4 Quantum statistics at equilibrium

4.1 Canonical density matrices

In the present section we project the above declared indifference among quantum states onto the formalism of quantum statistics. We assign the appropriate density matrices to the most common statistical ensembles. To that end we consider the diagonal Hamiltonian[18] (Eq. (14)) associated with the (complete) basis made of bound many-particle eigenstates $|j\rangle$ with energies ϵ_j. The *microcanonical density matrix* assumes uniform distribution (Eq. (18)) over all states at the energy shell E

$$\hat{\rho} = z^{-1} \sum_j \delta(E - \epsilon_j)|j\rangle\langle j| = z^{-1}\delta(E - \hat{H}). \tag{78}$$

The proportionality factor (partition function) z is here to normalize (Eq.(26)) the density matrix, i.e. $z = \sum_j \delta(E - \epsilon_j)$.

The *canonical density matrix*, i.e. the density matrix for the heat exchanging quantum ensemble, will be defined accordingly by assigning a canonical Boltzmann weight (19) to each quantum microstate[19]

$$\hat{\rho} = \frac{\sum_j \mathrm{e}^{-\beta\epsilon_j}|j\rangle\langle j|}{\sum_j \mathrm{e}^{-\beta\epsilon_j}} = z^{-1} \exp(-\beta\hat{H}) \tag{79}$$

with canonical partition function $z \equiv \sum_j \mathrm{e}^{-\beta\epsilon_j} = \mathrm{Tr} \exp(-\beta\hat{H})$.

In the same way the *grand canonical density matrix* is constructed for grand canonical quantum ensemble. Assuming that the particle number $\hat{N}$ is well-defined for all the quantum microstates[20] $N(j)|j\rangle = \hat{N}|j\rangle$ we assign the grand canonical weight (20) for each state to yield

$$\hat{\rho} = z_G^{-1} \sum_j \mathrm{e}^{\beta(\bar{\mu}N(j)-\epsilon_j)}|j\rangle\langle j| = z_G^{-1}\mathrm{e}^{\beta(\bar{\mu}\hat{N}-\hat{H})}, \tag{80}$$

where the grand canonical partition function[21] reads $z_G = \mathrm{Tr}\ \mathrm{e}^{\beta(\bar{\mu}\hat{N}-\hat{H})}$.

[18] We use ϵ_j for many-particle energies, and reserve $\tilde{\epsilon}_j$ for single particle level energies in this section.

[19] The canonical density matrix is typically considered in Hilbert space $\mathbb{H}_N$ restricted to a fixed particle number. The same formula (79), but on the total many-body Hilbert space $\oplus_N \mathbb{H}_N$, is still correct for particles such as photons whose numbers cannot be controlled externally by reservoirs [8]. Consequences for collective vibrational excitations will be discussed in section 4.6.

[20] In other words that internal dynamics conserves particle number $[\hat{N}, \hat{H}] = 0$, which is true for any quantum mechanics, and thus most processes considered hereafter. Exception must be described within the quantum field theory, such as photon creation and annihilation processes of radiation, but even there final expression of Eq. (80) is correct prescription for grand canonical density matrix as will be demonstrated in section 5.1.

[21] Extension of Eq. (80) to more particle types and reservoirs is straightforward $\bar{\mu}\hat{N} \to \sum_\alpha \bar{\mu}_\alpha \hat{N}_\alpha$ but beyond our present concerns.

An attentive reader of the previous section might wonder to what extent it was really important to determine a specific value of the phase space equivalent $2\pi\hbar$ of a quantum state (for each canonical x, p pair)? Indeed, the transformation of the canonical density matrix (79) to the Wigner function

$$\rho_W \approx \frac{1}{z(2\pi\hbar)^{3N}} \exp\left(-\beta\mathcal{H}\right) \tag{81}$$

leads to the classical Boltzmann canonical density, comfortably absorbing transformation factor into the definition of the classical partition function $z_{\mathrm{cl}} \equiv z(2\pi\hbar)^{3N}$. The factor seems to be only a matter of normalization with little practical effect. However, the argument is limited to sparse particles. When we work with dense fermions or bosons in the classical phase space the knowledge of elementary phase space volume makes difference and becomes essential to correctly account for Pauli exclusion or boson condensation. Direct contact between the quantum and classical worlds can be experienced when modeling adsorption on surfaces, where a particle is rushing through phase space for a moment, at other times it is trapped by discrete surface binding quantum state.

