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"A Quantum Mechanical Formulation of the Nosé-Theorem"

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To my family

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Chapter 1

Introduction

It is well known that in classical statistical mechanics the temperature of a system appears as an intensive parameter T which is determined at thermal equilibrium. For the canonical ensemble T appears in the equilibrium distribution function f via

$$f = \frac{1}{Z(T)} e^{-H/kT} \tag{1.1}$$

where Z is a normalization constant proportional to T and k the Boltzmann constant. Another microscopic connection is due to the equipartition theorem which states that the average kinetic energy is related to the temperature by

$$< \sum_{i=1}^{N} p_i^2/2m >= \frac{3}{2} NkT \tag{1.2}$$

where N is the number of 3-dimensional particles considered. This theorem holds only for degrees of freedom which appear quadratic in the Hamilton function H - for general systems there is no statement possible. An ideal example where the equipartition theorem holds is the harmonic oscillator where the coordinates and momenta have a quadratic contribution to the energy since $H = p^2/2m + m\omega^2 r^2/2$.

In molecular dynamics simulations formula (1.2) is used for calculating the temperature of many-body systems. Since those simulations are carried out in the microcanonical ensemble the exact temperature value at a specific time step is unknown. Only after finishing the simulation cycle one can relate the average kinetic energy to the temperature. In contrast laboratory experiments are carried out in the canonical ensemble since holding the temperature constant is easy to execute. This contradiction between the simulation and the measurement of

a specific physical situation can be corrected by controlling the temperature during dynamical simulations. One method which fulfils this task is the Nosé-Hoover thermostat [1][2][3]. The Nosé-Hoover thermostat, which consist of a classical 'physical system' coupled to a classical 'heat bath', has the feature that the temperature appears as a heat bath parameter at which value the kinetic energy will fluctuate around. This is connected with the remarkable result that the Nosé-Hoover thermostat produces a canonical distribution for the physical variables (Nosé-theorem). With this tool a comparison of the simulation results and the laboratory results is possible. Since this is valid in the classical case the question arises if it is possible to formulate the Nosé-theorem for quantum systems.

If we go now over to quantum physics we observe that the equipartition theorem which is used for interpreting the temperature fails. The reason is that the spectrum of the energy of a physical system (e.g. the single harmonic oscillator from the example above) is discrete and one obtains a different canonical distribution function which contains an integer value n for the energy discretization. The density matrix reads

$$\hat{\rho} = \frac{1}{Z} e^{-\hat{H}/kT} = \frac{1}{Z} \sum_n e^{-(n+1/2)\hbar\omega/kT} |\Psi_n >< \Psi_n|, \tag{1.3}$$

where $|\Psi_n >$ denotes the energy eigenvectors. If one calculates now the average energy $< \hat{H} >$ one obtains

$$< \hat{H} >= \hbar\omega \frac{e^{-\hbar\omega/kT}}{1 - e^{-\hbar\omega/kT}} + \hbar\omega \frac{1}{2}. \tag{1.4}$$

This clearly gives the result that for low temperatures, when $\hbar\omega >> kT$, the average energy goes to $\hbar\omega/2$. At high temperatures, where

$$\hbar\omega << kT, \tag{1.5}$$

the result agrees with the one predicted by the equipartition theorem. From this we conclude that we can only interpret the temperature of a quantum system in a certain temperature limit as a fluctuation of the kinetic energy. This work shows a quantization of the Nosé-Hoover thermostat (chapter 2) from first principles, by using Dirac's constrained quantization method (chapter 3). In chapter 4 I show that for a temperature limit similar like the one used for the quantum harmonic oscillator a quantum Nosé-theorem can be formulated.

Another quantum formulation of the Nosé-Hoover thermostat has been provided by Sergi [4] introducing non-Hamiltonian Poisson brackets and commutators. Mentrup and Schnack presented [5] a quantum extension for coherent states.

Chapter 2

The Nosé-Hoover Thermostat

We describe a canonical ensemble if we surround a system consisting of N particles with coordinates (q, p) in phase space with a large external system (the heat bath). Nosé's [1][2] approach was instead to introduce a thermal variable s which describes together with its conjugate momentum p_s the heat bath. The variable s also describes the interaction of the heat bath with the system, namely we express the thermal interaction between the system and the heat bath by scaling all physical momenta p by s. This means that we can change each particle's velocity by changing the value of s, or respectively the value of p_s. The transformation of a particle's velocity can also be explained in an even deeper way by an additional rescaling of the system time t. So we end up with multiple relations of new and old variables which read

$$\begin{aligned} q_i' &= q_i \\ p_i' &= p_i/s \\ t' &= \int dt/s \end{aligned} \tag{2.1}$$

For a given particle its momenta read

$$p_i' = m_i \frac{dq_i'}{dt'} = s m_i \frac{dq_i'}{dt} = s m_i . \frac{dq_i}{dt} = s p_i \tag{2.2}$$

Here and from now on variables with primes shall be called real variables while variables without primes shall be called virtual variables.

Imagine now a Hamiltonian

$$H_{Nosé} = \sum_i \frac{p_i^2}{2 m_i s^2} + \Phi(q) + \frac{p_s^2}{2Q} + gkT \ln(s) \tag{2.3}$$

where we already see that Nosé modelled the interaction by replacing p_i with p_i/s in the usual kinetic energy term. Q represents the mass of s. T is the temperature of the heat bath. Applying the canonical formalism to $H_{Nosé}$ we obtain the equations of motion

$$\begin{aligned}
\frac{dq_i}{dt} &= \frac{\partial H_{Nosé}}{\partial p_i} = \frac{p_i}{m_i s^2} \\
\frac{dp_i}{dt} &= -\frac{\partial H_{Nosé}}{\partial q_i} = -\frac{d\Phi}{dq_i} \\
\frac{ds}{dt} &= \frac{\partial H_{Nosé}}{\partial p_s} = \frac{p_s}{Q} \\
\frac{dp_s}{dt} &= -\frac{\partial H_{Nosé}}{\partial s} = \sum_i \frac{p_i^2}{m_i s^3} - gkT/s.
\end{aligned} \tag{2.4}$$

We now transform the equations of motion according to the rules 2.1. Additional we introduce the relation $p'_s = p_s/s$.

$$\begin{aligned}
\frac{dq'_i}{dt'} &= s\frac{dq'_i}{dt} = s\frac{dq_i}{dt} = \frac{p_i}{m_i s} = \frac{p'_i}{m_i} \\
\frac{dp'_i}{dt'} &= s\frac{d}{dt}\frac{p_i}{s} = \frac{dp_i}{dt} - \frac{1}{s}\frac{ds}{dt}p_i = -\frac{\partial \Phi}{\partial q'_i} - \frac{1}{s}\frac{ds}{dt'}p'_i \\
\frac{ds'}{dt'} &= s\frac{ds'}{dt} = s\frac{ds}{dt} = s'^2 p'_s/Q \\
\frac{dp'_s}{dt'} &= s\frac{d}{dt}\frac{p_s}{s} = \frac{dp_s}{dt} - \frac{1}{s}\frac{ds}{dt}p_s = \sum_i \frac{p'^2_i}{m_i s} - gkT/s - \frac{1}{s}\frac{ds}{dt'}p'_s.
\end{aligned} \tag{2.5}$$

Hoover's idea [6] was now to introduce the variable $\xi = (1/s)ds/dt' = sp'_s/Q$ to end up with

$$\begin{aligned}
\frac{dq'_i}{dt'} &= \frac{p'_i}{m_i} \\
\frac{dp'_i}{dt'} &= -\frac{\partial \Phi}{\partial q'_i} - \xi p'_i \\
\frac{dlns'}{dt'} &= \xi \\
\frac{d\xi}{dt'} &= \left(\sum_i \frac{p_i^2}{m_i} - gkT\right)/Q.
\end{aligned} \tag{2.6}$$

These equations of motion are referred to be the Nosé-Hoover thermostat. Usually one drops the third differential equation since it is decoupled from the others, although this would destroy the canonical form of the equations. Nevertheless one can calculate the canonical equilibrium distribution of both formulations of the Nosé-Hoover thermostat as shown in the next section. What is the interpretation of the equations of motion above? The equations $\dot{q}$ and $\dot{p}$ describe the frictional motion of the particles in a given potential Φ. The difference to classic frictional

theories is that the friction coefficient ξ is not a constant but a (canonical) variable. Assume now that the time derivative of ξ is positive which means that the kinetic energy of the particles is higher than the value $gkT/2$. An increasing friction coefficient means that the friction force decreases each particle's velocity until the kinetic energy drops below $gkT/2$. This results in $\dot{\xi} < 0$. When ξ decreases the velocities begin to increase - the system is heated up. In the long turn the particle's kinetic energy will fluctuate around $gkT/2$.

2.1 Derivation of the generalized Liouville equation

This derivation concerning the generalized Liouville equation follows Evans and Morriss [7]. We consider an ensemble of macroscopically identical systems which are distributed over a set of microstates. Then we investigate a fraction of δn systems located at a point $\Gamma = (q, p) = (q_1, ..., q_{3N}, p_1, ..., p_{3N})$ around a volume element $(\delta q, \delta p)$. Then we can define the density distribution function $f(q, p, t)$ by

$$\delta n = f(q, p, t)\delta q \delta p. \tag{2.7}$$

Of course the total ensemble number is fixed and that is why we can normalize f by integrating over the whole phase space

$$1 = \int f(q, p, t)\delta r \delta p. \tag{2.8}$$

Consider now a trajectory in phase space which passes through the volume element $\delta q \delta p$ we can calculate the number of configurations entering e.g. a face perpendicular to the q_1 axis

$$f(q_1, ..., t)\dot{q_1}(q_1, ..., t)\delta q_2 ... \delta q_{3N}\delta p \tag{2.9}$$

and similar for a face shifted to $q_1 + \delta q_1$

$$\begin{aligned} &f(q_1 + \delta q_1, ..., t)\dot{q_1}(q_1 + \delta q_1, ..., t)\delta q_2 ... \delta q_{3N}\delta p \approx \\ &\left(f(q_1, ..., t) + \frac{\partial f}{\partial q_1}\delta q_1\right)\left(\dot{q_1}(q_1, ..., t) + \frac{\partial \dot{q_1}}{\partial q_1}\delta q_1\right)\delta q_2 ... \delta q_{3N}\delta p. \end{aligned} \tag{2.10}$$

The total number of δn changing in time in the q_1 direction must read

$$\frac{d}{dt}\delta n_{q_1} = -\left(\dot{q_1}\frac{\partial f}{\partial q_1} + f\frac{\partial \dot{q_1}}{\partial q_1}\right)\delta q \delta p \tag{2.11}$$

or along all coordinate and momentum directions

$$\frac{d}{dt}\delta n = -\left(f\frac{\partial}{\partial \Gamma}\cdot\dot{\Gamma} + \dot{\Gamma}\cdot\frac{\partial f}{\partial \Gamma}\right)\delta q \delta p. \tag{2.12}$$

