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Review of quantum statistical mechanics

Thermodynamics is used to describe the bulk properties of matter in or near equilibrium. Many scientists, notably Boyle, Carnot, Clausius, Gay-Lussac, Gibbs, Joule, Kelvin, and Rumford, contributed to the development of the field over three centuries. Quantities such as mass, pressure, energy, and so on are readily defined and measured. Classical statistical mechanics attempts to understand thermodynamics by the application of classical mechanics to the microscopic particles making up the system. Great progress in this field was made by physicists like Boltzmann and Maxwell. Temperature, entropy, particle number, and chemical potential are thus understandable in terms of the microscopic nature of matter. Classical mechanics is inadequate in many circumstances however, and ultimately must be replaced by quantum mechanics. In fact, the ultraviolet catastrophe encountered by the application of classical mechanics and electromagnetism to blackbody radiation was one of the problems that led to the development of quantum theory. The development of quantum statistical mechanics was achieved by a number of twentieth century physicists, most notably Planck, Einstein, Fermi, and Bose. The purpose of this chapter is to give a mini-review of the basic concepts of quantum statistical mechanics as applied to noninteracting systems of particles. This will set the stage for the functional integral representation of the partition function, which is a cornerstone of modern relativistic quantum field theory and the quantum statistical mechanics of interacting particles and fields.

1.1 Ensembles

One normally encounters three types of ensemble in equilibrium statistical mechanics. The *microcanonical* ensemble is used to describe an isolated system that has a fixed energy E, a fixed particle number N, and a fixed

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volume V. The *canonical* ensemble is used to describe a system in contact with a heat reservoir at temperature T. The system can freely exchange energy with the reservoir, but the particle number and volume are fixed. In the *grand canonical* ensemble the system can exchange particles as well as energy with a reservoir. In this ensemble the temperature, volume, and chemical potential μ are fixed quantities. The standard thermodynamic relations are summarized in appendix section A1.1.

In the canonical and grand canonical ensembles, $T^{-1} = \beta$ may be thought of as a Lagrange multiplier that determines the mean energy of the system. Similarly, μ may be thought of as a Lagrange multiplier that determines the mean number of particles in the system. In a relativistic quantum system, where particles can be created and destroyed, it is most straightforward to compute observables in the grand canonical ensemble. For that reason we use the grand canonical ensemble throughout this book. There is no loss of generality in doing so because one may pass over to either of the other ensembles by performing an inverse Laplace transform on the variable μ and/or the variable β. See appendix section A1.2.

Consider a system described by a Hamiltonian H and a set of conserved number operators $\hat{N}_i$. (A hat or caret is used to denote an operator for emphasis or whenever there is the possibility of an ambiguity.) In QED, for example, the number of electrons minus the number of positrons is a conserved quantity, not the number of electrons or positrons separately, because of reactions like $e^+e^- \to e^+e^+e^-e^-$. These number operators must be Hermitian and must commute with H as well as with each other. They must also be extensive (scale with the volume of the system) in order that the usual macroscopic thermodynamic limit can be taken. The statistical density matrix $\hat{\rho}$ is the fundamental object in equilibrium statistical mechanics:

$$\hat{\rho} = \exp\left[-\beta\left(H - \mu_i \hat{N}_i\right)\right] \tag{1.1}$$

Here and throughout the book a repeated index is assumed to be summed over. In QED the sum would run over two conserved number operators if one allowed for both electrons and muons. The statistical density matrix is used to compute the ensemble average of any desired observable, represented by the operator $\hat{A}$, via

$$A = \langle \hat{A} \rangle = \frac{\mathrm{Tr}\, \hat{A}\hat{\rho}}{\mathrm{Tr}\, \hat{\rho}} \tag{1.2}$$

where Tr denotes the trace operation.

