



Constant-Temperature Dynamics in the Wigner Representation of Quantum Mechanics

Mireille Merlise Megnidio-Tchoukouegno

Submitted in fulfillment of the academic
requirements for the degree of Master of Science
in School of Physics
University of KwaZulu-Natal Pietermaritzburg

To the loving memory of my late mother, Mawouet Madeleine.

Acknowledgments

My deepest gratitude goes to my supervisor, Dr Alessandro Sergi, for his guidance, financial support, motivation and understanding during my Msc work. He was always available for discussions and cooperation. I am very grateful to the School of Physics for providing the facilities for my research.

I owe much to staff members of the School of Physics of the University of KwaZulu-Natal, Pietermaritzburg for their support during this period of hard work. I am specifically thankful to Dr Naven Chetty and Daniel Uken who proofread parts of my dissertation and made usefull comments that helpt to improve the quality of the dissertation, and also to Ravene.

I am very grateful to my loving husband Medard for his love and support during my MSc research work. He was like a second supervisor to me. Among other things, he assisted me in editing my work.

I am so grateful to friends and colleagues at the School of Physics for their support and diverse situations. Special thanks to Miguel and Emmanuel. My sincere appreciation to all the members of the Cameroonian Community in Pietermaritzburg. Thanks to you guys, on many occasions I felt at home far from home.

Finally, I am thankful to my whole family in Cameroon and abroad, including my dear father, my brothers and sisters, uncles and aunts. My humble gratitude goes to the Hayfields congregation in Pietermaritzburg for their spiritual support.

Declaration

The research work described in this thesis was carried out in the School of Physics, University of KwaZulu-Natal Pietermaritzburg, from February 2010 to June 2011 under the supervision of Dr Alessandro Sergi.

This thesis presents original work by the author and has not been submitted in any form for any degree or diploma to any University. Where use has been made of the work of others it is duly acknowledged in the text.

June, 2011.

Student: _____
Mireille Merlise Megnidio-Tchoukouegno
Date

Supervisor: _____
Dr Alessandro Sergi
Date

Abstract

This dissertation deals with theory and algorithms for computer simulations of classical and quantum systems in the canonical ensemble. First, the approach of Nosé-Hoover and its generalization, known as the Nosé-Hoover chain dynamics, are introduced. Such methods are used in classical molecular dynamics simulations to control the temperature of particle systems through a coupling to a few additional fictitious variables, mimicking an infinite thermal reservoir. In order to introduce the extension of the Nosé-Hoover method to quantum systems, the features of the Wigner representation of quantum mechanics are reviewed. Finally, a recent approach [A. Sergi and F. Petruccione, *J. Phys. A* **41** 355304 (2008)], which extends the Nosé-Hoover and Nosé-Hoover chain equations in quantum phase space, is described. Such a method is applied to a single harmonic mode, and the conditions for quantum-to-classical transitions as a function of the thermodynamical temperature are studied by means of numerical simulations. It is shown that, in the case of strong coupling, the open system dynamics simulated by Nosé-Hoover chain equations leads to quantum-classical transition of the Wigner function of the harmonic mode. Agreement between the numerical and analytical results is also found. The algorithms and results illustrated are of interest to the numerical simulation of the quantum dissipative dynamics of more general systems.

Contents

1	Introduction	1
2	Classical Molecular Dynamics at Constant Temperature	4
2.1	Molecular Dynamic basics	5
2.1.1	Microcanonical ensemble	7
2.1.2	Canonical ensemble	9
2.2	Nosè-Hoover thermostat	10
2.2.1	Extended-Hamiltonian formulation	10
2.3	Nosè-Hoover chain thermostats	17
3	Theory of Quantum Mechanics	21
3.1	Schrödinger Picture of Quantum Mechanics	25
3.2	Heisenberg Picture of Quantum Mechanics	27
3.3	Quantum statistical mechanics	28
3.4	Density matrix	30
4	Wigner Representation of Quantum Mechanics	35
4.1	Wigner formulation of quantum mechanics in phase space . .	35
4.2	Derivation of the quantum Wigner-Liouville equation	43
4.2.1	Extraneous solutions of the quantum Wigner-Liouville equation.	50

5	Wigner Quantum Dynamics at Constant Temperature	52
5.1	Wigner’s quantum statistical mechanics	53
5.2	Nosè-Hoover dynamics in Wigner quantum phase space . . .	54
5.3	Nosè-Hoover chain dynamics in Wigner quantum phase space	58
6	Quantum-Classical Transition of a Harmonic Mode in a Ther-	
	mal Nosè-Hoover Chain Bath	63
6.1	Thermostated harmonic mode	64
6.2	Quantum-classical limit	66
6.3	Numerical results and discussion	68
6.3.1	NVE dynamics	69
6.3.2	Nosè-Hoover (NVT) dynamics	70
6.3.3	Nosè-Hoover chain (NVT) dynamics	70
7	Conclusions	81
A	Time-reversible Nosè-Hoover Algorithm	83
B	Time-reversible Nosè-Hoover Chain Algorithm	85
C	Wigner Distribution for an Ensemble at Temperature T	89
C.1	Equilibrium Wigner function for a harmonic oscillator	91

Chapter 1

Introduction

Algorithms for simulating dynamics of many body quantum systems are an open area of research. Monte Carlo techniques and Molecular Dynamics [1] methods are used to simulate a wide variety of classical systems, but there are no such general methods for quantum mechanics. Quantum mechanics is much more difficult to simulate on a computer because the computational resources required for calculations often far exceed what is available.

The development of efficient algorithms for simulating quantum dynamics is of importance to a number of fields and specifically to the fields of open quantum systems[2], quantum information theory [3] and quantum optics [4]. Open quantum systems are often realized by putting a system of interest in contact with a thermal bath of harmonic degrees of freedom with specified spectral density [2, 5]. It is thus desirable to be able to control the temperature of the system in quantum dynamics simulations.

In classical Molecular Dynamics simulations the methods of Nosè-Hoover and its generalization, known as the Nosè-Hoover chain, are used to control the temperature of particle systems. This is done by coupling the system of interest to a few additional fictitious variables, mimicking an infinite thermal reservoir. By means of these fictitious variables, the algorithms are able to describe thermodynamical baths, which generally require a large number

of degrees of freedom to simulate. These Nosè-Hoover methods are formulated using phase-space equations. To use them in quantum simulations, a quantum phase space is required. This is achieved by using the Wigner representation to represent the quantum dynamics in terms of phase-space functions.

The first formulation able to represent quantum mechanics in phase space was provided by Wigner in 1932 [6]. He introduced the phase-space Wigner function to study quantum corrections to classical statistical mechanics. This phase-space formulation of quantum mechanics offers a structure in which quantum phenomena can be described using classical mechanics in the appropriate classical limit [7]. It does this by transforming quantum operators into functions of phase space. As a result of this, it becomes possible to implement Molecular Dynamics methods to quantum dynamics.

The theory of [8] presents the extension of the Nosè-Hoover and Nosè-Hoover chain equations in quantum phase space. This theory was used to show how the constant-temperature constraints can be introduced in quantum dynamics through the Wigner phase-space formulation. In this case the temperature, which is a classical concept [9], has been introduced to the quantum dynamics by the direct coupling of the classical thermostat to the quantum subsystem in phase space. The Nosè-Hoover equations of motion were introduced in quantum phase space so as to define a Nosè-Wigner dynamics. This is of interest to study quantum-to-classical transitions as a function of temperature.

In this work, a classical thermostat has been directly coupled to the quantum subsystem in phase space. The so-called Nosè-Wigner dynamics has been applied to a single harmonic mode, and it is shown that at low temperature, the Nosè-Wigner distribution function approaches the classical canonical distribution. The conditions for these quantum-to-classical transitions as a function of the thermodynamical temperature are studied by

means of numerical simulations. It is shown that, in the case of strong coupling, the open system dynamics simulated by Nosè-Hoover chain equations leads to the classical limit of the Wigner function of the harmonic mode.

The dissertation is organized as follows: Chapter 2 deals with classical Molecular Dynamics simulation at constant temperature. The simulation method is described and thermal averages are calculated as a function of thermodynamical temperature, in terms of Nosè-Hoover and Nosè-Hoover chain thermostats. The Wigner representation of quantum mechanics is reviewed and a quantum-classical approximation of the Wigner-Liouville law of motion for the continuous potentials is derived in Chapter 4. This is done in order to introduce the Nosè-Hoover approach in quantum dynamics. In Chapter 5 the Nosè-Hoover and Nosè-Hoover chain equations of motion in quantum phase space are introduced, to define Nosè-Wigner dynamics, as a function of temperature. The results of the numerical integration of the Wigner distribution function are given in Chapter 6. It is shown how the use of the Nosè-Hoover chain dynamics causes the Wigner distribution function for the one dimensional harmonic mode to approach the classical limit. Similar calculations have been done for the momentum distribution to show how it can approach an appropriate classical limit. Chapter 7 presents the conclusions and future area of research. The Appendices contain derivations and algorithms relevant to the theory.

Chapter 2

Classical Molecular Dynamics at Constant Temperature

This chapter discusses a computational method, Molecular Dynamics Simulation (MDS), commonly used in computational physics to study many-particle classical systems. It is a deterministic method based on numerical solutions of ordinary differential equations defining the dynamics of the degrees of freedom for the classical system. This method was initially introduced in the microcanonical ensemble. The theory of this method was extended to the canonical ensemble, to control temperature instead of energy. This dictated that the system be placed in contact with a thermal bath which requires a large number of degrees of freedom to simulate. This is inconvenient to simulate on a computer, as it would require large amounts of memory. To solve this problem, Nosè and Hoover extended the method of MDS [10] in order to make constant-temperature simulations possible on a computer. This chapter starts with a brief summary of the basics of Molecular Dynamics and introduces the microcanonical and canonical ensembles

to calculate classical statistical averages in phase space. The theory of Nosè-Hoover [11] is then summarized as well as its extension, the Nosè-Hoover chain method. The extended Hamiltonians [12, 13, 14] of these formulations are discussed and classical statistical averages are calculated in the canonical ensemble.

2.1 Molecular Dynamic basics

Molecular Dynamics Simulation is a form of computer simulation in which the dynamics of many particles systems are numerically calculated. This is done for a finite period of time, once the interaction between the particles is specified. This computational method, calculating the time-dependent behaviour of a molecular system, is based upon Newton's equation of motion, $\mathbf{F} = m\mathbf{a}$, where \mathbf{F} is the force exerted on the particle, m is its mass and \mathbf{a} is its acceleration. From the knowledge of the force on each particle, it is possible to determine the acceleration of each particle in the system. If the initial conditions of the system, namely the positions and momenta of the particles, are known, then integration of the equations of motion yield trajectories that describe the position, velocity and acceleration of the particles as functions of time. From these trajectories, the average values of properties can be determined.

Consider a classical system of N particles in a fixed volume. The motion of this system is governed by Newton's equations of motion [15]

$$\mathbf{F}_k = m_k \mathbf{a}_k, \quad k = 1, \dots, N \quad (2.1)$$

where m_k is the mass of particle k , \mathbf{a}_k is its acceleration and \mathbf{F}_k the force acting upon it due to the interactions with the others particles. In classical mechanics, the Hamilton equations of motion dictate a correlation between

the position and momenta of the particles

$$\begin{cases} \dot{r}_k = \frac{\partial}{\partial p_k} H(r, p) \\ \dot{p}_k = -\frac{\partial}{\partial r_k} H(r, p) = F_k \end{cases} \quad (2.2)$$

where r_k and p_k denote position and momentum coordinates for the k^{th} particle. H is the Hamiltonian of the system, which is defined in phase space by

$$H(r, p) = \sum_{k=1}^N \frac{p_k^2}{2m_k} + V(r). \quad (2.3)$$

The above Hamiltonian represents the total energy of the system and does not explicitly depend on time. A multidimensional notation is being used, where r and p denote the positions and momenta of all the particles in the system. It follows from the Hamilton equations of motion that the Hamiltonian is conserved in a closed system:

$$\begin{aligned} \frac{d}{dt} H(r, p) &= \sum_{k=1}^N \frac{\partial H}{\partial p_k} \dot{p}_k + \frac{\partial H}{\partial r_k} \dot{r}_k \\ &= -\sum_{k=1}^N \frac{\partial H}{\partial p_k} \frac{\partial H}{\partial r_k} + \sum_{k=1}^N \frac{\partial H}{\partial r_k} \frac{\partial H}{\partial p_k} = 0. \end{aligned} \quad (2.4)$$

Newton's equations or Hamilton's equations are the equations of motion governing the dynamics of the particles. These equations of motion and the particle's interaction potential are the essential elements for Molecular Dynamics Simulation.

The MDS method can be implemented on the computer using the following procedure: time is discretised into small intervals δt . Simulation starts at $t = 0$ with initial positions and velocities of the particles. At each time step, the forces on the particles are computed and combined with the current positions and velocities to generate new positions and velocities. The force acting on each particle is assumed to be constant during the time interval. The particles are then moved to the new positions, and an updated set of

forces is computed and a new dynamics cycle goes on. This is repeated until the time evolution of the system has been computed to the desired time. After that, the averages of properties of the system are computed. But experiment measures many types of averages and to use computer simulation as the numerical equivalent of experiment, it is important to know how these averages are related. Therefore, statistical mechanics is needed.

Molecular Dynamics Simulation generates information at the microscopic level, including particle positions and velocities. This microscopic information can be converted to macroscopic observables, such as temperature, pressure and energy by using statistical mechanics. These measurable properties are formulated in terms of ensemble averages. An ensemble is a collection of all possible systems with different microscopic states but identical macroscopic or thermodynamic states. In the following, attention will be given to the microcanonical ensemble and canonical ensemble.

2.1.1 Microcanonical ensemble

This ensemble is characterized by constant particle number N , constant volume V and constant total energy E ; and is denoted as the NVE ensemble. In this ensemble, the equilibrium distribution function takes the following form

$$f(r, p) = Z^{-1} \delta(E - H), \quad (2.5)$$

where the quantity

$$Z = \int d^N r d^N p \delta(E - H) \quad (2.6)$$

is the normalization constant, known as the partition function. The function $\delta(E - H)$ is known as the delta of Dirac, and is zero everywhere in phase space, except when $H - E = 0$. The above expression of the distribution function can aid in defining ensemble averages in statistical mechanics. An ensemble average is the average taken over a large number of replicas of the system considered simultaneously. The ensemble average for an observable

A is given by

$$\langle A \rangle_{ensemble} = \int d^N r d^N p A(r^N, p^N) f(r^N, p^N), \quad (2.7)$$

where $A(r^N, p^N)$ is the observable and $f(r^N, p^N)$ is the distribution function. It follows from Eq. (2.7) that the integration is for all possible variables of coordinates r and p and can be calculated once the distribution function is known. This integral is extremely difficult to calculate because all possible system states need to be determined. In MDS the points in the ensemble are calculated sequentially, in time. In this case, the time average of a classical system of N particles using Molecular Dynamics technique can be expressed as

$$\langle A \rangle_{time} = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau A(r^N(t), p^N(t)) dt \quad (2.8)$$

where τ is the simulation time and $A(r^N, p^N)$ is the instantaneous value of A . In these simulations, the total energy is a constant of motion, in other words it does not change in time. The time averages are measured in an ensemble that is very similar to the microcanonical ensemble. Thus, one might be led to assume that the time averages are equivalent to the ensemble averages in the microcanonical ensemble [1]. To calculate an ensemble average, the MDS must pass through all possible states corresponding to particular thermodynamic constraints. The dilemma is that, time averages by MDS can be calculated, but experimental observables are assumed to be ensemble averages. Resolving this, leads to one of the most fundamental axioms of statistical mechanics, the ergodic hypothesis [1], stating that the time average equals the ensemble average.

$$\langle A \rangle_{time} = \langle A \rangle_{ensemble}. \quad (2.9)$$

Hence, computing the average of a function of the coordinates and momenta of many particles by time averaging is equivalent to computing it by ensemble averaging. Using this hypothesis produces limitations and inconveniences

because Eq.(2.9) is not true in general; many examples of systems are not ergodic in practice. In reality, experiments are done at constant temperatures and constant pressures, therefore, to compare the results of simulations with experiments it is better to perform calculations in the canonical ensemble.

2.1.2 Canonical ensemble

Experiments are usually done in the canonical ensemble, which is characterized by constant particle number N , constant volume V , constant temperature T and is denoted as the NVT ensemble. To ensure that the temperature of the system is constant, the system is placed in contact with a thermal bath or reservoir. This reservoir has a large number of microscopic degrees of freedom making simulation difficult on a computer. The system is governed by the canonical distribution function [11]

$$f_c(r^N, p^N) = Z_c^{-1} e^{-\beta H(r,p)}, \quad (2.10)$$

where

$$Z_c = \int d^N r d^N p e^{-\beta H(r,p)} \quad (2.11)$$

is the canonical partition function and $\beta = 1/k_B T$ is the inverse of the product between the temperature and the Boltzmann constant k_B . Thus, the thermal average in the canonical ensemble can be considered to be:

$$\langle A \rangle = \int d^N r d^N p A(r^N, p^N) f_c(r^N, p^N). \quad (2.12)$$

It is difficult to solve Eq. (2.12) because of the need to simulate the infinite number of degrees of freedom of the bath. Nosè solved this problem and Hoover refined it later. They found that constant-temperature trajectories can be generated by using just two additional degrees of freedom, one position coordinate and one momentum coordinate, known as Nosè variables.

2.2 Nosè-Hoover thermostat

Nosè-Hoover dynamics is a deterministic method used in MDS to maintain the temperature of the system. In his approach, Nosè introduced an extended Hamiltonian containing the coordinates of the original subsystem, augmented with an extra variable η with its conjugated momentum p_η . The dimensionality of Nosè extended phase space is $2N + 2$, a number that can be simulated computationally.

2.2.1 Extended-Hamiltonian formulation

The Hamiltonian of the subsystem with phase-space coordinates (r, p) is

$$H(r, p) = \frac{p^2}{2m} + V(r), \quad (2.13)$$

where $V(r)$ is the potential energy. To represent the thermal bath, Nosè added two additional degrees of freedom (η, p_η) . The Nosè Hamiltonian can be written as

$$H_{NH}(r, \eta, p, p_\eta) = \frac{p^2}{2m} + V(r) + \frac{p_\eta^2}{2m_\eta} + gk_B T \eta \quad (2.14)$$

with the phase-space point of the extended system $X = (r, \eta, p, p_\eta)$. Here, and henceforth, the NH subscript denotes Nosè-Hoover quantities. The constant g is the number of degrees of freedom of the subsystem and m_η is a fictitious mass associated with the extra degrees of freedom. H_{NH} is a conserved quantity,

$$\frac{dH_{NH}}{dt} = \frac{\partial H_{NH}}{\partial p} \dot{p} + \frac{\partial H_{NH}}{\partial r} \dot{r} + \frac{\partial H_{NH}}{\partial p_\eta} \dot{p}_\eta + \frac{\partial H_{NH}}{\partial \eta} \dot{\eta} = 0. \quad (2.15)$$

From the knowledge of the extended-Hamiltonian, the Nosè-Hoover equations of motion are postulated as

$$\dot{r} = \frac{p}{m} \quad (2.16)$$

$$\dot{\eta} = \frac{p_\eta}{m_\eta} \quad (2.17)$$

$$\dot{p} = -\frac{\partial V}{\partial r} - p \frac{p_\eta}{m_\eta} \quad (2.18)$$

$$\dot{p}_\eta = \frac{p^2}{m} - g k_B T. \quad (2.19)$$

It follows from Eq. (2.18) that the acceleration of the particles is determined not only by the force $-\frac{\partial V}{\partial r} = F(r)$ but also by the term $p \frac{p_\eta}{m_\eta}$ which behaves like a friction term. Moreover, this friction term can take both negative and positive sign. This comes from the fact that there is an acceleration associated with p_η determined by Eq. (2.19). Such acceleration, \dot{p}_η is driven by the imbalance between the kinetic energy of the physical particles and the external temperature $k_B T$. This is how the Nosè-Hoover equations control the mechanism between the internal temperature and the external temperature T , with the controller variable p_η .

The equations of motion above cannot be derived by following Hamiltonian theory from the Nosè Hamiltonian. The Hamiltonian theory imposes that an infinite number of degrees of freedom should be considered when the thermodynamic constraints of the system are implemented. In this case, Nosè abandoned the Hamiltonian theory structure and used a non-Hamiltonian formalism which does not satisfy the Jacobi relation [13, 16]. With this general formalism it has been shown that the thermodynamic constraints can be achieved with a small number of degrees of freedom. To

this end, an antisymmetric matrix $\mathcal{B}_{ij}^N = -\mathcal{B}_{ji}^N$ has been introduced [11]

$$\mathcal{B}^N = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -p \\ 0 & -1 & p & 0 \end{bmatrix}, \quad (2.20)$$

so that Nosè's equations of motion can be written in the following form

$$\begin{bmatrix} \dot{r} \\ \dot{\eta} \\ \dot{p} \\ \dot{p}_\eta \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -p \\ 0 & -1 & p & 0 \end{bmatrix} \begin{bmatrix} \frac{\partial H_{NH}}{\partial r} \\ \frac{\partial H_{NH}}{\partial \eta} \\ \frac{\partial H_{NH}}{\partial p} \\ \frac{\partial H_{NH}}{\partial p_\eta} \end{bmatrix}, \quad (2.21)$$

and in a compact form as [11]

$$\begin{aligned} \dot{X}_k &= L_{NH} X_k \\ &= \{X_k, H_{NH}\}_{\mathcal{B}^N} \\ &\equiv \sum_{i,j=1}^{2(N+1)} \frac{\partial X_k}{\partial X_i} \mathcal{B}_{ij}^N \frac{\partial H_{NH}}{\partial X_j} = \mathcal{B}_{kj}^N \frac{\partial H_{NH}}{\partial X_j}, \end{aligned} \quad (2.22)$$

where L_{NH} represents the Nosè-Liouville operator, defined as

$$L_{NH} = \dot{X}_k \frac{\partial}{\partial X_k}. \quad (2.23)$$

The second equality on the right-hand side of Eq. (2.22) is the Nosè bracket and the repeated indices imply summation. Under the ergodic hypothesis, it will be proven that Eqs. (2.16)-(2.19) can generate averages in the canonical ensemble.

In this case, let $f_{NH}(r, p, t)$ be the Nosè distribution function. The Liouville equation for the Nosè distribution function is

$$\begin{aligned} \frac{\partial}{\partial t} f_{NH} &= -\frac{\partial}{\partial X_k} (\dot{X}_k f_{NH}) \\ &= -\dot{X}_k \frac{\partial f_{NH}}{\partial X_k} - \frac{\partial \dot{X}_k}{\partial X_k} f_{NH} \\ &= -L_{NH} f_{NH} - K_{NH} f_{NH}, \end{aligned} \quad (2.24)$$

where K_{NH} is defined as the compressibility of the phase space and is given by

$$\begin{aligned}
K_{NH} &= \sum_{k=1}^{2(N+1)} \frac{\partial \dot{X}_k}{\partial x_k} \\
&= \sum_{k,j=1}^{2(N+1)} \left(\frac{\partial B_{kj}^N}{\partial X_k} \frac{\partial H_{NH}}{\partial X_j} + B_{kj}^N \frac{\partial^2 H_{NH}}{\partial X_j \partial X_k} \right) \\
&= \sum_{k,j=1}^{2(N+1)} \frac{\partial B_{kj}^N}{\partial X_k} \frac{\partial H_{NH}}{\partial X_j} + \sum_{k=1}^{2(N+1)} B_{kk}^N \frac{\partial^2 H_{NH}}{\partial X_k^2}. \quad (2.25)
\end{aligned}$$

All the diagonal terms of B^N are equal to zero, so

$$\sum_{k=1}^{2(N+1)} B_{kk}^N \frac{\partial^2 H_{NH}}{\partial X_k^2} = 0,$$

therefore

$$K_{NH} = \sum_{k,j=1}^{2(N+1)} \frac{\partial B_{kj}^N}{\partial X_k} \frac{\partial H_{NH}}{\partial X_j}. \quad (2.26)$$

At equilibrium, the Nosè distribution function f_{NH} no longer depends on time, therefore

$$\frac{\partial f_{NH}(r,p)}{\partial t} = 0. \quad (2.27)$$

Eq. (2.24) thus becomes

$$\left(K_{NH} + L_{NH} \right) f_{NH} = 0. \quad (2.28)$$

Now that the Nosè distribution function no longer depends explicitly on time, its total time derivative is written as follows

$$\begin{aligned}
\frac{d}{dt} f_{NH} &= \frac{\partial f_{NH}}{\partial t} + \dot{X}_k \frac{\partial f_{NH}}{\partial X_k} \\
&= \dot{X}_k \frac{\partial f_{NH}}{\partial X_k} = L_{NH} f_{NH}. \quad (2.29)
\end{aligned}$$

Hence, for equilibrium distribution functions, one can use $\frac{d}{dt} = L_{NH}$. Since the Nosè Hamiltonian is conserved by the Nosè-Liouville operator, it follows

that the results of the Liouville operator applied to any function of the Hamiltonian is equal to zero

$$L_{NH}g(H_{NH}) = 0 \quad (2.30)$$

where g is an arbitrary function of the Hamiltonian. In order to obtain a solution of Eq. (2.28), it is useful to define a function W by

$$\frac{dW}{dt} = K_{NH}, \quad (2.31)$$

and the Nosè partition function Z_{NH} by,

$$Z_{NH} = \int d^N r d^N p d^N \eta d^N p_\eta e^{-\beta H_{NH}}. \quad (2.32)$$

With all the above ingredients, the solution of Eq. (2.28) can be written in the following form

$$f_{NH} \propto Z_{NH}^{-1} e^{-W} \delta(E - H_{NH}). \quad (2.33)$$

This can be verified by the direct substitution of Eq. (2.33) into Eq. (2.28)

$$K_{NH} Z_{NH}^{-1} e^{-W} \delta(E - H_{NH}) + L_{NH} \left(Z_{NH}^{-1} e^{-W} \delta(E - H_{NH}) \right) = 0. \quad (2.34)$$

The second term of Eq. (2.34) can be rewritten as

$$\begin{aligned} L_{NH} \left(Z_{NH}^{-1} e^{-W} \delta(E - H_{NH}) \right) &= e^{-W} L_{NH} \left(Z_{NH}^{-1} \delta(E - H_{NH}) \right) \\ &\quad + Z_{NH}^{-1} \delta(E - H_{NH}) L_{NH} e^{-W} \end{aligned} \quad (2.35)$$

but since $\delta(E - H_{NH})$ is a function of H_{NH} , the Liouville operator acting upon it will yield zero. Thus

$$L_{NH} \left(Z_{NH}^{-1} e^{-W} \delta(E - H_{NH}) \right) = Z_{NH}^{-1} \delta(E - H_{NH}) L_{NH} e^{-W}. \quad (2.36)$$

Now using the fact that L_{NH} can be replaced by $\frac{d}{dt}$ one obtains

$$\begin{aligned} Z_{NH}^{-1} \delta(E - H_{NH}) L_{NH} e^{-W} &= Z_{NH}^{-1} \delta(E - H_{NH}) \frac{d}{dt} e^{-W} \\ &= -\frac{dW}{dt} Z_{NH}^{-1} \delta(E - H_{NH}) e^{-W} \\ &= -K_{NH} Z_{NH}^{-1} \delta(E - H_{NH}) e^{-W} \end{aligned} \quad (2.37)$$

Substituting Eq. (2.37) into Eq. (2.34) yields zero. One can conclude that Eq. (2.28) is the solution of the Liouville equation for the Nosè distribution function at equilibrium.