Together with the normalization above and

$$\frac{1}{\delta q \delta p}\frac{d}{dt}\delta n = \frac{\partial}{\partial t}\frac{\delta n}{\delta q \delta p} = \frac{\partial f}{\partial t} \tag{2.13}$$

we obtain the generalized Liouville equation which describes the time evolution a phase space function with respect to the additional contraction of the phase space itself

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \Gamma} \cdot (\dot{\Gamma} f) = 0. \tag{2.14}$$

The total time derivative of f is given by

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \dot{\Gamma} \cdot \frac{\partial f}{\partial \Gamma}. \tag{2.15}$$

Then the Liouville equation reads

$$\frac{df}{dt} = -\left(\frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma}\right) f. \tag{2.16}$$

For the Nosé-Hoover system the phase space does not only consists of the (q, p) variables, but rather of four variables $\Gamma = (q, p, s, \xi)$. So the Liouville equation would read explicitly

$$\frac{df}{dt} = -\left(\frac{\partial}{\partial q} \cdot \dot{q} + \frac{\partial}{\partial p} \cdot \dot{p} + \frac{\partial}{\partial s} \cdot \dot{s} + \frac{\partial}{\partial \xi} \cdot \dot{\xi}\right) f. \tag{2.17}$$

2.1.1 Equilibrium solution for the Nosé-Hoover thermostat

In the literature the Nosé-Hoover thermostat is often referred to as two different systems since the equation for $\dot{s}$ becomes redundant. Both systems describe of course the same dynamics in phase space, but one has take care of the generalized Liouville equation since the term $\partial\dot{\Gamma}/\partial\Gamma$ vanishes in one case. This term is called phase space contraction factor since it describes the shrinking of the phase space volume.

- For the Nosé-Hoover system which is described by all four differential equations of (2.6) the so-called phase space contraction factor is

  $$\Lambda \equiv \frac{\partial}{\partial \Gamma} \cdot \dot{\Gamma} = 0 \tag{2.18}$$

  which means that the Liouville theorem $df/dt = 0$ known from classical mechanics holds. The equilibrium solution $\partial f/\partial t = 0$ of the equation

  $$0 = \dot{\Gamma} \cdot \frac{\partial f}{\partial \Gamma} \tag{2.19}$$

  reads

  $$f(\Gamma) = Ce^{\sum_i \frac{p_i^2}{2m_i} + \Phi(q) + \frac{Q}{2}\xi^2 + gkTlns}. \tag{2.20}$$

- For the Nosé-Hoover system which is described only by the first three equations of (2.6)- which are the equations for $\dot{q}, \dot{p}$,and $\dot{\xi}$ - the phase space contraction factor reads

$$\Lambda = -g\xi. \tag{2.21}$$

So we have to solve the generalized equilibrium Liouville equation

$$\dot{\Gamma} \cdot \frac{\partial f}{\partial \Gamma} + g\xi f = 0. \tag{2.22}$$

The solution reads

$$f(\Gamma) = Ce^{\frac{1}{kT}\left(\sum_i \frac{p_i^2}{2m_i} + \Phi(q) + \frac{Q}{2}\xi^2\right)}. \tag{2.23}$$

2.2 Production of canonical ensemble for $H_{Nosé}$

The Hamiltonian $H_{Nosé}$ has an interesting feature namely it generates a canonical distribution for the variables (q, p) [2]. To show this we make the following calculation. For the Nosé-Hoover system given by the Hamiltonian

$$H_{Nosé} = \sum_i^N \frac{p_i^2}{2m_i s^2} + \Phi(q) + \frac{p_s^2}{2Q} + gkT\ln(s) \tag{2.24}$$

we express the equilibrium distribution function in a δ function form as $\delta(H_{Nosé} - E)$ where E is the time-constant value of $H_{Nosé}$. The partition function then reads

$$Z = \frac{1}{N!h^{3N}} \int dp_s \int ds \int dp \int dq \delta(H_0(p/s, q) + p_s^2/2Q + gkTlns - E). \tag{2.25}$$

where $H_0(p, q) = \sum_i \frac{p_i^2}{2m} + \Phi(q)$. After the variable transformation $p_i' = p_i/s$, $q_i' = q_i$ which changes the volume element as

$$dpdq = s^{3N} dp'dq', \tag{2.26}$$

we obtain

$$Z = \frac{1}{N!h^{3N}} \int dp_s \int dp' \int dq' \int ds s^{3N} \delta(H_0(p', q') + p_s^2/2Q + gkTlns - E). \tag{2.27}$$

We can use the general rule for distribution of functions to express them as a zero of the function itself. The formula reads $\delta(f(s)) = \delta(s - s_0)/f'(s)$ where s_0 is the zero of $f(s)$, $f(s_0) = 0$ with

$$f(s) = H_0(p', q') + p_s^2/2Q + gkTlns - E. \tag{2.28}$$

So s_0 is

$$s_0 = e^{-\frac{1}{gkT}(H_0(p',q')+p_s^2/2Q-E)} \tag{2.29}$$

and the derivative $f'(s) = gkT/s$. Now the partition function becomes

$$Z = \frac{1}{N!h^{3N}}\frac{1}{gkT}\int dp_s \int dp' \int dq' \int ds s^{3N+1}\delta(s - e^{-\frac{1}{gkT}(H_0(p',q')+p_s^2/2Q-E)}). \tag{2.30}$$

After integrating with respect to s we obtain

$$Z = \frac{1}{N!h^{3N}}\frac{1}{gkT}\left[\int dp_s e^{\frac{3N+1}{gkT}(E-\frac{p_s^2}{2Q})}\right]\left[\int dp' \int dq' e^{-\frac{3N+1}{gkT}H_0(p',q')}\right]. \tag{2.31}$$

Choosing $g = 3N + 1$ the partition function Z of the extended system reads exactly (up to constant) as the canonical partition function Z_c given by

$$Z_c = \int dp' \int dq' e^{-H_0(p',q')/kT} \tag{2.32}$$

with the usual equilibrium distribution function

$$f_c(p', q') = e^{-H_0/kT}. \tag{2.33}$$

Writing down the formulas for the microcanonical (extended) ensemble average and the canonical (physical) ensemble average of an observable A we gain the surprising result that we can identify both! With the above result we get

$$\begin{aligned} < A(p/s, q) >_{mc} = & \frac{1}{Z}\int dpdqdp_s dsA(p/s, q)\delta(H_{Nosé} - E) = \\ & \frac{1}{Z_c}\int A(p', q')f_c(p', q')dp'dq' =< A(p', q') >_c . \end{aligned} \tag{2.34}$$

The calculation above is in the literature named Nosé-Theorem and it is the key point of thermostating systems. A microcanonical extended system (constant energy) consisting of q, p, s and p_s variables produces in terms of averages a canonical distribution (constant temperature) for the q and p variables. An alternative proof - calculating the delta distribution with the zeros concerning the p_s variables - is presented in appendix A.

2.3 Time scaling transformations in Hamiltonian systems

We now consider the following time scaling transformation which preserves the symplectic structure of a Hamiltonian system. This was already mentioned in the literature [10][11]. Assume we have a Hamilton function $H = H(X_i, \tilde{X}_i; \lambda)$, which is a function of its coordinates $X_i = X_i(\lambda)$

and its canonical conjugates $\tilde{X}_i = \tilde{X}_i(\lambda)$. The parameter λ represents the Hamiltonian time of the system. The system has the following equations of motion

$$\frac{d}{d\lambda}X_i = \frac{\partial H}{\partial \tilde{X}_i} \quad \frac{d}{d\lambda}\tilde{X}_i = -\frac{\partial H}{\partial X_i}. \tag{2.35}$$

In another Hamiltonian time t the equations of motion would read

$$\frac{dX_i}{dt}\frac{1}{f} = \frac{\partial H}{\partial \tilde{X}_i} \quad \frac{d\tilde{X}_i}{dt}\frac{1}{f} = -\frac{\partial H}{\partial X_i}, \tag{2.36}$$

where $f(X_i, \tilde{X}_i) := d\lambda/dt$. One usually scales the time after calculating the equations of motion (this destroys the Hamiltonian structure since H does not determine the equations of motion in time t), but this step can be skipped when we go over to a constrained Hamiltonian system which features already the new time t. We call the procedure which is necessary for this a time scaling transformation. A time scaling transformation transforms a system with Hamiltonian H in the time λ to a constrained system with Hamiltonian H^* in the time t where $f(X_i, \tilde{X}_i) = d\lambda/dt$ represents the time scaling. The Hamiltonian H^* is given by the rule

$$H^*(X_i, \tilde{X}_i; t) := f(X_i; \tilde{X}_i)H(X_i, \tilde{X}_i; \lambda), \tag{2.37}$$

together with the constraint $H = 0$. This time scaling transformation gives the same equations of motion as equation (2.36) since

$$\frac{dX_i}{dt} = \frac{\partial H^*}{\partial \tilde{X}_i} = \frac{\partial f}{\partial \tilde{X}_i}H + f\frac{\partial H}{\partial \tilde{X}_i} = f\frac{\partial H}{\partial \tilde{X}_i} \tag{2.38}$$

and

$$\frac{d\tilde{X}_i}{dt} = -\frac{\partial H^*}{\partial X_i} = -\frac{\partial f}{\partial X_i}H - f\frac{\partial H}{\partial X_i} = -f\frac{\partial H}{\partial X_i}, \tag{2.39}$$

where the constraint $H = 0$ ensures that the first term on the right side vanishes. Alternatively we can write

$$H^* = f(H - \underline{H}) = 0 \tag{2.40}$$

with the constraint $H = \underline{H}$ which means that the Hamiltonian has for all times and phase space trajectories the value $\underline{H}$.

