CHAPTER V

THE QUANTUM MECHANICAL MODEL

A problem of the particle moving in a potential field is the general theme underlying the theoretical approaches to many problems in physical and chemical science. The Brownian motion theory has led to an understanding of such phenomena [8] as interstitial diffusion in solids, reaction rates in chemical physics, macroscopic quantum tunneling in Josephson systems, and fission in nuclear physics. In the previous chapter we have summarized the classical theory of Brownian motion and consider some notions which are used in the theory. In this chapter we shall discuss further, the theory of quantum Brownian motion by path integral. The Feynman-Vernon theory is very useful to study the problem.

Microscopic Model

Let us consider a quantum Brownian particle of mass M moving in an external potential $V(q,t)$ which may depend explicitly on time. Then a Lagrangian function L_B of this particle can be written as

$$L_B = \frac{1}{2} m\dot{q}^2 - V(q,t) . \tag{5.1}$$

The Brownian particle is suspend in a heat bath environment which consists of n harmonic oscillators with mass m and coordinate x_j. The Lagrangian L_h of a heat bath is

$$L_h = \sum_{k=1}^{n} \left(\frac{1}{2} m\dot{x}_k^2 - \frac{1}{2} m\omega_k^2 x_k^2 \right) . \tag{5.2}$$

The Brownian particle coupled with the heat bath through interaction which is the coordinate q of the Brownian particle. The Lagrangian L_I of this interaction is

$$L_I = -q\sum_{k=1}^{n} c_k x_k \ , \tag{5.3}$$

where c_k is the coupling constant between q and each of the harmonic oscillators.

To summarize, we shall describe the Brownian motion phenomena by using a model where the heat bath environment consist of a set of n harmonic oscillators coupled linearly to the coordinate q of the Brownain particle. The Brownian motion of the particle arises because of its interaction with the heat bath. Now, the complete system under study is therefore governed by the total Lagrangian L as follows

$$L = L_B + L_I + L_h . \tag{5.4}$$

And the corresponding action A in the time interval $0 \le t \le T$ is

$$\begin{aligned} A &= A[q(t), x(t)] = A_B + A_I + A_h , \\ A_B &= \int_0^T dt\, L_B , \quad A_I = \int_0^T dt\, L_I , \quad A_h = \int_0^T dt\, L_h \end{aligned} \tag{5.5}$$

where we use $x(t)$ for $\left(x_1(t), x_2(t), \ldots, x_n(t)\right)$, so

$$A = \int_0^T dt \left[\frac{1}{2}M\dot{q}^2 - V(q,t) - q\sum_{k=1}^{n} c_k x_k + \sum_{k=1}^{n}\left(\frac{1}{2}m\dot{x}_k^2 - \frac{1}{2}m\omega_k^2 x_k^2\right)\right]. \tag{5.6}$$

We can write the density matrix $\rho(q_0, q_0'; x_0, x_0')$ at time $t = 0$ for our system as

$$\rho(q_0, q_0'; x_0, x_0') = \left\langle \psi^*(q_0', x_0')\psi(q_0, x_0)\right\rangle , \tag{5.7}$$

on at time $t > 0$. From chapter IV we know that the density matrix $\rho(q_0, q_0'; x_0, x_0')$ can be split into two parts, say the density matrix $\rho_B(q_0, q_0')$ which describes the Brownian particle only and $\rho_h(x_0, x_0')$ for the heat bath only. In this case $\rho(q_0, q_0'; x_0, x_0')$ is simply the form

$$\rho(q_0, q_0'; x_0, x_0') = \rho_B(q_0, q_0')\, \rho_h(x_0, x_0') . \tag{5.8}$$

This is an important initial condition. The density matrix of the whole system is in the form

$$\begin{aligned} \rho(q_u, q_u'; x_u, x_u') = \int_{-\infty}^{\infty} & dq_0 dq_0' dx_0 dx_0' K(q_u, x_u, u; q_0, x_0, o) \\ & \times K^*(q_u', x_u', u; q_0', x_0', o)\, \rho(q_0, q_0')\, \rho(x_0, x_0') . \end{aligned} \tag{5.9}$$

