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Time-Dependent Probability Density of Statistical Mechanics

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Methods based on the density matrix for calculating the time-dependent probability density of a quantum system approaching equilibrium are presented. Explicit expressions are derived for the time-dependent probability density for a double-well potential. The effects of tunneling and transitions between energy levels on the probability density are discussed. For the case of closely spaced energy levels, a partial differential form of the density matrix equation is derived and used to calculate time-dependent probability densities.

KEY WORDS: Probability density; density matrix; tunneling phenomena.

1. INTRODUCTION

The probability density $\bar{P}(\mathbf{r})$ of a quantum system at equilibrium at temperature T can be calculated by solving the time-independent Schrödinger equation for the wave functions $\phi_n(\mathbf{r})$ and the eigenvalues ϵ_n and then summing the series

$$\bar{P}(\mathbf{r}) = Q^{-1} \sum_n \exp(-\epsilon_n/kT)\, |\phi_n(\mathbf{r})|^2 \tag{1}$$

where Q is the parition function and k is Boltzmann's constant. If the quantum system does not interact strongly with its surroundings, the equilibrium

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probability density depends only on the properties of the system. On the other hand, the time-dependent probability density depends both on the properties of the system and on the interaction potential between the system and its surroundings. A practical method based on the density matrix for treating the interaction between a quantum system and its surroundings has been proposed by Redfield.(1,2) It is the purpose of this paper to use a modified form of Redfield's method to obtain the time-dependent probability density of a quantum system approaching equilibrium. The case of discrete energy levels will be treated first and an explicit expression for the time-dependent probability density for a double-well potential will be derived. Next the case of closely spaced energy levels will be studied, a partial differential equation for the time-dependent probability density will be derived, and explicit solutions will be given.

2. DENSITY MATRIX EQUATION FOR PROBABILITY DENSITY

Consider an ensemble whose members consist of a quantum system of interest surrounded by a temperature bath.(1,2) The Hamiltonian of the system $\hat{H}_S(\mathbf{r})$ and the Hamiltonian of the bath $\hat{H}_B(\mathbf{R})$ are both considered to be time independent. There is a weak interaction between the system and the bath, represented by the time-independent interaction operator $\hat{H}_I(\mathbf{r}, \mathbf{R})$. The variables $\mathbf{r}$ and $\mathbf{R}$ are the generalized coordinates of the system and bath, respectively. The total Hamiltonian for the combination of the system and bath is

$$\hat{H}(\mathbf{r}, \mathbf{R}) = \hat{H}_S(\mathbf{r}) + \hat{H}_B(\mathbf{R}) + \hat{H}_I(\mathbf{r}, \mathbf{R}) \tag{2}$$

The eigenfunctions $\phi_n(\mathbf{r})$ and $\Phi_{fu}(\mathbf{R})$ of the system and bath are given by

$$\hat{H}_S(\mathbf{r})\phi_n(\mathbf{r}) = \epsilon_n\phi_n(\mathbf{r}) \tag{3}$$

$$\hat{H}_B(\mathbf{R})\Phi_{fu}(\mathbf{R}) = E_f\Phi_{fu}(\mathbf{R}) \tag{4}$$

where ϵ_n and E_f are the eigenvalues of the system and bath, respectively, and u is a degeneracy parameter.

The wave function $\Psi(\mathbf{r}, \mathbf{R}, t)$ of each member of the ensemble varies with time according to the Schrödinger equation

$$i\hbar\, \partial\Psi(\mathbf{r}, \mathbf{R}, t)/\partial t = \hat{H}(\mathbf{r}, \mathbf{R})\Psi(\mathbf{r}, \mathbf{R}, t) \tag{5}$$

One can expand $\Psi(\mathbf{r}, \mathbf{R}, t)$ in terms of the wave functions $\phi_n(\mathbf{r})$ and $\Phi_{fu}(\mathbf{R})$:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_n \sum_f \sum_u a_{nfu}(t) \exp[-i(\epsilon_n + E_f)t/\hbar]\phi_n(\mathbf{r})\Phi_{fu}(\mathbf{R}) \tag{6}$$