The Nosè distribution function becomes:

$$f_{NH} = Z_{NH}^{-1} e^{-\int K_{NH} dt} \delta(E - H_{NH}). \quad (2.38)$$

To write Nosè's distribution function explicitly, let us consider the following expression

$$H_T = \frac{p^2}{2m} + V(r) + \frac{p_\eta^2}{2m_\eta}. \quad (2.39)$$

The total time derivative of H_T is given by

$$\frac{dH_T}{dt} = -3Nk_B T \frac{p_\eta}{m_\eta}, \quad (2.40)$$

which is related to the compressibility by

$$K_{NH} = -3N \frac{p_\eta}{m_\eta} = \beta \frac{dH_T}{dt}. \quad (2.41)$$

The canonical averages can be written as

$$\begin{aligned} \langle A \rangle_{NH} &= \int dr dp d\eta dp_\eta e^{-\beta H_T} \delta(E - H_{NH}) A(r, p) \\ &= \int dr dp e^{-\beta \left(\frac{p^2}{2m} + V(r) \right)} A(r, p) \int d\eta \delta(E - H_{NH}) \int dp_\eta e^{-\beta \frac{p_\eta^2}{2m_\eta}}. \end{aligned} \quad (2.42)$$

Equation. (2.42) is split into three integrals. The second integral can be performed by using the following identity

$$\delta(f(\eta)) = \sum_{\eta_0} \frac{\delta(\eta - \eta_0)}{\frac{df}{d\eta}(\eta_0)} \quad (2.43)$$

where the sum runs over the zeros η_0 of $f(\eta)$. The identity leads to

$$f(\eta) = E - H_{NH} \quad (2.44)$$

$$f(\eta) = 0 \rightarrow \eta_0 = \frac{E - H_T}{3Nk_B T} \quad (2.45)$$

$$\frac{df}{d\eta}(\eta_0) = 3Nk_B T \quad (2.46)$$

$$\delta(f(\eta)) = \frac{\delta(\eta - \beta(H_T - E)/3N)}{3Nk_B T}, \quad (2.47)$$

and gives

$$\int d\eta \delta(E - H_{NH}) = \frac{1}{3Nk_B T}. \quad (2.48)$$

The Gaussian integral over p_η

$$\int dp_\eta e^{-\beta \frac{p_\eta^2}{2m_\eta}} \quad (2.49)$$

can be easily calculated by using the standard integral with limits

$$\int_{-\infty}^{\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}}, \quad (2.50)$$

and identifying $a = \beta/2m_\eta$ to give

$$\int dp_\eta e^{-\beta \frac{p_\eta^2}{2m_\eta}} = \sqrt{2\pi m_\eta k_B T}. \quad (2.51)$$

Finally, the average in the canonical ensemble takes the form

$$\begin{aligned} \langle A \rangle_N &= \frac{1}{3Nk_B T} \sqrt{2\pi m_\eta k_B T} \int dr dp e^{-\beta \left(\frac{p^2}{2m} + V(r) \right)} A(r, p) \\ &\equiv \langle A \rangle_C. \end{aligned} \quad (2.52)$$

Thus, Eq. (2.52) shows that, the classical average in the canonical ensemble can be calculated using Nosè-Hoover dynamics.

The Nosè-Hoover algorithm (see Appendix A), while capable of dealing with one conservation law, does not give enough flexibility to deal with more than one δ -function in the partition function. This restriction renders the Nosè-Hoover method problematic. To increase the size of the phase space and thus make the system ergodic, Martyna *et al.* [17] suggested a scheme where the Nosè-Hoover thermostat is coupled to another thermostat or to a whole chain of thermostats known as the Nosè-Hoover chain. To maintain the tensorial notation to a minimum the chain is limited to only two thermostat variables.

2.3 Nosè-Hoover chain thermostats

Consider a one-dimensional system, coupled with two Nosè-Hoover chain thermostats, a phase-space point of the entire system is denoted by $X = (r, \eta_1, \eta_2, p, p_{\eta_1}, p_{\eta_2})$. The conserved Hamiltonian of the total system is

$$H_{(NHC)}(r, \eta_1, \eta_2, p, p_{\eta_1}, p_{\eta_2}) = \frac{p^2}{2m} + V(r) + \frac{p_{\eta_1}^2}{2m_{\eta_1}} + \frac{p_{\eta_2}^2}{2m_{\eta_2}} + gk_B T(\eta_1 + \eta_2), \quad (2.53)$$

where η_1 and η_2 are the two thermostat variables with conjugated momenta p_{η_1} and p_{η_2} ; m_{η_1}, m_{η_2} are fictitious masses associated with the extra degrees of freedom. The number of degrees of freedom $g = 3N$ is fixed to ensure that one obtains the canonical distribution function. It is the number of degrees of freedom of the subsystem in configuration space, k_B is the Boltzmann constant and T is the thermostat temperature. The equations of motion are given by

$$\dot{r} = \frac{p}{m} \quad (2.54)$$

$$\dot{\eta}_1 = \frac{p_{\eta_1}}{m_{\eta_1}} \quad (2.55)$$

$$\dot{\eta}_2 = \frac{p_{\eta_2}}{m_{\eta_2}} \quad (2.56)$$

$$\dot{p} = -\frac{\partial V}{\partial r} - p \frac{p_{\eta_1}}{m_{\eta_1}} \quad (2.57)$$

$$\dot{p}_{\eta_1} = \frac{p^2}{m} - gk_B T - p_{\eta_1} \frac{p_{\eta_2}}{m_{\eta_2}} \quad (2.58)$$

$$\dot{p}_{\eta_2} = \frac{p_{\eta_1}^2}{m_{\eta_1}} - gk_B T. \quad (2.59)$$

This yields the following antisymmetric matrix [12]

$$\mathcal{B}^{NHC} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -p & 0 \\ 0 & -1 & 0 & p & 0 & -p_{\eta_1} \\ 0 & 0 & -1 & 0 & p_{\eta_1} & 0 \end{bmatrix}. \quad (2.60)$$

Once the antisymmetric matrix is known, it is a simple matter to rewrite Eqs.(2.54)-(2.59) in tensorial form with all elements explicitly shown

$$\begin{aligned}
\begin{bmatrix} \dot{r} \\ \dot{\eta}_1 \\ \dot{\eta}_2 \\ \dot{p} \\ \dot{p}_{\eta_1} \\ \dot{p}_{\eta_2} \end{bmatrix} &= \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -p & 0 \\ 0 & -1 & 0 & p & 0 & -p_{\eta_1} \\ 0 & 0 & -1 & 0 & p_{\eta_1} & 0 \end{bmatrix} \begin{bmatrix} \frac{\partial H_{NHC}}{\partial r} \\ \frac{\partial H_{(NHC)}}{\partial \eta_1} \\ \frac{\partial H_{(NHC)}}{\partial \eta_2} \\ \frac{\partial H_{(NHC)}}{\partial p} \\ \frac{\partial H_{(NHC)}}{\partial p_{\eta_1}} \\ \frac{\partial H_{(NHC)}}{\partial p_{\eta_2}} \end{bmatrix} \\
&= \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -p & 0 \\ 0 & -1 & 0 & p & 0 & -p_{\eta_1} \\ 0 & 0 & -1 & 0 & p_{\eta_1} & 0 \end{bmatrix} \begin{bmatrix} \frac{\partial V}{\partial r} \\ gk_B T \\ gk_B T \\ \frac{p}{m} \\ \frac{p_{\eta_1}}{m_{\eta_1}} \\ \frac{p_{\eta_2}}{m_{\eta_2}} \end{bmatrix}, \quad (2.61)
\end{aligned}$$

and the general form

$$\dot{X}_k = \sum_{i,j=1}^{2(N+1)} \frac{\partial X_k}{\partial X_i} \mathcal{B}_{ij}^{(NHC)} \frac{\partial H_{(NHC)}}{\partial X_j} = \mathcal{B}_{kj}^{(NHC)} \frac{\partial H_{(NHC)}}{\partial X_j}. \quad (2.62)$$

The Liouville equation for the Nosè-Hoover chain's distribution function of the system is

$$\begin{aligned}
\frac{\partial}{\partial t} f_{(NHC)} &= -\frac{\partial}{\partial X_k} (\dot{X}_k f_{(NHC)}) \\
&= -\dot{X}_k \frac{\partial f_{(NHC)}}{\partial X_k} - \frac{\partial \dot{X}_k}{\partial X_k} f_{(NHC)} \\
&= -L_{(NHC)} f_{(NHC)} - K_{(NHC)} f_{(NHC)} = 0 \quad (2.63)
\end{aligned}$$

where the compressibility of the phase space is expressed as

$$\begin{aligned}
K_{(NHC)} &= -3N \frac{p_{\eta_1}}{m_{\eta_1}} + \frac{p_{\eta_2}}{m_{\eta_2}} \\
&= \beta \frac{dH'_T}{dt}
\end{aligned}$$

with

$$H'_T = \frac{p^2}{2m} + V(r) + \frac{p_{\eta_1}^2}{2m_{\eta_1}} + \frac{p_{\eta_2}}{m_{\eta_2}}. \quad (2.64)$$

Similar to the way the Nosè-Hoover distribution function was solved, one finds that the following Nosè-Hoover chain distribution function is the solution of Eq.(2.63)

$$f_{(NHC)}(r, p) = \frac{e^{-W'} \delta(E - H_{(NHC)})}{\int d^N r d^N p d^N \eta_1 d^N \eta_2 d^N p_{\eta_1} d^N p_{\eta_2} e^{-\beta H_{(NHC)}}} \quad (2.65)$$

where

$$W' = \int K_{(NHC)} dt. \quad (2.66)$$

For the Nosè-Hoover chain method, the canonical averages can be written as

$$\langle A \rangle_{(NHC)} = \int dr dp d\eta_1 d\eta_2 dp_{\eta_1} dp_{\eta_2} e^{-\beta H'_T} \delta(E - H_{(NHC)}) A(r, p). \quad (2.67)$$

Using Eq. (2.43), the integral over η_1 and η_2 becomes

$$\int d\eta_1 \delta(E - H_{(NHC)}) = \frac{1}{3Nk_B T} \quad (2.68)$$

$$\int d\eta_2 \delta(E - H_{(NHC)}) = \frac{1}{3Nk_B T} \quad (2.69)$$

and the Gaussian integrals over p_{η_1} and p_{η_2} are given by

$$\int dp_{\eta_1} e^{-\beta \frac{p_{\eta_1}^2}{2m_{\eta_1}}} = \sqrt{2\pi m_{\eta_1} k_B T} \quad (2.70)$$

$$\int dp_{\eta_2} e^{-\beta \frac{p_{\eta_2}^2}{2m_{\eta_2}}} = \sqrt{2\pi m_{\eta_2} k_B T}. \quad (2.71)$$

Ultimately, the result for the average is written as

$$\begin{aligned} \langle A \rangle_{(NHC)} &= \frac{1}{(3Nk_B T)^2} \sqrt{2\pi m_{\eta_1} k_B T} \sqrt{2\pi m_{\eta_2} k_B T} \int dr dp e^{-\beta H} A(r, p) \\ &\equiv \langle A \rangle_C. \end{aligned} \quad (2.72)$$

It has thus been shown that canonical ensemble averages can be determined by using Nosè-Hoover chain dynamics.

The non-Hamiltonian Nosè dynamics simulation is a well-known method in MDS. In practice, it is used to calculate dynamical properties at constant temperature and study phase-space transitions. Generally, the Nosè-Hoover Chain algorithm (see Appendix B) [17] gives a correct canonical distribution function and a satisfactory solution to the practical ergodicity problems [18].

Chapter 3

Theory of Quantum

Mechanics

This chapter discusses some pictures of quantum mechanics. The first picture was developed by Heisenberg in the form of matrix mechanics and the second one was described by Schrödinger in the form of wave mechanics. Both approaches are special cases of a formulation of quantum mechanics due to Dirac [19] in which abstract vectors of a linear space and abstract operators on the space are used. The chapter starts with a brief summary of the mathematical tools of quantum mechanics and introduces Heisenberg's picture and Schrödinger's picture of quantum mechanics.

Linear vector spaces in quantum mechanics

In his formulation of quantum mechanics, Dirac termed a vector a "ket" and denoted it by the symbol $|\dots\rangle$. He then defined a linear space with the kets as the elements of this space. In this space, the scalar product of two vectors $|\psi\rangle$ and $|\varphi\rangle$ can be written in the compact form as $\langle\psi|\varphi\rangle$. The bracket notation led Dirac to term the vector $\langle\psi|$ a "bra" vector.

Complete orthonormal basis set

Let $\phi_1, \phi_2, \dots, \phi_n$ be a set of n vectors in a linear vector space S . A basis $\phi_1, \phi_2, \dots, \phi_n$ is said to be complete if any vector ψ in the space S may be expressed uniquely as a linear combination of the ϕ_i :

$$\psi = c_1\phi_1 + c_2\phi_2 + \dots + c_n\phi_n = \sum_{i=1}^n c_i\phi_i. \quad (3.1)$$

For a basis of kets $|\phi_i\rangle$, the completeness property can be written as

$$|\psi\rangle = \sum_{i=1}^n c_i|\phi_i\rangle. \quad (3.2)$$

The basis of kets $|\phi_i\rangle$ is said to be an orthonormal basis if

$$\langle\phi_i|\phi_j\rangle = \delta_{ij}, \quad i, j = 1, \dots, n, \quad (3.3)$$

where δ_{ij} is the Krönecker delta function. To determine a coefficient c_j one should form the scalar product of $|\phi_j\rangle$ and $|\psi\rangle$. Thus

$$\langle\phi_j|\psi\rangle = \sum_{i=1}^n c_i\langle\phi_j|\phi_i\rangle = \sum_{i=1}^n c_i\delta_{ij} = c_j, \quad (3.4)$$

when the basis kets are orthonormal. With $i = j$, it follows from (3.2) and (3.4) that the statement of a complete orthonormal basis can be written as

$$|\psi\rangle = \sum_{i=1}^n \langle\phi_i|\psi\rangle|\phi_i\rangle. \quad (3.5)$$

Operators

An operator on a vector space transforms each vector of the space into either the same vector or another vector of the space. Thus

$$X|u\rangle = |v\rangle \quad (3.6)$$

where $|u\rangle$ and $|v\rangle$ are kets of the same space and X is an operator of the space.

An operator is completely specified if its action on every ket of the space is known.

In quantum mechanics, operators on the vector spaces are usually linear. An operator X is said to be linear if it associates with every ket $|u\rangle$ another ket $|v\rangle$ as

$$X(|u\rangle + |v\rangle) = X|u\rangle + X|v\rangle \quad (3.7)$$

where the distribution law holds, and also if

$$X(\lambda|u\rangle) = \lambda X|u\rangle \quad (3.8)$$

where the operator commutes with the complex number λ . Let $|u\rangle$ and $|v\rangle$ be two kets. The matrix element of an operator X between the states $|u\rangle$ and $|v\rangle$ is the scalar product in the form

$$\chi_{uv} = \langle u|X|v\rangle. \quad (3.9)$$

A diagonal matrix element of the operator X in the state $|u\rangle$ is then $\langle u|X|u\rangle$. If one considers an orthonormal basis $|u\rangle$, the trace of an operator X , written TrX , is defined by

$$TrX = \sum_u \langle u|X|u\rangle. \quad (3.10)$$

Adjoint operators

For all $|u\rangle$ and $|v\rangle$ of the vector space, the adjoint operator written X^\dagger of the operator X is defined by

$$\langle u|X^\dagger|v\rangle = \langle v|X|u\rangle^*. \quad (3.11)$$

Hermitian operators

An operator X is said to be Hermitian or self-adjoint if it is equal to its adjoint, that is if:

$$X^\dagger = X. \quad (3.12)$$

It follows from (3.12) and (3.11) that a Hermitian operator satisfies the relation

$$\langle u|X|v\rangle = \langle v|X|u\rangle^* \quad (3.13)$$

for all $|u\rangle$ and $|v\rangle$ of the vector space. The general properties of Hermitian operators can be found for example in [20].

Eigenvectors and eigenvalues of an operator

Let X be an operator. $|u\rangle$ is called an eigenvector of X with associated eigenvalue λ if

$$X|u\rangle = \lambda|u\rangle, \quad (3.14)$$

where λ is a complex number. When the operator X is Hermitian, its eigenvalues and eigenvectors satisfy the following properties

- (i) The eigenvalues of a Hermitian operator are real.
- (ii) Eigenvectors belonging to different eigenvalues of a Hermitian operator X are orthogonal.

The property (i) can be obtained using the fact that a diagonal matrix element of X written as $\langle u|X|u\rangle$, is real.

Observables

An operator X is said to be an observable if it is linear and Hermitian and also if its eigenkets $|x_i\rangle$ are a basis of the vector space on which X operates. To be more precise, the eigenkets $|x_i\rangle$ are a complete orthonormal set, so that from the definition of the complete orthonormal basis set, an arbitrary ket $|\varphi\rangle$ can be expanded as

$$|\varphi\rangle = \sum_{i=1}^n c_{x_i} |x_i\rangle = \sum_{i=1}^n \langle x_i|\varphi\rangle |x_i\rangle. \quad (3.15)$$

3.1 Schrödinger Picture of Quantum Mechanics

The Schrödinger picture of quantum mechanics was formulated by Erwin Schrödinger in 1926 to describe how the quantum state of a physical system changes in time [20]. In the standard interpretation of quantum mechanics, the quantum state, also called a wave function or state vector, is the most complete description that can be given to a physical system. In the Schrödinger picture, the state evolves in time and the operators are constant.

In quantum mechanics, the quantum state of a particle, namely the position $q(t)$ and the conjugate momentum $p(t)$ of the particle, is defined at a given time by a wave function $\psi(q, t)$. The so-called wave function $\psi(q, t)$ contains all the information it is possible to know about the particle. The knowledge of the wave function allows one to calculate the probability of finding, at a given time t , the particle in a volume $d^3q = dx dy dz$. The probability is determined by the following expression

$$dP = |\psi(q, t)|^2 d^3q. \quad (3.16)$$

The sum of probabilities of all possible values of coordinates of the system must, by definition, equal to one

$$\int |\psi(q, t)|^2 d^3q = 1. \quad (3.17)$$

Let us consider an arbitrary physical quantity A which describes the state of a quantum system at a given time t . In quantum mechanics, the physical quantity can take a value, called an eigenvalue A_n , where $n = 0, 1, 2, 3, \dots$. The eigenvalue is defined as a result of an arbitrary physical measurement. Each eigenvalue A_n is associated with a wave function of the system ψ_n called an eigenfunction. The probability P_n of obtaining the eigenvalue A_n for a measurement at time t is represented in the form

$$P_n = \frac{|c_n|^2}{\sum_n |c_n|^2}, \quad (3.18)$$

where the summation extends over all n and c_n are constant coefficients. It is apparent from (3.18) that the sum of probabilities over all states ψ_n is equal to one. For any $\psi(q, t)$, this probability P_n can be determined by decomposing $\psi(q, t)$ in terms of the functions $\psi_n(q)$ given by

$$\psi(q, t) = \sum_n c_n \psi_n(q). \quad (3.19)$$

Finally, the time-dependent equation defining the evolution of the wave function $\psi(q, t)$ is the Schrödinger equation written in general form as

$$i\hbar \frac{\partial}{\partial t} \psi(q, t) = \hat{H} \psi(q, t), \quad (3.20)$$

where \hat{H} is the Hamiltonian operator of the system. Equation. (3.20) is as central to quantum mechanics as Newton's law is to classical mechanics. The partial differential equation can be solved when the potential is time independent using separation of variables. Let $\psi(q, t) = \theta(t)\phi(q)$. Substituting in Eq. (3.20), one see that $\theta(t)$ satisfies the ordinary differential equation

$$\theta'(t) = -\frac{i\hat{H}}{\hbar} \theta(t) \quad (3.21)$$

and $\phi(q)$ satisfies the ordinary differential equation

$$-\frac{\hbar^2}{2m} \phi''(q) + V(q)\phi(q) - \hat{H}\phi(q) = 0. \quad (3.22)$$

Solving Eq. (3.21) one gets

$$\theta(t) = A e^{-\frac{i\hat{H}}{\hbar} t} \quad (3.23)$$

and finally, one can write

$$\psi(q, t) = e^{-\frac{i\hat{H}}{\hbar} t} \psi(q) \quad (3.24)$$

where $\psi(q) = A\phi(q)$ and $\phi(q)$ is a solution of Eq. (3.22). The solutions of Eq. (3.20) describe not only atomic, molecular and subatomic systems but also macroscopic systems [20]. In his picture, Schrödinger used his wave equation

to evaluate the wave function $\psi(q, t_1)$ and calculated the expectation value of an arbitrary operator $\hat{\chi}$ at a future time $t = t_1$ as

$$\langle \chi(t_1) \rangle = \int \psi^*(q, t_1) \hat{\chi} \psi(q, t_1) dq. \quad (3.25)$$

In his picture Heisenberg adopted an equivalent point of view of describing a quantum state in quantum mechanics.

3.2 Heisenberg Picture of Quantum Mechanics

Werner Heisenberg was the first to describe quantum mechanics in the form called matrix mechanics in 1925 [20]. This form is the basis of Dirac's bra and ket notation for quantum states and the wave function. In the Heisenberg picture of quantum mechanics, the state of the system is constant while the operators evolve in time. This picture stands in contrast with the Schrödinger formulation in which the operators are constant and the states evolve in time. In the Heisenberg picture, an operator $\hat{\chi}$ changes in time according to the Heisenberg equation of motion

$$\frac{d\hat{\chi}(t)}{dt} = \frac{i}{\hbar} [\hat{H}, \hat{\chi}(t)] + \left(\frac{\partial \hat{\chi}}{\partial t} \right), \quad (3.26)$$

where $[\hat{H}, \hat{\chi}(t)] = \hat{H}\hat{\chi}(t) - \hat{\chi}(t)\hat{H}$ is the commutator of \hat{H} and $\hat{\chi}(t)$. It is a simple matter to derive Eq. (3.26) using Eq. (3.25). Consider the fact that the Heisenberg picture and the Schrödinger picture of quantum mechanics are equivalent. Writing explicitly the time dependence of the wave function $\psi(q, t)$ in the form

$$\psi(q, t) = e^{-i\hat{H}t/\hbar} \psi(q), \quad (3.27)$$

the expectation value of an observable $\hat{\chi}$ can be written as

$$\langle \chi(t) \rangle = \int \psi^*(q) e^{i\hat{H}t/\hbar} \hat{\chi} e^{-i\hat{H}t/\hbar} \psi(q) dq, \quad (3.28)$$

and the operator as a function of time is defined as

$$\hat{\chi}(t) = e^{i\hat{H}t/\hbar} \hat{\chi} e^{-i\hat{H}t/\hbar}. \quad (3.29)$$

Taking the time derivative of equation (3.29) one obtains

$$\begin{aligned}
\frac{d\hat{\chi}(t)}{dt} &= \frac{i}{\hbar}\hat{H}e^{i\hat{H}t/\hbar}\hat{\chi}e^{-i\hat{H}t/\hbar} + e^{i\hat{H}t/\hbar}\frac{\partial\hat{\chi}}{\partial t}e^{-i\hat{H}t/\hbar} + e^{i\hat{H}t/\hbar}\hat{\chi}\left(-\frac{i}{\hbar}\hat{H}e^{-i\hat{H}t/\hbar}\right) \\
&= \frac{i}{\hbar}\hat{H}\hat{\chi}(t) + \frac{\partial\hat{\chi}}{\partial t} - \frac{i}{\hbar}\hat{\chi}(t)\hat{H} \\
&= \frac{i}{\hbar}[\hat{H}, \hat{\chi}(t)] + \left(\frac{\partial\hat{\chi}}{\partial t}\right).
\end{aligned} \tag{3.30}$$

In this equation, the operator is explicitly a function of time. But only operators without explicit time-dependence will be considered, and the Heisenberg equation of motion simplifies to

$$\frac{d\hat{\chi}(t)}{dt} = \frac{i}{\hbar}[\hat{H}, \hat{\chi}(t)]. \tag{3.31}$$

3.3 Quantum statistical mechanics

The statistical theories developed in the previous chapter can be extended to the treatment of quantum systems. The intrinsic statistical character of quantum mechanics is due to the constraints imposed by the Heisenberg uncertainty principle [21] which states that the particle cannot be at a definite position in coordinate space and at the same time have a definite momentum. It follows from Eq. (3.20) that the quantum state and operators are propagated in time without any indeterminacy in the time evolution of a quantum state. But the indeterminacy appears when a physical quantity is measured. The only way to solve the problem is to interpret the results of the measurement of those various physical quantities using statistical techniques.

