

Chapter 2

Electronic Density of States of Porous Silicon

In this Chapter, we investigate the electronic structure of porous silicon. First, we propose a model of porous silicon structure as a disordered system. Thence the density of states is determined using Feynman's path integral technique of disordered system. Subsequently an analytic expression of density of states is obtained as well as its low- and high-energy limits. We also discuss the band gap and mobility gap of porous silicon in the last Section.

2.1 Our Model for Porous Silicon

We use the same primitive structure of porous silicon as that of Sawada et al. (1994), an irregular structure obtained by removing some silicon atoms randomly from a perfect silicon crystal, and most dangling bonds of silicon atoms are terminated by hydrogen atoms (Sawada et al., 1994). We also consider that Si-H bond formation prevents reconstruction around vacancies. Therefore, this structure retains partially original crystal symmetries, which is consistent with experimental facts (Barla et al., 1984; Sugiyama and Nittono, 1990). In a sense, porous silicon can be viewed as a disordered assembly of three-dimensional quantum wells which are produced from random potential fluctuation from the system. It is clear that the quantum confinement is implied in our model through the potential fluctuation. This structure leads to the reduction of density of states in the vicinity of the crystalline silicon band edges, as in the quantum confinement model, and

the electrons (or holes) near band edge are localized. The reduction of density of states can be seen from analytical approximated density of states which is derived using Feynman's path-integral method for disordered systems (Sa-yakanit, 1979). We also note that good details of calculation technique in Feynman's path-integrals of disordered systems can be found in an M.Sc. thesis of Varagorn Piputnchonlathee (1996).

From the above discussion and by using the effective mass and the one electron approximations, electrons can move freely in the conduction band (as well as holes in the valence band). Removals of some atoms associated with occurring of potential barriers are called "scatterers". Thus, following the method of Samathiyakanit (1974), we model porous silicon as a system of an electron (or hole) moving among a set of N_1 rigid scatterers, confined within a volume Ω , and having a density $n_1 = N_1/\Omega$. However, occurrence of the potential barriers is equivalent to occurrence of the potential wells among the potential barriers. Such a system is described by the Hamiltonian,

$$H = \frac{1}{2}m\dot{\mathbf{x}}^2 + \sum_{i=1}^{N_2} v_2(\mathbf{x} - \mathbf{x}'_i) \quad (2.1)$$

where N_2 is the number of wells, m is the effective mass of electron (or hole) and $v_2(\mathbf{x} - \mathbf{x}'_i)$ is the potential of a well seen by an electron (or hole) at point \mathbf{x} due to a well at point \mathbf{x}'_i which is also assumed in a Gaussian form, as of the scatterer potential v_1 (see Appendix A), which is

$$v_2(\mathbf{x} - \mathbf{x}'_i) = -v_0 \exp \left[-\frac{|\mathbf{x} - \mathbf{x}'_i|^2}{l^2} \right] \quad (2.2)$$

where l is related to the autocorrelation length and v_0 is the strength of the potential well.

2.2 Feynman's Path-Integral Formalism

About fifty years ago, Feynman (1948) invented a new formulation for quantum mechanics called path integrals. This formalism was motivated by the paper of Dirac (1945) entitled "On The Analogy between Classical and Quantum Mechanics". Rather than beginning with the Hamiltonian of a system, the Lagrangian is considered instead allowing us not involve to the commutation relations. The foundation concept is the amplitude, $\Phi [\mathbf{x}[(\tau)]]$, of a system moving along any path equal to the exponential of the phase of that path, where the phase is the ratio of the action, $S [\mathbf{x}[(\tau)]]$, along the path and Planck's constant. In notations

$$\Phi [\mathbf{x}[(\tau)]] = \exp \left[i \frac{S [\mathbf{x}[(\tau)]]}{\hbar} \right]. \quad (2.3)$$

Then we can define a propagator, which is an amplitude for a system going from one point to another point during a finite time, as a sum of $\Phi [\mathbf{x}[(\tau)]]$ over all possible paths. That is,

$$K (\mathbf{x}_2, \mathbf{x}_1; t, 0) = \sum_{\text{all possible paths}} \Phi [\mathbf{x}(\tau)], \quad (2.4)$$

where K is the propagator. Since the summation over all possible paths is not a precise mathematical definition, thus a path integral is introduced. For a propagator, we can write down its expression, using a path integral, as

$$K (\mathbf{x}_2, \mathbf{x}_1; t, 0) = \int D(\mathbf{x}(\tau)) \exp \left[\frac{i}{\hbar} S [\mathbf{x}[(\tau)]] \right], \quad (2.5)$$

where $D(\mathbf{x}(\tau))$ denote as path-integration. For more about path integrals, Feynman and Hibbs' book (1965) is the best one which gives us rather complete knowledge.

Now, we shall turn back to our problem. According to our model, the Lagrangian of our system is

$$L = \frac{1}{2}m\dot{\mathbf{x}}^2 - \sum_{i=1}^{N_2} v_2(\mathbf{x} - \mathbf{x}'_i). \quad (2.6)$$

Using the path integral formalism, the propagator can be written as

$$K'(\mathbf{x}_2, \mathbf{x}_1; t, 0; [\mathbf{x}']) = \int D(\mathbf{x}(\tau)) \exp \left[\frac{i}{\hbar} \int_0^t d\tau \left(\frac{1}{2}m\dot{\mathbf{x}}^2 - \sum_{i=1}^{N_2} v_2(\mathbf{x} - \mathbf{x}'_i) \right) \right], \quad (2.7)$$

where $[\mathbf{x}']$ is a set of positions of wells. From this propagator, the system properties obviously depend on a configuration of wells which is random. But in practice we measure these quantities many times on the identical prepared system. It should be an average value, instead of the particular one, that will be obtained from measurements. Kohn and Luttinger (1957) have shown that in general we can substitute the specific value of any function by its ensemble average provided that the wells are truly independent.

Follow the foregoing discussion, we shall define the average propagator $K(\mathbf{x}_2, \mathbf{x}_1; t, 0)$ as the sum over all configurations of the specific propagator $K'(\mathbf{x}_2, \mathbf{x}_1; t, 0; [\mathbf{x}'])$ weighted with the probability $P([\mathbf{x}'])$ that the system having the configuration $[\mathbf{x}']$. The average propagator can be expressed mathematically by

$$K(\mathbf{x}_2, \mathbf{x}_1; t, 0) = \sum_{\text{all configuration}} P([\mathbf{x}']) K'(\mathbf{x}_2, \mathbf{x}_1; t, 0; [\mathbf{x}']). \quad (2.8)$$

