolet cathstrophe cannot occur or if they obey quantum mechanical laws and consist of fermionic particles (plus possibly bosonic particles with charges of only one sign).

Bibliography: [DL67], [LL72], [Li01]

Appendix A2. The subadditivity method

A simple consequence of the assumptions is that the exponential in (5.2) can be bounded above by $e^{\beta BN}e^{-\frac{\beta}{2m}\sum_{i=1}^N \mathbf{p}_i^2}$ so that

$$\begin{aligned}&1\le Z_{gc}(\beta,\lambda,V)\le e^{Ve^{\beta\lambda}e^{\beta B}\sqrt{2m\beta^{-1}}^d}\quad\Rightarrow\\ &0\le\frac{1}{V}\log Z_{gc}(\beta,\lambda,V)\le e^{\beta\lambda}e^{\beta B}\sqrt{2m\beta^{-1}}^d\end{aligned}\tag{A2.1}$$

Consider for simplicity the case of a hard core interaction with *finite range*, *c.f.* (7.2). Consider a sequence of boxes Ω_n with sides 2^nL_0 where $L_0>0$ is arbitrarily fixed $>2R$. The *partition function* $Z_{gc}(\beta,z)$ relative to the volume Ω_n is $Z_n=\sum_{N=0}^\infty\frac{z^N}{N!}\int_{\Omega_n}d\mathbf{P}d\mathbf{Q}e^{-\beta\Phi(\mathbf{Q})}$ because the integral over the $\mathbf{P}$ variables can be explicitly performed and included in z^N if z is defined as $z=e^{\beta\lambda}\big(2m\beta^{-1}\big)^{d/2}$.

Then the box Ω_n contains 2^d boxes Ω_{n-1} for $m\ge1$ and

$$1\le Z_n\le Z_{n-1}^{2^d}e^{\beta B2d(L_{n-1}/R)^{d-1}2^{2d}}\tag{A2.2}$$

because the corridor of width $2R$ around the boundaries of the 2^d cubes Ω_{n-1} filling Ω_n has volume $2RL_{n-1}2^d$ and contains at most $(L_{n-1}/R)^{d-1}2^d$ particles each of which interacts with at most 2^d other particles. Therefore $\beta p_n\stackrel{def}{=}L_n^d\log Z_n\le L_{n-1}^d\log Z_{n-1}+\beta B\gamma_d2^{-n}(L_0/R)^{d-1}$ for some $\gamma_d>0$. Hence $0\le\beta p_n\le\beta p_{n-1}+\Gamma_d2^{-n}$ for some $\Gamma_d>0$ and p_n is bounded above and below uniformly in n: so that the limit (7.1) exists on the sequence $L_n=L_02^n$ and defines a function $\beta p_\infty(\beta,\lambda)$.

A box of arbitrary size L can be filled with about $(L/L_{\overline{n}})^d$ boxes of side $L_{\overline{n}}$ with $\overline{n}$ so large that, prefixed $\delta>0$, $|p_\infty-p_n|<\delta$ for all $n\ge\overline{n}$. Likewise a box of size L_n can be filled by about $(L_n/L)^d$ boxes of size L if n is large. The latter remarks lead to conclude, by standard inequalities, that the limit in (7.1) exists and coincides with p_∞.

The *subadditivity* method just demonstrated for finite range potentials with hard core can be extended to the potentials satisfying just stability and temperedness, *c.f.* Sect.7.

Bibliography: [Ru69], [Ga99].

Appendix A3. An infrared inequality

The infrared inequalities stem from *Bogoliubov's inequality.* Consider as an example the problem of crystallization of Sect.13. Let $\langle\cdot\rangle$ denote average over a canonical equilibrium state with Hamiltonian $H=\sum_{j=1}^N\frac{\mathbf{p}_j^2}{2}+U(\mathbf{Q})+\varepsilon W(\mathbf{Q})$ with given temperature and density parameters β,ρ, $\rho=a^{-3}$. Let $\{X,Y\}=\sum_j(\partial_{p_j}X\,\partial_{q_j}Y-\partial_{q_j}X\,\partial_{p_j}Y)$ be the Poisson bracket. Integration by parts, *with periodic boundary conditions*, yields

$$\langle A^*\{C,H\}\rangle \equiv -\frac{\int A^*\{C,e^{-\beta H}\}d\mathbf{P}d\mathbf{Q}}{\beta Z_c(\beta,\rho,N)} \equiv -\beta^{-1}\langle\{A^*,C\}\rangle \tag{A3.1}$$

as a general identity. The latter identity implies, for $A=\{C,H\}$,

$$\langle\{H,C\}^*\{H,C\}\rangle = -\beta^{-1}\langle\{C,\{H,C^*\}\}\rangle \tag{A3.2}$$

