

Chapter 2

Ensemble Theory in Statistical Physics: Free Energy Potential

Abstract In this chapter, we discuss the basic formalism of statistical physics. Also, we consider in detail the concept of the free energy potential.

Similar to Chap. 1, this chapter is a prerequisite. As required for further discussions, we consider understanding of the free energy concept, its connection with the probability of fluctuations,

$$W_{fluctuation}^{ensemble} = e^{\frac{\Psi_{equilibrium} - \Psi_{fluctuation}}{T^{res}}}, \quad (2.1)$$

and with the partial partition function,

$$\Psi_{fluctuation} = -T^{res} \ln Z_{fluctuation}. \quad (2.2)$$

The reader who is proficient in these concepts may skip this chapter.

Since the purpose of this chapter is to refresh in memory the class studied by students only 1 or 2 quarters ago, we generally avoid rigorous discussions or mathematical proofs. Instead, we illustrate the formalism by simple examples and multiple figures. This provides intuitive understanding of all concepts discussed in the following chapters and simultaneously introduces terminology utilized in the following discussions.

For the reader not familiar with statistical physics, we recommend to follow thoroughly all the formulae below because the chapter has been developed to serve as a “guide” to basic concepts of statistical physics. Although we consider the discussions presented here to be sufficient for understanding of the following results, for further study we refer the reader to brilliant textbooks, e.g., Landau and Lifshitz (1980).

2.1 Basic Definitions

Statistical physics studies systems with high number of degrees of freedom. A classical example is a gas, 1 mol of which contains $N_A \propto 6 \cdot 10^{23}$ particles, where N_A is the *Avogadro constant*. This is important because many results in statistical

physics are valid only when the number of degrees of freedom is infinite: $N \rightarrow +\infty$. This limit is called *the thermodynamic limit of infinite number of degrees of freedom* or, simply, *the thermodynamic limit*.

A system is called *an ideal system* if its particles or degrees of freedom do not interact with each other. For example, *an ideal gas* is a gas with noninteracting, noncolliding particles.

However, the above definition is not completely correct because such a gas would never reach the state of thermal equilibrium. For example, if initially half of the gas particles have velocities 10 m/s while the other half have 20 m/s, and particles do not interact or collide, the gas will keep the velocities of its particles unchanged and we will never see the Maxwell–Boltzmann distribution.

Therefore, to reach the state of thermal equilibrium, there must always be present some (maybe weak but nonzero) interaction among the degrees of freedom. For example, we can modify the definition of ideal gas to be a gas whose particles can collide, but these events are extremely rare. So, observing the system for a long period of time, we will see how it evolves toward an equilibrium state. On the contrary, for short time intervals we can neglect particle collisions as improbable events and consider the system to be completely without particle interactions. Therefore, the possibility to consider the system ideal significantly depends on the duration of the time interval during which we intend to investigate the system's behavior.

Besides the interactions of particles or degrees of freedom with each other, we consider their interactions with *external fields*. An example is a magnetic system in a nonzero magnetic field h . We will always consider external fields to be supported as constant and not depending on the state of the system considered.

Constant external field is an example of *boundary conditions* imposed on a system. Other examples may include systems maintained at constant volume, pressure, temperature, etc. In particular, *an isolated system* is a system with prohibited energy and particle exchange, and maintained at constant volume: $E, V, N = \text{const}$.

If a property of a system can fluctuate for the given set of boundary conditions, we call this property the system's *fluctuating parameter*. For example, for a system maintained at constant temperature, its energy can fluctuate and is, therefore, a fluctuating parameter. If pressure is also maintained constant, another fluctuating parameter is the system's volume.

In the case when a phase transition is present in the system, the phases are distinguished by the values of fluctuating parameters. For example, for the gas–liquid phase transition at constant pressure, two phases are distinguished by the values of the volume; while for a ferromagnetic system the role of a parameter distinguishing phases is played by the system's magnetization. Such fluctuating parameters are often called *order parameters* because they describe the appearance of an order in a system below its critical point. We will discuss this definition in more detail in the following chapters.