Suppose that the wells are completely random or uniformly distributed, we have

$$P([\mathbf{x}']) d[\mathbf{x}'] = \frac{1}{\Omega^{N_2}} d\mathbf{x}'_1 \dots d\mathbf{x}'_{N_2}, \quad (2.9)$$

where Ω is the volume of a porous silicon. Consequently,

$$K(\mathbf{x}_2, \mathbf{x}_1; t, 0) = \int D(\mathbf{x}(\tau)) \exp \left[\frac{i}{\hbar} \int_0^t d\tau \frac{1}{2} m \dot{\mathbf{x}}^2 \right] \cdot \left\{ \int \frac{d\mathbf{x}'}{\Omega} \exp \left[-\frac{i}{\hbar} \int_0^t d\tau v_2(\mathbf{x} - \mathbf{x}') \right] \right\}^{N_2}. \quad (2.10)$$

Now, consider the term inside the curly braces of eq.(2.10), putting in a new form, as

$$\int \frac{d\mathbf{x}'}{\Omega} \exp \left[-\frac{i}{\hbar} \int_0^t d\tau v_2(\mathbf{x} - \mathbf{x}') \right] = \int \frac{d\mathbf{x}'}{\Omega} \exp \left(\left[-\frac{i}{\hbar} \int_0^t d\tau v_2(\mathbf{x} - \mathbf{x}') \right] - 1 \right) + 1 \quad (2.11)$$

Applying the identity,

$$\lim_{\Omega \rightarrow \infty} \left[1 + \frac{a}{\Omega} \right]^N = \exp \left[\frac{aN}{\Omega} \right], \quad (2.12)$$

and eq.(2.11) into the last term of eq.(2.10), this is reduced to

$$\left\{ \int \frac{d\mathbf{x}'}{\Omega} \exp \left[-\frac{i}{\hbar} \int_0^t d\tau v_2(\mathbf{x} - \mathbf{x}') \right] \right\}^{N_2} = \exp \left[n_2 \int d\mathbf{x}' \left(\exp \left[-\frac{i}{\hbar} \int_0^t d\tau v_2(\mathbf{x} - \mathbf{x}') \right] - 1 \right) \right] \quad (2.13)$$

where $n_2 = N_2/\Omega$ is the wells concentration. Then, the exponential exponent is expanded into Taylor series and since $n_2 \rightarrow \infty$, $v_2 \rightarrow 0$ so that $n_2 v_2^2$ is finite. We keep up the terms up to the second power of $v_2(\mathbf{x} - \mathbf{x}'_i)$. The average propagator

eq.(2.10) becomes

$$K(\mathbf{x}_2, \mathbf{x}_1; t, 0) = \int D(\mathbf{x}(\tau)) \exp \left[\frac{i}{\hbar} \left(\int_0^t d\tau \frac{1}{2} m \dot{\mathbf{x}}^2 - n_2 \int_0^t d\tau \int d\mathbf{x}' v_2(\mathbf{x} - \mathbf{x}') + \frac{i}{2\hbar} n_2 \int_0^t d\tau \int_0^t d\sigma \int d\mathbf{x}' v_2(\mathbf{x}(\tau) - \mathbf{x}') v_2(\mathbf{x}(\sigma) - \mathbf{x}') \right) \right] \quad (2.14)$$

Note that the assumption we used above allows us completely describe the system by the first and second moments of the potential. That is, the distribution of the potential is Gaussian or normal. This means that a system of an electron moving in weak and dense scatterers is equivalent to that of an electron moving in the Gaussian random potential.

Since the second term of the exponent is a time integral of the first term in Taylor expansion of potential energy of the system, this is then interpreted as a mean potential energy of the system. So, we define the mean potential energy due to all wells E_0 and the autocorrelation function $W(\mathbf{x}(\tau) - \mathbf{x}(\sigma))$ as following:

$$E_0 = n_2 \int d\mathbf{x}' v_2(\mathbf{x} - \mathbf{x}') \quad (2.15)$$

and

$$W(\mathbf{x}(\tau) - \mathbf{x}(\sigma)) = \int d\mathbf{x}' v_2(\mathbf{x}(\tau) - \mathbf{x}') v_2(\mathbf{x}(\sigma) - \mathbf{x}'), \quad (2.16)$$

The autocorrelation function is an important function which tells us the effect of a potential at one point on a potential at another point. If the potential at any two points are uncorrelated then it is called the Gaussian-white-noise random potential. The autocorrelation function of this potential is given by

$$W(\mathbf{x}(\tau) - \mathbf{x}(\sigma)) = \text{constant} \cdot \delta(\mathbf{x}(\tau) - \mathbf{x}(\sigma)). \quad (2.17)$$

By using these two functions, the average propagator can be written as

$$K(\mathbf{x}_2, \mathbf{x}_1; t, 0) = \int D(\mathbf{x}(\tau)) \exp \left[\frac{i}{\hbar} S[\mathbf{x}(\tau)] \right], \quad (2.18)$$

where

$$S[\mathbf{x}(\tau)] = \int_0^t d\tau \left[\frac{1}{2} m \dot{\mathbf{x}}^2 - E_0 + \frac{i}{2\hbar} n_2 \int_0^t d\sigma W(\mathbf{x}(\tau) - \mathbf{x}(\sigma)) \right]. \quad (2.19)$$

For the potential applied in our model, the mean potential energy due to all wells which is at the same position as the mean potential energy due to all scatterers, can be demonstrated as

$$E_0 = n_1 \int d\mathbf{x}' v_1(\mathbf{x} - \mathbf{x}') = n_1 v_0 \left(\frac{\pi a_0^2}{4 \ln 2} \right)^{3/2}, \quad (2.20)$$

and the autocorrelation is given by

$$W(\mathbf{x}(\tau) - \mathbf{x}(\sigma)) = v_0^2 \left(\frac{\pi L^2}{4} \right)^{3/2} \exp \left[-\frac{|\mathbf{x}(\tau) - \mathbf{x}(\sigma)|^2}{L^2} \right], \quad (2.21)$$

where $L = \sqrt{2} l$ denotes the autocorrelation length.

In addition, it should be noted that the mean potential energy caused by all wells, E_0 , is interpreted as upshifted energy resulted from all scatterers or disordered structure of porous silicon. So the upshifted energy is, indeed, confinement energy which is well known in crystalline silicon model. However, the shift exists in both valence and conduction bands so that the confinement energy from our model, ΔE , is twice of the mean potential energy, i.e.

$$\Delta E = 2E_0 \quad (2.22)$$

where E_0 is defined by eq.(2.20).

2.3 The Density of States

The density of states $\rho(E)$ (see Omar, 1975) can be defined by

$$\rho(E) dE = \text{a number of states between an energy interval } E \text{ and } E + dE \text{ per unit volume.} \quad (2.23)$$

This definition gives us a qualitative picture of the density of states, but does not explicitly express the formula for calculation. The usual formula for the density of states is concerned with the number-of-states function $N(E)$, which provides a number of states having energy less than or equal to E ,

$$\rho(E) = \frac{d}{dE} N(E). \quad (2.24)$$

Another formula which is directly related to the energy eigenvalue E_i eigenstate φ_i can be written as

$$\rho(E) = \frac{1}{\Omega} \sum_i \delta(E - E_i), \quad (2.25)$$

where δ is the Dirac delta function.

