

School of Physics & Astronomy

PHS4200/PHS4021 Statistical Mechanics

Lecture 7: Density Operators in Quantum Statistical Mechanics

7.1 Introduction

In classical statistical mechanics, a microstate of a system at an instant of time corresponds to a point (\mathbf{q}, \mathbf{p}) in phase space, with a classical statistical ensemble described by a density function $\rho(\mathbf{q}, \mathbf{p})$. However, the Heisenberg uncertainty principle precludes the simultaneous measurement of position and momentum, and it is therefore necessary to construct a statistical ensemble using the language of quantum mechanics; namely, using operators and wavefunctions. Here we examine the formal methods of quantum statistical mechanics - in particular the density operator formalism, which generalises the classical theory of statistical distributions (e.g., the Boltzmann distribution). In essence the density operator, or its equivalent matrix representation, describes quantum statistical probabilities based on the wavefunction and the Boltzmann probabilities of the energy levels.

7.2 The Density Operator

Quantum mechanical systems are described by a state vector $|\Psi(t)\rangle$ in Hilbert space¹ \mathcal{H} . The state vector evolves according to the Schrödinger equation:

$$i\hbar \frac{d|\Psi(t)\rangle}{dt} = \hat{H}|\Psi(t)\rangle, \quad (7.1)$$

where \hat{H} is the Hamiltonian operator of the system. The formal solution to Eq. (7.1) is given by:

$$|\Psi(t)\rangle = \hat{U}(t - t_0)|\Psi(t_0)\rangle = e^{-i\hat{H}(t-t_0)/\hbar}|\Psi(t_0)\rangle. \quad (7.2)$$

The state vector at time t_0 can be expressed as a linear superposition of orthonormal basis vectors $|\phi_\alpha\rangle$, i.e.,

$$|\Psi(t_0)\rangle = \sum_{\alpha} c_{\alpha}(t_0)|\phi_{\alpha}\rangle \quad (c_{\alpha}(t_0) \in \mathbb{C}), \quad (7.3)$$

where a measurement on the system at t_0 has a probability $|c_{\alpha}(t_0)|^2$ of being found in the state $|\phi_{\alpha}\rangle$. At time t the state of a system will be characterised by the wavefunction $\Psi(\mathbf{q}, t) = \langle \mathbf{q} | \Psi(t) \rangle$, which is just the state vector in the coordinate representation. The probability density is given by $|\Psi(\mathbf{q}, t)|^2$. If a quantum mechanical system is in given microstate, described by the state vector $|\Psi_n(t)\rangle$, or the wavefunction $\Psi_n(\mathbf{q}, t)$, then we say that it is a pure state. The corresponding expectation value of an operator $\hat{A} = \hat{A}(\hat{\mathbf{Q}}, \hat{\mathbf{P}})$, in the state $|\Psi_n(t)\rangle$, is given by:

¹ To be more precise the quantum mechanical state of a physical system is represented by a ray in Hilbert space (http://en.wikipedia.org/wiki/Hilbert_space). A ray is an equivalence class of normalised state vectors, i.e., all state vectors $a|\Psi\rangle$ ($a \in \mathbb{C}$, $a \neq 0$), which have the same “direction” as $|\Psi\rangle$ correspond to the same physical state. However, physicists customarily use the word vector rather than ray. For a discussion of rays and vectors see e.g.,

<http://www.itpa.lt/~kvantas/BK/04/03/AJP00348.pdf>

$$\langle \hat{A} \rangle = \langle \Psi_n | \hat{A} | \Psi_n \rangle. \quad (7.4)$$

In statistical mechanics we need to introduce an additional probability w_n to describe an ensemble being in various quantum states $|\Psi_n(t)\rangle$. These mixed states are described by an ensemble average:

$$\langle \hat{A} \rangle = \sum_n w_n \langle \Psi_n | \hat{A} | \Psi_n \rangle. \quad (7.5)$$

Introducing a set of complete orthonormal basis vectors $\{|\phi_\alpha\rangle\}$, allows Eq. (7.5) to be written as:

$$\begin{aligned} \langle \hat{A} \rangle &= \sum_n w_n \langle \Psi_n | \hat{A} \hat{I} | \Psi_n \rangle \\ &= \sum_n w_n \langle \Psi_n | \hat{A} \left(\sum_\alpha |\phi_\alpha\rangle \langle \phi_\alpha| \right) | \Psi_n \rangle \\ &= \sum_\alpha \langle \phi_\alpha | \left(\sum_n w_n |\Psi_n\rangle \langle \Psi_n| \right) \hat{A} | \phi_\alpha \rangle, \end{aligned} \quad (7.6)$$

where we have used the closure relation $\sum_m |\phi_\alpha\rangle \langle \phi_\alpha| = \hat{I}$. Equation (7.6) can also be written as:

$$\begin{aligned} \langle \hat{A} \rangle &= \sum_\alpha \langle \phi_\alpha | \left(\sum_n w_n |\Psi_n\rangle \langle \Psi_n| \right) \hat{A} | \phi_\alpha \rangle \\ &= \text{Tr}(\hat{\rho} \hat{A}), \end{aligned} \quad (7.7)$$

where the density operator is defined as:

$$\hat{\rho} = \sum_n w_n |\Psi_n\rangle \langle \Psi_n|. \quad (7.8)$$

Note that a pure state is specified by $w_n = 1$ for some $|\Psi_n\rangle$, with $n = m$, and $w_n = 0$ for all other state vectors, so that the density operator simplifies to $\hat{\rho} = |\Psi_m\rangle \langle \Psi_m|$.

Example 7.1: Construct the density operator for a pure state consisting of a completely polarised beam of electrons in the “up state” in the z -direction, described by:

$$|S_z+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}.$$

Solution

The density operator for this pure state is given by:

$$\hat{\rho} = |S_z+\rangle \langle S_z+| = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}.$$

Note that for a pure state $\hat{\rho}^2 = \hat{\rho}$, which you can readily confirm using this example.