If the property of a system is proportional to the number N of degrees of freedom in the system, we call this property *the extensive parameter* (e.g., energy, entropy, heat capacity, volume, magnetization, etc.). On the contrary, if the property of a system is not proportional to N , we call this property *the intensive parameter* (e.g., temperature, pressure, chemical potential, specific heat capacity, specific magnetization, etc.).

The last definition we should introduce is the definition of *an ensemble*. Let us investigate a particular system. If we observe the system's behavior, we see that it evolves, jumping from one state into another. If we consider, for example, gas particles when they follow their trajectories, the gas as a whole will keep moving from its current state into the next, into the next, into the next, and so on.

But instead of observing the behavior of one particular system, we can build an ensemble of systems. All systems in the ensemble are identical and differ from one another only by their initial conditions. In other words, instead of observing a chain of states $\{\}_1 \rightarrow \{\}_2 \rightarrow \{\}_3 \rightarrow \dots$ for one particular system, we can consider the ensemble of systems which initially are in states $\{\}_1, \{\}_2, \{\}_3, \dots$. The *ergodic hypothesis* claims that these two modeling techniques of the system's behavior are equivalent.

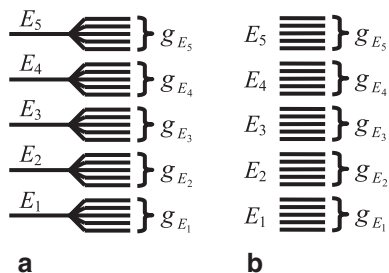
2.2 Energy Spectrum

Firstly we consider an isolated system whose Hamiltonian does not depend on time explicitly. For such a system, we find a discrete or continuous energy spectrum of *microstates* $\{E\}$ as eigenfunctions of the Hamiltonian operator. For simplicity, we consider in this chapter only discrete energy spectra although all our formulae are valid for the case of continuous spectra as well.

We make no assumptions about the structure of the spectrum, requiring only for the dependence of the spectrum density to be exponential on the number of degrees of freedom $N \rightarrow +\infty$ in the system. This requirement is valid for the majority of systems and, as we will see below, is in fact, crucial for the formalism of statistical physics.

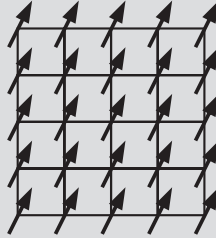
Each eigenvalue E of the Hamiltonian (as a possible value of the system's energy) is called *an energy level*. Generally for an ideal system, many eigenfunctions $\{E\}$ correspond to the same Hamiltonian eigenvalue E . Then this energy level E is called *degenerate* while the number of microstates $\{E\}$ belonging to this eigenvalue E is called *the degeneracy* g_E of this energy level. This is schematically presented in Fig. 2.1a where microstates $\{E\}$ (shown as horizontal lines to the right) are combined into energy levels E_i (shown as horizontal lines to the left) with degeneracies g_{E_i} .

Fig. 2.1 A schematic representation of an energy spectrum. **a** Microstates are combined into energy levels E_i with degeneracies g_{E_i} . **b** Microstates are combined into groups with energies E_i and statistical weights g_{E_i}



Problem 2.2.1

Find the energy spectrum for the Ising model without spin interactions. For simplicity, assume that the model consists only of $N = 3$ spins.



Solution: The Ising model (Ising 1925) is described in detail in Chap. 3. Here we present only the brief description of the Ising model without spin interactions which will be utilized as an example for the rest of this chapter. The model is built on the base of an absolutely rigid lattice whose geometry is currently not important. At each lattice site, a spin (a magnetic moment μ) is located. As it is known from quantum mechanics, the spin of an electron can have only two projections $\pm \frac{1}{2}$ on an axis of an external magnetic field h . In the Ising model, a spin also can have only two projections on the axis of the magnetic field h . But now these projections are chosen to be ± 1 where the multiplier $1/2$ has been lost for the purpose of convenience.

