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Lecture Notes 2: Basic Principles of Statistical Mechanics

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1 Introduction

Gibbs distributions, and methods to study them, play a fundamental role in problems of modern coding and constraint satisfaction. They can be viewed as purely mathematical objects, but some insight can be gained by understanding why they are natural objects in the context of physical models. This is the goal of this chapter.

Statistical mechanics describes the behavior of large systems or ”macroscopic systems” that are composed of a large number of degrees of freedom. For example condensed matter systems are composed of $O(10^{23})$ atoms, molecules, magnetic moments, spins, etc. Many problems of coding and computer science also involve a large number of degrees of freedom (e.g. bits) also. A precise knowledge and description of the motion of each molecule in a macroscopic system would be impossible and is in fact inessential to the understanding of the macroscopic properties of the system. The general approach of statistical mechanics is to replace the fully deterministic description in terms of laws of motion by a probabilistic description based on appropriate probability distributions, that one has to guess.[1]

The correct probabilistic description is known only for systems which have reached thermal equilibrium, for which the macroscopic laws of usual thermodynamics apply. Gibbs distributions introduced in this chapter only describe those. We will derive Gibbs distributions from two “natural” principles which one can take as the definition of “thermal equilibrium”.

Systems that do not fall in this category are said to be “out of equilibrium” and their fundamental probabilistic description(s) (if this is even possible) is not elucidated (such systems range all the way from stationary heat or electric flows up to the more fancy living systems).

The Gibbs measures that we seek do not depend on the detailed form of the microscopic dynamics for the degrees of freedom (the equations of motion of Newton for classical particles or of Heisenberg for a quantum system) but only on the fact that there exist conserved quantities. In fact even if the dynamics is unknown, or unspecified, or random, we can write down the Gibbs measures simply in terms of the conserved quantities.

The prime example of a conserved quantity is the energy of an isolated system. We will stick to the simple case where there is only one conserved quantity, namely the energy. It will also be useful to have a concrete working example in mind. The following is a toy model which turns out to be one of the most important and most studied models of classical statistical mechanics. More will be said about it in the third lecture.

Example 1 (Lattice gas model) *Replace continuum space by a discrete d-dimensional grid (see figure 1, $d = 3$ may seem the most relevant case but other values of d are of also*

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[1] At the turn of the 19th to 20th century this constituted an important shift of paradigm, which emerged through the works of Helmholtz, Maxwell, Boltzmann, Planck, Gibbs, Einstein and others.

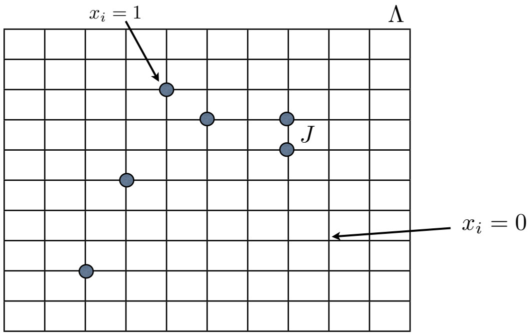

Figure 1: The lattice gas model. At most one particle occupies a lattice site. There is an energy cost for neighboring particles.

of great importance both theoretically and practically). Particles (e.g. atoms) can occupy the vertices of this grid and at most one atom is present on a vertex. We will call V *the set of vertices and* E *the set of edges. The configuration of the system is described by a vector* $(x_1, \cdots, x_{|V|})$ *where* $x_i = 1$ *if an atom is present at vertex* i *and* $x_i = 0$ *if vertex* i *is empty. We suppose that only neighboring atoms interact and that the interaction energy is* $-J$ *(*$J < 0$ *corresponds to repulsion and* $J > 0$ *to attraction). The total energy function, also called Hamiltonian in physics, or cost function in computer science, is then*

$$\mathcal{H}(x_1, \ldots, x_{|V|}) = -J \sum_{(i,j)\in E} x_i x_j - \mu \sum_{i\in V} x_i, \tag{1}$$

The real number μ *is a cost associated to the presence or absence of a particle (this might be a chemical affinity or a chemical potential). The detailed dynamics* $x_i(t)$, $i \in V$ *as a function of time* t *is not specified here. We only assume that the dynamics is such that the total energy, call it* E, *of the system is conserved. This means that at any time* t *we have*

$$\mathcal{H}(x_1(t), \ldots, x_{|V|}(t)) = E \tag{2}$$

The set of configurations satisfying this equation is called the energy surface and is denoted Γ_E. *Note that* $\Gamma_E \subset \{0,1\}^{|V|}$.

