

Partition function (statistical mechanics)

Partition functions describe the statistical properties of a system in thermodynamic equilibrium. It is a function of temperature and other parameters, such as the volume enclosing a gas. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives.

There are actually several different types of partition functions, each corresponding to different types of statistical ensemble (or, equivalently, different types of free energy.) The **canonical partition function** applies to a canonical ensemble, in which the system is allowed to exchange heat with the environment at fixed temperature, volume, and number of particles. The **grand canonical partition function** applies to a grand canonical ensemble, in which the system can exchange both heat and particles with the environment, at fixed temperature, volume, and chemical potential. Other types of partition functions can be defined for different circumstances; see partition function (mathematics) for generalizations.

Canonical partition function

Definition

As a beginning assumption, assume that a thermodynamically large system is in constant thermal contact with the environment, with a temperature T , and both the volume of the system and the number of constituent particles fixed. This kind of system is called a canonical ensemble. Let us label with s ($s = 1, 2, 3, \dots$) the *exact* states (microstates) that the system can occupy, and denote the total energy of the system when it is in microstate s as E_s . Generally, these microstates can be regarded as analogous to discrete quantum states of the system.

The **canonical partition function** is

$$Z = \sum_s e^{-\beta E_s},$$

where the "inverse temperature", β , is conventionally defined as

$$\beta \equiv \frac{1}{k_B T}$$

with k_B denoting Boltzmann's constant. The term $\exp(-\beta E_s)$ is known as the Boltzmann factor. In systems with multiple quantum states s sharing the same E_s , it is said that the energy levels of the system are degenerate. In the case of degenerate energy levels, we can write the partition function in terms of the contribution from energy levels (indexed by j) as follows:

$$Z = \sum_j g_j \cdot e^{-\beta E_j},$$

where g_j is the degeneracy factor, or number of quantum states s which have the same energy level defined by $E_j = E_s$.

The above treatment applies to *quantum* statistical mechanics, where a physical system inside a finite-sized box will typically have a discrete set of energy eigenstates, which we can use as the states s above. In *classical* statistical mechanics, it is not really correct to express the partition function as a sum of discrete terms, as we have done. In classical mechanics, the position and momentum variables of a particle can vary continuously, so the set of microstates is actually uncountable. In this case we must describe the partition function using an integral rather than a sum. For instance, the partition function of a gas of N identical classical particles is

$$Z = \frac{1}{N! h^{3N}} \int \exp[-\beta H(p_1 \cdots p_N, x_1 \cdots x_N)] d^3 p_1 \cdots d^3 p_N d^3 x_1 \cdots d^3 x_N$$

where

\mathbf{p}_i indicate particle momenta

\mathbf{x}_i indicate particle positions

d^3 is a shorthand notation serving as a reminder that the \mathbf{p}_i and \mathbf{x}_i are vectors in three dimensional space, and

H is the classical Hamiltonian.

The reason for the $N!$ factor is discussed below. For simplicity, we will use the discrete form of the partition function in this article. Our results will apply equally well to the continuous form. The extra constant factor introduced in the denominator was introduced because, unlike the discrete form, the continuous form shown above is not dimensionless. To make it into a dimensionless quantity, we must divide it by h^{3N} where h is some quantity with units of action (usually taken to be Planck's constant).

In quantum mechanics, the partition function can be more formally written as a trace over the state space (which is independent of the choice of basis):

$$Z = \text{tr}(e^{-\beta\hat{H}}),$$

where \hat{H} is the quantum Hamiltonian operator. The exponential of an operator can be defined using the exponential power series. The classical form of Z is recovered when the trace is expressed in terms of coherent states ^[1] and when quantum-mechanical uncertainties in the position and momentum of a particle are regarded as negligible. Formally, one inserts under the trace for each degree of freedom a resolution of the identity

$$\mathbf{1} = \int |x, p\rangle \langle x, p| \frac{dx dp}{h}$$

where $|x, p\rangle$ is a normalised Gaussian wavepacket centered at position x and momentum p . Thus,

$$Z = \int \text{tr} \left(e^{-\beta\hat{H}} |x, p\rangle \langle x, p| \right) \frac{dx dp}{h} = \int \langle x, p| e^{-\beta\hat{H}} |x, p\rangle \frac{dx dp}{h}$$

A coherent state is an approximate eigenstate of both operators \hat{x} and \hat{p} , hence also of the Hamiltonian \hat{H} , with errors of the size of the uncertainties. If Δx and Δp can be regarded as zero, the action of \hat{H} reduces to multiplication by the classical Hamiltonian, and Z reduces to the classical configuration integral.

