Mathematical aspects of wetting

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Abstract. Wetting phenomena, as well as other aspects of the coexistence of phases, can be modelled, from a microscopic point of view, by a lattice gas, like the Ising model, or an interface model.

In the first part of the talk, I describe some basic facts and results of the theory, many of which have been obtained with the help of correlation inequalities.

In a second part of the talk, I present some recent results of a joint work with K. Alexander and F. Dunlop, that concern an interface model. This system presents a sequence of layering transitions, whose levels increase with the temperature, and complete wetting above a certain value of this quantity.

1 Introduction

Principle: When two phases are in contact, a portion of the total free energy of the system is proportional to the area of the surface of contact, and to a coefficient, the surface tension, which is specific for each pair of substances. Equilibrium will accordingly be obtained when the free energy of the surfaces in contact is a minimum.

Figure 1

When one of the substances involved is anisotropic, such as a crystal, the contribution to the total free energy of each element of area depends on its orientation. The minimum surface free energy for a given volume determines then the ideal form of the crystal in equilibrium.

It is only in recent times that equilibrium crystals have been produced in the laboratory. Most crystals grow under non-equilibrium conditions and is a subsequent relaxation of the macroscopic crystal that restores the equilibrium.

Figures 2, 3

Suppose that we have a drop of some fluid, $+$, over a flat substrate, w, while both are exposed to air, $-$. We have then three different surfaces of contact, and the total free energy of the system consists of three parts, associated to these three surfaces. A drop of fluid $+$ will exist if

$$\tau^{W+} + \tau^{+-} > \tau^{W-}.$$

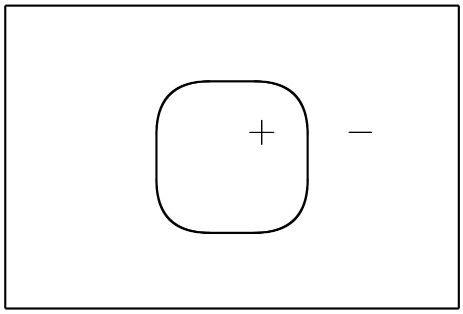
A film of fluid $+$ is formed (complete wetting), if

$$\tau^{W+} + \tau^{+-} = \tau^{W-}.$$

In the first case, the contact angle θ measures the degree of wetting. It is given by the Young's equation

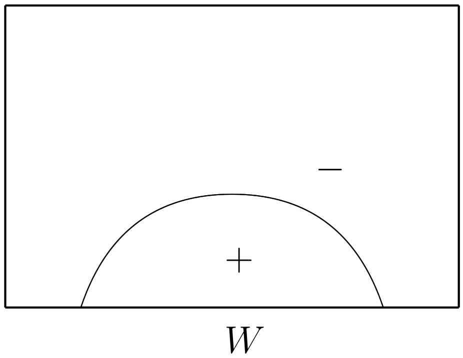
$$\tau^{+-} \cos\theta = \tau^{W-} - \tau^{W+}$$

(it is assumed here that τ^{+-} is isotropic, an irrelevant hypothesis in the following study).

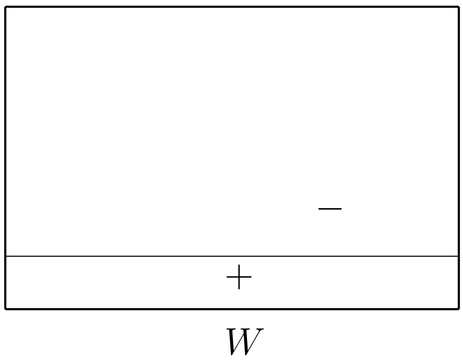


Two phases: $\tau^{+-} > 0$ (3 dim.).

Young's equation:
$\tau^{+-} \cos\theta = \tau^{W-} - \tau^{W+}$



Partial wetting: $\tau^{W+} + \tau^{+-} > \tau^{W-}$.