The grand canonical partition function

$$Z = Z(V, T, \mu_1, \mu_2, \ldots) = \mathrm{Tr}\, \hat{\rho} \tag{1.3}$$

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is the single most important function in thermodynamics. From it all the thermodynamic properties may be determined. For example, the pressure, particle number, entropy, and energy are, in the infinite-volume limit, given by

$$\begin{aligned} P &= \frac{\partial(T \ln Z)}{\partial V} \\ N_i &= \frac{\partial(T \ln Z)}{\partial \mu_i} \\ S &= \frac{\partial(T \ln Z)}{\partial T} \\ E &= -PV + TS + \mu_i N_i \end{aligned} \tag{1.4}$$

1.2 One bosonic degree of freedom

As a simple example consider a time-independent single-particle quantum mechanical mode that may be occupied by bosons. Each boson in that mode has the same energy ω. There may be 0, 1, 2, or any number of bosons occupying that mode. There are no interactions between the particles. This system may be thought of as a set of noninteracting quantized simple harmonic oscillators. It will serve as a prototype of the relativistic quantum field theory systems to be introduced in later chapters. We are interested in computing the mean particle number, energy, and entropy. Since the system has no volume there is no physical pressure.

Denote the state of the system by $|n\rangle$, which means that there are n bosons in the system. The state $|0\rangle$ is called the vacuum. The properties of these states are

$$\langle n|n'\rangle = \delta_{nn'} \qquad \text{orthogonality} \tag{1.5}$$

$$\sum_{n=0}^{\infty} |n\rangle\langle n| = 1 \qquad \text{completeness} \tag{1.6}$$

One may think of the bras $\langle n|$ and kets $|n\rangle$ as row and column vectors, respectively, in an infinite-dimensional vector space. These vectors form a complete set. The operation in (1.5) is an inner product and the number 1 in (1.6) stands for the infinite-dimensional unit matrix.

It is convenient to introduce creation and annihilation operators, $a^\dagger$ and a, respectively. The creation operator creates one boson and puts it in the mode under consideration. Its action on a number eigenstate is

$$a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle \tag{1.7}$$

Similarly, the annihilation operator annihilates or removes one boson,

$$a|n\rangle = \sqrt{n}\,|n-1\rangle \tag{1.8}$$

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unless $n = 0$, in which case it annihilates the vacuum,

$$a|0\rangle = 0 \tag{1.9}$$

Apart from an irrelevant phase, the coefficients appearing in (1.7) and (1.8) follow from the requirements that $a^\dagger$ and a be Hermitian conjugates and that $a^\dagger a$ be the number operator $\hat{N}$. That is,

$$\hat{N}|n\rangle = a^\dagger a|n\rangle = n|n\rangle \tag{1.10}$$

As a consequence the commutator of a with $a^\dagger$ is

$$[a, a^\dagger] = aa^\dagger - a^\dagger a = 1 \tag{1.11}$$

We can build all states from the vacuum by repeated application of the creation operator:

$$|n\rangle = \frac{1}{\sqrt{n!}}(a^\dagger)^n|0\rangle \tag{1.12}$$

Next we need a Hamiltonian. Up to an additive constant, it must be ω times the number operator. Starting with a wave equation in nonrelativistic or relativistic quantum mechanics the additive constant emerges naturally. One finds that

$$H = \tfrac{1}{2}\omega\left(aa^\dagger + a^\dagger a\right) = \omega\left(a^\dagger a + \tfrac{1}{2}\right) = \omega\left(\hat{N} + \tfrac{1}{2}\right) \tag{1.13}$$

The additive term $\frac{1}{2}\omega$ is the zero-point energy. Usually this term can be ignored. Exceptions arise when the vacuum changes owing to a background field, such as the gravitational field or an electric field, as in the Casimir effect. We shall drop this term in the rest of the chapter and leave it as an exercise to repeat the following analysis with the inclusion of the zero-point energy.

