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Non-equilibrium Thermodynamics for Quantum Systems

D. Bedeaux

The extension of the scheme of mesoscopic non-equilibrium thermodynamics developed for quantum mechanical systems by Bedeaux and Mazur (2001) is discussed. This scheme gives a master equation for the density matrix of the system. Onsager relations are given. Application to a spin system gives the Bloch equations. The application to a one-dimensional harmonic oscillator results in equations which make it possible to calculate the Green functions. For the last case we derive, as a new alternative, quantum mechanical Langevin equations. Compared to the classical Langevin equations a new element is random velocity. The correlation of the random velocity with the random force then results from the zero point motion of the oscillator. The application of mesoscopic non-equilibrium thermodynamics to these well known problems illustrates the usefullness of this method.

1 Introduction

Onsager (1931) gave a systematic formulation of the reciprocal relations and showed that they were a general consequence of the invariance of the microscopic equations of motion under time reversal. After this ground breaking work it took ten years before Meixner (1941, 1942, 1943) and, independently a little later, Prigogine (1947) set up a consistent phenomenological theory of irreversible processes, incorporating both Onsager's reciprocity theorem and the explicit calculation of the entropy source strength. At the end of the forties, de Groot and Mazur joined as founding fathers of this new field. After more than a decade of rapid development, in 1962 they published their now classical monograph "Non-Equilibrium Thermodynamics" (de Groot and Mazur, 1962, 1985). After this period, the work shifted to on the one hand the statistical mechanical foundation of the field and on the other hand to phenomena far from equilibrium.

The work on the statistical mechanical foundation in those days was done using the apparently reasonable assumption that the macroscopic relaxation phenomena could be obtained systematically from the microscopic description. On the microscopic level, relaxation was essentially different. The macroscopic relaxation phenomena would arise when one considered large numbers of particles. Alder and Wainwright (1967, 1970) reported that molecular dynamic simulations showed that the autocorrelation function of the velocity of a single particle decayed algebraically in proportion to $t^{-3/2}$. They needed macroscopic hydrodynamics to explain this. This changed our understanding of the microscopic foundation of macroscopic phenomena completely. Much work was done in subsequent years to show how microscopic degrees of freedom are coupled to macroscopic ones. Macroscopic behaviour makes itself be felt all the way from the microscopic to the macroscopic world. It becomes important to understand physical behaviour on all length and time scales, in particular also in the mesoscopic[1] domain describing phenomena between the microscopic and the macroscopic world. The present interest in phenomena and structures on a nm-scale show how important this mesocopic domain has become.

It became important to apply the methods developed for the macroscopic world in this mesoscopic domain. In recent years Rubi and Mazur (1994, 1998, 2000) pioneered the use of internal variables for this purpose, a method which dates back to the early days of the field of non-equilibrium thermodynamics (Prigogine and Mazur, 1953) but which was never really used. Mazur (1999) also included the treatment of fluctuations into the macroscopic formalism of non-equilibrium thermodynamics. The central quantity in this generalization is, as usual in non-equilibrium thermodynamics, the entropy S of the system. In the macroscopic theory the entropy is a function of a set of macroscopic state variables $\boldsymbol{\alpha} = (\alpha_1, \alpha_2, ...)$. In

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[1] Mesoscopic is used here in the original sense introduced by van Kampen (1992) (chapter 3, page 57) to signify "...the stochastic description in terms of macroscopic variables....It comprises both the deterministic laws and the fluctuations about them".

the mesoscopic version, the entropy is (van Kampen, 1992), using Gibbs' entropy postulate, the functional

$$S(t) = S\left(\{P(\boldsymbol{\alpha},t)\}\right) = -k_B \int P(\boldsymbol{\alpha},t) \ln \frac{P(\boldsymbol{\alpha},t)}{P_{eq}(\boldsymbol{\alpha})} d\boldsymbol{\alpha} + S_{eq} \tag{1}$$

where $P(\boldsymbol{\alpha},t)$ is the probability density that the system is in state $\boldsymbol{\alpha}$ at time t. Furthermore, $P_{eq}(\boldsymbol{\alpha})$ and S_{eq} are the probability density and the entropy in equilibrium, and k_B denotes Boltzmann's constant.