Meaning and significance

It may not be obvious why the partition function, as we have defined it above, is an important quantity. First, let us consider what goes into it. The partition function is a function of the temperature T and the microstate energies E_1, E_2, E_3, \dots . The microstate energies are determined by other thermodynamic variables, such as the number of particles and the volume, as well as microscopic quantities like the mass of the constituent particles. This dependence on microscopic variables is the central point of statistical mechanics. With a model of the microscopic constituents of a system, one can calculate the microstate energies, and thus the partition function, which will then allow us to calculate all the other thermodynamic properties of the system.

The partition function can be related to thermodynamic properties because it has a very important statistical meaning. The probability P_s that the system occupies microstate s is

$$P_s = \frac{1}{Z} e^{-\beta E_s}.$$

$e^{-\beta E_s}$ is the well-known Boltzmann factor. (For a detailed derivation of this result, see canonical ensemble.) The partition function thus plays the role of a normalizing constant (note that it does *not* depend on s), ensuring that the probabilities sum up to one:

$$\sum_s P_s = \frac{1}{Z} \sum_s e^{-\beta E_s} = \frac{1}{Z} Z = 1.$$

This is the reason for calling Z the "partition function": it encodes how the probabilities are partitioned among the different microstates, based on their individual energies. The letter Z stands for the German word *Zustandssumme*, "sum over states". This notation also implies another important meaning of the partition function of a system: it counts the (weighted) number of states a system can occupy. Hence if all states are equally probable (equal energies) the partition function is the total number of possible states. Often this is the practical importance of Z .

Calculating the thermodynamic total energy

In order to demonstrate the usefulness of the partition function, let us calculate the thermodynamic value of the total energy. This is simply the expected value, or ensemble average for the energy, which is the sum of the microstate energies weighted by their probabilities:

$$\langle E \rangle = \sum_s E_s P_s = \frac{1}{Z} \sum_s E_s e^{-\beta E_s} = -\frac{1}{Z} \frac{\partial}{\partial \beta} Z(\beta, E_1, E_2, \dots) = -\frac{\partial \ln Z}{\partial \beta}$$

or, equivalently,

$$\langle E \rangle = k_B T^2 \frac{\partial \ln Z}{\partial T}.$$

Incidentally, one should note that if the microstate energies depend on a parameter λ in the manner

$$E_s = E_s^{(0)} + \lambda A_s \quad \text{for all } s$$

then the expected value of A is

$$\langle A \rangle = \sum_s A_s P_s = -\frac{1}{\beta} \frac{\partial}{\partial \lambda} \ln Z(\beta, \lambda).$$

This provides us with a method for calculating the expected values of many microscopic quantities. We add the quantity artificially to the microstate energies (or, in the language of quantum mechanics, to the Hamiltonian), calculate the new partition function and expected value, and then set λ to zero in the final expression. This is analogous to the source field method used in the path integral formulation of quantum field theory.

Relation to thermodynamic variables

In this section, we will state the relationships between the partition function and the various thermodynamic parameters of the system. These results can be derived using the method of the previous section and the various thermodynamic relations.

As we have already seen, the thermodynamic energy is

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}.$$

The variance in the energy (or "energy fluctuation") is

$$\langle (\Delta E)^2 \rangle \equiv \langle (E - \langle E \rangle)^2 \rangle = \frac{\partial^2 \ln Z}{\partial \beta^2}.$$

The heat capacity is

$$C_v = \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{k_B T^2} \langle (\Delta E)^2 \rangle.$$

The entropy is

$$S \equiv -k_B \sum_s P_s \ln P_s = k_B (\ln Z + \beta \langle E \rangle) = \frac{\partial}{\partial T} (k_B T \ln Z) = -\frac{\partial A}{\partial T}$$

where A is the Helmholtz free energy defined as $A = U - TS$, where $U = \langle E \rangle$ is the total energy and S is the entropy, so that

$$A = \langle E \rangle - TS = -k_B T \ln Z.$$

Partition functions of subsystems

Suppose a system is subdivided into N sub-systems with negligible interaction energy. If the partition functions of the sub-systems are $\zeta_1, \zeta_2, \dots, \zeta_N$, then the partition function of the entire system is the *product* of the individual partition functions:

$$Z = \prod_{j=1}^N \zeta_j.$$

If the sub-systems have the same physical properties, then their partition functions are equal, $\zeta_1 = \zeta_2 = \dots = \zeta$, in which case

$$Z = \zeta^N.$$

However, there is a well-known exception to this rule. If the sub-systems are actually identical particles, in the quantum mechanical sense that they are impossible to distinguish even in principle, the total partition function must be divided by a $N!$ (N factorial):

$$Z = \frac{\zeta^N}{N!}.$$

This is to ensure that we do not "over-count" the number of microstates. While this may seem like a strange requirement, it is actually necessary to preserve the existence of a thermodynamic limit for such systems. This is known as the Gibbs paradox.