The propagator $K(q_u, x_u, u; q_0, x_0, 0)$ in Eq.(5.9) is

$$K(q_u, x_u, u; q_0, x_0, 0) = \int Dq(t) Dx(t)\, exp(iA/\hbar) , \tag{5.10}$$

where the action A is of the Eq.(5.5). Notice that ρ describes the behavior of complete system, but we are not interested in the behavior of the heat bath. We want access to the properties of the Brownian particle regardless of the specific behavior of the heat bath. All we need is its influence on the Brownain particle. Then we have to trace out the final coordinates of the heat bath, in the other words we have to integrate its coordinates, or we have to sum over all its final states. So, the effective density matrix or the reduced density matrix is

$$\begin{aligned} \tilde{\rho}(q_u, q_u', u) &= Tr_h\, \rho(q_u, q_u'; x_u, x_u') \\ &= \int dx_u dx_u' \delta(x_u - x_u')\, \rho(q_u, q_u'; x_u, x_u') \end{aligned} \tag{5.11}$$

$$\tilde{\rho}(q_u, q'_u, u) = \int dq_0 dq'_0 J(q_u, q'_u; q_0, q'_0)\, \rho_B(q_0, q'_0, 0), \tag{5.12}$$

where

$$J(q_u, q'_u; q_0, q'_0) = \int Dq(t) Dq'(t)\, exp\{(i/\hbar)(A_B[q(t)] - A_B[q'(t)])\}\, F[q(t), q'(t)], \tag{5.13}$$

and

$$\begin{aligned} F[q(t), q'(t)] &= \int dx_0 dx'_0 dx_u dx'_u \delta(x_u - x'_u)\, \rho_h(x_0, x'_0) \\ &\times \int Dx(t) Dx'(t)\, exp\{(i/\hbar)(A_I[q(t), x(t)] - A_I[q'(t), x'(t)] + A_h[x(t)] - A_h[x'(t)])\}. \end{aligned} \tag{5.14}$$

The influence functional $F[q(t), q'(t)]$ describes all of the effect of the heat bath surrounding which is composed of n harmonic oscillators which do not interact with each other. By using the property of the influence functional in Eq.(4.23) of chapter IV it leads us to calculate the influence functional of each oscillator separately and then the effective influence functional is the product of these influence functional. The influence functional of the j^{th} oscillator is

$$\begin{aligned} F_j[q(t), q'(t)] &= \int dx_{j0} dx'_{j0} dx_{ju} dx'_{ju} \delta(x_{ju} - x'_{ju})\, \rho_h(x_{j0}, x'_{j0}) \\ &\times \int Dx_j(t)\, exp\left\{\frac{i}{\hbar}\left[\frac{1}{2}m\dot{x}_j^2 - \frac{1}{2}m\omega_j^2 x_j^2 - qc_j x_j\right]\right\} \\ &\times \int Dx'_j(t)\, exp\left\{-\frac{i}{\hbar}\left[\frac{1}{2}m\dot{x}'^2_j - \frac{1}{2}m\omega_j^2 x'^2_j - qc_j x'_j\right]\right\}. \end{aligned} \tag{5.15}$$

The two path integrals in this equation are conjugate to each other and they have been calculated in Eq.(3.50) of chapter III. For our case, we have $f(t) = q(t)$ and the end points $a = 0,\ b = u$. The density matrix of a harmonic oscillator has also been calculated in chapter III but it is not normalized. To normalize the density matrix of the oscillator we divide it by the partition function of the oscillator. So, one gets the density matrix $\rho_h\left(x_{ju}, x_{j0}\right)$ of the j^{th} oscillator as:

$$\rho_h\left(x_{j0}, x'_{j0}\right) = \left(\frac{1}{2\sinh\left(\omega_j \hbar\beta/2\right)}\right)\left(\frac{m\omega_j}{2\hbar\pi \sinh\left(\omega_j \hbar\beta\right)}\right)^{1/2} \times \exp\left\{-\frac{m\omega_j}{2\hbar \sinh\left(\omega_j \hbar\beta\right)}\left[\left(x_{j0}{}^2 + x'_{j0}{}^2\right)\cosh\omega_j \hbar\beta - 2x_{j0}x'_{j0}\right]\right\}. \quad (5.16)$$

Substituting the result of the two path integrals and density matrix of Eq.(5.16) into Eq.(5.15) and then integrating over all variables x_{k0}, x'_{k0}, x_{ku}, x'_{ku} gives the result

$$F_j\left[q(t), q'(t)\right] = \exp\left\{-\frac{1}{\hbar}\int_0^{t_f} dt \int_0^{t} ds\,\left[q(t) - q'(t)\right]\left[\alpha_j(t-s)q(s) - \alpha_j^*(t-s)q'(s)\right]\right\}. \quad (5.17)$$

where

$$\alpha_j(t-s) = \frac{c_j^2}{2m\omega_j}\coth\frac{\hbar\omega_j}{2kT}\cos\omega_j(t-s) - i\frac{c_j^2}{2m\omega_j}\sin\omega_j(t-s). \quad (5.18)$$