In the mesoscopic theory one proceeds, following the general scheme of non-equilibrium thermodynamics, to calculate from eq.(1) the entropy production. One then sets up linear phenomenological laws between the "currents" and "thermodynamic forces", occurring therein. Subsequently one derives, using conservation of probability, differential equations obeyed by $P(\boldsymbol{\alpha},t)$. The latter describe the dynamics of the fluctuations of $\boldsymbol{\alpha}$.

Suppose now, however, that the system is a quantum system. What happens under these circumstances to the mesoscopic non-equilibrium thermodynamic scheme? This problem was treated by Bedeaux and Mazur (2001). In this contribution we will extract some of the more interesting aspects of this analysis. The second section gives the general theory. The state of the system is described in non-equilibrium quantum statistical mechanics by the two index density matrix ρ of which the mesoscopic entropy is now a functional. For its form an expression analogous to Gibbs' entropy postulate is used. An explicit expression is found for the two index "thermodynamic force matrix" conjugate to the two index "current matrix" $d\rho/dt$. The formalism is found to lead to a master equation for the density matrix. The properties of the various terms in this equation are discussed. Onsager relations are given for the four index Onsager matrix.

The general formalism is applied to two problems which have been extensively discussed in the literature. The first is a spin system, which is discussed in the third section. The second is a one-dimensional damped harmonic oscillator, which is discussed in Sections 4 and 5. The reason for this choice is to show that non-equilibrium thermodynamics is a simple method to obtain results presently found using various alternative approaches. For the spin system the Redfield equation is found. Using the symmetries in the problem the Bloch equations (Abragam, 1961) are subsequently obtained. In Section 4 for the damped harmonic oscillator, the appropriate Onsager matrix is constructed. In Section 5 we construct a quantum mechanical Langevin equation for the oscillator. This gives a new alternative to describe the dynamics of a quantum mechanical system. A discussion of the various results and a conclusion are presented in the last section.

2 Mesoscopic Non-equilibrium Thermodynamics for Quantum Systems

The state of a system in quantum statistical mechanics is described by the density matrix ρ. The density matrix is Hermitian and its trace is taken equal to one

$$Tr\left(\rho\right) = 1 \tag{2}$$

The expectation value of an observable A is given by

$$\langle A \rangle = Tr\left(A\rho\right) \tag{3}$$

If the system is insulated from the environment, the time evolution of the density matrix is given by the Liouville-von Neuman equation

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}\left[H,\rho\right] = -\frac{i}{\hbar}\left[H\rho - \rho H\right] \tag{4}$$

where H is the Hamiltonian. The equilibrium density matrix for a system in contact with a heat bath with a temperature T is

$$\rho_{eq} = e^{-H/k_BT}/Tr\left(e^{-H/k_BT}\right) \tag{5}$$

The entropy of the system is, in analogy to the Gibbs' entropy postulate, given by

$$\begin{aligned} S - S_{eq} &= -k_B Tr\left[\rho \ln\left(\rho_{eq}^{-1}\rho\right)\right] = -k_B Tr\left[\rho \sum_{j=1}^{\infty} \frac{(-1)^{j-1}}{j} \left(\rho_{eq}^{-1}\delta\rho\right)^j\right] \\ &= -k_B Tr\left[\left(\sum_{j=1}^{\infty} \frac{(-1)^{j-1}}{j} \left(\delta\rho\rho_{eq}^{-1}\right)^j\right)\rho\right] = -k_B Tr\left[\ln\left(\rho\rho_{eq}^{-1}\right)\rho\right] \end{aligned} \tag{6}$$

where

$$\delta\rho \equiv \rho - \rho_{eq} \tag{7}$$

The logarithm of a matrix is defined by the sum given above. Expanding the entropy to the second order in the deviation of equilibrium $\delta\rho$, one gives

$$S = -\frac{1}{2} k_B Tr\left[\delta\rho\rho_{eq}^{-1}\delta\rho\right] + S_{eq} \tag{8}$$