Generally, we consider the lattice with N spins, where N is infinite in the thermodynamic limit: $N \rightarrow +\infty$. Let index i enumerate the sites of the lattice. If the spin at site i has projection $\sigma_i = +1$ on the axis of magnetic field, then its energy is $-\mu h$. For projection $\sigma_i = -1$, we have energy $+\mu h$. The Hamiltonian of the system equals the sum of the spin energies:

$$H_{\{\sigma\}} = -\mu h \sum_{i=1}^N \sigma_i. \quad (2.3)$$

As we see from (2.3), the Ising model without spin interactions is nothing more than a *two-level system*, where each degree of freedom is allowed to have only two values of energy: $\varepsilon = \pm \mu h$. As an example, we utilize here the Ising model but not the two-level system with the purpose to acquaint the reader with the former.

The formulation of the model above has been oversimplified. Nevertheless, it corresponds to the rigorous formulation; we only need to put “caps” of quantum operators over the Hamiltonian and over the spins:

$$\hat{H} = -\mu h \sum_{i=1}^N \hat{\sigma}_i. \quad (2.4)$$

Microstates $\{\sigma\}$, as the eigenfunctions of Hamiltonian (2.4), correspond to the realizations of different spin orientations on the lattice. In other words, prescribing for each spin its orientation (along the field, $\sigma_i = +1$, or against the field, $\sigma_i = -1$), we are forming a particular microstate $\{\sigma\}$ of the system.

In the case of $N=3$ (which corresponds to the formulation of our problem), there are only eight microconfigurations $\{\sigma\}$ of spin orientations on the lattice: $\{\uparrow\uparrow\uparrow\}$, $\{\uparrow\uparrow\downarrow\}$, $\{\uparrow\downarrow\uparrow\}$, $\{\downarrow\uparrow\uparrow\}$, $\{\uparrow\downarrow\downarrow\}$, $\{\downarrow\uparrow\downarrow\}$, $\{\downarrow\downarrow\uparrow\}$, and $\{\downarrow\downarrow\downarrow\}$, where the symbol “ \uparrow ” denotes a spin oriented “up” (along the field) while the symbol “ \downarrow ” denotes a spin oriented “down” (against the field). These microconfigurations correspond to the following microstates: $\{E = -3\mu h\}$, $\{E = -\mu h\}$, $\{E = -\mu h\}$, $\{E = -\mu h\}$, $\{E = \mu h\}$, $\{E = \mu h\}$, $\{E = \mu h\}$, and $\{E = 3\mu h\}$.

$$\begin{array}{l}
 E = 3\mu h \quad \text{---} \quad \{3\mu h\} \quad \left. \vphantom{\begin{array}{c} \{3\mu h\} \\ \{3\mu h\} \\ \{3\mu h\} \end{array}} \right\} g_{3\mu h} = 1 \\
 E = \mu h \quad \text{---} \quad \left. \begin{array}{c} \{\mu h\} \\ \{\mu h\} \\ \{\mu h\} \end{array} \right\} g_{\mu h} = 3 \\
 E = -\mu h \quad \text{---} \quad \left. \begin{array}{c} \{-\mu h\} \\ \{-\mu h\} \\ \{-\mu h\} \end{array} \right\} g_{-\mu h} = 3 \\
 E = -3\mu h \quad \text{---} \quad \{-3\mu h\} \quad \left. \vphantom{\begin{array}{c} \{-3\mu h\} \\ \{-3\mu h\} \\ \{-3\mu h\} \end{array}} \right\} g_{-3\mu h} = 1
 \end{array}$$

Therefore, the energy spectrum of the system consists of four energy levels. Only one microstate $\{\uparrow\uparrow\uparrow\}$ (which we have denoted as $\{-3\mu h\}$) corresponds to energy level $E = -3\mu h$. Therefore, this level is not degenerate: $g_{-3\mu h} = 1$.

Three microstates $\{\uparrow\uparrow\downarrow\}$, $\{\uparrow\downarrow\uparrow\}$, and $\{\downarrow\uparrow\uparrow\}$ (which we have denoted as $\{-\mu h\}$) correspond to energy level $E = -\mu h$, and this level has triple degeneracy: $g_{-\mu h} = 3$. And so on.

Problem 2.2.2

Find the energy spectrum for the Ising model without spin interactions. Consider the model consisting of $N = 5$ spins.

Problem 2.2.3

Find the energy spectrum for the Ising model without spin interactions. Consider the case of the model with an arbitrary number of spins N .