Substituting Eq. (6) into Eq. (5), multiplying the result by

$$\exp[i(\epsilon_n' + E_f')t/\hbar]\phi_{n'}^*(\mathbf{r})\Phi_{f'u'}^*(\mathbf{R})$$

and integrating over all values of **r** and **R**, one finds that the coefficients of the expansion (6) vary with time according to the equation

$$i\hbar\, da_{n'f'u'}/dt = \sum_{n}\sum_{f}\sum_{u} a_{nfu} \exp[i(\epsilon_{n'} - \epsilon_n + E_{f'} - E_f)t/\hbar]\, G_{n'f'u'nfu} \tag{7}$$

where

$$G_{n'f'u'nfu} = \iint \phi^*_{n'} \Phi^*_{f'u'} \hat{H}_I \phi_n \Phi_{fu}\, d\mathbf{r}\, d\mathbf{R} \tag{8}$$

We are particularly interested in obtaining the ensemble-averaged probability density $\bar{P}(\mathbf{r}, t)$ of the system, where $\bar{P}(\mathbf{r}, t)\, d\mathbf{r}$ is the probability that a system of the ensemble has coordinates in $d\mathbf{r}$ at $\mathbf{r}$ at time t. To derive an expression for $\bar{P}(\mathbf{r}, t)$, we first multiply the wave function (6) by its complex conjugate and perform an ensemble average to obtain the probability distribution $\bar{P}(\mathbf{r}, \mathbf{R}, t)$ for the combination of system and bath:

$$\begin{aligned}\bar{P}(\mathbf{r}, \mathbf{R}, t) &= \langle |\Psi(\mathbf{r}, \mathbf{R}, t)|^2 \rangle \\ &= \sum_{n}\sum_{n'}\sum_{f}\sum_{f'}\sum_{u}\sum_{u'} \langle a^*_{n'f'u'} a_{nfu} \rangle \exp[i(\epsilon_{n'} - \epsilon_n + E_{f'} - E_f)t/\hbar] \\ &\quad \times \phi^*_{n'}(\mathbf{r}) \phi_n(\mathbf{r}) \Phi^*_{f'u'}(\mathbf{R}) \Phi_{fu}(\mathbf{R})\end{aligned} \tag{9}$$

where the brackets denote an ensemble average. Next, integrating Eq. (9) over the coordinates of the bath, we obtain

$$\begin{aligned}\bar{P}(\mathbf{r}, t) &= \int \bar{P}(\mathbf{r}, \mathbf{R}, t)\, d\mathbf{R} \\ &= \sum_{n}\sum_{n'}\sum_{f}\sum_{u} \langle a^*_{n'fu} a_{nfu} \rangle \exp[i(\epsilon_n{}' - \epsilon_n)t/\hbar] \phi^*_{n'}(\mathbf{r}) \phi_n(\mathbf{r})\end{aligned} \tag{10}$$

where use has been made of the orthonormality property of the wave functions $\Phi_{fu}(\mathbf{R})$. The total density matrix in the Heisenberg representation is defined as

$$\rho^H_{nfun'f'u'} = \langle a^*_{n'f'u'} a_{nfu} \rangle \tag{11}$$

$$= \rho_{nfun'f'u'} \exp[i(\epsilon_n - \epsilon_{n'} + E_f - E_{f'})t/\hbar] \tag{12}$$

where $\rho_{nfun'f'u'}$ is the total density matrix in the Schrödinger representation. In most applications, one is concerned with the properties of the system only, not the bath. For these cases it is convenient to use the reduced density matrix, which is defined as

$$\sigma^H_{nn'} = \sum_{f}\sum_{u} \langle a^*_{n'fu} a_{nfu} \rangle \tag{13}$$

$$= \sigma_{nn'} \exp[i(\epsilon_n - \epsilon_n{}')t/\hbar] \tag{14}$$

where $\sigma^H_{nn'}$ and $\sigma_{nn'}$ are the reduced density matrices of the system in the Heisenberg and Schrödinger representations, respectively. Finally, combining

Eqs. (10), (13), and (14), we obtain an expression for the probability density of the system

$$\bar{P}(\mathbf{r}, t) = \sum_{n} \sum_{n'} \sigma_{nn'}(t)\phi_{n'}^{*}(\mathbf{r})\phi_{n}(\mathbf{r}) \tag{15}$$

