

General Properties of Polymer Systems

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Abstract. We prove the existence of the thermodynamic limit for the pressure and show that the limit is a convex, continuous function of the chemical potential.

The existence and analyticity properties of the thermodynamic limit for the correlation functions is then derived; we discuss in particular the Mayer Series and the virial expansion.

In the special case of Monomer-Dimer systems it is established that no phase transition is possible; moreover it is shown that the Mayer Series for the density is a series of Stieltjes, which yields upper and lower bounds in terms of Padé approximants.

Finally it is shown that the results obtained for polymer systems can be used to study classical lattice systems.

1. Introduction

In the last decade the mechanism of phase transitions has been intensively investigated by studying properties of rather simple models. One of those models, the Polymer Model [1] (also called quasi-crystalline model), consists of a lattice which is fully covered with non-overlapping “monomers” (molecule occupying one site of the lattice) and “polymers” (rigid system of molecules which can be placed on the lattice in such a way that each molecule of the polymer coincide with one site of the lattice).

This model appears for example in the study of adsorption of poly-atomic molecules on a surface; in this case the monomers represent the empty sites. This same model describes physical systems consisting of molecules with unpaired electrons; these molecules then interact to form long chains or polymers. Finally we shall recall that this is also the model which is introduced in the study of liquids consisting of molecules of different sizes or in the so-called cell-cluster theory of liquid state [2].

On the other hand this model is very general since any classical lattice systems (as defined by Ruelle [3]) can be reduced to a system of polymers on the same lattice; this is the “association problem”. In some special cases the polymer system associated with the classical lattice

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system can be further simplified if one consider polymers on a lattice with different geometry [4].

In the present article we study the properties of the polymer model and we prove the existence of the thermodynamic limit for the pressure as well as analyticity properties for the correlation functions at sufficiently high density of monomers. This is obtained using the same formalism and techniques as introduced in the case of classical lattice systems.

Let us mention finally that the more general polymer model in which the molecules which constitute the polymer can be in several possible states can also be reduced to the simple polymer model described above.

2. Polymer Systems

2.1. Definitions

In this section we describe the model and give the definitions which we shall use in this article.

We consider a finite set A consisting of $N(A)$ points in \mathbb{R}^v called sites, which are denoted by small letters x, y, \dots . With $X = \{x_1, \dots, x_n\}$ a finite subset of A , a "Polymer X " is a rigid system of n particles which can be placed on A in such a way as to cover X . The polymers consisting of one particle will be called "monomers", of two particles "dimers", ... of n particles " n -mers". Polymers are placed on A and we assume that each site is covered by one and only one particle.

A configuration of the polymer system is therefore defined as a partition $\{X_1, \dots, X_k\}$ of the set A ; we recall that by definition of a partition, we have:

$$A = \bigcup_{i=1}^k X_i \quad X_i \neq \emptyset \quad X_i \cap X_j = \emptyset \quad \text{if } i \neq j.$$

The state of the system is defined as usual by a probability measure $P_A(\{X_1, \dots, X_k\})$ on the configuration space; for polymer systems this measure is characterised by a positive, bounded function $\Phi(X)$ defined on subsets $X \subset A$, which is interpreted as the "*activity of the Polymer X* ", and

$$P_A(\{X_1, \dots, X_k\}) = Q_A^{-1} \prod_{i=1}^k \Phi(X_i) \quad (1)$$

where

$$Q_A = \sum_{\substack{\text{all partitions } i \\ A = \cup X_i}} \prod \Phi(X_i) \quad \text{is the "Partition Function"}. \quad (2)$$

The pressure p_A is defined by:

$$\beta p_A = \frac{1}{N(A)} \text{Log } Q_A \quad \text{where } \beta = \frac{1}{kT}. \quad (3)$$

We shall also study the correlation functions $\varrho_A(X_1; \dots; X_p)$ which are defined as the probability of finding polymers X_1, \dots, X_p . With the above probability measure we have:

$$\begin{aligned} \varrho_A(X_1; \dots; X_p) &= 0 \quad \text{if } X_i \cap X_j \neq \emptyset \quad \text{for some } i \neq j \\ \varrho_A(X_1; \dots; X_p) &= Q_A^{-1} \prod_{i=1}^p \Phi(X_i) \left\{ \sum_{\substack{\text{all partitions} \\ A \setminus \cup X_i = \cup Y_j}} \Pi \Phi(Y_j) \right\} \\ &\quad \text{if } X_i \cap X_j = \emptyset \quad \text{for all } i \neq j. \end{aligned} \tag{4}$$

With these definitions the correlation functions have in particular the following properties

$$\text{i) } 0 \leq \varrho_A(X_1; \dots; X_p) \leq 1, \tag{5}$$

$$\text{ii) } \varrho_A(X) = \Phi(X) \frac{\partial}{\partial \Phi(X)} \text{Log } Q_A = \frac{1}{\beta} \frac{\partial}{\partial \mu(X)} \text{Log } Q_A \tag{6}$$

$$\text{where } \beta \mu(X) = \text{Log } \Phi(X) \tag{7}$$

and the density of “ n -mers” $\varrho_A^{(n)}$ is defined by

$$\varrho_A^{(n)} = \frac{1}{N(A)} \sum_{\substack{X \subset A \\ N(X)=n}} \varrho_A(X) = \sum_{\substack{X \subset A \\ N(X)=n}} \frac{\partial p_A}{\partial \mu(X)} \tag{8}$$

where the sum is restricted to those subsets containing $N(X) = n$ elements.

Finally if A is a subset of \mathbb{Z}^v , we shall say that the activity is translationally invariant if it satisfies

$$\Phi(\tau_a X) = \Phi(X) \quad \text{for all } a \in \mathbb{Z}^v \quad \text{and } X \subset \mathbb{Z}^v$$

and

$$\tau_a X = \{x_1 + a, \dots, x_n + a\} \quad \text{for all } X = \{x_1, \dots, x_n\}.$$

2.2. Notation and Algebraic Formalism

In order to obtain a concise formulation of the problem, we shall make use of an algebraic formalism which has already been used extensively in statistical mechanics [5].

Let $X = \{x_1, \dots, x_p\}$ and $Y = \{y_1, \dots, y_q\}$ denote subsets of A .

If $X \cap Y = \emptyset$ we shall write $X \cup Y$ as $X + Y$.

If $Y \subset X$ we shall write $X \setminus Y$ as $X - Y$.

We shall denote by $N(X)$ the number of elements in the subset X ; finally

$\sum_{X=\Sigma X_i}$ will mean “sum over all partitions of X ”.

Let V_A be the complex vector space of bounded functions $\Psi(X)$ defined on the subsets $X \subset A$; this vector space is a commutative algebra with unit element $\mathbb{1}$ for the $*$ -product defined by:

$$\forall \Psi_1, \Psi_2 \in V_A, \quad (\Psi_1 * \Psi_2)(X) = \sum_{Y \subset X} \Psi_1(Y) \Psi_2(X - Y). \quad (9)$$

The unit element $\mathbb{1}$ is the vector defined by:

$$\mathbb{1}(X) = \begin{cases} 1 & \text{if } X = \emptyset \\ 0 & \text{if } X \neq \emptyset. \end{cases} \quad (10)$$

We also define a mapping Γ of $V_A^+ = \{\Psi \mid \Psi \in V_A, \Psi(\emptyset) = 0\}$ on $\mathbb{1} + V_A^+$ by means of the $*$ -exponential:

$$\Gamma \Psi = \mathbb{1} + \sum_{n=1}^{\infty} \frac{1}{n!} \Psi^{*n} \quad (11)$$

which gives explicitly:

$$(\Gamma \Psi)(X) = \sum_{X = \sum X_i} \prod_i \Psi(X_i). \quad (12)$$

Finally we define an operation $D_X: \Psi \rightarrow D_X \Psi$

$$(D_X \Psi)(Y) = \Psi(X + Y) \delta_{\emptyset, X \cap Y} \quad (13)$$

where

$$\delta_{\emptyset, T} = \begin{cases} 1 & \text{if } \emptyset = T \\ 0 & \text{if } \emptyset \neq T. \end{cases}$$

This operation satisfies in particular the following relations:

$$\begin{aligned} D_x(\Psi_1 * \Psi_2)(Y) &= [(D_x \Psi_1 * \Psi_2)(Y) + (\Psi_1 * D_x \Psi_2)(Y)] \delta_{\emptyset, \{x\} \cap Y} \\ (D_x \Gamma \Psi)(Y) &= (D_x \Psi * \Gamma \Psi)(Y) \delta_{\emptyset, \{x\} \cap Y} \\ (D_X \Gamma \Psi)(Y) &= \sum_{X = \sum_{i=1}^q X_i} (D_{X_1} \Psi * \dots * D_{X_q} \Psi * \Gamma \Psi)(Y) \delta_{\emptyset, X \cap Y}. \end{aligned} \quad (14)$$

There is one more property of the mapping Γ which we shall need later:

Defining

$$\lambda^N \Psi \quad \text{by} \quad (\lambda^N \Psi)(X) = \lambda^{N(X)} \Psi(X) \quad \forall \lambda \in \mathbb{C} \quad (15)$$

we have

$$\Gamma(\lambda^N \Psi) = \lambda^N \Gamma \Psi.$$

2.3. Algebraic Formulation of the Polymer System and Scaling Property

Taking $\Phi(\emptyset) = 0$, the algebraic formalism just introduced, enables us to write the partition function and the correlation functions in the

following form:

$$Q_A = (\Gamma \Phi)(A), \tag{16}$$

$$\varrho_A(X_1; \dots; X_p) = \prod_{i=1}^p \Phi(X_i) \frac{(\Gamma \Phi)\left(A - \sum_{i=1}^p X_i\right)}{(\Gamma \Phi)(A)} \quad \text{if } X_i \cap X_j = \emptyset. \tag{17}$$

This expression for the correlation functions suggests to introduce the reduced correlation functions $\bar{\varrho}_A(X)$ defined as:

$$\bar{\varrho}_A(X) = \frac{(\Gamma \Phi)(A - X)}{(\Gamma \Phi)(A)} \tag{18}$$

which gives:

$$\varrho_A(X_1; \dots; X_p) = \prod_{i=1}^p \Phi(X_i) \quad \bar{\varrho}_A\left(\sum_i X_i\right) \tag{19}$$

Using this formalism we obtain at once the following *sum rules*:

$$\sum_{X \ni x} \varrho_A(X) = 1 \tag{20}$$

and

$$\sum_{n=1}^{\infty} n \varrho_A^{(n)} = \frac{1}{N(A)} \sum_{X \subset A} N(X) \varrho_A(X) = 1. \tag{21}$$

Indeed Eq. (14) yields:

$$Q_A = (\Gamma \Phi)(A) = (D_x \Gamma \Phi)(A - x) = \sum_{X \ni x} \Phi(X) (\Gamma \Phi)(A - X)$$

dividing both sides by Q_A gives Eq. (20).

Eq. (21) follows from:

$$\sum_{X \subset A} N(X) \varrho_A(X) = \sum_{x \in A} \sum_{X \ni x} \varrho_A(X) = N(A).$$

We notice that these sum rules express only the fact that each site is occupied by one and only one particle.

In the cases where A is taken to be a finite subset of \mathbb{Z}^v , $\bar{\varrho}_A$ will be defined for all $X \subset \mathbb{Z}^v$ by:

$$\bar{\varrho}_A(X) = \chi_A(X) \frac{(\Gamma \Phi)(A - X)}{(\Gamma \Phi)(A)}$$

where χ_A is the characteristic function of the set of subsets of A (in the set of subsets of \mathbb{Z}^v).

We shall write $Q_A[\Phi]$ and $\varrho_A[\Phi]$ when we want to investigate the dependence of Q_A and ϱ_A on the activity Φ . From the property (15) of the mapping Γ , we deduce immediately the following *scaling properties*:

For all $\lambda \in \mathbb{C}$

$$Q_A[\Phi] = \lambda^{-N(A)} Q_A[\lambda^N \Phi] \tag{22}$$

therefore

$$\begin{aligned} \beta p_A[\Phi] &= \beta p_A[\lambda^N \Phi] - \text{Log } \lambda \\ \varrho_A[\Phi] &= \varrho_A[\lambda^N \Phi] \\ \bar{\varrho}_A[\Phi] &= \lambda^N \bar{\varrho}_A[\lambda^N \Phi]. \end{aligned}$$

This scaling property implies in particular the following:

Proposition. Consider a system made up only of monomers and αn -mers (n fixed; $\alpha = 1, 2, \dots$) and such that the activity $\Phi(x)$ of the monomers is constant $\Phi(x) = z$.

- i) The set of zeros of the partition function Q_A as function of the complex variable z possess the symmetry C_n with respect to the origin ($C_n =$ cyclic group of order n).
- ii) The domain of analyticity of the correlation function in the complex variable z possess the symmetry C_n .

3. Thermodynamic Limit for the Pressure

To study the existence and properties of this thermodynamic limit, we shall consider A to be a finite subset of \mathbb{Z}^v and we shall assume the activity to be *translationally invariant*.

The activity will be said to be *stable* if it satisfies the following condition:

$$\|\Phi\| = \sum_{X \ni 0} \frac{|\Phi(X)|}{N(X)} < \infty \tag{23}$$

3.1. Existence of the Limit

Lemma 1. If the activity Φ is stable and non-negative ($\Phi(X) \geq 0 \forall X \subset \mathbb{Z}^v$) then

i) $\text{Log } z \leq \beta p_A \leq \|\Phi\|$

where $z = \Phi(x)$ is the activity of monomers.

ii) for $z > 0$, the function $-N(A) p_A$ is subadditive with respect to A .

Proof. i) The lower bound is a direct consequence of the scaling property (22):

$$z^{-N(A)} Q_A[\Phi] = Q_A[z^{-N} \Phi] = 1 + \sum_{p=1}^{N(A)-1} \sum_{A = \sum_{i=1}^p X_i} z^{-N(A)} \prod_{i=1}^p \Phi(X_i) \geq 1$$

therefore $-\text{Log } z + \beta p_A \geq 0$.

The upper bound follows from the stability condition since:

$$\begin{aligned} Q_A[\Phi] &= (\Gamma\Phi)(A) = \sum_{A=\Sigma X_i} \prod_i \Phi(X_i) = \sum_{A=\Sigma X_i} \prod_i \sum_{x \in X_i} \frac{\Phi(X_i)}{N(X_i)} \\ &\leq \sum_p \frac{1}{p!} \prod_{i=1}^p \sum_{x \in A} \sum_{X_i \ni x} \frac{\Phi(X_i)}{N(X_i)} \leq \exp N(A) \|\Phi\| \end{aligned}$$

therefore

$$\beta p_A = \frac{1}{N(A)} \text{Log } Q_A \leq \|\Phi\|$$

$$\begin{aligned} \text{ii) } Q_{A_1+A_2} &= (\Gamma\Phi)(A_1+A_2) = (D_{A_1}\Gamma\Phi)(A_2) \\ &= (\Gamma\Phi)(A_1)(\Gamma\Phi)(A_2) + \sum_{A_1=\Sigma X_j} \sum_{\substack{S \subset A_2 \\ S \neq \emptyset}} (D_{X_1}\Phi * \dots * D_{X_q}\Phi)(S)(\Gamma\Phi)(A_2 - S) \end{aligned}$$

therefore

$$Q_{A_1+A_2} \geq Q_{A_1} Q_{A_2}$$

and

$$-N(A_1+A_2) p_{A_1+A_2} \leq -N(A_1) p_{A_1} - N(A_2) p_{A_2}.$$

Theorem 1. For any non-negative, stable activity $\Phi(X)$ such that $\Phi(x) = z \neq 0$, the following limit exists and is finite

$$\beta p = \lim_{A \rightarrow \infty} \beta p_A$$

$$\text{Log } z \leq \beta p \leq \|\Phi\|$$

when A tends to ∞ in the following sense [6]

- a) $A \rightarrow \infty$ in the sense of Van Hove,
- b) there exists $C > 0$ and for each A , a parallelepiped $A(b)$ with sides (b_1, \dots, b_ν) such that $A \subset A(b)$, $N(A(b))^{-1} N(A) > C > 0$ and $b \rightarrow \infty$.

Proof. The subadditivity of $-N(A) p_A$ and the fact that $-\beta p_A \geq -\|\Phi\|$ implies that the following limit exists

$$\lim_{a \rightarrow \infty} p_{A(a)} = \sup_a p_{A(a)} = p$$

where $a \rightarrow \infty$ means that each side of the parallelepiped $A(a)$ tends to ∞ .

To show the existence of the limit in the more general sense we consider a sequence of volume A_j which tends to ∞ in the sense of our theorem.

1) By definition of Van Hove Convergence, for all a there exists unions of parallelepipeds with sides a , say A_j^-, A_j^+ such that:

$$A_j^- \subset A_j \subset A_j^+ \quad \text{and} \quad \frac{N(A_j^\pm)}{N(A_j)} \xrightarrow{j \rightarrow \infty} 1.$$

Introducing the quantity $f_A = \beta p_A - \text{Log } z$, Lemma 1 implies that f_A is positive and $-N(A) f_A$ is subadditive; from this follows that

$$f_{A_j} \geq \frac{N(A_j^-)}{N(A_j)} f_{A(a)}$$

therefore $\liminf f_{A_j} \geq \sup_a f_{A(a)} = f = \beta p - \text{Log } z$.