We know from the property of the influence functional that $F = \prod_j F_j$ so the effective influence functional is

$$F\left[q(t), q'(t)\right] = \exp\left\{-\frac{1}{\hbar}\int_0^{t_f} dt \int_0^{t} ds\,\left[q(t) - q'(t)\right]\left[\alpha(t-s)q(s) - \alpha^*(t-s)q'(s)\right]\right\} \quad (5.19)$$

in which the function $\alpha(t-s)$ is

$$\alpha(t-s) = \alpha_R(t-s) + i\alpha_I(t-s), \quad (5.20)$$

$$\alpha_R(t-s) = \sum_{j=1}^{n} \alpha_{jR} = \sum_{j=1}^{n} \frac{c_j^2}{2m\omega_j} \coth\frac{\hbar\omega_j}{2kT} \cos\omega_j(t-s) \qquad (5.21)$$

and

$$\alpha_I(t-s) = -\sum_{j=1}^{n} \alpha_{jI} = -\sum_{j=1}^{n} \frac{c_j^2}{2m\omega_j} \sin\omega_j(t-s). \qquad (5.22)$$

Finally, we can write the propagator for he density matrix as

$$\begin{aligned} J[q_B, q'_B; q_0, q'_0] = \int Dq(t)Dq'(t)\ \exp\frac{i}{\hbar}\{\ & A_B[q] - A_B[q'] \\ & - \int_0^{t_B} dt \int_0^{t} ds\, [q(t) - q'(t)]\alpha_I(t-s)[q(s)+q'(s)]\ \} \\ & \times exp - \frac{1}{\hbar}\int_0^{t_B} dt \int_0^{t} ds\, [q(t) - q'(t)]\alpha_R(t-s)[q(s)-q'(s)]\,. \qquad (5.23) \end{aligned}$$

Now if we have the reduced density matrix at time $t = 0$, the equation (5.12) and (5.23) will give us its time development. There is no dependence on coordinates of the heat bath environment any longer.

A Particle Subject to Classical Random Forces

In this section we shall discuss some behavior of a particle under influence of classical random forces. Supposing that the particle of mass m and its coordinate at time t is $q(t)$ is acted upon by an external force $F(t)$. The action of this system is

$$A = A[q(t)] = A_0[q(t)] - \int_0^{t_B} dt\, q(t)F(t)\ , \qquad (5.24)$$

where $A_0[q(t)]$ is an action of the particle which is not disturbed by the forces. The characteristic of the force is a random process. No one can know it more explicitly as a function of time, but we can only know its probability $P[F(t)]DF(t)$. More specifically the probability density $P[F(t)]$ is a Gaussian type of distribution. Now the propagator of our system for each value of $F(t)$ is a double path integral:

$$\int Dq(t)Dq'(t)\ \exp\frac{i}{\hbar}\left\{A_0[q(t)]-A_0[q'(t)]-\int_0^{t_b}dt[q(t)-q'(t)]F(t)\right\}. \qquad (5.25)$$

By reasoning of the random type of $F(t)$, we then have to average the propagator (5.25) with the weight $P[F(t)]DF(t)$ to give the effective propagator $J(q_T,q'_T;q_0,q'_0)$ for our problem as

$$J(q_b,q'_b;q_0,q'_0)=\int Dq(t)Dq'(t)\ \phi[Q(t)]\exp\frac{i}{\hbar}\{A_0[q(t)]-A_0[q'(t)]\}, \qquad (5.26)$$

$$Q(t)=\frac{q(t)-q'(t)}{\hbar}$$

where $\phi[Q(t)]$ is the characteristic functional which is in the form

$$\phi[Q(t)]=\int DF(t)\ P[F(t)]\exp\left(-i\int_0^{t_b}dt\,Q(t)F(t)\right) \qquad (5.27)$$

The characteristic functional $\phi[Q(t)]$ here is the average of all the effects of the random force $F(t)$. The form of Eq.(5.26) is a way to calculate the propagator of the problem by averaging the random external force $F(t)$ first. This form is more convenient than calculating by average (5.25) directly because all of the moment mean value, mean square value or correlation functional of $F(t)$, etc., can be determined directly from the characteristic functional $\phi[Q(t)]$, viz.,

$$\left\langle F(t')\right\rangle = -i\frac{\delta\phi[Q(t)]}{\delta Q(t')}\bigg|_{Q(t')=0}$$

$$\left\langle F(t')F(s')\right\rangle = -i\frac{\delta^2\phi[Q(t)]}{\delta Q(t')\delta Q(s')}\bigg|_{Q(t)=0} . \tag{5.28}$$