2.4 Dettmann formulation of the Nosé-Hoover thermostat

An example where the above method is applied, is the Nosé-Hoover Thermostat. Nosé's original deviation starts with a Hamiltonian $H_{Nosé} = H_{Nosé}(q, p, s, p_s; t)$. After deriving the equations

of motion Nosé transforms the variables with a noncanonical time transformation: $\{q(t), p(t), s(t), p_s(t)\} \rightarrow \{q'(t'), p'(t'), s'(t'), p'_s(t')\}$. The transformation laws read

$$q' = q \qquad p' = p/s \qquad s' = s \qquad p'_s = p_s/s \qquad dt/dt' = s. \tag{2.41}$$

Dettmann's idea [8][9][12] was to define the Hamiltonian $H_D := H^* = fH_{Nosé} = sH_{Nosé}$ (where $\underline{H} = 0$ is chosen) , which vanishes, because of the constraint $H_{Nosé} = 0$. H_D reads

$$H_D = \sum_i \frac{p_i^2}{2m_i s} + s\Phi(q) + s\frac{p_s^2}{2Q} + gkTs\ln(s). \tag{2.42}$$

The equations of motion derived with the Hamiltonian H_D and the constraint that $H_{Nosé}$=0 read

$$\begin{aligned} \frac{dq_i}{dt} &= s\frac{\partial H_{Nosé}}{\partial p_i} = \frac{p_i}{m_i s} \\ \frac{dp_i}{dt} &= -s\frac{\partial H_{Nosé}}{\partial q_i} = -s\frac{d\Phi}{dq_i} \\ \frac{ds}{dt} &= s\frac{\partial H_{Nosé}}{\partial p_s} = s\frac{p_s}{Q} \\ \frac{dp_s}{dt} &= -s\frac{\partial H_{Nosé}}{\partial s} = \sum_i \frac{p_i^2}{m_i s^2} - gkT. \end{aligned} \tag{2.43}$$

To obtain the final result, we use the definitions (2.41) and its time derivatives. If we drop the $'$ we end up with the Nosé-Hoover equations of motion

$$\begin{aligned} \frac{dq_i}{dt} &= \frac{p_i}{m_i} \\ \frac{dp_i}{dt} &= -\frac{d\Phi}{dq_i} - p_i p_s/Q \\ \frac{ds}{dt} &= s\frac{\partial H_{Nosé}}{\partial p_s} = s\frac{p_s}{Q} \\ \frac{dp_s}{dt} &= -s\frac{\partial H_{Nosé}}{\partial s} = \sum_i \frac{p_i^2}{m_i} - gkT. \end{aligned} \tag{2.44}$$

With this we derived the Nosé dynamics without making use of a time scaling. Also here the third equation for s becomes redundant.

2.5 Production of canonical ensemble for H_D

The Nosé-Theorem holds also for the case where we use the Dettmann Hamiltonian to describe canonical averages [12]. H_D can be written as

$$H_D = sH_0(p/s, q) + s\frac{p_s^2}{2Q} + gkTsln(s), \tag{2.45}$$

where $H_0(p,q) := \sum_i p_i^2/2m_i + \Phi(q)$. The only difference concerning the calculation done in section 2.2 is that the δ function reads with the help of $\delta(f(s)) = \delta(s-s_0)/|f'(s_0)|$ where s_0 is the only zero of f, where

$$f(s) = H_D - E = sH_0(p/s,q) + s\frac{p_s^2}{2Q} + gkTsln(s) - E. \tag{2.46}$$

Next we use $E = 0$ which represents the fact that the initial value of H_D is zero. After the transformations $p_i/s \to p_i'$ and $q_i \to q_i'$ we obtain

$$\begin{aligned}\delta(H_D - E)dsdp_sdpdq &= \delta(H_D)s^{3N}dsdp_sdp'dq' \\ &= \delta(s - e^{-\frac{1}{gkT}(H_0(p',q')+p_s^2/2Q)})s^{3N}dsdp_sdp'dq'/|H_0(p',q') + \frac{p_s^2}{2Q} + gkTln(s_0) + gkT|.\end{aligned} \tag{2.47}$$

After the s integration we obtain a similar result as in section (2.2) namely

$$\frac{1}{gkT}e^{-\frac{3N}{gkT}(H_0(p',q')+p_s^2/2Q)}dp_sdp'dq'. \tag{2.48}$$

Note that in the formula for $f'(s_0)$ there is no gkT/s term in the denominator as in the Nosé-Hoover case. This reduces the constant g in the s integral to $g = 3N$, since the constraint lowers the number of degrees of freedom by one. The p_s integration gives a constant and we obtain the result that the Nosé-Theorem holds also concerning the Dettmann Hamiltonian. We obtain

$$\begin{aligned}< A(p/s,q) >_{mc} = &\frac{1}{Z}\int dpdqdp_sdsA(p/s,q)\delta(H_D) = \\ &\frac{1}{Z_c}\int A(p',q')f_c(p',q')dp'dq' =< A(p',q') >_c,\end{aligned} \tag{2.49}$$

for an observable A where f_c is again the equilibrium distribution function.

Chapter 3

Dirac Quantization of Constrained Systems

3.1 Dirac's generalized Hamiltonian dynamics

This chapter describes Dirac's method to quantize constrained systems. We follow closely Dirac's approach given in [13]. In usual dynamic theories one starts with a Lagrangian function $L(q, \dot{q})$ which is a function of the coordinates and velocities. Here the point above the space coordinate means the derivative with respect to the time, $\dot{q} = dq/dt$. The Lagrange equation reads

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_n} = \frac{\partial L}{\partial q_n}. \tag{3.1}$$

To go over to the Hamilton formalism one defines the momentum variable p by

$$\dot{p}_n = \frac{\partial L}{\partial \dot{q}_n} \tag{3.2}$$

so that ones has the dynamical variables p and q. Usually the momenta are assumed to be independent of the coordinates but concerning constrained systems this does not hold. In general a constrained system is a system which also consists of additional relations (constraints) which are described by M functions Φ_m

$$\Phi_m(q, p) = 0. \tag{3.3}$$

This clearly means that not all q's and p's are independent. We call these constraints primary constraints. If we look at the variation of H which reads

$$\begin{aligned}&\delta H = \delta(p_n\dot{q}_n - L) = \\ &\delta p_n\dot{q}_n + p_n\delta\dot{q}_n - \frac{\partial L}{\partial q_n}\delta q_n - \frac{\partial L}{\partial \dot{q}_n}\delta\dot{q}_n = \\ &\delta p_n\dot{q}_n - \frac{\partial L}{\partial q_n}\delta q_n.\end{aligned} \tag{3.4}$$

we see that H is independent of the velocities $\dot{q}_n$ because its variation does not depend on the variation of $\dot{q}_n$. The last equation can be rewritten as

$$\left(\frac{\partial H}{\partial q_n} + \frac{\partial L}{\partial q_n}\right)\delta q_n + \left(\frac{\partial H}{\partial p_n} - \dot{q}_n\right)\delta p_n = 0. \tag{3.5}$$

We use Theorem 1.2 in [14] which states that for arbitrary variations tangent on the surface $\Phi_m(q,p) = 0$ of the function

$$0 = \lambda_n\delta q_n + \mu_n\delta p_n \tag{3.6}$$

it follows

$$\lambda_n = u_m\frac{\partial\Phi_m}{\partial q_n} \quad \mu_n = u_m\frac{\partial\Phi_m}{\partial p_n} \tag{3.7}$$

for some u_m. With this we obtain

$$\begin{aligned}\dot{q}_n &= \frac{\partial H}{\partial p_n} + u_m\frac{\partial\Phi_m}{\partial p_n} \\ -\frac{\partial L}{\partial q_n} &= \frac{\partial H}{\partial q_n} + u_m\frac{\partial\Phi_m}{\partial q_n} = -\dot{p}_n.\end{aligned} \tag{3.8}$$

To simplify the formalism it is useful to introduce the algebra of Poisson brackets of two functions $f(q,p)$ and $g(q,p)$ which is defined by

$$\{f,g\} = \frac{\partial f}{\partial q_n}\frac{\partial g}{\partial p_n} - \frac{\partial f}{\partial p_n}\frac{\partial g}{\partial q_n}. \tag{3.9}$$

The Poisson bracket has four properties: Antisymmetry,

$$\{f,g\} = -\{g,f\}. \tag{3.10}$$

Linearity,

$$\{f_1 + f_2, g\} = \{f_1,g\} + \{f_2,g\}. \tag{3.11}$$

There exists also a 'product law',

$$\{fg,h\} = f\{g,h\} + \{f,h\}g. \tag{3.12}$$

And the Jacobi identity also holds:

$$\{f,\{g,h\}\}+\{g,\{h,f\}\}+\{h,\{f,g\}\}=0. \tag{3.13}$$

Consider now the time derivative of a function $g=g(q,p)$ which reads

$$\dot{g}=\frac{\partial g}{\partial q_n}\dot{q}_n+\frac{\partial g}{\partial p_n}\dot{p}_n. \tag{3.14}$$

Together with the equations of motion above we can write then instead

$$\dot{g}=\{g,H\}+u_m\{g,\Phi_m\}. \tag{3.15}$$

Here we introduce a new notation for equality: Instead of writing

$$\Phi=0 \tag{3.16}$$

we write

$$\Phi\approx 0. \tag{3.17}$$

The symbol '$\approx$' means that all constraints are allowed to be set equal to zero only after evaluating all Poisson brackets. We say that the constraints are 'weakly zero'. For ordinary equality we use '=' which is called 'strongly zero'. Furthermore one can identify two function $f\approx g$ if they coincide on the submanifold defined by the constraints.

As already said the primary constraints are all those constraints which define our dynamical system. Since those constraints are functions identical to zero it is clear that the time evolution of something that is equal to zero must stay zero, too. Let us set $g=\Phi_{m'}$ in the above equation. We obtain

$$\dot{\Phi}_{m'}=\{\Phi_{m'},H\}+u_m\{\Phi_{m'},\Phi_m\}\approx 0. \tag{3.18}$$

There may now arise three different cases: *a*) it could be possible to obtain an equation of the form $0=0$ which we do not have to bother any more. *b*) we obtain a condition on the u_m. *c*) a new equation arises which looks like $\chi(q,p)=0$. Such an equation is nothing else than a new constraint which must also fullfill the above time evolution. All such constraints which arise from the primary ones are collected to a new set which we call secondary constraints. One has to carry on and evaluate all time evolutions until all u_m's are fixed. The distinction between primary and secondary constraints is now of importance, although in the final form the opposite is true. So we end up with M primary constraints and K secondary ones which form together

a set of $M + K = J$ constraints $\Phi_j \approx 0$ in total. So what is left is a system described by the formula

$$\{\Phi_j, H\} + u_m \{\Phi_j, \Phi_m\} \approx 0. \tag{3.19}$$

where the index j runs over all J constraints. The index m runs only over all M primary constraints, obviously $M \leq J$. The above equation can be thought of an inhomogenous vector equation. Its general solution for the u_m is

$$u_m = U_m + V_m \tag{3.20}$$

where U_m describes the solution of the inhomogenous components and V_m the homogenous solution of

$$V_m \{\Phi_j, \Phi_m\} \approx 0. \tag{3.21}$$

V_m itself consists of all linearly independent solutions V_a^m, $a = 1, ..., A$ of the formula above. So the general solutions reads

$$u_m = U_m + v_a V_a^m \tag{3.22}$$

with total arbitrary coefficients v_a. So in total our constrained system obeys the time evolution

$$\dot{g} \approx \{g, H' + v_a \Phi_a\} \tag{3.23}$$

where

$$\begin{aligned} H' &= H + U_m \Phi_m \\ \Phi_a &= V_a^m \Phi_m \\ H_T &:= H' + v_a \Phi_a. \end{aligned} \tag{3.24}$$

H_T is called the total Hamiltonian and H' is called first-class Hamiltonian. The equations of motions read simply

$$\dot{g} \approx \{g, H_T\} \tag{3.25}$$

which are they same as the original Lagrangian ones.

