Kapitel 4

Bosons and fermions in thermodynamic equilibrium

In this chapter we consider a quantum many-particle system in thermodynamic equilibrium. In contrast to the quantum-mechanical description which is based on a given many-particle state or wave function here the system is in general in a *mixed state*, i.e. in an incoherent superposition of pure quantum states[1]. The central quantity which describes such states is the density operator ρ which we discuss in the next section.

4.1 Averages in a mixed state. Density operator

Let us rewrite the computation of an expectation value of operator $\hat{A}$ in a pure state $|\Psi\rangle$ of a N-particle system by introducing a projection operator onto this state,

$$\langle \hat{A} \rangle_\Psi = \langle \Psi | \hat{A} | \Psi \rangle = \mathrm{Tr}\, \hat{P}_\Psi \hat{A} \,, \tag{4.1}$$

$$\hat{P}_\Psi = |\Psi\rangle\langle\Psi| \tag{4.2}$$

Let us prove relation (4.1). To this end we switch to an arbitrary representation of the state. As an example we take the coordinate representation in terms of coordinate product states for all particles, $|R\rangle = |\mathbf{r}_1\mathbf{r}_2\dots\mathbf{r}_N\rangle$. The first expression in Eq. (4.1) then becomes

$$\langle \Psi | \hat{A} | \Psi \rangle = \int dR_1 dR_2 \Psi^*(R_1) \langle R_1 | \hat{A} | R_2 \rangle \Psi(R_2) \,. \tag{4.3}$$

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[1] The case of a pure state is, of course, included as as special case.

This has to be compared to the expression with the trace which is the sum over the diagonal matrix elements,

$$\begin{aligned}\mathrm{Tr}\,\hat{P}_\Psi \hat{A} &= \int dR_1 \langle R_1|\Psi\rangle\langle\Psi|\hat{A}|R_1\rangle \\ &= \int dR_1 dR_2 \langle R_1|\Psi\rangle\langle\Psi|R_2\rangle\langle R_2|\hat{A}|R_1\rangle \qquad (4.4)\\ &\equiv \langle\hat{A}\rangle_\Psi\,,\end{aligned}$$

which coincides with expression (4.3).

Mixed state. This expression with the projection operator has the advantage that it is straightforwardly generalized to mixed states. In the following we will consider a complete orthonormal set $|\Psi^i$ of eigenstates of the hamiltonian, i.e. solutions of the stationary Schrödinger equation $\hat{H}|\Psi^i\rangle = E_i|\Psi^i\rangle$ with $E_1 \leq E_2 \leq E_3 \dots$ and $\langle\Psi^i|\Psi^k\rangle = \delta_{ik}$. Now, if our system is in contact with a bath which gives rise to random exchange of energy (and particles) our system will typically not remain in a single pure state but undergo random excitations into other eigenstates. Averaging over a sufficiently long time will lead to a finite positive real probability W_i that the state $|\Psi^i\rangle$ will be realized, giving rising to a *mixed state*,

$$\hat{P}_\Psi \to \hat{\rho} = \sum_i W_i \hat{P}_{\Psi^{(i)}} = \sum_i W_i |\Psi^{(i)}\rangle\langle\Psi^{(i)}| \qquad (4.5)$$

$$0 \leq W_i \leq 1, \quad \sum_i W_i = 1\,. \qquad (4.6)$$

In Eq. (4.5) we defined the density operator that was introduced by Landau and von Neumann. The normalization of the density operator is given by

$$1 = \mathrm{Tr}\,\hat{\rho} = \int dR \langle R|\hat{\rho}|R\rangle = \sum_i W_i \int dR\, |\Psi^{(i)}(R)|^2\,. \qquad (4.7)$$

In the special case of thermodynamic equilibrium the probabilities are known and depend on the thermodynamic ensemble.