In our problem we assume that the probability distribution is the Gaussian distribution:

$$\exp\left\{-(1/2)\int_0^{t_0}dt\int_0^{t}ds\, F(t)B(t-s)F(s)\right\} .$$

The convenient form of the probability distribution $P[F(t)]$ is

$$P[F(t)] = \frac{1}{\xi}\exp\left\{-\frac{1}{2}\int_0^{t_0}dt\int_0^{t}ds\, F(t)B(t-s)F(s)\right\} , \tag{5.29}$$

where ξ is a normalizing factor in the form:

$$\xi = \int DF(t)\ \exp\left\{-\frac{1}{2}\int_0^{t_0}dt\int_0^{t}ds\, F(t)B(t-s)F(s)\right\} .$$

The characteristic functional corresponding with $P[F(t)]$ can be written in the form

$$\phi[Q(t)] = \exp\left(-\int_0^{t_0}dt\int_0^{t}ds\, Q(t)W(t-s)Q(s)\right) . \tag{5.30}$$

By using Eq.(5.28) one can get the results

$$\left\langle F(t)\right\rangle = 0,$$

$$\left\langle F(t)F(s)\right\rangle = W(t-s) . \tag{5.31}$$

This result is very familiar. The first equation shows that the average value of the random force vanishes and the other show that $W(t-s)$ in Eq.(5.30) is the correlation function of the force.

The Propagator J

The effect of the random classical forces to the particle which has been discussed in the previous section is very useful to consider the Brownian motion problem in the classical limit from the microscopic model or the quantum mechanical model. To do that we first insert Eq.(5.30) back into Eq.(5.26), the propagator J reads

$$J(q_u, q'_u; q_0, q'_0) = \int Dq(t)Dq'(t)\ \exp\frac{i}{\hbar}\left\{A_0[q(t)] - A_0[q'(t)]\right\} \times \exp\left\{-\int_0^u dt \int_0^t ds\ Q(t)W(t-s)Q(s)\right\} \tag{5.32}$$

Eq.(5.32) is very similar to Eq.(5.23) except for the imaginary part that appears in the exponent of Eq.(5.23). Regardless of this difference we see that the real part of Eq.(5.23) and Eq.(5.32) play the same role, i.e., the physical meaning of $\hbar\alpha_R(t-s)$ in Eq.(5.23) and $W(t-s)$ are the same, the correlation of forces. So far in our discussion, $\hbar\alpha_R(t-s)$ must give the correlation of forces in the classical regime. Now we want some conditions which make our quantum mechanical model reproduce the correlation between the stochastic forces acting on the classical Brownian particle. To do that we investigate the behavior of $\hbar\alpha_R(t-s)$ for high temperature, say $kT \geq \hbar\omega_j$. From the Eq.(5.21), viz.,

$$\hbar\alpha_R(t-s) = \hbar\sum_{j=1}^{n}\frac{c_j^2}{2m\omega_j}\coth\frac{\hbar\omega_j}{2kT}\cos\omega_j(t-s), \tag{5.33}$$

and the limit of high temperature Eq.(5.33) becomes

$$\hbar\alpha_R(t-s)=\frac{kT}{m}\sum_{j=1}^{n}\frac{c_j^2}{\omega_j^2}\cos\omega_j(t-s)+O(\hbar^2) \tag{5.34}$$

to neglect the higher order term $O(\hbar^2)$, the result is the classical correlation of forces to which our quantum mechanical model led us. We desire to compare Eq.(5.34) to the well-known correlation of forces

$$\langle F(t)F(s)\rangle = 2\eta\, kT\delta(t-s) \tag{5.35}$$

given by the classical theory of the Browning motion which has been discussed in the previous chapter. Before comparing, we first have to consider a continuum of oscillators. Assuming that the density of the oscillators is $\rho_D(\omega)$, then

$$\hbar\alpha_R(t-s)\approx\frac{kT}{m}\int_0^{\infty}d\omega\rho_D(\omega)\frac{c^2(\omega)}{\omega^2}\cos\omega(t-s)\ . \tag{5.36}$$

Now, we come to the important step in answering which condition is required to make the quantum mechanical model reproduce the classical theory of the Browning motion. If we choose the following condition:

$$\rho_D(\omega)c^2(\omega)=\begin{cases}\dfrac{2m\eta\omega^2}{\pi} & for \quad \omega<\Omega \\ 0 & for \quad \omega>\Omega\end{cases} \tag{5.37}$$

where Ω is the high frequency cutoff in the distribution of the oscillators, this condition (5.36) becomes

$$\hbar\alpha_R(t-s)\approx\frac{2\eta\, kT}{\pi}\int_0^{\Omega}d\omega\,\cos\omega\,(t-s) \tag{5.38}$$

