4 Liquid-Vapor Equilibrium

In this chapter, we develop a rigorous theory of the liquid-vapor equilibrium. In particular, we will provide a version of the van der Waals–Maxwell theory of condensation, that was briefly presented in Section 1.1.6. For that, we will study the lattice gas and construct the main two thermodynamic quantities associated to it, namely the *free energy* and the *pressure*, under general two-body interactions. The latter will be studied for different types of microscopic interactions:

1. When particles do not interact with each other except through exclusion, the thermodynamic quantities can be computed explicitly (like in the ideal gas). This will be done in Section 4.7, where the **hard-core gas** will be studied in detail.

2. In the **nearest-neighbor** gas (Section 4.8), only neighboring particles attract each other, and a direct link with the Ising model, as introduced in Chapter 3, can be made. A satisfactory qualitative thermodynamical description of the condensation phenomenon will then be obtained by importing results from Chapter 3.

3. The **van der Waals gas** (Section 4.9) is the mean-field version of the lattice gas, and is a reformulation in this language of the Curie–Weiss model of Chapter 2. As we will see, this model displays a number of unphysical properties. Nevertheless, it turns out that Maxwell's construction appears naturally as a consequence of the Legendre transform.

4. Finally, we consider **Kac interactions** (Section 4.10), in which a small parameter $\gamma > 0$ is used to tune the range of the interaction. By sending the range of the interaction to infinity, in the so-called **van der Waals limit**, we will make a bridge between the two previous models, restoring the correct behavior of the thermodynamic potentials, and put Maxwell's construction on rigorous grounds.

In contrast to most other chapters, this one focuses more on the study of the *thermodynamic potentials*, free energy and pressure, rather than on the Gibbs distribution and its sensitivity to boundary conditions. Typical configurations under the relevant Gibbs distributions will nevertheless be briefly discussed in Sections 4.6 and 4.12.1.

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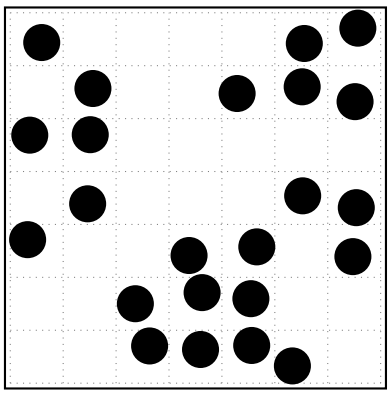

Figure 4.1: In the lattice gas approximation, the vessel is divided into imaginary cells, such that each cell can contain at most one particle.

Remark 4.1. In order to ease the physical interpretation of the results obtained, we will adopt, in this chapter, the convention used in physics: namely, we will keep the inverse temperature β outside the Hamiltonian, and will add a multiplicative constant $\frac{1}{\beta}$ in front of the free energy and pressure. ◇

We will rely on some results on real convex functions; these are collected in Appendix B.2.

4.1 The lattice gas approximation

The lattice gas was introduced informally in Chapter 1, Section 1.2.4. Consider a gas contained in a vessel. We will build a model based on van der Waals' [1] two main assumptions concerning the interactions between the particles that compose the gas:

- *repulsion*: at short distances, particles interact in a repulsive way (as small, impenetrable spheres).
- *attraction*: attractive forces act at larger distances.

In order to avoid the many technicalities inherent to the continuum (and because this book is about lattice models), we will introduce a natural discretization. Although it might appear as a significant departure from reality, we will see that it leads to satisfactory results and allows a good qualitative understanding of the corresponding phenomena.

In the **lattice gas approximation**, the vessel is partitioned into imaginary microscopic cubic cells of sidelength 1 (in some suitable units), and it is assumed that *each cell can be either empty or occupied by exactly one particle*; see Figure 4.1. Since it prevents particles from overlapping, this assumption embodies the short-range repulsive part of the interaction. Each cell is identified with a vertex $i \in \Lambda$, where Λ is some finite subset of $\mathbb{Z}^d$. As an additional simplification, we only keep track of the cells that are occupied, and not of the exact position of each particle inside its cell.

Turning to the attractive part of the interaction, we assume that a pair of particles in cells i and j contributes an amount $-K(i,j) \leq 0$ to the total energy, where

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$K(i,j)$ decreases to zero when $\|j-i\|_2 \to \infty$. We also assume that $K(\cdot,\cdot)$ is **translation invariant**: $K(i,j) = K(0,j-i)$, and **symmetric**: $K(0,-j) = K(0,j)$. The total interaction energy of the system is thus

$$-\sum_{\substack{\{i,j\}\subset\Lambda \\ i \text{ and } j \text{ occupied}}} K(i,j)\,.$$

Later, some specific choices for $K(i,j)$ will be considered.

It is natural to associate to every cell $i \in \Lambda$ its **occupation number** (notice that in Chapter 3, the corresponding random variables were denoted n_i)

$$\eta_i \stackrel{\text{def}}{=} \begin{cases} 1 & \text{if } i \text{ contains a particle,} \\ 0 & \text{otherwise.} \end{cases}$$

A **configuration** of the lattice gas in the vessel is therefore given by the set of occupation numbers, $\eta = (\eta_i)_{i\in\Lambda}$, and is thus an element of $\{0,1\}^\Lambda$. Using occupation numbers, one can consider the interaction between pairs of cells i and j, $-K(i,j)\eta_i\eta_j$, which can be non-zero only if i and j both contain a particle.

Definition 4.2. *Let $\Lambda \Subset \mathbb{Z}^d$, $\eta \in \{0,1\}^\Lambda$. The **Hamiltonian of the lattice gas in Λ** is*

$$\mathscr{H}_{\Lambda;K}(\eta) \stackrel{\text{def}}{=} -\sum_{\{i,j\}\subset\Lambda} K(i,j)\eta_i\eta_j \tag{4.1}$$

We will actually be mostly interested in systems with **finite-range** interactions, that is, those for which

$$r \stackrel{\text{def}}{=} \inf\bigl\{R \geq 0 : K(i,j) = 0 \text{ if } \|j-i\|_2 > R\bigr\} < \infty.$$

More generally, in order to have a well-defined thermodynamic limit, we will need to assume that the maximal interaction between a particle and the rest of the system is bounded. In our case, this condition can be written

$$\kappa \stackrel{\text{def}}{=} \sup_{i\in\mathbb{Z}^d} \sum_{j\neq i} K(i,j) = \sum_{j\neq 0} K(0,j) < \infty,$$

since $-\kappa$ represents the interaction of a particle with the rest of an infinite system in which each other cell contains a particle.

The **number of particles** in a configuration η can be expressed as

$$N_\Lambda(\eta) \stackrel{\text{def}}{=} \sum_{i\in\Lambda} \eta_i\,,$$

and the **empirical density** is defined by

$$\rho_\Lambda \stackrel{\text{def}}{=} \frac{N_\Lambda}{|\Lambda|}\,.$$

When studying the lattice gas in a large vessel, we will either assume that the number of particles is fixed (describing a fluid confined to some hermetically sealed container), or that this number can fluctuate (the system can exchange particles with an external reservoir). As explained in Chapter 1, these two descriptions of the gas are called respectively **canonical** and **grand canonical**. They will both be associated to a thermodynamic potential (respectively, the free energy and the pressure), which will contain the relevant information about the thermodynamic behavior of the system.

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Remark 4.3. Except in our discussion in Section 4.12.1, we will only consider free boundary condition in this chapter. The reason for this is that we are mostly interested in thermodynamic potentials and the latter turn out to be insensitive to the chosen boundary condition, for precisely the same reason as in Chapter 3. ⋄

4.2 Canonical ensemble and free energy

In the canonical ensemble (Section 1.2.2), the number of particles is fixed.

Definition 4.4. *Let $\Lambda \Subset \mathbb{Z}^d$, $N \in \{0,1,2,\dots,|\Lambda|\}$. The **canonical Gibbs distribution at inverse temperature β** is the probability distribution on $\{0,1\}^\Lambda$ defined by*

$$\nu_{\Lambda;\beta,N}(\eta) \stackrel{\text{def}}{=} \frac{\exp(-\beta \mathscr{H}_{\Lambda;K}(\eta))}{\mathbf{Q}_{\Lambda;\beta,N}} \mathbf{1}_{\{N_\Lambda(\eta)=N\}}, \tag{4.2}$$

*where the **canonical partition function** is defined by*

$$\mathbf{Q}_{\Lambda;\beta,N} \stackrel{\text{def}}{=} \sum_{\substack{\eta\in\{0,1\}^\Lambda:\\ N_\Lambda(\eta)=N}} \exp\bigl(-\beta \mathscr{H}_{\Lambda;K}(\eta)\bigr). \tag{4.3}$$

The thermodynamic potential describing an infinite system of fixed density at equilibrium is the *free energy*. It is convenient to first define the **free energy in a finite region** Λ as a function of a continuous parameter $\rho \in [0,1]$. For that, assume first that ρ is such that $\rho|\Lambda| \in \{0,1,\dots,|\Lambda|\}$ and let

$$f_{\Lambda;\beta}(\rho) \stackrel{\text{def}}{=} \frac{-1}{\beta|\Lambda|} \log \mathbf{Q}_{\Lambda;\beta,\rho|\Lambda|}. \tag{4.4}$$

This defines a function on $\{0, \frac{1}{|\Lambda|}, \frac{2}{|\Lambda|}, \dots, \frac{|\Lambda|-1}{|\Lambda|}, 1\}$, which can be extended to a continuous function on $[0,1]$ by interpolating linearly on each interval $[\frac{k}{|\Lambda|}, \frac{k+1}{|\Lambda|}]$.

When taking the thermodynamic limit $\Lambda \Uparrow \mathbb{Z}^d$ (for a definition, see page 83) in the canonical ensemble, the number of particles will increase with the size of the system, $N \to \infty$, but the density of particles will remain constant. To simplify, we will not consider the thermodynamic limit along general sequences Λ_n that converge in the sense of van Hove, but rather use everywhere sequences of **parallelepipeds**, that is, sets of the form $\bigl([a_1,b_1]\times[a_2,b_2]\times\cdots\times[a_d,b_d]\bigr)\cap\mathbb{Z}^d$. Arguments similar to those used in Section 3.2.2 can be used to remove this restriction. We denote by $\mathscr{R}$ the collection of all parallelepipeds.

Theorem 4.5. *Let $\mathscr{R} \ni \Lambda_n \Uparrow \mathbb{Z}^d$. Let $\rho \in [0,1]$ and $N_n \in \mathbb{N}$ be such that $\frac{N_n}{|\Lambda_n|} \to \rho$. The limit*

$$f_\beta(\rho) \stackrel{\text{def}}{=} \lim_{n\to\infty} f_{\Lambda_n;\beta}(N_n/|\Lambda_n|) \tag{4.5}$$

*exists, does not depend on the choice of the sequences $(\Lambda_n)_{n\geq 1}$ and $(N_n)_{n\geq 1}$, and is called the **free energy**. Moreover, the convergence is uniform on compact subsets of $(0,1)$ and $\rho \mapsto f_\beta(\rho)$ is convex and continuous on $[0,1]$.*

To prove Theorem 4.5, the first ingredient is the following basic property of the canonical partition function:

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Lemma 4.6. *Consider two disjoint regions $\Lambda, \Lambda' \Subset \mathbb{Z}^d$. If $N \le |\Lambda|$ and $N' \le |\Lambda'|$, then*

$$\mathbf{Q}_{\Lambda\cup\Lambda';\beta,N+N'} \ge \mathbf{Q}_{\Lambda;\beta,N}\mathbf{Q}_{\Lambda';\beta,N'}\,. \tag{4.6}$$

Proof. In $\mathbf{Q}_{\Lambda\cup\Lambda';\beta,N+N'}$, we obtain a lower bound by keeping only the configurations in which Λ contains N particles and Λ' contains N' particles. Moreover, since $K(i,j) \ge 0$, we can ignore the interactions between pairs of particles at vertices $i \in \Lambda$, $j \in \Lambda'$. After summing separately over the configurations in Λ and Λ', we get (4.6). □

The second ingredient is the following "continuity" property of the partition function with respect to the number of particles in the vessel:

Lemma 4.7. *Let $\Lambda \Subset \mathbb{Z}^d$ and $N \in \{0,1,\dots,|\Lambda|-1\}$. Then,*

$$\tfrac{|\Lambda|-N}{N+1}\mathbf{Q}_{\Lambda;\beta,N} \le \mathbf{Q}_{\Lambda;\beta,N+1} \le e^{\beta\kappa}\,\tfrac{|\Lambda|-N}{N+1}\mathbf{Q}_{\Lambda;\beta,N}\,. \tag{4.7}$$

Proof. Observe that

$$\begin{aligned}\mathbf{Q}_{\Lambda;\beta,N+1} &= \sum_{\substack{\eta\in\{0,1\}^\Lambda:\\ N_\Lambda(\eta)=N+1}} \exp\bigl(-\beta\mathscr{H}_{\Lambda;K}(\eta)\bigr)\\ &= \frac{1}{N+1}\sum_{\substack{\eta\in\{0,1\}^\Lambda:\\ N_\Lambda(\eta)=N}}\ \sum_{\substack{\eta'\in\{0,1\}^\Lambda:\\ \eta'_i\ge\eta_i,\forall i\\ N_\Lambda(\eta')=N+1}} \exp\bigl(-\beta\mathscr{H}_{\Lambda;K}(\eta')\bigr)\,.\end{aligned}$$

Since $\mathscr{H}_{\Lambda;K}(\eta) - \kappa \le \mathscr{H}_{\Lambda;K}(\eta') \le \mathscr{H}_{\Lambda;K}(\eta)$ and since there are exactly $|\Lambda| - N$ terms in the sum over η', this proves (4.7). □

Exercise 4.1. *Using Lemma 4.7, show that, for all $\epsilon > 0$, when Λ is large, $\mathbf{Q}_{\Lambda;\beta,N} \le \epsilon\mathbf{Q}_{\Lambda;\beta,N+1}$ if $\frac{N}{|\Lambda|}$ is sufficiently small, and $\mathbf{Q}_{\Lambda;\beta,N+1} \le \epsilon\mathbf{Q}_{\Lambda;\beta,N}$ if $\frac{N}{|\Lambda|}$ is sufficiently close to 1.*

Proof of Theorem 4.5: For simplicity, we do not include β in the notation of the partition functions. Let $\rho \in [0,1]$. We will first take for N_n the particular sequence $N_n = \lceil \rho|\Lambda_n|\rceil$, and show the existence of the limit

$$f_\beta(\rho) = \lim_{n\to\infty} \frac{-1}{\beta|\Lambda_n|}\log \mathbf{Q}_{\Lambda_n;\lceil\rho|\Lambda_n|\rceil}\,. \tag{4.8}$$

The boundary cases $\rho = 0$, $\rho = 1$, can be computed explicitly:

$$f_\beta(0) = 0\,, \qquad f_\beta(1) = -\tfrac{\kappa}{2}\,. \tag{4.9}$$

For intermediate densities, we use a subadditivity argument. For convenience, we write (4.7) as follows:

$$c^{-1}\mathbf{Q}_{\Lambda;N} \le \mathbf{Q}_{\Lambda;N+1} \le c\,\mathbf{Q}_{\Lambda;N}\,, \tag{4.10}$$

for some $c > 1$ that can be chosen uniformly if $\frac{N}{|\Lambda|}$ belongs to some closed interval $[a,b] \subset (0,1)$.

Let $\rho \in (0,1)$. For all disjoint $\Lambda', \Lambda'' \in \mathscr{R}$, with $\Lambda = \Lambda' \cup \Lambda'' \in \mathscr{R}$, we have $\lceil\rho|\Lambda|\rceil \ge \lceil\rho|\Lambda'|\rceil + \lceil\rho|\Lambda''|\rceil - 2$. Therefore, applying (4.10) twice, followed by (4.6),

$$\mathbf{Q}_{\Lambda;\lceil\rho|\Lambda|\rceil} \ge c^{-2}\mathbf{Q}_{\Lambda';\lceil\rho|\Lambda'|\rceil}\mathbf{Q}_{\Lambda'';\lceil\rho|\Lambda''|\rceil}\,.$$

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It follows that the numbers $a(\Lambda) \stackrel{\text{def}}{=} -\log(c^{-2}\mathbf{Q}_{\Lambda;\lceil\rho|\Lambda|\rceil})$ enjoy the following subadditivity property:

$$a(\Lambda' \cup \Lambda'') \le a(\Lambda') + a(\Lambda'')\,.$$

Moreover, these numbers are translation invariant: $a(\Lambda + i) = \Lambda$. This implies (see Lemma B.6) that

$$\lim_{n\to\infty} \frac{a(\Lambda_n)}{|\Lambda_n|} \quad \text{exists and equals} \quad \inf_{\Lambda\in\mathscr{R}} \frac{a(\Lambda)}{|\Lambda|}\,.$$

This shows the existence of the limit in (4.8) but also provides the following useful upper bound, valid for all $\Lambda \in \mathscr{R}$:

$$\mathbf{Q}_{\Lambda;\lceil\rho|\Lambda|\rceil} \le c^2 e^{-\beta f_\beta(\rho)|\Lambda|}\,. \tag{4.11}$$

Remark 4.8. Before going further, let us derive some simple bounds on $f_\beta(\rho)$, which we will need later. First, we can bound the energy of each configuration η appearing in $\mathbf{Q}_{\Lambda;\lceil\rho|\Lambda|\rceil}$ (everywhere below, $\Lambda \in \mathscr{R}$):

$$-\beta\mathscr{H}_{\Lambda;K}(\eta) = \tfrac{1}{2}\beta \sum_{i\in\Lambda} \eta_i \sum_{\substack{j\in\Lambda\\ j\neq i}} K(i,j)\eta_j \le \tfrac{1}{2}\beta\kappa\lceil\rho|\Lambda|\rceil\,,$$

which gives

$$\mathbf{Q}_{\Lambda;\lceil\rho|\Lambda|\rceil} \le e^{\frac{1}{2}\beta\kappa\lceil\rho|\Lambda|\rceil} \binom{|\Lambda|}{\lceil\rho|\Lambda|\rceil}. \tag{4.12}$$

Approximating the combinatorial factor using Stirling's formula as in (B.2), we can write, when $|\Lambda|$, N and $|\Lambda| - N$ are large,

$$\binom{|\Lambda|}{N} = \frac{1+o(1)}{\sqrt{2\pi N(1-\frac{N}{|\Lambda|})}} \Big\{ \big(\tfrac{N}{|\Lambda|}\big)^{\frac{N}{|\Lambda|}} \big(1-\tfrac{N}{|\Lambda|}\big)^{1-\frac{N}{|\Lambda|}} \Big\}^{-|\Lambda|}. \tag{4.13}$$

Therefore, letting

$$s^{\text{l.g.}}(\rho) \stackrel{\text{def}}{=} -\rho\log\rho - (1-\rho)\log(1-\rho)\,, \tag{4.14}$$

using (4.12) and taking the thermodynamic limit, we obtain

$$-\tfrac{1}{2}\kappa\rho - \tfrac{1}{\beta}s^{\text{l.g.}}(\rho) \le f_\beta(\rho) \le 0\,. \tag{4.15}$$

This bound implies in particular that $f_\beta(\rho)$ is finite, since $\kappa < \infty$. One can also use $-\beta\mathscr{H}_{\Lambda;K}(\eta) \ge 0$, which gives

$$f_\beta(\rho) \le -\tfrac{1}{\beta}s^{\text{l.g.}}(\rho)\,. \tag{4.16}$$

Alternatively, one can bound the partition function from below by keeping a single configuration,

$$\mathbf{Q}_{\Lambda;\lceil\rho|\Lambda|\rceil} \ge e^{-\beta\mathscr{H}_{\Lambda;K}(\eta_*)}\,. \tag{4.17}$$

Exercise 4.2. *Show that there is a configuration η_*, contributing to $\mathbf{Q}_{\Lambda;\lceil\rho|\Lambda|\rceil}$, such that*

$$\mathscr{H}_{\Lambda;K}(\eta_*) = -\tfrac{1}{2}\kappa\rho|\Lambda| + o(|\Lambda|)\,. \tag{4.18}$$

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Using (4.18) in (4.17) gives

$$f_\beta(\rho) \le -\tfrac{1}{2}\kappa\rho\,. \tag{4.19}$$

◇

Let us now assume that $(N_n)_{n\ge1}$ is an arbitrary sequence satisfying $\frac{N_n}{|\Lambda_n|} \to \rho$. We can again use (4.10) repeatedly and get, for large n,

$$c^{-|N_n-\lceil\rho|\Lambda_n|\rceil|}\mathbf{Q}_{\Lambda_n;\lceil\rho|\Lambda_n|\rceil} \le \mathbf{Q}_{\Lambda_n;N_n} \le c^{|N_n-\lceil\rho|\Lambda_n|\rceil|}\mathbf{Q}_{\Lambda_n;\lceil\rho|\Lambda_n|\rceil}\,.$$

Since $\frac{N_n-\lceil\rho|\Lambda_n|\rceil}{|\Lambda_n|} \to 0$, this shows that the limit in (4.5) exists and coincides with the one in (4.8).

Let $I = [a,b] \subset (0,1)$. Using (4.7) for $\frac{N}{|\Lambda|}, \frac{N+1}{|\Lambda|} \in I$,

$$\left|f_{\Lambda;\beta}\left(\tfrac{N+1}{|\Lambda|}\right) - f_{\Lambda;\beta}\left(\tfrac{N}{|\Lambda|}\right)\right| \le \tfrac{1}{|\Lambda|}\left\{\kappa + \tfrac{1}{\beta}\sup_{\rho\in I}\log\left(\tfrac{1-\rho}{\rho}\right)\right\}.$$

From this, one easily deduces the existence of $C = C(\beta, I) > 0$ such that, for all $\Lambda \Subset \mathbb{Z}^d$,

$$|f_{\Lambda;\beta}(\rho) - f_{\Lambda;\beta}(\rho')| \le C|\rho-\rho'|\,, \qquad \forall \rho,\rho' \in I\,. \tag{4.20}$$

Combined with the already established pointwise convergence, (4.20) implies uniform convergence on I. Moreover, the limiting function $f_\beta(\rho)$ is continuous (actually, C-Lipschitz) on I. Using (4.15)–(4.19) yields $\lim_{\rho\downarrow0} f_\beta(\rho) = 0$ and $\lim_{\rho\uparrow1} f_\beta(\rho) = -\frac{\kappa}{2}$, which by (4.9) guarantees continuity at 0 and 1.