Thus, a knowledge of $\sigma_{nn'}$ as a function of time is all that is required to determine the time-dependent probability density. One can make use of the Hermitian property of the reduced density matrix,

$$\sigma_{nm}^{*} = \sigma_{mn} \tag{16}$$

to derive a more convenient form of Eq. (15):

$$\bar{P}(\mathbf{r}, t) = \sum_{n} \sigma_{nn}(t)[\phi_{n}(\mathbf{r})]^{2} + 2 \sum_{m>n} \sum_{n} |\sigma_{nm}(t)|\phi_{n}(\mathbf{r})\phi_{m}(\mathbf{r}) \cos \theta_{nm} \tag{17}$$

where we have let

$$\sigma_{nm} = |\sigma_{nm}| \exp(i\theta_{nm}) \tag{18}$$

and all the functions $\phi_{n}(\mathbf{r})$ are to be taken as real without loss of generality.

Redfield assumed that the interaction operator $\hat{H}_{I}(\mathbf{r}, \mathbf{R})$ could be expressed as the sum of products of operators involving the system or bath alone:

$$\hat{H}_{I}(\mathbf{r}, \mathbf{R}) = \sum_{q} \hat{H}_{b}{}^{q}(\mathbf{R})L^{q}(\mathbf{r}) \tag{19}$$

Substituting Eq. (19) into Eq. (8) yields

$$G_{nfun'f'u'} = \sum_{q} H_{fuf'u'}^{q} L_{nn'}^{q} \tag{20}$$

where

$$L_{nn'}^{q} = \int \phi_{n}{}^{*}(\mathbf{r})L^{q}(\mathbf{r})\phi_{n'}(\mathbf{r})\, d\mathbf{r} \tag{21}$$

$$H_{fuf'u'}^{q} = \int \Phi_{fu}^{*}(\mathbf{R})\hat{H}_{b}{}^{q}(\mathbf{R})\Phi_{f'u'}(\mathbf{R})\, d\mathbf{R} \tag{22}$$

He also assumed that the bath can be considered to remain in thermal equilibrium for all time so that the total density matrix could be expressed as

$$\rho_{nfun'f'u'} = \sigma_{nn'}p(\omega_{f})\, \delta_{ff'}\, \delta_{uu'} \tag{23}$$

where

$$p(\omega_{f}) = [\exp(-\hbar\omega_{f}/kT)]/\sum_{f'} \sum_{u'} \exp(-\hbar\omega_{f'}/kT) \tag{24}$$

and where ω_{f} are the eigenvalues of the bath E_{f} divided by $\hbar$. Combining Eq. (7) with Eqs. (11)–(14) and (20)–(24) and using perturbation theory, Redfield found that it was possible to calculate the rate of change of the reduced density matrix by the equation

$$d\sigma_{nn'}/dt = i\omega_{n'n}\sigma_{nn'} + \sum_{m}\sum_{m'} R_{nn'mm'}\sigma_{mm'} \tag{25}$$

where the matrix $R_{nn'mm'}$ is called the relaxation matrix and its elements are given by

$$\begin{aligned} R_{nn'mm'} = \hbar^{-2}\sum_{q}\sum_{q'} \{ & L^{q}_{nm}L^{q'}_{m'n'}[j_{qq'}(\omega_{nm}) + j_{qq'}(\omega_{n'm'})] \\ & - \delta_{nm}\sum_{\gamma} L^{q}_{m'\gamma}L^{q'}_{\gamma n'}j_{qq'}(\omega_{m'\gamma})\exp(\hbar\omega_{m'\gamma}/kT) \\ & - \delta_{n'm'}\sum_{\gamma} L^{q}_{n\gamma}L^{q'}_{\gamma m}j_{qq'}(\omega_{m\gamma})\exp(\hbar\omega_{m\gamma}/kT)\} \end{aligned} \tag{26}$$

where

$$j_{qq'}(\omega) = \pi\sum_{u}\sum_{u'}\int d\nu\, p(\nu)H^{q}_{\nu-\omega,u,\nu,u'}H^{q'}_{\nu,u',\nu-\omega,u}\eta_u(\nu - \omega)\eta_{u'}(\nu) \tag{27}$$