To be more precise, let us consider a system which is described by a specific state $|\psi\rangle$. The system is then said to be in a pure state. This state vector can be represented in terms of orthonormal basis functions, $|\varphi_i\rangle$ as

$$|\psi\rangle = \sum_i c_i |\varphi_i\rangle \tag{3.32}$$

where summation extends over all i and the $c_i = \langle \varphi_i | \psi \rangle$ are some constant coefficients. Let us consider now a self-adjoint operator $\hat{\chi} = \hat{\chi}^\dagger$ for which

$$\hat{\chi}|\varphi_i\rangle = a_i|\varphi_i\rangle, \quad i = 1, \dots, n, \quad (3.33)$$

where a_i is a real number. When the state vector of the system is known, the probabilities of finding all the possible result are also known. If the state of the system is normalized, then the matrix element or expectation value of the observable, that is, when the system is in a pure state $|\psi\rangle$, is written as

$$\bar{\chi} = \int \psi^*(q, t) \hat{\chi} \psi(q, t) dq = \langle \psi | \hat{\chi} | \psi \rangle. \quad (3.34)$$

Substituting Eq. (3.32) into Eq. (3.34) will help us to define the expectation value $\langle \chi \rangle$ as the sum of all the eigenvalues χ_j of the given quantity, each multiplied by the corresponding probability $|c_j|^2$. This can be verified as follows

$$\begin{aligned} \bar{\chi} &= \sum_i \sum_j c_i c_j^* \langle \varphi_i | \hat{\chi} | \varphi_j \rangle \\ &= \sum_i \sum_j c_i c_j^* \chi_j \langle \varphi_i | \varphi_j \rangle \\ &= \sum_i \sum_j c_i c_j^* \chi_j \delta_{ij} \\ &= \sum_j |c_j|^2 \chi_j. \end{aligned} \quad (3.35)$$

It follows from Eq. (3.35) that when all the information about the initial condition of the system is known, the results of the measurements of the physical quantities are given by statistical averages. This is not surprising because it satisfies the Heisenberg uncertainty principle of quantum mechanics which does not exist in classical mechanics. All the theory given above is available only when one has all the information about the state of the system. However, it is not possible in practice to have all the information about the state of the system. To take into account the partial information, one has to introduce a useful mathematical tool, the density matrix.

3.4 Density matrix

The description of a system by means of a wave function is a particular case corresponding to a density matrix for a pure state given by

$$\hat{\rho} = |\psi\rangle\langle\psi|. \quad (3.36)$$

For this state, the wave function completely determines the state of a physical system and it is defined by a ket vector $|\psi\rangle$. More often, when considering a system to be in a statistical ensemble of different state vectors, that is, mixed states, it is not possible to use a pure state description of quantum mechanics.

A system described by a statistical mixed states does not gives us enough information about the quantum state. This is not the case with the state which is a linear superposition of states. It follows from this that, with a system described by a statistical mixed state, it is not possible to know what state the subsystem is in; it is only possible to determine the probabilities that the subsystem is in each accessible state. Thus it implies the introduction of a statistical ensemble of identical systems, and the probabilities then give the fraction of the ensemble in each microstate.

Since the single system is replaced by an ensemble of identical systems, averages of observables cannot be determined according to Eq. (3.35). Averages for the ensemble should now be calculated by expressing the average of each accessible state and summing all the terms, each multiplied by the corresponding probability associated with that state. In this case, the average value of this specific system is [21]

$$\begin{aligned} \langle\chi\rangle &= \sum_k \gamma_k \bar{\chi}_k \\ &= \sum_k \gamma_k \sum_i \sum_j c_i c_j^* \langle i|\hat{\chi}|j\rangle \end{aligned} \quad (3.37)$$

where γ_k is the probability that the system is in the state $|\psi^{(k)}\rangle$. These

probabilities are all positive, and must satisfy the normalisation condition

$$\sum_k \gamma_k = 1. \quad (3.38)$$

From Eq. (3.37), let us introduce the function ρ_{ji} defined by

$$\rho_{ji} = \sum_k \gamma_k c_j^k c_i^{k*}. \quad (3.39)$$

This function is a matrix element, in terms of which the average can be expressed:

$$\langle \chi \rangle = \sum_i \sum_j \chi_{ij} \rho_{ji}. \quad (3.40)$$

The matrix element can be written in an abstract bracket form according to Dirac's convention [19] as

$$\rho_{ji} = \langle j | \hat{\rho} | i \rangle. \quad (3.41)$$

With the above expression of the matrix element ρ_{ji} , one can now define the operator $\hat{\rho}$ which is called the von Neumann density matrix [21]. Knowledge of the density matrix allows the calculation of the average value of any quantum operator $\hat{\chi}$ which is given in terms of a product of operators as

$$\begin{aligned} \langle \hat{\chi} \rangle &= \sum_i \sum_j \chi_{ij} \langle j | \hat{\rho} | i \rangle \\ &= \sum_i \sum_j \langle i | \hat{\chi} | j \rangle \langle j | \hat{\rho} | i \rangle \\ &= \sum_i \langle i | \hat{\chi} \hat{\rho} | i \rangle \sum_j | j \rangle \langle j | \\ &= \sum_i \langle i | \hat{\chi} \hat{\rho} | i \rangle \end{aligned} \quad (3.42)$$

with $\sum_j | j \rangle \langle j | = 1$, known as the closure relation. Eq. (3.42) gives the average as a sum of the diagonal matrix elements of the matrix product of $\hat{\chi}$ and $\hat{\rho}$, or the trace. Since the trace of a matrix is basis independent, the identity $Tr(AB) = Tr(BA)$ can be used, and the average of the observable can be written as

$$\langle \hat{\chi} \rangle = Tr\{\hat{\rho}\hat{\chi}\} = Tr\{\hat{\chi}\hat{\rho}\}. \quad (3.43)$$

From this result, one can conclude that the mixed state can be described using the density matrix.

Just as the Schrödinger equation describes how pure states evolve in time, the von Neumann equation derived below describes how the density matrix evolves in time. To see this, let us consider the expectation value of the operator $\hat{\chi}$ at time t

$$\begin{aligned}\langle\chi(t)\rangle &= \text{Tr}\left(\hat{\chi}(t)\hat{\rho}\right) \\ &= \text{Tr}\left(e^{i\hat{H}t/\hbar}\hat{\chi}e^{-i\hat{H}t/\hbar}\hat{\rho}\right),\end{aligned}\quad (3.44)$$

where \hat{H} is not a function of time. Using the fact that the trace of an operator under unitary transformations is invariant, the above expression can be written as

$$\begin{aligned}\langle\chi(t)\rangle &= \text{Tr}\left(\hat{\chi}e^{-i\hat{H}t/\hbar}\hat{\rho}e^{i\hat{H}t/\hbar}\right) \\ &= \text{Tr}\left(\hat{\chi}\hat{\rho}(t)\right),\end{aligned}\quad (3.45)$$

where the last line defined the density matrix as a function of time. The von Neumann equation of motion for the density matrix can be expressed by taking the time derivative of $\hat{\rho}(t)$. One gets

$$\begin{aligned}\frac{\partial}{\partial t}\hat{\rho}(t) &= \frac{\partial}{\partial t}\left(e^{-i\hat{H}t/\hbar}\hat{\rho}e^{i\hat{H}t/\hbar}\right) \\ &= \frac{i\hat{H}}{\hbar}e^{-i\hat{H}t/\hbar}\hat{\rho}e^{i\hat{H}t/\hbar} + e^{-i\hat{H}t/\hbar}\hat{\rho}\left(\frac{i\hat{H}}{\hbar}\right)e^{i\hat{H}t/\hbar} \\ &= -\frac{i}{\hbar}\left[\hat{H},\hat{\rho}(t)\right].\end{aligned}\quad (3.46)$$

The so-called density matrix operator obeys many important properties which will be necessary to enumerate. It follows from the following properties that the density matrix can be interpreted as a probability. The first property is

$$\text{Tr}\hat{\rho} = 1. \quad (3.47)$$

This can be easily proven using Eq. (3.38) and Eq. (3.39) as follow

$$\begin{aligned}
Tr\hat{\rho} &= \sum_i \rho_{ii} \\
&= \sum_k \gamma_k c_i^k c_i^{k*} \\
&= \sum_k \gamma_k \sum_i |c_i^k|^2 \\
&= \sum_k \gamma_k = 1.
\end{aligned} \tag{3.48}$$

The second property,

$$\rho = \rho^\dagger, \tag{3.49}$$

is that the density matrix is a Hermitian operator. From the definition of the matrix element in Eq. (3.37), one can say that the density matrix is a Hermitian operator. This can be demonstrated as follows

$$\begin{aligned}
(\rho_{ij})^* &= \left(\sum_k \gamma_k c_i^k c_j^{k*} \right)^* \\
&= \sum_k \gamma_k c_i^{k*} c_j^k = \rho_{ji}.
\end{aligned} \tag{3.50}$$

Finally, the third property,

$$\langle u|\rho|u \rangle \geq 0, \tag{3.51}$$

implies that the diagonal elements of the density matrix are nonnegative. This can be easily verified using Eq. (3.38) and Eq. (3.47).

Representation of the state can be introduced using Dirac notation as $\psi(r) \equiv \langle r|\psi \rangle$ and $\psi^*(r) = \langle \psi|r \rangle$ in coordinate space, and $\psi(p) \equiv \langle p|\psi \rangle$ and $\psi^*(p) = \langle \psi|p \rangle$ in momentum space.

Using the above notation, the density matrix can be represented, for example, in coordinate space as

$$\rho(r, r') \equiv \langle r|\hat{\rho}|r' \rangle. \tag{3.52}$$

Analogously, it can be represented in momentum space as

$$\rho(p, p') \equiv \langle p|\hat{\rho}|p' \rangle. \tag{3.53}$$

It can also be represented in an infinite number of different ways in phase space. One such representation is that proposed originally by Wigner [6].

Chapter 4

Wigner Representation of Quantum Mechanics

In this chapter, the Wigner formulation of quantum mechanics in phase space will be introduced and it will be shown how the Weyl transform given in [22] was exploited to define the Wigner function in phase space. This function will be used to evaluate time-dependent quantum averages. Some of the Wigner function properties which make it quite useful in applications are also illustrated. For example, it can be used to evaluate more difficult and interesting expectation values, such as time-dependent thermal correlation functions [23]. The law of motion for the Wigner function, known as the Wigner-Liouville equation, can be used to introduce quantum propagation in time and is particularly suited to develop quantum-classical approximation schemes.

4.1 Wigner formulation of quantum mechanics in phase space

The Wigner representation of quantum mechanics was used to represent quantum dynamics in terms of phase-space functions. In 1932 Wigner was

the first to formulate quantum mechanics in phase space. This was done by introducing a phase-space function to study quantum corrections to classical statistical mechanics.

The statistical character of quantum mechanics is particularly apparent in Wigner's phase-space formulation [6, 24, 25, 26]. In this approach, which is equivalent to the Schrödinger formalism [19, 27], quantum effects are introduced both through correction terms to the classical law of motion and through constraints on the initial conditions. In the Wigner representation of quantum mechanics, the Wigner function substitutes wave functions or density matrices. The Wigner function is a quasi-distribution in phase space.

To introduce the Wigner function, the definition of the Weyl transform is needed. Consider an arbitrary operator $\hat{\chi}$. The Weyl transform $\tilde{\chi}$ is defined as [22]

$$\tilde{\chi}(r, p) = \int d\xi \exp[-\frac{i}{\hbar}p\xi] \langle r + \frac{\xi}{2} | \hat{\chi} | r - \frac{\xi}{2} \rangle. \quad (4.1)$$

The above expression is represented in terms of matrix elements of the operator in the position basis. Analogously, it can be represented in terms of matrix elements of the operator in the momentum basis

$$\tilde{\chi}(r, p) = \int d\eta \exp[\frac{i}{\hbar}r\eta] \langle p + \frac{\eta}{2} | \hat{\chi} | p - \frac{\eta}{2} \rangle. \quad (4.2)$$

The Weyl transform has important characteristics which will be explained below. A useful property is that the integral over phase space of the product of Weyl transforms of two operators is equal to the trace of their product [22]

$$Tr[\hat{\chi}_1 \hat{\chi}_2] = \frac{1}{2\pi\hbar} \iint \tilde{\chi}_1(r, p) \tilde{\chi}_2(r, p) dr dp. \quad (4.3)$$

Firstly, Schrödinger describes quantum mechanics using operators acting on a wave function in coordinate space and Heisenberg did it by using operators given by matrices. Weyl found a way to convert an operator into a function of phase space by using his transformation. Following this idea, Wigner introduced his representation stating that quantum mechanics could

be described not only by operators, but by functions as well. The Wigner function of N particles is obtained as the Weyl transform of the density matrix divided by $(2\pi\hbar)^N$

$$\begin{aligned} f_W(r, p) &= \frac{1}{(2\pi\hbar)^N} \int d^N \xi \exp\left[\frac{i}{\hbar} p \cdot \xi\right] \left\langle r - \frac{\xi}{2} \left| \hat{\rho} \right| r + \frac{\xi}{2} \right\rangle \\ &= W\left\{ \hat{\rho} \left(r - \left(\frac{\xi}{2}\right), r + \left(\frac{\xi}{2}\right) \right) \right\}. \end{aligned} \quad (4.4)$$

Equation. (4.4) defines the Wigner function with the Weyl transform of the density matrix. This equation introduces a phase-space representation for quantum-mechanical operators. Using Eq. (4.2) the Wigner function can be also introduced starting from the momentum representation of the density operator as

$$f_W(r, p) = \frac{1}{(2\pi\hbar)^N} \int d^N \eta \exp\left[\frac{i}{\hbar} r \cdot \eta\right] \left\langle p - \frac{\eta}{2} \left| \hat{\rho} \right| p + \frac{\eta}{2} \right\rangle. \quad (4.5)$$

For a pure state the Wigner function is simply

$$f_W(r, p) = \frac{1}{(2\pi\hbar)^N} \int d^N \xi \exp\left[\frac{i}{\hbar} p \cdot \xi\right] \psi\left(r - \frac{\xi}{2}\right) \psi^*\left(r + \frac{\xi}{2}\right) \quad (4.6)$$

where ψ^* is the complex conjugate of ψ . Analogously, for the momentum representation,

$$f_W(r, p) = \frac{1}{(2\pi\hbar)^N} \int d^N \eta \exp\left[\frac{i}{\hbar} p \cdot \eta\right] \psi\left(r - \frac{\eta}{2}\right) \psi^*\left(r + \frac{\eta}{2}\right). \quad (4.7)$$

It is also useful to define the inverse of the Weyl transform of the density matrix, for example, in the coordinate representation. Using Eq. (4.4), the inverse of the Weyl transform of the density matrix can be expressed by multiplying both sides of the equation by the integral $\int d^N p \exp\left[-\frac{i}{\hbar} p \cdot \xi'\right]$. It

becomes:

$$\begin{aligned}
\int d^N p \exp[-\frac{i}{\hbar} p \cdot \xi'] f_W(r, p) &= \frac{1}{(2\pi\hbar)^N} \int d^N \xi \exp[\frac{i}{\hbar} p \cdot \xi] \langle r - \frac{\xi}{2} | \hat{\rho} | r + \frac{\xi}{2} \rangle \\
&\times \int d^N p \exp[-\frac{i}{\hbar} p \cdot \xi'] \\
&= \frac{1}{(2\pi\hbar)^N} \int d^N \xi \int d^N p \exp[\frac{i}{\hbar} p \cdot (\xi - \xi')] \\
&\times \langle r - \frac{\xi}{2} | \hat{\rho} | r + \frac{\xi}{2} \rangle \\
&= \int d^N \xi \delta(\xi - \xi') \langle r - \frac{\xi}{2} | \hat{\rho} | r + \frac{\xi}{2} \rangle. \quad (4.8)
\end{aligned}$$

Using the properties of the delta function for the integral the above expression becomes

$$\begin{aligned}
\int d^N p \exp[-\frac{i}{\hbar} p \cdot \xi'] f_W(r, p) &= \langle r - \frac{\xi'}{2} | \hat{\rho} | r + \frac{\xi'}{2} \rangle \\
\langle r - \frac{\xi'}{2} | \hat{\rho} | r + \frac{\xi'}{2} \rangle &= \int d^N p \exp[-\frac{i}{\hbar} p \cdot \xi'] f_W(r, p), \quad (4.9)
\end{aligned}$$

which results in

$$\begin{aligned}
\rho(r - (\frac{\xi}{2}), r + (\frac{\xi}{2})) &= W^{-1}\{f_W(r, p)\} \\
&= \int d^N p \exp[-\frac{i}{\hbar} p \cdot \xi] f_W(r, p). \quad (4.10)
\end{aligned}$$

It follows directly from Eqs. (4.4) and (4.5) that the Wigner function satisfies the position-probability distribution,

$$\int_{-\infty}^{+\infty} f_W(r, p) dp = \langle r | \hat{\rho} | r \rangle, \quad (4.11)$$

and momentum-probability distribution

$$\int_{-\infty}^{+\infty} f_W(r, p) dr = \langle p | \hat{\rho} | p \rangle. \quad (4.12)$$

For a pure state, the position-probability distribution is given by

$$\int_{-\infty}^{+\infty} f_W(r, p) dp = |\psi(r)|^2, \quad (4.13)$$

analogously, the momentum-probability distribution is expressed as

$$\int_{-\infty}^{+\infty} f_W(r, p) dr = |\psi(p)|^2. \quad (4.14)$$

From the above two equations, it is easy to show that Eq. (3.47) implies that the Wigner function is normalised over phase space. This can be easily proven as follows.

Begin by taking the Weyl transform of the identity operator \hat{I} , and show that it is equal to 1:

$$\begin{aligned}
\tilde{I} &= \int d^N \xi \exp\left[\frac{i}{\hbar} p \cdot \xi\right] \left\langle r - \frac{\xi}{2} \left| \hat{I} \right| r + \frac{\xi}{2} \right\rangle \\
&= \int d^N \xi \exp\left[\frac{i}{\hbar} p \cdot \xi\right] \delta\left(r + \frac{\xi}{2} - r + \frac{\xi}{2}\right) \\
&= \int \exp\left[\frac{i}{\hbar} p \cdot \xi\right] \delta(\xi) d^N \xi = 1.
\end{aligned} \tag{4.15}$$

Referring to the trace of two operators given by Eq. (4.3), and using Eq. (4.4) one finds that

$$\begin{aligned}
Tr\left(\hat{\rho} \hat{I}\right) &= \frac{1}{(2\pi\hbar)^N} \iint \tilde{\rho}(r, p) \tilde{I}(r, p) dr dp \\
&= \iint f_W(r, p) dr dp = Tr[\hat{\rho}] = 1.
\end{aligned} \tag{4.16}$$

It is also possible to show that the Wigner function is real by using the condition (3.50). The complex conjugate of Eq. (4.4) can be expressed as

$$\begin{aligned}
\left(f_W(r, p)\right)^* &= \frac{1}{(2\pi\hbar)^N} \left(\int d^N \xi \exp\left[\frac{i}{\hbar} p \cdot \xi\right] \left\langle r - \frac{\xi}{2} \left| \hat{\rho} \right| r + \frac{\xi}{2} \right\rangle \right)^* \\
&= \frac{1}{(2\pi\hbar)^N} \int d^N \xi \exp\left[-\frac{i}{\hbar} p \cdot \xi\right] \left\langle r - \frac{\xi}{2} \left| \hat{\rho}^\dagger \right| r + \frac{\xi}{2} \right\rangle,
\end{aligned} \tag{4.17}$$

by changing the variable of integration from ξ to $-\xi$ and using the fact that the density matrix is hermitian, one obtains

$$\left(f_W(r, p)\right)^* = \frac{1}{(2\pi\hbar)^N} \int d^N \xi \exp\left[\frac{i}{\hbar} p \cdot \xi\right] \left\langle r - \frac{\xi}{2} \left| \hat{\rho} \right| r + \frac{\xi}{2} \right\rangle = f_W(r, p). \tag{4.18}$$

Thus Eq. (4.18) shows that $f_W(r, p)$ is real.

The expression given in Eq. (4.3) provides a way to calculate averages of any dynamical variable using the Wigner function. In this case, the average of any dynamical variable $\hat{\chi}$ in the state represented by the density matrix $\hat{\rho}$ is given by $Tr\{\hat{\rho}\hat{\chi}\}$. This trace can be expressed with the Wigner function.

To this end, it is useful to first define the Wigner representation of any operator $\hat{\chi}$, other than $\hat{\rho}$ as,

$$\chi_W(r, p) = \int d^N \xi \exp\left[\frac{i}{\hbar} p \cdot \xi\right] \langle r - \frac{\xi}{2} | \hat{\chi} | r + \frac{\xi}{2} \rangle. \quad (4.19)$$

Therefore, to find the phase-space expression of quantum averages in the Wigner formalism, it is necessary to write the trace in the position representation

$$Tr\{\hat{\rho}\hat{\chi}\} = \int d^N r_1 d^N r_2 \langle r_1 | \hat{\rho} | r_2 \rangle \langle r_2 | \hat{\chi} | r_1 \rangle. \quad (4.20)$$

Then, make the following change of variables

$$\begin{cases} r_1 &= r - \xi_1/2 \\ r_2 &= r + \xi_1/2, \end{cases} \quad (4.21)$$

so the Jacobian of the previous system is given by

$$|\mathbf{J}| = \begin{vmatrix} \frac{\partial r_1}{\partial r} & \frac{\partial r_1}{\partial \xi_1} \\ \frac{\partial r_2}{\partial r} & \frac{\partial r_2}{\partial \xi_1} \end{vmatrix} = 1. \quad (4.22)$$

The quantum average in Eq. (4.20) can be written as

$$\begin{aligned} Tr\{\hat{\rho}\hat{\chi}\} &= \int d^N r d^N \xi_1 \langle r - \xi_1/2 | \hat{\rho} | r + \xi_1/2 \rangle \langle r + \xi_1/2 | \hat{\chi} | r - \xi_1/2 \rangle \\ &= \int d^N r d^N \xi_1 d^N \xi_2 \langle r - \xi_1/2 | \hat{\rho} | r + \xi_1/2 \rangle \\ &\quad \times \langle r - \xi_2/2 | \hat{\chi} | r + \xi_2/2 \rangle \delta(\xi_1 + \xi_2), \end{aligned} \quad (4.23)$$

where the second term of the first line can be expressed in the following form using a delta function as

$$\langle r + \xi_1/2 | \hat{\chi} | r - \xi_1/2 \rangle = \int d\xi_2 \delta(\xi_2 + \xi_1) \langle r - \xi_2/2 | \hat{\chi} | r + \xi_2/2 \rangle. \quad (4.24)$$

Introducing the integral representation of the delta function written as

$$\delta(\xi_1 + \xi_2) = \frac{1}{(2\pi\hbar)^N} \int d^N p \exp\left[\frac{i}{\hbar} p \cdot (\xi_1 + \xi_2)\right], \quad (4.25)$$

Eq. (4.23) becomes

$$\begin{aligned}
Tr\{\hat{\rho}\hat{\chi}\} &= \int d^N r d^N \xi_1 d^N \xi_2 \langle r - \xi_1/2 | \hat{\rho} | r + \xi_1/2 \rangle \langle r - \xi_2/2 | \hat{\chi} | r + \xi_2/2 \rangle \\
&\quad \times \frac{1}{(2\pi\hbar)^N} \int d^N p \exp\left[\frac{i}{\hbar} p \cdot (\xi_1 + \xi_2)\right] \\
&= \int d^N r d^N p \frac{1}{(2\pi\hbar)^N} \int d^N \xi_1 \exp\left[\frac{i}{\hbar} p \cdot \xi_1\right] \langle r - \xi_1/2 | \hat{\rho} | r + \xi_1/2 \rangle \\
&\quad \times \int d^N \xi_2 \exp\left[\frac{i}{\hbar} p \cdot \xi_2\right] \langle r - \xi_2/2 | \hat{\chi} | r + \xi_2/2 \rangle. \tag{4.26}
\end{aligned}$$

Using the definition of the Weyl transform of the density matrix in Eq. (4.4), and the definition of the Weyl transform of an arbitrary quantum operator in Eq. (4.19), the above expression becomes

$$Tr\{\hat{\rho}\hat{\chi}\} = \int d^N r d^N p f_W(r, p) \chi_W(r, p). \tag{4.27}$$

Eq. (4.27) shows that quantum averages can be expressed as classical statistical averages in phase space. The similarity of these formulae to a classical phase-space average does not imply that quantum and classical theories are the same because there are important differences. The first is that, in general, the Wigner function cannot be interpreted as a true phase-space distribution function because it is not positive everywhere.

Consider two orthogonal states of a system ψ_1 and ψ_2 where their scalar product is equal to zero $\langle \psi_1 | \psi_2 \rangle = 0$. The trace product of two operators is the square of the scalar product of the two states, written as

$$Tr[\hat{\rho}_1 \hat{\rho}_2] = |\langle \psi_1 | \psi_2 \rangle|^2, \tag{4.28}$$

and for orthogonal states, the above expression is equal to zero. This is written as

$$\iint f_{W_1}(r, p) f_{W_2}(r, p) dr dp = 0. \tag{4.29}$$

It follows from Eq. (4.29) that $f_{W_1}(r, p)$ or $f_{W_2}(r, p)$ or both must be negative for some regions in phase space. For this reason the Wigner function cannot be interpreted as a probability in phase space.