Complete wetting: $\tau^{W+} + \tau^{+-} = \tau^{W-}$.

2 On the microscopic theory

We assume that the interatomic forces can be modelled by a lattice gas, and consider, as a simple example, the ferromagnetic Ising model. In a typical two-phase equilibrium state there is a dense component, which can be interpreted as a solid or liquid phase, and a dilute phase, which can be interpreted as the vapor phase.

Ising model

$\sigma_x = -1$ or 1, $x \in \mathbf{Z}^3$, empty or occupied site,
Λ is a parallelepiped, centered at the origin, of sides L_1, L_2, L_3, parallel to the axes. σ_Λ, a configuration on Λ, $\{\sigma_x, x \in \Lambda\}$.
The hamiltonian is,

$$H_\Lambda(\sigma_\Lambda \mid \bar{\sigma}) = -J \sum_{\langle x,y\rangle \cap \Lambda \neq \emptyset} \sigma_x \sigma_y,$$

$J > 0$, $\sigma_x = \bar{\sigma}_x$, when $x \notin \Lambda$, boundary condition.
Probability of the configuration σ_Λ, at the inverse temperature $\beta = 1/kT$:

$$\mu_\Lambda(\sigma_\Lambda \mid \bar{\sigma}) = Z^{\bar{\sigma}}(\Lambda)^{-1} \exp\big(-\beta H_\Lambda(\sigma_\Lambda \mid \bar{\sigma})\big),$$
$$Z^{\bar{\sigma}}(\Lambda) = \sum_{\sigma_\Lambda} \exp\big(-\beta H_\Lambda(\sigma_\Lambda \mid \bar{\sigma})\big).$$

The μ_Λ determine the Gibbs states of the infinite system.

For $\beta > \beta_c$, there are two different pure phases, two extremal translation invariant Gibbs states,

$$\mu^+ \text{ and } \mu^-,$$

associated with $\bar{\sigma}_x = 1$ and $\bar{\sigma}_x = -1$. Then, the spontaneous magnetization,

$$m^*(\beta) = \mu^+(\sigma_x) = -\mu^-(\sigma_x) > 0,$$

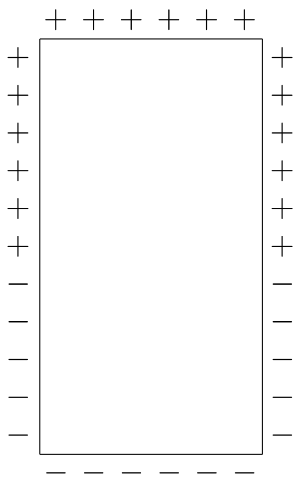
If $\beta \le \beta_c$, the Gibbs state is unique and $m^* = 0$.

The surface tension τ^{+-}, between the $+$ and $-$ phases, is

$$\tau^{+-}(\beta) = \lim_{\Lambda \to \infty} -\frac{1}{\beta L_1 L_2} \ln \frac{Z^{+-}(\Lambda_L)}{Z^+(\Lambda_L)} \; .$$

$Z^+(\Lambda)$ is the partition function with $\bar{\sigma} = +1$. $Z^{+-}(\Lambda)$ is the partition function with boundary conditions

$$\bar{\sigma}_x = \begin{cases} 1 & \text{if } x_3 \ge 0, \\ -1 & \text{if } x_3 < 0. \end{cases} \quad \text{or} \quad \bar{\sigma}_x = \begin{cases} 1 & \text{if } x \cdot \mathbf{n} \ge 0, \\ -1 & \text{if } x \cdot \mathbf{n} < 0. \end{cases}$$



Boundary conditions $+-$

The surface tension is the free energy, per unit area, due to the presence of the interface. In this expression the volume contributions proportional to the free energy of the coexisting phases, as well as the boundary effects, cancel, and only the contributions to the free energy due to the interface are left. The existence of such a quantity indicates that the macroscopic interface, separating the regions occupied by the pure phases in a large volume Λ, has a microscopic thickness and can therefore be regarded as a surface in a thermodynamic approach.