where $\eta_u(\nu)$ is the density of states and $\omega_{nm} = (\epsilon_n - \epsilon_m)/\hbar$. It is impractical to evaluate $j_{qq'}(\omega)$ as defined by Eq. (27) except for a few restricted cases since the calculation requires a complete knowledge of all the eigenfunctions and eigenvalues of the bath. Redfield has indicated that Eq. (27) can be taken as approximately equal to

$$j_{qq'}(\omega) = \tfrac{1}{2}[\exp(-\hbar\omega/2kT)]\int_{-\infty}^{+\infty} \langle A^{q}(0)A^{q'}(t)\rangle \exp(i\omega t)\, dt \tag{28}$$

where $A^{q}(t)$ is a randomly varying function of time associated with the interaction of the bath and the system and $\langle A^{q}(0)A^{q'}(t)\rangle$ is its correlation function.

Some of the elements of the relaxation matrix have physical significance. The terms R_{nnmm} are the probabilities of transition of the system from state m to state n per unit time caused by interaction with the bath. It can be shown that the matrix elements R_{nnmm} satisfy the relation

$$R_{nnmm} = R_{mmnn}\exp(\hbar\omega_{mn}/kT) \tag{29}$$

so that the transition probability from m to n is related to that from n to m. It can be shown that

$$\sum_{m} R_{nnmm}\sigma^{(T)}_{mm} = 0 \tag{30}$$

where $\sigma^{(T)}_{nm}$ is the equilibrium density matrix

$$\sigma^{(T)}_{nm} = \delta_{nm}\,[\exp(-\epsilon_n/kT)]/\sum_{n'}\exp(-\epsilon_{n'}/kT) \tag{31}$$

One can also prove that

$$\sum_{m} R_{nnmm} = 0 \tag{32}$$

It has been suggested by Redfield that those elements $R_{nn'mm'}$ of the relaxation matrix for which $\epsilon_n - \epsilon_{n'} \neq \epsilon_m - \epsilon_{m'}$ are in general ineffective in the relaxation process. This gives us the simplifying condition

$$R_{nn'mm'} = 0 \quad \text{if} \quad \epsilon_n - \epsilon_{n'} \neq \epsilon_m - \epsilon_{m'} \tag{33}$$

3. PROBABILITY DENSITY FOR TUNNELING PROCESSES

Studies of the kinetics of the tunneling process $YX + Z \rightarrow Y + XZ$, where group X is transferred through a barrier from group Y to group Z, and where the distance between group Y and group Z is fixed, have been carried out by considering that group X is bound by a double-well potential having two minima separated by a barrier. Successful use of the double-well potential has been made in analyzing the tunneling of hydrogen-bonded protons between nucleotide base pairs in DNA(3) and in investigating the general problem of tunneling in hydrogen bonds.(4) Recently, the effects of thermal vibrations on the kinetics of the tunneling process have been studied by solving the time-dependent Schrödinger equation for the double-well potential in which a fluctuating potential was included.(5) In this section it will be shown that the density matrix equations discussed in the previous section can also be used to take into account the effects of thermal vibrations on tunneling.

We consider the case of a particle in a double-well potential, which will be referred to as the system. The interaction of the surroundings on the system is taken to be a stochastic potential of the form

$$v(\mathbf{r}, t) = A(t)L(\mathbf{r}) \tag{34}$$

where $A(t)$ is a fluctuating potential whose correlation coefficient is $\langle A(0)A(t)\rangle$. According to Eq. (28), the spectral density is

$$j(\omega) = [\exp(-\hbar\omega/2kT)] \int_0^\infty \langle A(0)A(\tau)\rangle \cos(\omega\tau)\, d\tau \tag{35}$$

At time $t = 0$, we take the elements of the density matrix to be

$$\sigma_{nm}(0) = Q^{-1} \exp[-(\epsilon_n + \epsilon_m)/2kT] \exp(i\gamma_{nm}) \tag{36}$$

where Q is the partition function

$$Q = \sum_n \exp(-\epsilon_n/kT) \tag{37}$$

and where the phases γ_{nm} determine the initial probability density. For example, for certain values of γ_{nm}, the particle will be predominantly on one side of the double-well potential at time $t = 0$. Since the density matrix is Hermitian, $\gamma_{nn} = 0$.