To show that f_β is convex, we fix $\rho_1, \rho_2 \in (0,1)$ and consider the sequence of cubes $D_k = \{1,2,3,\dots,2^k\}^d$. For each k, D_{k+1} is the union of 2^d translates of D_k, denoted $D_k^{(1)},\dots,D_k^{(2^d)}$. We split these boxes into two groups, each subgroup containing $2^d/2$ boxes. Putting $\lceil\rho_1|D_k|\rceil$ particles in each box of the first group and $\lceil\rho_2|D_k|\rceil$ particles in each box of the second group, and using translation invariance,

$$\mathbf{Q}_{D_{k+1};\lceil\frac{\rho_1+\rho_2}{2}|D_{k+1}|\rceil} \ge c^{-2^d}\{\mathbf{Q}_{D_k;\lceil\rho_1|D_k|\rceil}\}^{2^d/2}\{\mathbf{Q}_{D_k;\lceil\rho_2|D_k|\rceil}\}^{2^d/2}.$$

This implies, after letting $k\to\infty$,

$$f_\beta\left(\tfrac{\rho_1+\rho_2}{2}\right) \le \tfrac{1}{2}\{f_\beta(\rho_1) + f_\beta(\rho_2)\}\,. \tag{4.21}$$

Convexity of $f_\beta(\rho)$ thus follows from its continuity (see Lemma B.11). □

4.3 Grand canonical ensemble and pressure

In the grand canonical ensemble (Section 1.2.3), the system can exchange particles with an external reservoir of fixed chemical potential μ (and inverse temperature β).

Remark 4.9. In this chapter, the letter μ always denotes the chemical potential, *not* a probability measure. ◇

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Definition 4.10. *Let $\mu \in \mathbb{R}$. The **grand canonical Gibbs distribution** at inverse temperature β is the probability distribution on $\{0,1\}^\Lambda$ defined by*

$$\nu_{\Lambda;\beta,\mu}(\eta) \stackrel{\text{def}}{=} \frac{\exp(-\beta\{\mathscr{H}_{\Lambda;K}(\eta) - \mu N_\Lambda(\eta)\})}{\Theta_{\Lambda;\beta,\mu}}, \tag{4.22}$$

*where the **grand canonical partition function** is defined by*

$$\Theta_{\Lambda;\beta,\mu} \stackrel{\text{def}}{=} \sum_{\eta\in\{0,1\}^\Lambda} \exp\bigl(-\beta\{\mathscr{H}_{\Lambda;K}(\eta) - \mu N_\Lambda(\eta)\}\bigr). \tag{4.23}$$

By summing over the possible number of particles, one gets the following simple relation between the canonical and grand canonical partition functions:

$$\Theta_{\Lambda;\beta,\mu} = \sum_{N=0}^{|\Lambda|} e^{\beta\mu N} \mathbf{Q}_{\Lambda;\beta,N}. \tag{4.24}$$

Exercise 4.3. *Let $\Lambda \Subset \mathbb{Z}^d$, and let $f, g : \{0,1\}^\Lambda \to \mathbb{R}$ be two nondecreasing functions. Using Theorem 3.50, prove that f and g are positively correlated: For all $\beta \geq 0, \mu \in \mathbb{R}$,*

$$\mathrm{Cov}_{\Lambda;\beta,\mu}(f,g) \geq 0,$$

where $\mathrm{Cov}_{\Lambda;\beta,\mu}$ denotes the covariance under $\nu_{\Lambda;\beta,\mu}$.

The thermodynamic potential describing an infinite system at equilibrium with a reservoir of particles at fixed chemical potential is the *pressure*. The **pressure in a finite volume** $\Lambda \Subset \mathbb{Z}^d$ is defined as

$$p_{\Lambda;\beta}(\mu) \stackrel{\text{def}}{=} \frac{1}{\beta|\Lambda|} \log \Theta_{\Lambda;\beta,\mu}, \quad \mu \in \mathbb{R}.$$

Observe that the derivative of the latter quantity yields the average density of particles under $\nu_{\Lambda;\beta,\mu}$:

$$\frac{\partial p_{\Lambda;\beta}}{\partial \mu} = \Bigl\langle \frac{N_\Lambda}{|\Lambda|} \Bigr\rangle_{\Lambda;\beta,\mu}. \tag{4.25}$$

We thus see that tuning the chemical potential allows one to control the average number of particles in the system. In particular, as discussed in Exercise 4.6 below, large negative values of μ result in a dilute (gas) phase, while large positive values of μ yield a dense (liquid) phase.

Theorem 4.11. *Let $\mathscr{R} \ni \Lambda_n \Uparrow \mathbb{Z}^d$. For all $\mu \in \mathbb{R}$, the limit*

$$p_\beta(\mu) \stackrel{\text{def}}{=} \lim_{n\to\infty} p_{\Lambda_n;\beta}(\mu) \tag{4.26}$$

*exists and does not depend on the choice of the sequence $(\Lambda_n)_{n\geq 1}$; it is called the **pressure**. Moreover, $\mu \mapsto p_\beta(\mu)$ is convex and continuous.*

Since p_β is convex, its derivative

$$\rho_\beta(\mu) \stackrel{\text{def}}{=} \frac{\partial p_\beta}{\partial \mu}(\mu) \tag{4.27}$$

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exists everywhere except possibly on a countable set of points (Theorem B.12) and will be called the **average (grand canonical) density**. The one-sided derivatives $\frac{\partial p_\beta}{\partial \mu^+}$ and $\frac{\partial p_\beta}{\partial \mu^-}$, are well defined at each μ. Theorem B.12, together with (4.25), also guarantees that, when $\rho_\beta(\mu)$ exists, it equals

$$\rho_\beta(\mu) = \lim_{n\to\infty} \Big\langle \frac{N_{\Lambda_n}}{|\Lambda_n|} \Big\rangle_{\Lambda_n;\beta,\mu}.$$

The existence of the limit in (4.26) will be seen to be a consequence of the existence of the free energy (see below), but it can also be proved directly:

Exercise 4.4. *Prove the existence of the pressure in Theorem 4.11 using the method suggested in Exercise 3.3.*

Theorem 4.11 leaves open the possibility that the pressure has affine pieces, along which an increase of the chemical potential μ would not result in an increase of the average density $\rho_\beta(\mu)$. This turns out to be impossible:

Theorem 4.12. *$\mu \mapsto p_\beta(\mu)$ is strictly convex and increasing.*

Proof. Differentiating (4.25) once again,

$$\frac{\partial^2 p_{\Lambda;\beta}}{\partial \mu^2} = \frac{\beta}{|\Lambda|} \mathrm{Var}_{\Lambda;\beta,\mu}(N_\Lambda),$$

where $\mathrm{Var}_{\Lambda;\beta,\mu}$ denotes the variance under $\nu_{\Lambda;\beta,\mu}$. Let us first observe that there exists $c > 0$, depending on β, κ and μ, such that

$$c < \nu_{\Lambda;\beta,\mu}\big(\eta_i = 1 \,|\, \eta_j = m_j, \forall\, j \in \Lambda \setminus \{i\}\big) < 1 - c, \qquad \forall\, i \in \Lambda, \tag{4.28}$$

for all choices of $m_j \in \{0,1\}$, $j \in \Lambda \setminus \{i\}$. In particular, $\mathrm{Var}_{\Lambda;\beta,\mu}(\eta_i) \geq c^2$) for all $i \in \Lambda$. Moreover, Exercise 4.3 guarantees that $\mathrm{Cov}_{\Lambda;\beta,\mu}(\eta_i, \eta_j) \geq 0$, so

$$\mathrm{Var}_{\Lambda;\beta,\mu}(N_\Lambda) = \sum_{i\in\Lambda} \mathrm{Var}_{\Lambda;\beta,\mu}(\eta_i) + \sum_{\substack{i,j\in\Lambda \\ i\neq j}} \mathrm{Cov}_{\Lambda;\beta,\mu}(\eta_i, \eta_j) \geq c^2\,|\Lambda|.$$

That p_β is increasing and strictly convex follows from the fact that $\frac{\partial^2 p_{\Lambda;\beta}}{\partial \mu^2} \geq \beta c^2 > 0$, uniformly in $\Lambda \Subset \mathbb{Z}^d$ (see Exercise B.5). □

Exercise 4.5. *Find the constant c in* (4.28).

Exercise 4.6. *Assuming that $p_\beta(\mu)$ exists, show that*

$$\lim_{\mu\to-\infty} p_\beta(\mu) = 0, \qquad \lim_{\mu\to+\infty} \frac{p_\beta(\mu)}{\mu} = 1. \tag{4.29}$$

Conclude that

$$\lim_{\mu\to-\infty} \rho_\beta(\mu) = 0, \qquad \lim_{\mu\to+\infty} \rho_\beta(\mu) = 1. \tag{4.30}$$

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4.4 Equivalence of ensembles

During our brief discussion of thermodynamics in Chapter 1, we saw that the entropy was related to the other thermodynamic potentials through Legendre transforms. We now check that similar relations between the free energy and pressure hold for the lattice gas.

Theorem 4.13. ***Equivalence of ensembles at the level of potentials*** *holds for the general lattice gas. That is, the free energy and pressure are each other's Legendre transform:*

$$f_\beta(\rho) = \sup_{\mu\in\mathbb{R}}\{\mu\rho - p_\beta(\mu)\} \qquad \forall \rho \in [0,1]\,, \tag{4.31}$$

$$p_\beta(\mu) = \sup_{\rho\in[0,1]}\{\rho\mu - f_\beta(\rho)\} \qquad \forall \mu \in \mathbb{R}\,. \tag{4.32}$$

Since each can be obtained from the other by a Legendre transform, f_β and p_β contain the same information about the system, and either of them can be used to study the thermodynamical behavior of the lattice gas.

Proof. We use (4.24). Since the $|\Lambda_n|+1$ terms of that sum are all nonnegative,

$$\max_N\{e^{\beta\mu N}\mathbf{Q}_{\Lambda_n;\beta,N}\} \le \Theta_{\Lambda_n;\beta,\mu} \le (|\Lambda_n|+1)\max_N\{e^{\beta\mu N}\mathbf{Q}_{\Lambda_n;\beta,N}\}\,.$$

By Exercise 4.1, we see that the maximum over N is attained for values of $\frac{N}{|\Lambda|}$ bounded away from 0 or 1. For those N, one can use (4.11):

$$\begin{aligned} e^{\beta\mu N}\mathbf{Q}_{\Lambda_n;\beta,N} &\le c^2\exp\big(\beta\{\mu\tfrac{N}{|\Lambda_n|} - f_\beta(\tfrac{N}{|\Lambda_n|})\}|\Lambda_n|\big) \\ &\le c^2\exp\big(\beta\sup_\rho\{\mu\rho - f_\beta(\rho)\}|\Lambda_n|\big)\,. \end{aligned}$$

This gives

$$\limsup_{n\to\infty}\tfrac{1}{\beta|\Lambda_n|}\log\Theta_{\Lambda_n;\beta,\mu} \le \sup_\rho\{\rho\mu - f_\beta(\rho)\}\,.$$

For the lower bound, we first use the continuity of $\rho\mapsto\rho\mu - f_\beta(\rho)$, and consider some $\rho_*\in[0,1]$ for which $\sup_\rho\{\rho\mu - f_\beta(\rho)\} = \rho_*\mu - f_\beta(\rho_*)$. Let $\epsilon>0$, and n be large enough to ensure that $\mathbf{Q}_{\Lambda_n;\beta,\lceil\rho_*|\Lambda_n|\rceil} \ge e^{-\beta f_\beta(\rho_*)|\Lambda_n| - \beta\epsilon|\Lambda_n|}$. Then, taking $N = \lceil\rho_*|\Lambda_n|\rceil$,

$$\begin{aligned} \max_N\{e^{\beta\mu N}\mathbf{Q}_{\Lambda_n;\beta,N}\} &\ge e^{\beta\mu\lceil\rho_*|\Lambda_n|\rceil}\mathbf{Q}_{\Lambda_n;\beta,\lceil\rho_*|\Lambda_n|\rceil} \\ &\ge \exp\Big(\beta\{\tfrac{\lceil\rho_*|\Lambda_n|\rceil}{|\Lambda_n|}\mu - f_\beta(\rho_*)\}|\Lambda_n| - \beta\epsilon|\Lambda_n|\Big)\,, \end{aligned}$$

which gives

$$\liminf_{n\to\infty}\tfrac{1}{\beta|\Lambda_n|}\log\Theta_{\Lambda_n;\beta,\mu} \ge \rho_*\mu - f_\beta(\rho_*) - \epsilon\,.$$

Since this holds for all $\epsilon>0$, (4.32) (and thereby the existence of the pressure) is proved. Then, $f_\beta(\rho)$ being convex and continuous, it coincides with the Legendre transform of its Legendre transform (Theorem B.19 [1]). This proves (4.31). □

[1] To apply that theorem, one needs to define $f_\beta(\rho)\stackrel{\text{def}}{=}+\infty$ for all $\rho\notin[0,1]$, so that $f_\beta:\mathbb{R}\to\mathbb{R}\cup\{\infty\}$ is convex and lower semi-continuous.

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The equivalence of ensembles allows to derive a further smoothness property for the free energy.

Corollary 4.14. *The free energy f_β is differentiable everywhere on* $(0,1)$.

Proof. If there existed a point ρ_* at which f_β were not differentiable, Theorem B.20 would imply that p_β is affine on some interval; this would contradict the claim of Theorem 4.12. □

4.5 An overview of the rest of the chapter

The existence of the free energy and pressure and the equivalence of ensembles, proved in the previous sections, hold under quite general assumptions (in our case: $\kappa < \infty$). In Section 4.6, we will see how these can be used to derive general properties of the canonical and grand canonical Gibbs distributions (similarly to what was done in earlier chapters for the Curie–Weiss and Ising models). Namely, the first concerns the typical density of particles, $\frac{N_\Lambda}{|\Lambda|}$, under the grand canonical distribution $\nu_{\Lambda;\beta,\mu}$, and the second concerns the geometrical properties of configurations under the canonical distribution $\nu_{\Lambda;\beta,N}$.

The remainder of this chapter is devoted to the study of particular cases. Our main concern will be to determine under which conditions *phase transitions* can occur at low temperature. For each of the models considered, we will study the qualitative properties of the free energy $f_\beta(\rho)$ and of the pressure $p_\beta(\mu)$. We will also express the pressure as a function of the density $\rho \in (0,1)$ and of the volume per particle $v \stackrel{\text{def}}{=} \rho^{-1}$, yielding two functions $\rho \mapsto \widetilde{p}_\beta(\rho)$, $v \mapsto \widehat{p}_\beta(v)$. Since the latter are considered at a fixed value of β, they are **isotherms of the pressure**.

A salient feature of the occurrence of phase transitions, in the canonical lattice gas, is the *condensation phenomenon*, that is, the coexistence of macroscopic regions with different densities, gas and liquid. Although a complete description of this phenomenon is outside the scope of this book, some aspects of the problem will be described in the complements at the end of the chapter (Section 4.12.1, see Figure 4.23).

4.6 Concentration and typical configurations

In this section, still under general assumptions (we only assume that $\kappa < \infty$), we use the existence of the free energy and pressure to derive properties of the Gibbs distributions.

4.6.1 Typical densities

In the grand canonical ensemble, the number of particles in Λ, N_Λ, can fluctuate, and we expect $\frac{N_\Lambda}{|\Lambda|}$ to concentrate around its average value, given by (4.25):

$$\Big\langle \frac{N_\Lambda}{|\Lambda|} \Big\rangle_{\Lambda;\beta,\mu} = \frac{\partial p_{\Lambda;\beta}}{\partial \mu}\,.$$

The next result characterizes the typical values of the density under $\nu_{\Lambda_n;\beta,\mu}$ as minimizers of a suitable function (compare with the similar results obtained in Section 2.2 in the context of mean-field models).

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Theorem 4.15. *Let $\mathscr{R} \ni \Lambda_n \Uparrow \mathbb{Z}^d$ and let $J \subset [0,1]$ be a closed interval. Then,*

$$\lim_{n\to\infty} \frac{1}{|\Lambda_n|} \log \nu_{\Lambda_n;\beta,\mu}\Big(\frac{N_{\Lambda_n}}{|\Lambda_n|} \in J\Big) = -\min_{\rho\in J} I_{\beta,\mu}(\rho)\,,$$

where

$$I_{\beta,\mu}(\rho) \stackrel{\text{def}}{=} \beta\big\{(f_\beta(\rho) - \mu\rho) - \min_{\rho'\in[0,1]} (f_\beta(\rho') - \mu\rho')\big\} \tag{4.33}$$

is called the ***rate function****.*

Proof. The proof follows the same steps as the proof of the equivalence of ensembles. Using the same decomposition as in (4.24),

$$\nu_{\Lambda;\beta,\mu}\big(\tfrac{N_\Lambda}{|\Lambda|} \in J\big) = \frac{1}{\Theta_{\Lambda;\beta,\mu}} \sum_{\substack{0\le N\le|\Lambda|:\\ N/|\Lambda|\in J}} e^{\beta\mu N} \mathbf{Q}_{\Lambda;\beta,N}\,.$$

The denominator $\Theta_{\Lambda;\beta,\mu}$ is treated using Theorem 4.13. For the numerator,

$$\max_{N:\,N/|\Lambda|\in J} \{e^{\beta\mu N}\mathbf{Q}_{\Lambda;\beta,N}\} \le \sum_{\substack{0\le N\le|\Lambda|:\\ N/|\Lambda|\in J}} e^{\beta\mu N}\mathbf{Q}_{\Lambda;\beta,N} \le (|\Lambda|+1) \max_{N:\,N/|\Lambda|\in J} \{e^{\beta\mu N}\mathbf{Q}_{\Lambda;\beta,N}\}\,,$$

and we can proceed as in the proof of Theorem 4.13. □

Consider the set of minimizers of $I_{\beta,\mu} \ge 0$:

$$\mathscr{M}_{\beta,\mu} \stackrel{\text{def}}{=} \big\{\rho \in [0,1] : I_{\beta,\mu}(\rho) = 0\big\}\,.$$

By continuity of $I_{\beta,\mu}$, $\mathscr{M}_{\beta,\mu}$ is closed. Since f_β is convex, so is $I_{\beta,\mu}$. Therefore, $\mathscr{M}_{\beta,\mu}$ is either a singleton, or a closed interval:

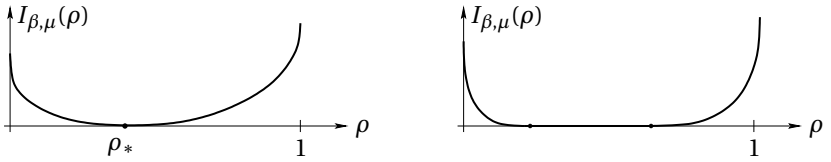

Figure 4.2: Depending on (β,μ), the minimizers of the rate function form either a singleton, $\mathscr{M}_{\beta,\mu} = \{\rho_*\}$ (on the left), or a closed interval (on the right).

Remark 4.16. Most of the plots given in this chapter were made to illustrate important features of the functions under consideration; in order to better emphasize the latter, we have often decided to accentuate them. Nevertheless, the qualitative properties have been preserved. Only those for the hard-core gas, and some of those for the van der Waals model, are drawn from an expression computed rigorously. ◇

Theorem 4.15 thus says that, in a grand canonical system with chemical potential μ, the particle density $\frac{N_\Lambda}{|\Lambda|}$ concentrates on $\mathscr{M}_{\beta,\mu}$, in the following sense: for any open set $G \subset [0,1]$, with $G \supset \mathscr{M}_{\beta,\mu}$, we have that

$$\text{as } \Lambda \Uparrow \mathbb{Z}^d\,, \quad \nu_{\Lambda;\beta,\mu}\Big(\frac{N_\Lambda}{|\Lambda|} \in G\Big) \to 1 \quad \text{exponentially fast in } |\Lambda|.$$

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Indeed, for any closed interval $J \subset [0,1] \setminus \mathscr{M}_{\beta,\mu}$, we have $\lambda \stackrel{\text{def}}{=} \min_{\rho\in J} I_{\beta,\mu}(\rho) > 0$ and, for any large enough box Λ,

$$\nu_{\Lambda;\beta,\mu}\Big(\frac{N_\Lambda}{|\Lambda|} \in J\Big) \le e^{-\frac{\lambda}{2}|\Lambda|}.$$

Densities outside $\mathscr{M}_{\beta,\mu}$ are therefore very atypical in large systems. Of course, it does not follow from the above theorem that all values in the set $\mathscr{M}_{\beta,\mu}$ are equally likely. Investigating this question requires a much more delicate analysis, taking into account *surface effects*; see the complements to this chapter (Section 4.12.1) for a discussion.

Remark 4.17. Using the equivalence of ensembles, one can also express $\mathscr{M}_{\beta,\mu}$ as

$$\mathscr{M}_{\beta,\mu} = \big\{\rho \in [0,1] : p_\beta(\mu) = \mu\rho - f_\beta(\rho)\big\}. \qquad \diamond$$

When the pressure is differentiable (that is, in the absence of a first-order phase transition), one knows exactly at which value the density concentrates:

Proposition 4.18. *Assume that p_β is differentiable at μ. Then, under $\nu_{\Lambda;\beta,\mu}$, the density $\frac{N_\Lambda}{|\Lambda|}$ concentrates on $\rho_\beta(\mu) \stackrel{\text{def}}{=} \frac{\partial p_\beta}{\partial \mu}$: for all $\epsilon > 0$, as $\Lambda \Uparrow \mathbb{Z}^d$,*

$$\nu_{\Lambda;\beta,\mu}\Big(\Big|\frac{N_\Lambda}{|\Lambda|} - \rho_\beta(\mu)\Big| \ge \epsilon\Big) \to 0, \qquad \textit{exponentially fast in } |\Lambda|.$$

Proof. If $\frac{\partial p_\beta}{\partial \mu}$ exists, then $\mathscr{M}_{\beta,\mu}$ must be a singleton (if it were an interval, f_β would be affine on that interval, a contradiction with Theorem B.20): $\mathscr{M}_{\beta,\mu} = \{\rho_*\}$. We only need to check that $\rho_* = \frac{\partial p_\beta}{\partial \mu}$. Using Remark 4.17, we see that ρ_* must satisfy $p_\beta(\mu) = \mu\rho_* - f_\beta(\rho_*)$. It thus follows from (4.32) that, for all $\epsilon > 0$,

$$p_\beta(\mu+\epsilon) - p_\beta(\mu) \ge \big\{(\mu+\epsilon)\rho_* - f_\beta(\rho_*)\big\} - p_\beta(\mu) = \epsilon\rho_*$$

and

$$p_\beta(\mu) - p_\beta(\mu-\epsilon) \le p_\beta(\mu) - \big\{(\mu-\epsilon)\rho_* - f_\beta(\rho_*)\big\} = \epsilon\rho_*,$$

which, dividing by ϵ and letting $\epsilon \downarrow 0$, gives $\frac{\partial p_\beta}{\partial \mu} = \rho_*$, proving the claim. □

4.6.2 Strict convexity and spatial homogeneity

In this section we describe typical configurations of particles in the canonical ensemble, by looking at how the density can vary from one point to another. More precisely, we will consider the canonical Gibbs distribution $\nu_{\Lambda;\beta,N}$ in a large box Λ, and assume that the density $\frac{N}{|\Lambda|} \simeq \rho$ belongs to some interval I on which the free energy is *strictly convex*:

$$f_\beta(\lambda\rho_1 + (1-\lambda)\rho_2) < \lambda f_\beta(\rho_1) + (1-\lambda) f_\beta(\rho_2),$$

for all $0 < \lambda < 1$ and all $\rho_1 < \rho_2$ in I. We will show that, under such conditions, the system is *homogeneous*: with high probability under $\nu_{\Lambda;\beta,N}$, all macroscopic sub-boxes of Λ have the same density ρ. (We have proved a similar claim in the microcanonical ensemble, in Section 1.3.1.)