Solution: *Magnetization* of the system in a microstate $\{\sigma\}$ is introduced as the sum of magnetic moments over the lattice:

$$M_{\{\sigma\}} \equiv \mu \sum_{i=1}^N \sigma_i. \quad (2.5)$$

Dividing the magnetization by the number of spins and by the value of the magnetic moment μ , we obtain *specific magnetization*:

$$m_{\{\sigma\}} \equiv \frac{1}{N} \sum_{i=1}^N \sigma_i \equiv \frac{M}{N\mu}. \quad (2.6)$$

It is easy to see that in the case of the Ising model without spin interactions the energy of the system depends on its magnetization bijectively: knowing energy, we can find magnetization and vice versa:

$$H_{\{\sigma\}} = -hM_{\{\sigma\}} = -\mu h N m_{\{\sigma\}}. \quad (2.7)$$

For convenience, we also introduce two more parameters: the number of spins along the field, N_{\uparrow} , and the number of spins against the field, N_{\downarrow} . The magnetization is, obviously, proportional to the difference between these two numbers,

$$M_{\{\sigma\}} = \mu(N_{\uparrow} - N_{\downarrow}), \quad (2.8)$$

while the sum of these numbers equals the total number of spins on the lattice,

$$N = N_{\uparrow} + N_{\downarrow}. \quad (2.9)$$

Therefore, if we know the energy of the system or its magnetization, we can bijectively find the numbers of spins along and against the field:

$$N_{\uparrow} = \frac{1}{2} \left(N - \frac{E}{\mu h} \right), \quad N_{\downarrow} = \frac{1}{2} \left(N + \frac{E}{\mu h} \right) \quad (2.10)$$

or

$$N_{\uparrow} = N \frac{1+m}{2}, \quad N_{\downarrow} = N \frac{1-m}{2}. \quad (2.11)$$

Vice versa, if we know N_{\uparrow} and N_{\downarrow} , we know the energy of the system

$$E = -\mu h (N_{\uparrow} - N_{\downarrow}). \quad (2.12)$$

This expression corresponds to the value of energy of a particular energy level. From (2.12) it is easy to see that two adjacent energy levels are separated by one spin “flip”:

$$|\Delta E| = 2\mu h, \quad (2.13)$$

where “2” comes from that a spin with one orientation disappears while a spin with the opposite orientation appears.

To find the degeneracy of energy level E , we should find how many microstates $\{\sigma\}$ correspond to numbers N_\uparrow and N_\downarrow , given by (2.10) and (2.11). In other words, for the given values of N_\uparrow and N_\downarrow , we have to find the number of microconfigurations by which N_\uparrow of N spins could be oriented along the field while the rest of spins would be oriented against the field:

$$g_E = \frac{N!}{N_\uparrow! N_\downarrow!}. \quad (2.14)$$

As we will see later, one of the most important mathematical formulae in statistical physics is Stirling’s approximation

$$N! = \left(\frac{N}{e}\right)^N \underline{\underline{O}}(N^\alpha), \quad (2.15)$$

where $\underline{\underline{O}}(N^\alpha)$ is the power-law dependence on N . In the thermodynamic limit, $N \rightarrow +\infty$, the power-law dependence $\underline{\underline{O}}(N^\alpha)$ on N is much “slower” than the “fast,” exponential dependence $(N/e)^N$. Further, we will often utilize the notation “ \approx_{\ln} ” of the *logarithmic accuracy* meaning that in the thermodynamic limit, $N \rightarrow +\infty$, we neglect all “slow” power-law multipliers in comparison with the “fast,” exponential dependencies on N . In particular, for Stirling’s approximation we have

$$N! \approx_{\ln} \left(\frac{N}{e}\right)^N. \quad (2.16)$$

Applying (2.16) to (2.14), for the energy level degeneracy we find

$$g_E = \left(\frac{N}{N_\uparrow}\right)^{N_\uparrow} \left(\frac{N}{N_\downarrow}\right)^{N_\downarrow} \underline{\underline{O}}(N^\alpha) \approx_{\ln} \left(\frac{N}{N_\uparrow}\right)^{N_\uparrow} \left(\frac{N}{N_\downarrow}\right)^{N_\downarrow} = \left(\frac{1+m}{2}\right)^{-N\frac{1+m}{2}} \left(\frac{1-m}{2}\right)^{-N\frac{1-m}{2}}. \quad (2.17)$$