In this section we will neglect transitions between energy levels and consider only tunneling phenomena. The density matrix equations (25) then reduce to

$$d\sigma_{nm}/dt = i\omega_{mn}\sigma_{nm} + R_{nmnm}\sigma_{nm} \tag{38}$$

where

$$R_{nmnm} = -\hbar^{-2}(L_{mm} - L_{nn})^2 j(0) \tag{39}$$

$$j(0) = \int_0^\infty \langle A(0)A(\tau)\rangle \, d\tau \tag{40}$$

$$L_{mm} = \int L(\mathbf{r})[\phi_{mm}(\mathbf{r})]^2 \, d\mathbf{r} \tag{41}$$

Equation (38) has the solution

$$\sigma_{nm}(t) = \sigma_{nm}(0) \exp(i\omega_{mn}t - D_{nm}t) \tag{42}$$

where

$$D_{nm} = -R_{nmnm} = \hbar^{-2}(L_{mm} - L_{nn})^2 \int_0^\infty \langle A(0)A(\tau)\rangle \, d\tau \tag{43}$$

Combining Eqs. (17), (36), and (42), we obtain an expression for the ensembled-averaged probability density:

$$\begin{aligned} \bar{P}(\mathbf{r}, t) = {} & Q^{-1} \sum_n [\phi_n(\mathbf{r})]^2 \exp(-\epsilon_n/kT) \\ & + 2Q^{-1} \sum_{m>n} \sum_n \phi_m(\mathbf{r})\phi_n(\mathbf{r}) \exp[-(\epsilon_n + \epsilon_m)/2kT] \exp(-D_{nm}t) \\ & \times (\cos\gamma_{mn} \cos\omega_{mn}t + \sin\gamma_{mn} \sin\omega_{mn}t) \end{aligned} \tag{44}$$

This probability distribution is in agreement with the one previously obtained by solving the Schrödinger equation for a fluctuating potential and then performing an ensemble average.(5) As discussed previously, this result shows that at sufficiently low temperatures the ensemble-averaged probability that a particle is on one side of a double-well potential may exhibit damped oscillations.

Equation (44) gives the probability density of a particle in a double-well potential as a function of time, but where transitions between energy levels have been neglected. Next, we will consider the effects of transitions. If the temperature is sufficiently low, the time dependence of the probability density can be determined by the two lowest energy eigenvalues of the system and their corresponding eigenfunctions. Making use of Eqs. (25), (26), (28), and (33), we obtain a coupled set of first-order ordinary differential equations with constant coefficients for the elements $\sigma_{11}(t)$, $\sigma_{21}(t)$, $\sigma_{22}(t)$ of the density matrix. Substituting the solution of the differential equation into Eq. (17) yields an expression for the ensemble-averaged probability density:

$$\begin{aligned}\bar{P}(\mathbf{r}, t) = {} & [\phi_1(\mathbf{r})]^2 Q^{-1}\exp(-\epsilon_1/kT) + [\phi_2(\mathbf{r})]^2 Q^{-1}\exp(-\epsilon_2/kT) \\ & + \{[\phi_1(\mathbf{r})]^2[\sigma_{11}(0) - Q^{-1}\exp(-\epsilon_1/kT)] \\ & + [\phi_2(\mathbf{r})]^2[\sigma_{22}(0) - Q^{-1}\exp(-\epsilon_2/kT)]\}\exp(-\lambda_1 t) \\ & + 2\phi_1(\mathbf{r})\phi_2(\mathbf{r})|\sigma_{21}(0)|\exp(-\lambda_2 t)\cos(\gamma_{21} - \omega_{21}t)\end{aligned} \tag{45}$$

where

$$\lambda_1 = 2(L_{12}/\hbar)^2 j(\omega_{21})[1 + \exp(\hbar\omega_{21}/kT)] \tag{46}$$

$$\lambda_2 = \hbar^{-2}(L_{22} - L_{11})^2 j(0) + (L_{12}/\hbar)^2 j(\omega_{21})[1 + \exp(\hbar\omega_{21}/kT)] \tag{47}$$

$$j(\omega) = [\exp(\hbar\omega/2kT)]\int_0^\infty \langle A(0)A(\tau)\rangle\cos(\omega\tau)\,d\tau \tag{48}$$

Here $\sigma_{11}(0)$ and $\sigma_{22}(0)$ are the values of the density matrix at time $t = 0$ and γ_{21} and $|\sigma_{21}(0)|$ are the phase and absolute value of σ_{21} at $t = 0$.