We will consider the thermodynamic limit along a sequence $\mathscr{R} \ni \Lambda \Uparrow \mathbb{Z}^d$ and, for each $0 < \alpha < 1$ and each Λ, consider a collection $\mathscr{D}_\alpha(\Lambda) \subset \mathscr{R}$ of subsets $\Lambda' \subset \Lambda$, translates of each other, with the property that $\frac{|\Lambda'|}{|\Lambda|} \to \alpha$ when $\Lambda \Uparrow \mathbb{Z}^d$.

Theorem 4.19. *Let $\mathscr{R} \ni \Lambda \Uparrow \mathbb{Z}^d$. Assume that $\frac{N}{|\Lambda|} \to \rho \in (0,1)$ and that f_β is strictly convex in a neighborhood of ρ. Fix $0 < \alpha < 1$. Then, for all small $\epsilon > 0$, as $\Lambda \Uparrow \mathbb{Z}^d$,*

$$\nu_{\Lambda;\beta,N}\Big(\exists \Lambda' \in \mathscr{D}_\alpha(\Lambda) \text{ such that } \Big|\frac{N_{\Lambda'}}{|\Lambda'|} - \rho\Big| \geq \epsilon\Big) \to 0\,, \tag{4.34}$$

exponentially fast in $|\Lambda|$.

Proof. Together with $\mathscr{R} \ni \Lambda \Uparrow \mathbb{Z}^d$, we consider $N \to \infty$ such that $\frac{N}{|\Lambda|} \to \rho \in (0,1)$. Fix $\epsilon > 0$ and some $\delta > 0$ (which will be fixed later), and cover $[0,1] \setminus (\rho - \epsilon, \rho + \epsilon)$ with closed intervals J_k, $k = 1, \dots, m$, of sizes $\leq \delta$, all at distance at least ϵ from ρ. We can assume that $m \leq 2/\delta$. We will first show that there exists $b_0 > 0$ such that, when Λ is large enough,

$$\nu_{\Lambda;\beta,N}\Big(\frac{N_{\Lambda'}}{|\Lambda'|} \in J_k\Big) \leq |\Lambda| e^{-b_0|\Lambda|}\,, \tag{4.35}$$

for all $\Lambda' \in \mathscr{D}_\alpha(\Lambda)$ and all k. Since there are at most $|\Lambda|$ sub-boxes $\Lambda' \in \mathscr{D}_\alpha(\Lambda)$ and since the number of intervals J_k is bounded, the main claim will then follow.

Consider some J_k. For definiteness, we assume that $\min J_k > \rho$ (the other case is treated similarly). We can of course assume that ρ, α and J_k are such that $\{N_{\Lambda'}/|\Lambda'| \in J_k\} \neq \varnothing$. First, decompose

$$\nu_{\Lambda;\beta,N}\Big(\frac{N_{\Lambda'}}{|\Lambda'|} \in J_k\Big) = \sum_{N' : \frac{N'}{|\Lambda'|} \in J_k} \nu_{\Lambda;\beta,N}(N_{\Lambda'} = N')\,. \tag{4.36}$$

Let $\Lambda'' \stackrel{\text{def}}{=} \Lambda \setminus \Lambda'$. If the interaction has finite range (see Exercise 4.7 below for the general case), then, for all configurations $\eta \in \{0,1\}^\Lambda$,

$$\mathscr{H}_{\Lambda;K}(\eta) = \mathscr{H}_{\Lambda';K}(\eta|_{\Lambda'}) + \mathscr{H}_{\Lambda'';K}(\eta|_{\Lambda''}) + O(|\partial\Lambda|)\,, \tag{4.37}$$

where, as usual, we denote by $\eta|_\Delta$ the restriction of $\eta \in \{0,1\}^\Lambda$ to $\Delta \subset \Lambda$. Therefore, letting $N'' \stackrel{\text{def}}{=} N - N'$,

$$\nu_{\Lambda;\beta,N}(N_{\Lambda'} = N') \leq e^{O(|\partial\Lambda|)} \frac{\mathbf{Q}_{\Lambda';\beta,N'}\mathbf{Q}_{\Lambda'';\beta,N''}}{\mathbf{Q}_{\Lambda;\beta,N}}\,.$$

For the denominator, we will use

$$\lim_{\Lambda \Uparrow \mathbb{Z}^d} \frac{1}{\beta|\Lambda|} \log \mathbf{Q}_{\Lambda;\beta,N} = -f_\beta(\rho)\,.$$

Let $N'_{\min} = \min\{N' : N'/|\Lambda'| \in J_k\}$, $N''_{\max} = N - N'_{\min}$. Using Lemma 4.7 repeatedly,

$$\mathbf{Q}_{\Lambda';\beta,N'} \leq \Big[e^{\beta\kappa}\big(\frac{1 - N'_{\min}/|\Lambda'|}{N'_{\min}/|\Lambda'|} \vee 1\big)\Big]^{N' - N'_{\min}} \mathbf{Q}_{\Lambda';\beta,N'_{\min}}\,,$$
$$\mathbf{Q}_{\Lambda'';\beta,N''} \leq \Big(\frac{(N''_{\max}+1)/|\Lambda''|}{1 - N''_{\max}/|\Lambda''|} \vee 1\Big)^{N''_{\max} - N''} \mathbf{Q}_{\Lambda'';\beta,N''_{\max}}\,.$$

As $\Lambda \Uparrow \mathbb{Z}^d$, we have

$$\frac{N'_{\min}}{|\Lambda'|} \to \rho^k_{\min} \stackrel{\text{def}}{=} \min J_k\,, \qquad \frac{N''_{\max}}{|\Lambda''|} \to \rho^k_{\max}\,,$$

where $\rho^k_{\max}$ satisfies

$$\alpha\rho^k_{\min} + (1-\alpha)\rho^k_{\max} = \rho\,.$$

Therefore, since $\Lambda' \in \mathscr{R}$ and $|\Lambda'|/|\Lambda| \to \alpha$,

$$\lim_{\Lambda \Uparrow \mathbb{Z}^d} \frac{1}{\beta|\Lambda|} \log \mathbf{Q}_{\Lambda';\beta,N'_{\min}} = -\alpha f_\beta(\rho^k_{\min})\,.$$

Observe that Λ'' is *not* a parallelepiped, but we can use Lemma 4.6 as follows:

$$\mathbf{Q}_{\Lambda'';\beta,N''_{\max}} \le \frac{\mathbf{Q}_{\Lambda;\beta,\tilde{N}}}{\mathbf{Q}_{\Lambda';\beta,\tilde{N}'}}\,, \tag{4.38}$$

where $\tilde{N}' \stackrel{\text{def}}{=} \lfloor \frac{N''_{\max}}{|\Lambda''|}|\Lambda'| \rfloor$, $\tilde{N} \stackrel{\text{def}}{=} N''_{\max} + \tilde{N}'$. Now, $\frac{\tilde{N}}{|\Lambda|} \to \rho^k_{\max}$, and $\frac{\tilde{N}'}{|\Lambda'|} \to \rho^k_{\max}$. Therefore,

$$\lim_{\Lambda \Uparrow \mathbb{Z}^d} \frac{1}{\beta|\Lambda|} \log \frac{\mathbf{Q}_{\Lambda;\beta,\tilde{N}}}{\mathbf{Q}_{\Lambda';\beta,\tilde{N}'}} = -(1-\alpha) f_\beta(\rho^k_{\max})\,.$$

We have thus proved that

$$\begin{aligned}\limsup_{\Lambda \Uparrow \mathbb{Z}^d} \frac{1}{\beta|\Lambda|} \log \max_{N' : \frac{N'}{|\Lambda'|} \in J_k} & \nu_{\Lambda;\beta,N}(N_{\Lambda'} = N') \\ & \le M_k\delta - \left\{\alpha f_\beta(\rho^k_{\min}) + (1-\alpha) f_\beta(\rho^k_{\max}) - f_\beta(\rho)\right\},\end{aligned}$$

where

$$M_k \stackrel{\text{def}}{=} \kappa + \log\Big(\frac{1-\rho^k_{\min}}{\rho^k_{\min}} \vee 1\Big) + \log\Big(\frac{\rho^k_{\max}}{1-\rho^k_{\max}} \vee 1\Big).$$

Observe that M_k is bounded uniformly in k. Namely, there exists $0 < \epsilon' < \epsilon$ (depending on ρ and α) such that $\rho^k_{\max} < \rho - \epsilon' < \rho + \epsilon < \rho^k_{\min}$ for all k. Moreover, by the strict convexity of f_β in a neighborhood of ρ, there exists some $b_0 > 0$ such that

$$\min_{1 \le k \le m} \left\{\alpha f_\beta(\rho^k_{\min}) + (1-\alpha) f_\beta(\rho^k_{\max}) - f_\beta(\rho)\right\} \ge 2b_0 > 0\,,$$

uniformly in m. One can thus take δ small enough so that $M_k\delta \le b_0$. The sum in (4.36) contains at most $|\Lambda|$ terms, which proves (4.35) for large enough Λ. □

Exercise 4.7. *Show that, when the interaction is not of finite range (but assuming $\kappa < \infty$),* (4.37) *becomes*

$$\mathscr{H}_{\Lambda;K}(\eta) = \mathscr{H}_{\Lambda';K}(\eta|_{\Lambda'}) + \mathscr{H}_{\Lambda'';K}(\eta|_{\Lambda''}) + o(|\Lambda|)\,,$$

so that the rest of the proof remains unchanged.

4.7 The hard-core lattice gas

Let us see what happens when

$$K(i,j) = 0$$

for all pairs i, j. This model, already considered in Chapter 1, is called the **hard-core lattice gas**, since the only interaction between the particles is the constraint of having at most one of them at each vertex. Due to the lack of an attractive part

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in its Hamiltonian, this model will not present a particularly interesting behavior, but it remains a good starting point, since its thermodynamic potentials can be computed explicitly.

When $K \equiv 0$, the canonical partition function becomes a purely combinatorial quantity, counting the configurations $\eta \in \{0,1\}^\Lambda$ with $N_\Lambda(\eta) = N$:

$$\mathbf{Q}^{\text{hard}}_{\Lambda;N} = \binom{|\Lambda|}{N}.$$

Since $\binom{|\Lambda|}{0} = \binom{|\Lambda|}{|\Lambda|} = 1$, we get $f^{\text{hard}}_\beta(0) = f^{\text{hard}}_\beta(1) = 0$. For intermediate densities, $0 < \rho < 1$, we use again (4.13)–(4.14), and obtain (see Figure 4.3)

$$f^{\text{hard}}_\beta(\rho) = -\tfrac{1}{\beta} s^{\text{l.g.}}(\rho)\,. \tag{4.39}$$

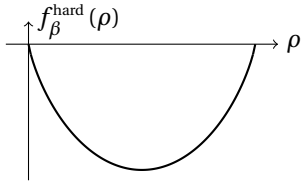

Figure 4.3: The free energy of the hard-core lattice gas, strictly convex at all temperatures.

The pressure can also be computed explicitly (see Figure 4.4), using either the equivalence of ensembles, or simply (4.24):

$$\Theta^{\text{hard}}_{\Lambda;\mu} = \sum_{N=0}^{|\Lambda|} \binom{|\Lambda|}{N} e^{\beta\mu N} = (1 + e^{\beta\mu})^{|\Lambda|}\,,$$

which yields

$$p^{\text{hard}}_\beta(\mu) = \frac{1}{\beta}\log(1 + e^{\beta\mu})\,. \tag{4.40}$$

The expressions obtained for $f^{\text{hard}}_\beta(\rho)$ and $p^{\text{hard}}_\beta(\mu)$ imply that these functions are analytic. We will now see how to express the pressure as a function of ρ rather than μ. To this end, one must answer the following question: can one realize a chosen average density ρ by suitably tuning μ?

Observe that the average density of particles,

$$\rho^{\text{hard}}_\beta(\mu) = \frac{\partial p^{\text{hard}}_\beta}{\partial\mu} = \frac{e^{\beta\mu}}{1 + e^{\beta\mu}}\,, \tag{4.41}$$

is smooth for all values of μ: when μ increases from $-\infty$ to $+\infty$, the density of the hard-core gas increases from 0 to 1 without discontinuities and exhibits no phase transition (see Figure 4.4). This absence of condensation is of course due to the lack of attraction between the particles.

By Proposition 4.18, we also know that the density of particles in a large grand canonical system, $\frac{N_\Lambda}{|\Lambda|}$, concentrates on $\rho^{\text{hard}}_\beta(\mu)$. Since $\rho^{\text{hard}}_\beta(\mu)$ is increasing in μ, the equation

$$\rho^{\text{hard}}_\beta(\mu) = \rho \tag{4.42}$$

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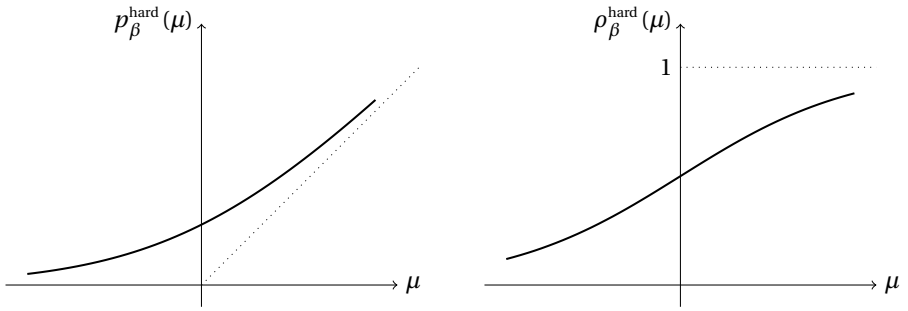

Figure 4.4: The pressure and average density of the hard-core lattice gas.

has a unique solution in μ, for each fixed $\rho \in (0,1)$. This solution can of course be given explicitly:

$$\mu_\beta^{\text{hard}}(\rho) = \tfrac{1}{\beta} \log \tfrac{\rho}{1-\rho}\,.$$

Therefore, densities $\rho \in (0,1)$ are in one-to-one correspondence with chemical potentials $\mu \in \mathbb{R}$. This bijection allows to express the pressure as a function of the density:

$$\widetilde{p}_\beta^{\text{hard}}(\rho) \stackrel{\text{def}}{=} p_\beta^{\text{hard}}(\mu_\beta^{\text{hard}}(\rho)) = -\tfrac{1}{\beta}\log(1-\rho)\,.$$

At low densities, $\log(1-\rho) \simeq -\rho$, which allows to recover the qualitative behavior provided by the equation of state of the ideal gas:

$$\beta \widetilde{p}_\beta^{\text{hard}}(\rho) = \rho + O(\rho^2) \qquad (\rho \text{ small})\,.$$

In terms of the **volume per particle**, $v = \rho^{-1}$,

$$\widehat{p}_\beta^{\text{hard}}(v) \stackrel{\text{def}}{=} \widetilde{p}_\beta^{\text{hard}}(v^{-1}) = -\tfrac{1}{\beta}\log\bigl(1-\tfrac{1}{v}\bigr)\,.$$

Remark 4.20. When v is large, $-\log(1-\frac{1}{v}) \simeq \frac{1}{v}$, and the above provides an approximation to the *Ideal Gas Law* (1.14), with $R = 1$,

$$pv = RT\,. \qquad \diamond$$

4.7.1 Parenthesis: equivalence of ensembles at the level of measures

Consider the canonical hard-core lattice gas along a sequence $\Lambda \Uparrow \mathbb{Z}^d$, $N \to \infty$, with $\frac{N}{|\Lambda|} \to \rho$. What can be said about the distribution of particles in a smaller subsystem $\Delta \subset \Lambda$, whose size remains fixed as $\Lambda \Uparrow \mathbb{Z}^d$?

Although the density of particles in Λ is fixed, close to ρ, the number of particles in Δ can fluctuate. We therefore expect to obtain, when $\Lambda \Uparrow \mathbb{Z}^d$, some distribution of the grand canonical type inside Δ, with a chemical potential μ to be determined; not surprisingly, it will be exactly the one obtained earlier through the relation (4.42).

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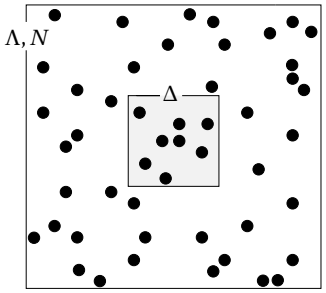

Figure 4.5: In a large system Λ with a fixed number of particles N, what can be said about the probability distribution describing a smaller subsystem $\Delta \subset \Lambda$?

Proposition 4.21. *Let $\Delta \Subset \mathbb{Z}^d$, $\Lambda \Uparrow \mathbb{Z}^d$, and assume that $\frac{N}{|\Lambda|} \to \rho \in (0,1)$. Let $\eta_\Delta \in \{0,1\}^\Delta$ be any configuration of particles in Δ. Then, as $\Lambda \Uparrow \mathbb{Z}^d$,*

$$\nu_{\Lambda;\beta,N}\big(\{\eta : \eta|_\Delta = \eta_\Delta\}\big) \longrightarrow \nu_{\Delta;\beta,\mu}(\eta_\Delta)\,, \tag{4.43}$$

where μ is the unique solution to (4.42).

Relation (4.43) is the simplest instance of **equivalence of ensembles at the level of measures**. A similar statement holds much more generally, at least away from phase transitions, but is substantially harder to establish [2].

Proof. The proof is a direct application of Stirling's formula: if $M = N_\Delta(\eta_\Delta)$,

$$\nu_{\Lambda;\beta,N}\big(\{\eta : \eta|_\Delta = \eta_\Delta\}\big) = \frac{\binom{|\Lambda|-|\Delta|}{N-M}}{\binom{|\Lambda|}{N}} = (1+o(1))\Big(1-\frac{N}{|\Lambda|}\Big)^{|\Delta|}\Big(\frac{N}{|\Lambda|-N}\Big)^M.$$

Since $\frac{N}{|\Lambda|} \to \rho$ and since (4.42) can be written as $\frac{\rho}{1-\rho} = e^{\beta\mu_\beta^{\mathrm{hard}}(\rho)}$,

$$\Big(\frac{N}{|\Lambda|-N}\Big)^M \longrightarrow \Big(\frac{\rho}{1-\rho}\Big)^M = \exp\{\beta\mu_\beta^{\mathrm{hard}}(\rho)M\}\,,$$

and

$$\Big(1-\frac{N}{|\Lambda|}\Big)^{|\Delta|} \longrightarrow (1-\rho)^{|\Delta|} = \frac{1}{(1+e^{\beta\mu_\beta^{\mathrm{hard}}(\rho)})^{|\Delta|}} = \frac{1}{\Theta_{\Delta;\beta,\mu_\beta^{\mathrm{hard}}(\rho)}}\,. \qquad \square$$

4.8 The nearest-neighbor lattice gas

In this section, we take further advantage of the binary nature of the lattice gas to link it precisely to the Ising ferromagnet. The occupation numbers $\eta_i \in \{0,1\}$ of the lattice gas can be mapped to Ising spins $\omega_i \in \{-1,+1\}$, by

$$\eta_i \mapsto \omega_i \stackrel{\mathrm{def}}{=} 2\eta_i - 1\,. \tag{4.44}$$

Expressed in terms of the Ising spins, the exponent in (4.22) becomes

$$\beta\big\{\mathscr{H}_{\Lambda;K}(\eta) - \mu N_\Lambda(\eta)\big\} = -\frac{\beta}{4}\sum_{\{i,j\}\subset\Lambda} K(i,j)\omega_i\omega_j - \frac{\beta}{4}(\kappa+2\mu)\sum_{i\in\Lambda}\omega_i - \beta(\tfrac{\mu}{2}+\tfrac{\kappa}{8})|\Lambda| + b_\Lambda\,,$$

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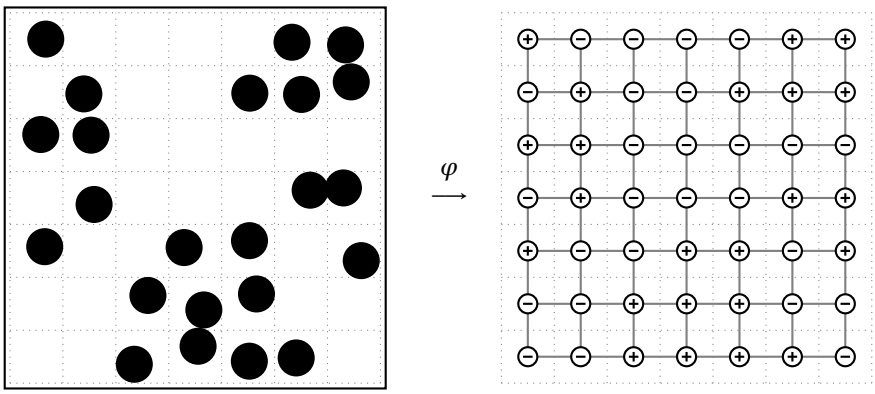

Figure 4.6: On the left, a configuration of the lattice gas, in which each cell i is either occupied by a particle, or empty. The occupation variables $\eta_i \in \{0,1\}$ are mapped to spin variables $\omega_i \in \{\pm 1\}$ (picture on the right) using the mapping (4.44).

where $b_\Lambda = o(|\Lambda|)$ (see exercise below). We thus see that the lattice gas is linked to an Ising ferromagnet with coupling constants $J_{ij} = \frac{\beta}{4} K(i,j) \geq 0$ and magnetic field $h' = \frac{\beta}{4}(\kappa + 2\mu)$.

Exercise 4.8. *Compute b_Λ, and show that*

$$\lim_{\Lambda \Uparrow \mathbb{Z}^d} \frac{|b_\Lambda|}{|\Lambda|} = 0 .$$

In order to take advantage of the results obtained in Chapter 3, in this subsection we restrict to the **nearest-neighbor lattice gas**, for which

$$K(i,j) \stackrel{\text{def}}{=} \mathbf{1}_{\{i \sim j\}} . \tag{4.45}$$

In this case, $\kappa = 2d$.