The limit defining the surface tension exits and $\tau^{+-} \geq 0$*.*
Moreover, $\tau^{+-} > 0$*, if* $\beta > \beta_c$*, and* $\tau^{+-} = 0$*, if* $\beta \leq \beta_c$*.*

Each configuration inside Λ can be described in a geometric way by specifying the set of *Peierls contours* which indicate the boundaries between the regions of spin 1 and the regions of spin -1.

The boundary condition $(+-)$ forces the system to produce a defect going transversally through the box Λ, a big Peierls contour that can be interpreted as the *microscopic interface* (also called a domain wall). The other defects that appear above and below the interface can be described by closed contours inside the pure phases.

Semi-infinite Ising model

Consider the Ising model on the semi-infinite space $\{x \in \mathbf{Z}^3\,; x_3 \geq 0\}$ and add a boundary magnetic field, $K > 0$, describing the properties of the wall.
Consider the model in the box

$$\Lambda' = \{x \in \Lambda : x_3 \geq 0\}.$$

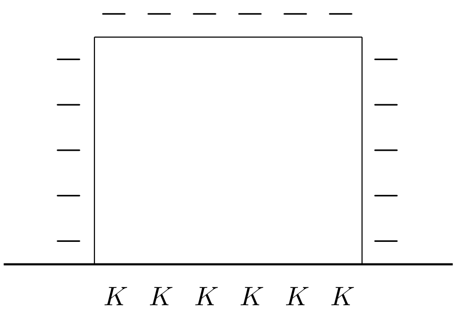
The hamiltonian is

$$H = -J \sum_{\langle xy\rangle \cap \Lambda' \neq \emptyset} \sigma_x \sigma_y - K \sum_{x \in \Lambda', x_3 = 0} \sigma_x .$$

Introduce the partition functions

$$Z^{W+}(\Lambda') \quad \text{and} \quad Z^{W-}(\Lambda'),$$

with respectively, $+$ and $-$ boundary conditions on that part of the boundary of Λ' which is not part of the wall.



Boundary conditions $W-$

The surface free energy contribution (per unit area) due to the presence of the wall, when we have the $-$ phase in the bulk, is

$$\tau^{\mathrm{w}-}(\beta, K) = -\lim_{\Lambda\to\infty} \frac{1}{\beta L_1 L_2} \ln \frac{Z^{W-}(\Lambda')}{Z^{+}(\Lambda)^{1/2}} \ ,$$

when we have the $+$ phase

$$\tau^{\mathrm{w}+}(\beta, K) = -\lim_{\Lambda\to\infty} \frac{1}{\beta L_1 L_2} \ln \frac{Z^{W+}(\Lambda')}{Z^{+}(\Lambda)^{1/2}} \ .$$

These limits exist, and $\tau^{\mathrm{w}-} \geq 0$, $\tau^{\mathrm{w}-} \geq 0$.
One can prove, as well, the existence of the Gibbs states $\mu^{\mathrm{w}-}$, $\mu^{\mathrm{w}+}$, *associated to the* $(-)$, $(+)$, *boundary conditions.*

The division by $Z^{+}(\Lambda)^{\frac{1}{2}}$ allows us to subtract from the total free energy, $\ln Z^{\mathrm{w}-}(\Lambda')$, the bulk term and all boundary terms which are not related to the presence of the wall.

The state $\mu^{\mathrm{w}-}$ describes the local equilibrium properties of the system near the wall, when deep inside the bulk the system is in the negative phase.

Similar considerations apply to the condition (w+).

Imagine that in the layer $x_3 = -1$ we take $\sigma_x = 1$, and drow the Peierls contours. Then, a *microscopic interface* appears when the boundary condition is (w$-$). It does not appear under the (w+) boundary condition.