Example 2 (Ising model) *The Ising model is very similar. there the degrees of freedoms describe magnetic moments localized at the sites of a crystal, here our grid* (V, E). *These are modeled by the so-called spin variable* $s_i = \pm$, $i \in V$. *The Hamiltonian is*

$$\mathcal{H}(s_1, \ldots, s_{|V|}) = -J \sum_{(i,j)\in E} s_i s_j - h \sum_{i\in V} s_i, \tag{3}$$

Mathematically speaking the lattice-gas and Ising models are equivalent. One can go from one to the other simply by performing the change of variable $x_i = \frac{1-s_i}{2}$ *or* $(-1)^{x_i} = s_i$ *and redefining the interaction constants.*

Remark. Real world systems have continuous degrees of freedom. For classical particle systems, $\{0,1\}^{|V|}$ is replaced by the phase space which is the set of all positions and velocities, and Γ_E really is a variety (surface). For magnetic systems spins $s_i = \pm$ are replaced by vectors. For quantum systems degrees of freedoms such as positions, velocities and spins are non commuting operators (matrices). Remarkably in all these mathematical settings the concepts of statistical mechanics are the same than in the discrete setting, which is our concern here.

2 Two postulates

There is no entirely logical or unique way of introducing a new physical law. Here we will derive the Gibbs distributions, starting from two economical postulates. The first one may seem reasonable. The second one is the mark of Boltzmann's genius (his famous simple formula (12)). The theory is validated by its experimental success.

2.1 The Ergodic Hypothesis

Let T be the experimental time scale on which we measure an observable quantity $\phi(x_1(t), \ldots, x_{|V|}(t))$ and let τ the microscopic dynamical time scale. In practice $T \gg \tau$. We assume that the result of the measure is an average

$$\frac{1}{T}\int_{-T/2}^{T/2} \phi(x_1(t), \ldots, x_{|V|}(t)) \equiv \langle \phi \rangle. \tag{4}$$

For an *isolated system*, the state (of the system) visits all configurations (in the lattice-gas, $(x_1, \ldots, x_{|V|}) \in \{0,1\}^{|V|}$) that are compatible with conservation of energy, $\Gamma_E = \{\underline{x} | \mathcal{H}(\underline{x}) = E\}$. This set is called the energy surface of the isolated system. The *ergodic hypothesis* assumes that the system spends an equal amount of time around each configuration on the energy surface. More precisely, under the assumptions that: i) the experimental time scale is much larger than the microscopic one, $\tau/T \to 0$, ii) the energy density is fixed $E/|V| = e$, iii) and the size of the system is very large $|V| \to \infty$, the above average can is calculated as follows:

$$\lim \frac{1}{T}\int_{-T/2}^{T/2} dt\, \phi(x_1(t), \ldots, x_{|V|}(t)) = \frac{\sum_{\underline{x}\in\{0,1\}^{|V|}} \mathbb{I}(\underline{x} \in \Gamma_E)\phi(\underline{x})}{\sum_{\underline{x}\in\{0,1\}^{|V|}} \mathbb{I}(\underline{x} \in \Gamma_E)}, \tag{5}$$

where $\underline{x} = (x_1, \ldots, x_{|V|})$ and $\Gamma_E = \{\underline{x} | \mathcal{H}(\underline{x}) = E\}$ is called the *energy surface.*

Definition 1 *We define the micro-canonical measure as*

$$\mu_{\text{micro}}(\underline{x}) = \frac{\mathbb{I}(\underline{x} \in \Gamma_E)}{\sum_{\underline{x}\in\{0,1\}^{|V|}} \mathbb{I}(\underline{x} \in \Gamma_E)}. \tag{6}$$

The ergodic hypothesis states that the time average of a measured quantity can be computed by taking the expected value with respect to the micro-canonical measure. We have replaced the detailed dynamical information by a measure.

From a modern perspective this hypothesis should be viewed at best as an attempt to justify the introduction of the micro-canonical measure. For all practical purposes, when the system has reached thermal equilibrium one can calculate expectation values thanks to the micro-canonical measure.