Example 7.2: Consider a partially polarised beam of electrons, which consists of a 50:50 mixture of two pure states, one of which is in the “up state” in the z -direction $|S_z+\rangle$, and the other is in the “up state” in the x -direction $|S_x+\rangle$. Construct the density operator for this mixed state.

Solution

The state $|S_z+\rangle$ is given in Example 7.1. It is straightforward to show that the state $|S_x+\rangle$ can be written as:

$$|S_x+\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} = \frac{1}{\sqrt{2}}(|S_z+\rangle + |S_z-\rangle).$$

The density operator (7.8) for this mixed state is then given by:

$$\begin{aligned} \hat{\rho} &= \sum_n w_n |\Psi_n\rangle\langle\Psi_n| \\ &= \frac{1}{2} |S_z+\rangle\langle S_z+| + \frac{1}{2} |S_x+\rangle\langle S_x+| \\ &= \frac{1}{2} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \end{pmatrix} + \frac{1}{2} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \end{pmatrix} \\ &= \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \frac{1}{4} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} = \begin{pmatrix} 3/4 & 1/4 \\ 1/4 & 1/4 \end{pmatrix}. \end{aligned}$$

Exercise 7.1: Show that the ensemble average calculated from Eq. (7.7) gives:

$$\langle \hat{S}_x \rangle = \text{Tr}(\hat{\rho} \hat{S}_x) = \frac{\hbar}{4}, \quad \langle \hat{S}_y \rangle = \text{Tr}(\hat{\rho} \hat{S}_y) = 0, \quad \text{and} \quad \langle \hat{S}_z \rangle = \text{Tr}(\hat{\rho} \hat{S}_z) = \frac{\hbar}{4}.$$

The density operator is Hermitian (*i.e.*, $\hat{\rho}^\dagger = \hat{\rho}$) and normalised, so that:

$$\text{Tr} \hat{\rho} = \text{Tr} \left(\sum_n w_n |\Psi_n\rangle\langle\Psi_n| \right) = \sum_n w_n \text{Tr}(|\Psi_n\rangle\langle\Psi_n|) = \sum_n w_n = 1. \quad (7.9)$$

Example 7.3: Show that $\text{Tr} |\Psi_n\rangle\langle\Psi_n| = 1$.

Solution

Expand the state $|\Psi_n\rangle$ in terms of set of complete orthonormal basis vectors $\{|\phi_\alpha\rangle\}$, *i.e.*,

$$|\Psi_n\rangle = \sum_\alpha c_\alpha |\phi_\alpha\rangle.$$

Hence we can write $\text{Tr} |\Psi_n\rangle\langle\Psi_n|$ as:

$$\begin{aligned} \text{Tr}(|\Psi_n\rangle\langle\Psi_n|) &= \sum_\mu \langle\phi_\mu|(|\Psi_n\rangle\langle\Psi_n|)|\phi_\mu\rangle \\ &= \sum_\mu \langle\phi_\mu| \left(\sum_\alpha c_\alpha |\phi_\alpha\rangle \right) \left(\sum_\beta c_\beta^* \langle\phi_\beta| \right) |\phi_\mu\rangle \\ &= \sum_\mu \sum_\alpha \sum_\beta c_\alpha c_\beta^* \langle\phi_\mu|\phi_\alpha\rangle \langle\phi_\beta|\phi_\mu\rangle \\ &= \sum_\mu \sum_\alpha \sum_\beta c_\alpha c_\beta^* \delta_{\mu\alpha} \delta_{\beta\mu} \\ &= \sum_\alpha |c_\alpha|^2 \\ &= 1. \end{aligned}$$

The density operator can also be expressed as a matrix, *i.e.*,

$$\begin{aligned}
\hat{\rho} &= \hat{\mathbf{I}}\hat{\rho}\hat{\mathbf{I}} = \left(\sum_{\alpha} |\varphi_{\alpha}\rangle\langle\varphi_{\alpha}| \right) \hat{\rho} \left(\sum_{\beta} |\varphi_{\beta}\rangle\langle\varphi_{\beta}| \right) \\
&= \sum_{\alpha} \sum_{\beta} \langle\varphi_{\alpha}|\hat{\rho}|\varphi_{\beta}\rangle |\varphi_{\alpha}\rangle\langle\varphi_{\beta}| \\
&= \sum_{\alpha} \sum_{\beta} \rho_{\alpha\beta} |\varphi_{\alpha}\rangle\langle\varphi_{\beta}|,
\end{aligned} \tag{7.10}$$

where the elements of the density matrix are $\rho_{\alpha\beta} = \langle\varphi_{\alpha}|\hat{\rho}|\varphi_{\beta}\rangle$.

7.2.1 Quantum Liouville Theorem

The density operator evolves in time according to a quantum version of the classical Liouville theorem (see Sec. 2.2). Starting from Eq. (7.8) we have:

$$\frac{\partial \hat{\rho}}{\partial t} = \sum_n w_n \left(\frac{\partial |\Psi_n\rangle}{\partial t} \langle\Psi_n| + |\Psi_n\rangle \frac{\partial \langle\Psi_n|}{\partial t} \right), \tag{7.11}$$

where the probability w_n does not have an explicit time dependence. The state vectors obey the Schrödinger time evolution equation, i.e.,

$$i\hbar \frac{\partial |\Psi_n\rangle}{\partial t} = \hat{H}|\Psi_n\rangle \quad \text{and} \quad -i\hbar \frac{\partial \langle\Psi_n|}{\partial t} = \langle\Psi_n|\hat{H}^{\dagger}. \tag{7.12}$$