4.8.1 The pressure

The parameters (β, μ) of the grand-canonical lattice gas are related to those of the nearest-neighbor Ising model, (β', h'), by the relations

$$\beta' = \tfrac{1}{4}\beta , \qquad h' = \tfrac{\beta}{4}(\kappa + 2\mu) .$$

By Exercise 4.8, for all $\epsilon > 0$, one can take n sufficiently large so that

$$e^{-\epsilon |\mathsf{B}(n)|} e^{\beta(\frac{\mu}{2} + \frac{\kappa}{8})|\mathsf{B}(n)|} \mathbf{Z}^{\varnothing}_{\mathsf{B}(n);\beta',h'} \leq \Theta_{\mathsf{B}(n);\beta,\mu} \leq e^{\epsilon |\mathsf{B}(n)|} e^{\beta(\frac{\mu}{2} + \frac{\kappa}{8})|\mathsf{B}(n)|} \mathbf{Z}^{\varnothing}_{\mathsf{B}(n);\beta',h'} .$$

We thus get, after taking the limits $n \to \infty$ and $\epsilon \downarrow 0$,

$$\beta p_\beta(\mu) = \psi_{\beta'}(h') + \tfrac{\beta\mu}{2} + \tfrac{\beta\kappa}{8} . \tag{4.46}$$

We can now extract qualitative information from the Ising model and translate it into the lattice gas language.

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For instance, we know from Theorem 3.9 that, in $d = 1$, $h' \mapsto \psi_{\beta'}(h')$ is everywhere analytic in h' (at all temperatures). This implies that the corresponding lattice gas has no phase transition, $\mu \mapsto p_\beta(\mu)$ being analytic everywhere. In fact, the exact solution of Theorem 3.9, together with (4.46), yields an explicit expression for $p_\beta(\mu)$.

When $d \geq 2$, it follows from the Lee–Yang Circle Theorem and Theorem 3.40 that $\psi_{\beta'}$ is analytic at least outside $h' = 0$. Therefore, to $h' = 0$ corresponds the unique value of the chemical potential at which the lattice gas can exhibit a first-order phase transition, namely:

$$\mu_* \stackrel{\text{def}}{=} -\tfrac{1}{2}\kappa .$$

We also know, from Theorem 3.34 and Peierls' argument, that there exists an inverse critical temperature $\beta_c(d) \in (0,\infty)$ such that a first-order phase transition does occur whenever $\beta' > \beta_c(d)$; see (3.27). We gather these results in the following

Theorem 4.22. *Let $\mu \mapsto p_\beta(\mu)$ denote the pressure of the nearest-neighbor lattice gas.*

1. *When $d = 1$, p_β is analytic everywhere.*
2. *When $d \geq 2$, p_β is analytic everywhere on $\{\mu : \mu \neq \mu_*\}$. Moreover, letting*

$$\beta_c^{\text{l.g.}} = \beta_c^{\text{l.g.}}(d) \stackrel{\text{def}}{=} 4\beta_c(d) ,$$

p_β is differentiable at μ_* if $\beta < \beta_c^{\text{l.g.}}$, but non-differentiable at μ_* if $\beta > \beta_c^{\text{l.g.}}$.

In particular, at all temperatures, the density of particles $\mu \mapsto \rho_\beta(\mu) = \frac{\partial p_\beta}{\partial \mu}$ exists (and is analytic) everywhere outside μ_*. Using (4.46), the latter can be related directly to the infinite-volume magnetization $m_{\beta'}$ of the Ising model:

$$\rho_\beta(\mu) = \frac{\partial p_\beta}{\partial \mu} = \frac{1}{\beta}\frac{\partial \psi_{\beta'}}{\partial h'}\frac{\partial h'}{\partial \mu} + \frac{1}{2} = \frac{1 + m_{\beta'}(h')}{2} .$$

(We write $m_{\beta'}(h')$ rather than $m(\beta', h')$, since we are mainly interested in the dependence on h'.) We call $(-\infty, \mu_*)$ the **gas branch** of the pressure, and $(\mu_*, +\infty)$ the **liquid branch**. Although the pressure is not differentiable at μ_* when $\beta > \beta_c^{\text{l.g.}}$, convexity guarantees that its one-sided derivatives are well defined and given by

$$\rho_l \stackrel{\text{def}}{=} \frac{\partial p_\beta}{\partial \mu^+}\Big|_{\mu_*} = \frac{1 + m^*_{\beta'}}{2} , \qquad \rho_g \stackrel{\text{def}}{=} \frac{\partial p_\beta}{\partial \mu^-}\Big|_{\mu_*} = \frac{1 - m^*_{\beta'}}{2} .$$

At μ_*, the grand-canonical system becomes sensitive to the boundary condition, and the density is only guaranteed to satisfy $\rho_g \leq \rho \leq \rho_l$. The reader can actually take a look back at the pictures of Figure 1.9 for the typical configurations of the lattice gas at low and high temperature. Observe that the densities ρ_g, ρ_l always satisfy

$$\rho_g + \rho_l = 1 . \tag{4.47}$$

(Let us mention that this property is really a consequence of the hidden spin-flip symmetry of the underlying Ising model, and does not hold in general lattice gases.) The pressure and the density have therefore the qualitative behavior displayed in Figure 4.7. (We remind the reader that the graphs shown in this section are only qualitative; their purpose is to emphasize the main features observed in the nearest-neighbor lattice gas.)

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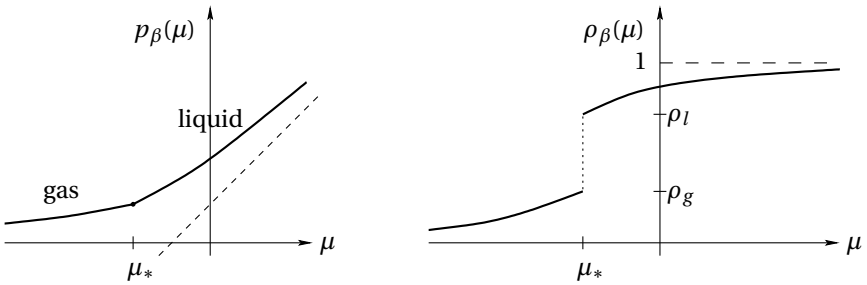

Figure 4.7: The pressure and density of the nearest-neighbor lattice gas, exhibiting a first-order phase transition when $\beta > \beta_c^{\text{l.g.}}$. The function $\mu \mapsto p_\beta(\mu)$ is analytic everywhere, except at μ_*, at which the one-sided derivatives differ, implying a jump in density, corresponding to the change from a gas of density ρ_g to a liquid of density ρ_l.

4.8.2 The free energy

In the canonical ensemble, we can obtain the main qualitative properties of the free energy using the fact that it is the Legendre transform of the pressure and applying Theorem B.20.

At high temperature, $\beta < \beta_c^{\text{l.g.}}$, the pressure is differentiable everywhere and the free energy is therefore strictly convex; see Figure 4.8. By Theorem 4.19, this implies that the typical configurations under the canonical Gibbs distribution are always spatially homogeneous, at all densities.

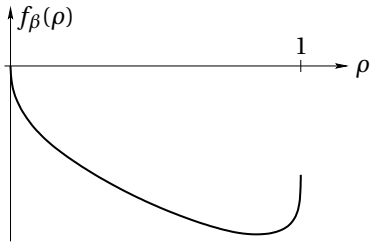

Figure 4.8: The free energy of the nearest-neighbor lattice gas is strictly convex when $\beta < \beta_c^{\text{l.g.}}$.

At low temperature, when $\beta > \beta_c^{\text{l.g.}}$, p_β is not differentiable at μ_* and, again by Theorem B.20, f_β is affine on the interval $[\rho_g, \rho_l]$, called the **coexistence plateau**. As for the pressure, we refer to $(0, \rho_g)$ as the **gas branch**, and to $(\rho_l, 1)$ as the **liquid branch**; see Figure 4.9.

Exercise 4.9. *Show that when $\beta > \beta_c^{\text{l.g.}}$, f_β is analytic on the gas and liquid branches.* Hint: *use Theorem 4.22, the strict convexity of the pressure, and the implicit function theorem.*

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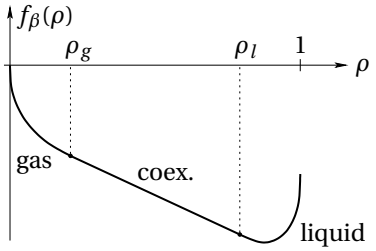

Figure 4.9: The free energy of the nearest-neighbor lattice gas, when $\beta > \beta_c^{l.g.}$, is analytic everywhere (see Exercise 4.9) except at ρ_g and ρ_l. On the coexistence plateau $[\rho_g, \rho_l]$, both gas and liquid are present in the system, in various proportions: there is *coexistence* and *phase separation*.

4.8.3 Typical densities

The typical density $\frac{N_\Lambda}{|\Lambda|}$ under the grand canonical Gibbs distribution $\nu_{\Lambda;\beta,\mu}$ can be characterized using the analysis following Theorem 4.15; see Figure 4.10.

When $\beta \le \beta_c^{l.g.}$ and for all $\mu \in \mathbb{R}$, the rate function $I_{\beta,\mu}$ is strictly convex and has a unique minimizer, $\mathscr{M}_{\beta,\mu} = \{\partial p_\beta / \partial \mu\}$, at which the density concentrates. The scenario is similar if $\beta > \beta_c^{l.g.}$ and $\mu \neq \mu_*$.

When $\beta > \beta_c^{l.g.}$ and $\mu = \mu_*$, the rate function attains its minima on the coexistence plateau: $\mathscr{M}_{\beta,\mu} = [\rho_g, \rho_l]$.

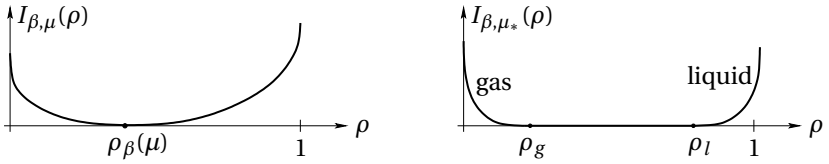

Figure 4.10: Values of the density at which the rate function does not attain its minimum are very unlikely to be observed in a large system distributed according to $\nu_{\Lambda;\beta,\mu}$. When $\beta < \beta_c^{l.g.}$, or when $\beta > \beta_c^{l.g.}$ and $\mu \neq \mu_*$ (on the left), $I_{\beta,\mu}(\rho)$ has a unique minimum at $\rho_\beta(\mu)$. When $\beta > \beta_c^{l.g.}$ and $\mu = \mu_*$ (on the right), $I_{\beta,\mu_*}(\rho)$ is minimal on the whole coexistence plateau.

Theorem 4.15 does not provide any information on the typical densities when $\mu = \mu_*$, beyond concentration on the coexistence plateau, and a more detailed analysis is necessary; this will be discussed in Section 4.12.1.

4.8.4 The pressure as a function of ρ and v.

Let us now express the pressure in terms of either the density ρ or the volume per particle $v = \rho^{-1}$.

When $\beta \le \beta_c^{l.g.}$, p_β is differentiable for all values of μ and $\rho_\beta(\mu) = \frac{\partial p_\beta}{\partial \mu}$ is continuous (Theorem B.12) and increasing. Remember from Exercise 4.6 that $\rho_\beta(\mu) \to 0$ as $\mu \to -\infty$, and $\rho_\beta(\mu) \to 1$ as $\mu \to +\infty$. Therefore, one can proceed as for the hardcore gas: for any $\rho \in (0,1)$, the equation

$$\rho_\beta(\mu) = \rho \tag{4.48}$$

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has a unique solution, which we denote $\mu_\beta^{\text{l.g.}}(\rho)$. We can thus define

$$\widetilde{p}_\beta(\rho) \stackrel{\text{def}}{=} p_\beta(\mu_\beta^{\text{l.g.}}(\rho)), \quad \rho \in (0,1). \tag{4.49}$$

When $\beta > \beta_c^{\text{l.g.}}$, existence of a solution to (4.48) is not guaranteed for all $\rho \in (0,1)$, because of the jump of $\rho_\beta(\mu)$ at μ_* (see Figure 4.7). In fact, inversion is only possible when $\rho < \rho_g$ or $\rho > \rho_l$; in this case, we also denote the inverse by $\mu_\beta^{\text{l.g.}}(\rho)$. To extend this function to a well-defined $\mu_\beta^{\text{l.g.}} : (0,1) \to \mathbb{R}$, we set

$$\mu_\beta^{\text{l.g.}}(\rho) \stackrel{\text{def}}{=} \mu_* \qquad \forall \rho \in [\rho_g, \rho_l]. \tag{4.50}$$

The reason for defining the inverse that way on the coexistence plateau is that, for finite systems, the average particle density in Λ, which is equal to $\frac{\partial p_{\Lambda;\beta}(\mu)}{\partial \mu}$, is increasing and differentiable (in fact, analytic) as a function of μ. In particular, to any density $\rho \in (0,1)$ is associated a unique value $\mu_{\Lambda;\beta}(\rho)$ of the chemical potential. The latter function being increasing, it is clear that it converges for all $\rho \in (0,1)$, as $\Lambda \Uparrow \mathbb{Z}^d$, to the function $\mu_\beta^{\text{l.g.}}(\rho)$ defined above. ◇

We can then define $\widetilde{p}_\beta(\rho)$ as in (4.49). Its qualitative behavior is sketched in Figure 4.11.

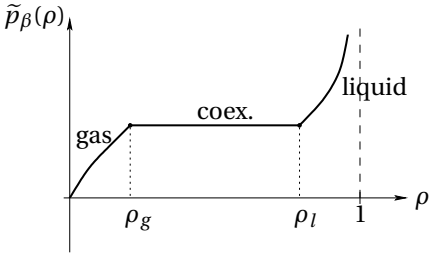

Figure 4.11: The pressure of the nearest-neighbor lattice gas at low temperature, as a function of the density $\rho \in (0,1)$.

Remark 4.23. In Section 5.7.2, we will see that the nearest-neighbor lattice gas also presents the ideal gas behavior at small densities:

$$\beta \widetilde{p}_\beta(\rho) = \rho + O(\rho^2), \qquad (\rho \text{ small}).$$

Using the *cluster expansion technique*, we will see in Theorem 5.12 that the coefficients of the **virial expansion** can actually be computed, yielding the exact higher-order corrections to the pressure at low density:

$$\beta \widetilde{p}_\beta(\rho) = \rho + b_2\rho^2 + b_3\rho^3 + \ldots \qquad (\rho \text{ small}). \qquad \diamond$$

Exercise 4.10. *Show that, when $\beta > \beta_c^{\text{l.g.}}$, $\rho \mapsto \widetilde{p}_\beta(\rho)$ is analytic on the gas and liquid branches.*

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Finally, we can also express the pressure as a function of the volume per particle, $v = \rho^{-1}$,

$$\widehat{p}_\beta(v) \stackrel{\text{def}}{=} \widetilde{p}_\beta(v^{-1}), \qquad v \in (1, \infty),$$

to obtain the qualitative behavior of the isotherms in a form directly comparable to the van der Waals–Maxwell theory. The sketch of a typical low temperature isotherm is given in Figure 4.12, where we have set $v_l \stackrel{\text{def}}{=} \rho_l^{-1}$ and $v_g \stackrel{\text{def}}{=} \rho_g^{-1}$.

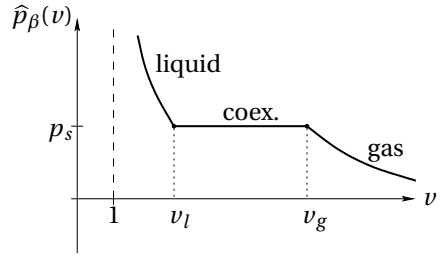

Figure 4.12: The pressure of the nearest-neighbor lattice gas at low temperature, as a function of the volume per particle $v > 1$. The value $v = 1$ plays the same role as $v = b$ in van der Waals' isotherms (Figure 1.4). The **saturation pressure** is given by $p_s = p_\beta(\mu_*)$.

4.9 The van der Waals lattice gas

In this section, we consider a lattice gas that does not fit in the general framework described earlier, but which will be important from the point of view of the van der Waals–Maxwell theory, especially in the next section.

Consider a lattice gas in a vessel $\Lambda \Subset \mathbb{Z}^d$, in which the interaction between the particles at vertices $i, j \in \Lambda$ is given by

$$K(i,j) \stackrel{\text{def}}{=} \frac{1}{|\Lambda|}. \tag{4.51}$$

This type of interaction is not physical, since the contribution to the total energy from a pair of particles depends on the size of the region Λ in which they live: it becomes of infinite range and tends to zero when $|\Lambda| \to \infty$. Nevertheless, the sum over the pairs of particles can be expressed as

$$\begin{aligned}\sum_{\{i,j\}\subset\Lambda} K(i,j)\eta_i\eta_j &= \frac{1}{2|\Lambda|}\sum_{i\in\Lambda}\sum_{\substack{j\in\Lambda\\ j\neq i}}\eta_i\eta_j \\ &= \frac{1}{2|\Lambda|}\sum_{i\in\Lambda}\eta_i\Big(\sum_{j\in\Lambda}\eta_j - \eta_i\Big) = \tfrac{1}{2}\rho_\Lambda^2|\Lambda| - \tfrac{1}{2}\rho_\Lambda,\end{aligned}$$

where $\rho_\Lambda \stackrel{\text{def}}{=} \frac{N_\Lambda}{|\Lambda|}$ is the empirical density. Since it is bounded, the second term $-\frac{1}{2}\rho_\Lambda$ does not contribute on the macroscopic scale and will be neglected.

Therefore, although not physically realistic, interactions of the form (4.51) lead to a model in which the square of the density appears explicitly in the Hamiltonian. In this sense, it can be considered as a microscopic toy model that embodies the

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main assumption made by van der Waals and discussed in Chapter 1. This model, with Hamiltonian

$$\mathscr{H}^{\mathrm{vW}}_{\Lambda;\mu} \stackrel{\mathrm{def}}{=} -\tfrac{1}{2}\rho_\Lambda^2|\Lambda| - \mu\rho_\Lambda|\Lambda|\,,$$

will be called the **van der Waals model**.

We already encountered the same interaction (formulated in the spin language) when considering the Curie–Weiss Model in Section 2.1 (remember in particular the Curie–Weiss Hamiltonian (2.4)). Therefore, this model could also be called the **mean-field** or **Curie–Weiss** lattice gas. A large part of the rest of this section will be the translation of the discussion of Section 2.1 in the lattice gas language. We nevertheless discuss a new important feature: its link with Maxwell's Construction.

Let us denote the canonical and grand canonical partition functions of the van der Waals model by $\mathbf{Q}^{\mathrm{vW}}_{\Lambda;\beta,N}$, respectively $\Theta^{\mathrm{vW}}_{\Lambda;\beta,\mu}$, and consider the associated free energy and pressure:

$$f^{\mathrm{vW}}_\beta(\rho) \stackrel{\mathrm{def}}{=} \lim_{n\to\infty} \frac{-1}{\beta|\Lambda_n|}\log \mathbf{Q}^{\mathrm{vW}}_{\Lambda_n;\beta,\lceil\rho|\Lambda_n|\rceil}\,, \quad \rho\in[0,1]\,,$$
$$p^{\mathrm{vW}}_\beta(\mu) \stackrel{\mathrm{def}}{=} \lim_{n\to\infty} \frac{1}{\beta|\Lambda_n|}\log \Theta^{\mathrm{vW}}_{\Lambda_n;\beta,\mu}\,, \qquad \mu\in\mathbb{R}\,.$$

The dependence of $K(i,j)$ on Λ prevents us from using Theorems 4.5 and 4.11 to show the existence of these limits. However, it is not difficult to compute the latter explicitly. Remember the definition of $s^{\mathrm{l.g.}}(\rho)$ in (4.14).

Theorem 4.24. *The above limits exist, and are given by*

$$f^{\mathrm{vW}}_\beta(\rho) = -\tfrac{1}{2}\rho^2 - \tfrac{1}{\beta}s^{\mathrm{l.g.}}(\rho)\,, \tag{4.52}$$
$$p^{\mathrm{vW}}_\beta(\mu) = \sup_{\rho\in[0,1]}\{\mu\rho - f^{\mathrm{vW}}_\beta(\rho)\}\,. \tag{4.53}$$

Exactly as we already saw in (2.5), the free energy splits into an **energy** term $-\frac{1}{2}\rho^2$ and an **entropy** term $-\frac{1}{\beta}s^{\mathrm{l.g.}}(\rho)$.

Proof. The simple structure of the Hamiltonian yields

$$\mathbf{Q}^{\mathrm{vW}}_{\Lambda;\beta,N} = \binom{|\Lambda|}{N} e^{\frac{1}{2}\beta\rho_\Lambda^2|\Lambda|}\,.$$

We then use (4.13) and get (4.52). For the pressure, we use a decomposition as the one in (4.24) and proceed as in the proof of (4.32). □

Of course, the properties of f^{vW}_β and p^{vW}_β can also be derived directly from those of the Curie–Weiss model. Therefore, parts of the material presented below has already been presented, in a different form, in Chapter 2.

By (4.53), p^{vW}_β is the Legendre transform of f^{vW}_β, but the converse is only true when f^{vW}_β is convex.

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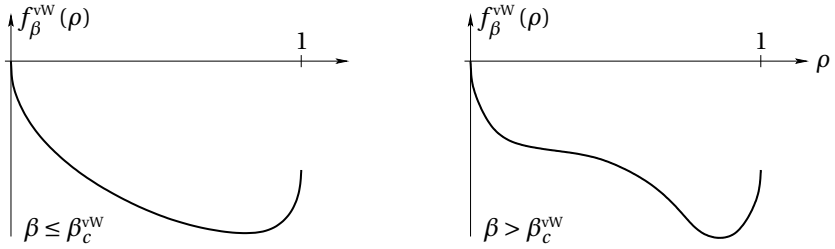

Figure 4.13: The free energy (4.52) of the van der Waals model at high (on the left) and low (on the right) temperatures.

4.9.1 (Non-)convexity of the free energy.

Since $f_\beta^{\mathrm{vW}}(\rho)$ is the sum of a concave energy term and of a convex entropy term, its convexity is not clear a priori. But an elementary computation shows that

$$\frac{\partial^2 f_\beta^{\mathrm{vW}}}{\partial \rho^2} \ge 0 \quad \forall \rho \in (0,1) \qquad \text{if and only if} \qquad \beta \le \beta_{\mathrm{c}}^{\mathrm{vW}}, \tag{4.54}$$

where the **critical inverse temperature** is

$$\beta_{\mathrm{c}}^{\mathrm{vW}} \stackrel{\mathrm{def}}{=} 4.$$

We can thus determine exactly when f_β^{vW} is the Legendre transform of p_β^{vW}:

1. When $\beta \le \beta_{\mathrm{c}}^{\mathrm{vW}}$, f_β^{vW} is convex and, since the Legendre transform is an involution on convex lower semicontinuous functions (Theorem B.19), this means that
$$f_\beta^{\mathrm{vW}}(\rho) = \sup_{\mu \in \mathbb{R}} \{\rho\mu - p_\beta^{\mathrm{vW}}(\mu)\}.$$
Therefore, *equivalence of ensembles holds at high temperature.*

2. When $\beta > \beta_{\mathrm{c}}^{\mathrm{vW}}$, f_β^{vW} is non-convex and therefore cannot be the Legendre transform of p_β^{vW} (see Exercise B.6): there exist values of ρ for which
$$f_\beta^{\mathrm{vW}}(\rho) \ne \sup_{\mu \in \mathbb{R}} \{\rho\mu - p_\beta^{\mathrm{vW}}(\mu)\}. \tag{4.55}$$
Therefore, *equivalence of ensembles does not hold at low temperature.*

The reader might wonder whether physical significance can be attached to the Legendre transform of the pressure, namely the right-hand side of (4.55). In fact, since the pressure is the Legendre transform of the free energy (by (4.53)), its Legendre transform is given by (see Theorem B.17)

$$\sup_{\mu \in \mathbb{R}} \{\rho\mu - p_\beta^{\mathrm{vW}}(\mu)\} = \mathrm{CE}\, f_\beta^{\mathrm{vW}}(\rho), \tag{4.56}$$

where $\mathrm{CE}\, f_\beta^{\mathrm{vW}}(\rho)$ is the **convex envelope** [2] **of** f_β^{vW}, defined by

$$\mathrm{CE}\, f_\beta^{\mathrm{vW}} \stackrel{\mathrm{def}}{=} \text{largest convex function } g \text{ such that } g \le f_\beta^{\mathrm{vW}}. \tag{4.57}$$

[2] A more precise definition can be found in Appendix B.2.3.