In our work, it is easy to use the formula eq.(2.25) since the Dirac delta function can be expressed in terms of the transformed propagator. With the energy expansion formula of the propagator (Feynman and Hibbs, 1965; Sakurai, 1985),

$$K(\mathbf{x}_2, \mathbf{x}_1; t, 0) = \sum_i \varphi_i(\mathbf{x}_2) \varphi_i^*(\mathbf{x}_1) \exp\left[-\frac{i}{\hbar} E_i t\right], \quad (2.26)$$

we have the trace of the propagator of the form

$$\text{Tr}K(\mathbf{x}_2, \mathbf{x}_1; t, 0) = \sum_i \exp\left[-\frac{i}{\hbar} E_i t\right]. \quad (2.27)$$

Taking a Fourier transform of both sides of eq.(2.27) leads to

$$\int_{-\infty}^{\infty} dt \text{Tr}K(\mathbf{x}_2, \mathbf{x}_1; t, 0) \exp\left[-\frac{i}{\hbar} E t\right] = 2\pi\hbar \sum_i \delta(E - E_i). \quad (2.28)$$

Note that the identities,

$$\delta(a) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dx \exp[iax] \quad (2.29)$$

and

$$\delta\left(\frac{a}{b}\right) = b\delta(a), \quad (2.30)$$

are used in the derivation of eq.(2.28). Now the required relation between the density of states and the propagator is obtained by comparing eq.(2.25) and eq.(2.28), we have

$$\rho(E) = \frac{1}{2\pi\hbar} \frac{1}{\Omega} \int_{-\infty}^{\infty} dt \operatorname{Tr} K(\mathbf{x}_2, \mathbf{x}_1; t, 0) \exp\left[\frac{i}{\hbar} Et\right]. \quad (2.31)$$

Because of translational invariant of the propagator, hence

$$\operatorname{Tr} K(\mathbf{x}_2, \mathbf{x}_1; t, 0) = \Omega K(0, 0; t, 0). \quad (2.32)$$

The density of states eq.(2.31) then becomes

$$\rho(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt K(0, 0; t, 0) \exp\left[\frac{i}{\hbar} Et\right], \quad (2.33)$$

The remaining problem for the density of states is the propagator which is determined in next Section.

2.3.1 The Approximated Density of States

In general, a lot of path integrals cannot be integrated out and our problem is one of these cases. Then an approximation method is needed inevitably. The most widely used methods in path integral formalism are perturbation and variational methods. Since this problem is not a perturbative-type problem, we reasonably choose a variational method.

The concept of this method is that the appropriate trial action with parameter can be adjusted such that the required path integral can be obtained with

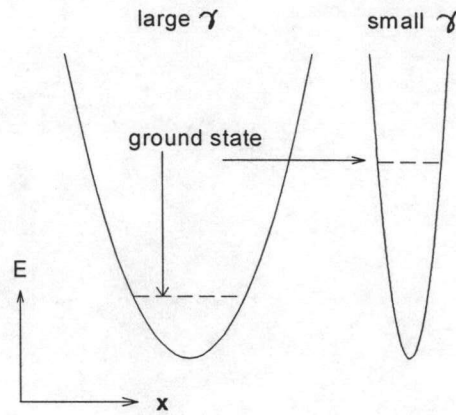


Figure 2.1: Schematic representation of harmonic well 's shapes and their associated ground states with small and large parameters γ

high accuracy. There are two criterias that indicate whether the chosen trial action is suitable or not. First, the path integral of this action should be carried out easily and exactly. Second, the physical meaning of the "real" and trial action must be likely. However, according to Feynman's polaron theory (1955) and Sa-yakanit 's work of density of states in a Gaussian random potential (1979), a harmonic trial action clearly corresponds to the above two criterias. Therefore, we use the following trial action of a harmonic oscillator having one parameter γ in our model,

$$S_0 = \int_0^t d\tau \frac{m}{2} \left[\dot{\mathbf{x}}^2(\tau) - \frac{\gamma^2}{2t} \int_0^t d\sigma |\mathbf{x}(\tau) - \mathbf{x}(\sigma)|^2 \right] \quad (2.34)$$

which associates with the trial propagator,

$$K_0(0, 0; t) = \left(\frac{m}{2\pi i \hbar t} \right)^{3/2} \left(\frac{\gamma t}{2 \sin(\gamma t/2)} \right)^3. \quad (2.35)$$

Actually, the parameter γ can indicate the shape of the harmonic well as depicted in Figure 2.1.

Of course, the last step of this method is to adjust the parameter. Such adjustment requires a rule or principle which enables us to find out the appropriate value of parameter. This is known as a variational principle. The discussion about the principle could not be considered yet in this Section.

2.3.1.1 The Approximated Propagator

As discussed above, in order to calculate the average propagator, we shall approximate the propagators with the help of the trial action. The approximation to be used is the first order cumulant expansion (Kubo, 1962). Let us first introduce a path integral average with respect to the trial action $S_0[\mathbf{x}(\tau)]$ denoted by

$$\langle O \rangle_0 = \frac{\int D(\mathbf{x}(\tau)) O \exp \left[\frac{i}{\hbar} S_0[\mathbf{x}(\tau)] \right]}{\int D(\mathbf{x}(\tau)) \exp \left[\frac{i}{\hbar} S_0[\mathbf{x}(\tau)] \right]}, \quad (2.36)$$

where O is a function to be averaged. Accordingly, the average propagator can be rewritten as

$$\begin{aligned} K(\mathbf{x}_2, \mathbf{x}_1; t, 0) &= \int D(\mathbf{x}(\tau)) \exp \left[\frac{i}{\hbar} (S - S_0) + \frac{i}{\hbar} S_0 \right] \\ &= K_0(\mathbf{x}_2, \mathbf{x}_1; t, 0) \left\langle \exp \frac{i}{\hbar} (S - S_0) \right\rangle_0, \end{aligned} \quad (2.37)$$

where K_0 is the trial propagator, eq.(2.35). The equation (2.37) for the average propagator is still an exact expression but still cannot be solved. The cumulant expansion,

$$\langle \exp [a] \rangle = \exp \left[\langle a \rangle + \frac{1}{2} \left(\langle a^2 \rangle - \langle a \rangle^2 - \frac{1}{3!} (\langle a^3 \rangle - 3 \langle a^2 \rangle \langle a \rangle + 2 \langle a \rangle^3 + \dots) \right) \right], \quad (2.38)$$

up to the first order allows us to get the approximated propagator,

$$K(\mathbf{x}_2, \mathbf{x}_1; t, 0) = K_0(\mathbf{x}_2, \mathbf{x}_1; t, 0) \exp \left[\frac{i}{\hbar} \langle S - S_0 \rangle_0 \right]. \quad (2.39)$$

Since the kinetic energy terms of both actions are identical, the exponent $\langle S - S_0 \rangle_0$ can be replaced by $\langle S' - S'_0 \rangle_0$, where the prime symbol means excluding the kinetic energy term. That is,

$$K(\mathbf{x}_2, \mathbf{x}_1; t, 0) = K_0(\mathbf{x}_2, \mathbf{x}_1; t, 0) \exp \left[\frac{i}{\hbar} \langle S' - S'_0 \rangle_0 \right]. \quad (2.40)$$

Since the trial propagator K_0 has been already carried out, the remaining work is to evaluate $\langle S' \rangle_0$ and $\langle S'_0 \rangle_0$.