Noting that the Hamiltonian operator is Hermitian ($\hat{H}^{\dagger} = \hat{H}$), we can write Eq. (7.11) as:

$$\begin{aligned}
\frac{\partial \hat{\rho}}{\partial t} &= \sum_n w_n \left(\frac{1}{i\hbar} \hat{H}|\Psi_n\rangle\langle\Psi_n| - \frac{1}{i\hbar} |\Psi_n\rangle\langle\Psi_n|\hat{H} \right) \\
&= \frac{1}{i\hbar} \hat{H} \left(\sum_n w_n |\Psi_n\rangle\langle\Psi_n| \right) - \left(\sum_n w_n |\Psi_n\rangle\langle\Psi_n| \right) \frac{1}{i\hbar} \hat{H} \\
&= \frac{1}{i\hbar} (\hat{H}\hat{\rho} - \hat{\rho}\hat{H}) \\
&= \frac{1}{i\hbar} [\hat{H}, \hat{\rho}].
\end{aligned} \tag{7.13}$$

Equation (7.13) is the quantum analogue of Liouville's theorem in classical mechanics. To see this, consider the total time derivative of the classical distribution $\rho = \rho(\mathbf{q}, \mathbf{p}, t)$ in Γ -space, i.e.,

$$\begin{aligned}
\frac{d\rho}{dt} &= \frac{\partial \rho}{\partial t} + \sum_i \left(\frac{\partial \rho}{\partial q_i} \frac{\partial q_i}{\partial t} + \frac{\partial \rho}{\partial p_i} \frac{\partial p_i}{\partial t} \right) \\
&= \frac{\partial \rho}{\partial t} + \sum_i \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right) \\
&= \frac{\partial \rho}{\partial t} + \{\rho, H\},
\end{aligned} \tag{7.14}$$

where we have used Hamilton's equations and the Poisson bracket is defined as (see Sec. 2.2):

$$\{A, B\} = \sum_i \left(\frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right). \tag{7.15}$$

Liouville's theorem requires $d\rho/dt = 0$, hence Eq. (7.14) becomes:

$$\frac{d\rho}{dt} = 0 \quad \Rightarrow \quad \frac{\partial \rho}{\partial t} = -\{\rho, H\} = \{H, \rho\}. \quad (7.16)$$

We now see that Eq. (7.16) is the classical analogue of Eq. (7.13), with the Poisson bracket playing the role of the commutator. This correspondence can be made explicit via the following identification:

$$\{H, \rho\} \leftrightarrow \frac{1}{i\hbar} [\hat{H}, \hat{\rho}]. \quad (7.17)$$

7.3 Quantum Ensembles

We can use the density operator formalism to describe ensembles in quantum statistical mechanics. For stationary ensembles it follows from Eq. (7.13) that $[\hat{H}, \hat{\rho}] = 0$. It is therefore convenient to use the energy eigenstates of the Hamiltonian operator, which are defined by:

$$\hat{H}|\varphi_n\rangle = E_n|\varphi_n\rangle. \quad (7.18)$$

In this basis the density operator (7.8) is diagonal, and for the canonical distribution we have:

$$\hat{\rho} = \sum_n w_n |\varphi_n\rangle\langle\varphi_n| = \sum_n \frac{e^{-\beta E_n}}{Z(\beta)} |\varphi_n\rangle\langle\varphi_n|. \quad (7.19)$$

where the partition function is given by:

$$Z(\beta) = \sum_n e^{-\beta E_n} = \sum_n \langle\varphi_n| e^{-\beta \hat{H}} |\varphi_n\rangle = \text{Tre}^{-\beta \hat{H}}. \quad (7.20)$$

We can also write

$$\sum_n e^{-\beta E_n} |\varphi_n\rangle\langle\varphi_n| = \sum_n |\varphi_n\rangle e^{-\beta E_n} \langle\varphi_n| = e^{-\beta \hat{H}} \sum_n |\varphi_n\rangle\langle\varphi_n| = e^{-\beta \hat{H}}. \quad (7.21)$$

and hence we have:

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\text{Tre}^{-\beta \hat{H}}}. \quad (7.22)$$

The ensemble average in the canonical ensemble is:

$$\langle \hat{A} \rangle = \text{Tr}(\hat{\rho} \hat{A}) = \frac{\text{Tr}(\hat{A} e^{-\beta \hat{H}})}{\text{Tre}^{-\beta \hat{H}}}. \quad (7.23)$$

For example, the internal energy is calculated as:

$$U = \langle \hat{H} \rangle = \frac{\text{Tr}(\hat{H} e^{-\beta \hat{H}})}{\text{Tre}^{-\beta \hat{H}}} = -\frac{\partial}{\partial \beta} \ln(\text{Tre}^{-\beta \hat{H}}). \quad (7.24)$$

Likewise the entropy is given by:

$$S = -\langle k_B \ln \hat{\rho} \rangle = -k_B \text{Tr}(\hat{\rho} \ln \hat{\rho}). \quad (7.25)$$

For the grand canonical ensemble the density operator becomes:

$$\hat{\rho}_G = \frac{e^{-\beta(\hat{H} - \mu \hat{N})}}{\text{Tre}^{-\beta(\hat{H} - \mu \hat{N})}}, \quad (7.26)$$

where μ is the chemical potential and \hat{N} is the number operator, which is required to describe

systems where the number of particles is not fixed.² As one would expect, all thermodynamic quantities can be obtained using the density operator formalism.