Canonical density operator. For example, in the canonical ensemble, where the system may exchange energy (but no particles) with the environment, the probabilities are given by the Boltzmann factor,

$$W_i^{\mathrm{c}}(N,V,T) = \frac{e^{-E_i/k_BT}}{Z^{\mathrm{c}}(N,V,T)} \qquad (4.8)$$

$$Z^{\mathrm{c}}(N,V,T) = \sum_i e^{-E_i/k_BT}\,, \qquad (4.9)$$

where $Z^{\mathrm{c}}(N,V,T)$ is the canonical partition function (sum of microstates) from which all other thermodynamic functions can be computed via standard relations. From these relations we can identify the canonical density operator as (we define $\beta=(k_B T)^{-1}$)

$$\hat{\rho}^{\mathrm{c}} = \frac{e^{-\beta\hat{H}}}{Z^{\mathrm{c}}(N,V,T)} \,. \tag{4.10}$$

This operator commutes with the hamiltonian, so the matrix of this operator in the eigenstates of $\hat{H}$ is diagonal

$$\rho^{\mathrm{c}}_{ij} = \langle\Psi^i|\hat{\rho}^{\mathrm{c}}|\Psi^j\rangle = \frac{e^{-\beta E_i}}{Z^{\mathrm{c}}(N,V,T)}\delta_{i,j}\,, \tag{4.11}$$

and one readily verifies that this expression also follows from the general definition (4.5). In most cases, however, the eigenstates of the hamiltonian are not known. Then the canonical density operator is not given by a diagonal matrix. Using for example coordinate eigenstates as a basis in the N-particle Hilbert space we obtain

$$\rho^{\mathrm{c}}(R,R') = \langle R|\hat{\rho}^{\mathrm{c}}|R'\rangle = \frac{\langle R|e^{-\beta\hat{H}}|R'\rangle}{Z^{\mathrm{c}}(N,V,T)}\,. \tag{4.12}$$

For the special case that $e^{-\beta\hat{H}} = e^{-\beta\hat{H}_1}e^{-\beta\hat{H}_2}$ and $\hat{H}_1|R\rangle = E_1(R)|R\rangle$, i.e. the states are eigenstates of $\hat{H}_1$, it follows

$$\rho^{\mathrm{c}}(R,R') = \frac{e^{-\beta E_1(R)}}{Z^{\mathrm{c}}(N,V,T)}\langle R|e^{-\beta\hat{H}_2}|R'\rangle\,, \tag{4.13}$$

and the difficult part of the problem has been reduced to computing the matrix elements of the second (non-diagonal) hamiltonian $\hat{H}_2$.

Grand canonical density operator. For the second example we consider the grand canonical ensemble, where the system may exchange energy and particles with the environment. Then the probabilities of the microstate i at a given particle number N is given by the modified Boltzmann factor,

$$W^{\mathrm{g}}_{i,N}(\mu,V,T) = \frac{e^{\beta(\mu N - E_{Ni})}}{Z^{\mathrm{g}}(\mu,V,T)} \tag{4.14}$$

$$Z^{\mathrm{g}}(\mu,V,T) = \sum_{N=0}^{\infty}\sum_i e^{\beta(\mu N - E_{Ni})}\,, \tag{4.15}$$

where μ is the chemical potential, and $Z^{\mathrm{g}}(\mu,V,T)$ is the grand canonical partition function (sum of microstates) from which all other thermodynamic functions can be computed via standard relations. This form assumes again that the grand canonical density operator is diagonal which means it is represented with respect to the joint eigenstates of the hamiltonian and the particle number operator, i.e. $[\hat{H}, \hat{N}] = 0$,

$$\hat{H}|iN\rangle = E_{Ni}|iN\rangle \,, \tag{4.16}$$

$$\hat{N}|iN\rangle = N|iN\rangle \,, \tag{4.17}$$

The general operator form is a generalization of the canonical density operator (4.10),

$$\hat{\rho}^{\mathrm{g}} = \frac{e^{\beta(\mu\hat{N}-\hat{H})}}{Z^{\mathrm{g}}(\mu, V, T)} \,. \tag{4.18}$$

We now ask ourselves how, in the present case, the definition of the density operator in terms of a superposition of projection operators, cf. (4.5) can be generalized to the grand ensemble. It is easy to verify the result,

$$\hat{\rho}^{\mathrm{g}} = \sum_{N=0}^{\infty}\sum_{i} W_{Ni}\, |iN\rangle\langle iN| \,, \tag{4.19}$$

$$0 \le W_{Ni} \le 1 \,, \quad \sum_{N=0}^{\infty}\sum_{i} W_{Ni} = 1 \,, \tag{4.20}$$

i.e., the density operator is the weighted sum of projections onto all eigenstates of the hamiltonian for any given particle number N. As before, the density operator is normalized, $\mathrm{Tr}\,\hat{\rho}^{\mathrm{g}} = 1$.