2) Let $A(b)$ be a paralleliped made up of parallelipeds $A(a)$ and such that $A(b) \supset A_j^+ \supset A_j$

$$\begin{aligned} N(A(b)) f_{A(b)} &\geq N(A_j) f_{A_j} + [N(A_b) - N(A_j^+)] f_{A(a)}, \\ f_{A_j} &\leq \frac{N(A(b))}{N(A_j)} f - \frac{N(A_b) - N(A_j^+)}{N(A_j)} f_{A(a)}. \end{aligned}$$

Since $f = \sup_a f_{A(a)}$, for all $\varepsilon > 0$ there exists a such that $f_{A(a)} > f - \varepsilon$; therefore

$$f_{A_j} \leq \frac{N(A_j^+)}{N(A_j)} f + \frac{N(A^{(b)})}{N(A_j)} \varepsilon.$$

Condition (a) and (b) implies then

$$\limsup f_{A_j} \leq f.$$

Finally using the scaling property (22) we obtain:

Corollary. *Theorem 1 remains valid for any activity of the form $\xi^{N(X)} \Phi(X)$ where ξ is a positive number and $\Phi(X)$ satisfies the conditions of Theorem 1.*

3.2. Convexity and Continuity Property¹

In this section we shall investigate the convexity and continuity properties of the functions p_A and p ; these properties are obtained in terms of the chemical potential $\mu(X)$ introduced in Section 2 as

$$\beta \mu(X) = \text{Log } \Phi(X).$$

The condition $\Phi(X)$ is stable and non-negative is equivalent to the condition $\mu(X) \in \mathcal{C}$ where

$$\mathcal{C} = \left\{ \mu(X) \mid \mu(X) \in \mathbb{R} \quad X \subset \mathbb{Z}^v \quad \text{and} \quad \sum_{X \geq 0} \frac{e^{\beta \mu(X)}}{N(X)} < \infty \right\}$$

Since we shall consider p_A as a functional of the chemical potential $\mu(X)$ we shall write:

$$p_A[\Phi] = P_A[\mu] \quad \text{where} \quad \Phi(X) = e^{\beta \mu(X)}.$$

¹ We recall that we have assumed in this chapter that Φ and μ are translationally invariant.

Finally we introduce the Banach Space \mathcal{B} of real chemical potential $v(X)$ satisfying:

$$\|v\| = \sup_{X \in \mathcal{Z}^v} |v(X)| < \infty . \tag{24}$$

- Lemma 2.** i) *The function $\mu \rightarrow P_A[\mu]$ is convex on \mathcal{C} .*
 ii) *For all $\mu \in \mathcal{C}$ and $v \in \mathcal{B}$*

$$|P_A[\mu + v] - P_A[\mu]| \leq \|v\| .$$

Hence for fixed $\mu \in \mathcal{C}$ the function $v \rightarrow P_A[\mu + v]$ is continuous on the Banach Space \mathcal{B} .

Proof. i) The convexity of \mathcal{C} follows from the convexity of the exponential; the convexity of P_A from Hölder inequality.

$$\begin{aligned} Q_A[\alpha\mu + (1 - \alpha)v] &= \sum_{A=\Sigma X_i} e^{\beta\alpha\Sigma\mu(X_i) + \beta(1-\alpha)\Sigma v(X_i)} \\ &\leq \left[\sum_{A=\Sigma X_i} e^{\beta\Sigma\mu(X_i)} \right]^\alpha \left[\sum_{A=\Sigma X_i} e^{\beta\Sigma v(X_i)} \right]^{1-\alpha} , \\ Q_A[\alpha\mu + (1 - \alpha)v] &\leq Q_A[\mu]^\alpha Q_A[v]^{1-\alpha} . \end{aligned}$$

- ii) We remark first that for all $\mu \in \mathcal{C}$ and $v \in \mathcal{B}$, $\mu + v \in \mathcal{C}$ since:

$$\sum_{X \geq 0} \frac{e^{\beta(\mu(X) + v(X))}}{N(X)} \leq e^{\beta\|v\|} \sum_{X \geq 0} \frac{e^{\beta\mu(X)}}{N(X)} < \infty .$$

Moreover:

$$Q_A[\mu + v] = \sum_{A=\Sigma X_i} e^{\beta\Sigma(\mu(X_i) + v(X_i))}$$

implies

$$\begin{aligned} e^{-\beta N(A)\|v\|} Q_A[\mu] &\leq Q_A[\mu + v] \leq e^{\beta N(A)\|v\|} Q_A[\mu] \\ -\|v\| + P_A[\mu] &\leq P_A[\mu + v] \leq \|v\| + P_A[\mu] . \end{aligned}$$

Theorem 2. *With*

$$P[\mu] = \lim_{A \rightarrow \infty} P_A[\mu] .$$

- i) *The function $\mu \rightarrow P[\mu]$ is convex on \mathcal{C} .*
 ii) *For fixed $\mu \in \mathcal{C}$, the function $v \rightarrow P[\mu + v]$ is continuous on the Banach space \mathcal{B} .*

This theorem is a direct consequence of Theorem 1 and Lemma 2.

3.3. Thermodynamic Limit for the Tangent Plane to the Graph of P

To conclude this paragraph we shall derive a result concerning the existence of the thermodynamic limit for the tangent plane to the graph of P . Following Ruelle [7] we introduce the average correlation func-

tion $\tilde{q}_A(X)$:

$$\tilde{q}_A(X) = \frac{1}{N(A)} \sum_{a \in \mathbb{Z}^v} \varrho_A(\tau_a X) \tag{25}$$

which represents the density of polymer of type X for the system A (i.e. the density of polymers having $N(X)$ elements and the same oriented shape as X).

Theorem 3. For fixed $\mu \in \mathcal{C}$, we consider the function $v \rightarrow P[\mu + v]$ defined on the Banach space \mathcal{B} . If the chemical potential $\mu(X)$ is such that $v \rightarrow P[\mu + v]$ has a unique tangent plane $\alpha^\mu[v]$ at the point $v = 0$, then when $A \rightarrow \infty$ in the sense of Theorem 1, we have:

i) $\lim_{A \rightarrow \infty} \sum_{X \geq 0} \tilde{q}_A^\mu(X) \frac{v(X)}{N(X)} = -\alpha^\mu[v]$ for all $v \in \mathcal{B}$,

ii) for every finite $X \subset \mathbb{Z}^v$ the following limit exists

$$\lim_{A \rightarrow \infty} \tilde{q}_A^\mu(X) = \tilde{q}^\mu(X)$$

and defines the infinite volume density of polymer of type X ,

iii) the following limit exists

$$\lim_{A \rightarrow \infty} \varrho_A^{(n)} = \varrho^{(n)} = \sum_{\substack{X \subset \mathbb{Z}^v \\ N(X)=n}} \frac{\partial p}{\partial v(X)}$$

and defines the density of n -mers for infinite systems (where $\varrho_A^{(n)}$ is defined by Eq. (8)).

Proof. i) For any finite A and any $\mu \in \mathcal{C}$, the function $v \rightarrow P_A[\mu + v]$ has a unique tangent plane at $v = 0$; indeed

$$\begin{aligned} \left. \frac{dP_A[\mu + \lambda v]}{d\lambda} \right|_{\lambda=0} &= -\alpha_A^\mu[v] = \frac{1}{Q_A} \frac{1}{N(A)} \sum_{A = \sum X_i} e^{\beta \sum \mu(X_i)} (\sum v(X_i)) \\ &= \frac{1}{Q_A} \frac{1}{N(A)} \sum_{X \subset A} v(X) \sum_{A-X = \sum Y_j} e^{\beta \sum \mu(X)} e^{\beta \sum \mu(Y_j)} \\ &= \frac{1}{N(A)} \sum_{X \subset A} v(X) \varrho_A(X) = \sum_{X \geq 0} \tilde{q}_A(X) \frac{v(X)}{N(X)}. \end{aligned}$$

Finally Eq. (21) implies that $\sum_X \varrho_A(X) \leq 1$ and therefore for all $v \in \mathcal{B}$, $\alpha_A^\mu[v]$ exists and satisfies

$$|\alpha_A^\mu[v]| \leq \|v\|.$$

The end of the proof is identical to the one given by Gallavotti and Miracle [8].

ii) This follows immediately from part (i).

We remark that the density of polymer of type X is up to the factor $-\frac{1}{N(X)}$ the functional derivative of P_A with respect to $v(X)$.

iii) From the definition of $\varrho_A^{(n)}$ we have:

$$\varrho_A^{(n)} = \sum_{\substack{X \\ N(X)=n}} \tilde{\varrho}_A(X) \frac{1}{N(X)} = -\alpha_A^\mu[v_n]$$

where $v_n(X) = \delta_{n, N(X)} \in \mathcal{B}$.

To conclude this theorem we remark [8] that if

$$-\left. \frac{dP(\mu + \lambda v)}{d\lambda} \right|_{\lambda=0} = \alpha^\mu[v]$$

exists for a certain $v \in \mathcal{B}$ then

$$\lim_{A \rightarrow \infty} \alpha_A^\mu[v] = \alpha^\mu[v].$$

Remarks. i) The existence of the thermodynamic limit was obtained only for the case $z \neq 0$; for the case $z = 0$, it is in fact possible to find two sequences of volume which tends to ∞ and such that the pressure converges to different values.

ii) The continuity of the pressure, and the functional derivative, was obtained relative to the chemical potential $v(X)$; this is connected with the fact that systems which do not have their activities $\Phi(X)$ equal to zero on the same subsets X are different physical systems.

iii) The results obtained in this section are in close analogy with those obtained for lattice systems; it is however interesting to notice that *in the case of polymers, the functional derivatives do not provide a complete description of the state of the system.* (Indeed by functional derivation one can obtain $\tilde{\varrho}(X)$ only for those X such that $\Phi(X) \neq 0$.)