By substituting S from eq.(2.19), the path integral average of S' is expressed as

$$\langle S' \rangle_0 = -E_0 t + \frac{i}{2\hbar} n_2 \int_0^t d\tau \int_0^t d\sigma \langle W(\mathbf{x}(\tau) - \mathbf{x}(\sigma)) \rangle_0, \quad (2.41)$$

where E_0 and $W(\mathbf{x}(\tau) - \mathbf{x}(\sigma))$ are given by eq.(2.20) and (2.21) respectively. To find the average of the autocorrelation function, we use its Fourier integral,

$$W(\mathbf{x}(\tau) - \mathbf{x}(\sigma)) = \frac{1}{(2\pi)^3} \int d\mathbf{k} W(\mathbf{k}) \exp [i\mathbf{k} \cdot (\mathbf{x}(\tau) - \mathbf{x}(\sigma))]. \quad (2.42)$$

The Fourier transforms of the autocorrelation function is given below

$$W(\mathbf{k}) = v_0^2 \left(\frac{\pi L^2}{2} \right)^3 \exp \left[-\frac{1}{4} L^2 k^2 \right] \quad (2.43)$$

Inserting eq.(2.42) into (2.41)

$$\begin{aligned} \langle S' \rangle_0 &= -E_0 t + \frac{i}{2\hbar} n_2 \int_0^t d\tau \int_0^t d\sigma \int \frac{d\mathbf{k}}{(2\pi)^3} W(\mathbf{k}) \langle \exp [i\mathbf{k} \cdot (\mathbf{x}(\tau) - \mathbf{x}(\sigma))] \rangle_0, \\ &= -E_0 t + \frac{i}{2\hbar} n_2 \int_0^t d\tau \int_0^t d\sigma \int \frac{d\mathbf{k}}{(2\pi)^3} W(\mathbf{k}) \exp [i\mathbf{k} \cdot A - k^2 B^2], \end{aligned} \quad (2.44)$$

where

$$A = \langle \mathbf{x}(\tau) - \mathbf{x}(\sigma) \rangle_0, \quad (2.45)$$

and

$$B = \frac{1}{2} \left(\frac{1}{3} \langle (\mathbf{x}(\tau) - \mathbf{x}(\sigma))^2 \rangle_0 - \langle \mathbf{x}(\tau) - \mathbf{x}(\sigma) \rangle_0^2 \right). \quad (2.46)$$

The last form of eq.(2.44) is the cumulant expansion of the previous form, by using the reason that only the first two cumulant functions are non-zero because S_0 is quadratic. Putting eq.(2.43) into (2.44) and applying the Gaussian integration formula for each Cartesian component of \mathbf{k} -integration, we get

$$\begin{aligned} \langle S' \rangle_0 &= -E_0 t + \frac{i}{2\hbar} (4\pi)^{-3/2} n_2 v_0^2 \left(\frac{\pi L^2}{2} \right)^3 \int_0^t d\tau \int_0^t d\sigma \\ &\quad \cdot \left(B + \frac{L^2}{4} \right)^{-3/2} \exp \left[-\frac{A^2}{4(B + L^2/4)} \right]. \end{aligned} \quad (2.47)$$

Now, we consider the average of the trial action, we have

$$\langle S'_0 \rangle_0 = -\frac{\gamma^2 m}{4t} \int_0^t d\tau \int_0^t d\sigma \langle |\mathbf{x}(\tau) - \mathbf{x}(\sigma)|^2 \rangle_0. \quad (2.48)$$

Because of the symmetry under interchanging between τ and σ of S'_0 , above equation can be written as

$$\langle S'_0 \rangle_0 = -\frac{\gamma^2 m}{4t} \int_0^t d\tau \int_0^t d\sigma \langle (\mathbf{x}(\tau) - \mathbf{x}(\sigma))^2 \rangle_0. \quad (2.49)$$

Here, the approximated propagator can be obtained by eq.(2.40), (2.47) and (2.49). Although, the terms such as A , B and $\langle (\mathbf{x}(\tau) - \mathbf{x}(\sigma))^2 \rangle_0$ are not solved explicitly yet, such averages can be obtained from (B.13) and (B.14). Therefore we need to find the forced classical action $S_{0,cl}^f$.

2.3.1.2 The Forced Classical Action $S_{0,cl}^f$

In order to obtain $S_{0,cl}^f$ and $S_{0,cl}$ corresponding to nonlocal harmonic trial action, eq.(2.34), we have to find the classical path by working on variation of the forced trial action $S_0^f(\omega)$ which includes effect of external force $\mathbf{f}(\tau)$ acting on the particle, then

$$\begin{aligned} S_0^f(\omega) &= \int_0^t d\tau L(\dot{\mathbf{x}}(\tau), \mathbf{x}(\tau), t) \\ &= \int_0^t d\tau \left[\frac{m}{2} \dot{\mathbf{x}}^2(\tau) - \frac{m}{2} \left(\frac{\omega^2}{2t} \right) \int_0^t d\sigma |\mathbf{x}(\tau) - \mathbf{x}(\sigma)|^2 + \mathbf{f}(\tau) \cdot \mathbf{x}(\tau) \right] \end{aligned} \quad (2.50)$$

At the extremum point,

$$\begin{aligned} \delta S_0^f(\omega) &= \int_0^t d\tau [m\dot{\mathbf{x}}(\tau) \cdot \delta\dot{\mathbf{x}}(\tau) + \mathbf{f}(\tau) \cdot \delta\mathbf{x}(\tau) \\ &\quad - \frac{m\omega^2}{2t} \int_0^t d\sigma (\mathbf{x}(\tau) - \mathbf{x}(\sigma)) \cdot \delta(\mathbf{x}(\tau) - \mathbf{x}(\sigma))] \end{aligned} \quad (2.51)$$

where $\delta\dot{\mathbf{x}}(\tau) = \delta \left[\frac{d}{dt} \mathbf{x}(\tau) \right] = \frac{d}{dt} \delta\mathbf{x}(\tau)$ and $\delta\mathbf{x}(t) = \delta\mathbf{x}(0) = 0$. Thus

$$\delta S_0^f(\omega) = - \int_0^t d\tau \left[m\ddot{\mathbf{x}}(\tau) + \frac{m\omega^2}{t} \int_0^t d\sigma (\mathbf{x}(\tau) - \mathbf{x}(\sigma)) - \mathbf{f}(\tau) \right] \cdot \delta\mathbf{x}(\tau) = 0 \quad (2.52)$$