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The regime $\beta > \beta_c^{\text{vW}}$ thus corresponds to CE $f_\beta^{\text{vW}} \neq f_\beta^{\text{vW}}$ (see Figure 4.14). In the next section, we will relate this to Maxwell's construction.

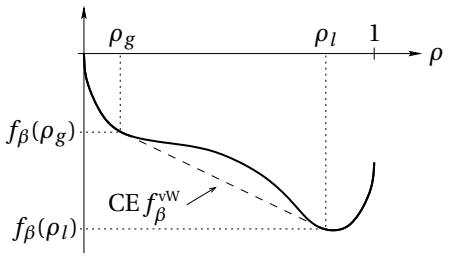

Figure 4.14: At low temperature, the free energy of the van der Waals model differs from its convex envelope. The points ρ_g and ρ_l will be identified below.

The non-convexity observed at low temperature in the van der Waals model is due to the fact that the geometry of the system plays no role: any pair of particles interacts in the same way, no matter how distant. Therefore, not surprisingly, we end up with the same conclusions as in van der Waals' theory when making the homogeneity assumption.

Convexity is known, since Chapter 1, to be a consequence of the variational principles satisfied by the fundamental functions of thermostatics. For systems with finite-range interactions, it appeared in the proof of Theorem 4.5. In the present setting, the argument can be formulated as follows. A system with density $\rho \in (\rho_g, \rho_l)$ living in Λ can always be split into two subsystems: a first one, with volume $|\Lambda_1| = \alpha|\Lambda|$ and density ρ_g and a second one with volume $|\Lambda_2| = (1-\alpha)|\Lambda|$ and density ρ_l, where α is chosen such that the overall density is unchanged: $\alpha\rho_g + (1-\alpha)\rho_l = \rho$. Indeed, the free energy density associated to these two systems is $\alpha f(\rho_g) + (1-\alpha) f(\rho_l)$, which is smaller than the free energy density of the original system: $\alpha f(\rho_g) + (1-\alpha) f(\rho_l) \leq f\big(\alpha\rho_g + (1-\alpha)\rho_l\big) = f(\rho)$.

The reason this does not occur in the van der Waals model is that it is impossible to split the system into two pieces in such a way that the energy of interaction between the two subsystems is negligible (that is, is $o(|\Lambda|)$). It is this peculiarity, ultimately due to the long-range nature of the interactions, which explains the unphysical features of these systems, such as the non-convexity of the free energy. In models with short-range interactions, such a splitting is indeed possible, and the spatial coexistence of gas and liquid phases occurs at the phase transition. ◇

4.9.2 An expression for the pressure; Maxwell's construction

We have already seen in (4.56) that the Legendre transform of the pressure is given by CE f_β^{vW}. At low temperature, CE f_β^{vW} is affine on a segment (Figure 4.14), and by Theorem B.20, this implies that p_β^{vW} has a point of non-differentiability. We make this analysis more explicit below.

Using (4.53), the analysis of the pressure $p_\beta^{\text{vW}}(\mu)$ for a fixed μ can be done through the study of the maxima of the function $\rho \mapsto \mu\rho - f_\beta^{\text{vW}}(\rho)$. Since f_β^{vW} is

differentiable, these can be found by solving

$$\frac{\partial f_\beta^{\mathrm{vW}}}{\partial \rho} = \mu\,, \tag{4.58}$$

which can be written as

$$\theta(\rho) = \beta(\rho + \mu)\,, \tag{4.59}$$

where $\theta(\rho) \stackrel{\mathrm{def}}{=} \log \frac{\rho}{1-\rho}$. We fix μ and make a qualitative analysis of the solutions (in ρ) to (4.59). Observe that $\theta(\rho) \to -\infty$ when $\rho \downarrow 0$, and $\theta(\rho) \to +\infty$ when $\rho \uparrow 1$. The graph of $\theta(\rho)$ therefore intersects the straight line $\rho \mapsto \beta(\rho+\mu)$ at least once, for all $\mu \in \mathbb{R}$ and $\beta > 0$; see Figure 4.15. However, the graph of $\theta(\rho)$ may intersect that line more than once. Actually, since $\theta'(\rho) \geq \theta'(\frac{1}{2}) = 4 = \beta_{\mathrm{c}}^{\mathrm{vW}}$, we see that this intersection is unique when $\beta \leq \beta_{\mathrm{c}}^{\mathrm{vW}}$, but not necessarily so when $\beta > \beta_{\mathrm{c}}^{\mathrm{vW}}$.

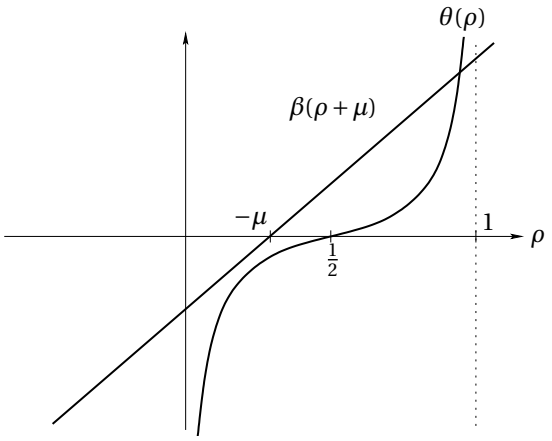

Figure 4.15: Solving (4.59).

The van der Waals pressure when $\beta \leq \beta_{\mathrm{c}}^{\mathrm{vW}}$

When $\beta \leq \beta_{\mathrm{c}}^{\mathrm{vW}}$, the unique solution to (4.59), denoted $\mu \mapsto \rho_\beta^{\mathrm{vW}}(\mu)$, is differentiable (analytic in fact) with respect to μ, and the pressure is given by

$$p_\beta^{\mathrm{vW}}(\mu) = \mu \rho_\beta^{\mathrm{vW}}(\mu) - f_\beta^{\mathrm{vW}}(\rho_\beta^{\mathrm{vW}}(\mu))\,. \tag{4.60}$$

Since $\rho_\beta^{\mathrm{vW}}(\mu) = \rho$ can be inverted to obtain $\mu_\beta^{\mathrm{vW}}(\rho)$, we can express the pressure as a function of the density; from (4.58),

$$\widetilde{p}_\beta^{\mathrm{vW}}(\rho) \stackrel{\mathrm{def}}{=} p_\beta^{\mathrm{vW}}(\mu_\beta(\rho)) = \frac{\partial f_\beta^{\mathrm{vW}}}{\partial \rho}\rho - f_\beta^{\mathrm{vW}}(\rho) = -\tfrac{1}{2}\rho^2 - \tfrac{1}{\beta}\log(1-\rho)\,. \tag{4.61}$$

Exercise 4.11. *Check* (4.61).

Once more, at low densities, (4.61) reduces to the equation of state for the ideal gas (1.14):

$$\beta \widetilde{p}_\beta^{\mathrm{vW}}(\rho) = \rho + O(\rho^2)\,.$$

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As a function of $v = \rho^{-1}$ (see Figure 4.19),

$$\widehat{p}_\beta^{\text{vW}}(v) = -\frac{1}{2v^2} - \frac{1}{\beta}\log\Bigl(1 - \frac{1}{v}\Bigr). \tag{4.62}$$

Once more, for fixed β, once v is taken large enough, $\widehat{p}_\beta^{\text{vW}}(v)$ is well approximated by the solution to

$$\Bigl(p + \bigl(\tfrac{1}{2} + \tfrac{1}{2\beta}\bigr)\frac{1}{v^2}\Bigr)(v-1) = \beta^{-1},$$

which is essentially van der Waals' expression (1.23), with $a = \frac{1}{2} + \frac{1}{2\beta}$ and $b = 1$.

The van der Waals pressure when $\beta > \beta_{\text{c}}^{\text{vW}}$

When $\beta > \beta_{\text{c}}^{\text{vW}}$, the pressure is also of the form (4.60), but the solution to (4.59) may not be unique. In that case, one must select those that correspond to a maxima of $\rho \mapsto \mu\rho - f_\beta(\rho)$. This can be made visually transparent by defining a new variable:

$$x \stackrel{\text{def}}{=} \rho - \tfrac{1}{2}.$$

(This change of variable symmetrizes the problem using a variable better suited than ρ. The analysis then reduces to the one done for the Curie–Weiss model, in Section 2.3.) After rearranging the terms, we are thus looking for the points $x \in \bigl[-\frac{1}{2}, \frac{1}{2}\bigr]$ that maximize the function

$$x \mapsto \varphi_\mu(x) \stackrel{\text{def}}{=} \bigl(\mu + \tfrac{1}{2}\bigr)x - g_\beta(x),$$

where $g_\beta(x) \stackrel{\text{def}}{=} -\frac{1}{2}x^2 - \frac{1}{\beta}s^{\text{l.g.}}(\frac{1}{2} + x)$, and where we have ignored a term that depends on μ but not on x. The advantage of working with the variable x is that $g_\beta(-x) = g_\beta(x)$. This shows that

$$\mu_*^{\text{vW}} \stackrel{\text{def}}{=} -\tfrac{1}{2}$$

is the only value of μ for which φ_μ is symmetric and has two distinct maximizers. For all other values of μ this maximizer is unique; see Figure 4.16.

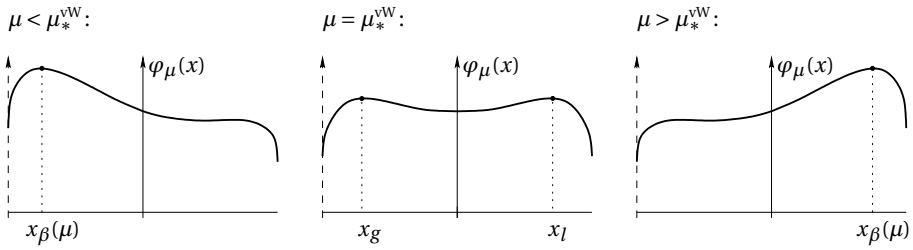

Figure 4.16: Left and right: the unique maximizer $x_\beta(\mu)$ of φ_μ when $\mu \neq \mu_*^{\text{vW}}$. Middle: The two maximizers x_g and x_l when $\mu = \mu_*$.

When μ increases from $\mu < \mu_*^{\text{vW}}$ to $\mu > \mu_*^{\text{vW}}$, the unique maximizer of $x \mapsto \varphi_\mu(x)$ jumps discontinuously from a value $x_g \stackrel{\text{def}}{=} \rho_g - \frac{1}{2} < 0$ to a value $x_l \stackrel{\text{def}}{=} \rho_l - \frac{1}{2} > 0$. We conclude that $\rho \mapsto \mu\rho - f_\beta^{\text{vW}}(\rho)$ has two distinct maximizers when $\mu = \mu_*^{\text{vW}}$: ρ_g and $\rho_l = 1 - \rho_g$. Moreover,

$$p_\beta^{\text{vW}}(\mu_*^{\text{vW}}) = \mu_*^{\text{vW}}\rho_g - f_\beta^{\text{vW}}(\rho_g) = \mu_*^{\text{vW}}\rho_l - f_\beta^{\text{vW}}(\rho_l). \tag{4.63}$$

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When $\mu \neq \mu_*^{\text{vW}}$, the maximizer is unique; we continue denoting it by $\rho_\beta^{\text{vW}}(\mu)$. Of course, $\rho_\beta^{\text{vW}}(\mu) < \rho_g$ when $\mu < \mu_*^{\text{vW}}$, $\rho_\beta^{\text{vW}}(\mu) > \rho_l$ when $\mu > \mu_*^{\text{vW}}$, and

$$\rho_g = \lim_{\mu \uparrow \mu_*^{\text{vW}}} \rho_\beta^{\text{vW}}(\mu), \quad \rho_l = \lim_{\mu \downarrow \mu_*^{\text{vW}}} \rho_\beta^{\text{vW}}(\mu).$$

Since we have, for $\mu \neq \mu_*^{\text{vW}}$,

$$\frac{\partial p_\beta^{\text{vW}}}{\partial \mu} = \frac{\partial}{\partial \mu}\{\mu \rho_\beta^{\text{vW}}(\mu) - f_\beta^{\text{vW}}(\rho_\beta^{\text{vW}}(\mu))\} = \rho_\mu^{\text{vW}}(\mu)$$

and since p_β^{vW} is convex (being a Legendre transform), Theorem B.12 then gives

$$\frac{\partial p_\beta^{\text{vW}}}{\partial \mu^-}\Big|_{\mu_*^{\text{vW}}} = \rho_g < \rho_l = \frac{\partial p_\beta^{\text{vW}}}{\partial \mu^+}\Big|_{\mu_*^{\text{vW}}}.$$

Remark 4.25. By Theorem B.20, the lack of differentiability of p_β^{vW} at μ_*^{vW} implies that its Legendre transform is affine on $[\rho_g, \rho_l]$ and μ_*^{vW} gives the slope of CE f_β^{vW} on $[\rho_g, \rho_l]$. Using the second and third terms in (4.63), we get

$$f_\beta^{\text{vW}}(\rho_l) - f_\beta^{\text{vW}}(\rho_g) = \mu_*^{\text{vW}}(\rho_l - \rho_g) = \frac{\partial f_\beta^{\text{vW}}}{\partial \rho}\Big|_{\rho_g}(\rho_l - \rho_g).$$

This is clearly seen on the graph of Figure 4.14. ◇

Let us then complete the description of the pressure in terms of the variables ρ and v. Since $\rho_\beta^{\text{vW}}(\mu)$ behaves discontinuously at μ_*^{vW}, we define its inverse as we did earlier (see page 189). For $\rho < \rho_g$ or $\rho > \rho_l$, $\rho_\beta^{\text{vW}}(\mu) = \rho$ has an inverse which we again denote $\mu_\beta^{\text{vW}}(\rho)$ and, for those densities, the pressure is obtained as in (4.61). Then,

$$\widetilde{\mu}_\beta(\rho) \stackrel{\text{def}}{=} \begin{cases} \mu_\beta^{\text{vW}}(\rho) & \text{if } \rho \in (0, \rho_g), \\ \mu_*^{\text{vW}} & \text{if } \rho \in [\rho_g, \rho_l], \\ \mu_\beta^{\text{vW}}(\rho) & \text{if } \rho \in (\rho_l, 1). \end{cases}$$

As a function of the density, $\widetilde{p}_\beta^{\text{vW}}(\rho) \stackrel{\text{def}}{=} p_\beta(\widetilde{\mu}_\beta^{\text{vW}}(\rho))$ then takes the following form (see Figure 4.17).

$$\widetilde{p}_\beta^{\text{vW}}(\rho) = \begin{cases} -\frac{1}{2}\rho^2 - \frac{1}{\beta}\log(1-\rho) & \text{if } \rho \in (0, \rho_g), \\ p_\beta^{\text{vW}}(\mu_*^{\text{vW}}) & \text{if } \rho \in [\rho_g, \rho_l], \\ -\frac{1}{2}\rho^2 - \frac{1}{\beta}\log(1-\rho) & \text{if } \rho \in (\rho_l, 1). \end{cases} \tag{4.64}$$

Remark 4.26. On the gas branch, at any temperature, we can use the Taylor expansion for $\log(1-\rho)$, and get

$$\beta \widetilde{p}_\beta^{\text{vW}}(\rho) = \rho + \tfrac{1}{2}(1-\beta)\rho^2 + \tfrac{1}{3}\rho^3 + \tfrac{1}{4}\rho^4 + \cdots$$

The above series, which in fact converges for all complex ρ inside the unit disk, is called the **virial expansion** for the pressure. It provides high-order corrections to the equation of the ideal gas. ◇

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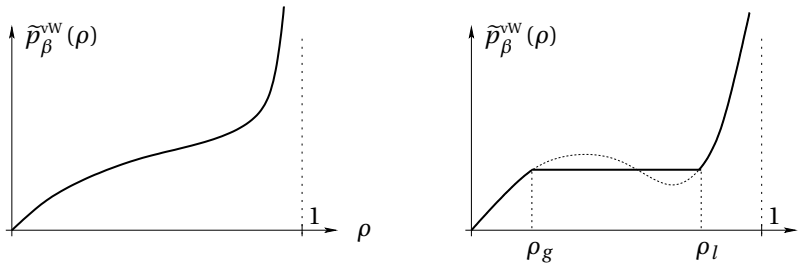

Figure 4.17: The pressure of the van der Waals model, as a function of the density. On the left, the regime $\beta \le \beta_c^{\mathrm{vW}}$, on the right, $\beta > \beta_c^{\mathrm{vW}}$.

Finally, we can express the pressure as a function of the volume per particle, $v = \rho^{-1}$. At low temperature, $\widehat{p}_\beta^{\mathrm{vW}}(v)$ presents a striking difference with its high-temperature counterpart, computed earlier. Namely, at low temperature, the expression (4.62) has to be replaced by a *constant* on the coexistence plateau $[v_l, v_g]$, where $v_l \stackrel{\text{def}}{=} \rho_l^{-1}$, $v_g \stackrel{\text{def}}{=} \rho_g^{-1}$. Quite remarkably, this constant is the same as the one provided by Maxwell's construction; see Figure 4.18.

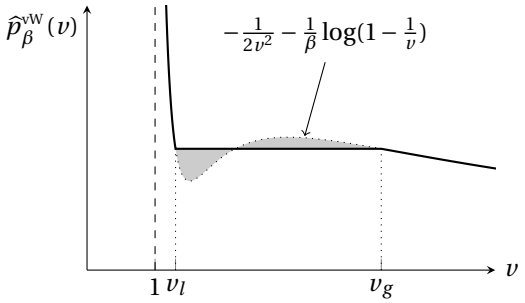

Figure 4.18: The pressure of the van der Waals model at low temperature, as a function of the volume per particle $v > 1$, obtained by applying the *equal area rule* (Maxwell construction) to an everywhere smooth function: the two shaded areas are equal. The coexistence plateau is at a height given by the saturation pressure $p_\beta^{\mathrm{vW}}(\mu_*^{\mathrm{vW}})$.

Theorem 4.27 (Maxwell's Construction)**.** *When* $\beta > \beta_c^{\mathrm{vW}}$,

$$\widehat{p}_\beta^{\mathrm{vW}}(v) = \mathrm{MC}\Big\{-\frac{1}{2v^2} - \frac{1}{\beta}\log\Big(1-\frac{1}{v}\Big)\Big\}. \tag{4.65}$$

Proof. As in (1.24), we must show that

$$\int_{v_l}^{v_g} \Big\{-\frac{1}{2v^2} - \frac{1}{\beta}\log\Big(1-\frac{1}{v}\Big)\Big\}\,\mathrm{d}v = p_\beta^{\mathrm{vW}}(\mu_*^{\mathrm{vW}})(v_g - v_l). \tag{4.66}$$

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A straightforward integration shows that this integral equals, after rearrangement,

$$\begin{aligned}\tfrac{1}{2}\Big[\tfrac{1}{v}\Big]_{v_l}^{v_g} - \tfrac{1}{\beta}\Big[(v-1)\log(v-1) - v\log v\Big]_{v_l}^{v_g} &= \tfrac{1}{2}\Big\{\tfrac{1}{v_g} - \tfrac{1}{v_l}\Big\} - \tfrac{1}{\beta}\Big[-v s^{\text{l.g.}}(\tfrac{1}{v})\Big]_{v_l}^{v_g} \\ &= -\tfrac{1}{2}\tfrac{v_g - v_l}{v_l v_g} - \tfrac{1}{\beta}\big\{v_l s^{\text{l.g.}}(\tfrac{1}{v_l}) - v_g s^{\text{l.g.}}(\tfrac{1}{v_g})\big\}.\end{aligned}$$

We then use the fact that $-\frac{1}{2} = \mu_*^{\text{vW}}$, $\frac{1}{v_l v_g} = \rho_l \rho_g = \rho_g(1-\rho_g)$, $s^{\text{l.g.}}(\frac{1}{v_l}) = s^{\text{l.g.}}(\rho_l) = s^{\text{l.g.}}(1-\rho_l) = s^{\text{l.g.}}(\rho_g) = s^{\text{l.g.}}(\frac{1}{v_g})$, as well as (4.63), to obtain

$$\begin{aligned}\int_{v_l}^{v_g}\Big\{-\frac{1}{2v^2} - \frac{1}{\beta}\log\Big(1-\frac{1}{v}\Big)\Big\}\,\mathrm{d}v &= (v_g - v_l)\big\{\mu_*^{\text{vW}}\rho_g + \tfrac{1}{2}\rho_g^2 + \tfrac{1}{\beta}s^{\text{l.g.}}(\rho_g)\big\} \\ &= (v_g - v_l)\big\{\mu_*^{\text{vW}}\rho_g - f_\beta(\rho_g)\big\} \\ &= (v_g - v_l)\,p_\beta^{\text{vW}}(\mu_*^{\text{vW}}).\end{aligned}$$

□

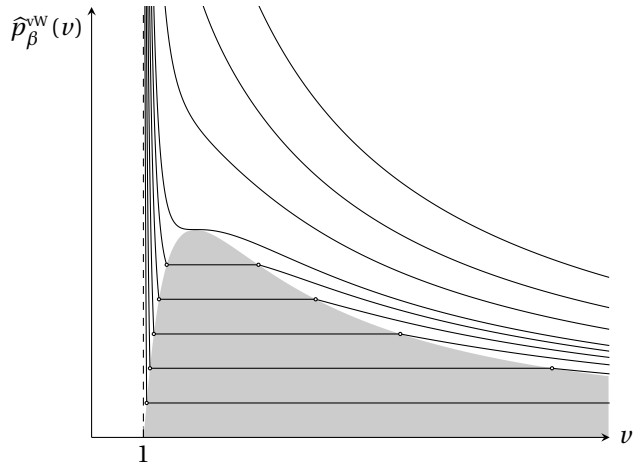

Figure 4.19: The pressure of the van der Waals–Maxwell model as a function of $v > 1$. The top four curves represent isotherms for values of $\beta \le \beta_c^{\text{vW}}$ (see (4.62)) and are smooth everywhere; the fourth one is the critical isotherm. The remaining curves correspond to values $\beta > \beta_c^{\text{vW}}$ and include a coexistence plateau due to Maxwell's Construction. The shaded region represents the values of the parameters (v, p) located on a coexistence plateau. These plots were obtained from (4.65).