Equation (2.17) is the typical representative of the degeneracy dependence on the number of degrees of freedom N in the system. Firstly, we see that both exponents, $N_\uparrow = N\frac{1+m}{2}$ and $N_\downarrow = N\frac{1-m}{2}$, are proportional to N , and,

therefore, the degeneracy of energy levels indeed depends exponentially on N . Secondly, N/N_{\uparrow} and N/N_{\downarrow} are intensive parameters (not proportional to N), and the singularity of the thermodynamic limit, $N \rightarrow +\infty$, is absent in them.

Therefore, we can conclude that the typical behavior of the energy-level degeneracy on the value of energy is presented by a “tendency” when something finite is raised to the “singular” power proportional to N .

And it is not important whether this dependence is increasing or decreasing with the increase of energy. For example, for the Ising model, the lowest energy level, when all spins are along the field, is not degenerate. Neither degenerate is the highest energy level, when all spins are against the field. Between these two extremes, the degeneracy initially grows with the increase of energy but then decreases back to unity. For both cases, what is important is that the dependence is exponential on N , when we can neglect all power-law dependences.

The spectrum presented in Fig. 2.1a corresponds to the case of an ideal system. If we consider a nonideal system (which cannot be converted into the ideal by variables’ change), the interactions among the degrees of freedom destroy the strict degeneracy when the energy levels “blur,” spreading their microstates all over the spectrum and mixing them with other energy levels. The sketch of the resulting spectrum is presented in Fig. 2.1b.

As we will see later, statistical mechanics very successfully “manipulates” the degeneracy of energy levels. Therefore, and for the spectrum of a nonideal system, we would like to introduce something analogous to the strict quantum degeneracy.

Let us unite closely located microstates $\{E\}$ (microstates $\{E\}$ with close values of energy) into groups with the averaged values of energy E_i , where g_{E_i} is the number of microstates in the group (Fig. 2.1b). We would like to call the quantity g_{E_i} , by analogy, the degeneracy. However, this term is reserved for the strict degeneration in quantum mechanics. Therefore, the special term, *the statistical weight*, is introduced, which sometimes is abbreviated as “*the stat-weight*.” In future, it will not be important for us whether we refer to the strict degeneracy in the sense of quantum mechanics or to the statistical weight as the number of microstates with close values of energy in the group. In both cases, we will refer to g_{E_i} by the term “statistical weight” without attributing it to the particular structure of the spectrum.

Students who begin to study statistical mechanics after such rigorous disciplines as theoretical or quantum mechanics are often confused by the fact that microstates are combined into groups “at will.” How many microstates do we unite into a particular group? Why cannot we make groups 2, 10, 100 times larger? We will obtain the answer to this question later. Now we only mention that the formalism of statistical physics “works” in such a way that it is not important how many microstates we unite into a particular group. In fact, the whole mechanism of statistical physics operates only because this combining can be performed arbitrarily.

2.3 Microcanonical Ensemble

A *microcanonical ensemble* (or *MCE*) is an ensemble of identical isolated systems (Fig. 2.2). The isolation boundary condition means that there are neither heat exchange $\delta Q^{\leftarrow} = 0$, nor work of external forces $\delta W^{\leftarrow} = 0$, nor particle exchange $\delta \Pi^{\leftarrow} = 0$.

Microstates $\{E, p\}$ of the considered system are the eigenfunctions of the system's Hamiltonian with the value of energy E corresponding to the condition of the system's isolation, $E = \text{const}$. Here, by p we have denoted some set of internal parameters distinguishing microstates with the same value of energy E . For example, for the Ising model from Problem 2.2.1, which consists of $N = 3$ spins and is isolated with energy $-\mu h$, there are only three microstates, $\{\uparrow\uparrow\downarrow\}$, $\{\uparrow\downarrow\uparrow\}$, and $\{\downarrow\uparrow\uparrow\}$, corresponding to this value of energy. The parameter p here denotes spin orientations on the lattice and can be equal, for example, to $\uparrow\uparrow\downarrow$.