7.4 Density Matrices in the Continuum Representation

In previous sections we used a discrete basis of eigenkets. We can generalise the density operator to the case where there is a continuum of states, e.g., in the coordinate basis we have:

$$\begin{aligned}\langle \hat{A} \rangle &= \text{Tr}(\hat{\rho} \hat{A}) = \int \langle q | \hat{\rho} \hat{A} | q \rangle dq \\ &= \int \langle q | \hat{\rho} \hat{A} | q \rangle dq \\ &= \iint \langle q | \hat{\rho} | q' \rangle \langle q' | \hat{A} | q \rangle dq dq'.\end{aligned}\tag{7.27}$$

The density matrix is a function of the coordinates, namely:

$$\begin{aligned}\hat{\rho}(q, q') &= \langle q | \hat{\rho} | q' \rangle \\ &= \langle q | \left(\sum_n w_n |\Psi_n\rangle \langle \Psi_n| \right) | q' \rangle \\ &= \sum_n w_n \langle q | \Psi_n \rangle \langle \Psi_n | q' \rangle \\ &= \sum_n w_n \Psi_n^*(q', t_0) \Psi_n(q, t_0).\end{aligned}\tag{7.28}$$

where the matrix elements (7.28) have been calculated at $t = t_0$. In general the wavefunctions satisfy the completeness condition:

$$\sum_n \Psi_n^*(q', t_0) \Psi_n(q, t_0) = \delta(q' - q),\tag{7.29}$$

where $\delta(q' - q)$ denotes the Dirac delta function (see Appendix B, Lecture 2). Likewise orthonormality of the wavefunctions requires:

$$\int \Psi_m^*(q, t_0) \Psi_n(q, t_0) dq = \delta_{mn}.\tag{7.30}$$

Exercise 7.2: Formulate the density matrix in the momentum or k -space representation.

7.4.1 Density Matrix for a Free Particle in a Box

The Hamiltonian for a free particle in one-dimension box of size L is given by:

$$\hat{H} = \frac{\hat{P}^2}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q^2}.\tag{7.31}$$

We assume that the eigenfunctions, $\phi_p(q) = \langle q | \phi_p \rangle$, of the Hamiltonian satisfy periodic boundary conditions, so that $\phi_p(q + L) = \phi_p(q)$.

² When the system has a fixed number of particles the eigenvalue of \hat{N} is just the particle number N . However, in general, particles can be created and annihilated, whence it is necessary to generalise the Hilbert space to Fock space, which may be thought of as a direct sum of Hilbert spaces, each with a fixed number of particles. A discussion of Fock space can be found at:

<http://www2.mathematik.hu-berlin.de/~kreimer/wp-content/uploads/SkriptQFTI.pdf>

https://en.wikipedia.org/wiki/Fock_space

The momentum eigenfunctions in the coordinate representation are none other than plane waves of the form:

$$\varphi_p(q) = \frac{1}{\sqrt{L}} e^{ipq/\hbar} \quad \text{or} \quad \varphi_k(q) = \frac{1}{\sqrt{L}} e^{ikq}, \quad \text{with} \quad k = \frac{2\pi}{L}n \quad (n = 0, \pm 1, \pm 2, \dots). \quad (7.32)$$

The corresponding eigenvalues are:

$$E_k = \frac{\hbar^2 k^2}{2m}. \quad (7.33)$$

We want to evaluate the density operator in the canonical ensemble. This is given by:

$$\hat{\rho} = \frac{e^{-\beta\hat{H}}}{\text{Tre}^{-\beta\hat{H}}} = \frac{1}{Z(\beta)} e^{-\beta\hat{H}}. \quad (7.34)$$

The corresponding density matrix is:

$$\begin{aligned} \hat{\rho}(q, q') &= \langle q | \hat{\rho} | q' \rangle \\ &= \frac{1}{Z(\beta)} \langle q | e^{-\beta\hat{H}} | q' \rangle \\ &= \frac{1}{Z(\beta)} \langle q | e^{-\beta\hat{H}} \left(\sum_k |\varphi_k\rangle \langle \varphi_k| \right) | q' \rangle \\ &= \frac{1}{Z(\beta)} \sum_k e^{-\beta E_k} \varphi_k^*(q') \varphi_k(q). \end{aligned} \quad (7.35)$$

If we let the size of the box become large the eigenvalues are quasi-continuous and we can replace the sum in Eq. (7.35) by an integral, i.e.,

$$\sum_k e^{-\beta E_k} \varphi_k^*(q') \varphi_k(q) \rightarrow \frac{L}{2\pi} \int_{-\infty}^{+\infty} e^{-\beta \hbar^2 k^2 / 2m} \varphi_k^*(q') \varphi_k(q) dk. \quad (7.36)$$

Substituting for the eigenfunctions (7.32) and evaluating the resulting complex Gaussian integral³ gives:

$$\begin{aligned} \frac{L}{2\pi} \int_{-\infty}^{+\infty} e^{-\beta \hbar^2 k^2 / 2m} \varphi_k^*(q') \varphi_k(q) dk &= \frac{L}{2\pi} \int_{-\infty}^{+\infty} e^{-\beta \hbar^2 k^2 / 2m} \frac{1}{L} e^{ik(q - q')} dk \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-\beta \hbar^2 k^2 / 2m + ik(q - q')} dk \\ &= \left(\frac{m}{2\pi\beta\hbar^2} \right)^{1/2} e^{-m(q - q')^2 / 2\beta\hbar^2}. \end{aligned} \quad (7.37)$$

It remains to evaluate the partition function, which is given by:

$$\begin{aligned} Z(\beta) &= \text{Tre}^{-\beta\hat{H}} = \int_0^L \langle q | e^{-\beta\hat{H}} | q \rangle dq \quad (\text{with } q = q') \\ &= L \left(\frac{m}{2\pi\beta\hbar^2} \right)^{1/2}. \end{aligned} \quad (7.38)$$

³ The complex Gaussian integral is given by:

$$\int_{-\infty}^{+\infty} e^{-\frac{1}{2}\alpha\xi^2 + iJ\xi} d\xi = \sqrt{\frac{2\pi}{\alpha}} e^{-J^2/2\alpha}.$$

Combining Eqs. (7.37) and (7.38) we obtain the density matrix for a free particle in the coordinate representation:

$$\begin{aligned}\hat{\rho}(q, q') &= \langle q | \hat{\rho} | q' \rangle \\ &= \frac{1}{Z(\beta)} \langle q | e^{-\beta \hat{H}} | q' \rangle \\ &= \frac{1}{L} e^{-m(q - q')^2 / 2\beta \hbar^2}.\end{aligned}\quad (7.39)$$

Note that the density matrix is symmetric in the coordinates (q, q') . The diagonal element $\langle q | \hat{\rho} | q \rangle = 1/L$ represents the probability density for the particle to found at q , which is independent of position (i.e., all positions within the one-dimensional box are equally likely).