The nonnegativeness property of the density matrix, given in Eq. (3.51), has its consequences in the Wigner representation due to the indeterminacy principle. To see this, consider two density operators given by $\hat{\rho}_1$ and $\hat{\rho}_2$. The trace of their product obeys the following constraints

$$0 \leq Tr\{\hat{\rho}_1\hat{\rho}_2\} \leq 1. \quad (4.30)$$

Using Eq. (4.3) and Eq. (4.4) the trace product of these two operators can be obtained

$$Tr\{\hat{\rho}_1\hat{\rho}_2\} = \frac{1}{(2\pi\hbar)^N} \iint (2\pi\hbar)^N f_{W_1}(r,p)(2\pi\hbar)^N f_{W_2}(r,p) d^N r d^N p, \quad (4.31)$$

so that Eq. (4.30) implies

$$0 \leq \int d^N r d^N p f_{W_1}(r,p) f_{W_2}(r,p) \leq \frac{1}{(2\pi\hbar)^N}. \quad (4.32)$$

For the special case $\hat{\rho}_1 = \hat{\rho}_2$, one gets

$$\int d^N r d^N p (f_W(r,p))^2 \leq \frac{1}{(2\pi\hbar)^N}, \quad (4.33)$$

which is an interesting property of functions. It shows that f_W cannot be too sharply peaked [7]. For example, imagine there is a Wigner function that vanishes outside some region of phase space of area σ and has the value σ^{-1} inside that region. Then Eq. (4.33) would lead to

$$\frac{1}{\sigma} \leq \frac{1}{(2\pi\hbar)^N}, \quad (4.34)$$

and this would imply

$$\sigma \geq (2\pi\hbar)^N. \quad (4.35)$$

This latter equation shows that the support area of f_W cannot be as small as one pleases. This result is related to the indeterminacy principle, and it has interesting implications for the quantum law of motion in the Wigner representation [7, 24].

4.2 Derivation of the quantum Wigner-Liouville equation

Let us consider an arbitrary quantum system and its representation in configuration space. As a starting point, one could think of a system of N quantum distinguishable particles with Cartesian coordinates r . The distinguishability hypothesis is not necessary, but it will be adopted not to be burdened with symmetry considerations [23]. The density matrix will be denoted with $\hat{\rho}(r, r')$. Averages of operators can be calculated as

$$a(t) = \langle \hat{A}(r, r') \rangle_t \equiv Tr \left\{ \hat{\rho}(r, r'; t) \hat{A}(r', r) \right\}. \quad (4.36)$$

The density matrix obeys the quantum Liouville equation of motion

$$\frac{\partial}{\partial t} \hat{\rho} = \frac{i}{\hbar} [\hat{\rho}, \hat{H}], \quad (4.37)$$

where \hat{H} is the Hamiltonian (energy operator) of the system

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{\Phi}(r), \quad (4.38)$$

m denotes the particle mass, $\hat{\Phi}$ is the potential energy operator and \hat{p} is the momentum operator.

The quantum Liouville equation (4.37) for the density matrix induces an equation of motion for the Wigner function. This can be obtained by taking the coordinate representation of Eq. (4.37)

$$\begin{aligned} \frac{\partial}{\partial t} \langle r | \hat{\rho} | r' \rangle &= \frac{i}{\hbar} \langle r | [\hat{\rho}, \hat{H}] | r' \rangle \\ &= \frac{i}{\hbar} \langle r | \left(\hat{\rho} \hat{H} - \hat{H} \hat{\rho} \right) | r' \rangle \\ &= \frac{i}{\hbar} \left[\langle r | \hat{\rho} \hat{H} | r' \rangle - \langle r | \hat{H} \hat{\rho} | r' \rangle \right], \end{aligned} \quad (4.39)$$

where a Dirac bra-ket notation has been introduced for the eigenfunction of the position operator \hat{r} of the system. By using the closure relation of the

position basis

$$\langle r|\hat{\rho}\hat{H}|r'\rangle = \int dr'' \langle r|\hat{\rho}|r''\rangle \langle r''|\hat{H}|r'\rangle \quad (4.40)$$

$$\langle r|\hat{H}\hat{\rho}|r'\rangle = \int dr'' \langle r|\hat{H}|r''\rangle \langle r''|\hat{\rho}|r'\rangle, \quad (4.41)$$

the right-hand side of Eq. (4.39) becomes

$$\begin{aligned} & \int dr'' \left(\langle r|\hat{\rho}|r''\rangle \langle r''|\hat{H}|r'\rangle - \langle r|\hat{H}|r''\rangle \langle r''|\hat{\rho}|r'\rangle \right) \\ &= \int dr'' \left(\rho(r, r'') \langle r''|\hat{H}|r'\rangle - \langle r|\hat{H}|r''\rangle \rho(r'', r') \right). \end{aligned} \quad (4.42)$$

Consider the matrix elements of the Hamiltonian,

$$\begin{aligned} \langle r''|\hat{H}|r'\rangle &= \langle r''|\left(\frac{\hat{p}^2}{2m} + \hat{\Phi}\right)|r'\rangle \\ &= \langle r''|\frac{\hat{p}^2}{2m}|r'\rangle + \langle r''|\hat{\Phi}|r'\rangle \\ &= \frac{\hat{p}^2}{2m} \langle r''|r'\rangle + \hat{\Phi} \langle r''|r'\rangle, \end{aligned} \quad (4.43)$$

the orthonormality condition $\langle r''|r'\rangle = \delta(r'' - r')$, and the position representation of the linear momentum operator in one-dimensional space $\hat{p} = -i\hbar \frac{\partial}{\partial r}$

$$\langle r''|\hat{H}|r'\rangle = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r''^2} \delta(r'' - r') + \Phi(r'') \delta(r'' - r'), \quad (4.44)$$

and similarly

$$\langle r|\hat{H}|r''\rangle = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r''^2} \delta(r - r'') + \Phi(r'') \delta(r - r''). \quad (4.45)$$

The commutator in Eq. (4.39) becomes

$$\begin{aligned} \langle r|[\hat{\rho}, \hat{H}]|r'\rangle &= \int dr'' \left[\rho(r, r'') \left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r''^2} + \Phi(r'') \right) \delta(r'' - r') \right. \\ &\quad \left. - \left[\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial r''^2} + \Phi(r'') \right) \delta(r - r'') \right] \rho(r'', r') \right] \\ &= \int dr'' \left[\rho(r, r'') \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \delta(r'' - r')}{\partial r''^2} \right) \right. \\ &\quad \left. + \rho(r, r'') \Phi(r'') \delta(r'' - r') \right] \\ &\quad - \int dr'' \left[\left(-\frac{\hbar^2}{2m} \frac{\partial^2 \delta(r - r'')}{\partial r''^2} \right) \rho(r'', r') \right. \\ &\quad \left. + \Phi(r'') \delta(r - r'') \rho(r'', r') \right] \end{aligned} \quad (4.46)$$

and for the integration the following symbols are used

$$\begin{aligned}
A &= \rho(r, r'') \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \delta(r'' - r')}{\partial r''^2} \right) \\
B &= \rho(r, r'') \Phi(r'') \delta(r'' - r') \\
C &= \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \delta(r - r'')}{\partial r''^2} \right) \rho(r'', r') \\
D &= \Phi(r'') \delta(r - r'') \rho(r'', r').
\end{aligned}$$

Using the properties of the Dirac function and by integrating by parts, the integrals of equation (4.46) are obtained. The solutions are given as

$$\int A dr'' = -\frac{\hbar^2}{2m} \int dr'' \delta(r'' - r') \frac{\partial^2 \rho(r, r'')}{\partial r''^2} \quad (4.47)$$

$$\int B dr'' = \rho(r, r') \Phi(r') \quad (4.48)$$

$$\int C dr'' = -\frac{\hbar^2}{2m} \int dr'' \delta(r - r'') \frac{\partial^2 \rho(r'', r')}{\partial r''^2} \quad (4.49)$$

$$\int D dr'' = \rho(r, r') \Phi(r). \quad (4.50)$$

Hence, Eq. (4.46) becomes

$$\begin{aligned}
\langle r | [\hat{\rho}, \hat{H}] | r' \rangle &= \int dr'' \left[-\frac{\hbar^2}{2m} \frac{\partial^2 \rho(r, r'')}{\partial r''^2} \delta(r'' - r') + \rho(r, r'') \Phi(r'') \delta(r'' - r') \right. \\
&\quad \left. + \frac{\hbar^2}{2m} \frac{\partial^2 \rho(r'', r')}{\partial r''^2} \delta(r - r'') - \Phi(r'') \rho(r'', r') \delta(r - r'') \right] \\
&= -\frac{\hbar^2}{2m} \frac{\partial^2 \rho(r, r')}{\partial r'^2} + \rho(r, r') \Phi(r') + -\frac{\hbar^2}{2m} \frac{\partial^2 \rho(r, r')}{\partial r^2} - \Phi(r) \rho(r, r') \\
&= \frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial r^2} - \frac{\partial^2}{\partial r'^2} \right) \rho(r, r') - \left(\Phi(r) - \Phi(r') \right) \rho(r, r'). \quad (4.51)
\end{aligned}$$

Using Eq. (4.51), the laws of the evolution for the density matrix can be rewritten as

$$\frac{\partial}{\partial t} \rho(r, r') = \frac{i\hbar}{2m} \left(\frac{\partial^2}{\partial r^2} - \frac{\partial^2}{\partial r'^2} \right) \rho(r, r') - \frac{i}{\hbar} \left(\Phi(r) - \Phi(r') \right) \rho(r, r'). \quad (4.52)$$

Then, the following change of variables can be performed

$$\begin{cases} r = \tilde{r} - \frac{\xi}{2} \\ r' = \tilde{r} + \frac{\xi}{2} \end{cases} \quad \begin{cases} \tilde{r} = \frac{r+r'}{2} \\ \xi = r' - r \end{cases} \quad (4.53)$$

with the Jacobian equal to

$$|\mathbf{J}| = \begin{vmatrix} \frac{\partial r}{\partial \tilde{r}} & \frac{\partial r}{\partial \xi} \\ \frac{\partial r'}{\partial \tilde{r}} & \frac{\partial r'}{\partial \xi} \end{vmatrix} = 1. \quad (4.54)$$

Using the variables in Eq. (4.53), the following results are found

$$\begin{aligned} \frac{\partial}{\partial r} &= \frac{\partial}{\partial \tilde{r}} \frac{\partial \tilde{r}}{\partial r} + \frac{\partial}{\partial \xi} \frac{\partial \xi}{\partial r} & \frac{\partial^2}{\partial r^2} &= \left(-\frac{\partial}{\partial \xi} + \frac{1}{2} \frac{\partial}{\partial \tilde{r}}\right) \left(-\frac{\partial}{\partial \xi} + \frac{1}{2} \frac{\partial}{\partial \tilde{r}}\right) \\ &= -\frac{\partial}{\partial \xi} + \frac{1}{2} \frac{\partial}{\partial \tilde{r}} & &= \frac{\partial^2}{\partial \xi^2} - \frac{\partial^2}{\partial \tilde{r} \partial \xi} + \frac{1}{4} \frac{\partial^2}{\partial \tilde{r}^2} \\ \frac{\partial}{\partial r'} &= \frac{\partial}{\partial \tilde{r}} \frac{\partial \tilde{r}}{\partial r'} + \frac{\partial}{\partial \xi} \frac{\partial \xi}{\partial r'} & \frac{\partial^2}{\partial r'^2} &= \left(\frac{\partial}{\partial \xi} + \frac{1}{2} \frac{\partial}{\partial \tilde{r}}\right) \left(\frac{\partial}{\partial \xi} + \frac{1}{2} \frac{\partial}{\partial \tilde{r}}\right) \\ &= \frac{\partial}{\partial \xi} + \frac{1}{2} \frac{\partial}{\partial \tilde{r}} & &= \frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \tilde{r} \partial \xi} + \frac{1}{4} \frac{\partial^2}{\partial \tilde{r}^2} \end{aligned} \quad (4.55)$$

so that the evolution equation for the density matrix becomes

$$\begin{aligned} \frac{\partial}{\partial t} \rho \left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2} \right) &= -\frac{i\hbar}{m} \frac{\partial^2}{\partial \tilde{r} \partial \xi} \rho \left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2} \right) \\ &\quad - \frac{i}{\hbar} \left(\Phi \left(\tilde{r} - \frac{\xi}{2} \right) - \Phi \left(\tilde{r} + \frac{\xi}{2} \right) \right) \rho \left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2} \right). \end{aligned} \quad (4.56)$$

To obtain the law of motion for the Wigner distribution function, the Fourier transform of Eq. (4.56) will be taken using the definition given in Eq. (4.4). The Fourier transform of the left-hand side of Eq. (4.56) is trivial and gives $\partial_t f_W(r, p)$. The Fourier transform of the first term on the right-hand side of Eq. (4.56) gives

$$\mathcal{F} \left\{ -\frac{i\hbar}{m} \frac{\partial^2}{\partial \tilde{r} \partial \xi} \rho \left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2} \right) \right\} = \frac{-i\hbar}{m} \frac{1}{(2\pi\hbar)^N} \int d^N \xi e^{\frac{i}{\hbar} p \xi} \frac{\partial^2}{\partial \tilde{r} \partial \xi} \rho \left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2} \right) \quad (4.57)$$

and by integration by parts one gets

$$\begin{aligned} -\frac{i\hbar}{m} \frac{\partial^2}{\partial \tilde{r} \partial \xi} \rho \left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2} \right) &= \frac{-i\hbar}{m} \frac{1}{(2\pi\hbar)^N} \frac{\partial}{\partial \tilde{r}} \int d^N \xi e^{\frac{i}{\hbar} p \xi} \left(-\frac{ip}{\hbar} \right) \\ &\quad \times \rho \left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2} \right) \\ &= -\frac{p}{m} \frac{\partial}{\partial \tilde{r}} f_W(\tilde{r}, p). \end{aligned} \quad (4.58)$$

The Fourier transform of the second term on the right-hand side of Eq. (4.56) gives

$$\begin{aligned}
& -\frac{i}{\hbar} \frac{1}{(2\pi\hbar)^N} \int d^N \xi \left[\Phi\left(\tilde{r} - \frac{\xi}{2}\right) - \Phi\left(\tilde{r} + \frac{\xi}{2}\right) \right] e^{\frac{i}{\hbar} p \xi} \rho\left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2}\right) \\
= & -\frac{i}{\hbar} \frac{1}{(2\pi\hbar)^N} \int d^N \xi d^N r' \delta\left(r' - \frac{\xi}{2}\right) [\Phi(\tilde{r} - r') - \Phi(\tilde{r} + r')] e^{\frac{i}{\hbar} p \xi} \\
& \times \rho\left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2}\right)
\end{aligned} \tag{4.59}$$

where the definition of the delta function has been used. Using the following integral representation of the Dirac delta function

$$\delta\left(r' - \frac{\xi}{2}\right) = \frac{1}{(2\pi\hbar)^N} \int d^N p' \exp\left[\frac{i}{\hbar} p' \left(r' - \frac{\xi}{2}\right)\right], \tag{4.60}$$

one gets

$$\begin{aligned}
= & -\frac{i}{\hbar} \frac{1}{(2\pi\hbar)^{2N}} \int d^N \xi d^N r' d^N p' e^{\frac{i}{\hbar} p' (r' - \frac{\xi}{2})} e^{\frac{i}{\hbar} p \xi} \\
& \times [\Phi(\tilde{r} - r') - \Phi(\tilde{r} + r')] \rho\left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2}\right),
\end{aligned} \tag{4.61}$$

which can be easily read as

$$\begin{aligned}
= & -\frac{i}{\hbar} \frac{1}{(2\pi\hbar)^{2N}} \int d^N \xi e^{\frac{i}{\hbar} p \xi} \int d^N r' d^N p' e^{-\frac{i}{\hbar} p' \frac{\xi}{2}} \\
& \times \left[\Phi(\tilde{r} - r') e^{\frac{i}{\hbar} p' r'} - \Phi(\tilde{r} + r') e^{\frac{i}{\hbar} p' r'} \right] \rho\left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2}\right).
\end{aligned} \tag{4.62}$$

Making the change of variables $r' = -r'$, the above expression can be written as

$$\begin{aligned}
&= -\frac{i}{\hbar} \frac{1}{(2\pi\hbar)^{2N}} \int d^N \xi e^{\frac{i}{\hbar} p \xi} \int d^N r' d^N p' e^{-\frac{i}{\hbar} p' \frac{\xi}{2}} \\
&\quad \times \left[\Phi(\tilde{r} - r') e^{\frac{i}{\hbar} p' r'} - \Phi(\tilde{r} + r') e^{-\frac{i}{\hbar} p' r'} \right] \rho\left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2}\right) \\
&= -\frac{i}{\hbar} \frac{1}{(2\pi\hbar)^{2N}} \int d^N \xi e^{\frac{i}{\hbar} p \xi} \int d^N r' d^N p' e^{-\frac{i}{\hbar} p' \frac{\xi}{2}} \Phi(\tilde{r} - r') \\
&\quad \times \left[e^{\frac{i}{\hbar} p' r'} - e^{-\frac{i}{\hbar} p' r'} \right] \rho\left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2}\right) \\
&= -\frac{i}{\hbar} \frac{1}{(2\pi\hbar)^{2N}} \int d^N \xi e^{\frac{i}{\hbar} p \xi} \int d^N r' d^N p' e^{-\frac{i}{\hbar} p' \frac{\xi}{2}} \Phi(\tilde{r} - r') \\
&\quad \times 2i \sin\left(\frac{p' r'}{\hbar}\right) \rho\left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2}\right) \\
&= \frac{2}{\hbar} \frac{1}{(2\pi\hbar)^N} \int d^N \xi \int \frac{d^N r' d^N p'}{(2\pi\hbar)^N} e^{\frac{i}{\hbar}(p - \frac{p'}{2})\xi} \Phi(\tilde{r} - r') \\
&\quad \times \sin\left(\frac{p' r'}{\hbar}\right) \rho\left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2}\right). \tag{4.63}
\end{aligned}$$

Then, performing the following change of variables

$$s = \frac{p'}{2} \quad d^N p' = 2^N d^N s, \tag{4.64}$$

Eq. (4.59) becomes

$$\begin{aligned}
&\frac{2^{N+1}}{\hbar(2\pi\hbar)^N} \int d^N \xi \frac{d^N r' d^N s}{(2\pi\hbar)^N} e^{\frac{i}{\hbar}(p-s)\xi} \Phi(\tilde{r} - r') \sin\left(\frac{2sr'}{\hbar}\right) \\
&\quad \times \rho\left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2}\right), \\
&= \frac{2}{\hbar(2\pi\hbar)^N} \int d^N r' d^N s \Phi(\tilde{r} - r') \sin\left(\frac{2sr'}{\hbar}\right) f_W(r, p - s). \tag{4.65}
\end{aligned}$$

Combining Eq. (4.58) and (4.65), one obtains the Wigner-Liouville equation of motion in the form

$$\begin{aligned}
\frac{\partial}{\partial t} f_W(r, p) &= -\frac{p}{m} \frac{\partial}{\partial r} f_W(r, p) \\
&\quad + \frac{2}{\hbar(\pi\hbar)^N} \int d^N r' d^N s \Phi(r - r') \sin\left(\frac{2sr'}{\hbar}\right) f_W(r, p - s). \tag{4.66}
\end{aligned}$$

Equation (4.66) provides the law of evolution of the Wigner function. It is an integro-differential equation permitting the representation of quantum

evolution in phase space. Recent attempts to apply such an equation to study condensed matter systems can be found in Refs. [23, 28, 29].

Consider the potential term in Eq. (4.56)

$$-\frac{i}{\hbar} \left[\Phi \left(\tilde{r} - \frac{\xi}{2} \right) - \Phi \left(\tilde{r} + \frac{\xi}{2} \right) \right] \rho \left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2} \right). \quad (4.67)$$

If the potential is continuous, then a Taylor expansion can be performed

$$f(x) = \sum_{k=0}^{\infty} \frac{(x-x_0)^k}{k!} f^{(k)}(x_0). \quad (4.68)$$

Now consider the following change of variables

$$x_0 = \tilde{r} \quad , \quad x = \tilde{r} - \xi/2$$

$$\Phi \left(\tilde{r} - \frac{\xi}{2} \right) = \Phi(\tilde{r}) - \frac{\partial \Phi(\tilde{r})}{\tilde{r}} \frac{\xi}{2} + \frac{1}{2} \frac{\partial^2 \Phi(\tilde{r})}{\partial \tilde{r}^2} \frac{\xi^2}{4} - \dots \quad (4.69)$$

$$\Phi \left(\tilde{r} + \frac{\xi}{2} \right) = \Phi(\tilde{r}) + \frac{\partial \Phi(\tilde{r})}{\tilde{r}} \frac{\xi}{2} + \frac{1}{2} \frac{\partial^2 \Phi(\tilde{r})}{\partial \tilde{r}^2} \frac{\xi^2}{4} + \dots \quad (4.70)$$

so that

$$\Phi \left(\tilde{r} - \frac{\xi}{2} \right) - \Phi \left(\tilde{r} + \frac{\xi}{2} \right) = -2 \sum_{\substack{n=1 \\ \text{odd}}} \left(\frac{\xi}{2} \right)^n \frac{1}{n!} \frac{\partial^n \Phi(\tilde{r})}{\partial \tilde{r}^n}. \quad (4.71)$$

With this result, Eq. (4.67) becomes

$$\frac{2i}{\hbar} \sum_{\substack{n=1 \\ \text{odd}}} \left(\frac{\xi}{2} \right)^n \frac{1}{n!} \frac{\partial^n \Phi(\tilde{r})}{\partial \tilde{r}^n} \rho \left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2} \right) \quad (4.72)$$

Taking the Wigner-transformed it is found that:

$$\begin{aligned} & \frac{1}{(2\pi\hbar)^N} \frac{2i}{\hbar} \sum_{\substack{n=1 \\ \text{odd}}} \frac{1}{n!} \frac{\partial^n \Phi(\tilde{r})}{\partial \tilde{r}^n} \int d^N \xi \left(\frac{\xi}{2} \right)^n e^{\frac{i}{\hbar} p \xi} \rho \left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2} \right) \\ &= \frac{1}{(2\pi\hbar)^N} \frac{2i}{\hbar} \sum_{\substack{n=1 \\ \text{odd}}} \frac{1}{n!} \frac{\partial^n \Phi(\tilde{r})}{\partial \tilde{r}^n} \int d^N \xi \left(\frac{\hbar}{2i} \right)^n \frac{\partial^n}{\partial p^n} e^{\frac{i}{\hbar} p \xi} \rho \left(\tilde{r} - \frac{\xi}{2}, \tilde{r} + \frac{\xi}{2} \right) \\ &= \sum_{\substack{n=1 \\ \text{odd}}} \frac{1}{n!} \left(\frac{\hbar}{2i} \right)^{n-1} \frac{\partial^n \Phi(\tilde{r})}{\partial \tilde{r}^n} \frac{\partial^n}{\partial p^n} f_W(\tilde{r}, p). \end{aligned} \quad (4.73)$$

where in the second equality, the following expression

$$\xi e^{\frac{i}{\hbar} p \xi} = \frac{\hbar}{i} \frac{\partial}{\partial p} e^{\frac{i}{\hbar} p \xi} \quad (4.74)$$

has been used. Therefore, the quantum Wigner-Liouville equation for a continuous potential can be written as

$$\frac{\partial}{\partial t} f_W(r, p) = -\frac{p}{m} \frac{\partial}{\partial r} f_W(r, p) + \sum_{\substack{n=1 \\ \text{odd}}} \frac{1}{n!} \left(\frac{\hbar}{2i} \right)^{n-1} \frac{\partial^n \Phi(r)}{\partial r^n} \frac{\partial^n}{\partial p^n} f_W(r, p). \quad (4.75)$$

4.2.1 Extraneous solutions of the quantum Wigner-Liouville equation.

In Wigner's representation, the difference between classical and quantum mechanics does not reside merely in the difference between the quantum and classical Liouville equations of motion [30, 31]. To see this Eq. (4.75) can be re-arranged as

$$\begin{aligned} \frac{\partial}{\partial t} f_W(r, p) = & \left[-\frac{p}{m} \frac{\partial}{\partial r} + \frac{\partial \Phi(r)}{\partial r} \frac{\partial}{\partial p} \right] f_W(r, p) \\ & + \sum_{\substack{n=3 \\ \text{odd}}} \frac{1}{n!} \left(\frac{\hbar}{2i} \right)^{n-1} \frac{\partial^n \Phi(r)}{\partial r^n} \frac{\partial^n}{\partial p^n} f_W(r, p). \end{aligned} \quad (4.76)$$

If corrections of order $\vartheta(\hbar^2)$ can be neglected, the quantum Wigner-Liouville equation reduces to the classical Liouville equation [21]. However, such considerations can be misleading because the correction terms in Eq. (4.75) or (4.76) are of order \hbar^n only formally. As a matter of fact, correction terms in Eq. (4.76) also contain n -th order derivatives of f_W with respect to p . Since, as it will be shown in the following, f_W depends on \hbar , such derivatives can generate factors of $1/\hbar$ that would cancel the explicit \hbar factors in Eq. (4.76). In other words, the Wigner representation makes apparent that the quantum law of motion also involves quantum initial conditions which must be obeyed by their solution. This is also true in the Schödinger formulation of quantum mechanics, because the wave function depends on \hbar . However,

as it is within the Wigner representation, it cannot be disregarded at any level. An obvious example is provided by the quantum harmonic oscillator. Because the potential is harmonic, the correction terms in Eq. (4.76) are identically zero, so that the quantum Wigner-Liouville equation and the classical Liouville equation coincide. However, it is clear that the quantum oscillator is far from being a classical object. Quantum effects, in this case, are solely contained in quantum initial conditions, Eq. (4.33), and in the fact that the Wigner function of a mixed state must be expressible as

$$f_W(r, p) = \sum_k \alpha_k f_W^{(k)}(r, p), \quad (4.77)$$

with

$$0 \leq \alpha_k \leq 1, \quad \sum_k \alpha_k = 1, \quad (4.78)$$

where $f_W^{(k)}$ is the Wigner function of pure states $|\psi^{(k)}\rangle$. If the coefficients of the linear combination in Eq. (4.77) obey the properties in Eq. (4.78), then one has a physically meaningful quantum solution; otherwise, no meaning can be attached to the solutions of Eq. (4.76). It can be shown that once constraints (4.33) and (4.77) are satisfied initially, they remain satisfied under time evolution according to the Wigner-Liouville equation.