4.10 Kac interactions and the van der Waals limit

Although Maxwell's construction was obtained rigorously in the previous section, it was only proved to occur in a model with non-physical interactions. It therefore remains to understand whether the van der Waals–Maxwell theory can be given a precise meaning in the framework of equilibrium statistical mechanics, but starting from *finite-range* interactions. This will be done in this section.

Consider a lattice gas in a large vessel, with a fixed density. We have seen how van der Waals' main simplifying hypothesis could be realized in a model (the van

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der Waals model), in which a quadratic term ρ_Λ^2 appears in the Hamiltonian, as a consequence of the non-local structure of the interaction.

As explained earlier, the *local* density of a real gas at fixed overall density ρ can undergo large fluctuations, in particular in the coexistence regime. This makes it possible to observe the true physical phenomenon of interest: condensation.

Instead of making homogeneity assumptions on the density, we introduce a class of interactions that allows one to compute the energy in large but finite regions, whatever the density of particles is (in that region). To this end, we will consider some initial pair interaction, given by some function φ, and then *scale it* in an appropriate way:

Definition 4.28. *Let $\varphi : \mathbb{R}^d \to \mathbb{R}_{\geq 0}$ be a Riemann-integrable function with compact support, satisfying $\varphi(-x) = \varphi(x)$ and*

$$\int \varphi(x)\,\mathrm{d}x = 1\,. \tag{4.67}$$

*The **Kac interaction associated to φ with scaling parameter** $\gamma > 0$ is*

$$K_\gamma(i,j) \stackrel{\text{def}}{=} \gamma^d \varphi\big(\gamma(j-i)\big)\,.$$

We will mostly be interested in small values of γ,that is, when the interaction of a particle at $i \in \mathbb{Z}^d$ is essentially the same with all the other particles located in a neighborhood of i of diameter γ^{-1}. The smaller γ, the more particles interact, but the less a pair $\{i,j\}$ contributes to the total energy. In this respect, the interaction K_γ is similar, at a microscopic scale, to the van der Waals model. Nevertheless, because φ is compactly supported, *K_γ always has a finite range of order γ^{-1}*. Let us denote the maximal interaction of a particle with the rest of the system by $\kappa_\gamma = \sum_{j\neq 0} K_\gamma(0,j)$.

Exercise 4.12. *Show, using* (4.67)*, that*

$$\lim_{\gamma \downarrow 0} \kappa_\gamma = 1\,. \tag{4.68}$$

A possible choice for φ is

$$\varphi(x) \stackrel{\text{def}}{=} \begin{cases} 2^{-d} & \text{if } \|x\|_\infty \leq 1\,, \\ 0 & \text{if } \|x\|_\infty > 1\,. \end{cases} \tag{4.69}$$

The scaling of this function, for some $0 < \gamma < 1$, is depicted in Figure 4.20.

The canonical and grand canonical partition functions associated to $\mathscr{H}_{\Lambda;K_\gamma}$ will be denoted $\mathbf{Q}_{\Lambda;\gamma,\beta,N}$, respectively $\Theta_{\Lambda;\gamma,\beta,\mu}$. The free energy and pressure will be denoted $f_{\Lambda;\gamma,\beta}(\rho)$, respectively $p_{\Lambda;\gamma,\beta}(\mu)$.

We will consider a two-steps limiting procedure: first, we will take the thermodynamic limit at a fixed positive value of γ (below, $\Lambda \Uparrow \mathbb{Z}^d$ actually means using $\mathscr{R} \ni \Lambda_n \Uparrow \mathbb{Z}^d$):

$$f_{\gamma,\beta}(\rho) = \lim_{\Lambda \Uparrow \mathbb{Z}^d} f_{\Lambda;\gamma,\beta}(\rho)\,, \qquad p_{\gamma,\beta}(\mu) = \lim_{\Lambda \Uparrow \mathbb{Z}^d} p_{\Lambda;\gamma,\beta}(\mu)\,.$$

The existence of these limits is guaranteed by Theorems 4.5 and 4.11. In the second step, we will let the parameter γ tend to 0.

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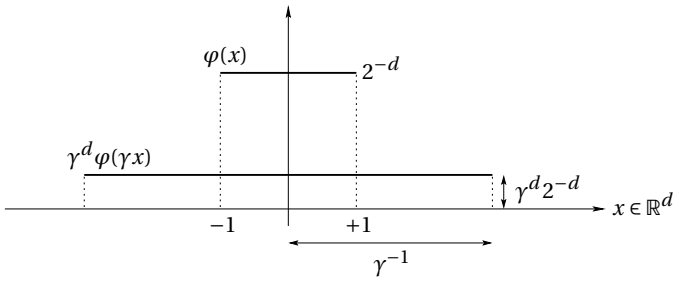

Figure 4.20: The function φ in (4.69)

Definition 4.29. *The limit $\gamma \downarrow 0$ is called the **van der Waals limit**[2]. When they exist, we denote the limits by*

$$f_{0^+,\beta}(\rho) \stackrel{\text{def}}{=} \lim_{\gamma\downarrow 0} f_{\gamma,\beta}(\rho)\,, \qquad p_{0^+,\beta}(\mu) \stackrel{\text{def}}{=} \lim_{\gamma\downarrow 0} p_{\gamma,\beta}(\mu)\,.$$

Remark 4.30. To summarize, the relevant limiting procedure, in the study of Kac interactions, is $\lim_{\gamma\downarrow 0}\lim_{\Lambda\Uparrow\mathbb{Z}^d}\{\dots\}$. Observe that if the limits are taken in the other order, $\lim_{\Lambda\Uparrow\mathbb{Z}^d}\lim_{\gamma\downarrow 0}\{\dots\}$, this yields the hard-core model of Section 4.7. Indeed, for all fixed $i, j \in \mathbb{Z}^d$,

$$\lim_{\gamma\downarrow 0} K_\gamma(i,j) = 0\,. \tag{4.70}$$

Therefore,

$$\lim_{\Lambda\Uparrow\mathbb{Z}^d}\lim_{\gamma\downarrow 0} f_{\Lambda;\gamma,\beta}(\rho) = \lim_{\Lambda\Uparrow\mathbb{Z}^d} f^{\text{hard}}_{\Lambda;\beta}(\rho) = f^{\text{hard}}_{\beta}(\rho) = -\tfrac{1}{\beta}s^{\text{l.g.}}(\rho)\,,$$
$$\lim_{\Lambda\Uparrow\mathbb{Z}^d}\lim_{\gamma\downarrow 0} p_{\Lambda;\gamma,\beta}(\mu) = \lim_{\Lambda\Uparrow\mathbb{Z}^d} p^{\text{hard}}_{\Lambda;\beta}(\mu) = p^{\text{hard}}_{\beta}(\mu) = \tfrac{1}{\beta}\log(1+e^{\beta\mu})\,,$$

as seen in (4.39) and (4.40)). Therefore, taking the limits in that order does not lead to interesting phenomena. ◇

4.10.1 van der Waals limit of the thermodynamic potentials

When $\gamma \downarrow 0$, Kac interactions become, loosely speaking, infinitely weak and of infinite range. We therefore expect $p_{0^+,\beta}$ and $f_{0^+,\beta}$ to be related to the thermodynamic potentials of the van der Waals model, in some sense.

Notice also that, since $p_{\gamma,\beta}$ and $f_{\gamma,\beta}$ are convex, their limits as $\gamma \downarrow 0$ must also be convex. Since we know that non-convexity does occur in the van der Waals model at low temperature, some new feature is to be expected.

Theorem 4.31 (van der Waals limit of Kac interactions)**.** *For all $\beta > 0$,*

$$f_{0^+,\beta}(\rho) = \text{CE}\, f^{\text{vW}}_{\beta}(\rho)\,, \qquad \forall \rho \in [0,1]\,, \tag{4.71}$$
$$p_{0^+,\beta}(\mu) = p^{\text{vW}}_{\beta}(\mu)\,, \qquad \forall \mu \in \mathbb{R}\,. \tag{4.72}$$

[2] This limit is also called **mean field**, **Kac** or **Lebowitz–Penrose limit**.

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The most remarkable feature of this result is that the limiting behavior of Kac interactions is described by the van der Waals model, *but with a free energy having the correct convexity property.* (We remind the reader that the convex envelope did not appear naturally in the van der Waals model, but only when considering the Legendre transform of the pressure in (4.56).) Remember that

$$f_\beta^{\mathrm{vW}}(\rho) = -\tfrac{1}{2}\rho^2 - \tfrac{1}{\beta} s^{\mathrm{l.g.}}(\rho)\,.$$

The double limiting procedure $\lim_{\gamma\downarrow 0}\lim_{\Lambda\Uparrow\mathbb{Z}^d}\{\cdot\}$ thus leads to two main features. The first is the appearance of a quadratic term in the free energy, $-\frac{1}{2}\rho^2$, without it having been introduced artificially in the Hamiltonian. Here, as will be seen, it stems from the interaction of a particle with the rest of the system, which provides a non-vanishing contribution even in the limit $\gamma \downarrow 0$. The second new feature is of course the geometric modification of f_β^{vW} by the convex envelope. This modification is non-trivial at low temperature, since it leads to the appearance of an *affine portion* on the graph of the free energy, as seen earlier; see Figure 4.21.

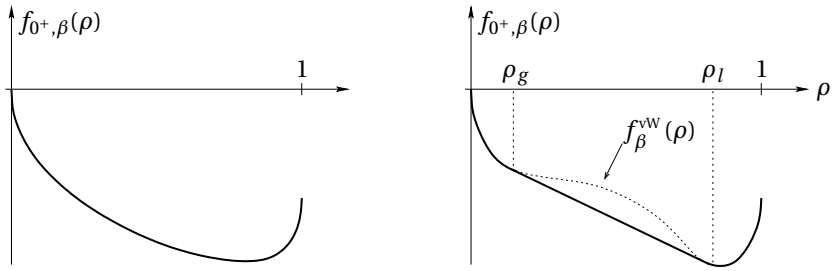

Figure 4.21: The van der Waals limit of the free energy; left: $\beta \le \beta_c^{\mathrm{vW}}$, right: $\beta > \beta_c^{\mathrm{vW}}$.

Proof of (4.71)**:**

Since the temperature plays no role in the proof below, we will usually omit β from the notations.

As the mechanism of the proof will show, the appearance of the convex envelope in (4.71) is precisely due to the fact that, for finite-range interactions, the system is free to let the density of particles vary from place to place.

We thus use an intermediate scale, $\ell \in \mathbb{N}$, which we assume to be large, of the form $\ell = 2^p$, but smaller than the scale of the interaction, $\ell \ll \gamma^{-1}$. In the end, we shall consecutively take the limits $\Lambda \Uparrow \mathbb{Z}^d$, then $\gamma \downarrow 0$ and finally $\ell \uparrow \infty$.

By Theorem 4.5, the free energy can be computed using a sequence of cubic boxes $\Lambda \Uparrow \mathbb{Z}^d$ whose sidelength is always a multiple of ℓ. We therefore consider a partition of $\mathbb{Z}^d$ into cubes $\Lambda^{(\alpha)}$, $\alpha = 1, 2, \dots$, of sidelength ℓ (see Figure 4.22). For simplicity, we can assume that $\Lambda^{(1)}$ always contains the origin, that Λ is a cube of sidelength $\ell 2^n$, given by the union of M cubes of the partition and centered on the cube $\Lambda^{(1)}$, and denote these cubes by $\Lambda^{(1)}, \dots, \Lambda^{(M)}$.

We fix ρ and take $N = \lceil \rho|\Lambda| \rceil$. The starting point is to consider all possible arrangements of the N particles in the boxes $\Lambda^{(\alpha)}$, by writing

$$\mathbf{Q}_{\Lambda;\gamma,N} = \sum_{\substack{N_1,\dots,N_M:\\ N_1+\cdots+N_M=N}} \mathbf{Q}_{\Lambda;\gamma,N}(N_1,\dots,N_M)\,, \tag{4.73}$$

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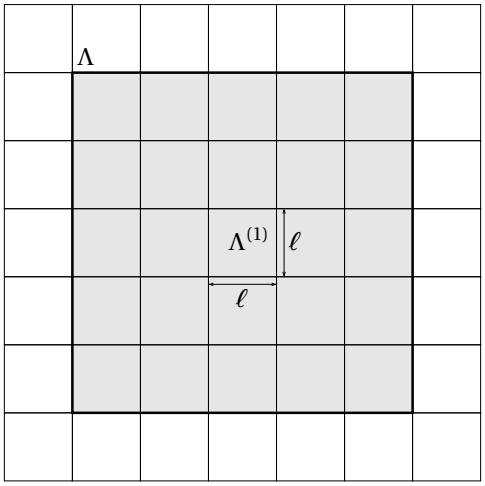

Figure 4.22: $\mathbb{Z}^d$ is partitioned into cubes $\Lambda^{(\alpha)}$, $\alpha = 1,2,\ldots$, of sidelength ℓ. The box Λ is assumed to be built from boxes of the partition, and centered on the box $\Lambda^{(1)}$.

where $\mathbf{Q}_{\Lambda;\gamma,N}(N_1,\ldots,N_M)$ denotes the canonical partition function in which the sum is restricted to configurations in which $\Lambda^{(\alpha)}$ contains N_α particles, $\alpha = 1,\ldots,M$. We then express the Hamiltonian in a way that takes into account the location of the particles among the boxes $\Lambda^{(\alpha)}$:

$$\mathscr{H}_{\Lambda;K_\gamma} = \sum_\alpha \mathscr{H}_{\Lambda^{(\alpha)};K_\gamma} + \sum_{\substack{\{\alpha,\alpha'\}\\ \alpha\neq\alpha'}} I_\gamma(\alpha,\alpha')\,,$$

where $I_\gamma(\alpha,\alpha')$ represents the interactions between the particles in $\Lambda^{(\alpha)}$ and those in $\Lambda^{(\alpha')}$:

$$I_\gamma(\alpha,\alpha') = -\sum_{i\in\Lambda^{(\alpha)}}\sum_{j\in\Lambda^{(\alpha')}} K_\gamma(i,j)\eta_i\eta_j\,.$$

By defining

$$\overline{K}_\gamma(\alpha,\alpha') \stackrel{\text{def}}{=} \max_{i\in\Lambda^{(\alpha)},\, j\in\Lambda^{(\alpha')}} K_\gamma(i,j)\,,$$
$$\underline{K}_\gamma(\alpha,\alpha') \stackrel{\text{def}}{=} \min_{i\in\Lambda^{(\alpha)},\, j\in\Lambda^{(\alpha')}} K_\gamma(i,j)\,,$$

we have

$$-\overline{K}_\gamma(\alpha,\alpha')N_{\Lambda^{(\alpha)}}N_{\Lambda^{(\alpha')}} \le I_\gamma(\alpha,\alpha') \le -\underline{K}_\gamma(\alpha,\alpha')N_{\Lambda^{(\alpha)}}N_{\Lambda^{(\alpha')}}\,. \tag{4.74}$$

Upper bound. Since $f_\gamma(\rho)$ is convex, its limit as $\gamma\downarrow 0$ is also convex, and therefore continuous (Exercise B.3 and Proposition B.9). (Continuity at 0 and 1 follows from (4.9), (4.15), (4.16) and (4.19).) It is thus sufficient to prove an upper bound for (4.71) for densities ρ belonging to a dense subset of $(0,1)$. So, let us fix a dyadic density, of the form $\rho = \frac{k}{2^m}$, $0 < k < 2^m$. By construction, when ℓ is large enough, $N_* \stackrel{\text{def}}{=} \lceil \rho|\Lambda^{(\alpha)}|\rceil = \rho|\Lambda^{(\alpha)}|$ for each α. We thus get a lower bound on the partition

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function by keeping only the configurations in which each box $\Lambda^{(\alpha)}$ contains exactly N_* particles:

$$\mathbf{Q}_{\Lambda;\gamma,N} \geq \mathbf{Q}_{\Lambda;\gamma,N}(N_*,\dots,N_*)\,. \tag{4.75}$$

Using (4.74) and performing separately the sums over the configurations of N_* particles in each box $\Lambda^{(\alpha)}$,

$$\begin{aligned}\mathbf{Q}_{\Lambda;\gamma,N}(N_*,\dots,N_*) &\geq \{\mathbf{Q}_{\Lambda^{(1)};\gamma,N_*}\}^M \prod_{\substack{\{\alpha,\alpha'\}\\ \alpha\neq\alpha'}} e^{\beta \underline{K}_\gamma(\alpha,\alpha')N_*^2} \\ &= \{\mathbf{Q}_{\Lambda^{(1)};\gamma,N_*}\}^M \exp\Big(\tfrac{1}{2}\beta N_*^2 \sum_{\alpha=1}^{M} \sum_{\substack{\alpha'=1\\(\alpha'\neq\alpha)}}^{M} \underline{K}_\gamma(\alpha,\alpha')\Big)\,.\end{aligned}$$

Now,

$$\sum_{\substack{\alpha'=1\\(\alpha'\neq\alpha)}}^{M} \underline{K}_\gamma(\alpha,\alpha') = \sum_{\substack{\alpha'\geq 1\\(\alpha'\neq\alpha)}} \underline{K}_\gamma(\alpha,\alpha') - \sum_{\substack{\alpha'\geq 1\\(\Lambda^{(\alpha')}\not\subset\Lambda)}} \underline{K}_\gamma(\alpha,\alpha')\,. \tag{4.76}$$

By translation invariance, the first sum on the right-hand side does not depend on α, which can thus be assumed to be equal to 1. Then, since K_γ has finite range, say R_γ, the second sum is (finite and) non-zero only if $\Lambda^{(\alpha)}$ is at distance at most R_γ from Λ^{c}. It thus represents a boundary term, of order $(R_\gamma/\ell)^d|\partial^{\mathrm{ex}}\Lambda|$. Since we take the thermodynamic limit *before* the limit $\gamma\downarrow 0$, we get, after letting $\Lambda \Uparrow \mathbb{Z}^d$ (along that specific sequence of cubes),

$$f_\gamma(\rho) \leq \frac{-1}{\beta|\Lambda^{(1)}|}\log \mathbf{Q}_{\Lambda^{(1)};\gamma,N_*} - \frac{\rho^2}{2}|\Lambda^{(1)}| \sum_{\alpha'>1} \underline{K}_\gamma(1,\alpha')\,. \tag{4.77}$$

Exercise 4.13. *For all fixed $\ell\in\mathbb{N}$,*

$$\lim_{\gamma\downarrow 0}|\Lambda^{(1)}| \sum_{\alpha'>1} \underline{K}_\gamma(1,\alpha') = \int \varphi(x)\,\mathrm{d}x = \lim_{\gamma\downarrow 0}|\Lambda^{(1)}| \sum_{\alpha'>1} \overline{K}_\gamma(1,\alpha')\,. \tag{4.78}$$

We can now compute the van der Waals limit. By (4.70), $\lim_{\gamma\downarrow 0}\mathbf{Q}_{\Lambda;\gamma,N_*} = \mathbf{Q}^{\mathrm{hard}}_{\Lambda;N_*}$ and, since we assumed that $\int\varphi(x)\,\mathrm{d}x = 1$, (4.77) and (4.78) yield

$$\limsup_{\gamma\downarrow 0} f_\gamma(\rho) \leq f^{\mathrm{hard}}_{\Lambda^{(1)}}(\rho) - \tfrac{1}{2}\rho^2\,.$$

Taking $\ell\to\infty$ gives

$$\limsup_{\gamma\downarrow 0} f_\gamma(\rho) \leq -\tfrac{1}{2}\rho^2 - \tfrac{1}{\beta}s^{\mathrm{l.g.}}(\rho) = f^{\mathrm{vW}}_\beta(\rho)\,.$$

This bound holds for all dyadic $\rho\in(0,1)$. Since $f_\gamma(\rho)$ is convex, $\limsup_{\gamma\downarrow 0} f_\gamma(\rho)$ also is; in particular, it is continuous. This implies that this last upper bound holds for all $\rho\in(0,1)$, and, using again the convexity of $\limsup_{\gamma\downarrow 0} f_\gamma(\rho)$,

$$\limsup_{\gamma\downarrow 0} f_\gamma(\rho) \leq \mathrm{CE}\, f^{\mathrm{vW}}_\beta(\rho)\,.$$

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Lower bound. We start by bounding (4.73) as follows:

$$\mathbf{Q}_{\Lambda;\gamma,N} \le \mathscr{N}(N;M) \max_{\substack{N_1,\dots,N_M:\\ N_1+\cdots+N_M=N}} \mathbf{Q}_{\Lambda;\gamma,N}(N_1,\dots,N_M)\,,$$

where $\mathscr{N}(N;M)$ is the number of M-tuples $(N_1,\dots,N_M)$ with $N_1+\cdots+N_M=N$.