Exercise 7.3: Show that Eq. (7.38) is in agreement with the partition function calculated in Example 3.2.

It is instructive to calculate the expectation value of the Hamiltonian, i.e.,

$$\begin{aligned}\langle \hat{H} \rangle &= \text{Tr}(\hat{\rho} \hat{H}) = \text{Tr}(\hat{H} \hat{\rho}) \\ &= -\frac{\hbar^2}{2m} \int_0^L \left[\langle q | \frac{\partial^2}{\partial q^2} \frac{1}{L} e^{-m(q - q')^2 / 2\beta \hbar^2} | q' \rangle \right]_{q=q'} dq \\ &= -\frac{\hbar^2}{2mL} \int_0^L \left[\langle q | \left(-\frac{m}{\beta \hbar^2} + \frac{m^2(q - q')^2}{\beta^2 \hbar^2} \right) e^{-m(q - q')^2 / 2\beta \hbar^2} | q' \rangle \right]_{q=q'} dq \quad (7.40) \\ &= \frac{1}{2\beta L} \int_0^L \langle q | q \rangle dq \\ &= \frac{1}{2\beta} \quad \text{or} \quad \frac{1}{2} k_B T.\end{aligned}$$

This is exactly what the equipartition theorem would predict for a single degree of freedom!

Exercise 7.4: Repeat the calculation leading to Eq. (7.40) using Eq. (7.24), i.e.,

$$\langle \hat{H} \rangle = \text{Tr}(\hat{\rho} \hat{H}) = \frac{\text{Tr}(\hat{H} e^{-\beta \hat{H}})}{\text{Tr} e^{-\beta \hat{H}}} = -\frac{\partial}{\partial \beta} \ln(\text{Tr} e^{-\beta \hat{H}}).$$

7.4.2 Density Matrix for the Quantum Oscillator

The quantum harmonic oscillator in one dimension is described by the Hamiltonian:

$$\hat{H} = \frac{\hat{P}^2}{2m} + \frac{1}{2} m \omega^2 \hat{Q}^2 = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q^2} + \frac{1}{2} m \omega^2 q^2, \quad (7.41)$$

where ω is the angular frequency of the oscillator. The energy eigenvalues are given by:

$$E_n = \left(n + \frac{1}{2} \right) \hbar \omega \quad (n = 0, 1, 2, \dots) \quad (7.42)$$

with corresponding eigenfunctions:

$$\varphi_n(\xi) = \frac{1}{\sqrt{2^n n!}} \left(\frac{m\omega}{\pi \hbar} \right)^{1/4} H_n(\xi) e^{-\xi^2/2} \quad \text{where} \quad \xi = \left(\frac{m\omega}{\hbar} \right)^{1/2} q. \quad (7.43)$$

The Hermite polynomials are defined⁴ as:

$$H_n(\xi) = (-1)^n e^{\xi^2} \left(\frac{d}{d\xi} \right)^n e^{-\xi^2} \quad (n = 0, 1, 2, \dots). \quad (7.44)$$

The density matrix in the coordinate representation for the canonical ensemble is given by:

$$\hat{\rho}(q, q') = \langle q | \hat{\rho} | q' \rangle = \frac{1}{Z(\beta)} \langle q | e^{-\beta \hat{H}} | q' \rangle = \frac{1}{Z(\beta)} \sum_{n=0}^{\infty} e^{-\beta E_n} \phi_n^*(q') \phi_n(q) \quad (7.45)$$

The matrix elements $\langle q | e^{-\beta \hat{H}} | q' \rangle$ are:

$$\begin{aligned} \langle q | e^{-\beta \hat{H}} | q' \rangle &= \sum_{n=0}^{\infty} e^{-\beta E_n} \phi_n^*(q') \phi_n(q) \\ &= \left(\frac{m\omega}{\pi \hbar} \right)^{1/2} e^{-\frac{1}{2}(\xi^2 + \xi'^2)} \sum_{n=0}^{\infty} \frac{1}{2^n n!} e^{-\beta(n + \frac{1}{2})\hbar\omega} H_n(\xi) H_n(\xi'). \end{aligned} \quad (7.46)$$

The evaluation of the sum over states in Eq. (7.46) is rather involved. The reader is referred to the derivation by Kubo⁵, where it is shown that:

$$\langle q | e^{-\beta \hat{H}} | q' \rangle = \left(\frac{m\omega}{2\pi \hbar \sinh(\beta \hbar \omega)} \right)^{1/2} \exp \left(-\frac{m\omega}{4\hbar} [(q + q')^2 \tanh(\frac{1}{2}\beta \hbar \omega) + (q - q')^2 \coth(\frac{1}{2}\beta \hbar \omega)] \right). \quad (7.47)$$

The partition function is readily evaluated as the trace of the matrix elements in Eq. (7.47), i.e.,

$$\begin{aligned} Z(\beta) &= \text{Tr} e^{-\beta \hat{H}} \\ &= \int_{-\infty}^{+\infty} \langle q | e^{-\beta \hat{H}} | q \rangle dq \\ &= \left(\frac{m\omega}{2\pi \hbar \sinh(\beta \hbar \omega)} \right)^{1/2} \int_{-\infty}^{+\infty} \exp \left(-\frac{m\omega q^2}{\hbar} \tanh(\frac{1}{2}\beta \hbar \omega) \right) dq. \end{aligned} \quad (7.48)$$