3.1.1 First and second class constraints, Dirac brackets, gauge fixing

Before we move on let us define the following: A function $R = R(q, p)$ is called a first-class function, or first-class, if it has a vanishing Poisson bracket with all other Φ_j where $j = 1, ..., J$.

Otherwise it is called a second-class function, or second-class.
Also the following Theorem holds: The Poisson bracket of two first-class functions is also first-class. Proof: Let R and S be first class. Then the brackets

$$\{R, \Phi_j\} = r_{jj'}\Phi_{j'} \tag{3.26}$$

$$\{S, \Phi_j\} = s_{jj'}\Phi_{j'} \tag{3.27}$$

can of course be constructed via a linear combination of all constraints. Then

$$\begin{aligned}\{\{R,S\},\Phi_j\} &= \{\{R,\Phi_j\},S\} - \{\{S,\Phi_j\},R\} \\ &= \{r_{jj'}\Phi_{j'},S\} - \{s_{jj'}\Phi_{j'},R\} \\ &= r_{jj'}\{\Phi_{j'},S\} + \{r_{jj'},S\}\Phi_{j'} - s_{jj'}\{\Phi_{j'},R\} - \{s_{jj'},R\}\Phi_{j'} \approx 0.\end{aligned} \tag{3.28}$$

So we have proven that $\{R, S\}$ is first-class. Together with primary and secondary constraints we can distinguish between four different types of constraints, although the division of primary and secondary is independent of first-class and second-class. Using this it is easy to show that the Hamiltonian H' defined in the previous chapter is first-class and that the total Hamiltonian H_T consists of the sum of a first-class Hamiltonian with first-class constraints, per definition. So what's the meaning of the arbitrary coefficients v_a which appear in H'? Physically speaking a dynamical state is defined by a given initial set of q's and p's and not by the coefficients v_a. The initial set of course defines all later physical states but the functions v_a come in and therefore all states at a later time have to correspond to the same physical state (for different v's. Say that at time $t = 0$ a function g takes its value $g(t = 0) = g_0$ then at later time δt the time evolutions reads

$$\begin{aligned}g(\delta t) &= g_0 + \dot{g}\delta t \\ &= g_0 + \{g, H_T\}\,\delta t \\ &= g_0 + \delta t\left(\{g, H'\} + v_a\{g, \Phi_a\}\right).\end{aligned} \tag{3.29}$$

For a different v_a, say v'_a the difference between the time evolution would read

$$\Delta g(\delta t) = \epsilon_a\{g, \Phi_a\}, \tag{3.30}$$

where $\epsilon_a = \delta t(v_a - v'_a)$ is a small and arbitrary number. This means that changing our total Hamiltonian by adding the additional term $\epsilon_a\Phi_a$ does change the q's and p's but not the physical state of the system at this time. In a similar manner one can show that also the functions $\{\Phi_a, \Phi_{a'}\}$ and $\{H', \Phi_a\}$ do not change the physical state since all those brackets are

first-class itself (as shown by the theorem above). So in general we can say that all first-class constraints are generators of transformations which do not change the physical state. We call this transformations gauge transformations.

Since all physical observables can not depend on arbitrary functions we have to get rid of this arbitrariness by imposing gauge fixing conditions. As we already saw the first-class constraints are generators of gauge freedom, therefore we have to eliminate them. By choosing a new set of constraints $\chi_{a'}$ where $a' = 1, ..., A$ such that the bracket

$$det\left(\{\chi_{a'}, \Phi_a\}\right) \neq 0, \tag{3.31}$$

- where this inequality must be understood weakly - we create a 1-to-1 correspondence between a physical state and a set of q's and p's. Since the number of gauge fixing constraints is equal to the number of initial first-class constraints, they both form a complete second-class set such that no first-class constraint is left. This means that no arbitrary functions are left and the physical state is exactly determined. Since now only second-class constraints are left (let us call them from now on Φ_s where $s = 1, ..., S = 2A$) the consistency relation for them reads

$$0 \approx \{\Phi_s, H_T\} = \{\Phi_s, H\} + U_{s'} \{\Phi_s, \Phi_{s'}\}. \tag{3.32}$$

Then the unknown coefficients read

$$U_{s'} = -\{\Phi_{s'}, \Phi_{s''}\}^{-1} \{\Phi_{s''}, H\}. \tag{3.33}$$

So the time evolution of a function $f = f(q, p)$ reads

$$\begin{aligned} \dot{f} &= \{f, H_T\} = \{f, H\} - \{f, \Phi_s\} \{\Phi_s, \Phi_{s'}\}^{-1} \{\Phi_{s'}, H\} \\ &:= \{f, H\}_D, \end{aligned} \tag{3.34}$$

where we have introduced with $\{.,.\}_D$ the so-called Dirac bracket which fulfills the same properties as the Poisson bracket, namely
antisymmetry,

$$\{f, g\}_D = -\{g, f\}_D. \tag{3.35}$$

Linearity,

$$\{f_1 + f_2, g\}_D = \{f_1, g\}_D + \{f_2, g\}_D. \tag{3.36}$$

A 'product law',

$$\{fg, h\}_D = f\{g, h\}_D + \{f, h\}_D g. \tag{3.37}$$

And the Jacobi identity,

$$\{f,\{g,h\}_D\}_D + \{g,\{h,f\}_D\}_D + \{h,\{f,g\}_D\}_D = 0. \tag{3.38}$$

The Dirac bracket describes the same equations of motion for the physical system than the Poisson bracket because they are weakly equal since

$$\{\Phi_s, H_T\} \approx 0 \tag{3.39}$$

because H_T is first-class. Thus we can write

$$\begin{aligned} \dot{g} &\approx \{g, H_T\}_D \\ &= \{f, H_T\} - \{f, \Phi_s\}\{\Phi_s, \Phi_{s'}\}^{-1}\{\Phi_{s'}, H_T\} \end{aligned} \tag{3.40}$$

for the time evolution of an arbitrary phase space function. More than that the Dirac bracket of any function g with a Φ_s is strongly equal to zero since

$$\{g, \Phi_s\}_D = \{g, \Phi_s\} - \{g, \Phi_{s'}\}\{\Phi_{s'}, \Phi_{s''}\}^{-1}\{\Phi_{s''}, \Phi_{s'}\} = 0. \tag{3.41}$$

So we can interpret $\Phi_s = 0$ s a strong equation. For two general function F and G we define the Dirac bracket by

$$\{F, G\}_D = \{F, G\} - \{F, \Phi_s\}\{\Phi_s, \Phi_{s'}\}^{-1}\{\Phi_{s'}, G\}. \tag{3.42}$$

Adopting the Schrödinger picture the time evolution of a wave vector $|\Psi(t_0)>$ is given by the Schrödinger equation

$$i\hbar\frac{d}{dt}|\Psi> = \hat{H}_T|\Psi>, \tag{3.43}$$

where $\hat{H}_T = \hat{H}_T(\hat{X})$ and $\hat{X} = (\hat{q}, \hat{p})$ represents the position and momentum operator by replacing $q \to \hat{q}$ and $p \to \hat{p}$. With this we can write down the expectation value of an operator $\hat{B} = \hat{B}(\hat{X})$ which reads

$$<\hat{B}> = <\Psi|\hat{B}|\Psi>. \tag{3.44}$$

We also end up with the equations for the constraints $\hat{\Phi}_s$ which must read

$$\hat{\Phi}_s|\Psi> = 0. \tag{3.45}$$

This of course implies that

$$\left[\hat{\Phi}_s, \hat{\Phi}_{s'}\right]|\Psi> = 0, \tag{3.46}$$

too. If we define the commutator with the Poisson bracket,

$$[\hat{F}, \hat{G}] = i\hbar \{F, G\}_{X=\hat{X}} \tag{3.47}$$

- where the subscript $X = \hat{X}$ means that we replace all observables with their corresponding operators after working out the Poisson bracket - we would end up with the condition $\{\Phi_s, \Phi_{s'}\}_{X=\hat{X}} = 0$. Since we have only second class constraints left (after fixing the gauge!) enforcing the above condition is impossible. Using the Dirac bracket $\{\Phi_s, \Phi_{s'}\}_{D,X=\hat{X}}$ instead of the Poisson bracket for the definition of the commutator one obtains as a condition for the constraints

$$\{\Phi_s, \Phi_{s'}\}_D = 0, \tag{3.48}$$

which is always true since the Dirac bracket of any function with a second class constraint vanishes as proven above. With this we define the quantum mechanical commutators by the rule

$$[\hat{F}, \hat{G}] := i\hbar \{F, G\}_{D,X=\hat{X}} \tag{3.49}$$

instead of using Poisson brackets.

3.1.2 Time dependent constraints

Until now we have only considered time independent constraints. Now we derive the Dirac formalism for time dependent constraints according to Mukunda [15]. Let's start with a phase space function $f = f(\Gamma, t)$ which depends explicitly on time. Here the symbol Γ stands for all phase space variables which we have to consider when we calculate the Dirac/Poisson-brackets. The time evolution of f reads

$$\frac{d}{dt} f(\Gamma, t) \approx \frac{\partial f}{\partial t} + \{f, H + \lambda_\nu \Phi_\nu\}. \tag{3.50}$$

When we set $f = \Phi_\mu$ we get

$$\frac{d}{dt} \Phi_\mu \approx \frac{\partial \Phi_\mu}{\partial t} + \{\Phi_\mu, H + \lambda_\nu \Phi_\nu\} \approx 0 \tag{3.51}$$

where we used the fact that the constraints are conserved in time and that the matrix $\{\Phi_\mu, \Phi_\nu\}$ is invertible. From this we calculate the λ_ν:

$$\lambda_\nu \approx -\{\Phi_\nu, \Phi_\mu\}^{-1} \left(\{\Phi_\mu, H\} + \frac{\partial \Phi_\mu}{\partial t} \right) \tag{3.52}$$

and plug them in in the above equation. We obtain

$$\begin{aligned}\frac{d}{dt}f(\Gamma,t) \approx \frac{\partial f}{\partial t} + \{f,H\} - \{f,\Phi_\nu\}\{\Phi_\nu,\Phi_\mu\}^{-1}\left(\{\Phi_\mu,H\} + \frac{\partial \Phi_\mu}{\partial t}\right) = \\ = \frac{\partial f}{\partial t} + \{f,H\}_D - \{f,\Phi_\nu\}\{\Phi_\nu,\Phi_\mu\}^{-1}\frac{\partial \Phi_\mu}{\partial t}.\end{aligned} \tag{3.53}$$

In the next chapter we derive the equations of motion for the relativistic particle, which can be considered as a constrained system. There two constraints arise: $\Phi_1 = H(\Gamma)$ and a special gauge $\Phi_2 = \Phi_2(\Gamma, t)$.