Exercise 4.14. *Show that, for all* $\rho \in (0,1)$,

$$\lim_{\ell\to\infty}\lim_{\Lambda\Uparrow\mathbb{Z}^d} \frac{1}{|\Lambda|}\log \mathscr{N}(\lceil\rho|\Lambda|\rceil;M) = 0\,. \tag{4.79}$$

Then, using again (4.74),

$$\mathbf{Q}_{\Lambda;\gamma,N}(N_1,\dots,N_M) \le \Big\{\prod_\alpha \mathbf{Q}_{\Lambda^{(\alpha)};\gamma,N_\alpha}\Big\} \prod_{\substack{\{\alpha,\alpha'\}\\ \alpha\neq\alpha'}} e^{\beta\overline{K}_\gamma(\alpha,\alpha')N_\alpha N_{\alpha'}}\,.$$

For the first product, we write

$$\mathbf{Q}_{\Lambda^{(\alpha)};\gamma,N_\alpha} = \exp\big(-\beta f_{\Lambda^{(1)};\gamma}(\tfrac{N_\alpha}{|\Lambda^{(\alpha)}|})|\Lambda^{(1)}|\big)\,.$$

For the second, we use $N_\alpha N_{\alpha'} \le \frac{1}{2}(N_\alpha^2+N_{\alpha'}^2)$ and the same argument given after (4.76) to obtain

$$\prod_{\substack{\{\alpha,\alpha'\}\\ \alpha\neq\alpha'}} e^{\beta\overline{K}_\gamma(\alpha,\alpha')N_\alpha N_{\alpha'}} \le e^{c|\partial^{\mathrm{ex}}\Lambda|}\exp\Big(\tfrac{1}{2}\beta\overline{\kappa}_\gamma|\Lambda^{(1)}|\sum_{\alpha=1}^M\big(\tfrac{N_\alpha}{|\Lambda^{(\alpha)}|}\big)^2\Big),$$

where c depends on γ and ℓ, and

$$\overline{\kappa}_\gamma \stackrel{\mathrm{def}}{=} |\Lambda^{(1)}|\sum_{\alpha'>1}\overline{K}_\gamma(1,\alpha')\,.$$

By Lemma 4.13, $\overline{\kappa}_\gamma \to 1$ as $\gamma\downarrow 0$. If we define $g_{\Lambda^{(1)},\gamma}(\rho) \stackrel{\mathrm{def}}{=} -\frac{1}{2}\overline{\kappa}_\gamma\rho^2 + f_{\Lambda^{(1)};\gamma}(\rho)$, then

$$\begin{aligned}\frac{-1}{\beta|\Lambda|}\log\mathbf{Q}_{\Lambda;\gamma,N} \ge{}& \frac{-1}{\beta|\Lambda|}\log\mathscr{N}(N;M)\\ &+ \min_{\substack{N_1,\dots,N_M:\\ N_1+\cdots+N_M=N}} \frac{1}{M}\sum_{\alpha=1}^M g_{\Lambda^{(1)};\gamma}\big(\tfrac{N_\alpha}{|\Lambda^{(\alpha)}|}\big) - \frac{c|\partial^{\mathrm{ex}}\Lambda|}{\beta|\Lambda|}\,.\end{aligned}$$

Now, for each M-tuple $(N_1,\dots,N_M)$ above,

$$\begin{aligned}\frac{1}{M}\sum_{\alpha=1}^M g_{\Lambda^{(1)};\gamma}\big(\tfrac{N_\alpha}{|\Lambda^{(\alpha)}|}\big) &\ge \frac{1}{M}\sum_{\alpha=1}^M \mathrm{CE}\, g_{\Lambda^{(1)};\gamma}\big(\tfrac{N_\alpha}{|\Lambda^{(\alpha)}|}\big)\\ &\ge \mathrm{CE}\, g_{\Lambda^{(1)};\gamma}\Big(\frac{1}{M}\sum_{\alpha=1}^M\tfrac{N_\alpha}{|\Lambda^{(\alpha)}|}\Big) = \mathrm{CE}\, g_{\Lambda^{(1)};\gamma}\big(\tfrac{N}{|\Lambda|}\big)\,.\end{aligned}$$

For the first inequality, we used that $g \ge \mathrm{CE}\, g$, and then that $\mathrm{CE}\, g$ is convex (see Exercise B.2). Since $\frac{N}{|\Lambda|}\to\rho$,

$$f_\gamma(\rho) \ge \liminf_{\Lambda\Uparrow\mathbb{Z}^d}\frac{-1}{\beta|\Lambda|}\log\mathscr{N}(N;M) + \mathrm{CE}\, g_{\Lambda^{(1)};\gamma}(\rho)\,.$$

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By (4.79), the first term on the right-hand side will vanish once we take the limit $\ell \to \infty$. To take the van der Waals limit in the second term, we first observe that

$$\lim_{\gamma \downarrow 0} g_{\Lambda^{(1)};\gamma}(\rho) = -\tfrac{1}{2}\rho^2 + f^{\text{hard}}_{\Lambda^{(1)}}(\rho)\,, \tag{4.80}$$

uniformly in $\rho \in (0,1)$, and rely on the following

Exercise 4.15. *Let $f_n : [a,b] \to \mathbb{R}$ be a sequence of functions converging uniformly to $f : [a,b] \to \mathbb{R}$. Then* $\mathrm{CE}\, f_n$ *converges uniformly to* $\mathrm{CE}\, f$.

We therefore get, for all $\rho \in [a,b] \subset [0,1]$,

$$\liminf_{\gamma \downarrow 0} f_\gamma(\rho) \geq \liminf_{\Lambda \Uparrow \mathbb{Z}^d} \frac{-1}{\beta|\Lambda|} \log \mathscr{N}(N;M) + \mathrm{CE}\big\{-\tfrac{\rho^2}{2} + f^{\text{hard}}_{\Lambda^{(1)}}(\rho)\big\}\,.$$

We finally take the limit $\ell \to \infty$, which yields

$$\liminf_{\gamma \downarrow 0} f_\gamma(\rho) \geq \mathrm{CE}\, f^{\text{vW}}_\beta(\rho)\,.$$

This concludes the proof of (4.71). □

Proof of (4.72)**:**

For a fixed $\mu \in \mathbb{R}$, we take $\gamma \downarrow 0$ on both sides of

$$p_{\gamma,\beta}(\mu) = \sup_{\rho \in [0,1]} \{\rho\mu - f_{\gamma,\beta}(\rho)\}\,.$$

We first show that the right-hand side converges to $\sup_{\rho\in[0,1]}\{\rho\mu - f_{0^+,\beta}(\rho)\}$.

Since they are fixed, let us omit β and μ from the notations. Let $F_\gamma(\rho) \stackrel{\text{def}}{=} \rho\mu - f_\gamma(\rho)$ and $F_{0^+}(\rho) \stackrel{\text{def}}{=} \lim_{\gamma\downarrow 0} F_\gamma(\rho) = \rho\mu - f_{0^+}(\rho)$. As we already know, F_{0^+} attains its maximum away from 0 and 1. Therefore we can take $\delta > 0$ small enough so that $\sup_\rho F_{0^+}(\rho) = \sup_{\rho\in K} F_{0^+}(\rho)$, where $K = [\delta, 1-\delta]$. Observe that, because $\rho \mapsto F_{0^+}(\rho)$ is concave and by our choice of δ, $\partial^+ F_{0^+}(\delta) > 0$ and $\partial^- F_{0^+}(1-\delta) < 0$; by Theorem B.12, this implies that $\partial^+ F_\gamma(\delta) > 0$, $\partial^- F_\gamma(1-\delta) < 0$, for all small enough $\gamma > 0$. Since the family $(f_\gamma)_{\gamma>0}$ is bounded by (4.15)–(4.19), the convergence $f_\gamma \to f_{0^+}$ is uniform on K (Lemma B.10). This implies

$$\limsup_{\gamma\downarrow 0} \sup_{\rho\in K} F_\gamma(\rho) = \sup_{\rho\in K} F_{0^+}(\rho)\,,$$

which implies what we wanted. Therefore, in terms of the Legendre transform $(\cdot)^*$, we have obtained $p_{0^+} = (f_{0^+})^* = (\mathrm{CE}\, f^{\text{vW}})^*$. But, by Corollary B.18, $(\mathrm{CE}\, f^{\text{vW}})^* = (f^{\text{vW}})^* = p^{\text{vW}}$. □

4.11 Bibliographical references

Lattice models of gases have been studied since the early stages of statistical mechanics; Boltzmann, in particular, already considered similar approximations as a computational device. See the book of Gallavotti [130] and references therein.

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Thermodynamic potentials and equivalence of ensembles. The construction of the thermodynamic potentials and the derivation of their general convexity properties are classical and can be found in several sources. A very general approach can be found in the important work of Lanford [205]. A classical reference for the existence of the pressure is the book of Ruelle [289]. See also, the more recent book of Presutti [279], in which the equivalence of ensembles is proved at the level of thermodynamic potentials. More on the equivalence of ensembles at the level of measures can be found in Section 6.14.1.

Van der Waals lattice gas. The van der Waals model studied in Section 4.9 incorporates the main assumptions made by van der Waals [339] about the interactions of a gas of particles, which we had already discussed in Chapter 1. As already mentioned in Chapter 2, the Curie–Weiss version of the van der Waals lattice gas model was introduced independently by many people, including Temperley [328], Husimi [167] and Kac [183]. Our treatment of its pressure, as a function of the variables ρ and v, was taken from Dorlas' book [90].

Ising lattice gas. The mapping between the Ising model and the lattice gas appeared first explicitly in [220].

Kac limit. The first justification of Maxwell's construction based on the van der Waals limit was given by Kac, Uhlenbeck and Hemmer [184] for a one-dimensional gas of hard rods. The result was then substantially generalized by Lebowitz and Penrose [215]; our proof of Theorem 4.31 follows essentially theirs. A general reference covering much more material on systems with Kac interactions is Presutti's book [279]. More bibliographical references on Kac interactions will be given in the complements.

4.12 Complements and further reading

4.12.1 The phase separation phenomenon

In the current chapter, we have provided a satisfactory description of the condensation phenomenon in terms of the thermodynamic potentials, but we have not discussed what really happens during condensation, as observed in typical configurations. In this section, we provide a brief description of what can be said about this problem from a mathematical point of view. To keep the discussion as simple as possible, only the nearest-neighbor lattice gas will be considered, although much of what follows can be extended to general finite-range ferromagnetic interactions. Detailed information and more references can be found in the review [28].

Consider the nearest-neighbor lattice gas in $\mathsf{B}(n) \subset \mathbb{Z}^d$, $d \geq 2$. We have seen in Theorem 4.15 that, in the grand canonical ensemble with $\mu = \mu_*$, the typical values of the density lie in the interval $[\rho_g, \rho_l]$, on which the rate function $I_{\beta,\mu}$ vanishes. In particular, this result does not allow us to discriminate between the various possible values of the density in this interval. There is a reason for that: in this regime, the average density in the box is in fact very sensitive to the boundary condition and thus cannot be derived using only the thermodynamic limit of the pressure and of the free energy.

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Similarly, in the canonical ensemble with $\rho \in [\rho_g, \rho_l]$, the lack of strict convexity of the free energy prevents us from using Theorem 4.19 to determine the typical values of the local density in various subsets of the box $\Lambda = \mathsf{B}(n)$ for such values of ρ. As we will see, in this regime, typical values of the *local* density are still given by ρ_g and ρ_l. However, on a macroscopic scale, typical configurations are not homogeneous anymore, but exhibit *phase coexistence*. Namely, in order to satisfy the constraint that the overall density in Λ is ρ, the system reacts by *spatially segregating* the gas and liquid phases: for example, if the boundary condition favors the gas phase, there is spontaneous creation of a droplet of liquid phase surrounded by the gas phase, as depicted in Figure 4.23.

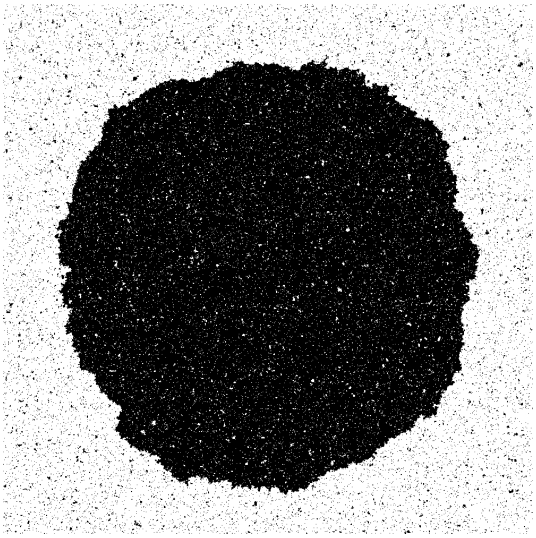

Figure 4.23: A typical configuration of the nearest-neighbor lattice gas in a box of size 500×500 in the canonical ensemble at inverse temperature $\beta = 2$ (with a boundary condition favoring the gas phase). The simulation was made by fixing the density to the value $\rho = \frac{1}{2} \in (\rho_g, \rho_l)$. Clearly, spatial homogeneity in the sense of (4.34) is no longer true; phase separation occurs. In a typical configuration, a macroscopic liquid droplet of density ρ_l appears, immersed in a gas phase of density ρ_g. This droplet's shape is described, asymptotically, by a Wulff crystal (see below).

In the thermodynamic limit, the droplet's macroscopic shape becomes deterministic, with microscopic fluctuations. Namely, let us denote by $V \subset \Lambda$ the droplet. The following occurs with a probability tending to 1 as $\Lambda \uparrow \mathbb{Z}^d$:

1. Up to microscopic corrections, its *volume* is given by $|V| = \frac{\rho - \rho_g}{\rho_l - \rho_g} |\Lambda|$. In this way, the average density in Λ is indeed ρ, since

$$\rho_l |V| + \rho_g (|\Lambda| - |V|) \simeq \rho |\Lambda| .$$

2. The *shape* of the droplet converges to a deterministic shape characterized as a minimizer of a surface functional involving the *surface free energy*, to be defined below.

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These two statements will be given a more precise form in Theorem 4.33 below. We will see that the macroscopic geometry of the regions occupied by the gas and liquid phases depends strongly on the boundary condition and thus, again, cannot be deduced using only the thermodynamic limit of the pressure and of the free energy. In order to go further, we need to go beyond such bulk quantities, and consider corrections coming from surface effects.

Surface corrections to the pressure

In order to discuss corrections to the pressure, we need to consider non-trivial boundary conditions. Similarly to what we did in Chapter 3, we consider the Hamiltonian

$$\mathscr{H}_{\Lambda;\mu_*}(\eta) \stackrel{\text{def}}{=} - \sum_{\{i,j\}\in\mathscr{E}_\Lambda^{\text{b}}} \eta_i\eta_j - \mu_* \sum_{i\in\Lambda} \eta_i \,,$$

defined on infinite configurations $\eta \in \Omega \stackrel{\text{def}}{=} \{0,1\}^{\mathbb{Z}^d}$. Let

$$\Omega_\Lambda^1 \stackrel{\text{def}}{=} \left\{\eta\in\Omega : \eta_i = 1 \text{ for all } i\notin\Lambda\right\}, \qquad \Omega_\Lambda^0 \stackrel{\text{def}}{=} \left\{\eta\in\Omega : \eta_i = 0 \text{ for all } i\notin\Lambda\right\}.$$

We denote by $\nu^1_{\Lambda;\beta,\mu^*}$ and $\nu^0_{\Lambda;\beta,\mu^*}$ the corresponding Gibbs distributions in Λ:

$$\nu^1_{\Lambda;\beta,\mu^*}(\eta) \stackrel{\text{def}}{=} \frac{e^{-\beta\mathscr{H}_{\Lambda;\mu_*}(\eta)}}{\Theta^1_{\Lambda;\beta,\mu_*}} \mathbf{1}_{\{\eta\in\Omega^1_\Lambda\}}, \qquad \nu^0_{\Lambda;\beta,\mu^*}(\eta) \stackrel{\text{def}}{=} \frac{e^{-\beta\mathscr{H}_{\Lambda;\mu_*}(\eta)}}{\Theta^0_{\Lambda;\beta,\mu_*}} \mathbf{1}_{\{\eta\in\Omega^0_\Lambda\}},$$

where $\Theta^1_{\Lambda;\beta,\mu_*}$ and $\Theta^0_{\Lambda;\beta,\mu_*}$ are the associated partition functions.

Using the mapping between the lattice gas and the Ising model, it is easy to check that these two probability measures correspond exactly to the Gibbs distribution of the Ising model, at inverse temperature $\beta/4$ and with magnetic field $h=0$, in Λ with $+$, respectively $-$, boundary condition. It thus follows from the analysis in Chapter 3 that, when $\beta > \beta_{\text{c}}^{\text{l.g.}}$, typical configurations under $\nu^1_{\Lambda;\beta,\mu^*}$ have a (homogeneous) density larger than $1/2$, while typical configurations under $\nu^0_{\Lambda;\beta,\mu^*}$ have a (homogeneous) density smaller than $1/2$. They thus describe, respectively, the liquid and gas phases.

Let us now turn to the corresponding finite-volume pressures:

$$p^1_{\Lambda;\beta} \stackrel{\text{def}}{=} \frac{1}{\beta|\Lambda|}\log\Theta^1_{\Lambda;\beta,\mu_*}, \qquad p^0_{\Lambda;\beta} \stackrel{\text{def}}{=} \frac{1}{\beta|\Lambda|}\log\Theta^0_{\Lambda;\beta,\mu_*}.$$

(For simplicity, we do not indicate μ_* in the notations for the pressures.) As usual, since the boundary condition plays no role in the definition of the thermodynamic pressure, $p^1_{\Lambda;\beta}$ and $p^0_{\Lambda;\beta}$ both converge to p_β in the thermodynamic limit, which implies in particular that

$$p^1_{\Lambda;\beta}|\Lambda| = p_\beta|\Lambda| + o(|\Lambda|)\,,$$

and similarly for $p^0_{\Lambda;\beta}$. In fact, it follows from the proof of Theorem 3.6 that the error $o(|\Lambda|)$ is in fact a *boundary term*, that is, it is $O(|\partial^{\text{in}}\Lambda|)$. It should thus not come as a surprise that this error term depends in general on the choice of the boundary condition. We therefore expect a more accurate description of the following type:

$$\begin{aligned} p^1_{\Lambda;\beta}|\Lambda| &= p_\beta|\Lambda| - \tau^1_\beta|\partial^{\text{in}}\Lambda| + o(|\partial^{\text{in}}\Lambda|)\,,\\ p^0_{\Lambda;\beta}|\Lambda| &= p_\beta|\Lambda| - \tau^0_\beta|\partial^{\text{in}}\Lambda| + o(|\partial^{\text{in}}\Lambda|)\,. \end{aligned} \tag{4.81}$$

Revised version, August 22 2017
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Here, $-\tau^1_\beta$ (resp. $-\tau^0_\beta$) should be interpreted as the contribution *per unit of area* to $p^1_{\Lambda;\beta}|\Lambda|$ (resp. $p^0_{\Lambda;\beta}|\Lambda|$), resulting from the interaction between the phase contained inside Λ and the boundary of the box. (The negative signs are introduced to respect the conventions, making τ^1_β and τ^0_β non-negative.)

Surface tension. Up to now, we have only considered the correction to the pressure in cases in which the boundary condition typically induces homogeneous configurations inside the box. We now consider what happens when the boundary condition induces the presence of a macroscopic interface. The surface tension measures the free energy (per unit of area) associated to an interface. It is given by a function $\tau_\beta(\cdot)$ defined on $\{\mathbf{n} \in \mathbb{R}^d : \|\mathbf{n}\|_2 = 1\}$, where $\mathbf{n}$ represents the direction perpendicular to the interface.

In order to induce the presence of a macroscopic interface, we proceed as in Section 3.10.7. Let us fix a direction $\mathbf{n} \in \mathbb{R}^d$ and define, for each $i \in \mathbb{Z}^d$,

$$\eta^{\mathbf{n}}_i \stackrel{\text{def}}{=} \begin{cases} 0 & \text{if } i \cdot \mathbf{n} \geq 0, \\ 1 & \text{otherwise,} \end{cases}$$

where $i \cdot \mathbf{n}$ denotes the scalar product on $\mathbb{R}^d$. This boundary condition is illustrated in Figure 4.24; it is a natural generalization of Dobrushin's boundary condition, which was introduced in Section 3.10.7. As explained there, the boundary condition $\eta^{\mathbf{n}}$ leads to the presence of an interface, separating the lower part of the box (filled with liquid) from its upper half (filled with gas).

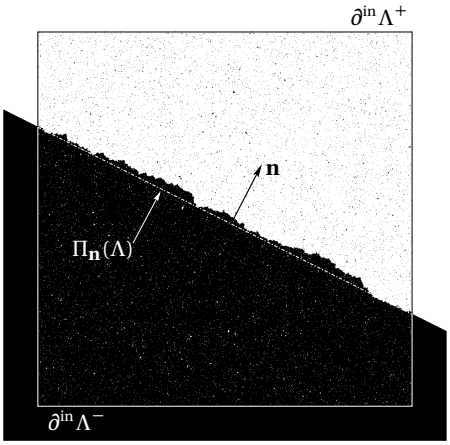

Figure 4.24: A picture representing the construction of the surface tension $\tau_\beta(\mathbf{n})$, by fixing a boundary condition in which all cells below (resp. above) the plane $\{x \cdot \mathbf{n} = 0\}$ are occupied by particles (resp. vacant).

Let us now extract the contribution to the pressure $p^{\mathbf{n}}_{\Lambda;\beta}$ due to this interface.

Let $\Pi_{\mathbf{n}}(\Lambda) \stackrel{\text{def}}{=} \{x \in [-n, n]^d : x \cdot \mathbf{n} = 0\}$ be the intersection of the hyperplane orthogonal to $\mathbf{n}$ with the box (seen as a subset of $\mathbb{R}^d$). In the discussion below, we assume that $\mathbf{n}$ has its last coordinate positive. This will allow to refer to the parts of Λ located *above* and *below* $\Pi_{\mathbf{n}}(\Lambda)$.

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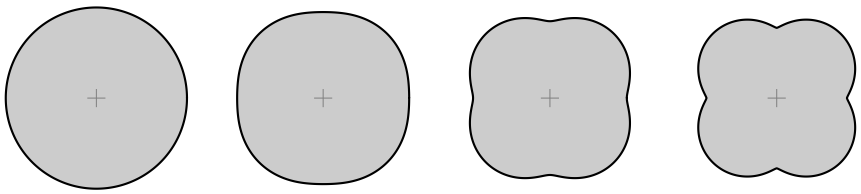

Figure 4.25: The surface tension of the two-dimensional nearest-neighbor lattice gas (as a function of the direction) for $\beta = 2.0$, 4.0, 8.0 and 16.0 (the scale differs for each value of β).

With the boundary condition $\eta^{\mathbf{n}}$, two contributions to the pressure should come from $\partial^{\text{in}}\Lambda$: one coming from the contact of the liquid with the lower part of the boundary of the box (below $\Pi_{\mathbf{n}}(\Lambda)$), denoted $-\tau^1_\beta|\partial^{\text{in}}\Lambda^-|$, and the other coming from the contact of the gas with the upper part of the boundary of the box (above $\Pi_{\mathbf{n}}(\Lambda)$), denoted $-\tau^0_\beta|\partial^{\text{in}}\Lambda^+|$.

Finally, the third contribution to the pressure should come from the *interface* that crosses the box, whose existence is forced by the choice of the boundary condition; it should depend on $\mathbf{n}$ and be proportional to $|\Pi_{\mathbf{n}}(\Lambda)|$ (that is, the area of $\Pi_{\mathbf{n}}(\Lambda)$). The decomposition of the pressure into its volume and surface contributions should therefore be

$$p^{\mathbf{n}}_{\Lambda;\beta}|\Lambda| = p_\beta|\Lambda| - \tau^0_\beta|\partial^{\text{in}}\Lambda^+| - \tau^1_\beta|\partial^{\text{in}}\Lambda^-| - \tau_\beta(\mathbf{n})|\Pi_{\mathbf{n}}(\Lambda)| + o(|\partial^{\text{in}}\Lambda|)\,. \tag{4.82}$$

Using (4.82), (4.81) and the fact that $|\partial^{\text{in}}\Lambda| = 2|\partial^{\text{in}}\Lambda^\pm|$, we get

$$\begin{aligned}\tau_\beta(\mathbf{n})|\Pi_{\mathbf{n}}(\Lambda)| &= -p^{\mathbf{n}}_{\Lambda;\beta}|\Lambda| + \tfrac{1}{2}(p^0_{\Lambda;\beta} + p^1_{\Lambda;\beta})|\Lambda| + o(|\partial^{\text{in}}\Lambda|) \\ &= -\frac{1}{\beta}\log\frac{\Theta^{\mathbf{n}}_{\Lambda;\beta,\mu_*}}{\left(\Theta^0_{\Lambda;\beta,\mu_*}\Theta^1_{\Lambda;\beta,\mu_*}\right)^{1/2}} + o(|\partial^{\text{in}}\Lambda|)\,.\end{aligned}$$

This then leads to the following natural definition.

