

### 31.11 Thermodynamic limit

How can we study the thermodynamic limit of a system? The Hamiltonian in this limit is meaningless; it is generally a non-convergent infinite sum. For example, see the Ising Hamiltonian; it is an infinite sum of  $\pm 1$ . Consequently, the Boltzmann factor is almost always 0 or  $\infty$ .

Because the purpose of thermodynamic limit is to study the bulk properties of a system, we should take the van Hove limit.<sup>1</sup> Thus, in order to consider thermodynamic limit we prepare nested sequences of volumes whose surfaces are not very complicated. A finite system must have, usually, a boundary, so boundary conditions must be imposed. The reader might think the boundary conditions lose significance in the thermodynamic limit, but this is not always the case. We already know that for 2-Ising model, the up-spin boundary condition far away indeed affects what we observe around us, if  $T < T_c$ . In most interesting cases boundary effects are crucial.

In this section a procedure to take the thermodynamic limit is outlined with the aid of a lattice model with finite-range interactions. Suppose we wish to study an infinite lattice  $L$ . We prepare nested sequence  $\{V_i\}$  of (van Hove) volumes converging to  $L$  (i.e.,  $V_1 \subset V_2 \subset \dots \subset L$ ).

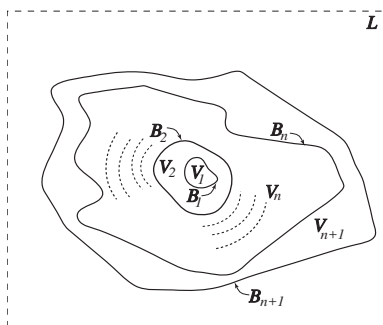


Fig. 5.2.1 An increasing nested sequence of finite systems to define thermodynamic limit.  $L$  is the infinite lattice and  $V_i$  are finite systems with van Hove volumes with explicit boundary conditions  $B_i$  (= the minimal sufficient condition to fix the system energy uniquely when the state in  $V_i$  is given).

For each finite volume system a boundary condition  $B$  must be specified.<sup>2</sup> Let us write the volume-boundary condition pair as  $(V, B)$ . Let us make the canonical distribution for  $(V, B)$ :

$$\mu_{V,B} = \frac{1}{Z_{V,B}} e^{-\beta H_V(B)}, \quad (0.0.1)$$

where  $H_V(B)$  is the Hamiltonian for the system with the volume  $V$ <sup>3</sup> and the boundary condition  $B$  (thus  $H_V(B)$  includes the surface interaction terms). Make the totality of  $\mu_{V,B}$  choosing all possible  $V \subset L$  and  $B$ . Then, we take a sequence  $\{\mu_{V_i, B_i}\}$  that converges to a probability measure  $\mu$  (defined on the set of microstates on  $L$ ). The limit points (= probability measures) available through this construction (that is, accumulation points of  $M$ ) are called the *Gibbs measures* (however, read the fine-lettered explanation on the “totality

<sup>1</sup>Roughly speaking, this implies that we take the large system size limit so that the surface area  $\times L$  scales as the system volume, where  $L$  is the representative length scale of the system.

<sup>2</sup>For the Ising model the interaction is nearest neighbor, so we have only to specify the spins just outside the boundary. However, if the interaction is wider-ranged, we must specify a lot about the external ‘spin configurations.’

<sup>3</sup>Here,  $V$  denotes a bounded (and singly connected) subset of the whole lattice, but occasionally also denotes its volume.

of Gibbs measure” below).

To speak about ‘convergence’ we must specify the topology of the space  $M$ . That is, we must be able to tell which canonical distribution of the form (0.0.1) is close to which. Since our aim is statistical mechanics, it is sensible to define the closeness of two distributions by the closeness of thermodynamic observables computed by these distributions. Therefore, we interpret the statement “The probability measure sequence  $\{\mu_i\}$  converges to  $\mu$ ,” as “all the thermodynamic observables computed by this sequence converge to those computed by  $\mu$ .”