Now we shall define the function $\Delta(\tau)$ as

$$\Delta(\tau) = \frac{1}{\pi}\int_0^{\Omega} d\omega \cos\omega\tau \,. \tag{5.39}$$

If Ω is large, say $\Omega \to \infty$, one can see (from Eq.(5.38)) that

$$\Delta(\tau) \overset{\Omega\to\infty}{\longrightarrow} \delta(\tau). \tag{5.40}$$

By the help of the function $\Delta(\tau)$, Eq.(5.38) can be rewritten in the form

$$\hbar\alpha_R(t-s) = 2\eta\, kT\Delta(t-s) \tag{5.41}$$

One can see from Eq.(5.41) and the expression (5.40) that if Ω is large, say $\Omega \to \infty$, Eq.(5.41) turns to Eq.(5.35). This is to say that the quantum mechanical model which is introduced in the previous section with the condition (5.37) shall recover Eq.(5.35). In other words, we shall regain Eq.(5.35) when we consider the time much longer than the typical time Ω^{-1}. The physical meaning of this is the low-frequency behavior of the condition (5.37) which is important in this case. This fact is in harmony with the classical theory of Brownian motion since Eq.(5.35) is valid only when we consider times longer than the typical relaxation time of the reservoir.

So far, we have considered a particle coupled to a finite number of harmonic oscillators. However, the environment oscillator can only be considered as a proper heat bath causing dissipation if the spectrum of the environment oscillator is quasi-continuous, so we introduce a spectral density of the environment through

$$I(\omega) = \sum_{j=1}^{n} \frac{\pi c_j^2}{2m\omega_j}\delta\left(\omega-\omega_j\right). \tag{5.42}$$

Then Eq.(5.21) and (5.22) can be written as

$$\alpha_R(t-s) = \int_0^{\infty}\frac{d\omega}{\pi}\; I(\omega)\coth\frac{\hbar\omega}{2kT}\cos\omega(t-s) \,, \tag{5.43}$$

and

$$\alpha_I(t-s) = -\int_0^{\infty} \frac{d\omega}{\pi} I(\omega) \sin \omega_j (t-s) \ . \tag{5.44}$$

Because the distribution of oscillators is already fixed by the condition (5.37), by using this condition in Eq.(5.43) and (5.44) one gets

$$\alpha_R(t-s) = \int_0^{\Omega} d\omega \frac{\eta\ \omega}{\pi} \ \coth \frac{\hbar\omega}{2kT} \cos\omega(t-s) \ , \tag{5.45}$$

and

$$\begin{aligned} \alpha_I(t-s) &= -\int_{-\Omega}^{\Omega} d\omega \frac{\eta\ \omega}{2\pi} \ \sin\omega(t-s) \\ &= \frac{\eta}{2\pi} \frac{d}{d(t-s)} \int_{-\Omega}^{\Omega} d\omega \ \cos\omega(t-s) \\ &= \frac{\eta}{\pi} \frac{d\Delta(t-s)}{d(t-s)} \end{aligned} \tag{5.46}$$

So, for the large Ω one gets

$$\alpha_I(t-s) = \eta \ \frac{d}{d(t-s)} \delta(t-s) \, . \tag{5.47}$$

Finally, using (5.45) and (5.46) in (5.23) we have

$$\begin{aligned} J[q_u, q'_u; q_0, q'_0] = \int Dq(t) Dq'(t) \ \exp \frac{i}{\hbar} \{ & A_B[q] - A_B[q'] \\ & - \int_0^u dt \int_0^t ds \, [q(t) - q'(t)] \frac{d\Delta(t-s)}{d(t-s)} [q(s) + q'(s)] \ \} \\ \times exp - \frac{I}{\hbar} \int_0^{\Omega} d\omega \frac{\eta\omega}{\pi} \coth \frac{\hbar\omega}{2kT} & \int_0^u dt \int_0^t ds \, [q(t) - q'(t)] \ \cos\omega(t-s) \ [q(s) - q'(s)] \end{aligned} \tag{5.48}$$