General results

Some general rigorous results can then be proved (J. Fröhlich, C.E. Pfister)

Remark that the states $\mu^{\mathrm{w}+}$ and $\mu^{\mathrm{w}-}$ are invariant by translations parallel to the plane $x_3 = 0$. Let z denote the site $(0,0,z)$. Introduce the magnetizations,

$$m^{\mathrm{w}-}(z) = \mu^{\mathrm{w}-}(\sigma_z), \quad \text{and} \quad m^{\mathrm{w}-} = \mu^{\mathrm{w}-}(\sigma_0),$$

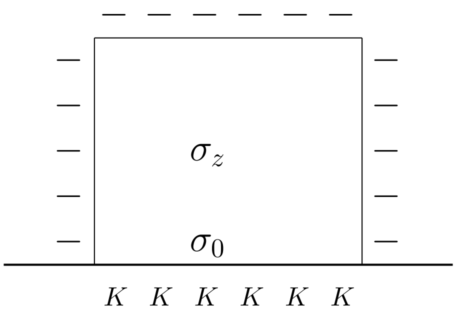
and similarly $m^{\mathrm{w}+}(z)$ and $m^{\mathrm{w}+}$.
Their connection with the surface free energies is given by

$$\tau^{\mathrm{w}-}(\beta,K) - \tau^{\mathrm{w}+}(\beta,K) = \int_0^K (m^{\mathrm{w}+}(\beta,K') - m^{\mathrm{w}-}(\beta,K'))dK'.$$

Theorem 1 *We have*

$$\begin{aligned} \tau^{\mathrm{w}-}(\beta,K) - \tau^{\mathrm{w}+}(\beta,K) &\le \tau^{+-}(\beta,K), \\ m^{\mathrm{w}+}(\beta,K) - m^{\mathrm{w}-}(\beta,K) &\ge 0. \end{aligned}$$

The last difference is a decreasing function with respect to K. Also, $\tau^{\mathrm{w}-} - \tau^{\mathrm{w}+} = \tau^{+-}$, if $K \ge J$.



We recall that $\tau^{\mathrm{w}-}(K) - \tau^{\mathrm{w}+}(K) = \int_0^K (m^{\mathrm{w}+}(K') - m^{\mathrm{w}-}(K'))dK'$.

COROLLARY 1 *If $m^{\mathrm{w}+} > m^{\mathrm{w}-}$ for $K = K_0$, then for $K < K_0$,*

$$m^{\mathrm{w}+} > m^{\mathrm{w}-} \quad \textit{and}$$
$$\tau^{\mathrm{w}-} - \tau^{\mathrm{w}+} < \tau^{+-}.$$

We have partial wetting and $\mu^{\mathrm{w}-} \neq \mu^{\mathrm{w}+}$.

COROLLARY 2 *If $m^{\mathrm{w}+} = m^{\mathrm{w}-}$ for $K = K_0$, then for $K \geq K_0$,*

$$m^{\mathrm{w}+} = m^{\mathrm{w}-} \quad \textit{and}$$
$$\tau^{\mathrm{w}-} - \tau^{\mathrm{w}+} = \tau^{+-}.$$

We have complete wetting and $\mu^{\mathrm{w}-} = \mu^{\mathrm{w}+}$.
Moreover, $m^{\mathrm{w}-}(z) \to m^*$ (the spontaneous magnetization) when $z \to \infty$.

REMARK At zero temperature $m^{\mathrm{w}+} = 1$ and $m^{\mathrm{w}-} = -1$. One can prove that, also at low temperature, namely, if $\beta(J - K) \geq \beta_0$ (some constant), we have $m^{\mathrm{w}+} > m^{\mathrm{w}-}$. Hence there is always partial wetting if the temperature is low enough. Moreover, $m^{\mathrm{w}+}(z) \to m^*$ and $m^{\mathrm{w}-}(z) \to -m^*$ when $z \to \infty$.