It is not obvious that the identity (5) should be exactly true, or that it is even necessary. We have not specified very precisely how we take the limits $\frac{\tau}{T} \to 0$ and $|V| \to +\infty$; we have not specified to which class of functions ϕ we want to apply the hypothesis; we have not specified what are the initial conditions of the trajectory $\underline{x}(t)$; etc. All these daunting problems have been the subject of much debates and efforts and the hypothesis has played an important historical role. In mathematics, an outcome of these efforts is a deep branch of mathematics called "ergodic theory". The hypothesis has been proven for simple systems with only a few particles (a finite number of them) and simple dynamical laws. The first proof goes back to Sinai (around 1970) for one particle in a billiard shaped region, whose dynamics is given by straight lines reflecting at the billiard walls, and has since then been extended to a finite fixed number of hard spheres in the billiard. Note that such systems with a small number of degrees of freedom are not at all the concern of (traditional) statistical mechanics.

We summarize this discussion by formulating our first principle:

Postulate 1. *For a macroscopic isolated system with conserved energy, measurable quantities can be calculated as averages with respect to the micro-canonical measure.*

2.2 Boltzmann's Principle

Set

$$W(E) = \sum_{\underline{x} \in \{0,1\}^{|V|}} \mathbb{I}(\underline{x} \in \Gamma_E). \tag{7}$$

For the systems of interest the above expression has an exponential behavior as the size of the system grows.

$$\sum_{\underline{x} \in \{0,1\}^{|V|}} \mathbb{I}(\underline{x} \in \Gamma_E) \simeq \exp(\mathcal{S}(E)), \tag{8}$$

with $\mathcal{S}(E) = O(|V|)$. Define the *Boltzmann entropy* as

$$\mathcal{S}_{Boltz}(E) = \ln W(E). \tag{9}$$

A priori, this is a purely mathematical combinatorial quantity.

Example 3 *Let us consider the lattice gas model introduced in the previous example for the simple case* $J = 0$. *Pick* E/μ *lattice nodes among* $|V|$ *nodes with the state* $+1$ *and the rest* 0. *Hence,*

$$W(E) = \binom{|V|}{E/\mu} \simeq \exp\left(|V| h_2(\frac{E}{\mu|V|})\right), \tag{10}$$

where $h_2(\cdot)$ is the binary entropy function. In the infinite size limit we have

$$s(e) = \lim_{\substack{|V|\to\infty \\ E/|V|=e}} \frac{\mathcal{S}(E)}{|V|} = h_2\left(\frac{E}{\mu|V|}\right) = h_2\left(\frac{e}{\mu}\right), \tag{11}$$

where $e = E/|V|$. Note that this is a concave function (for physicaly sensible Hamiltonians the Boltzmann entropy is a concave of e; this is not always the case in computer science and coding problems with hard constraints).

Postulate 2. *(Boltzmann) The thermodynamic entropy measured in an experiment*[2] *and the Boltzmann entropy (a pure counting object) are equal. More precisely,*

$$\mathcal{S}_{Thermo} = k_B \mathcal{S}_{Boltz}, \tag{12}$$

where

$$\frac{\partial \mathcal{S}_{Thermo}}{\partial E} = \frac{1}{T}. \tag{13}$$

and T is the temperature measured by a thermometer. Here k_B is Boltzmann's constant that relates temperature units of the thermometer with energy units. It is not really a fundamental constant: one can always measure temperature in units of energy and set $k_B = 1$ (this is not usual practice though).

This postulate makes the connection between statistical mechanics and thermodynamics. It allows to compute thermodynamic quantities such as thermodynamic entropy and free energy (intuitively free energy is the amount of energy that can be transformed into work while maintaining the temperature and other quantities - volume or pressure - constant).