3.2 Parameter invariant theories - the relativistic particle

A relativistic particle moves in the four dimensional Minkowski space described by the metric

$$\eta_{\mu\nu} = diag(1,-1,-1,-1). \tag{3.54}$$

Its Action reads

$$S\left[x^\mu(\tau)\right] = -m\int_{\tau_1}^{\tau_2} d\tau \left(\frac{dx^\mu}{d\tau}\frac{dx_\mu}{d\tau}\right)^{1/2}. \tag{3.55}$$

Applying Euler's Theorem one already sees that the Hamiltonian corresponding to the Lagrangian $L = -m\sqrt{\dot{x}^2}$ must vanish since L is homogenous of the first degree in the velocities. Here and for the following we use the point above the variables as a derivative with respect to τ. Nevertheless the action of the particle is invariant under time transformations (this means reparametrizations).

Generally: Imagine a Lagrangian $L = L(x, dx/dt)$. Now take the time t and set equal to a new degree of freedom x_0. Then define the new Lagrangian [14][16] L^*

$$L^* = L\frac{dt}{d\tau} = L\frac{dx_0}{d\tau} = \frac{dx_0}{d\tau}L\left(x, \frac{dx/d\tau}{dx_0/d\tau}\right) \tag{3.56}$$

Notice that the new Lagrangian L^* contains one more degree of freedom than the old one L. But the actions

$$\int L^* d\tau = \int L dt \tag{3.57}$$

Since in the case of the relativistic particle L is homogenous in the first degree of the velocities L^* is too. This mean L^* gives us also a weakly vanishing Hamiltonian. If we apply Dirac's

formalism, where the Hamiltonian H is weakly zero - and this is the only constraint, which is primary and first class - we can set the first class Hamiltonian H' in

$$H_T = H' + v_a \Phi_a \tag{3.58}$$

equal to zero. So we end up with an expression for the total Hamiltonian

$$H_T = v_a \Phi_a \tag{3.59}$$

and furthermore the time evolution of a phase space function g reads then

$$\dot{g} \approx v_a \left\{ g, \Phi_a \right\}. \tag{3.60}$$

Since the $v's$ are arbitrary we can multiply both sides of the above equation with a factor $d\tau/dt$ to go from time τ over to time t. This means

$$\frac{dg}{dt} \approx v'_a \left\{ g, \Phi_a \right\}, \tag{3.61}$$

where $v'_a := v_a d\tau/dt$. Now let us go back to the relativistic particle. Applying the canonical formalism the canonical momenta are given by the formula

$$\pi_\mu = \frac{\partial L}{\partial \dot{x}_\mu} = -m \frac{\dot{x}_\mu}{\sqrt{\dot{x}^2}}. \tag{3.62}$$

One sees that the relation

$$\pi^2 = m^2 \tag{3.63}$$

holds. This is a primary constraint and it shall be written in the equivalent form

$$\Phi_1 = \sqrt{\pi_i^2 + m^2} - \pi_0 \approx 0. \tag{3.64}$$

One easily sees that $H = \pi_\mu \dot{x}^\mu - L$ is equal to zero. Following the Dirac procedure we end up with a total Hamiltonian [17]

$$H_T = \lambda_1 \Phi_1, \tag{3.65}$$

where Φ_1 is a primary first class constraint, so λ_1 can not be determined. This means that this theory is a gauge theory. We choose a gauge fixing constraint Φ_2 of the form

$$\Phi_2 = x_0 - \tau. \tag{3.66}$$

With these constraints we get no other constraints from Dirac's procedure. The new total Hamiltonian reads

$$H_T = \lambda_1 \Phi_1 + \lambda_2 \Phi_2. \tag{3.67}$$

Here the time evolution of the constraints read

$$\begin{aligned} \frac{d\Phi_1}{d\tau} &= \lambda_2 \{\Phi_1, \Phi_2\} \approx 0, \\ \frac{d\Phi_2}{d\tau} &= \frac{\partial \Phi_2}{\partial \tau} + \lambda_1 \{\Phi_2, \Phi_1\} \approx 0. \end{aligned} \tag{3.68}$$

It follows immediately that $\lambda_2 = 0$ and $\lambda_1 = 1/\{\Phi_2, \Phi_1\} = -1$. Since $H = \Phi_1 \approx 0$ equation (3.53) reads

$$\frac{d}{d\tau} f(\Gamma, \tau) \approx \frac{\partial f}{\partial \tau} + \{f, \Phi_1\}_D - \{f, \Phi_i\} \{\Phi_i, \Phi_j\}^{-1} \frac{\partial \Phi_j}{\partial \tau}. \tag{3.69}$$

As one can check the Dirac-bracket $\{f, \Phi_1\}_D$ vanishes since

$$\begin{aligned} \{f, \Phi_1\}_D = &\{f, \Phi_1\} - \{f, \Phi_1\} (-1/\{\Phi_1, \Phi_2\}) \{\Phi_2, \Phi_1\} + \\ &\{f, \Phi_2\} (-1/\{\Phi_2, \Phi_1\}) \{\Phi_1, \Phi_1\} = 0. \end{aligned} \tag{3.70}$$

What is left is

$$\frac{d}{d\tau} f(\Gamma, \tau) \approx \frac{\partial f}{\partial \tau} - \{f, \Phi_\nu\} \{\Phi_\nu, \Phi_\mu\}^{-1} \frac{\partial \Phi_\mu}{\partial \tau}. \tag{3.71}$$

With this the equations of motion $Z = (x^\mu, \pi_\mu)$ of the relativistic particle read

$$\begin{aligned} \frac{d}{d\tau} Z \approx &- \{Z, \Phi_1\} \{\Phi_1, \Phi_2\}^{-1} \frac{\partial \Phi_2}{\partial \tau} = \\ &- \{Z, H\} (-1)(-1) = \\ &\left\{ Z, \pi_0 - \sqrt{\pi_i^2 + m^2} \right\}, \end{aligned} \tag{3.72}$$

which results in

$$\begin{aligned} \dot{x}^0 &= 1 \\ \dot{x}^i &= -\pi_i/\pi_0 \\ \dot{\pi}_\mu &= 0. \end{aligned} \tag{3.73}$$

Adopting the Schrödinger picture we quantize this system by replacing $x^\mu \to \hat{x}^\mu$ and $\pi \to \hat{\pi}_\mu$. The commutators are calculated using the Dirac brackets (equation (3.42)). The result reads $[\hat{x}^\mu, \hat{\pi}_\nu] = i\hbar \delta^\mu_\nu$.

Chapter 4

The Quantum Nosé-Hoover Thermostat

4.1 Choice of gauge fixing

Using Dirac's quantization method we can now quantize the Dettmann Hamiltonian system where the Hamiltonian $H_{Nosé}$ appears as a constraint. Let us now recall the Nosé-Hoover-thermostat described some chapters above. Dettmanns Hamiltonian reads

$$H_D = sH_{Nosé} = s\left(\sum_i \frac{p_i^2}{2ms^2} + \frac{p_s^2}{2Q} + \phi(r) + gkTln(s) - \underline{H}\right) \tag{4.1}$$

where

$$\Phi_1 = H_{Nosé} - \underline{H} \approx 0. \tag{4.2}$$

Following the Dirac procedure the total Hamiltonian is a linear combination of the constraint with a multiplier ν which has to be determined.

$$H_T = \nu\Phi_1. \tag{4.3}$$

Since this constraint is first class and no secondary constraints arise we have to make a gauge fixing to get rid of the gauge freedom. This is obtained by introducing another constraint which has a non-vanishing Poisson bracket with the original one. Together with the time dependent gauge

$$\Phi_2 = s - t/Q \approx 0 \tag{4.4}$$

we end up with a total Hamiltonian which reads

$$H_T = \nu\Phi_1 + \mu\Phi_2. \tag{4.5}$$

We obtain for the time derivative of the gauge given with the Poisson bracket of H_T

$$0 \approx \dot{\Phi}_2 = \{\Phi_2, H_T\} = \frac{\partial\Phi_2}{\partial t} + \nu\{\Phi_2, \Phi_1\} + \mu\{\Phi_2, \Phi_2\}. \tag{4.6}$$

and further

$$\nu = \frac{1}{p_s}. \tag{4.7}$$

The time derivative of the first constraint gives us the result that μ must vanish

$$0 \approx \dot{\Phi}_1 = \{\Phi_1, H_T\} = \nu\{\Phi_1, \Phi_1\} + \mu\{\Phi_1, \Phi_2\}. \tag{4.8}$$

So the total Hamiltonian

$$H_T = \frac{1}{p_s}\left(\sum_i \frac{p_i^2}{2ms^2} + \frac{p_s^2}{2Q} + \phi(r) + gkTln(s) - \underline{H}\right) \tag{4.9}$$

determines the following equations of motion

$$\begin{aligned} \dot{s} &= 1/Q \\ \dot{r_i} &= \frac{1}{p_s}\frac{p_i}{ms^2} \\ \dot{p_s} &= \frac{1}{p_s}\left(-\frac{p_i^2}{ms^3} + gkT\right) \\ \dot{p}_i &= \frac{1}{p_s}\phi'(r) \end{aligned}. \tag{4.10}$$

We can also calculate the equations of motion for $Z = (s, r_i, p_s, p_i)$ via equation (3.53):

$$\begin{aligned} \frac{d}{dt}Z \approx &-\{Z, \Phi_1\}\{\Phi_1, \Phi_2\}^{-1}\frac{\partial\Phi_2}{\partial t} = \\ &\{Z, H_{Nosé} - \underline{H}\}\frac{1}{p_s}. \end{aligned} \tag{4.11}$$

This gives the same result as above because we can pull the $1/p_s$ inside the bracket (weak equality).