The time rate of change of the entropy to this order is found to be

$$\frac{dS}{dt} = -\frac{1}{2} k_B Tr\left[\left(\rho_{eq}^{-1}\delta\rho + \delta\rho\rho_{eq}^{-1}\right)\frac{d\rho}{dt}\right] = Tr\left[X\frac{d\rho}{dt}\right] \tag{9}$$

where the cyclic invariance of the trace was used. The thermodynamic force

$$X \equiv \eth S/\eth\rho = -\frac{1}{2} k_B \left(\rho_{eq}^{-1}\delta\rho + \delta\rho\rho_{eq}^{-1}\right) \tag{10}$$

is conjugate to the flux $d\rho/dt$. Here $\eth$ indicates a functional derivative. For the insulated system it follows, using the Liouville-von Neumann equation (4), the equilibrium density matrix (5) and eq.(9), that the entropy is independent of time (see the derivation of eq.(16) below). When the system is coupled to the environment, the Liouville-von Neumann equation is no longer valid. Eq.(9) then gives a positive entropy production when the system is not in equilibrium. In non-equilibrium thermodynamics, the thermodynamic force is taken to be sufficiently small for $d\rho/dt$ to be linear in the thermodynamic force. The resulting "master equation" is

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \mathbf{L}X \tag{11}$$

The super-matrix **L** maps the space of observables, of which ρ is an element, onto itself. If one uses a complete orthonormal set of functions in Hilbert space, the density matrix is a two-index matrix and **L** a four-index matrix.

The properties of this super-matrix are listed below. Since the thermodynamic force X is Hermitian, **L** may be chosen Hermitian in the last two indices

$$L_{ijkl} = L_{ijlk}^{*} \tag{12}$$

Using this property of **L** one may then replace X in the master equation by the non-Hermitian form

$$X = -k_B \rho_{eq}^{-1}\delta\rho \tag{13}$$

Furthermore, in view of eq.(2)and using the cyclic invariance of the trace, we have

$$\frac{d}{dt}Tr(\rho) = Tr\left(\frac{d\rho}{dt}\right) = -\frac{i}{\hbar}Tr(H\rho - \rho H) + Tr(\mathbf{L}X) = Tr(\mathbf{L}X) = 0 \tag{14}$$

so that **L** is traceless in the first two indices

$$\sum_i L_{iikl} = 0 \tag{15}$$

The entropy production is found by substituting the master equation into eq.(9)

$$\begin{aligned}\frac{dS}{dt} &= \frac{ik_B}{2\hbar}Tr\left(\left(\rho_{eq}^{-1}\delta\rho+\delta\rho\rho_{eq}^{-1}\right)\left(H\rho-\rho H\right)\right)+Tr\left[X\mathbf{L}X\right]\\ &= \frac{ik_B}{2\hbar}Tr\left(\left(\rho_{eq}^{-1}\delta\rho+\delta\rho\rho_{eq}^{-1}\right)\left(H\delta\rho-\delta\rho H\right)\right)+Tr\left[X\mathbf{L}X\right]\\ &= Tr\left[X\mathbf{L}X\right]\geq 0\end{aligned} \tag{16}$$

where the cyclic invariance of the trace and the fact that H and ρ_{eq}^{-1} commute were used.

Following Onsager the super matrix $\mathbf{L}$ must be Hermitian

$$L_{ijkl}=L_{lkji}^{*} \tag{17}$$

A proof of this relation is given in Bedeaux and Mazur (2001). $\mathbf{L}$ is referred to as the Onsager matrix. According to the second law, (16), it is non-negative definite. Using the Hermitian nature of $\mathbf{L}$, it follows that it is also traceless in the last two indices

$$\sum_k L_{ijkk}=0 \tag{18}$$

and Hermitian in its first two indices

$$L_{ijkl}=L_{jikl}^{*} \tag{19}$$

With eq.(13) for the thermodynamic force, the master equation may now be written in the form

$$\frac{d\rho}{dt}=-\frac{i}{\hbar}\left[H,\rho\right]-\mathbf{M}\delta\rho \tag{20}$$

where the master matrix is defined by

$$M_{ijkl}\equiv -k_B\sum_m L_{ijkm}(\rho_{eq}^{-1})_{ml} \tag{21}$$

Using the Onsager relations it follows that the master matrix satisfies

$$\sum_n M_{ijkn}\rho_{eq,nl}=-k_BL_{ijkl}=-k_BL_{lkji}^{*}=\sum_n \rho_{eq,ln}M_{nkji}^{*} \tag{22}$$

This is the usual relation for the master matrix and results in detailed balance for transition probabilities, and vice versa, when those are introduced.