4.2 Spaces of symmetrized wave functions

We next turn our attention to the concept of indistinguishability so specific in quantum mechanics. It is postulated that the wave functions of many particles of the same type must be symmetric for bosons (antisymmetric for fermions) with the respect to the transposition of particle coordinates, e.g. two-particle wave function satisfies

$$\psi(r_1, r_2) = \pm\psi(r_2, r_1).$$

Hilbert space of symmetrized (antisymmetrized[22]) many-body wave functions can be obtained as the linear extension over the Slater permanents (determinants)

$$\chi_{j_1,\ldots,j_N}(r_1, \ldots r_N) \propto \sum_{\{\Pi\}} (\pm 1)^{\mathrm{sgn}(\Pi)} \chi_{j_{\Pi(1)}}(r_1) \ldots \chi_{j_{\Pi(N)}}(r_N)$$

constructed from the products of single particle basis functions χ_j, Π stands for index permutations.

[22]Reader should be familiar with this construction of multi-particle states from the Hartree-Fock method of quantum chemistry.

For instance, out of two single-particle levels χ_a, χ_b one can construct only one antisymmetrized two-fermion state

wave function	energy	occupation number	2nd quantization
$(1/\sqrt{2})[\chi_a(r_1)\chi_b(r_2) - \chi_b(r_1)\chi_a(r_2)]$	$\tilde{\epsilon}_a+\tilde{\epsilon}_b$	$\|A:1\ 1\rangle$	$\hat{\chi}_a^\dagger\hat{\chi}_b^\dagger\|0\rangle$

while two bosons can occur in three symmetrized states

wave function	energy	occupation number	2nd quantization
$\chi_a(r_1)\chi_a(r_2)$	$2\tilde{\epsilon}_a$	$\|S:2\ 0\rangle$	$(\hat{\chi}_a^\dagger)^2\|0\rangle$
$\chi_b(r_1)\chi_b(r_2)$	$2\tilde{\epsilon}_b$	$\|S:0\ 2\rangle$	$(\hat{\chi}_b^\dagger)^2\|0\rangle$
$(1/\sqrt{2})[\chi_a(r_1)\chi_b(r_2) + \chi_b(r_1)\chi_a(r_2)]$	$\tilde{\epsilon}_a+\tilde{\epsilon}_b$	$\|S:1\ 1\rangle$	$\hat{\chi}_a^\dagger\hat{\chi}_b^\dagger\|0\rangle$

Three fermions cannot be placed on two (one-particle) levels at all, three bosons can assume four wave functions as follows.

wave function	energy	occupation number	2nd quantization
$\chi_a(r_1)\chi_a(r_2)\chi_a(r_3)$	$3\tilde{\epsilon}_a$	$\|S:3\ 0\rangle$	$(\hat{\chi}_a^\dagger)^3\|0\rangle$
$\chi_b(r_1)\chi_b(r_2)\chi_b(r_3)$	$3\tilde{\epsilon}_b$	$\|S:0\ 3\rangle$	$(\hat{\chi}_b^\dagger)^3\|0\rangle$
$(1/\sqrt{3})[\chi_a(r_1)\chi_a(r_2)\chi_b(r_3)$ $+\chi_a(r_1)\chi_b(r_2)\chi_a(r_3)$ $+\chi_b(r_1)\chi_a(r_2)\chi_a(r_3)]$	$2\tilde{\epsilon}_a+\tilde{\epsilon}_b$	$\|S:2\ 1\rangle$	$(\hat{\chi}_a^\dagger)^2\hat{\chi}_b^\dagger\|0\rangle$
$(1/\sqrt{3})[\chi_a(r_1)\chi_b(r_2)\chi_b(r_3)$ $+\chi_b(r_1)\chi_b(r_2)\chi_a(r_3)$ $+\chi_b(r_1)\chi_a(r_2)\chi_b(r_3)]$	$\tilde{\epsilon}_a+2\tilde{\epsilon}_b$	$\|S:1\ 2\rangle$	$\hat{\chi}_a^\dagger(\hat{\chi}_b^\dagger)^2\|0\rangle$

The notation of (anti-) symmetric wave functions in the left column of the tables becomes quickly expensive, therefore, more suitable representations of many-particle states have been developed. Apparently, any function in the left column can be identified by counting occupancy of either level χ_a or χ_b. In the third column of the tables we thus introduce the representation of the occupation numbers. When larger number of levels χ_k can be occupied, even this representation becomes costly. The technique of the second quantization (last column of tables) become feasible, where the symmetrization is encoded in the definition of bosonic operators satisfying the commutation relation

$$[\hat{\chi}_k, \hat{\chi}_l^\dagger] = \delta_{kl} \tag{82}$$

and antisymmetrization in the definition of fermionic operators satisfying the anticommutation relation

$$\{\hat{\chi}_k, \hat{\chi}_l^\dagger\} = \delta_{kl}. \tag{83}$$