#### At least one Gibbs state exists

An argument goes like...<sup>4</sup>

Here, we mean by a lattice system a system consisting of discrete entities fixed at lattice points that can take (at most) countably many states. The existence of a convergent sequence in  $\{\mu_{V,B}\}$  is shown by the *diagonal argument*. We take a countable list of bounded thermodynamic observables  $\{Q_i\}$  (i.e., we make a list of observables such as internal energy density, magnetization density, etc.) Let us write the expectation value of observable  $Q$  with respect to  $\mu$  as  $\mu(Q)$ . Let us first make a sequence  $\{\mu_{V,B}(Q_1)\}$  of observation results of  $Q_1$ . Since this is a bounded sequence, we can choose a converging subsequence  $\{\mu_{1i}(Q_1)\}$ . Next, we make the sequence  $\{\mu_{1i}(Q_2)\}$  for observable  $Q_2$ , and choose a convergent subsequence  $\{\mu_{2i}(Q_2)\}$ . Repeat this procedure to make  $\{\mu_{ki}\}$  for all  $k \in \mathbf{N}$ . Now, choose the diagonal elements and make a sequence  $\{\mu_{kk}\}$ . By construction  $\{\mu_{kk}(Q_i)\}$  converges for any  $Q_i$ . Thus we may conclude that  $\{\mu_{kk}\}$  converges to a  $\mu$ , which is a Gibbs measure. Thus, there is at least one Gibbs measure for any reasonable lattice model.

A possible definition of the phase transition for a system is the occurrence of qualitative change in the set of the totality of the Gibbs states of the system. For example, if the temperature is lowered, the number of (pure) Gibbs states changes 1 to 2 for 2-Ising model (see Sect. 5.4). This temperature is the critical point = the second order phase transition point.

#### The totality of Gibbs states

In the text thermodynamic limit is understood as a limit reached by a sequence of increasingly large systems, and the Gibbs measure is defined as a measure obtained in this sequence limit. However, in mathematical physics, the Gibbs measure is directly defined without any limiting procedure (classically by the DLR (Dobrushin-Lanford-Ruelle) equation, quantum-mechanically by the KMS (Kubo-Martin-Schwinger) condition, for example).<sup>5</sup> The totality  $K$  of the Gibbs measures defined directly is the convex linear hull of the Gibbs measures defined sequentially.  $K$  is a nonempty convex set and any state in it must be one of the following (a) or (b):<sup>6</sup>

- (a)  $\mu \in K$  cannot be expressed as a linear combination of other members of  $K$ . Such states are called *pure states*.**r** (**r**to symmetry breaking)
- (b)  $\mu \in K$  can be uniquely decomposed into a linear combination of pure states. Such states are called *mixed states*.

Physically, pure states correspond to macroscopic states that can be observed locally for a sufficiently large single system.<sup>7</sup> Do not confuse pure Gibbs states and thermodynamic single

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<sup>4</sup>That  $\{\mu_{V,B}\}$  is a compact set with respect to the vague topology is perhaps the best argument for mathematicians. The argument here with the aid of the diagonal argument is quite general, but sounds rather artificial. For general systems, more physical arguments would not be available.

<sup>5</sup> A good reference is R. B. Israel, *Convexity in the Theory of Lattice Gases* (Introduction by A. S. Wightman) (Princeton Univ. Press 1979). The introduction by Wightman should be read by everyone.

<sup>6</sup>That is,  $K$  is a Choquet simplex.

<sup>7</sup>Here, ‘locally’ implies that we observe a large but finite volume at around, e.g., the origin (or in front of us).

phases (pure phases). A mixed state corresponds, as illustrated in Fig. 5.1.3, to an ensemble containing different (pure) states and has nothing to do with individual samples to have more than one phases.<sup>8</sup>

The macroscopic thermodynamic state we observe in a single system corresponds to a pure Gibbs state. Precisely speaking, a pure Gibbs state corresponds to a unique thermodynamic state of the system. However, a thermodynamic state is defined as the equivalence class with respect to the thermodynamic coordinate values, so it corresponds to an equivalence class of pure Gibbs states with respect to the thermodynamic coordinate values. For example, if two phases coexist in a pure Gibbs state, the phase boundary plane is also specified in space; however, thermodynamic states are indifferent to the actual (normal) direction of the phase boundary.

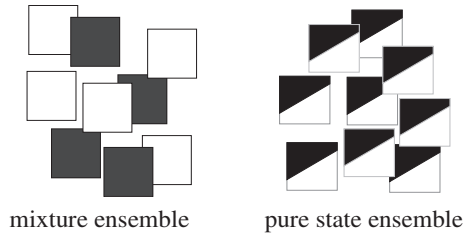


Fig. 5.1.3 Two kinds of ensemble; a pure Gibbs state corresponds to an actual state of a single sample observable by a single observation. Notice that both ensembles give the same expectation values for thermodynamic quantities. In this illustration the left figure exhibits a mixture Gibbs state made of thermodynamically pure phase samples, and the right figure exhibits a pure Gibbs states whose samples contain thermodynamically coexisting phases.

We have reached an idea that the phase transition is a point where the Gibbs state of the system changes qualitatively. It is also natural to expect that at such a point thermodynamic functions should have certain qualitative changes (have singularities). Let us consider the singular points of thermodynamic functions.

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<sup>8</sup>Sequentially defined limits need not be pure states.