It may be verified that the equilibrium distribution is a right eigenfunction of the master matrix with an eigenvalue of zero:

$$\left(M\rho_{eq}\right)_{ij}=\sum_{kl}M_{ijkl}\rho_{eq,lk}=-k_B\sum_{klm}L_{ijkm}(\rho_{eq}^{-1})_{ml}\rho_{eq,lk}=-k_B\sum_k L_{ijkk}=0 \tag{23}$$

where the traceless nature of the Onsager matrix in the last two indices was used, cf. eq.(18). The master equation can therefore also be written in the form

$$\frac{d\rho}{dt}=-\frac{i}{\hbar}\left[H,\rho\right]-\mathbf{M}\rho \tag{24}$$

Eq.(23) shows that the equilibrium density matrix, which contains the Hamilton operator, remains unchanged in spite of the fluctuations induced by the interaction with the external world. This property was found in this case as a consequence of the Onsager relations, which made it possible to derive eq.(18) from eq.(15). It is the quantum mechanical equivalent of, for instance, the use of Maxwell's velocity distribution by Einstein in his description of the diffusion of a Brownian particle. A microscopic derivation of the master equation in the form given in eq.(24) has been given using projection operators, see e.g. Zwanzig (1964).

In the following sections the above equations are applied to two well-known examples. The first is a spin in a magnetic field and the second is the damped harmonic oscillator. On the one hand it will be found that the above scheme leads in a straightforward manner to the usual description for these examples. On the other hand, in particular in the second example, new insight is gained and some new equations are found.

3 The Bloch Equation

Consider a spin in a magnetic field B along the z-axis. The Hamiltonian is

$$H = \mu B S_z \tag{25}$$

where μ is the magnetic moment and S_z the spin along the z-axis. The spins along the x, y and z-axes are given by

$$S_x = \frac{1}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_y = \frac{i}{2}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}, \quad S_z = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{26}$$

The density matrix can be written as

$$\rho = \begin{pmatrix} \rho_{++} & \rho_{+-} \\ \rho_{-+} & \rho_{--} \end{pmatrix} \tag{27}$$

where $\rho_{++} + \rho_{--} = 1$, ρ_{++} and ρ_{--} are real and $\rho_{+-} = \rho^*_{-+}$. For the average values of the spins one finds

$$\begin{aligned} \langle S_x \rangle &= Tr\left(S_x \rho\right) = \frac{1}{2}\left(\rho_{-+} + \rho_{+-}\right), \quad \langle S_y \rangle = Tr\left(S_y \rho\right) = \frac{i}{2}\left(\rho_{-+} - \rho_{+-}\right) \\ \langle S_z \rangle &= Tr\left(S_z \rho\right) = \frac{1}{2}\left(\rho_{++} - \rho_{--}\right) \end{aligned} \tag{28}$$

It follows that the density matrix may be written as

$$\rho = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + 2\langle S_x \rangle S_x + 2\langle S_y \rangle S_y + 2\langle S_z \rangle S_z \tag{29}$$

In equilibrium the density matrix is given by

$$\begin{aligned} \rho_{eq} &= \exp\left(-\frac{\mu B S_z}{k_B T}\right) / \left[\exp\left(-\frac{\mu B}{2k_B T}\right) + \exp\left(\frac{\mu B}{2k_B T}\right)\right] \\ &= \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} - S_z \tanh\left(\frac{\mu B}{2k_B T}\right) \end{aligned} \tag{30}$$

With these results the master equation (22) becomes

$$\begin{aligned} \frac{d\rho}{dt} &= 2S_x \frac{d\langle S_x \rangle}{dt} + 2S_y \frac{d\langle S_y \rangle}{dt} + 2S_z \frac{d\langle S_z \rangle}{dt} = -\frac{i}{\hbar}\left[H, \rho\right] - \mathbf{L}\left(\rho - \rho_{eq}\right) \\ &= -2\frac{i}{\hbar}\mu B \langle S_y \rangle S_x + 2\frac{i}{\hbar}\mu B \langle S_x \rangle S_y \\ &\quad -2\mathbf{M}\left[\langle S_x \rangle S_x + \langle S_y \rangle S_y + \left(\langle S_z \rangle + \frac{1}{2}\tanh\left(\frac{\mu B}{2k_B T}\right)\right) S_z\right] \end{aligned} \tag{31}$$