QUESTION: *Is there a situation of complete wetting at higher temperatures ? Here K takes a fixed value, characteristic of the substrate, such that $K < J$.*

It is an open problem in dimension 3.

3 SOS interface

Consider the Ising model in the box Λ' with the boundary condition (w$-$). Put $\sigma_x = -1$ for all x above the microscopic interface, and $\sigma_x = 1$ for all x below it. Moreover, assume that this interface is the graph of a function, $x \in \mathbf{Z}^2 \to \phi_x$. We obtain then the following SOS (solid-on-solid) interface model.

$$x \in \mathbf{Z}^2, \quad \phi_x \geq 0, \quad \text{integer}$$

$$H_\Lambda(\phi_\Lambda \mid \bar{\phi}) = 2J \sum_{\langle x,x'\rangle \cap \Lambda \neq \emptyset} |\phi_x - \phi_{x'}| - 2(J-K) \sum_{x \in \Lambda} \delta(\phi_x) + 2J|\Lambda|$$

$$\mu_\Lambda(\phi_\Lambda \mid \bar{\phi}) = Z^{\bar{\phi}}(\Lambda)^{-1} \exp\big(-\beta H_\Lambda(\phi_\Lambda \mid \bar{\phi})\big)$$
$$Z^{\bar{\phi}}(\Lambda) = \sum_{\phi_\Lambda} \exp\big(-\beta H_\Lambda(\phi_\Lambda \mid \bar{\phi})\big)$$

$$\tau^{\text{w}-} = -\lim_{\Lambda \to \infty} \frac{1}{\beta L_1 L_2} \ln Z^{(0)}(\Lambda)$$
$$\tau^{\text{w}-} = 0$$
$$\tau^{+-} = -\lim_{\Lambda \to \infty} \frac{1}{\beta L_1 L_2} \ln \tilde{Z}^{(0)}(\Lambda)$$

In $\tilde{Z}$ the usual SOS model is considered, without the second term in the hamiltonian, the ϕ_x taking positive or negative values.

Theorem 2 (Chalker's) The following results are known

$$\textit{if}\quad 2\beta(J-K) > -\ln\frac{1-e^{-2\beta J}}{16(1+e^{-2\beta J})},\quad \textit{then}\quad \rho_0 > 0,$$
$$\textit{if}\quad 2\beta(J-K) < -\ln(1-e^{-8\beta J}),\quad \textit{then}\quad \rho_0 = 0.$$

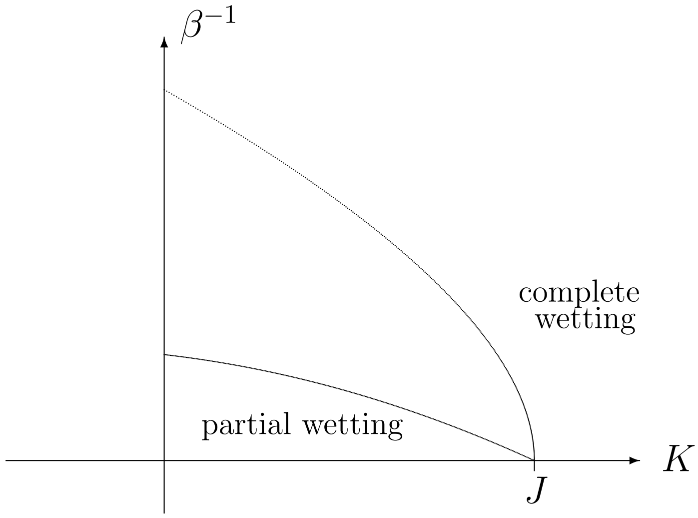


Illustration of Chalker's results.