3 Gibbs Measure

The micro-canonical measure described earlier, only characterizes an isolated system. However, real macroscopic systems are not isolated. One should also notice that in practice, in order to reach thermal equilibrium it is necessary to put systems in contact with a thermal bath. For simplicity, let us again take our lattice gas model where we have a large isolated system denoted by the graph $G = (V, E)$. It is best to think of G as being infinite, $G = \mathbb{Z}^d$. We assume that this large system has reached thermal equilibrium with temperature T. Therefore, we know that it is described by

$$\mu_{\text{micro}}(\underline{x}) = \frac{\mathbb{I}(\underline{x} \in \Gamma_E)}{\sum_{\underline{x}\in\{0,1\}^{|V|}} \mathbb{I}(\underline{x} \in \Gamma_E)}. \tag{14}$$

Now, let us consider a much smaller but still macroscopic system $S \subset V$ (see Figure 2). The main question we answer in this section is what is the induced measure on S? The

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[2] We do not review here what thermodynamic entropy is and how it is measured. This was understood by Carnot, Clausius, Joule, Helmholtz and others in their work on heat engines in the 19th century. For us, equation (13) defines $\mathcal{S}_{Thermo}$.

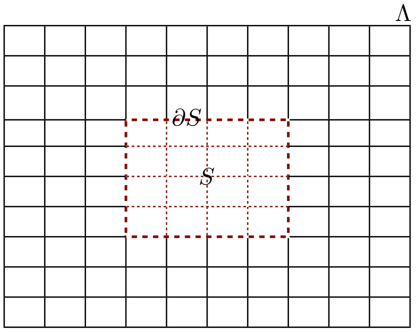

Figure 2: The system S is embedded in a thermal bath V. The total system V is considered as an isolated system and its total energy E is conserved. We compute the induced measure on S.

probability that the configuration of this smaller systems is $x_1, \dots, x_{|S|}$ reads

$$\mu_{ind}(x_1, \dots, x_{|S|}) = \sum_{x_{|S|+1}, \dots, x_{|V|}} \mu(x_1, \dots, x_{|V|}) = \frac{\sum_{x_{|S|+1}, \dots, x_{|V|}} \mathbb{I}(\underline{x} \in \Gamma_E)}{\sum_{x_1, \dots, x_{|V|}} \mathbb{I}(\underline{x} \in \Gamma_E)}. \tag{15}$$

The total energy can be written as,

$$\begin{aligned} E &= \mathcal{H}(x_1, \dots, x_{|V|}) \\ &= \mathcal{H}_S(x_1, \dots, x_{|S|}) + \mathcal{H}_{V \setminus S}(x_{S+1}, \dots, x_{|V|}) + \mathcal{H}_{int}, \end{aligned}$$

where $\mathcal{H}_{int}$ is the term capturing the interactions between particles in the sets S and V. Note that in general we have $\mathcal{H}_S = O(|S|)$, $\mathcal{H}_{V \setminus S} = O(|V \setminus S|)$ and $\mathcal{H}_{int} = O(|\partial S|)$. Since $O(|V \setminus S|) \gg O(|S|) \gg O(|\partial S|)$, the term $\mathcal{H}_{int}$ can be neglected from the above expression for energy. Note however that this is the term that allows S to reach thermal equilibrium through the interactions with the bath. For fixed $x_1, \dots, x_{|S|}$ we get

$$\begin{aligned} \mu_{ind}(x_1, \dots, x_{|S|}) &= \frac{\sum_{x_{|S|+1}, \dots, x_{|V|}} \mathbb{I}((x_{|S|+1}, \dots, x_{|V|}) \in \Gamma_{E - \mathcal{H}_S(x_1, \dots, x_{|S|})})}{\sum_{x_1, \dots, x_{|S|}} \sum_{x_{|S|+1}, \dots, x_{|V|}} \mathbb{I}((x_{|S|+1}, \dots, x_{|V|}) \in \Gamma_{E - \mathcal{H}_S(x_1, \dots, x_{|S|})})} \\ &= \frac{\exp(\mathcal{S}(E - \mathcal{H}_S(x_1, \dots, x_{|S|})))}{\sum_{x_1, \dots, x_{|S|}} \exp(\mathcal{S}(E - \mathcal{H}_S(x_1, \dots, x_{|S|})))} \\ &\overset{(a)}{=} \frac{\exp(\mathcal{S}(E) - \mathcal{H}_S(x_1, \dots, x_{|S|}) \frac{\partial \mathcal{S}}{\partial E} + \dots)}{\sum_{x_1, \dots, x_{|S|}} \exp(\mathcal{S}(E) - \mathcal{H}_S(x_1, \dots, x_{|S|}) \frac{\partial \mathcal{S}}{\partial E} + \dots)} \\ &\overset{(b)}{=} \frac{\exp\left(-\frac{\mathcal{H}_S(x_1, \dots, x_{|S|})}{k_B T}\right)}{\sum_{x_1, \dots, x_{|S|}} \exp\left(-\frac{\mathcal{H}_S(x_1, \dots, x_{|S|})}{k_B T}\right)}, \end{aligned}$$

where in (a) we used the Taylor expansion and in (b) the Boltzmann's principle. The resulting measure is nothing else than the Gibbs measure.