We can simplify this expression to integrate the term containing the derivative of $\Delta(t-s)$ function by parts. It is straightforward to do that and the result is

$$\int_0^{t_f} dt \int_0^{t} ds \left[q(t)-q'(t)\right] \frac{d\Delta(t-s)}{d(t-s)} \left[q(s)+q'(s)\right]$$
$$= -\int_0^{t_f} dt\eta\left[q^2(t)-q'^2(t)\right]\Delta(0) + \int_0^{t_f} dt\eta\left[q(t)-q'(t)\right]\Delta(t)\left[q(0)+q'(0)\right]$$
$$-\frac{\eta}{2}\int_0^{t_f} dt\int_0^{t} ds\left[q(t)-q'(t)\right]\Delta(t-s)\left[\dot{q}(s)+\dot{q}'(s)\right] . \qquad (5.49)$$

From Eq.(5.44), the definition of function $\Delta(\tau)$, one get the value of $\Delta(0)$ as:

$$\Delta(0) = \frac{\Omega}{\pi} \qquad (5.50)$$

For large Ω the function $\Delta(\tau)$ becomes to Dirac delta function$\delta(\tau)$ by means of (5.40). By using this limit in Eq.(5.49) and substitute the value of $\Delta(0)$ from Eq(5.50), the result on the right hand side is

$$-\frac{\eta\Omega}{\pi}\int_0^{t_f} dt\left[q^2(t)-q'^2(t)\right] + \frac{1}{\eta}\left[q^2(0)-q'^2(0)\right]$$
$$+\frac{\eta}{2}\int_0^{t_f} dt\left[q(t)\dot{q}(t)+q(t)\dot{q}'(t)-q'(t)\dot{q}(t)-q'(t)\dot{q}'(t)\right] . \qquad (5.51)$$

The limit of large Ω simply reflects the fact that we are interested in time $t \approx \omega^{-1} >> \Omega^{-1}$. Consequently the second term in (5.51) clearly much smaller than the first one so that we can neglect it. After we do that Eq.(5.51) becomes

$$-\frac{\eta\Omega}{\pi}\int_0^{t_f} dt\left[q^2(t)-q'^2(t)\right] + \frac{\eta}{2}\int_0^{t_f} dt\left[q(t)\dot{q}(t)+q(t)\dot{q}'(t)-q'(t)\dot{q}(t)-q'(t)\dot{q}'(t)\right] . \qquad (5.52)$$

For further considerations about the frequency shift, we define the relaxation constant γ as

$$\gamma = \frac{\eta}{2M} \ , \tag{5.53}$$

and the frequency shift $\Delta\omega$ as

$$\Delta\omega = \frac{4\gamma\ \Omega}{\pi} \ . \tag{5.54}$$

We can finally write (5.48) as

$$\begin{aligned} J[q_t, q'_t; q_0, q'_0] = \int Dq(t) Dq'(t)\ \exp\frac{i}{\hbar}\{\ A_r[q] - A_r[q'] \\ - M\gamma \int_0^t dt \left[q(t)\dot{q}(t) - q'(t)\dot{q}'(t) + q(t)\dot{q}'(t) - q'(t)\dot{q}(t)\right]\ \} \\ \times exp - \frac{1}{\hbar}\frac{2M\gamma}{\pi}\int_0^{\Omega} d\omega\ \ \omega \coth\frac{\hbar\omega}{2kT}\int_0^t dt \int_0^t ds\ [q(t) - q'(t)]\ \cos\omega(t-s)\ [q(s) - q'(s)] \end{aligned} \tag{5.55}$$

where we have introduced S_r as the renormalized action given by

$$A_r = \int_0^t dt \left[\frac{1}{2}M\dot{q}^2 - V(q)\right] + \int_0^t dt\, \frac{1}{2}M(\Delta\omega)^2 q^2 . \tag{5.56}$$

In other words A_r is the action which the potential $V(t)$ renormalized by the subtraction of the harmonic term with frequency. From now on we shall call it the renormalized potential $V_r(q)$

$$V_r(q) = V(q) - \frac{1}{2}M(\Delta\omega)^2 q^2 . \tag{5.57}$$

So Eq.(5.56) can be written in the form

$$A_r = \int_0^t dt \left[\frac{1}{2}M\dot{q}^2 - V_r(q)\right] . \tag{5.58}$$

The Fokker-Planck Equation

An expression for the propagator of the reduced density matrix of a particle interacting with a heat bath of harmonic oscillators has been derived in Eq.(5.55). We also showed that in classical limit, the real exponential of Eq.(5.55) reduces to the characteristic functional of the stochastic force acting on the Brownian particle. At the same time we gave a definite form for the additional imaginary part of the integrand, i.e. the term involving $q\dot{q}$, etc., in Eq.(5.55). Now we shall discuss this part of the integrand and try to answer whether this term is makes sense. In other words we want to know: is that term compatible with the classical Brownian motion of a particle? In order to answer this question we shall to investigate the equation of motion for the density matrix in the classical region. To compare this equation to the one of a classical Brownian particle we must write it down to the phase-space representation. That is the only way we can compare it to the equation of motion in phase-space distribution in classical physics. The way we can perform the transformation from the Hilbert to the phase-space is by using the so-called Wigner distribution function.