Therefore, we can obtain a classical equation

$$\ddot{\mathbf{x}}_c(\tau) + \omega^2 \mathbf{x}_c(\tau) = \frac{\omega^2}{t} \int_0^t d\sigma \mathbf{x}_c(\sigma) + \frac{\mathbf{f}(\tau)}{m} \quad (2.53)$$

and we can solve eq.(2.53) by introducing the Green's function $g(\tau, \sigma)$ corresponding to following equation :

$$\left(\frac{d^2}{d\tau^2} + \gamma^2 \right) g(\tau, \sigma) = \delta(\tau - \sigma) \quad (2.54)$$

of which

$$g(\tau, \sigma) = -\frac{1}{\omega \sin \omega t} [\sin \omega(t-z) \sin \omega \sigma \Theta(\tau - \sigma) + \sin \omega(t - \sigma) \sin \omega \tau \Theta(\sigma - \tau)] \quad (2.55)$$

where Θ is the Heaviside step function and we use the boundary condition $\mathbf{x}(0) = \mathbf{x}_1$ and $\mathbf{x}(t) = \mathbf{x}_2$. From eq.(2.53), we use eq.(2.55) and get

$$\begin{aligned} \mathbf{x}_c(\tau) &= \frac{1}{\sin \gamma \tau} (\mathbf{x}_2 \sin \gamma \tau - \mathbf{x}_1 \sin \gamma(t - \tau)) \\ &+ \int_0^t \left[\frac{\omega^2}{t} \int_0^t d\sigma' \mathbf{x}_c(\sigma') + \frac{\mathbf{f}(\sigma')}{m} \right] g(\tau, \sigma) d\sigma \end{aligned} \quad (2.56)$$

Solving above integral equation yields

$$\begin{aligned} \mathbf{x}_c(\tau) &= \frac{1}{\sin \omega t} (\mathbf{x}_2 \sin \omega \tau + \mathbf{x}_1 \sin \omega(t - \tau)) - \frac{2}{\sin \omega t} \left(\sin \frac{\omega \tau}{2} \sin \frac{\omega(t - \tau)}{2} \right) \\ &\times \left[(x_2 + x_1) \sin \frac{\omega t}{2} - \frac{2}{m\omega} \int_0^t d\sigma \mathbf{f}(\sigma) \left(\sin \frac{\omega \sigma}{2} \sin \frac{\omega(\tau - \sigma)}{2} \right) \right] \\ &+ \int_0^t \frac{\mathbf{f}(\sigma)}{m} g(\sigma, \tau) d\sigma. \end{aligned} \quad (2.57)$$

The forced classical trial action $S_{0,cl}^f(\mathbf{x}_2, \mathbf{x}_1; t, \omega)$ is obtained by substituting eq.(2.57) into the expression

$$\begin{aligned} S_{0,cl}^f(\mathbf{x}_2, \mathbf{x}_1; t, \omega) &= S_{0,cl}(\mathbf{x}_2, \mathbf{x}_1; t, \omega) + \int_0^t d\tau \mathbf{f}(\tau) \cdot \mathbf{x}_c(\tau) \\ &= \frac{m}{2} \left[\int_0^t d\tau \dot{\mathbf{x}}_c^2(\tau) - \frac{\omega^2}{2t} \int_0^t d\tau \int_0^t d\sigma |\mathbf{x}(\tau) - \mathbf{x}(\sigma)|^2 \right. \\ &\quad \left. + \int_0^t d\tau \mathbf{f}(\tau) \cdot \mathbf{x}_c(\tau) \right] \end{aligned} \quad (2.58)$$

which is simplified, after integrating the first term by parts and invoking eq.(2.53), to be

$$S_{0,cl}^f(\mathbf{x}_2, \mathbf{x}_1; t, \omega) = \frac{m}{2} [\dot{\mathbf{x}}_c(t) \cdot \mathbf{x}_c(t) - \dot{\mathbf{x}}_c(0) \cdot \mathbf{x}_c(0)] + \frac{1}{2} \int_0^t d\tau \mathbf{f}(\tau) \cdot \mathbf{x}_c(\tau) \quad (2.59)$$

Thus, we get

$$\begin{aligned} S_{0,cl}^f(\mathbf{x}_2, \mathbf{x}_1; t, \omega) &= \frac{m\omega}{4} \cot \frac{\omega t}{2} |\mathbf{x}_2 - \mathbf{x}_1|^2 \\ &+ \frac{m\omega}{2 \sin \omega t} \left[\frac{2\mathbf{x}_2}{m\omega} \int_0^t d\tau \mathbf{f}(\tau) \left(\sin \omega \tau - 2 \sin \frac{\omega t}{2} \sin \frac{\omega}{2} (t - \tau) \sin \frac{\omega \tau}{2} \right) \right. \\ &+ \frac{2\mathbf{x}_1}{m\omega} \int_0^t d\tau \mathbf{f}(\tau) \left(\sin \omega (t - \tau) - 2 \sin \frac{\omega t}{2} \sin \frac{\omega}{2} (t - \tau) \sin \frac{\omega \tau}{2} \right) \\ &- \frac{2}{m^2 \omega^2} \int_0^t d\tau \int_0^t d\sigma \mathbf{f}(\tau) \cdot \mathbf{f}(\sigma) \left\{ \sin \omega (t - \tau) \sin \omega \sigma \right. \\ &\left. \left. - 4 \sin \frac{\omega}{2} (t - \tau) \sin \frac{\omega \tau}{2} \sin \frac{\omega}{2} (t - \sigma) \sin \frac{\omega \sigma}{2} \right\} \right] \quad (2.60) \end{aligned}$$

By means of eq.(2.58), the classical trial action $S_{0,cl}$ can be obtained by setting $\mathbf{f}(\tau)$ equal to zero. Hence, we find

$$S_{0,cl}(\mathbf{x}_2, \mathbf{x}_1; t, \omega) = \frac{1}{2} m\omega \cot \frac{\omega t}{2} |\mathbf{x}_2 - \mathbf{x}_1|^2 \quad (2.61)$$

2.3.1.3 Calculation of A , B and $\langle (\mathbf{x}(\tau) - \mathbf{x}(\sigma))^2 \rangle_0$

Using the forced classical trial action $S_{0,cl}^f$ from eq.(2.60), the first and second functional derivatives can be obtained

$$\begin{aligned} \frac{\delta}{\delta \mathbf{f}(\tau)} S_{cl}^f \Big|_{\mathbf{f}(\tau) \equiv 0} &= \frac{1}{\sin \gamma t / 2} \left(\mathbf{x}_2 \cos \frac{1}{2} \gamma (t - \tau) \sin \frac{1}{2} \gamma \tau \right. \\ &\left. + \mathbf{x}_1 \sin \frac{1}{2} \gamma (t - \tau) \cos \frac{1}{2} \gamma \tau \right) \quad (2.62) \end{aligned}$$

and

$$\left. \frac{\delta^2 S_{cl}^f}{\delta \mathbf{f}(\tau) \delta \mathbf{f}(\sigma)} \right|_{\mathbf{f}(\tau) \equiv 0} = -\frac{6}{m\gamma \sin \gamma t/2} \left[\Theta(\tau - \sigma) \sin \gamma(t - \tau) \sin\left(\frac{\gamma\sigma}{2}\right) \cos\frac{\gamma}{2}(\tau - \sigma) \right. \\ \left. + \Theta(\sigma - \tau) \sin \gamma(t - \sigma) \sin\left(\frac{\gamma\tau}{2}\right) \cos\frac{\gamma}{2}(\tau - \sigma) \right]. \quad (2.63)$$