(Anti-)Symmetrization of the density operator. So far we have completely neglected the spin symmetry of the N-particle system. The definition (4.5) involves projections onto eigenstates of the hamiltonian that are not (anti-)symmetrized. Therefore, we need to perform the (anti-)symmetrization *a posteriori*, as we discussed in Sec. 3.8.2:

$$\hat{\rho} \to \hat{\rho}^{\pm} = \sum_i W_i |\Psi^{(i)}\rangle^{\pm}\, {}^{\pm}\langle\Psi^{(i)}| = \hat{\rho}\,\lambda^{\pm}_{1\ldots N} \,. \tag{4.21}$$

We demonstrate the procedure for the general definition (4.5) in the coordinate representation,

$$\hat{\rho}^{\pm} \to \langle R|\hat{\rho}^{\pm}|R'\rangle = \sum_i W_i \Psi^{(i)}(R) \sum_P \mathrm{sign(P)}\Psi^{(\mathrm{i})\,*}(\mathrm{P[R']}) \tag{4.22}$$

$$= \sum_i W_i \Psi^{(i)\pm}(R)\Psi^{(i)\pm\,*}(R') \,, \tag{4.23}$$

where the proper normalization, Eq. (4.7), has to be fulfilled again. This is indeed obvious from the representation (4.23):

$$\begin{aligned}\mathrm{Tr}\,\hat{\rho}^{\pm} &= \int dR \sum_i W_i \Psi^{(i)\pm}(R)\Psi^{(i)\pm *}(R) \\ &= \sum_i W_i \int dR\, |\Psi^{(i)\pm}(R)|^2 = 1\,. \end{aligned} \tag{4.24}$$

Note that in our result (4.22) no pre-factor $1/N!$ appears, in contrast to the standard literature. This factor has no effect on the full density operators because it would also appear (or not) in the normalization, Z. However, all results that are computed directly from the partition function would be affected.

will be completed

4.2 Path Integral Monte Carlo (PIMC)

As for a quantum many-particle system in the ground state, also in thermodynamic equilibrium there exist only a few analytically solvable problems. These include the ideal gas (Boltzmann, Fermi or Bose gas). If the interaction is weak the problem can be solved by perturbation theory. Similarly, if the system is perturbed by a weak field, one can apply linear response theory. Beyond that, there exist a large number of many-body methods where special approximation are being derived that are adopted to specific physical situations. These methods are similar to nonequilibrium systems which we will discuss in the subsequent chapters. Instead, here we briefly summarize a different approach that is very efficient in thermodynamic equilibrium: path integral Monte Carlo (PIMC). It is based on an independent representation of quantum mechanics in terms of path integrals that was introduced by R. Feynman [FH65a] and further developed by many others, e.g. [Kle09].

For a general quantum many-particle problem the hamiltonian is the sum of different terms such as kinetic, potential and interaction energy. Then the density operator has a form similar to (4.13) where we assumed $\hat{H} = \hat{H}_1 + \hat{H}_2$ where $\hat{H}_1$ is diagonal in a certain representation (basis of its eigenstates), whereas $\hat{H}_2$ is not. In order to reduce the matrix elements of $e^{-\beta\hat{H}}$ to the manageable form (4.13), however, assumes that $[\hat{H}_1, \hat{H}_2] = 0$.