Isolating our system, we allow it to “visit” microstates with the given value of energy and prohibit “visiting” other microstates. *Strict isolation* means isolation strictly on one energy level (Fig. 2.3a) or strictly in one group of microstates (Fig. 2.3b).

But in nature no system with dense energy spectrum could be strictly isolated. There is always some uncertainty ΔE of isolation, which can include several energy levels (Fig. 2.4a) or several groups of microstates (Fig. 2.4b), if, of course, the energy spectrum is dense enough.

Similar to uncertainty of uniting microstates into groups, the uncertainty of the system's isolation does not influence the formalism of statistical physics. Let us discuss in detail why it is so.

Fig. 2.2 An isolated system

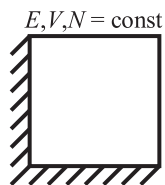


Fig. 2.3 The strict isolation on one energy level (a) or in one group of microstates (b)

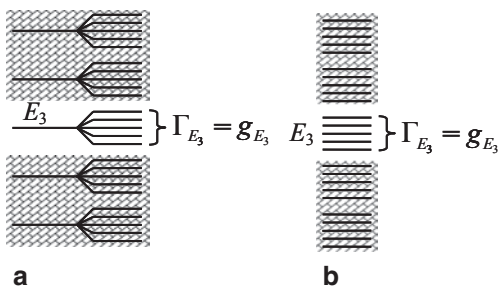
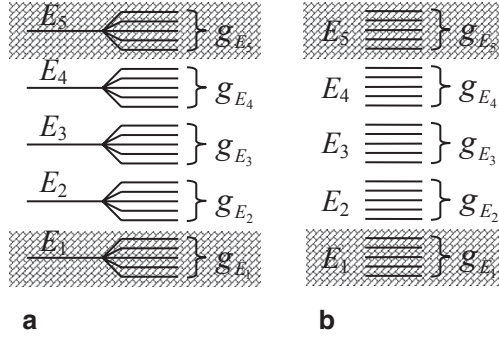


Fig. 2.4 The nonstrict isolation on three energy levels (a) or in three groups of microstates (b)



Firstly, we need to introduce a new term, *the statistical weight of an ensemble*, or, using slang, *the ensemble stat-weight*. What the statistical weight of a group of microstates is we already know: It is the number of microstates in the group. For the MCE, we utilize a similar definition—*the statistical weight of the MCE*, Γ^{MCE} , is the number of microstates which the system visits with nonzero probabilities. In other words, it is the number of microstates corresponding to the isolation conditions.

In the case of the strict isolation on one energy level E (in one group of microstates), the statistical weight of the MCE is the statistical weight g_E of this energy level (of this group of microstates):

$$\Gamma^{MCE} = g_E. \quad (2.18)$$

If the nonstrict isolation allows the system to visit k energy levels (groups) with close values of energy, the statistical weight of the MCE equals the sum of statistical weights of these levels (groups):

$$\Gamma^{MCE} = g_{E_1} + \dots + g_{E_k}. \quad (2.19)$$

Let $w_{\{E,p\}}$ be the probability distribution to observe the system in a microstate $\{E,p\}$ in the ensemble. If, for example, we consider a quantum system, this probability distribution is provided by the diagonalized statistical operator (quantum density matrix) $w_{\{E,p\}} \equiv \rho_{\{E,p\},\{E,p\}}$.

Liuville's theorem (Gibbs 1902) suggests that in equilibrium all microstates of the MCE are equiprobable:

$$w_{\{\tilde{E},p\}}^{MCE} = \begin{cases} \frac{1}{\Gamma^{MCE}}, & \tilde{E} = E \\ 0, & \tilde{E} \neq E \end{cases} = \frac{\delta_{\tilde{E},E}}{\Gamma^{MCE}}, \quad (2.20)$$

where E is the energy of isolation. Here we should again emphasize that distribution of probabilities (2.20) is equilibrium. For nonequilibrium cases, we are free to consider any arbitrary distribution of probabilities $w_{\{E,p\}}$. We will discuss this question in detail later.

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