Here, $\rho_0 = \mu^{(0)}(\phi_x = 0)$,

$\rho_0 > 0$ is equivalent to $\tau^{\mathrm{w}+} - \tau^{\mathrm{w}-} > \tau^{+-}$, i.e., partial wetting, and $\rho_0 = 0$, to $\tau^{\mathrm{w}+} - \tau^{\mathrm{w}-} = \tau^{+-}$, i.e., complete wetting.

ρ_0 is the quantity that corresponds to $m^{\mathrm{w}+} - m^{\mathrm{w}-}$ in the Ising model.

Layering transitions

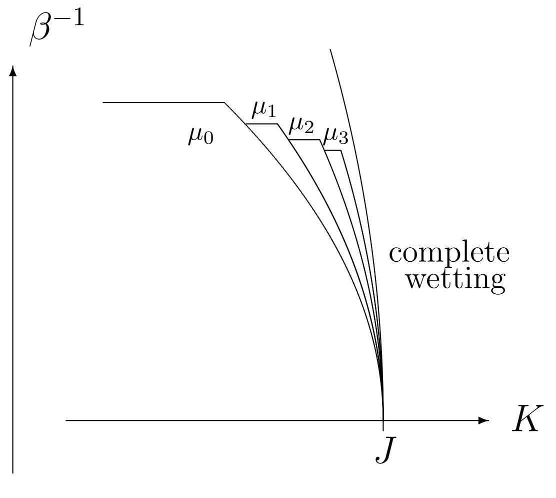
Joint work with K. Alexander and F. Dunlop (2008).
We use the notations:

$$u = 2\beta(J - K), \quad t = e^{-4\beta J}.$$

Theorem 3 *Let $n \geq 0$ integer, $\epsilon > 0$, there exists $t_0(n, \epsilon) > 0$, such that for $0 < t < t_0(n, \epsilon)$, if*

$$-\ln(1 - t^2) + (2 + \epsilon)t^{n+3} < u < -\ln(1 - t^2) + (2 - \epsilon)t^{n+2},$$

(1) The free energy $\tau^{\mathrm{w}-}$ is an analytic function of t, u, and $\rho_0 > 0$.
(2) There is a unique Gibbs state μ_n, the pure phase associated to the level n.



The regions in Theorem 3. Magnified view around the point $K = J, \beta^{-1} = 0$.

Remarks:

1. From the Figure we can see that if the parameter K is kept fixed, since it depends on the substrate, then the value n increases with the temperature.

2. The unicity of the Gibbs state means that the correlation functions converge, when $\Lambda \to \infty$, to a limit that does not depend on the chosen (uniformly bounded) boundary condition $\bar{\phi}_x$. Being unique and translation invariant this state represents a pure phase. In what sense it is associated to a level n would be clear from the proof. Let us say that for the typical configurations large portions of the interface are near to the level n.

3. We have, $t_0(n, \epsilon) \to 0$ when $n \to \infty$ or $\epsilon \to 0$.

The reason why $t_0(n, \epsilon)$ depends on ϵ, satisfying Remark 3, has an explanation. One may believe that the regions of unicity of the state extend in such a way that two neighboring regions, say those corresponding to the levels n and $n+1$, will have a common boundary where the two states μ_n and μ_{n+1} coexist. At this boundary there will be a first order phase transition, since the two Gibbs states are different. The curve of coexistence does not exactly coincide with the curve $u = -\ln(1 - t^2) + 2t^{n+3}$. The Theorem says that it is however very near to it, if the temperature is sufficiently low.