4. Thermodynamic Limit for the Correlation Functions

To study the existence and properties of the correlation functions for infinite systems, we shall first derive a set of equations which are satisfied by the reduced correlation functions of finite systems $\tilde{\varrho}_A$. From this set of equations, it is possible to extract several minimal subsets of equations equivalent to the full set; in particular one of those minimal subsets is analogous to the Kirkwood-Salsburg equations for classical continuous systems. We shall investigate this particular set of equations using the well-known methods of Banach space and Neumann series.

In this section we shall consider \mathcal{A} to be a subset of \mathbb{Z}^v ; however we do not restrict ourselves to the case of translation invariant activities.

4.1. Equations for the Correlation Functions

From the general properties of the mapping Γ introduced in § 2, we obtain:

$$\begin{aligned} & (\Gamma\Phi)(Z+Y) = (D_Y\Gamma\Phi)(Z) \\ & = (\Gamma\Phi)(Y)(\Gamma\Phi)(Z) + \sum_{Y=\sum Y_i} \sum_{\substack{S \subset Z \\ S \neq \emptyset}} (D_{Y_1}\Phi * \dots * D_{Y_q}\Phi)(S)(\Gamma\Phi)(Z-S). \end{aligned}$$

If $(\Gamma\Phi)(A) \neq 0$, writing $Z = A - X$ and with $Y \subset X \subset A$ we then have:

$$\bar{q}_A(X-Y) = (\Gamma\Phi)(Y)\bar{q}_A(X) + \sum_{Y=\sum Y_i} \sum_{\substack{S \subset A-X \\ S \neq \emptyset}} (D_{Y_1}\Phi * \dots * D_{Y_p}\Phi)(S)\bar{q}_A(X+S).$$

Therefore for any finite volume A , and for any activities such that $(\Gamma\Phi)(A) \neq 0$, the correlation functions satisfy for all X and $Y \subset X$:

$$(\Gamma\Phi)(Y)\bar{q}_A(X) = \chi_A(X)\bar{q}_A(X-Y) - \sum_{Y=\sum_{i=1}^q Y_i} \sum_{\substack{S_1, \dots, S_q \\ S_i \neq \emptyset \\ S_i \cap S_j = \emptyset}} \Pi\Phi(Y_i+S_i)\bar{q}_A(X+S). \quad (26)$$

This relation can also be written as²:

$$(\Gamma\Phi)(Y)\bar{q}_A(X) = \chi_A(X)\bar{q}_A(X-Y) - \sum_{\substack{S \neq \emptyset \\ S \cap X = \emptyset}} [(\Gamma\Phi)^{-1} * D_Y\Gamma\Phi](S)\bar{q}_A(X+S) \quad (27)$$

At this point we would like to find minimal subsets of (26) that are equivalent to the full set of equations.

Lemma 3. *If \bar{q}_A satisfies (26) for all $Y \subset X$ such that $N(Y) \leq n$, then it satisfies (26) for all Y such that $N(Y) = n+1$.*

Proof. Let $Y \subset X$ be any subset such that $N(Y) = n$.

From the relations and identities:

$$\begin{aligned} & (\Gamma\Phi)(Y+\{y\}) = \sum_{S \subset Y} \Phi(\{y\}+S)(\Gamma\Phi)(Y-S) \quad y \in X-Y, \\ & \sum_{S \subset Y} \Phi(\{y\}+S)\bar{q}_A(X-Y+S) \\ & = \sum_{S \subset Y} \Phi(\{y\}+S)[\bar{q}_A(X-Y+S) + \bar{q}_A(X-Y-\{y\})] \\ & \quad - \sum_{S \cap (X-Y) = \emptyset} \Phi(\{y\}+S)\bar{q}_A(X-Y+S) \\ & = \bar{q}_A(X-Y-\{y\}) - \sum_{\substack{Y_1 \subset Y \\ U_1 \cap X = \emptyset \\ U_1 \neq \emptyset}} \Phi(\{y\}+Y_1+U_1)\bar{q}_A(X+U_1-(Y-Y_1)) \end{aligned}$$

² $(\Gamma\Phi)^{-1}$ denotes the *-inverse of $\Gamma\Phi$.

and

$$\begin{aligned}
 & \sum_{S \subset Y} (\Gamma \Phi)(U + Y - S) \Phi(\{y\} + S) \\
 &= \sum_{S \subset Y + U} (\Gamma \Phi)(U + Y - S) \Phi(\{y\} + S) \\
 &\quad - \sum_{\substack{Y_1 \subset Y \\ U_1 \subset U \\ U_1 \neq \emptyset}} (\Gamma \Phi)(U - U_1 + Y - Y_1) \Phi(\{y\} + U_1 + Y_1) \\
 &= (D_{\{y\}+Y} \Gamma \Phi)(U) - \sum_{\substack{Y_1 \subset Y \\ U_1 \subset U \\ U_1 \neq \emptyset}} (\Gamma \Phi)(U - U_1 + Y - Y_1) \Phi(\{y\} + U + Y_1)
 \end{aligned}$$

the hypothesis of the lemma implies that for any $y \in X - Y$

$$\begin{aligned}
 (\Gamma \Phi)(\{y\} + Y) \bar{q}_A(X) &= \sum_{S \subset Y} \Phi(\{y\} + S) [(\Gamma \Phi)(Y - S) \bar{q}_A(X)] \\
 &= \sum_{S \subset Y} \Phi(\{y\} + S) \left[\chi_A(X) \bar{q}_A(X + S - Y) \right. \\
 &\quad \left. - \sum_{\substack{T \neq \emptyset \\ T \cap X = \emptyset}} [(\Gamma \Phi)^{-1} * D_{Y-S} \Gamma \Phi](T) \bar{q}_A(X + T) \right] \\
 &= \chi_A(X) \bar{q}_A(X - Y - \{y\}) \\
 &\quad - \sum_{\substack{Y_1 \subset Y \\ U_1 \cap X = \emptyset \\ U_1 \neq \emptyset}} \Phi(\{y\} + Y_1 + U_1) \chi_A(X) \bar{q}_A(X + U_1 - (Y - Y_1)) \\
 &\quad - \sum_{\substack{T \neq \emptyset \\ T \cap X = \emptyset}} \left\{ [(\Gamma \Phi)^{-1} * D_{\{y\}+Y} \Gamma \Phi](T) \bar{q}_A(X + T) \right. \\
 &\quad \left. + \sum_{Y_1 \subset Y} \sum_{U \subset T} \sum_{\substack{U_1 \subset U \\ U_1 \neq \emptyset}} \Phi(\{y\} + U_1 + Y_1) \right. \\
 &\quad \left. \cdot (\Gamma \Phi)^{-1}(T - U) (\Gamma \Phi)(U - U_1 + Y - Y_1) \bar{q}_A(X + T) \right\}.
 \end{aligned}$$

The last term being equal to:

$$\begin{aligned}
 & \sum_{Y_1 \subset Y} \sum_{\substack{T \neq \emptyset \\ T \cap X = \emptyset}} \sum_{\substack{U \subset T \\ U_1 = \emptyset}} \Phi(\{y\} + U_1 + Y_1) \\
 & \quad [(\Gamma \Phi)^{-1} * D_{Y-Y_1} \Gamma \Phi](T - U_1) \bar{q}_A(X + T) \\
 &= \sum_{\substack{Y_1 \subset Y \\ U_1 \cap X = \emptyset \\ U_1 \neq \emptyset}} \Phi(\{y\} + Y_1 + U_1) \\
 & \quad \cdot \sum_{S \cap (X + U_1) = \emptyset} [(\Gamma \Phi)^{-1} * D_{Y-Y_1} \Gamma \Phi](S) \bar{q}_A(X + U_1 + S).
 \end{aligned}$$

We can use once more the induction hypothesis to obtain finally:

$$(\Gamma\Phi)(Y + \{y\}) \bar{q}_A(X) = \chi_A(X) \bar{q}_A(X - Y - \{y\}) - \sum_{\substack{T \neq \emptyset \\ T \cap X = \emptyset}} [(\Gamma\Phi)^{-1} * D_{\{y\}+Y} \Gamma\Phi](T) \bar{q}_A(X + T).$$

Corollary. *The following set of equations is equivalent to the full set of Eqs. (26):*

$$\Phi(x_1) \bar{q}_A(X) = \chi_A(X) \bar{q}_A(X - x_1) - \sum_{\substack{S \neq \emptyset \\ S \subset A - X}} \Phi(x_1 + S) \bar{q}_A(X + S) \quad (28)$$

where x_1 is one of the points of the set X , for example the first in lexicographic order.

This last set of equations are the “Kirkwood-Salsburg equations for Polymer Systems”. Another subset of equations, analogous to the Mayer-Montroll equations, is obtained from (26) by taking $Y = X$:

$$(\Gamma\Phi)(X) \bar{q}_A(X) = \chi_A(X) \left[1 - \sum_{S \neq \emptyset} [(\Gamma\Phi)^{-1} * D_X \Gamma\Phi](S) \bar{q}_A(X + S) \right]. \quad (29)$$

It is expected that this set of equations is also equivalent to the full set (26).