Putting eq.(2.62) and (2.63) into (B.13) and (B.14), we get

$$\langle \mathbf{x}(\tau) \rangle_0 = \frac{1}{\sin \gamma t/2} \left(\mathbf{x}_2 \cos \frac{1}{2}\gamma(t - \tau) \sin \frac{1}{2}\gamma\tau \right. \\ \left. + \mathbf{x}_1 \sin \frac{1}{2}\gamma(t - \tau) \cos \frac{1}{2}\gamma\tau \right), \quad (2.64)$$

and, for $\tau > \sigma$,

$$\langle \mathbf{x}(\tau) \cdot \mathbf{x}(\sigma) \rangle_0 = \frac{6i\hbar}{m\gamma \sin \gamma t/2} \left[\sin \gamma(t - \tau) \sin\left(\frac{\gamma\sigma}{2}\right) \cos\frac{\gamma}{2}(\tau - \sigma) \right] \\ + \langle \mathbf{x}(\tau) \rangle_0 \cdot \langle \mathbf{x}(\sigma) \rangle_0 \quad (2.65)$$

and, for $\tau < \sigma$,

$$\langle \mathbf{x}(\tau) \cdot \mathbf{x}(\sigma) \rangle_0 = \frac{6i\hbar}{m\gamma \sin \gamma t/2} \left[\sin \gamma(t - \sigma) \sin\left(\frac{\gamma\tau}{2}\right) \cos\frac{\gamma}{2}(\tau - \sigma) \right] \\ + \langle \mathbf{x}(\tau) \rangle_0 \cdot \langle \mathbf{x}(\sigma) \rangle_0. \quad (2.66)$$

It can be easily obtained by inserting eq.(2.64) into (2.45) that

$$A = \left(\frac{\sin \frac{1}{2}\gamma(\tau - \sigma) \cos \frac{1}{2}\gamma(t - (\tau + \sigma))}{\sin \frac{1}{2}\gamma t} \right) (\mathbf{x}_2 - \mathbf{x}_1). \quad (2.67)$$

For B and $\langle (\mathbf{x}(\tau) - \mathbf{x}(\sigma))^2 \rangle_0$, we must separately substitute for $\tau > \sigma$ and $\tau < \sigma$ cases, eq.(2.65) and (2.66), into the new forms of them :

$$B = \frac{1}{6} \left[\langle \mathbf{x}^2(\tau) \rangle_0 - 2 \langle \mathbf{x}(\tau) \cdot \mathbf{x}(\sigma) \rangle_0 + \langle \mathbf{x}^2(\sigma) \rangle_0 \right. \\ \left. - \langle \mathbf{x}(\tau) \rangle_0^2 + 2 \langle \mathbf{x}(\tau) \rangle_0 \cdot \langle \mathbf{x}(\sigma) \rangle_0 - \langle \mathbf{x}(\sigma) \rangle_0^2 \right], \quad (2.68)$$

and

$$\langle (\mathbf{x}(\tau) - \mathbf{x}(\sigma))^2 \rangle_0 = \langle \mathbf{x}^2(\tau) \rangle_0 - 2 \langle \mathbf{x}(\tau) \cdot \mathbf{x}(\sigma) \rangle_0 + \langle \mathbf{x}^2(\sigma) \rangle_0. \quad (2.69)$$

Note that, in eq.(2.68), we have set

$$\langle (x(\tau) - x(\sigma))^2 \rangle_0 = \frac{1}{3} \langle (\mathbf{x}(\tau) - \mathbf{x}(\sigma))^2 \rangle_0 \quad (2.70)$$

because of the directional symmetry of the system. Now, we are able to write down B and $\langle (\mathbf{x}(\tau) - \mathbf{x}(\sigma))^2 \rangle_0$ as

$$B = i\hbar \left(\frac{\sin \frac{1}{2}\gamma |\tau - \sigma| \sin \frac{1}{2}\gamma (t - |\tau - \sigma|)}{m\gamma \sin \frac{1}{2}\gamma t} \right), \quad (2.71)$$

and

$$\begin{aligned} \langle (\mathbf{x}(\tau) - \mathbf{x}(\sigma))^2 \rangle_0 &= 6i\hbar \left(\frac{\sin \frac{1}{2}\gamma |\tau - \sigma| \sin \frac{1}{2}\gamma (t - |\tau - \sigma|)}{m\gamma \sin \frac{1}{2}\gamma t} \right) \quad (2.72) \\ &+ \left(\frac{\sin \frac{1}{2}\gamma (\tau - \sigma) \cos \frac{1}{2}\gamma (t - (\tau + \sigma))}{\sin \frac{1}{2}\gamma t} \right)^2 (\mathbf{x}_2 - \mathbf{x}_1)^2. \end{aligned}$$

It is worth to note that B has the following property

$$B(|\tau - \sigma|) = B(t - |\tau - \sigma|). \quad (2.73)$$

2.3.2 Evaluating the Approximated Density of States

According to the last two sections, it can be concluded that the approximated density of states defined through eq.(2.40) has a translational symmetry. This means that the formula for calculating it is given by eq.(2.33) in which only the diagonal element of the propagator is governed with. Then we set the condition $\mathbf{x}_2 = \mathbf{x}_1$, we have

$$A|_{\mathbf{x}_2=\mathbf{x}_1} = 0 \quad (2.74)$$

and

$$\langle (\mathbf{x}(\tau) - \mathbf{x}(\sigma))^2 \rangle_0 |_{\mathbf{x}_2=\mathbf{x}_1} = 6i\hbar \left(\frac{\sin \frac{1}{2}\gamma |\tau - \sigma| \sin \frac{1}{2}\gamma (t - |\tau - \sigma|)}{m\gamma \sin \frac{1}{2}\gamma t} \right). \quad (2.75)$$

In this condition, we apply eq.(2.74) to (2.47), $\langle S' \rangle_0$ becomes

$$\langle S' \rangle_0 |_{\mathbf{x}_2=\mathbf{x}_1} = -E_0 t + \frac{i}{2\hbar} (4\pi)^{-3/2} n_2 v_0^2 \left(\frac{\pi L^2}{2} \right)^3 \int_0^t d\tau \int_0^t d\sigma \left(B + \frac{L^2}{4} \right)^{-3/2}. \quad (2.76)$$

Based on the property eq.(2.73), the double-time integration can be reduced to a single integration as follows,

$$\int_0^t d\tau \int_0^t d\sigma \left(B (|\tau - \sigma|) + \frac{L^2}{4} \right)^{-3/2} = t \int_0^t dy \left(B (y) + \frac{L^2}{4} \right)^{-3/2}. \quad (2.77)$$

We obtain

$$\langle S' \rangle_0 |_{\mathbf{x}_2=\mathbf{x}_1} = -E_0 t + \frac{i}{2\hbar} \xi_L \left(\frac{L^2}{4} \right)^{3/2} t \int_0^t dy \left(B (y) + \frac{L^2}{4} \right)^{-3/2}, \quad (2.78)$$

where $\xi_L = n_2 v_0^2 (\pi L^2/4)^{3/2}$ and $y = |\tau - \sigma|$. $\xi_L^{1/2}$ is interpreted as the energy fluctuation around its mean energy (Saito, 1974).