This is the so-called Redfield equation. Given that the spin operators form a complete set in the subspace of Hermitian and traceless two-by-two matrices, the most general form of the master matrix is

$$\mathbf{M} = 2 \sum_{\nu,\nu'=x,y,z} M_{\nu\nu'} S_\nu S_{\nu'} \tag{32}$$

Both spin operators have two indices so that the master matrix has four. When applying this super-matrix to an arbitrary matrix A in order to obtain a matrix, one should contract the last two indices. This results in

$$\mathbf{M}A = 2 \sum_{\nu,\nu'=x,y,z} M_{\nu\nu'} S_\nu Tr\left(S_{\nu'} A\right) \tag{33}$$

Using then the rotational symmetry around the z-axis and parity it follows that the master matrix reduces to

$$\mathbf{M} = 2\left[M_2\left(S_xS_x + S_yS_y\right) + M_1S_zS_z\right] \tag{34}$$

Substituting this relation into eq.(31) gives

$$\begin{aligned}
\frac{d\langle S_x\rangle}{dt} &= -\frac{i}{\hbar}\mu B\langle S_y\rangle - M_2\langle S_x\rangle \\
\frac{d\langle S_y\rangle}{dt} &= \frac{i}{\hbar}\mu B\langle S_x\rangle - M_2\langle S_y\rangle \\
\frac{d\langle S_z\rangle}{dt} &= -M_1\left(\langle S_z\rangle + \frac{1}{2}\tanh\left(\frac{\mu B}{2k_BT}\right)\right)
\end{aligned} \tag{35}$$

These are the Bloch equations (Abragam, 1961). The two relaxation times for the spin along the field and normal to the field are given by $T_1 = 1/M_1$ and $T_2 = 1/M_2$ respectively.

4 Damped Harmonic Oscillator

Now consider a one-dimensional harmonic oscillator. The Hamiltonian is

$$H = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2x^2 \tag{36}$$

where m, p, ω and x are the mass, momentum, eigen frequency and the position of the oscillator, respectively. Using the raising and lowering operators

$$a^\dagger \equiv \sqrt{\frac{m}{2\hbar\omega}}\left(\frac{p}{m} + i\omega x\right) \quad \text{and} \quad a \equiv \sqrt{\frac{m}{2\hbar\omega}}\left(\frac{p}{m} - i\omega x\right) \tag{37}$$

the Hamiltonian becomes

$$H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right) \tag{38}$$

The commutation relations are

$$[x, p] = i\hbar \quad \text{and} \quad \left[a, a^\dagger\right] = 1 \tag{39}$$

The left and right eigen states of the Hamiltonian are

$$\langle n| = \langle 0|\, a^n \frac{1}{\sqrt{n!}} \quad \text{and} \quad |n\rangle = \frac{1}{\sqrt{n!}}\left(a^\dagger\right)^n|0\rangle \tag{40}$$

where $\langle 0|$ and $|0\rangle$ are the left and right ground state. One has

$$\langle n|\, H = \langle n|\,\hbar\omega\left(n + \frac{1}{2}\right) \quad \text{and} \quad H\,|n\rangle = \hbar\omega\left(n + \frac{1}{2}\right)|n\rangle \tag{41}$$

The equilibrium density matrix is, using this orthonormal set,

$$\begin{aligned}
\rho_{eq} &= \sum_{n=0}^{\infty}\exp\left(-\frac{\hbar\omega\left(n+\frac{1}{2}\right)}{k_BT}\right)|n\rangle\langle n|\left[\sum_{m=0}^{\infty}\exp\left(-\frac{\hbar\omega\left(m+\frac{1}{2}\right)}{k_BT}\right)\right]^{-1} \\
&= \left(1 - \exp\left(-\frac{\hbar\omega}{k_BT}\right)\right)\sum_{n=0}^{\infty}\exp\left(-\frac{\hbar\omega n}{k_BT}\right)|n\rangle\langle n|
\end{aligned} \tag{42}$$

The resulting equilibrium correlations are

$$\begin{aligned}
\langle p^2\rangle_{eq} &= m^2\omega^2\langle x^2\rangle_{eq} = \frac{1}{2}m\hbar\omega\coth\left(\frac{\hbar\omega}{2k_BT}\right) \\
\langle xp\rangle_{eq} &= -\langle px\rangle_{eq} = \frac{i\hbar}{2}
\end{aligned} \tag{43}$$