4.2. Kirkwood-Salsburg Equations for Polymers

Let \mathcal{B}_ξ be the complex Banach space of complex functions f defined on non empty finite subsets of \mathbb{Z}^v with the norm

$$\|f\|_\xi = \sup_X \frac{|f(X)|}{\xi^{N(X)}} \quad (30)$$

where ξ is a positive number to be chosen later on.

For any finite A , $\bar{q}_A(X) = \chi_A(X) \bar{q}_A(X)$; moreover for non negative activity

$$\bar{q}_A(X) \leq \frac{1}{\Pi \Phi(x_i)}.$$

Therefore for any finite A , and any non-negative activity Φ , $\bar{q}_A \in \mathcal{B}_\xi$ and satisfies $\|\bar{q}_A\|_\xi \leq 1$ if $\xi \Phi(x) > 1$ for all x .

We define on \mathcal{B}_ξ a linear operator K_Φ as follows: with $f \in \mathcal{B}_\xi$

$$(K_\Phi f)(x_1) = - \frac{1}{\Phi(x_1)} \sum_{\substack{S \neq \emptyset \\ S \neq x_1}} \Phi(x_1 + S) f(x_1 + S) \quad (31)$$

$$(K_\Phi f)(X) = \frac{1}{\Phi(x_1)} \left[f(X - x_1) - \sum_{\substack{S \neq \emptyset \\ S \cap X = \emptyset}} \Phi(x_1 + S) f(X + S) \right] \text{ if } N(X) \geq 2.$$

Lemma 4. For any activity Φ such that $\sum_{X \ni x} \xi^{N(X)} |\Phi(X)| < \infty$ for some ξ and such that

$$\min_x |\Phi(x)| \neq 0,$$

the operator K_Φ is a bounded operator on \mathcal{B}_ξ and its norm satisfies

$$\|K\|_\xi \leq \max \frac{1}{|\Phi(x)|} \frac{1}{\xi} \left[1 + \sum_{\substack{S \ni x \\ S \neq \emptyset}} |\Phi(x+S)| \xi^{N(x+S)} \right]. \quad (32)$$

This lemma follows immediately from the definition of K_Φ and \mathcal{B}_ξ . Let $\Delta(\xi)$ be the set of complex activities Φ such that

$$\|\Phi\|_\xi = \sup_x \sum_{X \ni x} |\Phi(X)| \xi^{N(X)} < \infty$$

and (33)

$$|\Phi(x)| > \sup_x \frac{1}{\xi} \left[1 + \sum_{\substack{S \ni x \\ S \neq \emptyset}} |\Phi(x+S)| \xi^{N(x+S)} \right] = R(\xi).$$

Lemma 5. The operator K_Φ defined on the Banach space \mathcal{B}_ξ is norm analytic in Φ for $\Phi \in \Delta(\xi)$; moreover in this same domain

$$\|K_\Phi\|_\xi < 1.$$

Proof. A very simple calculation shows that

$$\|K_\Phi - K_\Psi\|_\xi \leq \|\Psi - \Phi\|_\xi \quad \text{if } \Phi, \Psi \in \Delta(\xi). \quad (34)$$

Analyticity follows from the fact that K_Φ is of the form:

$$K_\Phi = \frac{1}{\Phi(x_1)} \cdot K'_\Phi$$

where $\frac{1}{\Phi(x_1)}$ is the operator defined by

$$\left(\frac{1}{\Phi(x_1)} f \right) (X) = \frac{1}{\Phi(x_1)} f(X)$$

for all $f \in \mathcal{B}_\xi$ and K'_Φ is the sum of two operators, one independent of Φ , the other linear in Φ .

Introducing the operator χ_A on \mathcal{B}_ξ defined by:

$$(\chi_A f) (X) = \chi_A(X) f(X) \quad \text{for all } f \in \mathcal{B}_\xi \quad (35)$$

and denoting by α the vector in \mathcal{B}_ξ defined by:

$$\alpha(X) = \delta_{N(X), 1} \frac{1}{\Phi(x)} \quad (36)$$

the “Kirkwood-Salsburg equations for polymers” appear as a linear equation on \mathcal{B}_ξ of the form:

$$\bar{Q}_A = \chi_A \alpha + \chi_A K_\Phi \bar{Q}_A. \tag{37}$$

We can now state the main result of this section:

Theorem 4. *Let $\Delta(\xi)$ be defined by (33); then for any $\Phi \in \Delta(\xi)$.*

I) *For any finite volume Λ , the “Kirkwood-Salsburg” equation*

$$\bar{Q}_\Lambda = \chi_\Lambda \alpha + \chi_\Lambda K_\Phi \bar{Q}_\Lambda$$

has a unique solution in \mathcal{B}_ξ , obtained by iteration. This solution is a norm analytic function of Φ in $\Delta(\xi)$ and satisfies

$$\|\bar{Q}_\Lambda\|_\xi \leq \left\{ 1 - \max_x \frac{1}{|\Phi(x)| \xi} \left[1 + \sum_{\substack{S \neq \emptyset \\ S \ni x}} |\Phi(x+S)| \xi^{N(S)+1} \right] \right\}^{-1} \tag{38}$$

II) *For any finite volume Λ , $Q_\Lambda[\Phi] \neq 0$, and the solution of the Kirkwood-Salsburg equation coincide with the definition (18).*

III) *The infinite volume equation*

$$\bar{Q} = \alpha + K_\Phi \bar{Q}$$

has a unique solution in \mathcal{B}_ξ , which is also analytic in $\Delta(\xi)$. Moreover if the activity is invariant under a certain subgroup T of translation then \bar{Q} is also invariant under T .

IV) *If the activity is invariant under a certain subgroup T of translations such that the quotient group \mathbb{Z}^v/T is finite (i.e. T is generated by v elementary translations)*

or if the activity has finite range,

then there exists a positive, decreasing function $\varepsilon(\lambda)$ such that

$$\lim_{\lambda \rightarrow \infty} \varepsilon(\lambda) = 0$$

and

$$|\bar{Q}_\Lambda(X) - \bar{Q}(X)| \leq \xi^{N(X)} \varepsilon(\lambda) \tag{39}$$

where λ is the minimum distance from $x_i \in X$ to the boundary of Λ .

V) *if the activity is invariant under a subgroup T of translation (such that the order of \mathbb{Z}^v/T is finite), then:*

$$\bar{Q}(X) = \lim_{\Lambda \rightarrow \infty} \frac{N(\mathbb{Z}^v/T)}{N(\Lambda)} \sum_{\tau \in T} \bar{Q}_\Lambda(\tau X) \tag{40}$$

where $N(\mathbb{Z}^v/T)$ is the order of the quotient group \mathbb{Z}^v/T and Λ tends to infinity in the sense of Van Hove. Moreover the convergence is uniform with respect to $\Phi(x)$ on every compact subset contained in $\Delta(\xi)$.

Proof. Part I follows from Lemma 1 and 2 and the fact that $\chi_A \alpha$ is a vector which is norm analytic for $\Phi \in A(\xi)$.

Part II is a consequence of the fact that $\bar{Q}_A(x)$ is analytic in $\Phi(x)$ and $\bar{Q}_A(x) = \frac{d}{d\Phi(x)} \text{Log } Q_A$.

Part III is obtained from Lemma 4 and 5 and the fact that if $\Phi(X)$ is invariant under a subgroup T then α and K_Φ are invariant under T .

Using the same argument as Ruelle [9], part IV will be proved if we can show that for $A \subset A' \subset A''$

$$\|\chi_A K_\Phi \chi_{A''} - \chi_A K_\Phi \chi_{A'}\|_\xi \leq \eta(\delta)$$

where δ is the minimum distance from A to the boundary of A' and $\eta(\delta)$ satisfies $\lim_{\delta \rightarrow \infty} \eta(\delta) = 0$.

This inequality follows from:

$$\begin{aligned} & |\chi_A(X) (K_\Phi \chi_{A''} f)(X) - \chi_A(X) (K_\Phi \chi_{A'} f)(X)| \\ & \leq \frac{1}{|\Phi(x_1)|} \sum_{\substack{S \neq \emptyset \\ S \neq x_1}} |\Phi(x_1 + S)| |f(X + S)| (1 - \chi_{A'}(S)) \end{aligned}$$

and the fact that $\Phi \in A(\xi)$ which yields

$$\|\chi_A K_\Phi \chi_{A''} - \chi_A K_\Phi \chi_{A'}\|_\xi \leq \sup_{x_1} \sum_{\substack{S \neq \emptyset \\ S \neq x_1 \\ S \subseteq A'}} |\Phi(x_1 + S)| \xi^{N(S)+1} \leq \eta(\delta)$$

where

$$\eta(\delta) = \sup_{x_1} \sum_{\substack{S \neq \emptyset \\ S \neq x_1 \\ S \subseteq B_\delta(x_1)}} |\Phi(x_1 + S)| \xi^{N(S)+1} \tag{41}$$

and $B_\delta(x_1)$ denotes the ball of radius δ centered at x_1 .