Definition 4.32. *Let* $\mathbf{n}$ *be a unit vector in* $\mathbb{R}^d$*. The* ***surface tension*** *per unit area, orthogonally to the direction* $\mathbf{n}$*, is defined by*

$$\tau_\beta(\mathbf{n}) \stackrel{\text{def}}{=} -\lim_{k\to\infty}\frac{1}{\beta|\Pi_{\mathbf{n}}(\mathsf{B}(k))|}\log\frac{\Theta^{\mathbf{n}}_{\mathsf{B}(k);\beta,\mu_*}}{\left(\Theta^0_{\mathsf{B}(k);\beta,\mu_*}\Theta^1_{\mathsf{B}(k);\beta,\mu_*}\right)^{1/2}}\,.$$

The existence of the above limit can be proved using a subadditivity argument. We refer to [244] for a proof in a more general setup.

The surface tension has a number of important properties, the main one, for our purposes, being the following: for all $\mathbf{n}$,

$$\tau_\beta(\mathbf{n}) > 0 \text{ if and only if } \beta > \beta_{\text{c}}^{\text{l.g.}}\,. \tag{4.83}$$

The proof can be found in [53] and [217]. More information on the surface tension can be found in the review [271].

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Equilibrium crystal shapes

We can then define a functional on subsets $\mathsf{V} \subset \mathbb{R}^d$ with a smooth boundary (sufficiently smooth, say, to have a well defined exterior unit normal $\mathbf{n}_x$ at almost all $x \in \partial\mathsf{V}$):

$$\mathscr{W}(\mathsf{V}) \stackrel{\text{def}}{=} \int_{\partial\mathsf{V}} \tau_\beta(\mathbf{n}_x) \mathrm{d}S_x \,,$$

where $\mathrm{d}S_x$ represents the infinitesimal surface element of $\partial\mathsf{V}$ at x.

We can now get back to the problem of describing the droplet mentioned at the beginning of the section. Let therefore $\Lambda = \mathsf{B}(n)$ with n large. Below, we also identify Λ with the subset of $\mathbb{R}^d$ given as the union of all closed unit cubes centered at the vertices of Λ.

Consider then the following variational problem [3]:

$$\textit{Minimize } \mathscr{W}(\mathsf{V}) \textit{ among all } \mathsf{V} \subset \Lambda \textit{ whose volume equals } |\mathsf{V}| = \tfrac{\rho-\rho_g}{\rho_l-\rho_g}|\Lambda|.$$

It can be shown that, up to translations, the solution to this problem is unique; we denote it by $\mathsf{V}_* = \mathsf{V}_*(\beta,\rho)$. As a matter of fact, it can be given explicitly. Consider the **Wulff shape** or **equilibrium crystal shape** associated to $\tau_\beta(\cdot)$, defined by (see Figure 4.26)

$$\mathsf{v}_* = \mathsf{v}_*(\beta) \stackrel{\text{def}}{=} \left\{ x \in \mathbb{R}^d \,:\, x \cdot \mathbf{n} \le \tau_\beta(\mathbf{n}) \text{ for every unit vector } \mathbf{n} \in \mathbb{R}^d \right\}.$$

A solution to the variational problem is then given by an appropriate dilation of v_* (together with translations), provided that it is not too large to fit inside Λ:

$$\mathsf{V}_* = \frac{\rho-\rho_g}{\rho_l-\rho_g}|\Lambda|\frac{\mathsf{v}_*}{|\mathsf{v}_*|}\,.$$

In the general case, the solution is also obtained starting from v_*, but with some modifications; see [28].

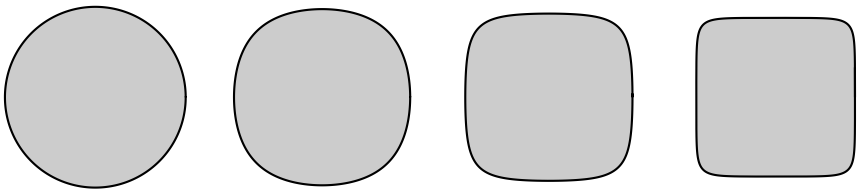

Figure 4.26: The equilibrium crystal shape for the two-dimensional Ising lattice gas at $\beta = 2.0$, 4.0, 8.0 and 16.0 (with the same fixed area).

Let us now state the result that characterizes the separation of phases. To keep things simple, and because the most precise results have been obtained in this context, we only discuss the two-dimensional case.

It will be convenient to describe the configurations using the Peierls contours introduced in section 3.7.2; in the lattice gas language, the latter separate empty vertices from those containing a particle.

Let us state a precise result, choosing a specific boundary condition:

[3] For this to make full sense, we should impose some regularity on the class of sets V involved, but we will abstain from discussing these issues here and refer to [28] for more information.

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Theorem 4.33. *Consider the two-dimensional nearest-neighbor lattice gas in the box $\Lambda = \mathsf{B}(n)$ with 0-boundary condition. Assume that $\beta > \beta_c^{\text{l.g.}}$, fix some $\rho \in (\rho_g, \rho_l)$ and set $N = \lfloor \rho |\Lambda| \rfloor$. Then,*

$$\lim_{n\to\infty} \nu^0_{\Lambda;\beta,N}(\mathscr{D}) = 1\,,$$

where $\mathscr{D}$ is the event defined as follows. There exist constants c_1, c_2, depending only on β, such that

- *all contours, except one which we denote by γ_0, have diameter at most $c_1 \log n$;*
- *the contour γ_0 has macroscopic size; it is closely approximated by a translate of V_*:*

$$\min_{x\in[-1,1]^2} n^{-1} d_{\mathbb{H}}\big(\gamma_0, x + \partial \mathsf{V}_*\big) \le c_2\, n^{-1/4} (\log n)^{1/2}\,,$$

where $d_{\mathbb{H}}(A;B)$ denotes the Hausdorff distance between A and B.

It can also be shown that the local density is given by ρ_g outside γ_0 and by ρ_l inside.

Together with the analysis of the thermodynamic potentials developed earlier in this chapter, this theory provides a satisfactory description of the condensation phenomenon at equilibrium.

The first result on phase separation is due to Minlos and Sinai [248], who showed that, at very low temperature, a unique large contour appears in Λ, whose shape is close to a square. (Their result actually holds in all $d \ge 2$.) For the two-dimensional model, the proper understanding of the role played by the surface tension, and the description of the scaling limit of this contour as the Wulff shape was first achieved by Dobrushin, Kotecký and Shlosman [79]. A different proof was then obtained by Pfister [270]. Building on the latter work, Ioffe managed to extend the proof to all $\beta > \beta_c(2)$ [170, 171]; the version stated above is due to Ioffe and Schonmann [173]. Extension to the Ising model in higher dimensions have been obtained by Bodineau [26] (at sufficiently low temperatures) and Cerf and Pisztora [64] (for all $\beta > \beta_c(d)$). A detailed analysis of the effect of boundary conditions on the equilibrium crystal shape is given in [272, 29]. Further relevant references and historical notes can be found in the review paper [28]. Similar results have been obtained for models with Kac interactions; see, for example, [18].

4.12.2 Kac interactions when γ is small but fixed

We saw in Theorem 4.31 that, at low temperature, the limiting free energy and pressure obtained via the van der Waals limit exhibit the characteristic features of a first-order phase transition. Let us make a few comments concerning what happens when studying these thermodynamic potentials when $\gamma > 0$ is small but fixed, not necessarily tending to 0.

First of all, observe that *regardless of the dimension of the system*, the functions obtained in the van der Waals limit are all given by some transformation of the *same* function $f^{\text{vW}}_\beta(\rho)$, that is, in the van der Waals limit $\gamma \downarrow 0$, the system loses its dependence on the dimension. This leads us to an important remark.

Namely, when $d = 1$, since $\gamma > 0$ corresponds to a potential with finite range interactions, the associated pressure $\mu \mapsto p_{\gamma,\beta}(\mu)$ is differentiable at all temperatures, as will be seen in Exercise 6.34 (in fact, it is even analytic [289, Theorem 5.6.2]). Therefore, by Theorem B.20, $\rho \mapsto f_{\gamma,\beta}(\rho)$ is always strictly convex when $\beta > \beta_c^{\text{vW}}$, for all $\gamma > 0$, and only becomes affine on the coexistence plateau *in the limit* $\gamma \downarrow 0$. This

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is of course not in contradiction with Theorem 4.31, since a convex but non-strictly convex function can be uniformly approximated arbitrarily well by a strictly convex function. Therefore when $\beta > \beta_c^{vW}$, when $d = 1$, the functions obtained in the van der Waals limit, $f_{0^+,\beta}(\rho)$ and $p_{0^+,\beta}(\mu)$, present non-analytic behaviors that are not representative of what happens when $\gamma > 0$, however small γ might be.

When $d \geq 2$, the situation is different, since we know that the Ising model exhibits a phase transition at sufficiently low temperature. One is thus naturally led to ask about the behavior of $f_{\gamma,\beta}$ and $p_{\gamma,\beta}$ for *small but fixed* values of $\gamma > 0$. This problem is not trivial since the interactions between two particles at fixed vertices (for example nearest neighbors) becomes small when γ is small.

The next theorem answers this question; it follows from the original works of Cassandro and Presutti [62] and Bovier and Zahradník [39], who introduced a convenient notion of contours for the Ising ferromagnet with Kac interactions.

Theorem 4.34. *($d \geq 2$) Let $\beta > \beta_c^{vW}$. There exists $\gamma_0 = \gamma_0(\beta) > 0$ such that, for all $0 < \gamma < \gamma_0$, $p_{\gamma,\beta}(\mu)$ is non-differentiable at $\mu_{*,\gamma} \stackrel{\text{def}}{=} -\kappa_\gamma/2$ and, as a consequence, $f_{\gamma,\beta}(\rho)$ is affine on $[\rho_{g,\gamma}, \rho_{l,\gamma}]$, where*

$$\rho_{g,\gamma} = \frac{\partial p_{\gamma,\beta}}{\partial \mu^-}\Big|_{\mu_{*,\gamma}} < \frac{\partial p_{\gamma,\beta}}{\partial \mu^+}\Big|_{\mu_{*,\gamma}} = \rho_{l,\gamma}.$$

Moreover, as $\gamma \downarrow 0$, $\rho_{g,\gamma} \to \rho_g$ and $\rho_{l,\gamma} \to \rho_l$, where ρ_g and ρ_l are the endpoints of the coexistence plateau of van der Waals' model.

Models with Kac interactions at small values of γ can be considered as *perturbations* of the mean-field behavior observed in the limit $\gamma \downarrow 0$. This allows for instance to compare the expectation of local observables with their mean-field counterparts, and extract useful information to study the model. This method was used by Lebowitz, Mazel and Presutti in [214] to provide one of the very few rigorous proofs of occurrence of a phase transition in the continuum.

For a much more detailed description of systems with Kac interactions, we refer the reader to the book of Presutti [279]. More comments on the case $\gamma > 0$ are made in the next section.

4.12.3 Condensation, metastability and the analytic structure of the isotherms

As we already said, from its very beginning, one of the central issues of statistical mechanics was to provide an explanation to the phase transitions observed in gases and liquids. In particular, the condensation phenomenon was used as a test to decide whether the theory of Boltzmann and Gibbs provided a sufficient structure on which phase transitions could be firmly understood. It was not even clear, at that time, whether a detailed study of the partition function could lead to a single function describing two distinct states, gas and liquid, or whether some additional hypotheses had to be made in order to allow for their coexistence.

The results obtained in this chapter, in particular those concerning the condensation phenomenon at low temperature, provide a satisfactory answer. Since condensation has been, historically, one of the cornerstones in the development of statistical mechanics, we will end this chapter with some comments regarding some of the first attempts made at describing condensation rigorously.

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Mayer's conjecture. The first notable attempt at obtaining a theoretical explanation of the condensation phenomenon, starting only from the partition function, was initiated by Mayer in the 1930s. In a series of papers with several coauthors, Mayer developed a theory to study the pressure of a model of particles in the continuum with pairwise interactions. Although not completely rigorous, his theory also firmly established the basis of the method invented by Ursell [337], known nowadays as the *cluster expansion* (see Chapter 5). We will not enter into too much detail, but rather sketch the argument he proposed for the mathematical description of condensation.

In [236], Mayer provided an expression for the coefficients a_n of the expansion of the pressure as a function of the **fugacity** $z \stackrel{\text{def}}{=} e^{\beta\mu}$:

$$\beta p_\beta(\mu) = a_1 z + a_2 z^2 + a_3 z^3 + \dots . \tag{4.84}$$

Mayer's argument then proceeded as follows. The series should converge at least for small values of z, which corresponds to large negative values of μ, that is, to a dilute phase. But if the series converges when $0 \le z < r_0$, and z is allowed to take complex values, then it defines a function, analytic in the disc $\{z \in \mathbb{C} : |z| < r_0\}$.

With a function describing the gas phase for small values of z at hand, Mayer associated the condensation phenomenon to *the first singularity encountered when continuing the pressure analytically along the real axis, from small to large values of* z. Let us assume that one such singularity is indeed encountered and denote it by z_s; see Figure 4.27. This way of defining the condensation point (the same characterization can be used when using other variables, like ρ or v) would later be referred to as **Mayer's conjecture**.

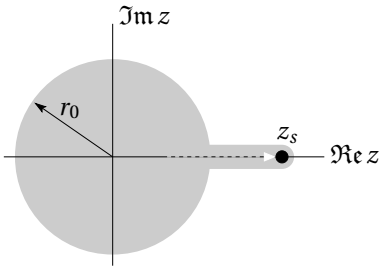

Figure 4.27: The determination of the condensation point according to Mayer: find the first singularity of the function defined by the series $a_1 z + a_2 z^2 + a_3 z^3 + \dots$, encountered along the positive real axis.

At that time, the question of whether Mayer's method could really describe the condensation phenomenon was debated (see [36]). One reason for that was that Mayer obtained (4.84) under several radical assumptions, one of them being that *the particles of the system are sufficiently far apart*, which is equivalent to assuming that the system is in a dilute (gas) phase. Therefore the equation of state given by the series had no reason a priori to be able to describe at the same time the dense (liquid) phase. This indicates that, in order for the full equation of state to be given, some other argument should be used to yield a second function describing the dense phase (large values of z). The two functions should then be combined, possibly using a thermodynamical argument similar to the Maxwell construction, in order for equilibrium to be described.

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But another question was raised. If a singularity z_s is indeed found on the positive real axis, closest to the origin, does it necessarily describe the true condensation point? Here, van der Waals and Maxwell's theory provides the immediate counter-example showing that condensation is not necessarily related to a singularity. Namely, consider the pressure of the van der Waals model at low temperature, computed in Section 4.9.2. On the gas branch, $\rho \in (0, \rho_g)$, we obtained

$$\widetilde{p}_\beta^{\text{vW}}(\rho) = -\tfrac{1}{2}\rho^2 - \tfrac{1}{\beta}\log(1-\rho)\,,$$

and Taylor expanded $\log(1-\rho)$ (Remark 4.26) to obtain the virial expansion

$$\beta\widetilde{p}_\beta^{\text{vW}}(\rho) = \rho + \tfrac{1}{2}(1-\beta)\rho^2 + \tfrac{1}{3}\rho^3 + \tfrac{1}{4}\rho^4 + \cdots$$

The radius of convergence of the latter series is equal to 1: it defines an analytic function on the unit disk $\{\rho \in \mathbb{C} : |\rho| < 1\}$ and, as ρ increases from $\rho = 0$, the first singularity along the positive real axis is encountered at $\rho = 1$, *not* at $\rho = \rho_g < 1$. This shows that, for this model, Mayer's way of determining the condensation point fails: the absence of a complex singularity at ρ_g makes it impossible to determine the position of the condensation point only from the knowledge of the values of the pressure on the gas branch.

Since the van der Waals–Maxwell theory remained of central importance at the time, theoretical physicists had good reasons to believe that its way of describing isotherms, by patching different branches together, was generic and should be a consequence of the first principles of statistical mechanics. It was therefore taken for granted at that time in the physics community that analytic continuations such as the one observed in van der Waals' theory were always possible. They were actually even given some importance, due to their relation to another important physical phenomenon.

Metastable states. Consider the isotherm of Figure 1.5. What is the significance of the part of van der Waals' isotherm $p(v)$ that is left out *after* Maxwell's construction, that is for $v \in [v_l, v_g]$?

From a mathematical point of view, $p(v)$ provides of course the unique *analytic continuation* from one of the branches of MC $p(v)$ to the other, along the paths $v \uparrow v_l$ and $v \downarrow v_g$. From an experimental point of view, an interesting observation can be made, which we have not described yet. Namely, if the experiment is done with care, it is actually possible to slowly drive a real gas along the path $v \downarrow v_g$, across v_g, without it starting to condense. The state obtained has a pressure which is larger than the saturation pressure, and is called a **super-saturated vapor**. It is not an equilibrium state, but what is called a **metastable gas state**. Such a state can have a very long lifetime, but a sufficiently strong external perturbation abruptly drives the system away from it, resulting in a mixture of equilibrium gas and liquid phases at the saturation pressure. Similarly, it is possible to observe a metastable liquid phase, the so-called **superheated liquid**, by slowly increasing v beyond v_l starting from the liquid phase.

Since metastable states are observed in the laboratory but are not equilibrium states in the sense of statistical mechanics, theoretical physicists considered analytic continuation as a way of at least defining their pressure [206].

Moving back to the case considered earlier, the analytic continuation of $\widetilde{p}_\beta(\rho)$ through ρ_g coming from the gas branch, as represented by the dotted line below, would therefore provide the pressure of a supersaturated vapor:

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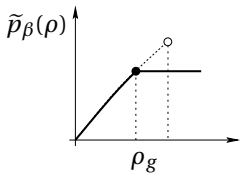

Singularity and the droplet mechanism. However, the true analytic structure of isotherms would later prove to be very different. In the 1960–1970s, an argument of a completely different nature suggested that the branches of an isotherm were separated by *singularities* preventing an analytic continuation. The argument was based on the use of the *droplet model*, whose pressure mimics the pressure of a single droplet of fluid immersed in a gas. This model was introduced for the first time by Andreev [11] and studied more systematically by Fisher [106] (see Exercise 4.16 below).

The striking feature suggested by this toy model was that the actual condensation phenomenon, namely the appearance of large stable droplets of liquid, was responsible for the presence of a singularity of the pressure at the condensation point.

These predictions were confirmed rigorously in the celebrated work [174] of Isakov, which we already mentioned in Section 3.10.9, Theorem 3.67. Isakov implemented rigorously the mechanism suggested by Andreev and Fisher, by giving a detailed study of the large contours (representing droplets) in the low-temperature Ising model ($d \geq 2$), as a function of the magnetic field. In essence, he showed that the coexistence of both phases, at $h = 0$, was responsible for the peculiar behavior of the derivatives of the pressure seen in (3.99).

When translated into the nearest-neighbor lattice gas language, Isakov's analysis implies that, when β is sufficiently large, all the thermodynamic potentials considered in Section 4.8 have singularities blocking analytic continuation at their transition points. For instance p_β, which is analytic on the branches $(-\infty, \mu_*)$ and (μ_*, ∞) by Theorem 4.22, has a singularity at μ_* that forbids analytic continuations along the paths $\mu \uparrow \mu_*$ and $\mu \downarrow \mu_*$. This can be shown to also prevent the existence of analytic continuations of f_β and $\widetilde{p}_\beta$ along $\rho \uparrow \rho_g$ or $\rho \downarrow \rho_l$, or of $\widehat{p}_\beta$ along $v \uparrow v_l$ or $v \downarrow v_g$ (see [112]).

These results strongly support Mayer's conjecture, at least for discrete spin systems with finite-range interactions: the condensation point can in principle be detected by studying a single branch up to its first singularity. They also definitely rule out the possibility of studying metastability by means of analytic continuation (see the bibliographical references given below).

Moreover, Isakov's result indicates that the global structure of the isotherms in "real" systems is more complex since the branches of the isotherms are represented by functions that cannot be united into one single analytic function. In particular, the pressure of a model with short range interactions *is not obtained by applying some Maxwell-type construction to a smooth function.* This sharp contrast with the van der Waals model comes from the fact that separation of phases (as briefly described in Section 4.12.1) occurs in systems with finite-range interactions, but not in mean-field models.

We mention further bibliographical references related to the topics discussed above. Interesting papers related to Mayer's conjecture include the papers of Kahn

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and Uhlenbeck [185], and Born and Fuchs [36]. In [204], Lanford and Ruelle ruled out the possibility of analytic continuation of the pressure, using an argument involving the variational principle for Gibbs states (this variational problem will be described later in Chapter 6).

Prior to the work of Isakov, various attempts had been made at describing metastability via analytic continuation for several toy models. These include papers of Schulman and coauthors [253, 281, 280].

In [114], the analysis of Isakov was generalized to the class of two-phase models with finite-range interactions considered in Pirogov–Sinai Theory (Chapter 7). The link between the absence of analytic continuation for finite-range models and the mean-field behavior of the van der Waals model was clarified in [113], where a Kać potential with a magnetic field was considered, and the disappearance of its singularity in the van der Waals limit was analyzed in detail.

Additional information on the non-analytic aspects of thermodynamic potentials at first-order phase transitions can be found in the review of Pfister [275] or in [112].

It is widely accepted, nowadays, that metastability is a dynamical phenomenon that does not enter the framework of equilibrium statistical mechanics. An important contribution to the understanding of metastability from such a point of view can be found in [297]. A modern presentation of metastability, from the point of view of stochastic dynamics, can be found in the books by Olivieri and Vares [258] and Bovier and den Hollander [38].

Exercise 4.16. *Consider, for $d \geq 2$,*

$$\psi_\beta(h) \stackrel{\text{def}}{=} \sum_{n\geq 1} e^{-\beta 2dn^{(d-1)/d}} e^{-hn},$$

which is a version of the droplet toy model considered by Fisher [106], formulated in the spin language. (The sum is to be interpreted as the pressure of a cubic droplet of $-$ spins immersed in a sea of $+$ spins, centered at the origin; if the droplet has volume n, $-\beta 2dn^{(d-1)/d}$ represents its surface energy, and $-hn$ the energy due to the effect of the magnetic field on its volume.) Verify that ψ_β is analytic in $H^+ \stackrel{\text{def}}{=} \{\mathfrak{Re}\, h > 0\}$. Then, show that ψ_β has no analytic continuation across $h = 0$ (along $h \downarrow 0$), by computing the limits

$$\lim_{h\downarrow 0} \frac{\mathrm{d}^k \psi_\beta}{\mathrm{d}h^k}\Big|_h$$

and showing that they have the same behavior as the one described in (3.99).

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