The master equation (20) gives the following equations for the average momentum and position

$$\begin{aligned}\frac{d\langle p\rangle}{dt} &= -\frac{im}{\hbar}Tr\left(p\left[H,\rho\right]\right) - Tr\left(p\mathbf{M}\delta\rho\right) = -m\omega^2\langle x\rangle - Tr\left(p\mathbf{M}\boldsymbol{\delta}\rho\right) \\ \frac{d\langle x\rangle}{dt} &= -\frac{i}{\hbar}Tr\left(x\left[H,\rho\right]\right) - Tr\left(x\mathbf{M}\boldsymbol{\delta}\rho\right) = \frac{1}{m}\langle p\rangle - Tr\left(x\mathbf{M}\boldsymbol{\delta}\rho\right)\end{aligned} \tag{44}$$

According to the usual macroscopic description for the damped oscillator, these equations should reduce to

$$\begin{aligned}\frac{d\langle p\rangle}{dt} &= -m\omega^2\langle x\rangle - \lambda\langle p\rangle \\ \frac{d\langle x\rangle}{dt} &= \frac{1}{m}\langle p\rangle\end{aligned} \tag{45}$$

As $\mathbf{M}$ is a four-index tensor, the most appropriate form to achieve this result is for $\mathbf{M}$ a quadratic form in p and x, or alternatively $a^\dagger$ and a. We find that the only such quadratic form is given by

$$\mathbf{M}\boldsymbol{\delta}\rho = -\lambda\boldsymbol{\delta}\rho + \frac{i\lambda}{\hbar}p\left[x,\boldsymbol{\delta}\rho\right] \tag{46}$$

For the time-dependence of the quadratic forms in eq.(43), one then finds

$$\begin{aligned}\frac{d\langle p^2\rangle}{dt} &= -2m\omega^2\left(\langle xp\rangle - \langle xp\rangle_{eq}\right) - 2\lambda\left(\langle p^2\rangle - \langle p^2\rangle_{eq}\right) \\ \frac{d\langle x^2\rangle}{dt} &= \frac{2}{m}\left(\langle xp\rangle - \langle xp\rangle_{eq}\right) \\ \frac{d\langle xp\rangle}{dt} &= \frac{d\langle px\rangle}{dt} = \frac{1}{m}\left(\langle p^2\rangle - \langle p^2\rangle_{eq}\right) - m\omega^2\left(\langle x^2\rangle - \langle x^2\rangle_{eq}\right) \\ &\quad -\lambda\left(\langle xp\rangle - \langle xp\rangle_{eq}\right)\end{aligned} \tag{47}$$

These expressions are identical to those found in the classical case. Deviation from the equilibrium values therefore decays in exactly the same manner as in the classical case. Only the final equilibrium value is different for the quantum mechanical case. In Bedeaux and Mazur (2001), the master equation was used to derive the Green functions for the oscillator. The expressions are rather complex and therefore not given here. The important thing to report is that they are identical to the Green functions found using the methods developped by Kubo (1957), Martin and Schwinger (1959) and Schwinger (1961).

5 The Quantum Langevin Equation and the Properties of the Random Force Matrix

Using eq.(44) for the momentum and position we have

$$\begin{aligned}\frac{d}{dt}\langle p\rangle &= -Tr\left\{\left(m\omega^2 x + \lambda p\right)\boldsymbol{\delta}\rho\right\} = Tr\left\{\frac{dp}{dt}\boldsymbol{\delta}\rho\right\} \\ \frac{d}{dt}\langle x\rangle &= -Tr\left\{\frac{p}{m}\boldsymbol{\delta}\rho\right\} = Tr\left\{\frac{dx}{dt}\boldsymbol{\delta}\rho\right\}\end{aligned} \tag{48}$$

In the classical description it is often practical and illuminating to use a Langevin equation rather than the equivalent description in phase space. We show below that one may do this also in the quantum mechanical case. The quantum Langevin equations are given by

$$\begin{aligned}\frac{dp(t)}{dt} &= -m\omega^2 x(t) - \lambda p(t) + f_p(t) \\ \frac{dx(t)}{dt} &= \frac{p(t)}{m} + f_x(t)\end{aligned} \tag{49}$$

The new elements are the random force matrix $f_p(t)$ and the random velocity matrix $f_x(t)$. To make this description complete we need to know the stochastic properties of these random force matrices.