Chapter 5

Wigner Quantum Dynamics at Constant Temperature

Modeling open quantum systems [2, 5] is ubiquitous in the theory and application of quantum information [3]. Typically, non-linear and non-Markovian effects still resist general solutions, and this will also be of interest to the emerging field of quantum biology [32]. For such reasons, the development of novel computational algorithms to simulate open quantum systems is an endeavour worth pursuing. To this end, a generalization of Wigner dynamics to constant-temperature conditions [8] has been introduced recently: the so-called Nosè-Wigner dynamics.

In the case of systems described by continuous interaction potentials admitting a convergent Taylor expansion, Wigner's approach to quantum mechanics [14] can be formulated with the Moyal bracket [33]. This provides an algebraic route to the formulation of quantum mechanics in phase space [33, 34]. Recently, generalized brackets have been used to define the equations of motion and statistical mechanics of non-Hamiltonian systems both in the classical [13, 14, 35] and in the quantum context [16, 36, 37]. In particular, it has been shown [16, 38] how to formulate constant-temperature dynamics for quantum-classical systems so that a reduced number of clas-

sical bath degrees of freedom can be used to simulate relaxation dynamics. This required combining the method of constant-temperature dynamics [10, 39] known as Nosè-Hoover dynamics in computer simulations of classical systems with quantum-classical dynamics [16, 37]. In classical molecular dynamics, the Nosè-Hoover equations [10, 39], and their variants [17] sample the canonical ensemble efficiently and can be formulated as non-Hamiltonian phase-space flows [13, 14, 35]. Recently, a formalism to tackle thermal effects in the simulation of open quantum systems via the generalization of Wigner dynamics to constant-temperature situations has been introduced [8]. To sketch the formalism, a generalized Moyal bracket has been defined by recasting it in suitable matrix form [14, 16, 35, 36]. This has generalized the theory given in Refs. [16, 38] to a full Wigner representation [8].

5.1 Wigner's quantum statistical mechanics

In the Wigner representation of quantum mechanics [6], quantum averages can be calculated in phase space as

$$\langle \chi \rangle = \int d^N r d^N p f_W(r, p; t) \chi_W(r, p), \quad (5.1)$$

where $\chi_W(r, p)$ is the Wigner equivalent of a quantum operator $\hat{\chi}$. The use of this Wigner form allows the expression for averages to be written in a way similar to that of classical statistical mechanics. In the following, H_W denotes the Wigner equivalent of the Hamiltonian operator of the system considered. When the interaction potential in H_W admits a convergent series expansion, the time evolution of the Wigner function can be written as

$$\begin{aligned} \frac{\partial}{\partial t} f_W(r, p, t) &= -\frac{i}{\hbar} \left(H_W e^{(i\hbar/2) \overleftarrow{\partial}_k B_{km}^c} \overrightarrow{\partial}_m f_W(t) - f_W(t) e^{(i\hbar/2) \overleftarrow{\partial}_k B_{km}^c} \overrightarrow{\partial}_m H_W \right) \\ &\equiv -\frac{i}{\hbar} \{H_W, f_W(t)\}_M, \end{aligned} \quad (5.2)$$

where the right-hand side defines the Moyal bracket [33]. In Eq.(5.2) a symplectic matrix \mathcal{B}^c has been introduced and it is written in block form as

$$\mathcal{B}^c = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}. \quad (5.3)$$

The notation $\partial_k \equiv \partial/\partial x_k$ has been used for the derivative with respect to the phase-space point $x = (r, p)$, and Einstein's convention of summation over repeated indices has been adopted.

The formal solution of Eq.(5.2) can be compactly written as

$$f_W(r, p, t) = \exp\left[-\frac{it}{\hbar}\{H_W, \dots\}_M\right] f_W(r, p, 0). \quad (5.4)$$

The right-hand side of Eq. (5.4) defines the quantum propagator in phase space, $\exp\left[-\frac{it}{\hbar}\{H_W, \dots\}_M\right]$. Equivalently, time averages can be calculated by considering the Wigner function at the initial time and evolving Wigner transformed operators according to

$$\chi_W(r, p, t) = \exp\left[\frac{it}{\hbar}\{H_W, \dots\}_M\right] \chi_W(r, p, 0). \quad (5.5)$$

From the above equation one sees that the time evolution is unitary.

5.2 Nosè-Hoover dynamics in Wigner quantum phase space

The theory of Ref. [8] can be summarized as follows. Assume one has a subsystem described by the Hamiltonian operator \hat{H} , which, once transformed into the Wigner representation, becomes a phase-space function $H_W(r, p)$, where (r, p) is the phase-space point comprised of coordinates r and momenta p . Moreover, let the system interact with a thermal bath. If $2N$ is the dimension of the subsystem, its dissipative dynamics can be represented *via* the deterministic Nosè-Hoover evolution of a system of dimension $2N + 2$ (or $2N + 2n$, with $n < 10$, in the case of Nosè-Hoover chains

[17]). Ultimately, the quantum phase space will be extended by adding two Nosè variables η, p_η , with fictitious mass m_η , as it is done in the classical Nosè-Hoover molecular dynamics approach [10, 39]. Hence, the phase-space point coordinates are given by $x = (r, \eta, p, p_\eta)$. Correspondingly, a quantum extended Nosè Hamiltonian has been introduced

$$H_W^N(x) = H_W(r, p) + \frac{p_\eta^2}{2m_\eta} + gk_B T \eta, \quad (5.6)$$

where g is the number of degrees of freedom, k_B is Boltzmann's constant and T is the fixed temperature of the canonical ensemble. In the extended phase space, the antisymmetric tensor field can be defined [12]

$$\mathcal{B}^N = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & -p \\ 0 & -1 & p & 0 \end{bmatrix}, \quad (5.7)$$

and the Moyal bracket as

$$\begin{aligned} \left\{ \chi_W^1, \chi_W^2 \right\}_M &\equiv \chi_W^1 \exp \left[\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^N \overrightarrow{\partial}_j \right] \chi_W^2 \\ &- \chi_W^2 \exp \left[\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^N \overrightarrow{\partial}_j \right] \chi_W^1, \end{aligned} \quad (5.8)$$

where χ_W^1 and χ_W^2 are arbitrary Wigner-transformed quantum operators. Although in the Hamiltonian of Eq. (5.6), the physical coordinates (r, p) and the additional Nosè coordinates η, p_η appear as independent from each other, they will be coupled through \mathcal{B}^N upon defining the generalized equations of motion. In fact, the antisymmetric tensor \mathcal{B}^N can be used to introduce an operator in the extended quantum phase space

$$\overrightarrow{\mathcal{M}}^N \equiv H_W^N \left(e^{\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^N \overrightarrow{\partial}_j} - e^{-\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^N \overrightarrow{\partial}_j} \right), \quad (5.9)$$

and define dynamics of Wigner-transformed operators as

$$\frac{\partial}{\partial t} \chi_W(x, t) = \frac{i}{\hbar} \overrightarrow{\mathcal{M}}^N \chi_W(x, t). \quad (5.10)$$

Equations (5.9) and (5.10) represent Nosè-Hoover dynamics in quantum phase space, or, Nosè-Wigner dynamics [8].

One can use a dynamical picture in which observables are fixed in time. Evolution is taken into account by the Wigner function $f_W(x, t)$ which is the Wigner-transformed density matrix operator [6]. In the extended phase space it is found that [8]:

$$f_W(x, t) = \exp\left[-\frac{it}{\hbar}\overrightarrow{\mathcal{M}}^{N, \dagger}\right] f_W(x), \quad (5.11)$$

where

$$\begin{aligned} \overrightarrow{\mathcal{M}}^{N, \dagger} &= H_W^N \left\{ \exp\left[\frac{i\hbar}{2}(\overleftarrow{\partial}_i \mathcal{B}_{ij}^N \overrightarrow{\partial}_j + \overleftarrow{\partial}_i(\partial_j \mathcal{B}_{ij}^N))\right] \right. \\ &\quad \left. - \exp\left[-\frac{i\hbar}{2}(\overleftarrow{\partial}_i \mathcal{B}_{ij}^N \overrightarrow{\partial}_j + \overleftarrow{\partial}_i(\partial_j \mathcal{B}_{ij}^N))\right] \right\}. \end{aligned} \quad (5.12)$$

This means that, under Nosè dynamics, the stationary Wigner function f_{We} , defined by $\partial_t f_{We} = 0$, obeys the following equation

$$\begin{aligned} -iL^N f_{We} - K^N f_{We} &= \sum_{n=1, \text{odd}} \frac{1}{n!} \left(\frac{\hbar}{2i}\right)^{n-1} \\ &\quad \times H_W^N [\overleftarrow{\partial}_i \mathcal{B}_{ij}^N \overrightarrow{\partial}_j + \overleftarrow{\partial}_i(\partial_j \mathcal{B}_{ij}^N)]^n f_{We}, \end{aligned} \quad (5.13)$$

where

$$K^N = (\partial_j \mathcal{B}_{ij}^N) \partial_j H_W^N = N \frac{p_\eta}{m_\eta} \quad (5.14)$$

$$iL^N = \mathcal{B}_{ij}^N (\partial_j H_W^N) \overrightarrow{\partial}_i \quad (5.15)$$

are the Nosè phase-space compressibility and the Nosè-Liouville operators respectively. Equations (5.11) and (5.13) contain the full quantum corrections to the dynamics of all the variables in the extended phase space. They define Nosè-Hoover dynamics in a completely quantum fashion. One of the main interests of such a generalization lies in the fact that, as in the classical case, just a pair of additional variables, namely the Nosè coordinates (η, p_η) , allows representation of thermal fluctuations, and therefore the process of relaxation toward thermodynamical equilibrium of a quantum system

by introducing a suitable non-Hamiltonian dynamics in the extended phase space. This is to be compared with a standard Hamiltonian formalism that would require coupling the physical coordinates, (r, p) , to a bath with an infinite number of degrees of freedom.

A classical approximation over the evolution of the Nosè variables, (η, p_η) , can be taken while retaining all the quantum corrections over the dynamics of the coordinates, (r, p) , of the physical system. This amounts to a quantum-classical approximation [40], and simplifies the analysis of the stationary Nosè-Hoover distribution in quantum phase space. As a matter of fact, when Nosè-Hoover dynamics is implemented within molecular dynamics computer simulations, a mass $m_\eta \approx N \times m$ is used to achieve a weak coupling to the Nosè “bath”. In such a way, while the temperature of the system is controlled, the equilibrium dynamical properties of the physical coordinates (r, p) are not significantly modified. In the present context, a small parameter $\mu = \sqrt{m/m_\eta}$ is naturally found in the theory so that one is allowed to perform a classical limit on the Nosè coordinates (η, p_η) . In this way, a quantum-classical description, along the lines described in [40], naturally arises. Therefore, within a quantum-classical approach, one could disregard all the quantum corrections on the evolution of the Nosè variables in the left-hand side of Eq. (5.13). Upon assuming a standard form for the Hamiltonian of the physical degrees of freedom, $H_W(r, p) = (p^2/2m) + V(r)$, the Nosè-Hoover equation for the stationary Wigner distribution function becomes

$$\begin{aligned} & \sum_{n=1, \text{odd}} \frac{1}{n!} \left(\frac{i\hbar}{2} \right)^{n-1} V(r) [\overleftarrow{\partial}_r \cdot \overrightarrow{\partial}_p]^n f_{We} \\ = & -(iL^N - K^N) f_{We}, \end{aligned} \quad (5.16)$$

where $\partial_r = \partial/\partial r$, $\partial_p = \partial/\partial p$, and K^N is the compressibility of the phase-space flow. Moreover, in order to calculate quantum averages as functions of (r, p) alone it is important to calculate the average of Eq. (5.15) over the now

classical Nosè variables. This turns out to be identical to the equations first proposed by Wigner [6], who showed how to obtain quantum corrections in the canonical ensemble in terms of an expansion of his distribution function in even powers of \hbar [6]:

$$f_{We} = \sum_{n=0}^{\infty} f_{We}^{(n)}. \quad (5.17)$$

The zeroth-order solution, $f_W^{(0)}$, to Eq. (5.16) is [13, 14, 35]

$$f_W^{(0)} \propto \delta(H_W^N) e^{-\int K^N dt}. \quad (5.18)$$

When averaging over η, p_η , $f_W^{(0)}$ becomes the Boltzmann's weight for the (r, p) variables. Moreover, averages of odd functions of the Nosè variables over $f_W^{(0)}$ are zero. Hence, the analysis of the correction terms, under the approximations of no quantum effects on the Nosè variables, can proceed as originally shown by Wigner [6]. The higher-order correction terms will all contain the zeroth-order term: $f_{We}^{(n)} = \hbar^n f_{We}^{(0)} \tilde{f}_{We}^{(n)}$, with $n \geq 2$. In principle, such correction terms could be used to calculate averages over an ensemble of dynamical trajectories including thermal fluctuations by means of Nosè-Hoover dynamics as defined through the operator $\vec{\mathcal{M}}^N$ introduced in Eq. (5.9).

5.3 Nosè-Hoover chain dynamics in Wigner quantum phase space

The Wigner Hamiltonian describes the evolution of a closed quantum system. Many situations require the system to be in contact with a thermal bath. Borrowing formalisms from the field of classical molecular dynamics, this can be represented deterministically in terms of additional fictitious variables by means of Nosè-Hoover chain dynamics of length two; it is straightforward to generalize the treatment to longer chains. Hence, the chain comprises the coordinates $\eta_1, p_{\eta_1}, \eta_2, p_{\eta_2}$, with fictitious mass Q , which is

assumed to be the same for η_1 and η_2 for simplicity. Consequently, the quantum phase-space point coordinates are given by $x = (r, \eta_1, \eta_2, p, p_{\eta_1}, p_{\eta_2})$.

As in the case of Nosè-Hoover dynamics, a quantum extended Hamiltonian can be introduced for the Nosè-Hoover chain

$$H_W^{(NHC)}(x) = H_W(r, p) + \frac{p_{\eta_1}^2}{2Q} + \frac{p_{\eta_2}^2}{2Q} + gk_B T \eta_1 + k_B T \eta_2, \quad (5.19)$$

where g is the number of degrees of freedom (equal to the number N of r coordinates), k_B is Boltzmann's constant and T is the fixed temperature of the thermal bath.

In the NHC extended quantum phase space, the antisymmetric tensor field can be defined as [12, 13, 14, 16, 38]

$$\mathcal{B}^{NHC} = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 & -p & 0 \\ 0 & -1 & 0 & p & 0 & -p_{\eta_1} \\ 0 & 0 & -1 & 0 & p_{\eta_1} & 0 \end{bmatrix}, \quad (5.20)$$

and the NHC Moyal bracket is given by

$$\begin{aligned} \left\{ \chi_W^1, \chi_W^2 \right\}_M &\equiv \chi_W^1 \exp \left[\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^{NHC} \overrightarrow{\partial}_j \right] \chi_W^2 \\ &- \chi_W^2 \exp \left[\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^{NHC} \overrightarrow{\partial}_j \right] \chi_W^1, \end{aligned} \quad (5.21)$$

where χ_W^1 and χ_W^2 are arbitrary Wigner-transformed quantum operators. From the Hamiltonian of Eq. (5.19), the physical coordinates (r, p) and the additional Nosè-Hoover chain coordinates $(\eta_1, p_{\eta_1}, \eta_2, p_{\eta_2})$ appear to be independent from each other. This is not true because they are coupled through the antisymmetric matrix \mathcal{B}^{NHC} and the generalized equations of motion. In fact, the antisymmetric tensor \mathcal{B}^{NHC} can be used to introduce in the extended quantum phase space an operator written as

$$\overrightarrow{\mathcal{M}}^{NHC} \equiv H_W^{(NHC)} \left(e^{\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^{NHC} \overrightarrow{\partial}_j} - e^{-\frac{i\hbar}{2} \overleftarrow{\partial}_i \mathcal{B}_{ij}^{NHC} \overrightarrow{\partial}_j} \right), \quad (5.22)$$

and the dynamics of Wigner-transformed operators can be defined as

$$\frac{\partial}{\partial t} \chi_W(x, t) = \frac{i}{\hbar} \mathcal{M}^{NHC} \chi_W(x, t). \quad (5.23)$$

Equation (5.23) couples the quantum subsystem of interest, with coordinates (r, p) , to the additional Nosè-Hoover chain coordinates describing a thermal bath.

To discuss the statistical features of the generalized dynamics defined by Eq. (5.23), it is more convenient to adopt a picture in which time evolution is taken into account by the Wigner function $f_W(x, t)$, while observables are fixed in time. In the extended phase space it is found that [8]:

$$f_W(x, t) = \exp \left[-\frac{it}{\hbar} \vec{\mathcal{M}}^{NHC, \dagger} \right] f_W(x), \quad (5.24)$$

where

$$\begin{aligned} \vec{\mathcal{M}}^{NHC, \dagger} &= H_W^{NHC} \left\{ \exp \left[\frac{i\hbar}{2} (\overleftarrow{\partial}_i \mathcal{B}_{ij}^{NHC} \overrightarrow{\partial}_j + \overleftarrow{\partial}_i (\partial_j \mathcal{B}_{ij}^{NHC})) \right] \right. \\ &\quad \left. - \exp \left[-\frac{i\hbar}{2} (\overleftarrow{\partial}_i \mathcal{B}_{ij}^{NHC} \overrightarrow{\partial}_j + \overleftarrow{\partial}_i (\partial_j \mathcal{B}_{ij}^{NHC})) \right] \right\}. \end{aligned} \quad (5.25)$$

Similar to the Nosè-Hoover case, the stationary Wigner function, f_{We} , generated by the NHC dynamics obeys the following equation of motion

$$\begin{aligned} -iL^{NHC} f_{We} - K^{NHC} f_{We} &= \sum_{n=1, \text{odd}} \frac{1}{n!} \left(\frac{\hbar}{2i} \right)^{n-1} \\ &\quad \times H_W^{(NHC)} [\overleftarrow{\partial}_i \mathcal{B}_{ij}^{NHC} \overrightarrow{\partial}_j + \overleftarrow{\partial}_i (\partial_j \mathcal{B}_{ij}^{NHC})]^n f_{We}, \end{aligned} \quad (5.26)$$

where

$$K^{NHC} = (\partial_j \mathcal{B}_{ij}^{NHC}) \partial_j H_W^{(NHC)} = -g \frac{p_{\eta_1}}{Q} - \frac{p_{\eta_2}}{Q} \quad (5.27)$$

$$iL^{NHC} = \mathcal{B}_{ij}^{NHC} (\partial_j H_W^{(NHC)}) \overrightarrow{\partial}_i \quad (5.28)$$

are the NHC phase-space compressibility and the NHC Liouville operators respectively. Equations (5.24) and (5.26) provide a full quantum description of the dynamics of all the variables in the extended phase space. A classical

approximation over the evolution of the NHC variables can be taken, while retaining all the quantum corrections over the dynamics of the coordinates (r, p) , of the physical system. This amounts to a quantum-classical approximation [40] and simplifies the analysis of the stationary NHC distribution in quantum phase space.

Thinking of a quantum-classical approach, all the quantum corrections on the evolution of the Nosè-Hoover chain variables in the left-hand side of Eq. (5.26) can be neglected. Upon assuming a standard form for the Hamiltonian of the physical degrees of freedom, $H_W(r, p) = (p^2/2m) + V(r)$, the NHC equation for the stationary Wigner distribution function can be written as

$$\begin{aligned} & \sum_{n=1, \text{odd}} \frac{1}{n!} \left(\frac{i\hbar}{2} \right)^{n-1} V(r) [\overleftarrow{\partial}_r \cdot \overrightarrow{\partial}_p]^n f_{We} \\ &= -(iL^{NHC} - K^{NHC}) f_{We}, \end{aligned} \quad (5.29)$$

where $\partial_r = \partial/\partial r$, $\partial_p = \partial/\partial p$.

Moreover, to calculate quantum averages of functions (r, p) alone it is important to calculate the average of Eq. (5.28) over the NHC variables, which have lost any quantum behavior after the quantum-classical approximation has been taking. This turns out to be similar to the equations first proposed by Wigner [6], who showed how to obtain quantum corrections in the canonical ensemble in terms of an expansion of his distribution function in even powers of \hbar [6]:

$$f_{We} = \sum_{n=0}^{\infty} f_{We}^{(n)}. \quad (5.30)$$

The zeroth-order solution, $f_W^{(0)}$, to Eq. (5.29) is [12, 13, 14]

$$f_W^{(0)} \propto \delta(H_W^{NHC}) e^{-\int k^{NHC} dt}. \quad (5.31)$$

Taking the average over $\eta_1, p_{\eta_1}, \eta_2, p_{\eta_2}$, the zeroth-order Wigner function $f_W^{(0)}$ becomes the Boltzmann's weight for the (r, p) variables. Moreover,

averages of odd functions of the NHC variables over $f_W^{(0)}$ are zero. Hence, the analysis of the correction terms, under the approximations of no quantum effects on the NHC variables, can proceed as originally shown by Wigner [6]. The higher-order correction terms will all contain the zeroth-order term: $f_{We}^{(n)} = \hbar^n f_{We}^{(0)} \tilde{f}_{We}^{(n)}$, with $n \geq 2$. Such correction terms can be used in order to calculate averages over an ensemble of dynamical trajectories including thermal fluctuations by means of Nosè-Hoover chain dynamics as defined through the operator $\overrightarrow{\mathcal{M}}^{NHC}$ introduced in Eq. (5.22).

Chapter 6

Quantum-Classical Transition of a Harmonic Mode in a Thermal Nosè-Hoover Chain Bath

Here there will be discussed a model used to describe quantum-classical transitions as a function of thermodynamical temperature, namely the harmonic mode. Since a full quantum-mechanical treatment is not computationally possible, one can think of using a quantum-classical method. This has been done by directly coupling the Nosè-Hoover and its generalizations, such as the Nosè-Hoover chain thermostat to the quantum subsystem in phase space. The dynamics of a one-dimensional harmonic mode is a useful model for studying the properties of constant-temperature quantum dynamics in phase space. The quantum-classical limit will also be discussed and it will be shown, by means of numerical simulations, how the quantum-classical transitions can be obtained by varying the thermodynamical temperature of the system. The results for the simulations performed comparing analytical

and numerical Wigner functions are displayed, showing their coincidence.

6.1 Thermostated harmonic mode

The theory discussed thus far can be applied to a system comprising a quantum subsystem coupled to a classical thermal bath. However, to perform numerical calculations, a model must be chosen to which the theory can be applied. An appropriate model to use for studying quantum-to-classical dynamics at constant temperature is a single harmonic mode. It is a well-studied model [7] to test a new theory and thus provide a way to check the efficacy and accuracy of the simulation. The harmonic mode which is interpreted as a quantum subsystem is coupled to a classical thermal bath. A single harmonic mode, with frequency ω and unit mass admits an analytical Wigner distribution function in the canonical ensemble, described as (see appendix C) [26]:

$$f_W(r, p) = \frac{1}{\pi} \tanh\left(\frac{\omega}{2}\beta\right) e^{-\frac{2}{\omega} \tanh\left(\frac{\omega}{2}\beta\right) H_W(r, p)} \quad (6.1)$$

where

$$H_W(r, p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 r^2 \quad (6.2)$$

is the Wigner-transformed Hamiltonian of a single mode. The Wigner quantum dynamics of harmonic modes takes a particularly simple form identical to classical Liouville dynamics. All the quantum effects of harmonic systems are contained in the initial conditions. Nevertheless, harmonic modes are interesting from a theoretical perspective because they can represent the degrees of freedom of fields in space-time. From a computational perspective, general techniques are being developed to represent the dynamics of arbitrary non-harmonic systems in terms of effective harmonic approximations [41, 42]. Equation (6.1) gives the solution of the Wigner-transformed Bloch equation for the canonical density matrix, assuming the unnormalized sta-

tistical operator has the form $\hat{\Omega}(\beta) = \exp[-\beta\hat{H}]$, typical of the canonical ensemble (see Appendix C). Now the Wigner distribution function given in Eq. (6.1) is stationary under constant-energy dynamics (preserving H_W) but it is not stationary under constant-temperature dynamics (which conserves H_W^N not H_W). This means that if one samples an initial phase-space point from $f_W(r, p)$ where β and ω are constant, and propagates the dynamics defined by the Hamiltonian H_W which is conserved in microcanonical ensemble, then the Wigner function obtained from NVE dynamics will not change in time. But this will not work in the canonical ensemble, because the NVT dynamics does not conserve H_W ; it conserves the Nosè-Hoover Hamiltonian H_W^N . Thus the combined use of Eq. (6.1) and constant-energy dynamics is legitimate for the calculation of static averages in the canonical ensemble. It amounts to a (computer) experiment to prepare the initial condition in a canonical ensemble at time $t < 0$, then adiabatically isolates the subsystem (specified by H_W) from the bath, and from $t = 0$ onward it evolves in a microcanonical manner. This preserves its Hamiltonian and thus its thermodynamical internal energy. Instead, whenever the dynamics do not take place in isolation from the thermal bath from $t = 0$ onward, constant-temperature dynamics, should be used consistently [43].