Definition 2 (Gibbs measure) *We define the Gibbs measure of the system S at thermal equilibrium with a bath of temperature T as*

$$\mu_{Gibbs}(x_1, \ldots, x_{|S|}) = \frac{1}{Z} \exp\left(-\frac{\mathcal{H}_S(x_1, \ldots, x_{|S|})}{k_B T}\right), \tag{16}$$

where the normalizing factor Z is called the partition function

$$Z = \sum_{x_1, \ldots, x_{|S|}} \exp\left(-\frac{\mathcal{H}_S(x_1, \ldots, x_{|S|})}{k_B T}\right)$$

Remark. In this derivation an important assumption was that $\mathcal{H}_{int}$ between the system and its complement can be neglected. For finite dimensional systems with local (i.e. finite range, or fast decaying with distance) interactions between particles this is always true. However if one deals with infinite dimensional systems (meaning here that $d \to +\infty$ or that the graph G cannot be metrically embedded in a finite dimensional space) or if the interactions are very long ranged this assumption may be problematic.

4 Free Energy, Entropy and Equivalence of Ensembles

The formulation in terms of the Gibbs measure above is also called *canonical ensemble* formulation. In practice which ensemble should one choose for the theoretical description of a large system: the micro-canonical or the canonical ? No system is really isolated and it would seem that the canonical description is more natural. However for large systems the energy fluctuations are negligible (of the order of the surface to be compared to the volume) and the micro-canonical can also be used. It is a matter of convenience which one to choose[3] and there are rules that allow to pass from one ensemble to another.

In the micro-canonical ensemble one computes the *entropy*

$$s(e) = \lim_{\substack{|V| \to \infty \\ E/|V| = e}} \frac{1}{|V|} \ln W(E). \tag{17}$$

In the canonical ensemble the relevant quantity is the *free energy*

$$f(T) = -k_B T \lim_{|S| \to \infty} \frac{1}{|S|} \ln Z. \tag{18}$$

One can show that free energy and entropy are related by a *Legendre transformation*,

$$f(T) = \min_e (e - k_B T s(e)). \tag{19}$$

Note that $f(T)$ is a concave function of T. Since $s(e)$ is concave, the Legendre transform can be inverted, and the entropy recovered from the free energy. This is what is meant by equivalence of ensembles.

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[3] In principle. An important condition is locality of interactions.

For completeness let us sketch the derivation of the last relation. The partition function can be written as

$$\sum_{x_1,\ldots,x_{|S|}} \exp\left(-\frac{\mathcal{H}_S(x_1,\ldots,x_{|S|})}{k_BT}\right) = \sum_E W(E)\exp(-\frac{E}{k_BT})$$

$$\approx |S|\int de\, e^{-|S|(\frac{e}{k_BT}-s(e))}$$

Taking the logarithm on both sides and going to the infinite size limit yields

$$\lim_{|S|\to+\infty}\frac{1}{|S|}\ln Z = -\min_e(\frac{e}{k_BT}-s(e)) \tag{20}$$

which is equivalent to the relationship between $f(T)$ and $s(e)$.

Remark. According to the physical situation, other measures or ensembles may be more convenient or relevant. When there are many conserved quantities besides energy, call them $I_j(\underline{x})$, $j=1,\ldots,g$, one can take for the statistical mechanics description of the system the measure (or ensemble),

$$\mu(\underline{x}) = \frac{1}{Z}\exp(-\sum_{j=1}^{g}\mu_j I_j(\underline{x})) \tag{21}$$

where the multipliers μ_j have thermodynamic interpretations. The multiplier associated to conserved energy is the inverse temperature; the one associated to conserved particle number is the chemical potential; the one associated to conserved volume is pressure, etc.... All the Legendre transformations between relevant thermodynamic quantities can be derived similarly than above.