The integral in Eq. (7.48) is a standard Gaussian integral (see Footnote 3), hence we have:

$$\begin{aligned} Z(\beta) &= \left(\frac{m\omega}{2\pi \hbar \sinh(\beta \hbar \omega)} \right)^{1/2} \int_{-\infty}^{+\infty} \exp \left(-\frac{m\omega q^2}{\hbar} \tanh(\frac{1}{2}\beta \hbar \omega) \right) dq \\ &= \left(\frac{m\omega}{2\pi \hbar \sinh(\beta \hbar \omega)} \right)^{1/2} \left(\frac{\pi \hbar}{m\omega \tanh(\frac{1}{2}\beta \hbar \omega)} \right)^{1/2}. \end{aligned} \quad (7.49)$$

Equation (7.49) can be simplified to give:

⁴ A table of Hermite polynomials can be found at:

https://en.wikipedia.org/wiki/Hermite_polynomials
<http://mathworld.wolfram.com/HermitePolynomial.html>

⁵ See Kubo, R., *Statistical Mechanics* (North-Holland, 1965). pp. 175-177. A pdf of this book can be found at:

<http://rafibakhsh.ir/wp-content/uploads/2014/10/Kubo-Statistical-mechanics.pdf>

A related calculation is carried out to evaluate the propagator (Green function) for the quantum oscillator in the Feynman path integral formalism. In this context the density matrix is closely related to the Euclidean propagator (see PHS4200 Advanced Quantum Mechanics, Lecture 5).

$$\begin{aligned}
Z(\beta) &= \frac{1}{\sqrt{2\sinh(\beta\hbar\omega)\tanh(\frac{1}{2}\beta\hbar\omega)}} \\
&= \frac{1}{\sqrt{4\sinh(\frac{1}{2}\beta\hbar\omega)\cosh(\frac{1}{2}\beta\hbar\omega)\tanh(\frac{1}{2}\beta\hbar\omega)}} \\
&= \frac{1}{2\sinh(\frac{1}{2}\beta\hbar\omega)}.
\end{aligned} \tag{7.50}$$

This result agrees with the partition function of the quantum oscillator obtained in Sec. 5.2. The diagonal element of the density matrix $\langle q|\hat{\rho}|q\rangle$ represents the probability density for the particle to found at q , i.e.,

$$\begin{aligned}
\hat{\rho}(q,q) &= \langle q|\hat{\rho}|q\rangle \\
&= \frac{1}{Z(\beta)}\langle q|e^{-\beta\hat{H}}|q\rangle \\
&= \left(\frac{m\omega\tanh(\frac{1}{2}\beta\hbar\omega)}{\pi\hbar}\right)^{1/2} \exp\left(-\frac{m\omega q^2}{\hbar}\tanh(\frac{1}{2}\beta\hbar\omega)\right).
\end{aligned} \tag{7.51}$$

In the high temperature limit ($\beta\hbar\omega \ll 1$), Eq. (7.51) reduces to the classical distribution for a harmonic oscillator, i.e.,

$$\langle q|\hat{\rho}|q\rangle = \left(\frac{m\omega\tanh(\frac{1}{2}\beta\hbar\omega)}{\pi\hbar}\right)^{1/2} \exp\left(-\frac{m\omega q^2}{\hbar}\tanh(\frac{1}{2}\beta\hbar\omega)\right) \xrightarrow{\beta\hbar\omega \ll 1} \left(\frac{m\omega^2}{2\pi k_B T}\right)^{1/2} e^{-m\omega^2 q^2/2k_B T}. \tag{7.52}$$

On the other hand, for low temperatures ($\beta\hbar\omega \gg 1$), we get the expected probability density for the ground state ($n = 0$) of the quantum mechanical oscillator.

$$\langle q|\hat{\rho}|q\rangle = \left(\frac{m\omega\tanh(\frac{1}{2}\beta\hbar\omega)}{\pi\hbar}\right)^{1/2} \exp\left(-\frac{m\omega q^2}{\hbar}\tanh(\frac{1}{2}\beta\hbar\omega)\right) \xrightarrow{\beta\hbar\omega \gg 1} \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-m\omega q^2/\hbar}. \tag{7.53}$$

Exercise 7.5: Carry out the steps leading to Eqs. (7.52) and (7.53).

Example 7.4: Show that in the high temperature limit ($\beta\hbar\omega \ll 1$) the density matrix reduces to that of a free particle as $\omega \rightarrow 0$.

Solution

In the high temperature limit Eq. (7.47) becomes:

$$\langle q|e^{-\beta\hat{H}}|q'\rangle = \left(\frac{m}{2\pi\hbar^2\beta}\right)^{1/2} \exp\left(-\frac{m\omega^2\beta}{8}(q + q')^2 - \frac{m}{2\hbar^2\beta}(q - q')^2\right),$$

As $\omega \rightarrow 0$ we recover the density matrix for a free particle [i.e., c.f. Eq. (7.37)]:

$$\langle q|e^{-\beta\hat{H}}|q'\rangle = \left(\frac{m}{2\pi\hbar^2\beta}\right)^{1/2} \exp\left(-\frac{m}{2\hbar^2\beta}(q - q')^2\right)$$

Example 7.5: Show that in the low temperature limit ($\beta\hbar\omega \gg 1$), we recover the ground state energy of the quantum oscillator.