The constant-temperature dynamics of the Wigner function of the harmonic degree of freedom can be represented in terms of the evolution of an ensemble of phase-space points. These initial values are obtained by sampling Eq. (6.1). For $t > 0$ the NH and NHC dynamics introduced by the generalized Moyal bracket in Eqs. (5.9) and (5.22) are integrated numerically to evolve the ensemble of points. The Wigner function can be reconstructed at any time using histograms.

6.2 Quantum-classical limit

The classical limit is a subtle topic in quantum mechanics and is not yet fully understood [7]. In particular, Michael Berry, among others, has proven that the quantum-to-classical limit ($\hbar \rightarrow 0$) is singular [44]. However, there is another way to achieve smoothly the quantum-to-classical transition; the thermodynamical temperature of the system is varied. In the high-temperature limit, it is possible to show that the Wigner distribution function becomes completely the classical canonical distribution function. It has

$$T \rightarrow \infty, \Rightarrow \beta \rightarrow 0. \quad (6.3)$$

Thus, the approximation to first-order Taylor series expansion of Eq. (6.1) can be taken; and the Wigner distribution function reduces to a classical probability distribution in phase space.

Recall that the Taylor expansion of the hyperbolic tangent is

$$\tanh x = x - \frac{1}{3}x^3 + \frac{2}{15}x^5 - \frac{17}{315}x^7 + \dots \text{for } |x| < \frac{\pi}{2}, \quad (6.4)$$

so

$$\tanh\left(\frac{\hbar\omega}{2}\beta\right) = \frac{\hbar\omega}{2}\beta - \frac{1}{3}\left(\frac{\hbar\omega}{2}\beta\right)^3 + \dots \text{for } \left|\frac{\hbar\omega}{2}\beta\right| < \frac{\pi}{2}. \quad (6.5)$$

Taking a first-order approximation, one obtains

$$\tanh\left(\frac{\hbar\omega}{2}\beta\right) = \frac{\hbar\omega}{2}\beta. \quad (6.6)$$

Equation (6.1) then becomes

$$f_W(r, p) = \frac{1}{\pi\hbar} \frac{\hbar\omega}{2} \beta e^{-\frac{2}{\hbar\omega} \frac{\hbar\omega}{2} \beta H_W(r, p)} \quad (6.7)$$

$$= \frac{\omega\beta}{2\pi} e^{-\beta H_W(r, p)}. \quad (6.8)$$

The factor $\frac{\omega}{2}\beta$ must be the inverse of the partition function for this to be

the classical canonical distribution function. This can be easily checked:

$$Z(\beta) = \iint dr dp e^{-\beta H(r,p)} \quad (6.9)$$

$$= \int dr e^{-\beta \frac{1}{2} m \omega^2 r^2} \int dp e^{-\beta \frac{p^2}{2m}} \quad (6.10)$$

$$= \sqrt{\frac{2\pi}{m\omega^2\beta}} \sqrt{\frac{2\pi m}{\beta}} \quad (6.11)$$

$$= \frac{2\pi}{\omega\beta}. \quad (6.12)$$

It has thus been shown that the classical canonical distribution function is recovered from the Wigner canonical distribution function in the high-temperature limit.

In the low-temperature limit, there is a transition of the Wigner distribution function from classical to quantum-mechanical behaviour. One finds that

$$T \rightarrow 0, \Rightarrow \beta \rightarrow \infty. \quad (6.13)$$

Let us write the extra term of Eq. (6.1) as

$$\tilde{\beta} = \frac{2}{\hbar\omega} \tanh\left(\frac{\hbar\omega}{2}\beta\right). \quad (6.14)$$

Then Eq. (6.1) becomes

$$f_W(r,p) = \frac{1}{\pi\hbar} \tanh\left(\frac{\hbar\omega}{2}\beta\right) e^{-\tilde{\beta} H_W(r,p)}. \quad (6.15)$$

If $\tilde{\beta} \neq \beta$ then the canonical Wigner distribution function contains all its quantum effects for a single harmonic mode. When the Nosè-Hoover thermostat is attached to the system it thermalises the system; and the quantum-to-classical transition can be achieved by increasing the value of β . That is, the classical canonical distribution function is recovered from the quantum Wigner distribution in the low-temperature limit. However, to get an accurate result, an ergodic Nosè-Hoover chain thermostat should be attached to the system [1]. Figure 6.14 illustrates this issue. With $\beta = 7.5$, the Wigner distribution function becomes completely classical and all its

quantum-mechanical behaviour disappears. Thus, it can be concluded that there is no definite boundary between the classical and the quantum world. It is possible to move from the quantum Wigner distribution function to the classical Boltzmann factor by increasing the value of β under *NHC* dynamics.

6.3 Numerical results and discussion

In part of the work reported here, Monte Carlo algorithms have been used to sample the Wigner distribution in phase space. The Wigner distribution function has been reconstructed in phase space using histograms. The result of a computer simulation of the initial Wigner function of the harmonic mode has been compared with the predictions of an approximate analytical theory applied to the same model. It is found that theory and computer simulation results are in agreement.

A trajectory in phase space is generated by sampling the initial conditions of the Wigner distribution function, running the dynamics at $t > 0$ under *NVE*, *NH* and *NHC* to evolve the ensemble of points. Histograms are used to reconstruct the Wigner distribution function. In quantum sampling at $t = 0$, analytical and numerical results of the Wigner function coincide. Then, the dynamics are run at $t > 0$ and it is observed that the Wigner distribution function is stationary under *NVE* dynamics with a different value of β . Using the *NH* and *NHC* algorithms, however, leads to a quantum-to-classical transition with higher values of β . This means that the quantum distribution function loses its quantum behaviour and becomes the classical distribution function.

It is useful to study the momentum-probability distribution in configuration space, in order to see how it can approach the classical limit. In this case, a numerical integration of the marginal probability distribution, given

as

$$f(p) = \int f_W(r, p) dq = \langle p | \hat{\rho} | p \rangle, \quad (6.16)$$

will be performed, where ρ is the density matrix. It would be desirable to show that, with each dynamical variable, an appropriate classical limit can be achieved under NHC dynamics.

For the calculations reported here, the oscillator angular frequency, \hbar , and all masses were taken to be unity, with different values of $\beta = 1/k_B T$. The time step in all cases was $\tau = 0.0025$ and all runs were calculated using 5×10^5 Monte Carlo sampling points. For the Nosè-Hoover simulations 10^5 time steps were used, for the NVE and Nosè-Hoover chain simulations 10^4 time steps were used.

In Figures 6.1 and 6.2, the theoretical result of a stationary solution of the Wigner distribution function with coordinates (r, p) , and the numerical result sampled at $t = 0$ for the different temperatures are compared. This comparison is important as a test of the theory before introducing the simulation with dynamics.

6.3.1 NVE dynamics

In this case, it is shown that the Monte Carlo method reproduces the behaviour of the Wigner distribution function at constant energy. Figure 6.3 depicts the quantum phase-space sampling, and displays the numerically calculated Wigner distribution function at $t = 0$, and at $t = 25$ for $\beta = 0.3$. It is instructive to see how the system reacts to a sudden decrease in the imposed temperature. It is found that in the microcanonical ensemble, the distribution function does not change with time. This is illustrated in figures 6.4, 6.5 and 6.6. From these results, it can be concluded that under constant energy, the Wigner distribution function does not change over time, even when the temperature is decreased.

6.3.2 Nosè-Hoover (NVT) dynamics

The effect of the Nosè-Hoover coupling with the Wigner distribution function is considered. The Nosè-Hoover method reproduces the behaviour of the Wigner distribution function, at a constant temperature within the numerical errors. For the low values of β the distribution function still has its quantum-mechanical behaviour. It disappears with the increasing values of β . As can be seen in figures 6.7 and 6.8, the distribution function at $t = 0$ is compared with the one generated by NH dynamics at $t = 250$ for the different temperatures. For $\beta = 5$ and $\beta = 7.5$ peaks become small and lead to the classical limit. Results are depicted in figures 6.9 and 6.10. The Wigner distribution function generated by the Nosè-Hoover thermostat does not yield a canonical distribution in phase space, even for very long simulations.

6.3.3 Nosè-Hoover chain (NVT) dynamics

The same analysis has been performed for the Wigner distribution function generated by the Nosè-Hoover chain thermostat. This case study shows that the Nosè-Hoover chain method yields good results for the Wigner distribution function in phase space, as presented in figures 6.11 and 6.12. The figures illustrate that the distribution function is dependent on the value chosen for the temperature. The distribution function, which is directly coupled to the thermostats, reacts to a sudden decrease in the imposed temperature and leads to the quantum-classical transition. The thermostats force a transition from quantum-mechanical behaviour to classical. The numerical results are displayed in figures 6.13 and 6.14. Within numerical error, the Nosè-Hoover chain thermostat coupled to the quantum subsystem can generate the correct distribution function in phase space and leads to the quantum-classical transition at low temperature for the harmonic mode.

In the previous paragraph, the Wigner distribution function in phase

space has been studied and showed how the thermalisation of the system can force a transition from quantum-mechanical behaviour to classical. Similar calculations have been done for the momentum-probability distribution obtained from the NHC dynamics for a harmonic oscillator. Even with the probability distribution of each dynamical variable under NHC dynamics, the quantum-classical transition can be achieved. The result of the simulation has been done where the expected transition is observed. For low temperatures, the numerical result of the the momentum-probability distribution at $t = 25$ obtained from the NHC dynamics is compared to the marginal classical distribution $e^{-\beta \frac{p^2}{2m}}$, called the Maxwell distribution, and the momentum-probability distribution at $t = 0$. When compared to the Maxwell distribution, the momentum-probability distribution at $t = 0$ is quantum in behaviour and the momentum-probability distribution at $t = 25$ obtained from the NHC dynamics is found to lose its quantum behaviour and return to the Maxwell distribution. Computational work has been done with two different values of β . Results are displayed in figures 6.15 and 6.16.

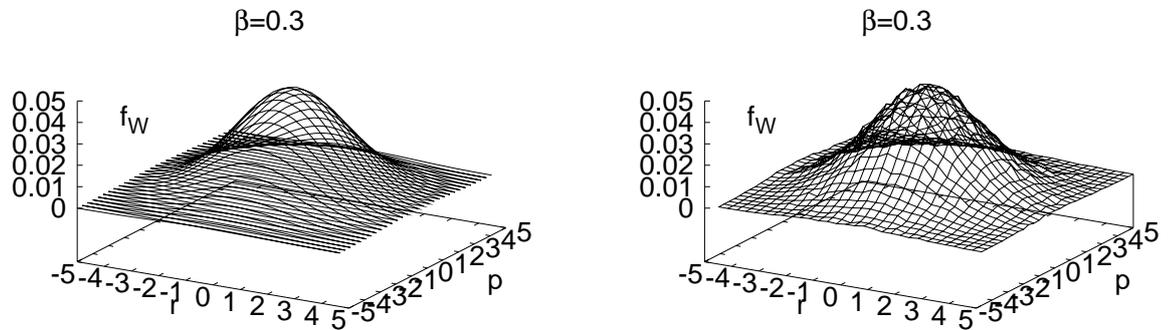


Figure 6.1: Comparison of analytical and numerical Wigner distribution functions for a harmonic oscillator sampled at $t = 0$ for $\beta = 0.3$. The left plot shows the analytical function while the right panel displays the numerical result. With the higher value of the temperature, fluctuations are large.

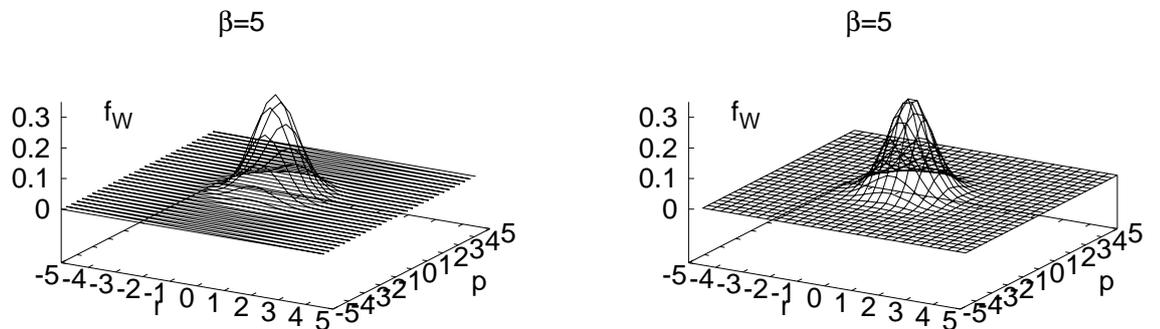


Figure 6.2: Comparison of analytical and numerical Wigner distribution functions for a harmonic oscillator sampled at $t = 0$ for $\beta = 5$. The left plot shows the analytical function, whereas the right panel displays the numerical result. Fluctuations become small when the value of the temperature is decreased. These figures illustrate that the numerical results are compatible with the analytical result.

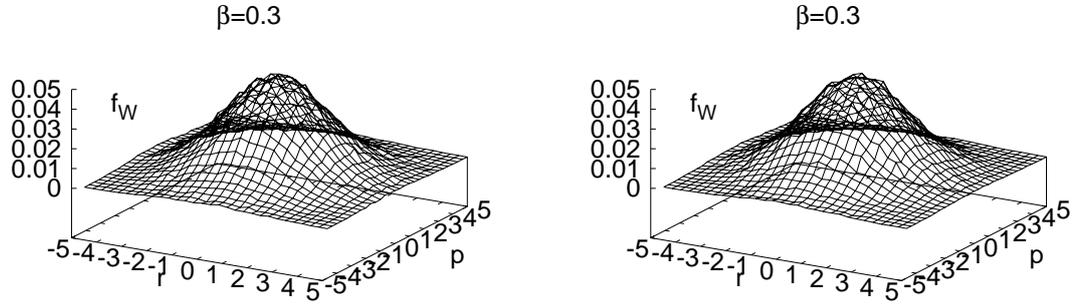


Figure 6.3: Numerical plots of the Wigner distribution function of a harmonic oscillator. The left plot is the result sampled at $t = 0$. The right panel displays the Wigner distribution function at $t = 25$ under the microcanonical ensemble (NVE). It follows from the result that the Wigner distribution function and the analytical Wigner distribution are still compatible. Fluctuations are large with the higher value of the temperature.

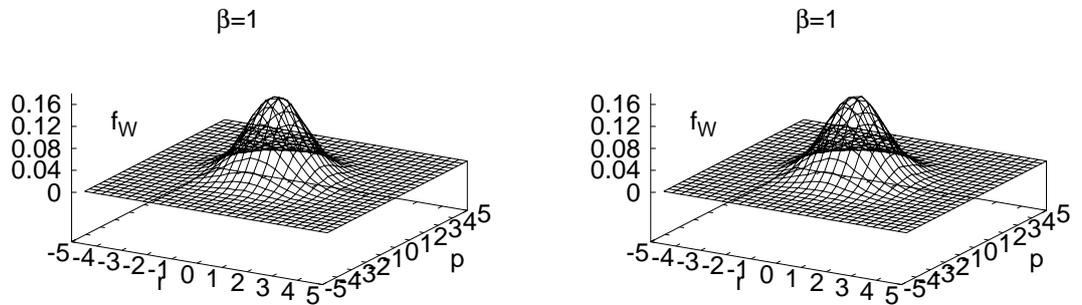


Figure 6.4: Numerical plots of the Wigner distribution function of a harmonic oscillator. The left plot is the result sampled at $t = 0$. The right panel displays the Wigner distribution function at $t = 25$ under the microcanonical ensemble (NVE). At this time the numerical Wigner distribution function still agrees with the analytical Wigner distribution at $t = 0$. Fluctuations become small when the value of the temperature is decreased.

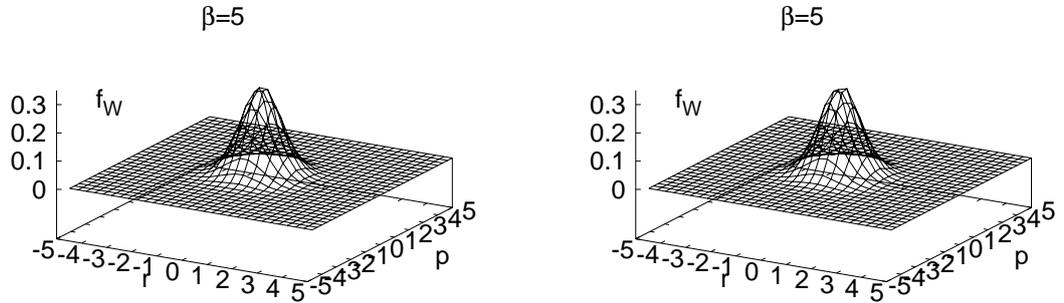


Figure 6.5: Numerical plots of the Wigner distribution function of a harmonic oscillator. The left plot is the result sampled at $t = 0$. The right panel displays the Wigner distribution function at $t = 25$ under the micro-canonical ensemble (NVE). At this time the result remains the same as the analytical quantum distribution.

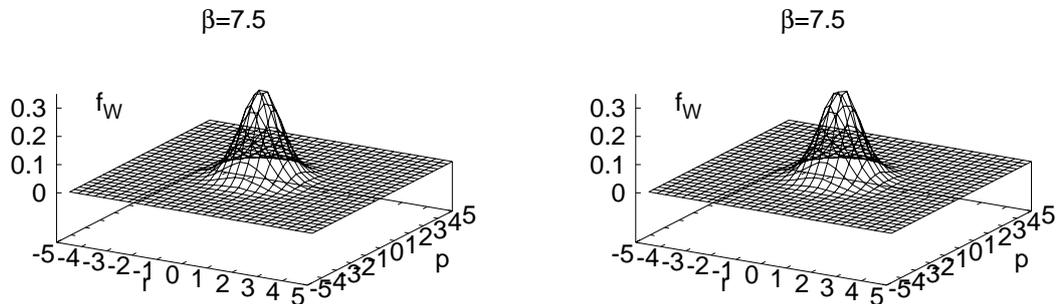


Figure 6.6: Numerical plots of the Wigner distribution function of a harmonic oscillator. The left plot is the result sampled at $t = 0$. The right panel displays the Wigner distribution function at $t = 25$ under the micro-canonical ensemble (NVE). It is remarked that, after certain values of β , the shape of the distribution function no longer changes. One can conclude that the distribution function obtained from NVE dynamics is stationary when $T \rightarrow 0$.

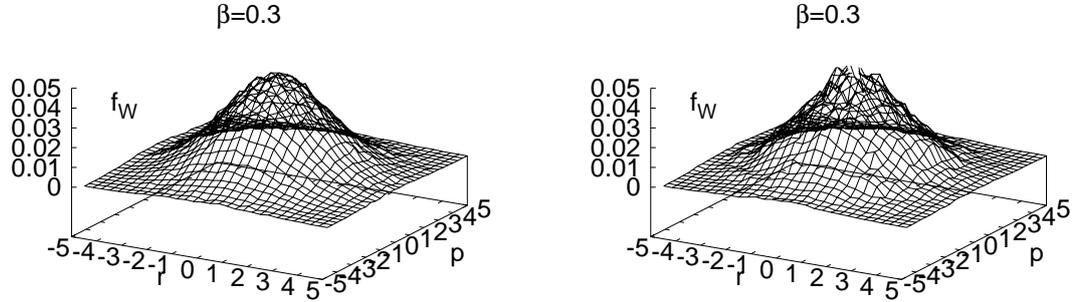


Figure 6.7: Plots of the Wigner distribution function of a harmonic oscillator. The left plot is the result sampled at $t = 0$, whereas the right panel displays the Wigner distribution function obtained from NH dynamics at $t = 250$. Over an extended period, the Wigner distribution function presented some imperfections due to the NH dynamics not recovering the correct canonical distribution.

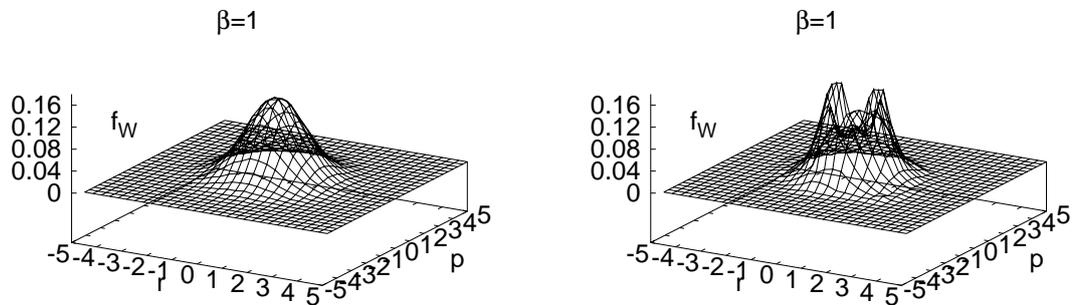


Figure 6.8: Plots of the Wigner distribution function of a harmonic oscillator. The left plot is the result sampled at $t = 0$, whereas the right panel displays the Wigner distribution function obtained from NH dynamics at $t = 250$. Some imperfections observed on the right plot are due to the NH dynamics not recovering the correct canonical distribution even at long times.

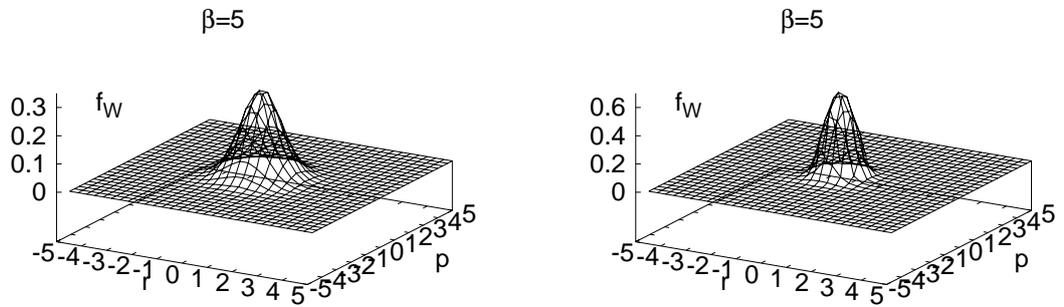


Figure 6.9: Plots of the Wigner distribution function for a harmonic oscillator. The left plot is the result sampled at $t = 0$. The right panel displays the Wigner distribution function obtained from NH dynamics at $t = 250$ where the quantum-mechanical behaviour progressively disappears leading to the classical case.

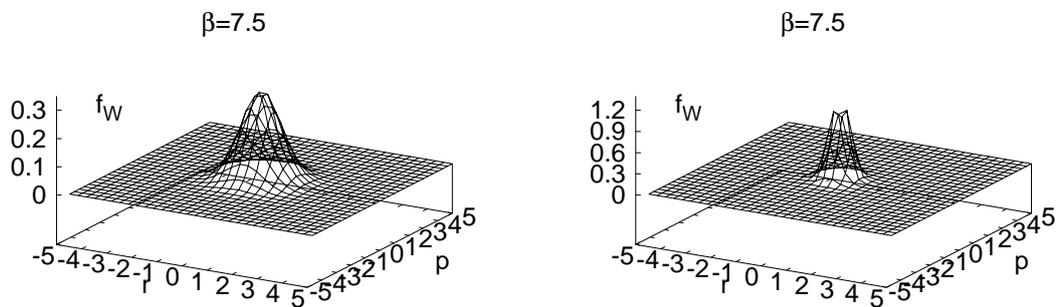


Figure 6.10: Plots of the Wigner distribution function for a harmonic oscillator. The left plot is the result sampled at $t = 0$. The right panel displays the Wigner distribution function obtained from NH dynamics at $t = 250$. At low temperature, the transition from quantum behaviour to classical can be noticed. The result is not accurate due to the NH dynamics limitations.

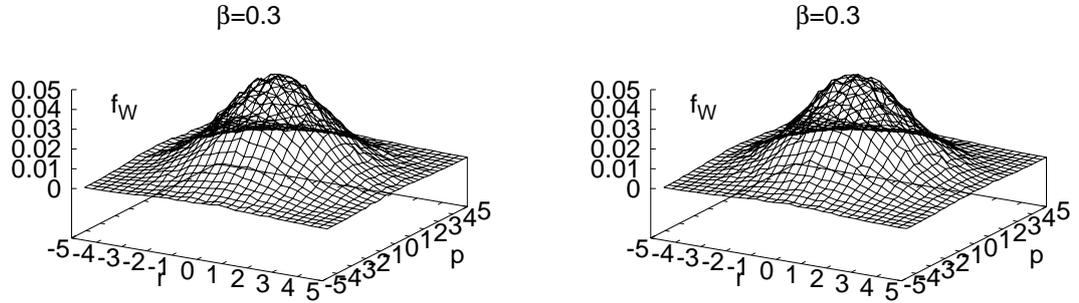


Figure 6.11: Plots of the Wigner distribution function for a harmonic oscillator. The left plot is the result sampled at $t = 0$ whereas the right panel displays the Wigner distribution function generated by the NHC dynamics at $t = 25$. The shape of the right plot compares well due to the capacity of NHC dynamics for recovering the correct canonical distribution function in phase space.