5 Marginals, thermodynamic limit

Usually the Gibbs measure contains too much information. It is often enough to calculate the first two marginals. More precisely,

$$\mu_i(x_i) = \sum_{\sim x_i}\mu_{Gibbs}(x_1,\ldots,x_{|S|}), \tag{22}$$

and

$$\mu_{i,j}(x_i,x_j) = \sum_{\substack{\sim x_i\\ \sim x_j}}\mu_{Gibbs}(x_1,\ldots,x_{|S|}). \tag{23}$$

It is usually enough to know the averages[4]

$$\langle x_i\rangle = \sum_{x_i} x_i\mu_i(x_i) = \sum_{x_1,\ldots,x_{|S|}} x_i\,\mu_{Gibbs}(x_1,\ldots,x_{|S|}), \tag{24}$$

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[4] The bracket $\langle - \rangle$ is the standard notation for expectations with respect to Gibbs distributions.

and

$$\langle x_i x_j \rangle = \sum_{x_i, x_j} x_i x_j \mu_{i,j}(x_i, x_j) = \sum_{x_1, \ldots, x_{|S|}} x_i x_j \, \mu_{Gibbs}(x_1, \ldots, x_{|S|}). \tag{25}$$

Note that for binary variables $x_i = 0, 1$ (or ± 1) these averages suffice to reconstruct the marginals μ_i and $\mu_{i,j}$.

The following covariance is usually called a *correlation function*

$$C_{i,j} = \langle x_i x_j \rangle - \langle x_i \rangle \langle x_j \rangle. \tag{26}$$

A simple but fundamental fact, is that these quantities can all be computed once the free energy is known. Let us modify slightly the Gibbs measure[5] by introducing extra "source" factors,

$$\mu^{\underline{\lambda}}_{Gibbs}(x_1, \ldots, x_{|S|}) = \frac{\exp\left(-\beta \mathcal{H}_S(x_1, \ldots, x_{|S|} + \sum_{i=1}^{|S|} \lambda_i x_i) \right)}{Z_{\underline{\lambda}}}, \tag{27}$$

where $\tilde{Z}$ is the normalization factor. The reader should check the very important identities

$$\langle x_i \rangle_{\underline{\lambda}} = \frac{\partial}{\partial \lambda_i} \ln Z_{\underline{\lambda}}, \tag{28}$$

and

$$\langle x_i x_j \rangle_{\underline{\lambda}} - \langle x_i \rangle_{\underline{\lambda}} \langle x_j \rangle_{\underline{\lambda}} = \frac{\partial^2}{\partial \lambda_i \partial \lambda_j} \ln Z_{\underline{\lambda}}. \tag{29}$$

To calculate the original quantities namely, $\langle x_i \rangle$ and $\langle x_i x_j \rangle$, we only need to compute $\ln Z_\lambda$ near $\underline{\lambda} = \underline{0}$. Let us warn the reader that it sometimes happens that $\ln Z$ is known at $\underline{\lambda} = 0$ but that for $\underline{\lambda}$ small the problem is orders of magnitude harder.

Statistical mechanics describes macroscopic systems. This regime is captured by computing the free energy and marginals in the infinite size limit,

$$\lim_{|S| \to +\infty} \frac{1}{|S|} \ln Z, \qquad \lim_{|S| \to +\infty} \langle x_i \rangle, \qquad \lim_{|S| \to +\infty} \langle x_i x_j \rangle. \tag{30}$$

This limit is called the *thermodynamic limit.* One of the ambitious mathematical statistical mechanics is to make sense of the thermodynamic limit for the Gibbs distribution itself. The reader can appreciate that this is not an obvious problem simply by the fact that an infinite number of variables will be involved and that the limits of the numerator and denominator do not make sense. The idea is to reconstruct the full measure from the limiting marginals. It turns out that the limits of marginals depend on boundary conditions or added infinitesimal perturbations (such as the $\lambda \to 0$ terms) and as a result the limiting Gibbs measures are not necessarily unique. This is the case precisely when phase transitions are present: a unique microscopic Hamiltonian can lead to many possible phases of matter (water-ice-gas) each being described by one of the limiting Gibbs measures. This fundamental feature of Gibbs distributions gained recognition only in the 1940-50's through the works of Bethe, Peierls, Onsager and has developed into a mathematical theory, beginning in the late 1960's (see history of Ising model in lecture 3).

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[5] Here we use the standard notation $\beta = \frac{1}{k_B T}$