The states $|n\rangle$ are simultaneous eigenstates of energy and particle number. We can assign a chemical potential to the particles. This is possible because there are no interactions to change the particle number. The partition function is easily computed:

$$\begin{aligned} Z &= \operatorname{Tr} \mathrm{e}^{-\beta(H-\mu\hat{N})} = \operatorname{Tr} \mathrm{e}^{-\beta(\omega-\mu)\hat{N}} \\ &= \sum_{n=0}^{\infty}\langle n|\mathrm{e}^{-\beta(\omega-\mu)\hat{N}}|n\rangle = \sum_{n=0}^{\infty}\mathrm{e}^{-\beta(\omega-\mu)n} \\ &= \frac{1}{1-\mathrm{e}^{-\beta(\omega-\mu)}} \end{aligned} \tag{1.14}$$

The mean number of particles is found from (1.4) to be

$$N = \frac{1}{\mathrm{e}^{\beta(\omega-\mu)} - 1} \tag{1.15}$$

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and the mean energy E is ωN. Note that N ranges continuously from zero to infinity as μ ranges from $-\infty$ to ω. Values of the chemical potential, in this system, are restricted to be less than ω on account of the positivity of the particle number or, equivalently, the Hermiticity of the number operator.

There are two interesting limits. One is the classical limit, where the occupancy is small, $N \ll 1$. This occurs when $T \ll \omega - \mu$. In this limit the exponential in (1.15) is large and so

$$N = \mathrm{e}^{-\beta(\omega-\mu)} \qquad \text{classical limit} \tag{1.16}$$

The other is the quantum limit, where the occupancy is large, $N \gg 1$. This occurs when $T \gg \omega - \mu$.

1.3 One fermionic degree of freedom

Now consider the same problem as in the previous section but for fermions instead of bosons. This is a prototype for a Fermi gas, and later on will help us to formulate the functional integral expression for the partition function involving fermions. These could be electrons and positrons in QED, neutrons and protons in nuclei and nuclear matter, or quarks in QCD.

The Pauli exclusion principle forbids the occupation of a single-particle mode by more than one fermion. Thus there are only two states of the system, $|0\rangle$ and $|1\rangle$. The action of the fermion creation and annihilation operators on these states is as follows:

$$\begin{aligned} \alpha^\dagger|0\rangle &= |1\rangle \\ \alpha|1\rangle &= |0\rangle \\ \alpha^\dagger|1\rangle &= 0 \\ \alpha|0\rangle &= 0 \end{aligned} \tag{1.17}$$

Therefore, these operators have the property that their square is zero when acting on any of the states,

$$\alpha\alpha = \alpha^\dagger\alpha^\dagger = 0 \tag{1.18}$$

Up to an arbitrary phase factor, the coefficients in (1.17) are chosen so that α and $\alpha^\dagger$ are Hermitian conjugates and $\alpha^\dagger\alpha$ is the number operator $\hat{N}$:

$$\hat{N}|n\rangle = n|n\rangle \tag{1.19}$$

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It follows that the creation and annihilation operators satisfy the anti-commutation relation

$$\{\alpha, \alpha^\dagger\} = \alpha\alpha^\dagger + \alpha^\dagger\alpha = 1 \tag{1.20}$$

The Hamiltonian is taken to be

$$H = \tfrac{1}{2}\omega\left(\alpha^\dagger\alpha - \alpha\alpha^\dagger\right) = \omega\left(\hat{N} - \tfrac{1}{2}\right) \tag{1.21}$$

This form follows from the Dirac equation. Notice that the zero-point energy is equal in magnitude but opposite in sign to the bosonic zero-point energy. In this chapter we drop this term for fermions, as we have for bosons.