Case of non-commuting operators. The problem is that, in many cases, $\hat{H}_1$ and $\hat{H}_2$ do not commute

$$e^{-\beta(\hat{H}_1+\hat{H}_2)} = e^{-\beta\hat{H}_1} e^{-\beta\hat{H}_2} e^{-\beta^2\hat{C}} \quad , \tag{4.25}$$

where the error term is obtained from the Baker-Campbell-Hausdorff formula as [DGB18]

$$\hat{C} = \frac{1}{2}[\hat{H}_1, \hat{H}_2] - \beta \left(\frac{1}{6}[\hat{H}_1, [\hat{H}_1, \hat{H}_2]] - \frac{1}{3}[[\hat{H}_1, \hat{H}_2], \hat{H}_2] \right) + \dots \ . \tag{4.26}$$

The interesting observation is that the commutator terms decrease with temperature because quantum effects are diminished. To take advantage of this property we exploit the (semi-)group property of the exponential function

$$e^{-\beta \hat{H}} = \prod_{\alpha=0}^{P-1} e^{-\epsilon \hat{H}} \ , \tag{4.27}$$

where $\epsilon = \beta/P$, and P is a positive integer number. We now use Eq. (4.27) and simultaneously insert $P-1$ unity operators of the form[2]

$$\hat{1} = \int \mathrm{d}\mathbf{R}_\alpha \ |\mathbf{R}_\alpha\rangle\langle\mathbf{R}_\alpha| \ , \tag{4.28}$$

into the partition function, where $|R\rangle$ are the eigenfunctions of $\hat{H}_1$ and form a complete orthonormal set.

4.2.1 Path integral

With this we obtain for the canonical partition function

$$Z^{\mathrm{c}} = \int \mathrm{d}\mathbf{X} \ \langle\mathbf{R}_0|e^{-\epsilon\hat{H}}|\mathbf{R}_1\rangle\langle\mathbf{R}_1| \dots |\mathbf{R}_{P-1}\rangle\langle\mathbf{R}_{P-1}|e^{-\epsilon\hat{H}}|\mathbf{R}_0\rangle \ . \tag{4.29}$$

Note that Eq. (4.29) is still exact and the integration is carried out over P sets of particle coordinates, $\mathrm{d}\mathbf{X} = \mathrm{d}\mathbf{R}_0 \dots \mathrm{d}\mathbf{R}_{P-1}$. Despite the increased dimensionality of the integral, this re-casting proves to be advantageous since each of the matrix elements must now be evaluated at a P times higher temperature and, for sufficiently many factors, we can introduce a high-temperature approximation, e.g., the primitive factorization[3]

$$e^{-\epsilon\hat{H}} \approx e^{-\epsilon\hat{H}_1} e^{-\epsilon\hat{H}_2} \ , \tag{4.30}$$

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[2] This is not necessarily a coordinate vector. It should be a complete set in N-particle Hilbert space.

[3] Higher order factorizations have also been studied and allow to use a much lower number of factors. An example is permutation blocking PIMC by Dornheim et al. For an overview and additional references, see Ref. [DGFB15].

which, according to the Trotter formula, becomes exact in the limit of $P \to \infty$

$$e^{-\beta(\hat{H}_1+\hat{H}_2)} = \lim_{P\to\infty} \left(e^{-\epsilon \hat{H}_1} e^{-\epsilon \hat{H}_2} \right)^P \ . \tag{4.31}$$

An interesting interpretation of Eq. (4.28) is given in terms of imaginary time path integrals. In particular, we note that the density operator is equivalent to a propagation in imaginary time by $\tau = -\mathrm{i}\beta$ (henceforth, we shall adopt the more conventional definition $\tau \to \tau/(-\mathrm{i}) \in [0, \beta]$). Therefore, Eq. (4.27) corresponds to the introduction of P imaginary ''time slices" of length ϵ and, a factorization like Eq. (4.30), to an "imaginary time propagator". Inserting Eq. (4.30) into (4.29) finally gives

$$Z^{\mathrm{c}} = \int \mathrm{d}\mathbf{X} \prod_{\alpha=0}^{P-1} \left(e^{-\epsilon E_1(\mathbf{R}_\alpha)} \rho_2(\mathbf{R}_\alpha, \mathbf{R}_{\alpha+1}; \epsilon) \right) \ , \tag{4.32}$$

where E_1 is the eigenvalue of the diagonal part, $\hat{H}_1$, i.e. $\hat{H}_1|R\rangle = E_1(R)|R\rangle$, whereas ρ_2 is the density matrix connected with the off-diagonal hamiltonian $\hat{H}_2$, i.e. $\rho_2(R, R'; \epsilon) = \langle R|e^{-\epsilon\hat{H}_2}|R'\rangle$.