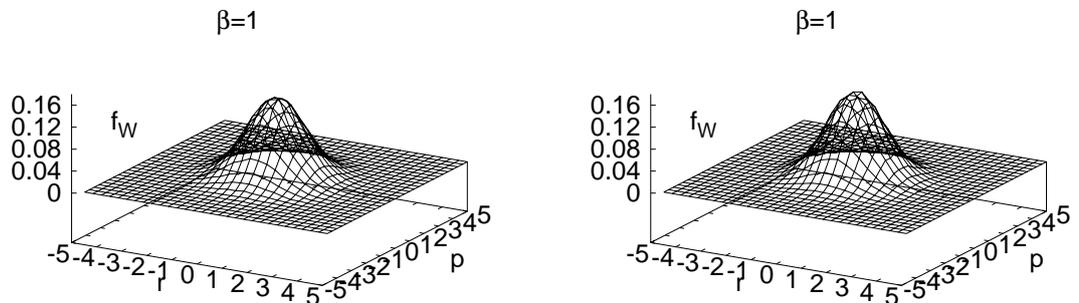


Figure 6.12: Plots of the Wigner distribution function for a harmonic oscillator. The left plot is the result sampled at $t = 0$ whereas the right panel displays the Wigner distribution function generated by the NHC dynamics at $t = 25$. It follows from the right plot that the NHC dynamics does recover the correct canonical distribution function in phase space. At this time, fluctuations in 6.11 compared to 6.12 are larger.

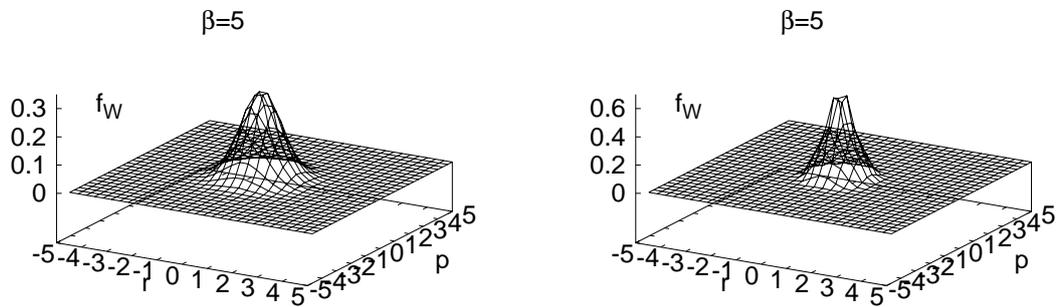


Figure 6.13: Plots of the Wigner distribution function for a harmonic oscillator. The left plot is the result sampled at $t = 0$. The right panel displays the Wigner distribution function generated by the NHC dynamics at $t = 25$ where the quantum character progressively disappears leading to the classical case.

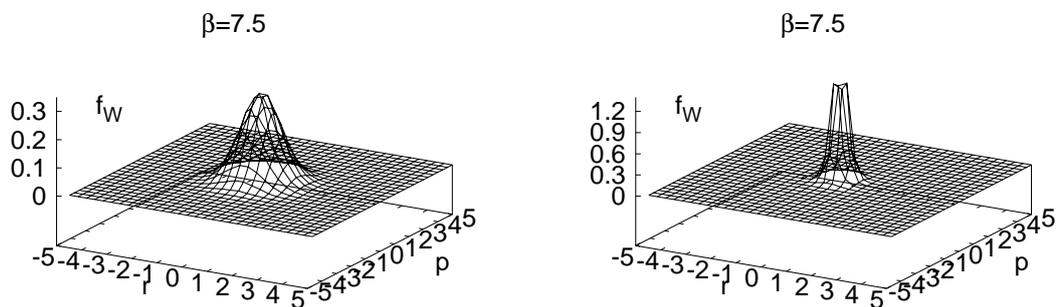


Figure 6.14: Plots of the Wigner distribution function for a harmonic oscillator. The left plot is the result sampled at $t = 0$ with a quantum character. The right panel displays the Wigner distribution function generated by the NHC dynamics at $t = 25$. The left plot still has all its quantum behaviour, while the right one shows the transition from quantum-mechanical behaviour to classical. At low temperature, the transition can be easily seen because of the ability of the NHC dynamics for recovering the correct canonical distribution in phase space.

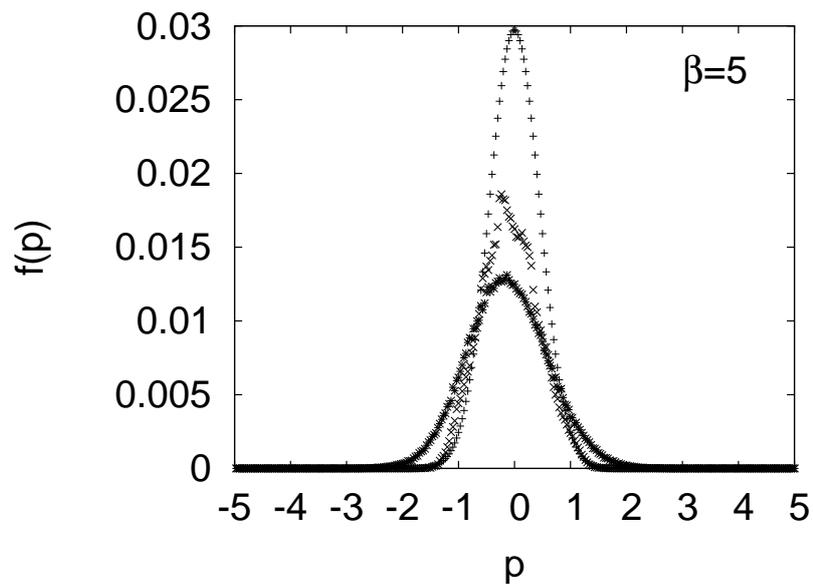


Figure 6.15: Plots of the marginal distribution of the harmonic oscillator. These plots show how the quantum-classical transition of the momentum-probability distribution obtained from NHC dynamics is approached. The line denoted by (*) represents the momentum-probability distribution sampled at $t = 0$. The line denoted by (\times) represents the momentum-probability distribution obtained from NHC dynamics at $t = 25$ and the (+) line represents the marginal classical distribution.

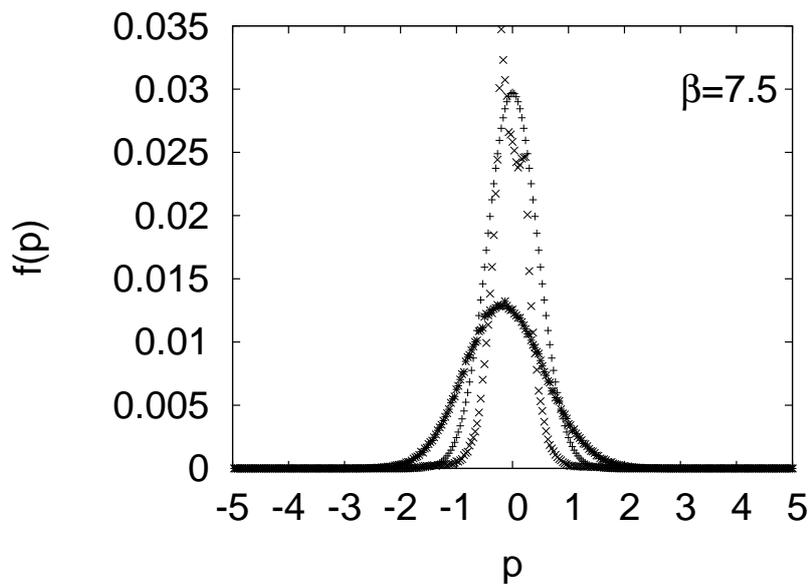


Figure 6.16: Plots of the marginal distribution of the harmonic oscillator. These plots show how the quantum-classical transition of the momentum-probability distribution obtained from NHC dynamics is approached. The line denoted by (*) represents the momentum-probability distribution sampled at $t = 0$. The line denoted by (x) represents the momentum-probability distribution obtained from NHC dynamics at $t = 25$ and the (+) line represents the marginal classical distribution.

Chapter 7

Conclusions

In this dissertation, a non-Hamiltonian approach to the simulation of quantum dynamics at constant temperatures has been discussed. The method is based on the Wigner formulation of quantum statistical mechanics and its unification with Nosè-Hoover techniques, to control the temperature, well-known in classical Molecular Dynamics. The aim was to better understand quantum dynamics features at constant temperatures. The study has shown that temperature control can lead to a quantum-classical transition in quantum phase space. Quantum-classical transitions were achieved by directly coupling the Nosè-Hoover thermostats to the harmonic mode of the Wigner function. In this case, the thermostats force a transition from the quantum distribution function to the classical distribution function.

Here, a brief summary of the various topics presented in the thesis is given. The Wigner representation of quantum mechanics has been used. Such a representation is typically adopted to illuminate the quantum-classical transition in phase space. Following this [8], a suitable generalization of the Moyal bracket [33] has allowed the use of classical Nosè-Hoover thermostats to control the temperature of the quantum degrees of freedom. The dynamics of a single harmonic oscillator was numerically integrated to show that the Wigner function is stationary under constant energy, which conserves

the Wigner-transformed Hamiltonian of a single mode (H_W) in a micro-canonical ensemble, and that the Wigner function obtained from NH and NHC dynamics can lead to the quantum-classical transition of the degree of freedom to which they are directly coupled. As known in pure classical contexts, it was found that, whereas the Nosè-Hoover dynamics is not ergodic, Nosè-Hoover chain dynamics samples the canonical distribution correctly. One of the main conclusions of this thesis is that, because temperature control in quantum dynamics can lead to the quantum-classical transition, care must be taken when using NHC dynamics within the Wigner formulation of quantum mechanics. The classical character of the thermal bath can be transferred to the quantum subsystem of interest, with which it is in contact. This has been numerically verified only for harmonic degrees of freedom, but it can be reasonably expected to hold for more general potentials as well. If one wants temperature control without the classical limit, it is possible not to couple the NHC fictitious variables directly to the quantum degrees of freedom. One can think of a quantum subsystem with coordinates (r, p) which are weakly coupled to a classical bath with coordinates (R, P) . The classical bath in turn is kept at constant temperature by coupling it to the NHC variables $(\eta_1, p_{\eta_1}, \eta_2, p_{\eta_2})$. Thus, the temperature of the classical bath is controlled but the weak coupling is expected to prevent the quantum subsystem from reaching the classical limit. Further numerical work is required in order to verify the validity of such a calculation scheme.

The formalism and the discussions presented here can be considered as preliminary steps towards a formulation of the dynamics of open quantum systems in contact with thermodynamical baths, without referring, as customary, to masters equations [2].

Future work will consist of applying the Wigner-Nosé dynamics to more complex computer models, suited to study tunneling processes in the condensed phase.

Appendix A

Time-reversible Nosè-Hoover Algorithm

The Liouville operator L_N is given as

$$\dot{x} = L_N x \quad (\text{A.1})$$

$$x(t) = \exp[tL_N]x(0). \quad (\text{A.2})$$

From Eqs.(2.16)-(2.19) the split Liouville operators are now

$$\dot{r} = L_1 r \quad L_1 = \frac{p}{m} \frac{\partial}{\partial r} \quad (\text{A.3})$$

$$\dot{p} = (L_2 + L_3)p \quad \begin{cases} L_2 = -\frac{\partial V}{\partial r} \frac{\partial}{\partial p} \\ L_3 = -p \frac{p_\eta}{m_\eta} \frac{\partial}{\partial p} \end{cases} \quad (\text{A.4})$$

$$\dot{\eta} = L_4 \eta \quad L_4 = \frac{p_\eta}{m_\eta} \frac{\partial}{\partial \eta} \quad (\text{A.5})$$

$$\dot{p}_\eta = L_5 p_\eta \quad L_5 = \left(\frac{p^2}{m} - g k_B T \right) \frac{\partial}{\partial p_\eta} = F_\eta \frac{\partial}{\partial p_\eta}. \quad (\text{A.6})$$

The total Liouville operator is

$$L_N = L_1 + L_2 + L_3 + L_4 + L_5. \quad (\text{A.7})$$

We can consider a small time step h and the symmetric Trotter factorization of the Liouville propagator:

$$e^{hL} \approx e^{L_5 h/2} e^{L_4 h/2} e^{L_3 h/2} e^{L_2 h/2} e^{L_1 h} e^{L_2 h/2} e^{L_3 h/2} e^{L_4 h/2} e^{L_5 h/2}. \quad (\text{A.8})$$

Using the identities

$$e^{c\partial/\partial x} f(x) \equiv f(x+c) \quad (\text{A.9})$$

$$e^{cx\partial/\partial x} f(x) \equiv f(xe^c), \quad (\text{A.10})$$

the direct translation technique gives the following pseudo-code of the algorithm ready to implemented

```

DO IT = 1, NTS
     $p_\eta = p_\eta + \frac{h}{2} F_\eta$ 
     $\eta = \eta + \frac{h}{2} \frac{p_\eta}{m_\eta}$ 
     $p = p \exp[-(h/2)p_\eta/m_\eta]$ 
     $p = p + \frac{h}{2} F(r)$ 
     $r = r + hp/m$ 
CALCULATE  $F(r)$ 
     $p = p + \frac{h}{2} F(r)$ 
     $p = p \exp[-(h/2)p_\eta/m_\eta]$ 
CALCULATE  $F_\eta$ 
     $\eta = \eta + \frac{h}{2} \frac{p_\eta}{m_\eta}$ 
     $p_\eta = p_\eta + \frac{h}{2} F_\eta$ 
END DO

```

Appendix B

Time-reversible Nosè-Hoover Chain Algorithm

The Liouville operator is given as

$$\dot{x} = L_N x \quad (\text{B.1})$$

$$x(t) = \exp[tL_N]x(0). \quad (\text{B.2})$$

From Eqs.(2.54)-(2.59) the split Liouville operators are now

$$\dot{q} = L_1 r \quad L_1 = \frac{p}{m} \frac{\partial}{\partial r} \quad (\text{B.3})$$

$$\dot{p} = (L_2 + L_3)p \quad \begin{cases} L_2 = -\frac{\partial V}{\partial r} \frac{\partial}{\partial p} \\ L_3 = -p \frac{p_{\eta_1}}{m_{\eta_1}} \frac{\partial}{\partial p} \end{cases} \quad (\text{B.4})$$

$$\dot{\eta}_1 = L_4 \eta_1 \quad L_4 = \frac{p_{\eta_1}}{m_{\eta_1}} \frac{\partial}{\partial \eta_1} \quad (\text{B.5})$$

$$\dot{\eta}_2 = L_5 \eta_2 \quad L_5 = \frac{p_{\eta_2}}{m_{\eta_2}} \frac{\partial}{\partial \eta_2} \quad (\text{B.6})$$

$$\dot{p}_{\eta_1} = L_6 p_{\eta_1} \quad \begin{aligned} L_6 &= \left(-p_{\eta_1} \frac{p_{\eta_2}}{m_{\eta_2}} + \frac{p^2}{m} - gk_B T \right) \frac{\partial}{\partial p_{\eta_1}} \\ &= \left(-p_{\eta_1} \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1} \right) \frac{\partial}{\partial p_{\eta_1}} \end{aligned} \quad (\text{B.7})$$

$$\dot{p}_{\eta_2} = L_7 p_{\eta_2} \quad L_7 = \left(\frac{p_{\eta_1}^2}{m_{\eta_1}} - gk_B T \right) \frac{\partial}{\partial p_{\eta_2}} = F_{\eta_2} \frac{\partial}{\partial p_{\eta_2}}. \quad (\text{B.8})$$

In L_6 there appears an operator with the form

$$L_6 = \left(-p_{\eta_1} \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1} \right) \frac{\partial}{\partial p_{\eta_1}} \quad (\text{B.9})$$

which can be developed following the derivation

$$\begin{aligned} \dot{p}_{\eta_1} &= -p_{\eta_1} \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1} \\ \frac{dp_{\eta_1}}{dt} &= -p_{\eta_1} \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1}. \end{aligned} \quad (\text{B.10})$$

Eq. (B.10) can be written in another form as

$$\begin{aligned} -\frac{m_{\eta_2}}{p_{\eta_2}} \frac{-\frac{p_{\eta_2}}{m_{\eta_2}}}{-p_{\eta_1} \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1}} \frac{dp_{\eta_1}}{dt} &= 1 \\ -\frac{m_{\eta_2}}{p_{\eta_2}} \frac{d}{dp_{\eta_1}} \left(\ln \left(-p_{\eta_1} \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1} \right) \right) \frac{dp_{\eta_1}}{dt} &= 1. \end{aligned}$$

By integrating from $t = 0$ to $t = \tau$ we have

$$\begin{aligned} -\frac{m_{\eta_2}}{p_{\eta_2}} \int_0^\tau \frac{d}{dt} \left[\ln \left(-p_{\eta_1} \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1} \right) \right] dt &= \int_0^\tau 1 dt \\ -\frac{m_{\eta_2}}{p_{\eta_2}} \left[\ln \left(-p_{\eta_1} \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1} \right) \right]_0^\tau &= \tau \\ -\frac{m_{\eta_2}}{p_{\eta_2}} \left[\ln \left(-p_{\eta_1} \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1} \right) - \ln \left(-p_{\eta_1}(0) \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1}(0) \right) \right] &= \tau. \end{aligned} \quad (\text{B.11})$$

Assume

$$\begin{aligned} p_{\eta_1}(0) &= p_{\eta_1} \\ F_{\eta_1}(0) &= F_{\eta_1}(\tau) = F_{\eta_1}. \end{aligned}$$

Eq. (B.11) gives

$$\ln \frac{-p_{\eta_1}(\tau) \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1}}{-p_{\eta_1} \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1}} = -\tau \frac{p_{\eta_2}}{m_{\eta_2}}.$$

Take the exponential and get

$$-p_{\eta_1}(\tau) \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1} = e^{-\tau \frac{p_{\eta_2}}{m_{\eta_2}}} \left(-p_{\eta_1} \frac{p_{\eta_2}}{m_{\eta_2}} + F_{\eta_1} \right)$$

giving

$$\begin{aligned}
p_{\eta_1}(\tau) &= p_{\eta_1} e^{-\tau \frac{p_{\eta_2}}{m_{\eta_2}}} + \frac{m_{\eta_2}}{p_{\eta_2}} F_{\eta_1} \left(1 - e^{-\tau \frac{p_{\eta_2}}{m_{\eta_2}}} \right) \\
&= p_{\eta_1} e^{-\tau \frac{p_{\eta_2}}{m_{\eta_2}}} + \tau F_{\eta_1} e^{-\tau \frac{p_{\eta_2}}{2m_{\eta_2}}} \frac{\sinh\left(\tau \frac{p_{\eta_2}}{2m_{\eta_2}}\right)}{\tau \frac{p_{\eta_2}}{2m_{\eta_2}}}.
\end{aligned}$$

The total Liouville operator is

$$L_N = L_1 + L_2 + L_3 + L_4 + L_5 + L_6 + L_7. \quad (\text{B.12})$$

We can again consider a small time step h and the symmetric Trotter factorization of the Liouville propagator:

$$e^{hL} \approx e^{L_7 h/2} e^{L_6 h/2} e^{L_5 h/2} e^{L_4 h/2} e^{L_3 h/2} e^{L_2 h/2} e^{L_1 h} e^{L_2 h/2} e^{L_3 h/2} e^{L_4 h/2} e^{L_5 h/2} e^{L_6 h/2} e^{L_7 h/2}.$$

A pseudo-code of the algorithm ready to implemente is given as

```

DO IT = 1, NTS
   $p_{\eta_2} = p_{\eta_2} + \frac{h}{2} F_{\eta_2}$ 
   $p_{\eta_1} = p_{\eta_1} \exp\left[-\frac{h}{2} \frac{p_{\eta_2}}{2m_{\eta_2}}\right] + \frac{\tau}{2} F_{\eta_1} \exp\left[-\frac{h}{2} \frac{p_{\eta_2}}{2m_{\eta_2}}\right]$ 
     $\times \frac{\sinh\left(\tau/2 \frac{p_{\eta_2}}{2m_{\eta_2}}\right)}{\tau/2 \frac{p_{\eta_2}}{2m_{\eta_2}}}$ 
   $\eta_2 = \eta_2 + \frac{h}{2} \frac{p_{\eta_1}}{m_{\eta_2}}$ 
   $\eta_1 = \eta_1 + \frac{h}{2} \frac{p_{\eta_1}}{m_{\eta_1}}$ 
   $p = p \exp\left[-(h/2)p_{\eta_1}/m_{\eta_1}\right]$ 
   $p = p + \frac{h}{2} F(r)$ 
   $r = r + hp/m$ 
CALCULATE  $F(r)$ 
   $p = p + \frac{h}{2} F(r)$ 
   $p = p \exp\left[-(h/2)p_{\eta_1}/m_{\eta_1}\right]$ 
   $\eta_1 = \eta_1 + \frac{h}{2} \frac{p_{\eta_1}}{m_{\eta_1}}$ 
   $\eta_2 = \eta_2 + \frac{h}{2} \frac{p_{\eta_1}}{m_{\eta_2}}$ 
CALCULATE  $F_{\eta_1}$ 
   $p_{\eta_1} = p_{\eta_1} \exp\left[-\frac{h}{2} \frac{p_{\eta_2}}{2m_{\eta_2}}\right] + \frac{\tau}{2} F_{\eta_1} \exp\left[-\frac{h}{2} \frac{p_{\eta_2}}{2m_{\eta_2}}\right]$ 
     $\times \frac{\sinh\left(\tau/2 \frac{p_{\eta_2}}{2m_{\eta_2}}\right)}{\tau/2 \frac{p_{\eta_2}}{2m_{\eta_2}}}$ 
CALCULATE  $F_{\eta_2}$ 
   $p_{\eta_2} = p_{\eta_2} + \frac{h}{2} F_{\eta_2}$ 
END DO

```

Appendix C

Wigner Distribution for an Ensemble at Temperature T

The canonical ensemble is specified by the parameters (N, V, T) indicating that the number N of particles, the volume V , and the temperature T are conserved. If $\beta = \frac{1}{k_B T}$ where k_B is Boltzmann's constant and T is the temperature [26], then the density matrix of the canonical ensemble is:

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

and $Z(\beta) = \text{Tr}(e^{-\beta \hat{H}})$ is the canonical partition function. The un-normalized density matrix $\hat{\Omega}$ then satisfies the equation

$$\frac{\partial \hat{\Omega}}{\partial \beta} = -\hat{H} \hat{\Omega} = -\hat{\Omega} \hat{H}, \quad (\text{C.2})$$

which is the Bloch [1932] equation for the density matrix of a canonical ensemble subject to the initial condition $\hat{\Omega}(\beta = 0) = \hat{I}$ where \hat{I} is the identity operator. This equation is utilized to derive an integro-differential equation for the temperature dependence of the Wigner distribution function of a canonical ensemble. Taking the Wigner-transformed of the Equation (C.2)

and using the product rule given by Groenewold [1946],

$$\begin{aligned}
\frac{\partial \Omega_W(r, p)}{\partial \beta} &= -H_W(r, p)e^{(\hbar/2i)\Lambda}\Omega_W(r, p) \\
&= -\Omega_W(r, p)e^{-(\hbar/2i)\Lambda}H_W(r, p) \\
&= -\frac{1}{2}\left(H_W(r, p)e^{(\hbar/2i)\Lambda}\Omega_W(r, p) + H_W(r, p)e^{(\hbar/2i)\Lambda}\Omega_W(r, p)\right) \\
&= -\frac{1}{2}\left(H_W(r, p)e^{(\hbar/2i)\Lambda}\Omega_W(r, p) + \Omega_W(r, p)e^{(\hbar/2i)\Lambda}H_W(r, p)\right) \\
&= -\frac{1}{2}H_W(r, p)\left(e^{(\hbar/2i)\Lambda} + e^{(\hbar/2i)\Lambda}\right)\Omega_W(r, p) \\
&= -H_W\cos\left(\frac{\hbar}{2}\Lambda\right)\Omega_W
\end{aligned} \tag{C.3}$$

where the operator Λ is the negative of the Poisson bracket written as

$$\Lambda = \overleftarrow{\frac{\partial}{\partial p}} \overrightarrow{\frac{\partial}{\partial r}} - \overleftarrow{\frac{\partial}{\partial r}} \overrightarrow{\frac{\partial}{\partial p}}.$$

Equation (C.3) is the Wigner-transformed of the Bloch equation. It was first derived by Oppenheim and Ross [45]. It is useful in the calculation of quantum-mechanical corrections of classical statistical mechanics. The initial condition for this equation is just the Wigner-transformed of $\hat{\Omega}(\beta = 0) = \hat{I} \rightarrow \Omega_W(\beta = 0) = 1$. It is proven as

$$\begin{aligned}
\Omega_W(\beta = 0) &= \int dz e^{\frac{i}{\hbar}pz} \langle r - \frac{z}{2} | \hat{1} | r + \frac{z}{2} \rangle \\
&= \int dz e^{\frac{i}{\hbar}pz} \langle r - \frac{z}{2} | r + \frac{z}{2} \rangle \\
&= \int dz e^{\frac{i}{\hbar}pz} \delta(r + \frac{z}{2} - r + \frac{z}{2}) \\
&= \int dz e^{\frac{i}{\hbar}pz} \delta(z) \\
&= 1
\end{aligned} \tag{C.4}$$

and it is worth noting that

$$f_W(r, p) = \frac{1}{\pi\hbar} \int_{-\infty}^{+\infty} dy \langle r - y | \hat{\rho} | r + y \rangle e^{\frac{2i}{\hbar}py}$$

does not obey the Wigner function of the Bloch equation because it must be multiplied by the β -dependent factor $(2\pi\hbar)Z(\beta)$ to obtain $\Omega_W(r, p)$. The

solution of Equation (C.3) in the multidimensional case is, to order \hbar^2 [6],

$$\begin{aligned} \Omega_W(r, p) = e^{-\beta H_W} & \left\{ 1 + (2\pi\hbar)^2 \left[\sum_k \left(\frac{-\beta^3}{8m_k} \frac{\partial^2 V}{\partial r_k^2} + \frac{\beta^3}{24m_k} \left(\frac{\partial V}{\partial r_k} \right)^2 \right) \right. \right. \\ & \left. \left. + \sum_{k,l} \frac{\beta^3}{24} \frac{p_k p_l}{m_k m_l} \frac{\partial^2 V}{\partial r_k \partial r_l} \right] \right\}. \end{aligned} \quad (\text{C.5})$$