Hence the Schwartz inequality $\langle A^*A\rangle\langle\{H,C\}^*\{H,C\}\rangle \ge |\langle\{A^*,C\}\rangle|^2$ combined with the two relations in (A3.1),(A3.2) yields *Bogoliubov's inequality*

$$\langle A^*A\rangle \ge \beta^{-1}\frac{|\langle\{A^*,C\}\rangle|^2}{\langle\{C,\{C^*,H\}\}\rangle} \tag{A3.3}$$

Let g,h be arbitrary complex (differentiable) functions and $\boldsymbol{\partial}_j=\boldsymbol{\partial}_{\mathbf{q}_j}$

$$A(\mathbf{Q}) \stackrel{def}{=} \sum_{j=1}^N g(\mathbf{q}_j),\qquad \mathbf{C}(\mathbf{P},\mathbf{Q}) \stackrel{def}{=} \sum_{j=1}^N \mathbf{p}_j h(\mathbf{q}_j) \tag{A3.4}$$

Then $H=\sum\frac12\mathbf{p}_j^2+\Phi(\mathbf{q}_1,\ldots,\mathbf{q}_N)$, if $\Phi(\mathbf{q}_1,\ldots,\mathbf{q}_N)=\frac12\sum_{j\ne j'}\varphi(|\mathbf{q}_j-\mathbf{q}_{j'}|)+\varepsilon\sum_j W(\mathbf{q}_j)$, so that $\{\mathbf{C},H\}\equiv\sum_j(h_j\boldsymbol{\partial}_j\Phi-\mathbf{p}_j(\mathbf{p}_j\cdot\boldsymbol{\partial}_j)h_j)$ with $h_j\stackrel{def}{=}h(\mathbf{q}_j)$. If h is real valued $\langle\{C,\{C^*,H\}\}\rangle$ becomes $\langle\sum_{jj'}h_jh_{j'}\boldsymbol{\partial}_j\cdot\boldsymbol{\partial}_{j'}\Phi(\mathbf{Q})\rangle+\langle\varepsilon\sum_j h_j^2\Delta W(\mathbf{q}_j)+\frac{4}{\beta}\sum_j(\boldsymbol{\partial}_jh_j)^2\rangle$ (integrals on $\mathbf{p}_j$ just replace $\mathbf{p}_j^2$ by $2\beta^{-1}$ and $\langle(\mathbf{p}_j)_i(\mathbf{p}_j)_{i'}\rangle=\beta^{-1}\delta_{i,i'}$). Therefore the average $\langle\{C,\{C^*,H\}\}\rangle$ becomes

$$\langle\frac12\sum_{jj'}(h_j-h_{j'})^2\Delta\varphi(|\mathbf{q}_j-\mathbf{q}_{j'}|)+\varepsilon\sum_j h_j^2\Delta W(\mathbf{q}_j)+4\beta^{-1}\sum_j(\boldsymbol{\partial}_jh_j)^2\rangle \tag{A3.5}$$

Choose $g(\mathbf{q})\equiv e^{-i(\boldsymbol{\kappa}+\mathbf{K})\cdot\mathbf{q}}$, $h(\mathbf{q})=\cos\mathbf{q}\cdot\boldsymbol{\kappa}$ and bound $(h_j-h_{j'})^2$ by $\boldsymbol{\kappa}^2\,(\mathbf{q}_j-\mathbf{q}_{j'})^2$, $(\boldsymbol{\partial}_jh_j)^2$ by $\boldsymbol{\kappa}^2$ and h_j^2 by 1. Hence (A3.5) is bounded above by $ND(\boldsymbol{\kappa})$ with

$$D(\boldsymbol{\kappa}) \stackrel{def}{=} \langle\,\boldsymbol{\kappa}^2\left(4\beta^{-1}+\frac{1}{2N}\sum_{j\ne j'}(\mathbf{q}_j-\mathbf{q}_{j'})^2|\Delta\varphi(\mathbf{q}_j-\mathbf{q}_{j'})|\right)\,+\,\varepsilon\frac1N\sum_j|\Delta W(\mathbf{q}_j)|\,\rangle \tag{A3.6}$$