Path integral in coordinate space. We now turn to the commonly studied case of the coordinate representation, where the eigenvectors of $\hat{H}_1$ comprise the coordinates of all particles[4], $|R\rangle = |\mathbf{r}_1\mathbf{r}_2 \dots \mathbf{r}_N\rangle$. In that case, the diagonal part of the hamiltonian is given by $\hat{H}_1 \to \hat{V}$, the operator of the potential energy where, for the eigenvalues, we have $E_1(R) \to V(\mathbf{R})$, denoting all potential energy terms. A typical factor (on "time slice" α) then has the form

$$V(\mathbf{R}_\alpha) = \sum_{i=1}^{N} V_{\mathrm{ext}}(\mathbf{r}_{\alpha,i}) + \sum_{k>i}^{N} W(|\mathbf{r}_{\alpha,i} - \mathbf{r}_{\alpha,k}|) \ , \tag{4.33}$$

where $W(r)$ is an arbitrary pair interaction, e.g., the Coulomb interaction, whereas $V_{\mathrm{ext}}(\mathbf{r})$ denotes an external potential.

The role of the second hamiltonian is now taken over by the kinetic energy operator, $\hat{T} = -\sum_{i=1}^{N} \hbar^2\nabla_i^2/2m$, and $\rho_2 \to \rho_0$ becomes the ideal part of the density matrix. The result is a Gaussian integral[5],

$$\rho_0(\mathbf{R}_\alpha, \mathbf{R}_{\alpha+1}, \epsilon) = \frac{1}{\lambda_\epsilon^{3N}} \prod_{k=1}^{N} \left[\exp\left(-\frac{\pi}{\lambda_\epsilon^2} (\mathbf{r}_{\alpha,k} - \mathbf{r}_{\alpha+1,k})^2 \right) \right] \ , \tag{4.34}$$

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[4] Note that this state is not (anti-)symmetrized. This can be a product of single-particle coordinate vectors.

[5] See problems, Sec. 4.4

with $\lambda_\epsilon = h/\sqrt{2\pi m k_B P \cdot T} = \hbar\sqrt{2\pi\epsilon/m}$ being the thermal DeBroglie wavelength corresponding to the P-fold increased temperature. In the limit $P \to \infty$, Eq. (4.34) becomes exact. An illustration of the path integral representation of three quantum particles is shown in the left part of Fig. 4.1. Each particle is represented by $P = 6$ high-temperature factors, leading to a set of 6 coordinates. Since the partition function is given by a trace the first and final coordinate of all particles coincide, so they are represented by closed loops (closed paths, "ring polymers"). Classical particles would correspond to straight vertical lines. In the case of quantum particles, the deviation from the straight line (variance of the coordinate fluctuations) is given by the thermal DeBroglie wavelength λ_T.

An illustration of the particle paths in three dimensions is shown in Fig. 4.2. It shows a snapshot of a real PIMC simulation for two cases: left, for a high temperature where each particle is given by a small cloud of particles. In the classical limit, all particles would shrink to a point (corresponding to a straight line in the one-dimensional representation). The right part shows the same system at a reduced temperature where the thermal DeBroglie wavelength increases and, therefore, the extension of the individual particles is large giving rise to significant particle overlap.

Path integral Monte Carlo (PIMC). The partition function Z^{c} is now given by a high-dimensional integral, Eq. (4.32) – the total dimension in case of N particles and P high-temperature factors is $N_{\mathrm{dim}} = 3NP$. In only very few cases these integrals can be computed analytically. The success of the path integral approach is largely due to the existence of highly efficient numerical integration routines that use random numbers and stochastic sampling methods (importance sampling, Metropolis algorithm).

4.2.2 (Anti-)Symmetrization of the partition function

So far the result for the partition function (4.32) involves a density operator that does not take into account the spin statistics. We have discussed before how (anti-)symmetry can be restored on the level of the density operator. One way is to perform an (anti-)symmetrization of the second argument of the density matrix, cf. Eq. (4.23). Then the partition function will contain an additional sum of $N!$ terms over all permutations of N particles. The previous result corresponds to the "identity permuation" whereas an example of the permutation of two particles is sketched in the right part of Fig. 4.1.