For $\langle S'_0 \rangle_0$ when $\mathbf{x}_2 = \mathbf{x}_1$, substitute eq.(2.75) into (2.49) we have

$$\langle S'_0 \rangle_0 |_{\mathbf{x}_2=\mathbf{x}_1} = -\frac{\gamma^2 m}{4t} \int_0^t d\tau \int_0^t d\sigma 6i\hbar \left(\frac{\sin \frac{1}{2}\gamma |\tau - \sigma| \sin \frac{1}{2}\gamma (t - |\tau - \sigma|)}{m\gamma \sin \frac{1}{2}\gamma t} \right). \quad (2.79)$$

Same as $\langle S' \rangle_0$, the double-time integration can be reduced to a single integration and can be simplified as follows

$$\begin{aligned} \langle S'_0 \rangle_0 |_{\mathbf{x}_2=\mathbf{x}_1} &= -\frac{3}{2} \frac{i\gamma\hbar}{\sin \frac{1}{2}\gamma t} \int_0^t d\sigma \sin \frac{1}{2}\gamma\sigma \sin \frac{1}{2}\gamma (t - \sigma) \\ &= \frac{3}{2} i\hbar \left(\frac{1}{2}\gamma t \cot \frac{1}{2}\gamma t - 1 \right). \end{aligned} \quad (2.80)$$

Combining eqs.(2.31), (2.35), (2.40), (2.78), (2.80) and (2.71) the approximated density of states can be written as

$$\begin{aligned} \rho(E) = & \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt \left(\frac{m}{2\pi i \hbar t} \right)^{3/2} \left(\frac{\gamma t}{\sin(\gamma t/2)} \right)^3 \\ & \cdot \exp \left[\frac{i}{\hbar} (E - E_0) t + \frac{3}{2} \left(\frac{1}{2} \gamma t \cot \gamma \frac{t}{2} - 1 \right) \right. \\ & \left. - \frac{\xi_L}{2\hbar^2} \left(\frac{L^2}{4} \right)^{3/2} t \int_0^t dy \left(B(y) + \frac{L^2}{4} \right)^{-3/2} \right]. \end{aligned} \quad (2.81)$$

However, the obtained density of states is still too complicate and cannot be calculated numerically then it is worth to separately consider it in two limiting case, low-energy and high-energy limits.

2.3.2.1 Low-Energy Limit

In a low-lying energy tail, we suppose that γ is large (Varagorn Piputnchonlathee, 1996). This means that we only consider the contribution from states of the large wells, which their energies are lower than that of the small well (see also Figure 2.1). Hence, we are able to approximate

$$\frac{\sin \frac{1}{2} \gamma |\tau - \sigma| \sin \frac{1}{2} \gamma (t - |\tau - \sigma|)}{\sin \frac{1}{2} \gamma t} \cong \frac{1}{2i}, \quad (2.82)$$

$$\left(\sin \frac{1}{2} \gamma t \right)^{-3} \cong -8i \exp \left[-i \frac{3}{2} \gamma t \right], \quad (2.83)$$

$$\frac{1}{2} \gamma t \cot \gamma \frac{t}{2} - 1 \cong \frac{i}{2} \gamma t. \quad (2.84)$$

By using eq.(2.82) and keeping only the term up to t^2 , eq.(2.77) can be integrated (Jeffrey, 1995) giving

$$\int_0^t d\tau \int_0^t d\sigma \left(B(|\tau - \sigma|) + \frac{L^2}{4} \right)^{-3/2} = \left[\frac{\hbar}{2m\gamma} + \frac{L^2}{4} \right]^{-3/2} t^2, \quad (2.85)$$

Applying eqs.(2.83), (2.84) and (2.85) to (2.81), the expression for the density of states becomes

$$\rho_L(E) = \frac{1}{2\pi\hbar} \left(\frac{m}{2\pi\hbar}\right)^{3/2} \left(\frac{E_\gamma}{\hbar}\right)^3 \int_{-\infty}^{\infty} dt (it)^{3/2} \cdot \exp \left[\frac{it}{\hbar} \left(E - E_0 - \frac{3}{4} E_\gamma \right) - \frac{t^2}{2\hbar^2} \xi_L \left(1 + 4 \frac{E_L}{E_\gamma} \right)^{-3/2} \right], \quad (2.86)$$

where $E_\gamma = \hbar\gamma$ and $E_L = \hbar^2/(2mL^2)$. Using the parabolic cylinder function $D_p(z)$ definition (Gradshteyn and Ryzhik, 1965),

$$\int_{-\infty}^{\infty} dt (it)^p \exp(-\beta^2 t^2 - iqt) = \frac{\sqrt{\pi}}{2^{p/2} \beta^{p+1}} \exp\left(\frac{-q^2}{8\beta^2}\right) D_p\left(\frac{q}{\beta\sqrt{2}}\right) \quad (2.87)$$

we have

$$\rho_L(E) = \frac{2^{-3/4}}{2\sqrt{\pi}\hbar} \left(\frac{m}{2\pi\hbar}\right)^{3/2} \left(\frac{E_\gamma}{\hbar}\right)^3 \left(\frac{\xi_L}{2\hbar^2} \left(1 + 4 \frac{E_L}{E_\gamma}\right)^{-3/2}\right)^{-5/4} \cdot \exp \left[-\frac{(E - E_0 - \frac{3}{4} E_\gamma)^2}{4\xi_L \left(1 + 4 \frac{E_L}{E_\gamma}\right)^{-3/2}} \right] \cdot D_{3/2} \left(-\frac{\sqrt{2}\hbar(E - E_0 - \frac{3}{4} E_\gamma)}{\xi_L \left(1 + 4 \frac{E_L}{E_\gamma}\right)^{-3/2}} \right) \quad (2.88)$$

Here, the density of states of porous silicon can be written down in the form which is obtained by Sa-yakanit, Sritrakool and Glyde (1982) for a heavily doped semiconductor

$$\rho_L(\eta; z) = \frac{L^{-3}}{E_L \xi_L'^{5/4} b^{3/4}(\eta; z)} \exp \left[\frac{-b(\eta; z)}{4\xi_L'} \right] D_{3/2} \left(\sqrt{\frac{b(\eta; z)}{\xi_L'}} \right), \quad (2.89)$$

where $\xi_L' = \xi_L/E_L^2$, $\eta = (E_0 - E)/E_L$, $z = E_\gamma/E_L$ and the two dimensionless functions are defined by

$$a(\eta; z) = \frac{1}{8\sqrt{2}\pi^2} \left(\frac{3}{4}z + \eta\right)^{3/2} (z + 4)^3 \quad (2.90)$$

and

$$b(\eta; z) = \left(\frac{3}{4}z + \eta\right)^2 \left(1 + \frac{4}{z}\right)^{3/2}. \quad (2.91)$$

It is important to note that the low-energy limit eq.(2.89) is valid only in low energy region (near bulk crystalline silicon band edge) or in the other word, the lower energy level is, the higher reliability of density of states will be.