If we let the initial conditions be

$$\sigma_{11}(0) = Q^{-1}\exp(-\epsilon_1/kT) \tag{49}$$

$$\sigma_{22}(0) = Q^{-1}\exp(-\epsilon_2/kT) \tag{50}$$

$$|\sigma_{21}(0)| = Q^{-1}\exp[-(\epsilon_1 + \epsilon_2)/2kT] \tag{51}$$

and consider the case where there are no transitions ($L_{12} = 0$), then the probability density of Eq. (45) reduces to that of Eq. (44). Thus, in this case, transitions give rise to an additional decay term with decay constant λ_1 and result in an increase in the magnitude of the decay constant λ_2 by the amount $(L_{12}/\hbar)^2 j(\omega_{21})[1 + \exp(\hbar\omega_{21}/kT)]$.

4. PARTIAL DIFFERENTIAL EQUATIONS

Consider a system with an infinite number of closely spaced discrete energy levels $\epsilon_0, \epsilon_1, \epsilon_2, \epsilon_3, \ldots$. We assume that transitions can occur only between neighboring energy levels so that

$$L_{nm}^q = 0 \qquad \text{for} \quad n > m + 1 \tag{52}$$

and that the elements R_{nnmm}, where $n = m + 1$, are of the same magnitude:

$$R_{nnmm} = D \qquad \text{for} \quad n = m + 1 \tag{53}$$

Condition (52) implies that

$$R_{nnmm} = 0 \quad \text{for} \quad n > m + 1 \tag{54}$$

According to Eqs. (25), (26), (29), and (52)–(54), the rate of change of the on-diagonal elements of the density matrix is given by

$$d\sigma_{ss}/dt = R_{sss-1s-1}\sigma_{s-1s-1} + R_{ssss}\sigma_{ss} + R_{sss+1s+1}\sigma_{s+1s+1} \tag{55}$$

where

$$R_{sss-1s-1} = D \tag{56}$$

$$R_{ssss} = -D[1 + \exp(\beta\hbar\omega_{ss-1})] \tag{57}$$

$$R_{sss+1s+1} = D\exp(\beta\hbar\omega_{s+1s}) \tag{58}$$

$$\beta = (kT)^{-1} \tag{59}$$

We now define functions $\omega(s)$ and $\sigma(s, t)$ by the relations

$$\omega(s) = \omega_{s+1s} \tag{60}$$

$$\sigma(s, t) = \sigma_{ss}(t) \tag{61}$$

and we will treat systems where these functions can be taken as continuous and differentiable. Expanding $\sigma(s + 1, t)$, $\sigma(s - 1, t)$, and $\omega(s - 1)$ in a Taylor series about s, e.g.,

$$\sigma(s + 1, t) = \sigma(s) + \frac{\partial\sigma(s)}{\partial s} + \frac{1}{2}\frac{\partial^2\sigma(s)}{\partial s^2} + \cdots \tag{62}$$

we obtain from Eq. (55) a partial differential equation for $\sigma(s, t)$

$$\frac{\partial\sigma(s, t)}{\partial t} = D\frac{\partial^2\sigma(s, t)}{\partial s^2} + D\beta\hbar\frac{\partial}{\partial s}[\omega(s)\sigma(s, t)], \qquad \beta = (kT)^{-1} \tag{63}$$

where we have used the conditions $\beta\hbar\omega \ll 1$ and $\beta\hbar|\partial\omega/\partial s| \ll 1$ and neglected higher order terms. Using a similar procedure for the $s = 0$ equation, we obtain the boundary condition

$$\frac{\partial\sigma(0, t)}{\partial s} + \beta\hbar\omega(0)\sigma(0, t) = 0 \tag{64}$$

At equilibrium, the elements of the density matrix are

$$\sigma_{ss} = Q^{-1}\exp(-\beta\epsilon_s) \tag{65}$$

Since the energy levels are closely spaced, Eq. (60) gives us

$$\omega(s) = (\epsilon_{s+1} - \epsilon_s)/\hbar = (1/\hbar)\,\partial\epsilon(s)/\partial s \tag{66}$$

Integrating Eq. (66) yields

$$\epsilon(s) = \hbar\int_0^s \omega(s)\,ds \tag{67}$$

Therefore Eq. (65) becomes

$$\sigma(s) = Q^{-1} \exp[-\beta\hbar \int_0^s \omega(s)\, ds] \tag{68}$$

It is readily confirmed that Eq. (68) satisfies Eq. (63) when $\partial\sigma/\partial t = 0$.