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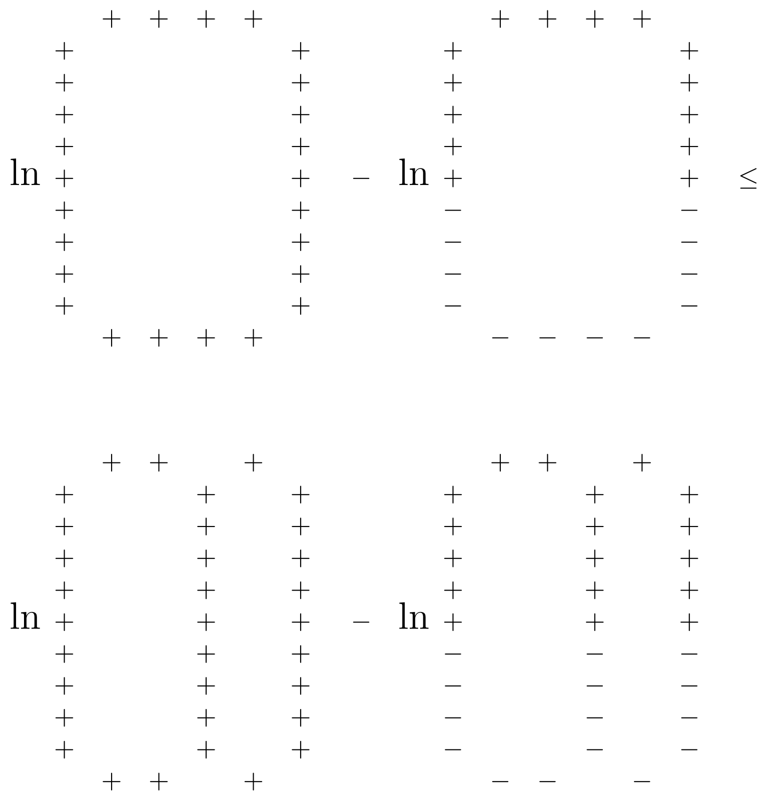
Proof that the limit τ^{+-} exits.

Let $f^{+-}(L_1, L_2) = \ln Z^+(\Lambda) - \ln Z^{+-}(\Lambda)$. The existence of the limit follows from the sub-additivity property $f^{+-}(L_1+L_1', L_2) \geq f^{+-}(L_1, L_2)+f^{+-}(L_1', L_2)$. But, from Griffiths (GKS) inequality, we have

$$\langle \sigma_x \rangle^+ \geq |\langle \sigma_x \rangle^{+-}|$$

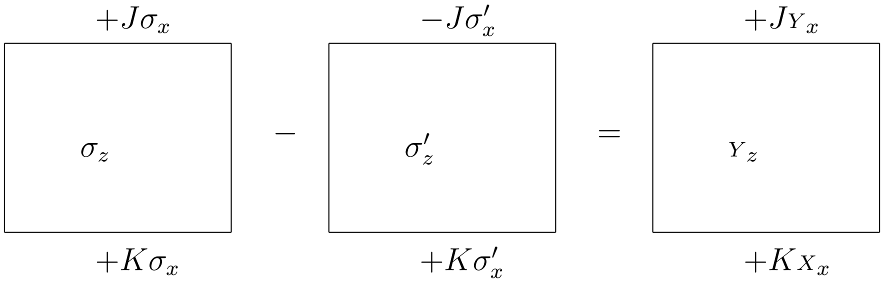


Similarly, one proves the existence of $\tau^{\mathrm{w}+}$ and $\tau^{\mathrm{w}-}$, and also that $\tau^{\mathrm{w}-} - \tau^{\mathrm{w}+} \leq \tau^{+-}$.

Proof that $m^{\mathrm{w}+} - m^{\mathrm{w}-} \geq 0$.

Griffiths (GKS) inequality tells us that

$$\langle \sigma_z \rangle^{\mathrm{w}+} - \langle \sigma_z \rangle^{\mathrm{w}-} \geq 0.$$



Proof that $m^{\mathrm{w}+} - m^{\mathrm{w}-}$ *is a decreasing function of* K.