We shall start by writing Eq.(5.55) when $2kT > \hbar\Omega >> \hbar\omega_h$, Ω being the cutoff frequency of the reservoir oscillators. This reads

$$J[q_t, q'_t; q_0, q'_0] = \int Dq(t)Dq'(t)\ \exp\frac{i}{\hbar}\{\ A_r[q] - A_r[q'] - M\gamma\int_0^t dt[q(t)\dot{q}(t) - q'(t)\dot{q}'(t) + q(t)\dot{q}'(t) - q'(t)\dot{q}(t)]\ \} \times exp - \frac{2M\gamma kT}{\hbar}\int_0^t dt\ [q(t) - q'(t)]^2 \qquad (5.59)$$

This expression becomes meaningless if we consider the classical limit $kT >> \hbar\omega_h$ (high temperature) and still keep it quantal form. However, this is the way to obtain an equation of motion for the reduced density matrix in the classical limit. Later we shall take the appropriate measures in order to be consistent with this approximation. We shall use Eq.(5.59) rather than (5.55) only to simplify our future expressions.

What we shall do now is to follow Feynman's procedure[11,12] when he derives the S   ödinger equation from the functional integration formalism. The procedure can begin by supposing that we have the reduced density matrix $\tilde{\rho}(q_t, q'_t, t)$ at a time t and wish to find its value $\tilde{\rho}(q_{t+\varepsilon}, q'_{t+\varepsilon}, t+\varepsilon)$ at $t+\varepsilon$ where $\varepsilon \to 0$. By Eq.(5.12) we have

$$\tilde{\rho}(q_{t+\varepsilon}, q'_{t+\varepsilon}, t+\varepsilon) = \int dq_t dq'_t J(q_{t+\varepsilon}, q'_{t+\varepsilon}; q_t, q'_t)\, \tilde{\rho}(q_t, q'_t, t) \qquad (5.60)$$

The propagator $J(q_{t+\varepsilon}, q'_{t+\varepsilon}; q_t, q'_t)$ in Eq.(5.60) can be written in a very simple form when $\varepsilon \to 0$. To do so we only need to remember that for small time intervals any regular path can be approximate by a straight line. Thus, functional integration over paths in short time intervals can be put equal to the value of the integrand times a normalization constant. Then,

$$J(q_{t+\varepsilon}, q'_{t+\varepsilon}; q_t, q'_t) \approx \frac{1}{C} \exp \frac{i}{\hbar} \left\{ \int_t^{t+\varepsilon} dt \left(\frac{1}{2} M\dot{q}^2 - V_r(q) \right) - \int_t^{t+\varepsilon} dt \left(\frac{1}{2} M\dot{q}'^2 - V_r(q') \right) \right.$$
$$\left. - M\gamma \int_t^{t+\varepsilon} dt \left[q(t)\dot{q}(t) - q'(t)\dot{q}'(t) + q(t)\dot{q}'(t) - q'(t)\dot{q}(t) \right] - \right\}$$
$$\times \exp - \frac{2M\gamma kT}{\hbar^2} \int_t^{t+\varepsilon} dt \left[q(t) - q'(t) \right]^2 \qquad (5.61)$$

All the integrals appearing above can be approximated when $\varepsilon \to 0$. We know that

$$\dot{q} \approx \frac{q_{t+\varepsilon} - q_t}{\varepsilon},\ \dot{q}' \approx \frac{q'_{t+\varepsilon} - q'_t}{\varepsilon},\ \int_t^{t+\varepsilon} dt z(q(t)) \approx \varepsilon z\left(\frac{q_{t+\varepsilon} + q_t}{2} \right) \qquad (5.62)$$