Moreover if the activity has finite range Δ , $\eta(\delta) = 0$ if $\delta > \delta_0$ where δ_0 is the diameter of the range; on the other hand if the activities are invariant under T

$$\eta(\delta) = \sup_{\tau \in \mathbb{Z}^v/T} \sum_{\substack{S \neq \emptyset \\ S \neq \tau x \\ S \subseteq B_\delta(\tau x)}} |\Phi(\tau x + S)| \xi^{N(S)+1}$$

and since

$$\sup_x \sum_{S \neq x} |\Phi(x + S)| \xi^{N(S)+1} < \infty$$

then $\lim_{\delta \rightarrow \infty} \eta(\delta) = 0$ since the order of \mathbb{Z}^v/T is finite.

Finally the proof of part V is identical with the one given in reference [8]; moreover the limit is uniform on every compact set contained in

$\Delta(\xi)$ since $|\bar{q}_A(X)|$ has a bound independent of X and which can be chosen independent of $\Phi(x)$ if Φ belongs to a compact set in $\Delta(\xi)$.

Remark. Part IV of the last theorem can be moreover extended to all $\Phi \in \Delta(\xi)$ which are the strong limit (in the norm $\|\cdot\|_\xi$) of Φ_δ

where

$$\Phi_\delta = \begin{cases} \Phi(X) & \text{if } |x_i - x_j| < \delta \text{ for all } i, j \\ 0 & \text{otherwise.} \end{cases}$$

In the study of phase transition one is usually interested in the domain of analyticity of \bar{q} as function of the monomer activity for fixed value of the activity of the other polymers. In this case the previous theorem reads:

Theorem 5. *The solutions \bar{q}_A and \bar{q} of the Kirkwood-Salsburg equations are analytic functions of the monomer activity $\Phi(x)$ in the domain:*

$$|\Phi(x)| > \max_x \frac{1}{\xi_0} \left[1 + \sum_{\substack{S \neq \emptyset \\ S \neq x}} |\Phi(x+S)| \xi_0^{N(S)+1} \right] = R(\xi_0) \quad (42)$$

where ξ_0 is the value of ξ such that $R(\xi_0)$ is minimum.

In particular if the activity is translationally invariant ξ_0 is the solution of

$$1 = \sum_{S \geq 0} (N(S) - 1) |\Phi(S)| \xi_0^{N(S)}. \quad (43)$$

Remark. In all those types of results, one would be interested to know how good is the domain of analyticity thus obtained; one can show that this is in particular *the best radius of convergence for systems consisting of monomers and n-mers (n fixed)*; indeed there exists special types of interactions (Van der Waals) for which the radius obtained in Theorem 4 is the exact radius of convergence.

4.3. Mayer Series and Virial Expansion

From Theorem 4, part V, we have that if $\Lambda \rightarrow \infty$ in the sense of Van Hove, and if the activity is invariant under translation, then

$$\lim_{\Lambda \rightarrow \infty} \frac{1}{N(\Lambda)} \sum_x \bar{q}_\Lambda(x) = \bar{q}^{(1)} = \frac{q^{(1)}}{z}$$

uniformly with respect to z on every compact subset contained in the exterior of the circle of radius $R(\xi_0)$.

Moreover since

$$\frac{1}{N(\Lambda)} \sum_x \bar{q}_\Lambda(x) - \frac{1}{z} = \frac{d}{dz} (\beta p_\Lambda - \text{Log } z)$$

and

$$\lim_{z \rightarrow \infty} (\beta p_A - \text{Log } z) = 0,$$

we have

$$\beta p_A = \text{Log } z - \int_z^\infty dz \left(\frac{1}{N(A)} \sum_x \bar{q}_A(x) - \frac{1}{z} \right)$$

$$\beta p = \lim_{A \rightarrow \infty} \beta p_A = \text{Log } z + \int_z^\infty dz \frac{1 - q^{(1)}}{z}.$$

In conclusion we have just proved:

Theorem 6. *If $A \rightarrow \infty$ in the sense of Van Hove, then the following limit exists*

$$\lim_{A \rightarrow \infty} \frac{1}{N(A)} \text{Log } Q_A = \beta p,$$

$$\lim_{A \rightarrow \infty} z \frac{d}{dz} \frac{1}{N(A)} \text{Log } Q_A = q^{(1)}$$

when the activity is translationally invariant and $|z| > R(\xi)$.

These limits continue analytically to $|z| > R(\xi_0)$ the physical pressure and density defined for $z > 0$. In particular the Mayer series

$$\beta p = \text{Log } z + \sum_{n=1}^\infty b_n z^{-n}, \tag{44}$$

$$q^{(1)} = 1 - \sum_{n=1}^\infty n b_n z^{-n} \tag{45}$$

has a radius of convergence of at least $R(\xi_0)^{-1}$ in z^{-1} .

Instead of the Mayer series (44) one would like to obtain an expansion of the pressure p in powers of the monomer density $q^{(1)}$, that is the *Virial expansion*; in our case $q^{(1)}$ being analytic around $z^{-1} = 0$, we shall look for an expansion in powers of $(1 - q^{(1)})$.

From

$$\bar{q}(x) = \sum_{k=0}^\infty (K^k \alpha)(x)$$

follows that

$$1 - q^{(1)} = -z \sum_{k=1}^\infty (K^k \alpha)(x)$$

and therefore the first non-zero coefficient of the Mayer series (45) is b_p , $p \geq 2$, where p is the smallest number > 1 such that $\Phi(X) \neq 0$ for some $N(X) = p$; moreover in this case

$$p b_p = \sum_{\substack{X \ni 0 \\ N(X) = p}} \Phi(X). \tag{46}$$

In particular $b_1 = 0$ and in general p and z will not be analytic in $q^{(1)}$ at $q^{(1)} = 1$; however we shall now derive the virial expansion for the special case of a system made up only of monomers and n p -mers (p fixed, $n = 1, 2, \dots$). For this special case we have:

$$1 - q^{(1)} = -z \sum_{l=1}^{\infty} (K^{pl}\alpha)(x) \tag{47}$$

that is

$$1 - q^{(1)} = \sum_{l=1}^{\infty} (pl) b_{pl} z^{-pl}, \tag{48}$$

$$\beta p - \text{Log } z = \sum_{l=1}^{\infty} b_{pl} z^{-pl}. \tag{49}$$

Since by assumption $pb_p \neq 0$, we may invert (48) in a neighborhood of $z^{-1} = 0$ and we obtain the virial expansion

$$\beta p - \text{Log } z = \sum_{n=1}^{\infty} c_n (1 - q^{(1)})^n \tag{50}$$

where

$$c_n = -\frac{1}{2i\pi} \int_c \frac{dz}{z} \frac{1}{n(1 - q^{(1)})^{n-1}}$$

if c is a circle of radius larger than $R(\xi_0)$.

From (47) follows that:

$$|1 - q^{(1)} + z(K^{pl}\alpha)(x)| = |1 - q^{(1)} - pb_p| \leq \frac{\|K\|_{\xi}^{2p}}{1 - \|K\|_{\xi}^p}$$

therefore for $|z| > R(\xi_0) = R$ ($R(\xi_0)$ defined by (42))

$$|1 - q^{(1)}| \geq \frac{|pb_p|}{|z|^p} - \frac{R^{2p}}{z^{2p} - z^p R^p}.$$

In conclusion we obtain:

$$|1 - q^{(1)}| \geq \frac{|pb_p|}{R^p} + 2 \left[1 - \left(1 + \frac{|pb_p|}{R^p} \right)^{\frac{1}{2}} \right]$$

on the circle $|z|^{-p} = R^{-p} - [R^p(|pb_p| + R^p)]^{-\frac{1}{2}}$.

We thus obtain the following theorem:

Theorem 7. *The radius of convergence of the virial expansion*

$$\beta p - \text{Log } z = \sum_{n=1}^{\infty} c_n (1 - q^{(1)})^n$$

is at least

$$|1 - q^{(1)}| = \frac{|pb_p|}{R^p} + 2 \left[1 - \left(1 + \frac{|pb_p|}{R^p} \right)^{\frac{1}{2}} \right]$$

where

$$pb_p = \sum_{\substack{X \neq 0 \\ N(X) = p}} \Phi(X)$$

and $R = R(\xi_0)$ was defined in (42).

Finally we shall remark that because of the scaling property:

$$\begin{aligned} \beta p[\Phi] &= \beta p[z^{-N} \Phi], \\ \varrho^{(1)}[\Phi] &= \varrho^{(1)}[z^{-N} \Phi] \end{aligned}$$

we can always choose $z = 1$ and thus obtain the usual form of the virial expansion:

$$\beta p = \sum_{n=1}^{\infty} c_n (1 - \varrho^{(1)})^n.$$

To conclude this section we mention the following generalization of Theorem 7:

Theorem 8. *For any polymer system the virial expansion*

$$\beta p - \text{Log } z = \sum_{n=1}^{\infty} c_n (1 - \varrho^{(1)})^{\frac{n}{m}}$$

where m is the smallest r such that $\Phi(x_1, \dots, x_r) \neq 0$ converges in a neighbourhood of $\varrho^{(1)} = 1$.

5. Monomer-Dimer Systems

For the special case of monomer-dimer systems the domain of analyticity of the pressure and the correlation functions, as functions of the monomer activity (obtained in § 4) can be extended by studying the zeros of the partition function.