4.2 Commutators

The Commutators are given by the formula

$$[\hat{A}, \hat{B}] = i\hbar\{A, B\}_{D, X=\hat{X}} \tag{4.12}$$

where $\{.,.\}_D$ is the Dirac bracket defined in the chapters above. This bracket depends on the gauge fixing we made. For the gauge constraint $\Phi_2 = s - t/Q \approx 0$ we obtain

$$\begin{aligned}\{s, p_s\}_D &= \{s, p_s\} - \{s, \Phi_i\} \{\Phi_i, \Phi_j\}^{-1} \{\Phi_j, p_s\} \\ &= 1 - \frac{\partial H_{Nosé}}{\partial p_s} \frac{Q}{p_s} - 0 = 0\end{aligned} \tag{4.13}$$

and

$$\begin{aligned}\{r_k, p_l\}_D &= \{r_k, p_l\} - \{r_k, \Phi_i\} \{\Phi_i, \Phi_j\}^{-1} \{\Phi_j, p_l\} \\ &= \delta_{kl} - 0 - 0 = 1.\end{aligned} \tag{4.14}$$

and all other combinations are zero. Therefore the commutators are

$$[s, p_s] = 0 \qquad [\hat{r}_i, \hat{p}_j] = i\hbar\delta_{ij}. \tag{4.15}$$

With this result we interpret s and p_s as ordinary functions since their commutator vanishes. r and p must be treated as operators with the usual commutator used in ordinary quantum mechanics. When we replace r and p with $\hat{r}$ and $\hat{p}$ we obtain for the total Hamiltonian, which becomes an operator,

$$\hat{H}_T(\hat{r}, \hat{p}, s, p_s) = \frac{1}{p_s} \left(\sum_i \frac{\hat{p}_i^2}{2ms^2} + \frac{p_s^2}{2Q} + \phi(\hat{r}) + gkTln(s) - \underline{H} \right). \tag{4.16}$$

Working in the framework of quantum statistical mechanics the microcanonical density matrix reads [18]

$$\hat{\rho}_{mc} = \sum_n p(E_n) |n><n| \tag{4.17}$$

for energy eigenvectors $|n>$ and energy eigenvalues E_n. Here $p(E_n)$ describes the probability of measuring the eigenvalue E_n and it is defined as

$$p(E_n) = \begin{cases} 1/Z(E)\Delta & E \leq E_n \leq E + \Delta \\ 0 \quad \text{otherwise.} \end{cases} \tag{4.18}$$

This means all eigenstates whose energy eigenvalues lie in the interval $[E, E+\Delta]$ occur with the same probability, where the quantity $Z(E)$ describes the number of energy eigenstates in the the interval $[E, E + \Delta]$. An alternative notation for the microcanonical density matrix reads

$$\hat{\rho}_{mc} = Z(E)^{-1} \delta(\hat{H} - E) \tag{4.19}$$

which yields together with the normalization $Tr\{\hat{\rho}_{mc}\} = 1$, where we have to trace over a complete set of eigenstates,

$$Z(E) = Tr\left\{\delta(\hat{H} - E)\right\}. \tag{4.20}$$

For the total Hamiltonian above the density matrix reads then

$$\hat{\rho}_{mc}(\hat{r}, \hat{p}, s, p_s) = Z(E)^{-1}\delta(\hat{H}_T - E) \tag{4.21}$$

which depends also on the classical variables s and p_s. The expectation value of an operator $\hat{B}$ in the energy eigenbasis $|n>$ can then be calculated with

$$< \hat{B} >_{mc} = Tr(\hat{B}\hat{\rho}_{mc}) = 1/Z \int\int dp_s ds \sum_n < n|\hat{B}\hat{\rho}_{mc}|n > . \tag{4.22}$$

For the canonical ensemble one usually looks at a system ($\hat{H}_1$) in contact with a heat bath ($\hat{H}_2$). The Hamiltonian of the total system in equilibrium reads

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{W} \approx \hat{H}_1 + \hat{H}_2, \tag{4.23}$$

where the interaction term W is negligibly small. Then one obtains the canonical density matrix of system 1 by tracing over the degrees of freedom of system 2 ($Z_{1,2}$ is the microcanonical partition sum of both systems):

$$\begin{aligned} \hat{\rho}_c &:= Tr_2\{\hat{\rho}_{mc}\} = Tr_2 \frac{\delta(\hat{H}_1 + \hat{H}_2 - E)}{Z_{1,2}(E)} = \frac{Z_2(E - \hat{H}_1)}{Z_{1,2}(E)} \\ &= \frac{Z_2(E - \tilde{E}_1 + \tilde{E}_1 - \hat{H}_1)}{Z_{1,2}(E)} \approx \frac{Z_2(E - \tilde{E}_1)}{Z_{1,2}(E)} e^{(\tilde{E}_1 - \hat{H}_1)/kT}, \end{aligned} \tag{4.24}$$

where we expanded the logarithm of $Z_2(E - \hat{H}_1)$ in $\hat{H}_1$ because the system 1 is much smaller than the system 2. The temperature T appears as the temperature of the heat bath

$$T = (k\frac{\partial}{\partial E} ln(Z_2(E - \tilde{E}_1)))^{-1}. \tag{4.25}$$

The canonical partition sum is defined as

$$Z_c := \frac{Z_{1,2}(E)}{Z_2(E - \tilde{E}_1)} e^{-\tilde{E}_1/kT} \tag{4.26}$$

and therefore we get

$$\hat{\rho}_c = Z_c^{-1} e^{-\hat{H}_1/kT} \tag{4.27}$$

for the canonical density matrix.

With this the canonical expectation value of an operator $\hat{B}$ in the energy eigenbasis reads

$$< \hat{B} >_c = Tr(\hat{B}\hat{\rho}_c) = 1/Z_c \int \int dp_s ds \sum_n < n|\hat{B}\hat{\rho}_c|n > . \tag{4.28}$$

for the total Hamiltonian (4.16) above.

4.3 The quantum Nosé-theorem

We start with the Hamiltonian $\hat{H}_T$ (4.16) consisting of quantum $(\hat{r}, \hat{p})$ and classical (s, p_s) degrees of freedom. In the following section we show that this Hamiltonian generates quantum canonical averages of observables, in other words it generates a canonical distribution for the $(\hat{r}, \hat{p})$ variables. The method is the following: 1) Write down the microcanonical partition sum of our total system. 2) Integrate out all heat bath variables (s, p_s) to obtain the partition sum which contains the reduced density distribution. The total Hamiltonian $\hat{H}_T$ (for simplicity $m = \hbar = \omega = 1$) for N harmonic oscillators reads

$$\hat{H}_T = \frac{1}{p_s}(\hat{H}_{Nosé} - \underline{H}) = \sum_{i=1}^{N} \frac{\hat{p_i}^2}{2s^2 p_s} + \frac{1}{p_s}\frac{\hat{r_i}^2}{2} + p_s/2Q + \frac{gkT}{p_s} ln(s) - \frac{1}{p_s}\underline{H}, \tag{4.29}$$

where we require $0 < \underline{H} << gkT$. To show that the canonical expectation value of an observable $\hat{B}$ is approximately generated by its microcanonical expectation value we proof that

$$< \hat{B}(\hat{r}\sqrt{s}, \hat{p}/\sqrt{s}) >_{mc} \approx < \hat{B}(\hat{r}, \hat{p}) >_c, \tag{4.30}$$

where

$$< \hat{B}(\hat{r}, \hat{p}) >_c := 1/Z_c Tr \left\{ \hat{B} e^{-\hat{H}_0(\hat{r},\hat{p})/kT} \right\} \tag{4.31}$$

and

$$< \hat{B}(\hat{r}\sqrt{s}, \hat{p}/\sqrt{s}) >_{mc} := 1/Z \int dp_s \int ds Tr \left\{ \hat{B}(\hat{r}\sqrt{s}, \hat{p}/\sqrt{s}) \delta(\frac{1}{p_s}\hat{H}_{Nosé}(\hat{r}, \hat{p}, s, p_s) - \frac{1}{p_s}\underline{H} - E) \right\}. \tag{4.32}$$

Above the operator $\hat{H}_0$ reads

$$\hat{H}_0(\hat{r}, \hat{p}) = \sum_i \frac{\hat{p_i}^2}{2} + \frac{\hat{r_i}^2}{2} \tag{4.33}$$

with the eigenvalues E_n given by

$$\hat{H}_0|n> = E_n|n> = \sum_{i=1}^{N}(n_i + 1/2)|n> = (n + N/2)|n> \tag{4.34}$$

where $n := \sum_{i=1}^{N} n_i$ and $|n>$ denotes the N-particle energy eigenstate. The average of an operator $\hat{B}$ in the microcanonical ensemble reads (multiplied by Z)

$$\begin{aligned}
&Z < \hat{B}(\hat{r}\sqrt{s}, \hat{p}/\sqrt{s}) >_{mc} = \int dp_s \int ds Tr \left\{ \hat{B}(\hat{r}\sqrt{s}, \hat{p}/\sqrt{s}) \delta(\frac{1}{p_s}\hat{H}_{Nosé}(\hat{r}, \hat{p}, s, p_s) - \frac{1}{p_s}\underline{H} - E) \right\} = \\
&\int dp_s \int ds Tr \left\{ \hat{B}(\hat{r}\sqrt{s}, \hat{p}/\sqrt{s}) \delta(\frac{1}{p_s}(\hat{H}_0(\hat{r}, \hat{p}/s) + p_s^2/2Q + gkTln(s) - \underline{H})) \right\} = \\
&\int dp_s \int ds Tr \left\{ \hat{B}(\hat{r}\sqrt{s}, \hat{p}/\sqrt{s}) \delta(\frac{1}{p_s}(\hat{H}_0(\hat{r}\sqrt{s}, \hat{p}/\sqrt{s})/s + p_s^2/2Q + gkTln(s) - \underline{H})) \right\} = \\
&\int dp_s \int ds Tr \left\{ \hat{B}(\hat{r}, \hat{p}) \delta(\frac{1}{p_s}(\hat{H}_0(\hat{r}, \hat{p})/s + p_s^2/2Q + gkTln(s) - \underline{H})) \right\}
\end{aligned} \tag{4.35}$$

where we set $E = 0$ (according to equation (2.47)) and used a unitary transformation $\hat{U}$ which transforms $\hat{r} \to \hat{r}/\sqrt{s}$ and $\hat{p} \to \hat{p}\sqrt{s}$ (similar done in [19][20]- see appendix B).