Consider the duplicated system

$$\begin{aligned} H^* &= H(\sigma \mid \mathrm{w}+) + H(\sigma' \mid \mathrm{w}-) \\ &= -(J/2) \sum_{\langle x,x' \rangle \subset \Lambda} \big(X_x X_y + Y_x Y_y \big) - K \sum_{x\colon x_3=0} X_x - J \sum_{x \in \partial\Lambda, x_3 \neq 0} Y_x, \end{aligned}$$

with

$$X_x = \sigma_x + \sigma'_x, \quad Y_x = \sigma_x - \sigma'_x.$$

Then

$$\langle \sigma_z \rangle^{\mathrm{w}+} - \langle \sigma'_z \rangle^{\mathrm{w}+} = \langle Y_z \rangle^*.$$

The conclusion then follows from Lebowitz inequalities.

Proof that $m^{\mathrm{w}+}(z) = m^{\mathrm{w}-}(z)$ *implies* $\mu^{\mathrm{w}+} = \mu^{\mathrm{w}-}$.

The proof is a consequence of FKG inequalities.
Consider the occupation variables $n_x = (1/2)(1 + \sigma_x)$.
The functions $n_{x_1} \dots n_{x_r}$ and $n_{x_1} + \dots + n_{x_r} - n_{x_1} \dots n_{x_r}$ are non-decreasing functions with respect to the usual order on the set of configurations.
Therefore,

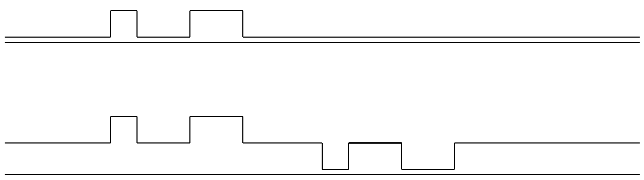
$$
\begin{aligned}
&\langle n_{x_1} \dots n_{x_r} \rangle^{\mathrm{w}+} \geq \langle n_{x_1} \dots n_{x_r} \rangle^{\mathrm{w}-}, \\
&\langle n_{x_1} \rangle^{\mathrm{w}+} + \dots + \langle n_{x_r} \rangle^{\mathrm{w}+} - \langle n_{x_1} \dots n_{x_r} \rangle^{\mathrm{w}+} \geq \\
&\langle n_{x_1} \rangle^{\mathrm{w}-} + \dots + \langle n_{x_r} \rangle^{\mathrm{w}-} - \langle n_{x_1} \dots n_{x_r} \rangle^{\mathrm{w}-}.
\end{aligned}
$$

Thus, if $\langle n_{x_i} \rangle^{\mathrm{w}+} = \langle n_{x_i} \rangle^{\mathrm{w}-}$, for $i = 1, \dots r$, we have $\langle n_{x_1} \dots n_{x_r} \rangle^{\mathrm{w}+} = \langle n_{x_1} \dots n_{x_r} \rangle^{\mathrm{w}-}$.

Remark on Theorem 3.

Though a general theory of the concerned systems does not exist, it has been realized that for an interesting class of systems, among which our model is included, one needs some extension of the Pirogov-Sinai theory of phase transitions. In such an extension certain states, called the *resticted ensembles*, play the role of the *ground states* in the usual theory. They can be defined as the restriction of the Gibbs probability measure to certain subsets of configurations. In the present case we consider, for each $n = 0, 1, 2, \ldots$, subsets of configurations which are in some sense near to the constant configurations $\phi_x = n$.

In this system the ground configuration is $\phi_x = 0$.
Let us compute the free energy $f(0)$ and $f(1)$ of the restricted ensembles at the levels $n = 0$ and $n = 1$.



$$f(0) = -u - t^2 e^{-u} - 2t^3 e^{-2u} + O(t^4)$$
$$f(1) = -t^2 e^{-u} - 2t^3 e^{2u} + O(t^4)$$

$$f(1) - f(0) = u - t^2 - 2t^3 + O(t^4) \quad \text{if } u = O(t^2)$$