5.1. Zeros of the Partition Function and Extension of the Domain of p and \bar{q}

Theorem 9. *The partition function $Q_A[\Phi]$ is different from zero for any complex activities such that $\text{Re } \Phi(x) > 0 \forall x \in A$ or $\text{Re } \Phi(x) < 0 \forall x \in A$ and $\Phi(x, y) \geq 0$ for all $x, y \in A$.*

We shall prove this theorem by induction using the recurrence formula (14) which gives:

$$Q_A[\Phi] = \Phi(x_i) Q_{A-x_i}[\Phi] + \sum_{\substack{x_j \in A \\ j \neq i}} \Phi(x_i, x_j) Q_{A-x_i-x_j}[\Phi]. \quad (51)$$

1. Let us first consider the case: $\operatorname{Re} \Phi(x) > 0$, $\Phi(x, y) \geq 0$.

i) $Q_{\{x\}}[\Phi] = \Phi(x)$,

$$Q_{\{x_1, x_2\}}[\Phi] = \Phi(x_1, x_2) + \Phi(x_1) \Phi(x_2)$$

therefore

$$Q_{\{x\}} \neq 0 \quad \text{and} \quad Q_{\{x_1, x_2\}} \neq 0$$

and

$$\operatorname{Re}[Q_{\{x_1, x_2\}}[\Phi] Q_{\{x_1\}}^*[\Phi]] = \operatorname{Re} \Phi^*(x_1) \Phi(x_1, x_2) + \operatorname{Re} \Phi(x_2) |\Phi(x_1)|^2 > 0.$$

ii) Assuming $Q_X[\Phi] \neq 0$ and

$$\operatorname{Re}[Q_X[\Phi] Q_{X-x_i}^*[\Phi]] > 0$$

for all X such that $N(X) \leq n-1$ and for all $x_i \in X$ let us show the same holds for all X such that $N(X) = n$; using (51) we have:

$$\begin{aligned} Q_X[\Phi] Q_{X-x_i}^*[\Phi] &= \left[\Phi(x_i) Q_{X-x_i} + \sum_{j \neq i} \Phi(x_i, x_j) Q_{X-x_i-x_j} \right] Q_{X-x_i}^* \\ &= \Phi(x_i) |Q_{X-x_i}|^2 + \sum_{j \neq i} \Phi(x_i, x_j) Q_{X-x_i}^* Q_{X-x_i-x_j}. \end{aligned}$$

Therefore

$$\operatorname{Re}(Q_X[\Phi] Q_{X-x_i}^*[\Phi]) > 0 \quad \text{for all } x_i \in X \quad (52)$$

and $Q_X[\Phi] \neq 0$.

2. Using the scaling property $|Q_\Lambda[\Phi]| = |Q_\Lambda[(-1)^N \Phi]|$ the theorem is also true for the case $\operatorname{Re} \Phi(x) < 0$ which concludes the proof. This theorem enables us to extend the domain of analyticity of the pressure and the correlation functions, and we have:

Theorem 10. *For monomer-dimer systems such that the activity is stable, translationally invariant, and satisfies $\Phi(x, y) \geq 0$, the following limit exists*

$$\lim_{\Lambda \rightarrow \infty} \frac{1}{N(\Lambda)} \operatorname{Log} Q_\Lambda = \beta p,$$

$$\lim_{\Lambda \rightarrow \infty} \bar{q}_\Lambda(X) = \bar{q}(X)$$

when $\Lambda \rightarrow \infty$ in the sense of Van Hove and $z \notin [-2iW^{\frac{1}{2}}, 2iW^{\frac{1}{2}}]$ where $W = \sum_{y \neq 0} \Phi(0, y)$. Moreover in this domain p and $\bar{q}(X)$ are the analytic continuation of the physical pressure and reduced correlation function (defined for $z \geq 0$).

Proof. The previous theorems imply that $p_A = \frac{1}{N(A)} \text{Log } Q_A$ and $\bar{q}_A(X)$ are analytic function of z in the plane cut by $[-2iW^{\frac{1}{2}}, 2iW^{\frac{1}{2}}]$; moreover p_A and $\bar{q}_A(X)$ are uniformly bounded on any compact subset of the z -plane cut by this segment: indeed from the proof of Lemma 1 follows that

$$\frac{1}{N(A)} \text{Log } |Q_A| \leq |z| + \frac{1}{2}W$$

while relations (51) and (52) yields for $\text{Re } z > 0$

$$\begin{aligned} |Q_A Q_{A-x}^*| &\geq \text{Re } Q_A Q_{A-x}^* \geq |\text{Re } z| |Q_{A-x}|^2, \\ |Q_A| &\geq |\text{Re } z| |Q_{A-x}| \geq |\text{Re } z|^{N(X)} |Q_{A-x}| \end{aligned}$$

and using the scaling relation $|Q_A[\Phi]| = |Q_A[(-1)^N \Phi]|$ this inequality remains valid for $\text{Re } z < 0$.

Therefore $|Q_A(X)| \leq |\text{Re } z|^{-N(X)}$.

This result together with Theorem 4 shows that $\bar{q}_A(X)$ is uniformly bounded on any compact subset of the z -plane cut by $[-2i\sqrt{W}, 2i\sqrt{W}]$.

Finally Theorem 4 and 6 imply that $\bar{p}_A \rightarrow p$ and $\bar{q}_A(X) \rightarrow \bar{q}(X)$ for $|z| > 2W^{\frac{1}{2}}$; we can therefore apply Vitali's theorem to conclude that p_A and $\bar{q}_A(X)$ converge uniformly on compact subsets to an analytic function on the z -plane cut by the segment $[-2iW^{\frac{1}{2}}, 2iW^{\frac{1}{2}}]$.

Conclusion

No phase transition can occur in monomer-dimer systems if the activity is stable, translationally invariant and satisfies $\Phi(x) \neq 0$ $\Phi(x, y) \geq 0$.

Finally Theorem 9 and 10 enable us to obtain other properties concerning the functions $q^{(1)}$ and p .

Theorem 11. *The monomer density*

$$q^{(1)}(z) = \sum_{j=0}^{\infty} a_j (-z^{-2})^j = \sum_{j=0}^{\infty} a_j (-\zeta)^j$$

is a series of Stieltjes in $\zeta = z^{-2}$ and therefore

$$q^{(1)}(z) = \int_0^{4W} \frac{df(y)}{1 + yz^{-2}}$$

where $f(y)$ is a bounded, non decreasing function.

Proof. Let $u = \frac{1-z}{1+z}$; Theorem 9 implies that $\bar{q}^{(1)}$, as function of u , is analytic in the circle $|u| < 1$; moreover from (52) follows that $\operatorname{Re} \bar{q}^{(1)} > 0$ for $|u| < 1$.

From those properties follows that [12] the function

$$F(w) = \frac{1}{\sqrt{1+w}} \bar{q}^{(1)}((1+w)^{-\frac{1}{2}})$$

is a series of Stieltjes in w ; therefore $q^{(1)}(z) = z\bar{q}^{(1)}(z)$ is a series of Stieltjes in $(z^{-2} - 1)$ and also a series of Stieltjes in $\zeta = z^{-2}$.

Theorem 12. Let $[N, M]$ (ζ) denote the Padé approximant for the series of Stieltjes of $q^{(1)}$; for z real, non negative, the monomer density satisfies:

$$\begin{aligned} [N, N] (\zeta = z^{-2}) &\geq q^{(1)}(z) \geq [N, N-1] (\zeta = z^{-2}) \\ -\frac{d}{d\zeta} [N, N] (\zeta = z^{-2}) &\leq \frac{1}{2} z^3 \frac{dq^{(1)}(z)}{dz} \leq \frac{d}{d\zeta} [N, N-1] (\zeta = z^{-2}) \end{aligned}$$

and the pressure is an increasing continuous function of the monomer density.

Proof. The first part of this theorem is a direct consequence [13] of Theorem 11. The last part follows from

$$\frac{dp}{dq^{(1)}} = \frac{q^{(1)}}{z \frac{dq^{(1)}}{dz}}$$

and the evaluation of the first Padé approximants:

$$[1, 0] (\zeta) = \frac{1}{1+W\zeta} \quad [1, 1] (\zeta) = \frac{1+a\zeta}{1+b\zeta}$$

$$a = W - W^{-1} \sum_s \Phi(0, s)^2$$

$$b = W + a.$$

6. The Association Problem

In this section we want to generalize an argument given by Green and Hurst [1] to show that the study of any classical lattice system can be reduced to the study of a polymer system on the same lattice.

6.1. Lattice Gas

We consider a classical system of particles on \mathbb{Z}^v such that at each lattice point there can be 0 or 1 particle; the system is described by the Hamiltonian:

$$H(X) = -\mu N(X) + U(X) \quad X \subset \mathbb{Z}^v$$

where the potential energy $U(X)$ is assumed to be translationally invariant and $U(X) = 0$ if $N(X) < 2$; with μ the chemical potential, the activity z is given by $z = e^{\beta\mu}$.