The unitary operator leaves the trace invariant if its argument is sandwiched with $\hat{U}$ and $\hat{U}^\dagger$ (because $\hat{U}\hat{U}^\dagger = \mathbf{1}$). $\hat{U}$ reads

$$U = e^{-\frac{i}{2}ln(\sqrt{s})(\hat{r}\hat{p}+\hat{p}\hat{r})} \tag{4.36}$$

and its action on the canonical variables $\hat{r}$ and $\hat{p}$ can be calculated via the known Baker-Campbell-Hausdorff formula. The commutators read $[s, p_s] = 0$ and $[\hat{r}, \hat{p}] = i\hbar$. We obtain

$$\begin{aligned}
\hat{U}\hat{r}\sqrt{s}\hat{U}^\dagger = e^{-\frac{i}{2}ln(\sqrt{s})(\hat{r}\hat{p}+\hat{p}\hat{r})}\hat{r}\sqrt{s}e^{\frac{i}{2}ln(\sqrt{s})(\hat{r}\hat{p}+\hat{p}\hat{r})} &= \hat{r}\sqrt{s} + \frac{1}{1!}\left[-\frac{i}{2}ln(\sqrt{s})(\hat{r}\hat{p}+\hat{p}\hat{r}), \hat{r}\sqrt{s}\right] \\
&+\frac{1}{2!}\left[-\frac{i}{2}ln(\sqrt{s})(\hat{r}\hat{p}+\hat{p}\hat{r}), \left[-\frac{i}{2}ln(\sqrt{s})(\hat{r}\hat{p}+\hat{p}\hat{r}), \hat{r}\sqrt{s}\right]\right] + ... = \\
&\hat{r}\sqrt{s}(1 - ln(\sqrt{s}) + \frac{1}{2!}ln^2(\sqrt{s}) + ...) = \\
&\hat{r}
\end{aligned} \tag{4.37}$$

and

$$\begin{aligned}
\hat{U}\frac{\hat{p}}{\sqrt{s}}\hat{U}^\dagger = e^{-\frac{i}{2}ln(\sqrt{s})(\hat{r}\hat{p}+\hat{p}\hat{r})}\frac{\hat{p}}{\sqrt{s}}e^{\frac{i}{2}ln(\sqrt{s})(\hat{r}\hat{p}+\hat{p}\hat{r})} &= \frac{\hat{p}}{\sqrt{s}} + \frac{1}{1!}\left[-\frac{i}{2}ln(\sqrt{s})(\hat{r}\hat{p}+\hat{p}\hat{r}), \frac{\hat{p}}{\sqrt{s}}\right] \\
&+\frac{1}{2!}\left[-\frac{i}{2}ln(\sqrt{s})(\hat{r}\hat{p}+\hat{p}\hat{r}), \left[-\frac{i}{2}ln(\sqrt{s})(\hat{r}\hat{p}+\hat{p}\hat{r}), \frac{\hat{p}}{\sqrt{s}}\right]\right] + ... = \\
&\frac{\hat{p}}{\sqrt{s}}(1 + ln(\sqrt{s}) + \frac{1}{2!}ln^2(\sqrt{s}) + ...) = \\
&\hat{p}.
\end{aligned} \tag{4.38}$$

With this result we can transform the arguments of every homogenous function as given by the formulas above.

We evaluate the trace in the N-particle position state $|x>$ and obtain

$$\begin{aligned} &Z < \hat{B}(\hat{r}\sqrt{s}, \hat{p}/\sqrt{s}) >_{mc} = \\ &\int dp_s \int ds \int dx < x|\hat{B}(\hat{r},\hat{p})\delta(\frac{1}{p_s}(\hat{H}_0(\hat{r},\hat{p})/s + p_s^2/2Q + gkTln(s) - \underline{H}))|x > . \end{aligned} \tag{4.39}$$

Changing the order of integrations gives us now (similar calculation for Z)

$$\begin{aligned} &Z < \hat{B}(\hat{r}\sqrt{s}, \hat{p}/\sqrt{s}) >_{mc} = \\ &\int dx < x|\hat{B}(\hat{r},\hat{p}) \int dp_s \int ds\delta(\frac{1}{p_s}(\hat{H}_0(\hat{r},\hat{p})/s + p_s^2/2Q + gkTln(s) - \underline{H}))|x > . \end{aligned} \tag{4.40}$$

We evaluated the trace in the basis of position eigenstates, but now we switch to the energy eigenstates $|n>$. The transformation of the eigenbasis reads

$$< x| = \sum_n < x|n >< n|. \tag{4.41}$$

We obtain

$$\begin{aligned} &Z < \hat{B}(\hat{r}\sqrt{s}, \hat{p}/\sqrt{s}) >_{mc} = \\ &\int dx < x|\hat{B}(\hat{r},\hat{p}) \int dp_s \int ds\delta(\frac{1}{p_s}(\hat{H}_0(\hat{r},\hat{p})/s + p_s^2/2Q + gkTln(s) - \underline{H}))|x >= \\ &\int dx \sum_n < x|n >< n|\hat{B}(\hat{r},\hat{p}) \int dp_s \int ds\delta(\frac{1}{p_s}(\hat{H}_0(\hat{r},\hat{p})/s + p_s^2/2Q + gkTln(s) - \underline{H}))|x >= \\ &\int dx \sum_n < n|\hat{B}(\hat{r},\hat{p}) \int dp_s \int ds\delta(\frac{1}{p_s}(\hat{H}_0(\hat{r},\hat{p})/s + p_s^2/2Q + gkTln(s) - \underline{H}))|x >< x|n >= \\ &\sum_n < n|\hat{B}(\hat{r},\hat{p}) \int ds \int dp_s\delta(\frac{1}{p_s}(\hat{H}_0(\hat{r},\hat{p})/s + p_s^2/2Q + gkTln(s) - \underline{H}))|n > \end{aligned} \tag{4.42}$$

Now comes the crucial point. We use the general formula for distributions used above, namely that $\delta(f(p_s)) = \sum_i \delta(p_s - p_{s_i})/|f'(p_{s_i})|$ where p_{s_i} are the zeros of $f(p_s)$, $f(p_{s_i}) = 0$. Since we trace in the energy eigenbasis we can replace the operator $\hat{H}_0$ with its eigenvalues E_n inside the delta function. In other words, we use the spectral theorem for functions of operators namely

$$\delta(\hat{H}_0 + ...) = \sum_n \delta(E_n + ...)|n >< n|. \tag{4.43}$$

With this replacement only the observable $\hat{B}(\hat{r},\hat{p})$ is left inside the bra-ket and the delta function can be treated by the formula above.

In order that the zeros of $f(p_s) = \frac{A}{p_s} + \frac{p_s}{2Q}$ exist, A must be negative where $A := E_n/s + gkTln(s) - \underline{H}$. Therefore

$$E_n < s\underline{H} - gkTsln(s) \tag{4.44}$$

The function on the right hand side reaches its maximum at $\tilde{s} = e^{-1+\underline{H}/gkT}$ which gives us a set of energy eigenvalues of

$$E_n < gkTe^{-1+\underline{H}/gkT} \tag{4.45}$$

for $n = 0, 1, 2, ..., n_{max}$ where

$$n_{max} = \lfloor E_{n_{max}} - N/2 \rfloor. \tag{4.46}$$

The so-called Gauss brackets mean we have to take the integer value which is closest to the value inside $\lfloor ... \rfloor$. Equation (4.45) has the property that the maximal value for E_n/gkT is always smaller than the fixed temperature T for $\underline{H} << gkT$. For the zeros of $f(p_s)$ we obtain the two functions

$$(p_s)_1 = \sqrt{-2QA} \quad (p_s)_2 = -\sqrt{-2QA} \tag{4.47}$$

where the square roots are always real because of 4.44. We can write the last integral of 4.42 as

$$\begin{aligned} &\sum_{n=0}^{n_{max}} < n|\hat{B}(\hat{r},\hat{p}) \int_{s_1}^{s_2} ds \int dp_s \delta(\frac{A}{p_s} + \frac{p_s}{2Q})|n >= \\ &\sum_{n=0}^{n_{max}} < n|\hat{B}(\hat{r},\hat{p}) \int_{s_1}^{s_2} ds \int dp_s \sum_{i=1}^{2} \frac{\delta(p_s - (p_s)_i)}{|\frac{1}{2Q} - \frac{A}{p_s^2}|}|n > \end{aligned} \tag{4.48}$$

where i is the index of the two zeros. Furthermore

$$\begin{aligned} &Z < \hat{B} >_{mc}= \\ &\sum_{n=0}^{n_{max}} < n|\hat{B}(\hat{r},\hat{p}) \int_{s_1}^{s_2} ds 2Q|n >= \\ &\sum_{n=0}^{n_{max}} 2Q < n|\hat{B}(\hat{r},\hat{p})(s_2 - s_1)|n >, \end{aligned} \tag{4.49}$$

where the s integration is carried out between the zeros of $A(s)$, s_1 and s_2 (see figure 4.1). In between the zeros the function $A(s)$ is negative (as required). The values s_1 and s_2 can not be calculated analytically, so one has to use numerical methods. A simple method to approximate s_1 is to set it equal to $s_1 \approx s_{min} = E_n/gkT$ where s_{min} is the minimum point of $A(s)$ (figure 4.1). Because $\underline{H} << gkT$ equation (4.45) states that E_n/gkT is small for $n = 1, 2, 3, ..., n_{max}$. This results in the fact that $s_1 \approx 0$ is negligible because it lies always left from the minimum $s_{min} \approx 0$. The formal solution of the zero s_2 reads

$$s_2 = -E_n / \left(gkTW(-E_n e^{-\underline{H}/gkT}/gkT) \right), \tag{4.50}$$

where W is the Product-Log function. An expansion for small E_n/gkT and small $\underline{H}/gkT$ up to the first order results in

$$s_2 \approx 1 + \frac{\underline{H}}{gkT} - \frac{E_n}{gkT} \approx e^{-E_n/gkT + \underline{H}/gkT}. \tag{4.51}$$

Approximating s_2 like this is the same as calculating the zero of the function $E_n + gkTln(s) - \underline{H}$. So in the end we just approximated the function $A(s)$ (figure 4.1). We end up with the result

$$\sum_{n=0}^{n_{max}} 2Q < n|\hat{B}(\hat{r},\hat{p})e^{-\hat{H}_0/gkT + \underline{H}/gkT}|n > . \tag{4.52}$$

The pre-factor $2Qe^{\underline{H}/gkT}$ contributes a constant term to our result which will cancel out when divided by the partition sum Z. For $g = 1$ we obtain

$$< \hat{B}(\hat{r}\sqrt{s}, \hat{p}/\sqrt{s}) >_{mc} \approx 1/Z_c Tr\left\{\hat{B}(\hat{r},\hat{p})e^{-\hat{H}_0(\hat{r},\hat{p})/kT}\right\} =< \hat{B}(\hat{r},\hat{p}) >_c \tag{4.53}$$

since all the constant factors are put into Z_c. This completes the proof. The difference of this result compared to the canonical distribution contains the terms of the sum where $n > n_{max}$. Fortunately high values of n have less contribution in the canonical distribution. The fact that $g = 1$, in contrast to the classical Nosé derivation where $g = 3N + 1$ (N particles in 3 dimensions), corresponds to the fact that g is the number of classical degrees of freedom involved (namely s). Since we performed a unitary transformation instead of an ordinary substitution (like in the classical case) the power of s in the integral is 1 instead of $3N + 1$.