Let us apply Eq. (63) to the case of a one-dimensional harmonic oscillator. Here $\omega(s) = \omega$, a constant, and the partial differential equation (63) becomes

$$\frac{\partial\sigma(s, t)}{\partial t} = D\frac{\partial^2\sigma}{\partial s^2} + D\beta\hbar\omega\frac{\partial\sigma}{\partial s} \tag{69}$$

We consider an ensemble of systems all of which are in state p at time $t = 0$. The elements of the density matrix at time $t = 0$ are

$$\sigma_{mn}(0) = \delta_{mp}\,\delta_{np} \tag{70}$$

According to condition (33), the differential equations (25) for the off-diagonal elements $d\sigma_{mn}/dt$ do not depend on the on-diagonal elements. Therefore, since all off-diagonal elements are zero at time $t = 0$, they will all be zero at any later time:

$$\sigma_{mn}(t) = 0 \qquad \text{if} \quad m \neq n \tag{71}$$

Thus for this case the behavior of the system is determined entirely by the on-diagonal elements.

Applying a Laplace transform to Eq. (69) and using the boundary condition (64) and the initial condition

$$\sigma(s, 0) = \delta(s - p) \tag{72}$$

yields the solution

$$\begin{aligned}\sigma(s, t) = {} & (4\pi Dt)^{-1/2}\{\exp[-(s + p)^2/4Dt] + \exp[-(s - p)^2/4Dt]\} \\ & \times \exp[-(\beta\hbar\omega/2)^2 Dt - (s - p)(\beta\hbar\omega/2)] \\ & + (\beta\hbar\omega/2)\exp(-s\beta\hbar\omega/2) \\ & \times \operatorname{erfc}[(s + p)(4Dt)^{-1/2} - (Dt)^{1/2}\beta\hbar\omega/2]\end{aligned} \tag{73}$$

We wish to use Eq. (73) to obtain an expression for the ensemble-averaged probability density of a harmonic oscillator at large time. The asymptotic expansion of Eq. (73) at large time is

$$\begin{aligned}\sigma(s, t) \approx {} & \beta\hbar\omega \exp(-\beta\hbar\omega s) \\ & + (p\beta\hbar\omega - 2)(\beta\hbar\omega)^{-2}(\pi D^3 t^3)^{-1/2}\exp(-Dt\beta^2\hbar^2\omega^2/4) \\ & \times (s\beta\hbar\omega/2 - 1)\exp[(p - s)\beta\hbar\omega/2]\end{aligned} \tag{74}$$

Since the off-diagonal elements of the density matrix are zero in this case, the ensemble-averaged probability density becomes

$$\bar{P}(x, t) = \sum_s \sigma(s, t)[\phi_s(x)]^2 \tag{75}$$

where $\phi_s(x)$ are the wave functions for the one-dimensional harmonic oscillator. Substituting Eq. (74) into Eq. (75) yields

$$\begin{aligned}\bar{P}(x, t) \approx{}& \beta\hbar\omega S(x, \beta)\\ &+ (p\beta\hbar\omega - 2)(\beta\hbar\omega)^{-2}(\pi D^3 t^3)^{-1/2}[\exp(-Dt\beta^2\hbar^2\omega^2/4)]\\ &\times [\exp(p\beta\hbar\omega/2)]\\ &\times \sum_s (s\beta\hbar\omega/2 - 1)[\exp(-s\beta\hbar\omega/2)][\phi_s(x)]^2\end{aligned} \tag{76}$$

where

$$S(x, \beta) = \sum_s [\exp(-s\beta\hbar\omega)][\phi_s(x)]^2 \tag{77}$$

The quantity $S(x, \beta)$ has been previously evaluated$^{(6)}$

$$\begin{aligned}S(x, \beta) ={}& (m\omega/2\pi\hbar)^{1/2}[\sinh(\beta\hbar\omega)]^{-1/2}\exp(\beta\hbar\omega/2)\\ &\times \exp[-(x^2 m\omega/\hbar)\tanh(\beta\hbar\omega/2)]\end{aligned} \tag{78}$$