This can be used to estimate the denominator in (A3.3). For the *l.h.s.* remark that $\langle A^*,A\rangle=|\sum_{j=1}^N e^{-i\mathbf{q}\cdot(\boldsymbol{\kappa}+\mathbf{K})}|^2$ and $|\langle\{A^*,\mathbf{C}\}\rangle|^2=|\langle\sum_j h_j\boldsymbol{\partial}\,g_j\rangle|^2=|\mathbf{K}+\boldsymbol{\kappa}|^2N^2(\rho_\varepsilon(\mathbf{K})+\rho_\varepsilon(\mathbf{K}+2\boldsymbol{\kappa}))^2$, hence (A3.3) becomes after multiplying both sides by the auxiliary function $\gamma(\boldsymbol{\kappa})$ (assumed even and vanishing for $|\boldsymbol{\kappa}|>\frac{\pi}{a}$) and summing over $\boldsymbol{\kappa}$,

$$D_1 \stackrel{def}{=} \frac1N\sum_{\boldsymbol{\kappa}}\gamma(\boldsymbol{\kappa})\langle\frac1N|\sum_{j=1}^N e^{-i(\mathbf{K}+\boldsymbol{\kappa})\cdot\mathbf{q}_j}|^2\rangle\,\ge\,\frac1N\sum_{\boldsymbol{\kappa}}\gamma(\boldsymbol{\kappa})\frac{|\mathbf{K}|^2}{4\beta}\frac{(\rho_\varepsilon(\mathbf{K})+\rho_\varepsilon(\mathbf{K}+2\boldsymbol{\kappa}))^2}{D(\boldsymbol{\kappa})} \tag{A3.7}$$

To apply (A3.3) the averages in (A3.6),(A3.7) have to be bounded above: this is a technical point that is discussed here as it illustrates a general method of using the results on the thermodynamic limits and their convexity properties to obtain estimates.

Note that $\langle \frac{1}{N}\sum_{\mathbf{k}}\gamma(\mathbf{k})d^d\mathbf{k}|\sum_{j=1}^N e^{-i\mathbf{k}\cdot\mathbf{q}_j}|^2\rangle$ is identically $\widetilde\varphi(0)+\frac{2}{N}\langle\sum_{j<j'}\widetilde\varphi(\mathbf{q}_j-\mathbf{q}_{j'})\rangle$ with $\widetilde\varphi(\mathbf{q})\stackrel{def}{=}\frac{1}{N}\sum_{\boldsymbol{\kappa}}\gamma(\boldsymbol{\kappa})e^{i\boldsymbol{\kappa}\cdot\mathbf{q}}$.

Let $\varphi_{\lambda,\zeta}(\mathbf{q})\stackrel{def}{=}\varphi(\mathbf{q})+\lambda\,\mathbf{q}^2|\Delta\varphi(\mathbf{q})|+\eta\widetilde\varphi(\mathbf{q})$ and let $F_V(\lambda,\eta,\zeta)\stackrel{def}{=}\frac{1}{N}\log Z^c(\lambda,\eta,\zeta)$ with Z^c the partition function in the volume Ω computed with energy $U'=\sum_{jj'}\varphi_{\lambda,\zeta}(\mathbf{q}_j-\mathbf{q}_{j'})+\varepsilon\sum_j W(\mathbf{q}_j)+\eta\,\varepsilon\sum|\Delta W(\mathbf{q}_j)|$. Then $F_V(\lambda,\eta,\zeta)$ is convex in λ,η and *it is uniformly bounded above and below* if $|\eta|,|\varepsilon|,|\zeta|\le 1$ (say) and $|\lambda|\le\lambda_0$: here $\lambda_0>0$ exists if $\mathbf{r}^2|\Delta\varphi(\mathbf{r})|$ satisfies the assumption set at the beginning of Sect.13 and the density is smaller than a close packing (this is because the potential U' will still satisfy conditions similar to (7.2) uniformly in $|\varepsilon|,|\eta|<1$ and $|\lambda|$ small enough).

Convexity and boundedness above and below in an interval imply bounds on the derivatives in the interior points: in this case on the derivatives of F_V with respect to λ,η,ζ at 0. The latter are identical to the averages in (A3.6),(A3.7). In this way the constants B_1,B_2,B_0 such that $D(\boldsymbol{\kappa})\le\boldsymbol{\kappa}^2B_1+\varepsilon B_2$ and $B_0>D_1$ are found.

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