For any finite volume A , the partition function Z_A and the correlation functions $\varrho_A(X)$ are defined as:

$$Z_A = \sum_{Y \subset A} e^{-\beta H(Y)} = \sum_{Y \subset A} z^{N(Y)} e^{-\beta U(Y)}$$

$$\varrho_A(X) = Z_A^{-1} \sum_{Y \subset A-X} e^{-\beta H(X+Y)} = Z_A^{-1} \sum_{Y \subset A-X} z^{N(X+Y)} e^{-\beta U(X+Y)}.$$

Finally we introduce the Ursell Functions $\Psi(X)$ defined by:

$$(\Gamma \Psi)(X) = e^{-\beta U(X)}; \quad \Psi(x) = 1.$$

Lemma 6. i) *The partition function Z_A for the lattice gas described by the activity z and the Ursell function $\Psi(X)$ is up to a factor $z^{N(A)}$ identical with the partition function of a polymer system described by the activity:*

$$\Phi(x) = \frac{1}{z} + 1 \quad \text{if } N(x) = 1,$$

$$\Phi(X) = \Psi(X) \quad \text{if } N(X) \geq 2$$

that is: $Z_{A,(z,\Psi)}^{\text{Lattice}} = z^{N(A)} Q_{A,(\frac{\delta}{z} + \Psi)}^{\text{Polymer}}$ where $\delta(X) = \delta_{N(X),1}$. (53)

ii) *The correlation functions $\varrho_A^{\text{Lattice}}(X)$ of the lattice gas are linear combinations of the correlation functions $\bar{\varrho}_A^{\text{Polymer}}(X)$ of the polymer system described by the activity $\Phi(X)$ given in part (i):*

$$\varrho_{A,(z,\Psi)}^{\text{Lattice}}(X) = \sum_{X = \sum X_i} \sum_{\substack{S_1, \dots, S_q \\ S_i \subset A-X \\ S_i \cap S_j = \emptyset}} \prod \Psi(X_j + S_j) \bar{\varrho}_{A,(\frac{\delta}{z} + \Psi)}^{\text{Polymer}}(X + \sum S_j). \quad (54)$$

Proof. i) $Z_{A,(z,\Psi)}^{\text{Lattice}} = \sum_{Y \subset A} z^{N(Y)} (\Gamma \Psi)(Y) = \Gamma(\delta + z^N \Psi)(A)$

therefore:

$$Z_{A,(z,\Psi)}^{\text{Lattice}} = Q_{A,(\delta + z^N \Psi)}^{\text{Polymer}} = z^{N(A)} Q_{A,(\frac{\delta}{z} + \Psi)}^{\text{Polymer}}.$$

$$\begin{aligned}
 \text{ii) } \varrho_{A,(z,\Psi)}^{\text{Lattice}} &= \frac{1}{Z_A} \sum_{Y \subset A-X} [D_X \Gamma(z^N \Psi)](Y) \\
 &= \frac{1}{Z_A} \sum_{Y \subset A-X} \sum_{X=\Sigma X_j} \sum_{\substack{S_1 \dots S_q \\ S_j \subset Y \\ S_i \cap S_j = \emptyset}} \prod_j (z^N \Psi)(X_j + S_j) [\Gamma(z^N \Psi)](Y - \Sigma S_j) \\
 &= \sum_{X=\Sigma X_j} \sum_{\substack{S_1 \dots S_q \\ S_j \subset A-X \\ S_i \cap S_j = \emptyset}} \prod_j (z^N \Psi)(X_j + S_j) \cdot \sum_{T \subset A-X-\Sigma S_j} \frac{\Gamma(z^N \Psi)(T)}{Z_A}.
 \end{aligned}$$

But

$$\frac{1}{Z_A} \sum_{T \subset A-X-S} \Gamma(z^N \Psi)(T) = \frac{1}{Z_A} \Gamma(\delta + z^N \Psi)(A - X - S) = \bar{\varrho}_{A,(\delta+z^N \Psi)}(X + S).$$

Using the scaling property (22) we arrive at the relation (54) which ends the proof.

Theorem 13. Consider a classical lattice gas described by the Hamiltonian $H(X) = -\mu N(X) + U(X)$ where the potential energy is invariant under translation.

1. If the Ursell functions $\Psi(X) = (\Gamma^{-1} e^{-\beta U})(X)$ satisfy the conditions

i) $\Psi(X) > 0$,

ii) $\sum_{X \neq \emptyset} \xi^{N(X)} \frac{\Psi(X)}{N(X)} < \infty$ for some $\xi > 0$

then the following limit exists and is finite:

$$\lim_{A \rightarrow \infty} \frac{1}{N(A)} \text{Log } Z_A^{\text{Lattice}} = p.$$

2. If there exists a real number ξ such that

$$\sum_{\substack{X \neq \emptyset \\ X \neq \emptyset}} |\Psi(0, X)| \xi^{N(X)} < \infty$$

then in the domain

$$\left| \frac{1+z}{z} \right| < \xi^{-1} \left\{ 1 + \sum_{\substack{X \neq \emptyset \\ X \neq \emptyset}} |\Psi(0, X)| \xi^{N(X)+1} \right\}$$

the following limit exists

$$\lim_{A \rightarrow \infty} \varrho_A^{\text{Lattice}}(X) = \varrho^{\text{Lattice}}(X)$$

and is analytic in z .

Proof. Part 1 follows from Lemma (6) and Theorem (6).

To show the second part, we use Theorem (5) which implies that for

$$\left| \frac{1}{z} + 1 \right| \geq \frac{1}{\xi} \left\{ 1 + \sum_{\substack{S \neq \emptyset \\ S \neq 0}} |\Psi(0, S)| \xi^{N(S)+1} \right\}$$

$\bar{\varrho}_{A, \frac{\delta}{z} + \Psi}^{\text{Polymer}}(X)$ and $\bar{\varrho}_{\frac{\delta}{z} + \Psi}^{\text{Polymer}}(X)$ are analytic in z ; moreover for any (z, Ψ) in this domain

$$|\varrho_{A, (z, \Psi)}^{\text{Lattice}}(X)| \leq \sum_{X = \sum X_i} \prod_j \sum_{S_j} |\Psi(X_j + S_j)| \xi^{N(X_j + S_j)} \cdot \|\bar{\varrho}_{A, (\frac{\delta}{z} + \Psi)}^{\text{Polymer}}\|_{\xi}$$

which yields

$$|\varrho_{A, (z, \Psi)}^{\text{Lattice}}(X)| \leq \sum_{q=1}^{N(X)} q^{N(X)} \left[\sum_S |\Psi(0, S)| \xi^{N(S)+1} \right]^q \|\bar{\varrho}_{A, (\frac{\delta}{z} + \Psi)}^{\text{Polymer}}\|_{\xi}.$$

Therefore the series defining $\varrho_{A, (z, \Psi)}^{\text{Lattice}}(X)$ is absolutely convergent; the rest follows from the uniform convergence of $\bar{\varrho}_A^{\text{Polymer}}$ to $\bar{\varrho}^{\text{Polymer}}$ when $A \rightarrow \infty$.

6.2. General Lattice System

We recall that with each point x of a finite set $A \subset \mathbb{Z}^v$ is associated a given subsystem whose states are numbered by $n_x \in \{0, 1, \dots, M\}$.

The configuration of this system A are characterised by the N -tuple:

$$n_A = (n_{x_1}, \dots, n_{x_N}) \quad N = N(A).$$

The correlation functions are defined by:

$$\varrho_A^{\text{Lattice}}(n_x) = \frac{1}{Q_A} \sum_{n_{A-x}} e^{-\beta H(n_A)}$$

where $Q_A^{\text{Lattice}} = \sum_{n_A} e^{-\beta H(n_A)}$ is the partition function

and $H(n_A) = U(n_A) - \mu(n_A)$

$$\mu(n_A) = \sum_x \mu(n_x);$$

$\mu(n_x)$ = chemical potential of the state n_x

$U(n_A)$ = potential energy corresponding to the configuration n_A .

In this case the *Ursell Functions* $\Psi(n_x)$ can again be introduced by means of a *-exponential where the *-product is defined by:

$$(f_1 * f_2)(n_x) = \sum_{Y \subset X} f_1(n_Y) f_2(n_{X-Y})$$

and we have:

$$e^{-\beta U(n_x)} = (\Gamma \Psi)(n_x) \quad \Psi(n_x) = 1.$$

We give without proof the following result:

Theorem 14. i) $Q_A^{\text{Lattice}} = Q_A^{\text{Polymer}}[\Phi]$

where

$$\Phi(X) = \sum_{n_x} e^{\beta \mu(n_x)} \Psi(n_x). \tag{55}$$

ii)

$$Q_A^{\text{Lattice}}(n_x) = \sum_{X = \sum_i X_i} \sum_{\substack{S_1, \dots, S_q \\ S_i \cap S_j = \emptyset}} \prod_i \sum_{n_{S_i}} e^{\beta \mu(n_{X_i} + S_i)} \Psi(n_{X_i} + S_i) \bar{Q}_A^{\text{Polymer}}(X + \sum S_i)$$

where $\Phi(X)$ is given by (55).

In conclusion from the existence and analyticity property of the pressure and correlation functions for polymer systems we can deduce analogous results for the pressure and correlation functions of general lattice systems.

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