The partition function is computed as in (1.14) except that the sum terminates at $n = 1$ on account of the Pauli exclusion principle:

$$\begin{aligned} Z &= \mathrm{Tr}\, \mathrm{e}^{-\beta(H-\mu\hat{N})} = \mathrm{Tr}\, \mathrm{e}^{-\beta(\omega-\mu)\hat{N}} \\ &= \sum_{n=0}^{1} \langle n|\mathrm{e}^{-\beta(\omega-\mu)\hat{N}}|n\rangle = \sum_{n=0}^{1} \mathrm{e}^{-\beta(\omega-\mu)n} \\ &= 1 + \mathrm{e}^{-\beta(\omega-\mu)} \end{aligned} \tag{1.22}$$

The mean number of particles is found from (1.4) to be

$$N = \frac{1}{\mathrm{e}^{\beta(\omega-\mu)} + 1} \tag{1.23}$$

and the mean energy E is ωN. Note that N ranges continuously from zero to unity as μ ranges from $-\infty$ to ∞. Unlike bosons, for fermions there is no restriction on the chemical potential.

As with bosons, there are two interesting limits. One is the classical limit, where the occupancy is small, $N \ll 1$. This occurs when $T \ll \omega - \mu$:

$$N = \mathrm{e}^{-\beta(\omega-\mu)} \qquad \text{classical limit} \tag{1.24}$$

which is the same limit as for bosons. The other is the quantum limit. When $T \to 0$ one obtains $N \to 0$ if $\omega > \mu$ and $N \to 1$ if $\omega < \mu$.

1.4 Noninteracting gases

Now let us put particles, either bosons or fermions, into a box with sides of length L. We neglect their mutual interactions, although in principle they must interact in order to come to thermal equilibrium. One can imagine including interactions, waiting until the particles come to equilibrium, and then slowly turning off the interactions. Such a noninteracting gas is often a good description of the atmosphere around us, electrons in a metal or white dwarf star, blackbody photons in a heated cavity or in the cosmic microwave background radiation, phonons in low-temperature materials, neutrons in a neutron star, and many other situations.

In the macroscopic limit the boundary condition imposed on the surface of the box is unimportant. For definiteness we impose the condition that the wave function vanishes at the surface of the box. (Also frequently used are periodic boundary conditions.) The vanishing of the wave function on the surface means that an integral number of half-wavelengths must fit in the distance L:

$$\lambda_x = 2L/j_x \quad \lambda_y = 2L/j_y \quad \lambda_z = 2L/j_z \tag{1.25}$$

where j_x, j_y, j_z are all positive integers. The magnitude of the x component of the momentum is $|p_x| = 2\pi/\lambda_x = \pi j_x/L$, and similarly for the y and z components. Amazingly, quantum mechanics tells us that these relations hold for both nonrelativistic and relativistic motion, for both bosons and fermions.

The full Hamiltonian is the sum of the Hamiltonians for each mode on account of the assumption that the particles do not interact. We use a shorthand notation in which $\mathbf{j}$ represents the triplet of numbers (j_x, j_y, j_z) that uniquely specifies each mode. Thus the Hamiltonian and number operator are

$$\begin{aligned} H &= \sum_{\mathbf{j}} H_{\mathbf{j}} \\ \hat{N} &= \sum_{\mathbf{j}} \hat{N}_{\mathbf{j}} \end{aligned} \tag{1.26}$$

Then the partition function is the product of the partition functions for each mode:

$$Z = \mathrm{Tr}\,\mathrm{e}^{-\beta(H-\mu\hat{N})} = \prod_{\mathbf{j}} \mathrm{Tr}\,\mathrm{e}^{-\beta(H_j-\mu\hat{N}_j)} = \prod_{\mathbf{j}} Z_{\mathbf{j}} \tag{1.27}$$

Each mode corresponds to the single bosonic or fermionic degree of freedom discussed previously.