We note that the second sum in Eq. (76) is equal to $S(x, \beta/2)$ and the first sum is equal to

$$-\frac{\beta}{2}\frac{\partial S(x, \beta/2)}{\partial\beta} = \sum_s \frac{s\beta\hbar\omega}{2}\exp\frac{-s\beta\hbar\omega}{2}[\phi_s(x)]^2 \tag{79}$$

Making use of Eqs. (76)–(79) and the condition $\beta\hbar\omega \ll 1$, we obtain an asymptotic solution for the ensemble-averaged probability density at large time

$$\begin{aligned}\bar{P}(x, t) \approx{}& (\beta m\omega^2/2\pi)^{1/2}\exp(-x^2\beta m\omega^2/2)\\ &+ (m/\pi\hbar^2\beta)^{1/2}[(p\beta\hbar\omega/2) - 1]U(x, t)\end{aligned} \tag{80}$$

where

$$\begin{aligned}U(x, t) ={}& (4\pi D^3 t^3)^{-1/2}\exp(-Dt\beta^2\hbar^2\omega^2/4)\\ &\times (x^2\beta m\omega^2 - 2)\exp(-x^2\beta m\omega^2/4)\end{aligned} \tag{81}$$

The second case that we consider involves a temperature change at time $t = 0$. For $t \leq 0$, we assume that the system is in thermal equilibrium at reciprocal temperature $\alpha = (kT')^{-1}$, so that the on-diagonal elements at $t = 0$ are

$$\sigma(s, 0) = \alpha\hbar\omega\exp(-\alpha\hbar\omega s) \tag{82}$$

and the off-diagonal elements are all zero. As in Eq. (71), the off-diagonal elements will then remain zero for all time. Again using Laplace transforms yields

$$\begin{aligned}\sigma(s, t) = {} & (\beta\hbar\omega/2)\exp(-s\beta\hbar\omega)\operatorname{erfc}[s(4Dt)^{-1/2} - (Dt)^{1/2}\beta\hbar\omega/2] \\ & + \alpha\hbar\omega\exp(-s\alpha\hbar\omega)\exp[\alpha(\alpha - \beta)\hbar^2\omega^2 Dt] \\ & - (\alpha\hbar\omega/2)\exp(-s\alpha\hbar\omega)\exp[\alpha(\alpha - \beta)\hbar^2\omega^2 Dt] \\ & \times \operatorname{erfc}[s(4Dt)^{-1/2} + (\tfrac{1}{2}\beta - \alpha)\hbar\omega(Dt)^{1/2}] \\ & + (\alpha - \beta)(\hbar\omega/2)\exp[(\alpha - \beta)\hbar\omega s + \alpha(\alpha - \beta)\hbar^2\omega^2 Dt] \\ & \times \operatorname{erfc}[s(4Dt)^{-1/2} - (\tfrac{1}{2}\beta - \alpha)\hbar\omega(Dt)^{1/2}] \qquad (83)\end{aligned}$$

Repeating the procedure used to derive Eq. (80), we obtain another asymptotic solution for the ensemble-averaged probability density at large time

$$\begin{aligned}\bar{P}(x, t) \approx {} & (\beta m\omega^2/2\pi)^{1/2}\exp(-x^2\beta m\omega^2/2) \\ & + (m/\pi\hbar^2\beta)^{1/2}\alpha(\beta - \alpha)(\alpha - \tfrac{1}{2}\beta)^{-2}U(x, t), \qquad \alpha > \beta \qquad (84)\end{aligned}$$

where $U(x, t)$ is given by Eq. (81).

In summary, methods based on the density matrix have been given for calculating the ensemble-averaged probability density as a function of time for a quantum system approaching equilibrium. Expressions for the time-dependent probability density have been derived for a particle in a double-well potential, and the processes of tunneling and transitions between energy levels have been studied. In addition, where the energy levels of a quantum system are closely spaced, a partial differential form of the density matrix equation has been derived, and exact and asymptotic solutions for the density matrix and probability density have been obtained.

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