Grand canonical partition function

Definition

In a manner similar to the definition of the canonical partition function for the canonical ensemble, we can define a **grand canonical partition function** for a grand canonical ensemble, a system that can exchange both heat and particles with the environment, which has a constant temperature T , and a chemical potential μ . The grand canonical partition function, although conceptually more involved, simplifies the theoretical handling of quantum systems because it incorporates in a simple way the spin-statistics of the particles (i.e. whether particles are bosons or fermions). A canonical partition function, which has a given number of particles is in fact difficult to write down because of spin statistics.

The grand canonical partition function \mathcal{Z} for an ideal quantum gas (a gas of non-interacting particles in a given potential well) is given by the following expression:

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{\{n_i\}} \prod_i e^{-\beta n_i (\epsilon_i - \mu)}$$

where N is the total number of particles in the gas, index i runs over every microstate (that is, a single particle state in the potential) with n_i being the number of particles occupying microstate i and ϵ_i being the energy of a particle in that microstate. The set $\{n_i\}$ is the collection of all possible occupation numbers for each of these microstates such that $\sum n_i = N$.

For example, consider the $N=3$ term in the above sum. One possible set of occupation numbers would be $n_1 = 0, 1, 0, 2, 0 \dots$ and the contribution of this set of occupation numbers to the $N=3$ term would be

$$\prod_i e^{-\beta n_i (\epsilon_i - \mu)} = e^{-\beta(\epsilon_1 - \mu)} e^{-2\beta(\epsilon_3 - \mu)}.$$

For bosons, the occupation numbers can take any integer values as long as their sum is equal to N . For fermions, the Pauli exclusion principle requires that the occupation numbers only be 0 or 1, again adding up to N .

Specific expressions

The above expression for the grand partition function can be shown to be mathematically equivalent to:

$$\mathcal{Z} = \prod_i \mathcal{Z}_i .$$

(The above product is sometimes taken over all states with equal energy, rather than over each state, in which case the individual partition functions must be raised to a power g_i where g_i is the number of such states. g_i is also referred to as the "degeneracy" of states.)

For a system composed of bosons:

$$\mathcal{Z}_i = \sum_{n_i=0}^{\infty} e^{-\beta n_i(\epsilon_i - \mu)} = \frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}}$$

and for a system composed of fermions:

$$\mathcal{Z}_i = \sum_{n_i=0}^1 e^{-\beta n_i(\epsilon_i - \mu)} = 1 + e^{-\beta(\epsilon_i - \mu)} .$$

For the case of a Maxwell-Boltzmann gas, we must use "correct Boltzmann counting" and divide the Boltzmann factor $e^{-\beta(\epsilon_i - \mu)}$ by $n_i!$.

$$\mathcal{Z}_i = \sum_{n_i=0}^{\infty} \frac{e^{-\beta n_i(\epsilon_i - \mu)}}{n_i!} = \exp(\exp(-\beta(\epsilon_i - \mu))) .$$

Relation to thermodynamic variables

Just as with the canonical partition function, the grand canonical partition function can be used to calculate thermodynamic and statistical variables of the system. As with the canonical ensemble, the thermodynamic quantities are not fixed, but have a statistical distribution about a mean or expected value.

Occupation numbers

The most probable occupation numbers are:

$$\langle n_i \rangle = - \left(\frac{\partial \ln(\mathcal{Z}_i)}{\partial \alpha} \right)_{\beta, V} = \frac{1}{\beta} \left(\frac{\partial \ln(\mathcal{Z}_i)}{\partial \mu} \right)_{\beta, V} ,$$

where $\alpha = -\beta \cdot \mu$.

For Boltzmann particles this yields:

$$\langle n_i \rangle = e^{-\beta(\epsilon_i - \mu)} .$$

For bosons:

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} .$$

For fermions:

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1} .$$

which are just the results found using the canonical ensemble for Maxwell-Boltzmann statistics, Bose-Einstein statistics and Fermi-Dirac statistics, respectively. (The degeneracy g_i is missing from the above equations because the index i is summing over individual microstates rather than energy eigenvalues.)