Using (5.62) in the expression for $J(q_{t+\varepsilon}, q'_{t+\varepsilon}; q_t, q'_t)$, Eq.(5.60) becomes (see appendix i)

$$\widetilde{\rho}(q,q',t+\varepsilon)=\int dQ_1 dQ_2 \exp\left\{\frac{iMQ_1^2}{2\varepsilon\hbar}-\frac{i\varepsilon}{\hbar}V_r\left(q-\frac{Q_1}{2}\right)-\frac{iMQ_2^2}{2\varepsilon\hbar}\right.$$
$$+\frac{i\varepsilon}{\hbar}V_r\left(q'-\frac{Q_2}{2}\right)-\frac{iM\gamma}{\hbar}\left(q-\frac{Q_1}{2}\right)Q_2+\frac{iM\gamma}{\hbar}\left(q'-\frac{Q_2}{2}\right)Q_1$$
$$-\frac{iM\gamma}{\hbar}\left(q-\frac{Q_1}{2}\right)Q_1+\frac{iM\gamma}{\hbar}\left(q'-\frac{Q_2}{2}\right)Q_2-\frac{2M\gamma kT\varepsilon}{\hbar^2}(q-q')^2$$
$$\left.-\frac{2M\gamma kT\varepsilon}{\hbar^2}(q-q')(Q_1-Q_2)-\frac{M\gamma kT\varepsilon}{2\hbar^2}(Q_1-Q_2)^2\right\}$$
$$\times\widetilde{\rho}(q-Q_1,q'-Q_2) \tag{5.63}$$

where $Q_1=q_{t+\varepsilon}-q_t$, $Q_2=q'_{t+\varepsilon}-q'_t$, $q_{t+\varepsilon}=q$ and $q'_{t+\varepsilon}=q'$. Expanding the Eq. (5.63) one concludes the following (see appendix ii):

a) The zero order term in ε gives us the normalization constant

$$C^2=\frac{2\pi\varepsilon\hbar}{M} \tag{5.64}$$

b) The first order term in ε gives us the desired equation of motion for reduced density matrix $\widetilde{\rho}$ in the semiclassical region,

$$\frac{\partial\widetilde{\rho}}{\partial t}=\frac{i\hbar}{2M}\frac{\partial^2\widetilde{\rho}}{\partial q^2}-\frac{i\hbar}{2M}\frac{\partial^2\widetilde{\rho}}{\partial q'^2}-\gamma(q-q')\frac{\partial\widetilde{\rho}}{\partial q}+\gamma(q-q')\frac{\partial\widetilde{\rho}}{\partial q'}$$
$$+\frac{V_r(q)}{i\hbar}\widetilde{\rho}-\frac{V_r(q')}{i\hbar}\widetilde{\rho}-\frac{2M\gamma kT}{\hbar^2}(q-q')^2\,\widetilde{\rho}. \tag{5.65}$$

Once again, we wish to emphasize that Eq.(5,65) is not the most general equation for $\widetilde{\rho}$. It is valid only when we have $2kT>\hbar\Omega>>\hbar\omega_h$. If were interested in obtaining something more general we would not have been allowed to write Eq.(5.59) instead of Eq.(5.55) and the last term of Eq.(5.65) would involve a time integration (it would depend on the past history of the system).

Now we want to compare the master equation (5.65) to the equation for the classical distribution in phase space. To do this we need now is the Wigner distribution or the Wigner transform of $\widetilde{\rho}$ which defined by

$$w(x,p,t)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}dy\, e^{\frac{ipy}{\hbar}}\,\widetilde{\rho}\,(x-\frac{y}{2},x+\frac{y}{2}) \tag{5.66}$$

In spite of presenting a purely quantal description of a system the Wigner distribution becomes very important when we are interested in a semi-classical region. This is because Wigner's theory is described directly in the classical phase space of the system. So if we take the Wigner transform of equation (5.65) we shall get (see appendic iii)

$$\frac{\partial w}{\partial t}=-\frac{1}{M}\frac{\partial pw}{\partial x}+\frac{\partial V_r' w}{\partial p}+2\gamma\frac{\partial pw}{\partial p}+D\frac{\partial^2 w}{\partial p^2} \tag{5.67}$$

where $D=2M\gamma kT=\eta kT$, which is the well-known Fokker-Planck equation describing the time development of the Wigner transform of the reduced density matrix of the system. This is a purely quantum mechanical equation. We know that $w(x,p,t)$ tends to the classical phase space distribution in this limit. Then we conclude that Eq. (5.67) describe the time development of the phase space distribution of a classical Brownian particle when $\hbar\to 0$. We also realize that the third term on the right-hand side of (5.67) is a direct consequence of the existence of the γ dependent term in the imaginary part of the exponent in (5.55). Therefore, the latter is responsibility of the appearance of a force of the form $\eta\dot{q}$ in the classical motion of a Browning particle. What we have achieved so far is that our quantum mechanical expression (5.55) for the propagator J is in total accordance with the equation believed to describe the classical motion of a Browning particle. It also means that the choice made for $\rho_D(\omega)c^2(\omega)$ in (5.37) is a very suitable one, allowing us to describe J solely in term of the phenomenological damping constant η.