C.1 Equilibrium Wigner function for a harmonic oscillator

For the harmonic oscillator, the Wigner-transformed Hamiltonian can be written as

$$H_W(r, p) = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 r^2.$$

The Bloch equation is then

$$\frac{\partial \Omega_W(r, p)}{\partial \beta} = - \left(\frac{p^2}{2m} + \frac{1}{2} m \omega^2 r^2 \right) \cos \left(\frac{\hbar}{2} \left[\overleftarrow{\frac{\partial}{\partial p}} \overrightarrow{\frac{\partial}{\partial r}} - \overleftarrow{\frac{\partial}{\partial r}} \overrightarrow{\frac{\partial}{\partial p}} \right] \right) \Omega_W. \quad (\text{C.6})$$

Using the Maclaurin series,

$$\begin{aligned} \cos \left(\frac{\hbar}{2} \left[\overleftarrow{\frac{\partial}{\partial p}} \overrightarrow{\frac{\partial}{\partial r}} - \overleftarrow{\frac{\partial}{\partial r}} \overrightarrow{\frac{\partial}{\partial p}} \right] \right) &= 1 - \frac{1}{2} \left(\frac{\hbar}{2} \right)^2 \left(\overleftarrow{\frac{\partial}{\partial p}} \overrightarrow{\frac{\partial}{\partial r}} - \overleftarrow{\frac{\partial}{\partial r}} \overrightarrow{\frac{\partial}{\partial p}} \right)^2 \\ &+ \frac{1}{4!} \left(\frac{\hbar}{2} \right)^4 \left(\overleftarrow{\frac{\partial}{\partial p}} \overrightarrow{\frac{\partial}{\partial r}} - \overleftarrow{\frac{\partial}{\partial r}} \overrightarrow{\frac{\partial}{\partial p}} \right)^4, \end{aligned}$$

and

$$\left(\overleftarrow{\frac{\partial}{\partial p}} \overrightarrow{\frac{\partial}{\partial r}} - \overleftarrow{\frac{\partial}{\partial r}} \overrightarrow{\frac{\partial}{\partial p}} \right)^2 = \frac{\overleftarrow{\partial^2}}{\partial p^2} \frac{\overrightarrow{\partial^2}}{\partial r^2} - 2 \frac{\overleftarrow{\partial^2}}{\partial p \partial r} \frac{\overrightarrow{\partial^2}}{\partial r \partial p} + \frac{\overleftarrow{\partial^2}}{\partial r^2} \frac{\overrightarrow{\partial^2}}{\partial p^2}$$

the Wigner function of the Bloch equation can be simplified by the Baker-Hausdorff Theorem: if $\hat{D} = [\hat{A}, \hat{B}]$ commutes with \hat{A} and \hat{B} then

$$\begin{aligned} e^{A+B} &= e^A e^B e^{-D/2} \\ e^{A-B} &= e^A e^{-B} e^{D/2} \end{aligned} \quad (\text{C.7})$$

with $A = \overleftarrow{\frac{\partial}{\partial p}} \overrightarrow{\frac{\partial}{\partial r}}$ and $B = \overleftarrow{\frac{\partial}{\partial r}} \overrightarrow{\frac{\partial}{\partial p}}$

$$\hat{D} = \left[\overleftarrow{\frac{\partial}{\partial p}} \overrightarrow{\frac{\partial}{\partial r}}, \overleftarrow{\frac{\partial}{\partial r}} \overrightarrow{\frac{\partial}{\partial p}} \right] = \frac{\overleftarrow{\partial}}{\partial p} \frac{\overrightarrow{\partial}}{\partial r} \cdot \frac{\overleftarrow{\partial}}{\partial r} \frac{\overrightarrow{\partial}}{\partial p} - \frac{\overleftarrow{\partial}}{\partial r} \frac{\overrightarrow{\partial}}{\partial p} \cdot \frac{\overleftarrow{\partial}}{\partial p} \frac{\overrightarrow{\partial}}{\partial r} = 0$$

then since $\overleftarrow{\partial} \overrightarrow{\partial}$ and $\overleftarrow{\partial} \overrightarrow{\partial}$ commutes

$$e^{\frac{i\hbar}{2} \left(\overleftarrow{\partial} \overrightarrow{\partial} - \overleftarrow{\partial} \overrightarrow{\partial} \right)} = e^{\frac{i\hbar}{2} \overleftarrow{\partial} \overrightarrow{\partial}} e^{-\frac{i\hbar}{2} \overleftarrow{\partial} \overrightarrow{\partial}}.$$

Consider also that

$$\overleftarrow{\partial} \overrightarrow{\partial} H_W(r, p) = 0,$$

Therefore

$$\begin{aligned} \frac{\partial \Omega_W(r, p)}{\partial \beta} &= -\left(\frac{p^2}{2m} + \frac{1}{2} m \omega^2 r^2 \right) \left[1 - \frac{\hbar^2}{8} \left(\frac{\overleftarrow{\partial}^2 \overrightarrow{\partial}^2}{\partial p^2 \partial r^2} - 2 \frac{\overleftarrow{\partial}^2 \overrightarrow{\partial}^2}{\partial p \partial r \partial r \partial p} + \frac{\overleftarrow{\partial}^2 \overrightarrow{\partial}^2}{\partial r^2 \partial p^2} \right) \right] \Omega_W \\ &= -\left(\frac{p^2}{2m} + \frac{1}{2} m \omega^2 r^2 \right) \Omega_W + \frac{\hbar^2}{8} \left(m \omega^2 \frac{\partial^2 \Omega_W}{\partial p^2} + \frac{1}{m} \frac{\partial^2 \Omega_W}{\partial r^2} \right) \\ &= -\left(\frac{p^2}{2m} + \frac{1}{2} m \omega^2 r^2 \right) \Omega_W + \frac{\hbar^2}{8} \left(\frac{1}{m} \frac{\partial^2 \Omega_W}{\partial r^2} + m \omega^2 \frac{\partial^2 \Omega_W}{\partial p^2} \right). \end{aligned} \quad (\text{C.8})$$

Equation. (C.8) is the Wigner-transformed Bloch equation for the harmonic oscillator. To solve this equation, let us make the ansatz

$$\Omega(r, p) = e^{-A(\beta)H(r, p) + B(\beta)} \quad (\text{C.9})$$

where A and B are the initial conditions $A(0) = B(0) = 0$. The derivatives of the Ω_W can be determined with respect to the spatial coordinate:

$$\frac{\partial \Omega_W(r, p)}{\partial r} = \Omega_W \left(-A(\beta) \frac{\partial H_W}{\partial r} \right) \quad (\text{C.10})$$

and hence

$$\frac{\partial^2 \Omega_W(r, p)}{\partial r^2} = \left(A^2(\beta) m^2 \omega^4 r^2 - A(\beta) m \omega^2 \right) \Omega_W. \quad (\text{C.11})$$

Similarly, with respect to the momentum coordinate:

$$\frac{\partial \Omega_W(r, p)}{\partial p} = \Omega_W \left(-A(\beta) \frac{\partial H_W}{\partial p} \right) \quad (\text{C.12})$$

and hence

$$\frac{\partial^2 \Omega_W(r, p)}{\partial p^2} = -\frac{A(\beta)}{m} \Omega_W + A^2(\beta) \frac{p^2}{m^2} \Omega_W. \quad (\text{C.13})$$

Finally, with respect to β :

$$\frac{\partial \Omega_W(r, p)}{\partial \beta} = \Omega_W \left(-\frac{\partial A}{\partial \beta} H_W + \frac{\partial B}{\partial \beta} \right). \quad (\text{C.14})$$

Therefore the transformed Wigner Bloch equation becomes

$$\begin{aligned} \Omega_W \left(-\frac{\partial A}{\partial \beta} H_W + \frac{\partial B}{\partial \beta} \right) &= -\left(\frac{p^2}{2m} + \frac{1}{2} m \omega^2 r^2 \right) \Omega_W \\ &+ \frac{\hbar^2}{8} \left(\frac{1}{m} \frac{\partial^2 \Omega_W}{\partial r^2} + m^2 \omega^2 \frac{\partial^2 \Omega_W}{\partial p^2} \right). \end{aligned} \quad (\text{C.15})$$

Dividing through by Ω_W the above equation becomes

$$\begin{aligned} -\frac{\partial A}{\partial \beta} H_W + \frac{\partial B}{\partial \beta} &= -H_W + \frac{\hbar^2}{8} \left[A^2 m \omega^4 r^2 - 2A\omega^2 + \omega^2 A^2 \frac{p^2}{m} \right] \\ &= -H_W + \frac{\hbar^2}{4} \left[-A\omega^2 + \omega^2 A^2 \left(\frac{p^2}{2m} + \frac{1}{2} m \omega^2 r^2 \right) \right] \\ &= -H_W + \frac{\hbar^2}{4} \left[-A\omega^2 + \omega^2 A^2 H_W \right] \\ &= -H_W + \left(\frac{\hbar\omega}{2} \right)^2 \left[-A + A^2 H_W \right]. \end{aligned} \quad (\text{C.16})$$

Thus

$$\begin{aligned} -\frac{\partial A}{\partial \beta} H_W + H_W &= -\frac{\partial B}{\partial \beta} + \left(\frac{\hbar\omega}{2} \right)^2 \left[-A + A^2 H_W \right] \\ &= -\frac{\partial B}{\partial \beta} - \left(\frac{\hbar\omega}{2} \right)^2 A + \left(\frac{\hbar\omega A}{2} \right)^2 H_W, \end{aligned} \quad (\text{C.17})$$

and

$$\left[-\frac{\partial A}{\partial \beta} + 1 - \left(\frac{\hbar\omega A}{2} \right)^2 \right] H_W = -\frac{\partial B}{\partial \beta} - \left(\frac{\hbar\omega}{2} \right)^2 A. \quad (\text{C.18})$$

This equation must hold for all r and p ; the terms in square brackets are independent of phase-space coordinates r and p , therefore they must vanish independently, that is

$$\frac{dA}{d\beta} - 1 + \frac{(\hbar\omega)^2}{4} A^2 = 0 \quad (\text{C.19})$$

and

$$\frac{\partial B}{\partial \beta} + \left(\frac{\hbar\omega}{2} \right)^2 A = 0. \quad (\text{C.20})$$

Equation. (C.19) can be integrated directly as

$$\begin{aligned}\frac{dA}{d\beta} &= 1 - \left(\frac{\hbar\omega}{2}\right)^2 A^2 \\ d\beta &= \frac{dA}{1 - \left(\frac{\hbar\omega}{2}\right)^2 A^2}.\end{aligned}\tag{C.21}$$

Consider the following identity,

$$\frac{1}{2} \frac{d}{dx} \ln\left(\frac{1+x}{1-x}\right) = \frac{1}{1-x^2},$$

and then make the following change of variables

$$\begin{aligned}\frac{\hbar\omega}{2}A &= x \\ dA &= \frac{2}{\hbar\omega}dx.\end{aligned}$$

Eq. (C.21) becomes

$$\begin{aligned}\beta &= \frac{2}{\hbar\omega} \int \frac{dx}{1-x^2} \\ &= \frac{2}{2\hbar\omega} \int dx \frac{d}{dx} \ln\left(\frac{1+x}{1-x}\right) \\ &= \frac{1}{\hbar\omega} \ln\left(\frac{1+x}{1-x}\right) \\ &= \frac{1}{\hbar\omega} \ln\left(\frac{1 + \frac{\hbar\omega}{2}A}{1 - \frac{\hbar\omega}{2}A}\right).\end{aligned}\tag{C.22}$$

Inverting Eq. (C.22) gives

$$\begin{aligned}\ln\left(\frac{1 + \frac{\hbar\omega}{2}A}{1 - \frac{\hbar\omega}{2}A}\right) &= \hbar\omega\beta \\ \frac{1 + \frac{\hbar\omega}{2}A}{1 - \frac{\hbar\omega}{2}A} &= e^{\hbar\omega\beta} \\ 1 + \frac{\hbar\omega}{2}A &= e^{\hbar\omega\beta} \left(1 - \frac{\hbar\omega}{2}A\right) \\ \frac{\hbar\omega}{2}A \left(e^{\hbar\omega\beta} + 1\right) &= e^{\hbar\omega\beta} - 1.\end{aligned}\tag{C.23}$$

Thus

$$\begin{aligned}
A &= \frac{2}{\hbar\omega} \frac{e^{\hbar\omega\beta} - 1}{e^{\hbar\omega\beta} + 1} \\
&= \frac{2}{\hbar\omega} \frac{e^{\hbar\omega\beta/2} \left(e^{\hbar\omega\beta/2} - e^{-\hbar\omega\beta/2} \right)}{e^{\hbar\omega\beta/2} \left(e^{\hbar\omega\beta/2} + e^{-\hbar\omega\beta/2} \right)} \\
&= \frac{2}{\hbar\omega} \frac{\left(e^{\hbar\omega\beta/2} - e^{-\hbar\omega\beta/2} \right)}{\left(e^{\hbar\omega\beta/2} + e^{-\hbar\omega\beta/2} \right)} \\
&= \frac{2}{\hbar\omega} \tanh\left(\frac{\hbar\omega}{2}\beta\right). \tag{C.24}
\end{aligned}$$

This can now be substituted into Eq. (C.20) to give

$$\begin{aligned}
\frac{\partial B}{\partial\beta} + \left(\frac{\hbar\omega}{2}\right)^2 \frac{2}{\hbar\omega} \tanh\left(\frac{\hbar\omega}{2}\beta\right) &= 0 \\
\frac{\partial B}{\partial\beta} + \frac{\hbar\omega}{2} \tanh\left(\frac{\hbar\omega}{2}\beta\right) &= 0, \tag{C.25}
\end{aligned}$$

and the solution of (C.25) is

$$B = -\frac{\hbar\omega}{2} \int d\beta \tanh\left(\frac{\hbar\omega}{2}\beta\right). \tag{C.26}$$

Recalling the hyperbolic functions

$$\begin{aligned}
\cosh x &= \frac{e^x + e^{-x}}{2} & \sinh x &= \frac{e^x - e^{-x}}{2} \\
\frac{d}{dx} \cosh x &= \sinh x & \frac{d}{dx} \sinh x &= \cosh x \\
\cosh^2 x - \sinh^2 x &= 1,
\end{aligned}$$

therefore

$$\frac{d}{dx} \ln(\cosh x) = \frac{\sinh x}{\cosh x} = \tanh x.$$

Using the change of variable below,

$$\begin{aligned}
x &= \frac{\hbar\omega}{2}\beta \\
dx &= \frac{\hbar\omega}{2} d\beta \tag{C.27}
\end{aligned}$$

Eq. (C.26) becomes

$$\begin{aligned}
B &= -\frac{\hbar\omega}{2} \frac{2}{\hbar\omega} \int dx \tanh x \\
&= -\int dx \frac{d}{dx} \ln(\cosh x) \\
&= -\ln(\cosh x) \\
B &= -\ln\left[\cosh\left(\frac{\hbar\omega}{2}\beta\right)\right]. \tag{C.28}
\end{aligned}$$

Therefore from Eq. (C.9),

$$\begin{aligned}
\Omega_W &= e^{-\frac{2}{\hbar\omega} \tanh\left(\frac{\hbar\omega}{2}\beta\right) H} e^{-\ln\left(\cosh\left(\frac{\hbar\omega}{2}\beta\right)\right)} \\
&= \frac{1}{\cosh\left(\frac{\hbar\omega}{2}\beta\right)} e^{-\frac{2}{\hbar\omega} \tanh\left(\frac{\hbar\omega}{2}\beta\right) H}. \tag{C.29}
\end{aligned}$$

To obtain the distribution function of the canonical ensemble, the normalization of Ω_W is needed

$$\begin{aligned}
Z(\beta) &= \iint dr dp \hat{\Omega} \\
&= \frac{1}{\cosh\left(\frac{\hbar\omega}{2}\beta\right)} \iint dr dp e^{-\frac{2}{\hbar\omega} \tanh\left(\frac{\hbar\omega}{2}\beta\right) \left(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 r^2\right)}. \tag{C.30}
\end{aligned}$$

The double integral can be factorised as:

$$Z(\beta) = \frac{1}{\cosh\left(\frac{\hbar\omega}{2}\beta\right)} \int dp e^{-\frac{2}{\hbar\omega} \tanh\left(\frac{\hbar\omega}{2}\beta\right) \frac{p^2}{2m}} \int dr e^{-\frac{2}{\hbar\omega} \tanh\left(\frac{\hbar\omega}{2}\beta\right) \frac{1}{2}m\omega^2 r^2}. \tag{C.31}$$

Both integrals are Gaussian and can be integrated as follow

$$\begin{aligned}
\int dp e^{-\frac{1}{\hbar\omega m} \tanh\left(\frac{\hbar\omega}{2}\beta\right) p^2} &= \sqrt{\frac{\pi}{\frac{1}{\hbar\omega m} \tanh\left(\frac{\hbar\omega}{2}\beta\right)}} \\
\int dr e^{-\frac{m\omega}{\hbar} \tanh\left(\frac{\hbar\omega}{2}\beta\right) r^2} &= \sqrt{\frac{\pi}{\frac{m\omega}{\hbar} \tanh\left(\frac{\hbar\omega}{2}\beta\right)}} \tag{C.32}
\end{aligned}$$

and

$$\begin{aligned}
Z(\beta) &= \frac{1}{\cosh(\frac{\hbar\omega}{2}\beta)} \frac{\pi}{\tanh(\frac{\hbar\omega}{2}\beta)} \frac{1}{\sqrt{\frac{1}{\hbar\omega m} \frac{m\omega}{\hbar}}} \\
&= \frac{\pi \hbar \cosh(\frac{\hbar\omega}{2}\beta)}{\cosh(\frac{\hbar\omega}{2}\beta) \sinh(\frac{\hbar\omega}{2}\beta)} \\
&= \frac{\pi \hbar}{\sinh(\frac{\hbar\omega}{2}\beta)}. \tag{C.33}
\end{aligned}$$

The Wigner-transformed distribution function corresponds to

$$f_W = \frac{1}{Z(\beta)} \Omega_W. \tag{C.34}$$

Finally

$$\begin{aligned}
f_W(r, p, \beta) &= \frac{\sinh(\frac{\hbar\omega}{2}\beta)}{\pi \hbar} \frac{e^{-\frac{2}{\hbar\omega} \tanh(\frac{\hbar\omega}{2}\beta) H}}{\cosh(\frac{\hbar\omega}{2}\beta)} \\
&= \frac{1}{\pi \hbar} \tanh\left(\frac{\hbar\omega}{2}\beta\right) e^{-\frac{2}{\hbar\omega} \tanh\left(\frac{\hbar\omega}{2}\beta\right) H(r,p)}. \tag{C.35}
\end{aligned}$$

Equation. (C.35) is the analytical Wigner distribution function in the canonical ensemble of the harmonic oscillator at temperature T . For $\hbar = 1$, Eq. (C.35) becomes

$$f_W(r, p) = \frac{1}{\pi} \tanh\left(\frac{\omega}{2}\beta\right) e^{-\frac{2}{\omega} \tanh\left(\frac{\omega}{2}\beta\right) H(r,p)} \tag{C.36}$$

Equation. (C.36) is an analytical stationary Wigner function in the canonical ensemble. The higher powers of \hbar provide the quantum corrections to the dynamics.

Bibliography

- [1] D. Frenkel and B. Smit. *Understanding Molecular Simulation*. (Academic Press, San Diego), (1996).
- [2] H. P. Breuer and F. Petruccione. *The Theory of Open Quantum Systems*. Oxford University Press, Oxford, (2002).
- [3] M. A. Nielsen and I. L. Chuang. *Quantum Computational and Quantum Information*. Cambridge University Press, Cambridge, (2000).
- [4] M. O. Scully and M. S. Zubairy. *Quantum Optics*. Cambridge University Press Cambridge, (1997).
- [5] U. Weiss. Quantum dissipative systems. *World Scientific, Singapore*, (2000).
- [6] E. Wigner. *Phys.Rev.*, **40**(749), (1932).
- [7] L. E. Ballentine. Quantum mechanics. a modern primer. *World Scientific, Singapore*, (2001).
- [8] A. Sergi and F. Petruccione. *J.Phys.A*, **41**(355304), (2008).
- [9] A. Sergi. Temperature in quantum dynamics. *Atti della Accademia Peloritana dei Pericolanti*, **87**(2, C1C0902001), (2009).
- [10] W. G. Hoover. *Phys.Rev.A*, **31**(1695), (1985).
- [11] A. Sergi and P. V. Giaquinta. *Phys.Essays*, **20**(4), (2007).

- [12] A. Sergi and M. Ferrario. Non-hamiltonian equations of motion with a conserved energy. *Phys.Rev.E*, **64**(056125), (2001).
- [13] A. Sergi. *Phys.Rev.E*, **67**(021101), (2003).
- [14] A. Sergi and P. V. Giaquinta. *J.Stat.Mech: Theory and Experiment*, **02**(P02013), (2007).
- [15] H. Fehske, R. Schneider, and A. Weiss. *Computational Many-Particle Physics, Lect. Notes Phys.* Springer, Berlin Heidelberg, (2008).
- [16] A. Sergi. *Phys.Rev.E*, **72**(066125), (2005).
- [17] G. J. Martyna, M. L. Klein, and M. E. Tuckerman. Nosè-Hoover chains: The canonical ensemble via continuous dynamics. *J.Chem.Phys*, **97**(2635-2645), (1992).
- [18] M. E. Tuckerman, B. J. Berne, and G. J. Martyna. Reversible multiple time scale molecular dynamics. *J.Chem.Phys*, **97**(3), (1992).
- [19] P. A. M. Dirac. *The Principles of Quantum Mechanics*. Oxford University Press,Oxford, (1958).
- [20] C. Cohen-Tannoudji, B. Diu, and F. Laloë. *Quantum Mechanics*. Wiley, New York, (1977).
- [21] R. Balescu. *Equilibrium and non-equilibrium statistical mechanics*. Wiley,New York, (1975).
- [22] W. B. Case. *Am. J. Phys*, **76**(10), (2008).
- [23] V. S. Filinov, S. Bonella, Y. E. Lozovik, A. V. Filinov, and I. Zacharov. "Quantum Molecular dynamics using Wigner representation" p.667 in *Classical and Quantum Dynamics in Condensed Phase Simulations, Proceedings of the International School of Physics, Lercici, B. J. Berne, G. Ciccotti, and D. F. Coker eds.* (World Scientific, Singapore), (1998).

- [24] H. Lee. *Phys.Rep*, **249**(147), (1995).
- [25] P. Carruthers and F. Zachariasen. *Rev.Mod.Phys*, **55**(245), (1983).
- [26] M. Hillery, R. F. O'Connell, M. O. Scully, and E. P. Wigner. *Phys.Rep*, **106**(121), (1984).
- [27] E. M. Lifshitz and L. D. Landau. *Quantum Mechanics:Non-Relativistic Theory*, volume **55**. Elsevier,Oxford, (1977).
- [28] V. S. Filinov. *Mol.Phys*, **88**(1517), (1996).
- [29] V. S. Filinov. *Mol.Phys*, **88**(1529), (1996).
- [30] P. R. Holland. *The Quantum Theory of Motion. An account of the de Broglie-Bohm Causal Interpretation of Quantum Mechanics*. Cambridge University Press,Cambridge, (1997).
- [31] E. J. Heller. *J.Chem.Phys*, **65**(1289), (1976).
- [32] P. Davies, The quantum life, in "How physics is changing biology" Special issue, *Physics World* **22** 24 (2009); J. Guck, Do cells care about physics?, in "How physics is changing biology" Special issue, *Physics World* **22** 31 (2009); S. Wang, Postcards from the brain, in "How physics is changing biology" Special issue, *Physics World* **22** 37 (2009); L. Sussking, Darwin's Legacy, in "How physics is changing biology" Special issue, *Physics World* **22** 42 (2009).
- [33] J. E. Moyal. *Proc. Cambridge Philos. Soc.*, **45**(99), (1949).
- [34] H. J. Groenewold. *Physica*, **12**(405), (1946).
- [35] A. Sergi. Variational principle and phase-space measure in non-canonical coordinates. *Atti della Accademia Peloritana dei Pericolanti*, **83**(C1A0501003), (2005).

- [36] A. Sergi. *J.Chem.Phys*, **126**(074109), (2007).
- [37] A. Sergi. *J.Chem.Phys*, **124**(024110), (2006).
- [38] A. Sergi. *J.Phys.A*, **40**(F347), (2007).
- [39] S. Nosè. *Mol.Phys*, **52**(255), (1984).
- [40] R. Kapral and G. Ciccotti. *J.Chem.Phys*, **110**(8919), (1999).
- [41] J. A. Poulsen, G. Nyman, and P. J. Rossky. *J.Chem.Phys*, **119**(12179), (2003).
- [42] F. Mintert and E. J. Heller. *Europhysics Letters*, **86**(50006), (2009).
- [43] M. M. Tchoukouegno and A. Sergi. Dynamical quantum-classical transitions of harmonic thermal baths. Unpublished, (2010).
- [44] M. V. Berry and K. E. Mount, *Rep.Prog.Phys*, **35**, 315 (1972); M. V. Berry, *Phyl Trans. Royal Soc. Lon*, **287**,237 (1977); *J.Phys.A*, **10**, 2083 (1977).
- [45] I. Oppenheim and J. Ross. *Phys.Rev*, **107**(28), (1957).