According to (1.4) it is $\ln Z$ that is of fundamental interest. From (1.27),

$$\ln Z = \sum_{j_x=1}^{\infty} \sum_{j_1=1}^{\infty} \sum_{j_z=1}^{\infty} \ln Z_{j_x,j_y,j_z} \tag{1.28}$$

In the macroscopic limit, $L \to \infty$, it is permissible to replace the sum from $j_x = 1$ to ∞ with an integral from $j_x = 1$ to ∞. (The correction to this approximation is proportional to the surface area L^2 and the relative contribution is therefore of order $1/L$.) We can then use $dj_x = Ld|p_x|/\pi$

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to write

$$\ln Z = \frac{L^3}{\pi^3} \int_0^\infty d|p_x| \int_0^\infty d|p_y| \int_0^\infty d|p_z| \ln Z(\mathbf{p}) \tag{1.29}$$

In all cases to be dealt with in this book the mode partition function depends only on the magnitude of the momentum components. Then the integration over p_x may be extended from $-\infty$ to ∞ if we divide by 2:

$$\ln Z = V \int \frac{d^3p}{(2\pi)^3} \ln Z(p) \tag{1.30}$$

Note the natural appearance of the phase-space integral $\int d^3x d^3p/(2\pi)^3$ in this expression.

Recalling the mode partition function from the previous sections we have

$$\ln Z = V \int \frac{d^3p}{(2\pi)^3} \ln \left(1 \pm \mathrm{e}^{-\beta(\omega-\mu)}\right)^{\pm 1} \tag{1.31}$$

where the upper sign (+) refers to fermions and the lower sign (−) refers to bosons. From (1.4) and (1.31) we obtain the pressure, particle number, and energy:

$$\begin{aligned} P &= \frac{T}{V} \ln Z \\ N &= V \int \frac{d^3p}{(2\pi)^3} \frac{1}{\mathrm{e}^{\beta(\omega-\mu)} \pm 1} \\ E &= V \int \frac{d^3p}{(2\pi)^3} \frac{\omega}{\mathrm{e}^{\beta(\omega-\mu)} \pm 1} \end{aligned} \tag{1.32}$$

These formulæ for N and E have the simple interpretation of phase-space integrals over the mean particle number and energy of each mode, respectively.

The dispersion relation $\omega = \omega(p)$ determines the energy for a given momentum. For relativistic particles $\omega = \sqrt{p^2 + m^2}$, where m is the mass. The nonrelativistic limit is $\omega = m + p^2/2m$. For phonons the dispersion relation is $\omega = c_\mathrm{s} p$, where c_s is the speed of sound in the medium.

There are a number of interesting and physically relevant limits. Consider the dispersion relation $\omega = \sqrt{p^2 + m^2}$. The classical limit corresponds to low occupancy of the modes and is the same for bosons (1.16) and fermions (1.24). The momentum integral for the pressure can be performed and written as

$$P = \frac{m^2 T^2}{2\pi^2} \, \mathrm{e}^{\mu/T} K_2\left(\frac{m}{T}\right) \qquad \text{classical limit} \tag{1.33}$$

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where K_2 is the modified Bessel function. The nonrelativistic limit of this is

$$P = T\left(\frac{mT}{2\pi}\right)^{3/2} \mathrm{e}^{(\mu-m)/T} \qquad \text{classical nonrelativistic limit} \tag{1.34}$$

Knowing the pressure as a function of temperature and chemical potential we can obtain all other thermodynamic functions by differentiation or by using thermodynamic identities.

The zero-temperature limit for fermions requires that $\mu > m$, otherwise the vacuum state is approached. In this limit all states up to the Fermi momentum $p_\mathrm{F} = \sqrt{\mu^2 - m^2}$ and energy $E_\mathrm{F} = \mu$ are occupied and all states above are empty. The pressure, energy density $\epsilon = E/V$, and number density $n = N/V$ are given by

$$\begin{aligned} P &= \frac{1}{16\pi^2}\left[2\mu^3 p_\mathrm{F} - m^2\mu p_\mathrm{F} - m^4 \ln\left(\frac{\mu + p_\mathrm{F}}{m}\right)\right] \\ \epsilon &= \frac{1}{16\pi^2}\left[\frac{2}{3}\mu p_\mathrm{F}^3 - m^2\mu p_\mathrm{F} + m^4 \ln\left(\frac{\mu + p_\mathrm{F}}{m}\right)\right] \\ n &= \frac{p_\mathrm{F}^3}{6\pi^2} \end{aligned} \tag{1.35}$$