Substitution into eq.(48) shows that the first moments are given by

$$\begin{aligned} \langle f_p(t) \rangle &= 0 \quad \text{and} \quad \langle f_p(t) \rangle_{eq} = 0 \\ \langle f_x(t) \rangle &= 0 \quad \text{and} \quad \langle f_x(t) \rangle_{eq} = 0 \end{aligned} \tag{50}$$

Averages containing the random force or velocity matrices are averages over the ensemble for the system plus the environment. Such averages reduce to the usual expression (3) for observables of the system alone.

In Bedeaux and Mazur (2001) it is shown using causality that the random force and velocity matrices satisfy the following "fluctuation-dissipation" theorems

$$\begin{aligned} \langle f_p(t) f_p(t') \rangle &= 2\lambda \left\langle p^2 \right\rangle_{eq} \delta(t-t') = \lambda m \hbar \omega \coth\left(\frac{\hbar\omega}{2k_B T}\right) \delta(t-t') \\ \langle f_p(t) f_x(t') \rangle &= -\frac{1}{2} i\hbar\lambda \delta(t-t') \\ \langle f_x(t) f_p(t') \rangle &= \frac{1}{2} i\hbar\lambda \delta(t-t') \\ \langle f_x(t) f_x(t') \rangle &= 0 \end{aligned} \tag{51}$$

Considering time-ordered products these relations reduce to

$$\begin{aligned} \langle T\{f_p(t) f_p(t')\} \rangle &= 2\lambda \left\langle p^2 \right\rangle_{eq} \delta(t-t') \\ \langle T\{f_p(t) f_x(t')\} \rangle &= 0 \\ \langle T\{f_x(t) f_p(t')\} \rangle &= 0 \\ \langle T\{f_x(t) f_x(t')\} \rangle &= 0 \end{aligned} \tag{52}$$

which is exactly the result that one obtains in the classical limit. This property has confused the discussion about the possibility of using a quantum mechanical Langevin equation because one neglected to introduce a random velocity. It then follows that the uncertainty relations are not fulfilled and from this contradictory result one has to conclude that a consistent description using a quantum mechanical Langevin is impossible (van Kampen, 1992). The quantum Langevin equation (49), together with the fluctuation-dissipation theorem (51) for the random force and velocity matrices, can be used as an alternative to the master equation (24) to calculate, for instance, the Green functions.

6 Discussion and Conclusions

Mesoscopic non-equilibrium thermodynamics for quantum systems has been shown to give a master equation for the density matrix. Similar to the classical case, reciprocal relations like those given by Onsager could be derived. The usefulness of the theory was verified by the application to two typical examples. The first was a spin system. For this case the master equation was found to reduce in a straightforward manner to the well-known Bloch equations. The present derivation places these equations within the general framework of non-equilibrium thermodynamics, which gives an interesting new dimension to them. The second example was the damped harmonic oscillator. The description for the second problem was worked out by Kubo (1957), Martin and Schwinger (1959), and Schwinger (1961). They describe the properties of the systems under consideration in terms of Green functions. This was a reason to also calculate these functions (Bedeaux and Mazur, 2001) using the master equation. The results are of the same nature as those found by Kubo, Martin and Schwinger. In the classical description of Brownian motion, one often uses a Langevin equation rather than the equivalent description in terms of a probability distribution in phase space. This is not done for quantum systems. We find that also for the quantum mechanical Brownian particle a Langevin equation can be derived. An interesting difference to the classical case is that one not only has to add a random force matrix to the time derivative of the momentum, but one also has to add a random velocity matrix to the time derivative of the position. The cross correlation of these two random matrices is found to contribute the terms due to the zero-point motion in the Green functions.

We conclude that mesoscopic non-equilibrium thermodynamics provides an appropriate method and framework to discuss irreversible processes occurring in quantum mechanical systems. In doing so, the method yields the dissipative equations obeyed and the description of the fluctuations around the average behaviour.

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Address: Prof. D. Bedeaux, Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, the Netherlands. e-mail: bedeaux@chem.leidenuniv.nl