4.4 Conclusion

It was shown that that the total Hamiltonian (4.16) generates approximately a canonical distribution after integrating out the heat bath variables. This Hamiltonian corresponds to the physical situation where N harmonic quantum oscillators are coupled to a heat bath. It must be noticed that the final form of the total Hamiltonian depends on the gauge fixing constraint I made. This choice of gauge fixing is not unique, if another one is chosen one will end up with a different total Hamiltonian (which will still be a linear combination of the Nosé-Hamiltonian and a multiplier). Also different commutators may arise from this.

Clearly an open question is if it is possible to generalize this quantum Nosé-Theorem to arbitrary potentials. The difficulty lies in the fact of finding a proper unitary transformation (to rescale the variables) such that one can derive an expression which contains the Hamiltonian $\hat{H}_0(\hat{q},\hat{p})$ (which describes the physical situation) from the total Hamiltonian $\hat{H}_T$.

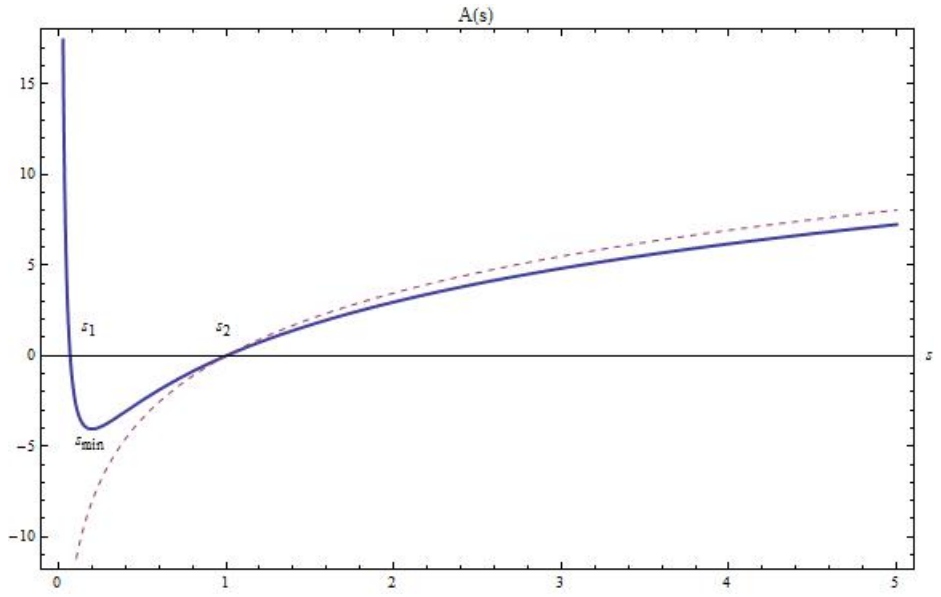

Figure 4.1: Thick line: Plot of $A(s)$ for $\underline{H} = 1$, $gkT = 5$ and $E_n = 1$. This results in the function $1/s + 5ln(s) - 1$. Dashed: The approximation $1 + 5ln(s) - 1$, s_1 and s_2 are the zeros of A, s_{min} is the minimum point of A.

A numerical simulation of this quantum Nosé-Theorem is of great interest but it has not yet been provided. It should be mentioned that the work of Grilli and Tosatti [19] treats a different but similar looking Hamiltonian where the physical variables are operators and the heat bath is also classical (see appendix B). They obtained an exact canonical distribution, which was also demonstrated with numerical simulations.

Appendix A

An Alternative Proof of the Classic Nosé-Theorem

Here I present an alternative derivation of the Nosé-Theorem where one calculates $\delta(f(p_s)) := \delta(H_0(p',q') + p_s^2/2Q + gkTlns - E)$ by first evaluating it with respect to the zeros of $f(p_s)$ and integrating out the s variable later. Equation (2.27) reads:

$$Z = \frac{1}{N!h^{3N}} \int dp_s \int dp' \int dq' \int dss^{3N} \delta(H_0(p',q') + p_s^2/2Q + gkTlns - E). \tag{A.1}$$

This implies

$$\delta(f(p_s)) = \sum_{i=1}^{2} \frac{\delta(p_s - (p_s)_i)}{|p_s/Q|} \tag{A.2}$$

where the zeros of $f(p_s)$ read

$$(p_s)_1 = \sqrt{2(EQ - H_0Q - gkTQln(s))} \quad (p_s)_2 = -\sqrt{2(EQ - H_0Q - gkTQln(s))}. \tag{A.3}$$

These zeros exist only when the minimum of f, $f((p_s)_{min})$, is negative, where $(p_s)_{min} = 0$ is the minimum point. This means

$$f((p_s)_{min}) = H_0(p',q') + gkTlns - E \leq 0. \tag{A.4}$$

We obtain

$$Z = \frac{1}{N!h^{3N}} \int dp' \int dq' \int_0^{e^{(E-H_0)/gkT}} dss^{3N} \left(\frac{2Q}{\sqrt{2(EQ - H_0Q - gkTQln(s))}} \right) \tag{A.5}$$

where the s integration is restricted to such values that A.4 is negative. For $g = 3N + 1$ our result reads

$$Z = \frac{\sqrt{2Q\pi}e^{E/kT}}{N!h^{3N}(3N+1)\sqrt{kT}} \int dp' \int dq' e^{-H_0(p',q')/kT} \tag{A.6}$$

which is clearly a canonical distribution.

Appendix B

The Grilli-Tosatti Thermostat

Grilli and Tosatti showed [19] that a Hamilton operator of the form

$$\hat{H}_{GT} = \sum_i \frac{\hat{p}_i^2}{2ms^2} + \hat{V}(s\hat{r}) + \frac{p_s^2}{2Q} + kTln(s) \tag{B.1}$$

produces a canonical distribution for the $(\hat{r}, \hat{p})$ quantum variables by integrating out the classical heat bath variables (s, p_s) in the microcanonical partition sum, so

$$< \hat{B}(\hat{r}, \hat{p}) >_c = 1/Z_c Tr \left\{ \hat{B} e^{-\hat{H}_0(\hat{r},\hat{p})/kT} \right\} \tag{B.2}$$

is equal

$$< \hat{B}(s\hat{r}, \hat{p}/s) >_{mc} = 1/Z \int dp_s \int ds Tr \left\{ \hat{B}(s\hat{r}, \hat{p}/s) \delta(\hat{H}_{GT}(s\hat{r}, \hat{p}/s, s, p_s) - E) \right\}. \tag{B.3}$$

After a rewriting

$$\begin{aligned} &Z < \hat{B} >_{mc} = \int dp_s \int ds Tr \left\{ \hat{B}(s\hat{r}, \hat{p}/s) \delta(\hat{H}_{GT}(s\hat{r}, \hat{p}/s, s, p_s) - E) \right\} = \\ &\int dp_s \int ds Tr \left\{ \hat{B}(s\hat{r}, \hat{p}/s) \delta(\hat{H}_0(s\hat{r}, \hat{p}/s) + p_s^2/2Q + kTln(s) - E) \right\} \end{aligned} \tag{B.4}$$

we evaluate the trace now in the energy eigenbasis and obtain

$$\begin{aligned} &Z < \hat{B} >_{mc} = \\ &\sum_n \int dp_s \int ds < n | \hat{B}(s\hat{r}, \hat{p}/s) \delta(\hat{H}_0(s\hat{r}, \hat{p}/s) + p_s^2/2Q + kTln(s) - E) | n > . \end{aligned} \tag{B.5}$$

We use a unitary transformation $\hat{U}$[20] which transforms $\hat{r} \to \hat{r}/s$ and $\hat{p} \to \hat{p}s$ and obtain

$$\begin{aligned} &Z < \hat{B} >_{mc} = \\ &\sum_n \int dp_s \int ds < n | \hat{B}(\hat{r}, \hat{p}) \delta(\hat{H}_0(\hat{r}, \hat{p}) + p_s^2/2Q + kTln(s) - E) | n >, \end{aligned} \tag{B.6}$$

where $\hat{U}$ reads

$$\hat{U} = e^{\frac{i}{2} ln(s)(\hat{r}\hat{p}+\hat{p}\hat{r})}. \tag{B.7}$$

Evaluating the zero of the delta distribution concerning s and integrating out p_s gives

$$< \hat{B}(s\hat{r},\hat{p}/s) >_{mc} = 1/Z_c \sum_n < n|\hat{B}(\hat{r},\hat{p})e^{-\hat{H}_0(\hat{r},\hat{p})/kT}|n > = < \hat{B}(\hat{r},\hat{p}) >_c \tag{B.8}$$

which completes the proof.

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List of Figures

4.1 Thick line: Plot of $A(s)$ for $\underline{H} = 1$, $gkT = 5$ and $E_n = 1$. This results in the function $1/s + 5ln(s) - 1$. Dashed: The approximation $1 + 5ln(s) - 1$, s_1 and s_2 are the zeros of A, s_{min} is the minimum point of A. 40

Abstract

This work is structured as follows: After an introduction Chapter 2 treats the Nosé-Hoover-Thermostat and the corresponding Nosé-Theorem which describes an interaction of a N particle system with a heat bath such that a canonical distribution is obtained when one integrates out the heath bath variables. In other words the microcanonical distribution for the whole system reduces to a canonical distribution for the N particles. Chapter 2 also provides an alternative deviation found by Dettmann using a constrained Hamiltonian system. Chapter 3 provides the theoretical background for quantizing a constrained system ('Dirac Quantization') and formulating a quantum version of the Nosé-Theorem. In Chapter 4 I show that the quantum mechanical Nosé-Theorem for N quantum harmonic oscillators generates a quantum canonical ensemble in the limit of high temperatures.

Zusammenfassung

Diese Arbeit ist aufgebaut wie folgt: Nach der Einführung behandelt Kapitel 2 den Nosé-Hoover Thermostaten und das Nosé-Theorem, in seiner ursprünglichen Herleitung. Das Nosé-Theorem beschreibt ein physikalisches N-Teilchen System in Wechselwirkung mit einem Wärmebad, mit der Eigenschaft, dass sich die mikrokanonische Dichteverteilung zu einer kanonischen Dichteverteilung reduziert, wenn man die Wärmebadvariablen ausintegriert. Ebenfalls gezeigt wird eine alternative Herleitung durch Dettmann, welche ein Hamiltonsches System mit Zwangskräften verwendet. Kapitel 3 ist eine Einführung in Diracs Quantisierungs Methode, welche anschließend (Kapitel 4) verwendet wird um das Nosé-Theorem quantenmechanisch zu formulieren. Es wird gezeigt, dass in der Näherung für große Temperaturen, N quantenmechanische Oszillatoren ein kanonisches Ensemble erzeugen.

Curriculum Vitae

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