Total number of particles

$$\langle N \rangle = - \left(\frac{\partial \ln(\mathcal{Z})}{\partial \alpha} \right)_{\beta, V} = \frac{1}{\beta} \left(\frac{\partial \ln(\mathcal{Q})}{\partial \mu} \right)_{\beta, V} .$$

Variance in total number of particles

$$\langle (\delta N)^2 \rangle = \left(\frac{\partial^2 \ln(\mathcal{Z})}{\partial \alpha^2} \right)_{\beta, V} .$$

Internal energy

$$\langle E \rangle = - \left(\frac{\partial \ln(\mathcal{Z})}{\partial \beta} \right)_{\mu, V} + \mu \langle N \rangle .$$

Variance in internal energy

$$\langle (\delta E)^2 \rangle = \left(\frac{\partial^2 \ln(\mathcal{Z})}{\partial \beta^2} \right)_{\mu, V} .$$

Pressure

$$P = k_B T \left(\frac{\partial \ln(\mathcal{Z})}{\partial V} \right)_N .$$

Mechanical equation of state

$$\langle PV \rangle = \frac{\ln \mathcal{Z}}{\beta} .$$

Relation to potential V

For the case of a non-interacting gas, using the "Semiclassical Approach" we can write (approximately) the inverse of the potential in the form:

$$\frac{1}{2i\pi} \int_{c-i\infty}^{c+i\infty} ds \frac{Z(s)}{\sqrt{\pi s}} e^{st} \sim V^{-1}(t)$$

$$s = \frac{1}{k_B T} \text{ (valid for high T)}$$

supposing that the Hamiltonian of every particle is $H=T+V$.

Finite quantum grand canonical ensemble

If the number of particles N is maintained small and finite, the orthodicity of the canonical ensemble is exploited to define a **finite quantum grand canonical partition function** for a finite quantum grand canonical ensemble.^[2] The only hypothesis in addition is that the system is ergodic, so the average in time is equivalent to the average on the possible configurations. A system is orthodic if the averages of the physical quantities on a given distribution recover the laws of thermodynamics. The canonical ensemble is natively orthodic so such properties is granted for the finite N grand canonical ensemble by construction. Said $H(N)$ the Hamiltonian of the system constituted by N electrons distributed between a two dimensional quantum dot of area Σ_1 containing only one or two electrons and a two dimensional finite and small gas of area Σ_2 , it can be separated by $H = H_1(N_1) + H_2(N_2)$ where $N_1 = 1, 2$. Consequently one defines the finite quantum grand partition function for identical particles from:

$$\mathcal{Z}(\Sigma, N, T) = \sum_{N_1=1}^2 \text{tr}(e^{-\beta \hat{H}_1})$$

$$\mathcal{Z} = e^{-c_A \Sigma_1 / k_B}$$

where the heat capacity per area unit at constant surface c_A is:

$$c_A = \frac{1}{A} \left(\frac{\partial U(A, N)}{\partial T} \right)_A = \frac{\pi^2}{3} g k_B^2 T$$

where the density of states per surface unit is $g(E)dE = m\pi^2/\hbar^2 dE$ for a two dimensional system ($d = 2$).

The generalized temperature is obtained by considering time ensembles instead of configuration space ensembles in the case of thermal and particle exchange between a small system of fermions (N even less than 10) with a single/double occupancy system which acts as single particle thermometer. The generalized temperature is expressed as the ratio of the average time of occupation τ_1 and τ_2 of the single/double occupancy system.^[3]

$$T = k^{-1} \ln 2 \frac{\tau_2}{\tau_1} \left(E - E_F \left(1 + \frac{3}{2N} \right) \right),$$

where E_F is the Fermi energy which tends to the ordinary temperature when N goes to infinity.

Discussion

Before specific results can be obtained from the grand canonical partition function, the energy levels of the system under consideration need to be specified. For example, the particle in a box model or particle in a harmonic oscillator well provide a particular set of energy levels and are a convenient way to discuss the properties of a quantum fluid. (See the gas in a box and gas in a harmonic trap articles for a description of quantum fluids.)

These results may be used to construct the grand partition function to describe an ideal Bose gas or Fermi gas, and can be used as well to describe a classical ideal gas. In the case of a mesoscopic system made of few particles like a quantum dot in a semiconductor, the finite quantum grand partition ensemble is required, for which the limit of a small finite N is maintained.

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