In the nonrelativistic limit,

$$\begin{aligned} P &= \frac{p_\mathrm{F}^5}{30\pi^2 m} \\ \epsilon &= mn + \frac{3}{2}P \qquad \text{nonrelativistic limit} \end{aligned} \tag{1.36}$$

Electrons and nucleons have spin 1/2 and these expressions need to be multiplied by 2 to take account of that! The low-temperature limit for bosons will be discussed in the next chapter.

Massless bosons with zero chemical potential have pressure

$$P = \frac{\pi^2}{90}T^4 \tag{1.37}$$

This is one of the most famous formulae in the thermodynamics of radiation fields.

If time reversal is a good symmetry, a detailed balance must occur among all possible reactions in equilibrium. For example, if the reaction $A + B \to C + D$ can occur then not only must the reverse reaction, $C + D \to A + B$, occur but it must happen at the same rate. Detailed balance implies relationships between the chemical potentials. It is shown in standard textbooks that, for the reactions just mentioned, the chemical potentials obey $\mu_A + \mu_B = \mu_C + \mu_D$. For a long-lived resonance

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that decays according to $X \to A + B$, the formation process $A + B \to X$ must happen at the same rate. The chemical potentials are related by $\mu_X = \mu_A + \mu_B$. Generally any reactions that are allowed by the conservation laws can and will occur. These conservation laws restrict the number of linearly independent chemical potentials. Consider, for example, a system whose only relevant conservation laws are for baryon number and electric charge. There are only two independent chemical potentials, one for baryon number (μ_B) and one for electric charge (μ_Q). Any particle in the system has a chemical potential which is a linear combination of these:

$$\mu_i = b_i \mu_B + q_i \mu_Q \tag{1.38}$$

Here b_i is the baryon number and q_i the electric charge of the particle of type i. These chemical potentials are all measured with respect to the total particle energy including mass. (The chemical potential μ_i^{NR}, as customarily defined in nonrelativistic many-body theory, is related to ours by $\mu_i^{\mathrm{NR}} = \mu_i - m_i$.) Bosons that carry no conserved quantum number, such as photons and π^0 mesons, have zero chemical potential. Antiparticles have a chemical potential opposite in sign to particles.

The electrically charged mesons π^+ and π^- have electric charges of $+1$ and -1 and therefore equal and opposite chemical potentials, μ_Q and $-\mu_Q$, respectively. The total conserved charge is the number of π^+ mesons minus the number of π^- mesons:

$$Q = V \int \frac{d^3p}{(2\pi)^3} \left(\frac{1}{\mathrm{e}^{\beta(\omega - \mu_Q)} - 1} - \frac{1}{\mathrm{e}^{\beta(\omega + \mu_Q)} - 1} \right) \tag{1.39}$$

and the total energy is

$$E = V \int \frac{d^3p}{(2\pi)^3} \left(\frac{\omega}{\mathrm{e}^{\beta(\omega - \mu_Q)} - 1} + \frac{\omega}{\mathrm{e}^{\beta(\omega + \mu_Q)} - 1} \right) \tag{1.40}$$

If the bosons have nonzero spin s, then the phase-space integrals must be multiplied by the spin degeneracy factor $2s + 1$. An analogous discussion can be given for fermions.

1.5 Exercises

1.1 Prove that the state $|n\rangle$ given in (1.12) is normalized to unity.

1.2 Referring to (1.17), let $|0\rangle$ and $|1\rangle$ be represented by the basis vectors in a two-dimensional vector space. Find an explicit 2×2 matrix representation of the abstract operators α and $\alpha^\dagger$ in this vector space.

1.3 Calculate the partition function for noninteracting bosons, including the zero-point energy. From it calculate the mean energy, particle number, and entropy. Repeat the calculation for fermions.