Solution

In the low temperature limit ($\beta\hbar\omega \gg 1$), Eq. (7.47) becomes:

$$\langle q|e^{-\beta\hat{H}}|q'\rangle = \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-\frac{1}{2}\beta\hbar\omega} \exp\left(-\frac{m\omega}{2\hbar}(q^2 + q'^2)\right),$$

and

$$\begin{aligned} \text{Tre}^{-\beta\hat{H}} &= \int_{-\infty}^{+\infty} \langle q|e^{-\beta\hat{H}}|q\rangle dq \\ &= \left(\frac{m\omega}{\pi\hbar}\right)^{1/2} e^{-\frac{1}{2}\beta\hbar\omega} \int_{-\infty}^{+\infty} \exp\left(-\frac{m\omega}{\hbar}q^2\right) dq \\ &= e^{-\frac{1}{2}\beta\hbar\omega}. \end{aligned}$$

From Eq. (7.24) we have:

$$\langle \hat{H} \rangle = \frac{\text{Tr}(\hat{H}e^{-\beta\hat{H}})}{\text{Tre}^{-\beta\hat{H}}} = -\frac{\partial}{\partial\beta} \ln(\text{Tre}^{-\beta\hat{H}}) = -\frac{\partial}{\partial\beta} \ln e^{-\frac{1}{2}\beta\hbar\omega} = \frac{1}{2}\hbar\omega,$$

which is the ground state energy of the quantum oscillator.

7.5 Density Matrix for a System of Particles

The density matrix formalism discussed in the preceding sections can be extended to describe a system of N particles. Let us consider N indistinguishable, non-interacting particles confined to a box of volume $V = L^3$. The density matrix for this system in the coordinate representation is:

$$\begin{aligned} \hat{\rho}(\mathbf{q}, \mathbf{q}') &= \langle q_1, q_2, \dots, q_{3N} | \hat{\rho} | q'_1, q'_2, \dots, q'_{3N} \rangle \\ &= \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N | \hat{\rho} | \mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N \rangle \\ &= \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N | \frac{e^{-\beta\hat{H}}}{Z(\beta, N)} | \mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N \rangle. \end{aligned} \quad (7.54)$$

where the partition function is given by:

$$\begin{aligned} Z(\beta, N) &= \text{Tre}^{-\beta\hat{H}} = \int \langle q_1, q_2, \dots, q_{3N} | e^{-\beta\hat{H}} | q_1, q_2, \dots, q_{3N} \rangle d^{3N}q \\ &= \int \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N | e^{-\beta\hat{H}} | \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N \rangle d^{3N}r. \end{aligned} \quad (7.55)$$

Since the particles are non-interacting, the energy of the N particle system may be written as:

$$E = \sum_{i=1}^N \frac{\hbar^2 |\mathbf{k}_i|^2}{2m}, \quad (7.56)$$

where $\mathbf{p}_i = \hbar\mathbf{k}_i$ is the momentum of an individual particle. The corresponding single-particle eigenfunctions are given by:

$$\varphi_{\mathbf{k}_i}(\mathbf{r}_i) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_i \cdot \mathbf{r}_i}, \quad \text{with} \quad \mathbf{k}_i = \frac{2\pi\mathbf{n}_i}{V^{1/3}} \quad (\mathbf{n}_i = 0, \pm 1, \pm 2, \dots). \quad (7.57)$$

A naive many-particle wavefunction (at time t_0) can be written as:

$$\langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N | \mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N \rangle = \Psi_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \prod_{i=1}^N \varphi_{\mathbf{k}_i}(\mathbf{r}_i). \quad (7.58)$$

with

$$\hat{H}\Psi_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E\Psi_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \text{ or } \hat{H}|\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N\rangle = E|\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N\rangle, \quad (7.59)$$

where the energy eigenvalues are given by Eq. (7.56). We can write the matrix elements as:

$$\begin{aligned}
& \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N | e^{-\beta \hat{H}} | \mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N \rangle \\
&= \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N | e^{-\beta \hat{H}} \mathbb{I} | \mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N \rangle \\
&= \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N | e^{-\beta \hat{H}} \left(\sum_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N} |\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N\rangle \langle \mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N| \right) | \mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N \rangle \\
&= \sum_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N} e^{-\beta E} \Psi_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N}^*(\mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_N).
\end{aligned} \tag{7.60}$$

The partition function is:

$$\begin{aligned}
Z(\beta, N) &= \text{Tre}^{-\beta \hat{H}} = \int \langle q_1, q_2, \dots, q_{3N} | e^{-\beta \hat{H}} | q_1, q_2, \dots, q_{3N} \rangle d^{3N} q \\
&= \int \langle \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N | e^{-\beta \hat{H}} | \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N \rangle d^{3N} \mathbf{r} \\
&= \sum_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N} e^{-\beta E} \int \Psi_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N}^*(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d^{3N} \mathbf{r} \\
&= \sum_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N} e^{-\beta E}.
\end{aligned} \tag{7.61}$$

Substituting for the energy eigenvalues (7.56) allows Eq. (7.61) to be written as:

$$\begin{aligned}
Z(\beta, N) &= \sum_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N} e^{-\beta E} \\
&= \sum_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N} \exp \left(\sum_{i=1}^N -\beta \frac{\hbar^2 |\mathbf{k}_i|^2}{2m} \right) \\
&= \prod_{i=1}^N \sum_{\mathbf{k}_i} \exp \left(-\beta \frac{\hbar^2 |\mathbf{k}_i|^2}{2m} \right) \\
&= \prod_{i=1}^N Z(\beta, 1) = [Z(\beta, 1)]^N.
\end{aligned} \tag{7.62}$$

The many-particle wavefunction (7.58) does not account for the indistinguishability of quantum particles. One might try to remedy this situation by inserting the Gibbs correction factor, as we did in classical statistical mechanics. In Sec. 5.1, we showed that the interchange of particle coordinates has no effect on the probability density. Therefore the many-particle wavefunction must be constructed in such a way as to respect this permutation symmetry. We can achieve this by introducing the permutation operator $\hat{\mathbf{P}}$, which generalises the exchange operator (see Sec. 5.1), and whose effect on the wavefunction is to produce an arbitrary permutation of the coordinates, i.e.,

$$\hat{\mathbf{P}} \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \Psi(\mathbf{r}_{P_1}, \mathbf{r}_{P_2}, \dots, \mathbf{r}_{P_N}), \tag{7.63}$$

where P_1, P_2, \dots, P_N is a permutation of the indices $1, 2, \dots, N$, which label the coordinates. If we now impose the permutation symmetry on the many-particle wavefunction (7.58), we can construct a wavefunction that respects the symmetry required by Bose-Einstein statistics, i.e.,

$$\Psi_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_N}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = C \sum_P \hat{\mathbf{P}} [\varphi_{\mathbf{k}_1}(\mathbf{r}_1) \varphi_{\mathbf{k}_2}(\mathbf{r}_2) \cdots \varphi_{\mathbf{k}_N}(\mathbf{r}_N)]. \tag{7.64}$$

where C is a normalisation constant and the sum is over all permutations of the indices $1, 2, \dots, N$. Likewise, for Fermi-Dirac statistics, we can construct an antisymmetric wavefunction:

$$\Psi_{k_1, k_2, \dots, k_N}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \hat{P}[\varphi_{k_1}(\mathbf{r}_1) \varphi_{k_2}(\mathbf{r}_2) \cdots \varphi_{k_N}(\mathbf{r}_N)], \quad (7.65)$$

where

$$(-1)^P = \begin{cases} +1 & \text{even permutation} \\ -1 & \text{odd permutation.} \end{cases} \quad (7.66)$$

ensures that the wavefunction is antisymmetric under the exchange of two indices. The normalisation constant is $(N!)^{-1/2}$. The antisymmetric wavefunction that describes fermions may also be written as a Slater determinant:

$$\Psi_{k_1, k_2, \dots, k_N}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{k_1}(\mathbf{r}_1) & \varphi_{k_1}(\mathbf{r}_2) & \cdots & \varphi_{k_1}(\mathbf{r}_N) \\ \varphi_{k_2}(\mathbf{r}_1) & \varphi_{k_2}(\mathbf{r}_2) & \cdots & \varphi_{k_2}(\mathbf{r}_N) \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \varphi_{k_N}(\mathbf{r}_1) & \varphi_{k_N}(\mathbf{r}_2) & \cdots & \varphi_{k_N}(\mathbf{r}_N) \end{vmatrix}. \quad (7.67)$$

The Pauli exclusion principle follows from the well known property of determinants; namely, if any two rows of the Slater determinant are identical, then the wavefunction vanishes. This situation occurs if two fermions are labelled with the same quantum numbers. Consequently, no two fermions can occupy the same one-particle state. However, for bosons the many-particle wavefunction is given by Eq. (7.64), which does not vanish if two or more particles are in the same state; hence the Pauli exclusion principle does not apply to bosons, and an arbitrary number of bosons may occupy the same one-particle state.

Example 7.5: Calculate the Slater determinant for a two-particle wavefunction and show that it vanishes if the two particles have the same quantum numbers.

Solution

The two-particle wavefunction is given by the Slater determinant:

$$\Psi_{k_1, k_2}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2!}} \begin{vmatrix} \varphi_{k_1}(\mathbf{r}_1) & \varphi_{k_1}(\mathbf{r}_2) \\ \varphi_{k_2}(\mathbf{r}_1) & \varphi_{k_2}(\mathbf{r}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} [\varphi_{k_1}(\mathbf{r}_1) \varphi_{k_2}(\mathbf{r}_2) - \varphi_{k_1}(\mathbf{r}_2) \varphi_{k_2}(\mathbf{r}_1)].$$

It is evident that the Slater determinant (and hence the wavefunction) vanishes if $\mathbf{k}_1 = \mathbf{k}_2$.

Exercise 7.6: Calculate the Slater determinant for a three-particle wavefunction. Show that the wavefunction vanishes if any two particles occupy the same one-particle state.

We can apply the above formalism to the case of an ideal gas, comprised of N indistinguishable, non-interacting particles (see Sec. 7.5). We will not carry out this calculation explicitly; however, we find that the Gibbs correction appears as a natural consequence of imposing the symmetry (or antisymmetry) on the many-particle wavefunction. Table 7.1 summarises the key concepts of classical and quantum statistical mechanics.

Table 7.1: Comparison of classical and quantum statistical mechanics.

Classical Statistical Mechanics	Quantum Statistical Mechanics
Distribution function (<i>c</i> -number) $\rho = \rho(\mathbf{q}, \mathbf{p})$	Density operator (<i>q</i> -number) $\hat{\rho}$
Normalisation $\frac{1}{N!h^{3N}} \int_{\Gamma} \rho(\mathbf{q}, \mathbf{p}) d^{3N}q d^{3N}p = 1$	Normalisation $\text{Tr} \hat{\rho} = 1$
Distribution function is real $\rho(\mathbf{q}, \mathbf{p}) \geq 0$ (<i>real</i>)	Density operator is Hermitian $\hat{\rho} = \hat{\rho}^\dagger$
Expectation value $\langle A \rangle = \frac{1}{N!h^{3N}} \int_{\Gamma} \rho(\mathbf{q}, \mathbf{p}) A(\mathbf{q}, \mathbf{p}) d^{3N}q d^{3N}p$	Expectation value $\langle \hat{A} \rangle = \text{Tr}(\hat{\rho} \hat{A})$
Liouville's equation: $\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0$	Quantum Liouville equation $i\hbar \frac{\partial \hat{\rho}}{\partial t} + [\hat{\rho}, \hat{H}] = 0$
$\rho(\mathbf{q}, \mathbf{p}) = \frac{e^{-\beta H}}{\frac{1}{N!h^{3N}} \int_{\Gamma} e^{-\beta H} d^{3N}q d^{3N}p}$	$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\text{Tr} e^{-\beta \hat{H}}}$

References

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- [2] Sethna, J. P., *Statistical Mechanics: Entropy, Order Parameters, and Complexity* (Oxford University Press, 2006). Chapter 7. A pdf of this textbook is available at:
<http://pages.physics.cornell.edu/~sethna/StatMech/EntropyOrderParametersComplexity.pdf>
- [3] https://en.wikipedia.org/wiki/Density_matrix
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