2.3.2.2 High-Energy Limit

In an another limit, high-energy limit case, the approximated density of states in this case can be obtained by taking the limit $\gamma \rightarrow 0$ (as discussed in low-energy limit) or equivalently $t \rightarrow 0$ which is physically understood by considering the pseudo-Heisenberg uncertainty relation $Et \geq \hbar$ (Van Miegham, 1992). Therefore, we are able to approximate

$$\frac{\gamma t}{2 \sin \frac{1}{2} \gamma t} \cong 1, \quad (2.92)$$

$$\frac{1}{2} \gamma t \cot \gamma \frac{t}{2} - 1 \cong 0, \quad (2.93)$$

and

$$\frac{\sin \frac{1}{2} \gamma |\tau - \sigma| \sin \frac{1}{2} \gamma (t - |\tau - \sigma|)}{\gamma \sin \frac{1}{2} \gamma t} \cong 0. \quad (2.94)$$

Inserting eqs.(2.94) to eq.(2.77), it can be integrated to obtain

$$\int_0^t d\tau \int_0^t d\sigma \left(B (|\tau - \sigma|) + \frac{L^2}{4} \right)^{-3/2} = \left(\frac{L^2}{4} \right)^{-3/2} t^2. \quad (2.95)$$

Combining eqs.(2.92), (2.93) and (2.95) with (2.81) we have

$$\rho_H(E) = \frac{m^{3/2}}{\pi^2 \hbar^3} \xi_L^{1/4} \left[\frac{\hbar^{1/2}}{\sqrt{2\pi}} \xi_L^{-1/4} \int_{-\infty}^{\infty} dt (it)^{-3/2} \exp \left[\frac{i}{\hbar} (E - E_0) t - \frac{\xi_L^2}{2\hbar^2} t^2 \right] \right] \quad (2.96)$$

By using parabolic cylinder function definition eq.(2.87) and the notation as in low energy limit, the approximated density of states in high energy limit becomes

$$\rho_H(\eta) = \frac{m^{3/2}}{\pi^2 \hbar^3} \xi_L^{1/4} \exp \left[-\frac{\eta^2}{4\xi_L} \right] D_{-3/2} \left(\frac{\eta}{\sqrt{\xi_L}} \right). \quad (2.97)$$

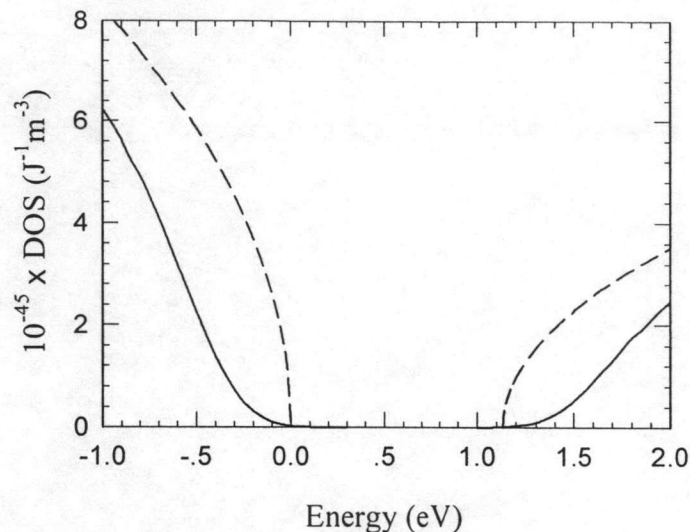


Figure 2.2: Density of states of porous silicon in high-energy limit eq.(2.97) for the valence band with hole effective mass of $0.58m_0$ (Singh, 1995) and conduction band with electron effective mass of $0.32m_0$ (Singh, 1995). The scatterer strength is 0.7 eV (Table 2.2) and the porosity is 72% (solid line). The dashed line represents parabolic density of states of perfect crystal.

We also note that the validity of the high energy limit eq.(2.97) is confined only in high energy region (far from bulk crystalline band edge). Alternately, we can also say that the higher energy level is, the higher reliability of density of states will be.

These two limit density of states will be used in calculation of the optical absorption of porous silicon in next Chapter. A specific example of the density of states of valence and conduction bands in high-energy limit (eq.(2.97)) is shown in Figure 2.2 and in low-energy limit is shown in Figure 2.3 as well.

Although we have set up the full expression for the density of states of porous silicon eq.(2.81), it has not been possible to evaluate the full expression exactly at all energies because of many built-in essential singularities. In order to solve this problem, we use the idea of matching density of states of Sa-yakanit and

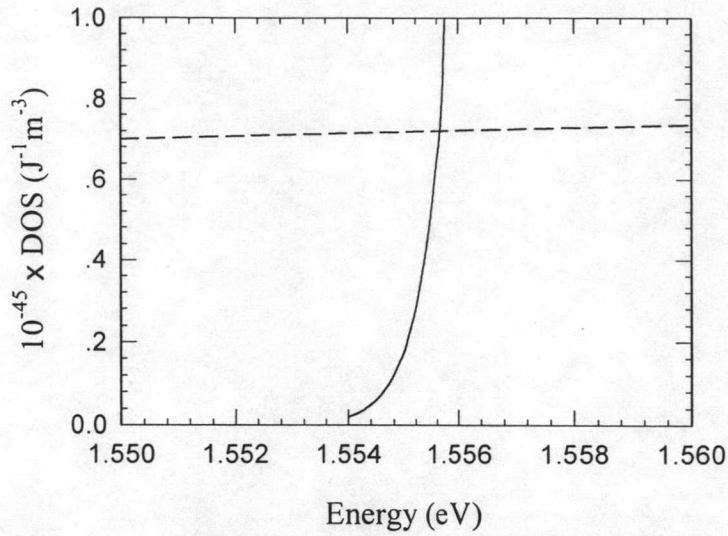


Figure 2.3: Density of states of porous silicon in low-energy limit eq.(2.89) (solid line) and high-energy limit eq.(2.97) (dashed line) for the valence band with hole effective mass of $0.58m_0$ (Singh, 1995) and conduction band with electron effective mass of $0.32m_0$ (Singh, 1995). The scatterer strength is 0.7 eV (Table 2.2) and the porosity is 72%.

Glyde (1980) in their work of heavily doped semiconductors. Then the chosen density of states for all energies is thus the low-energy limit density of states, $\rho_L(E)$, matched with the high-energy limit density of states, $\rho_H(E)$, in high energies, i.e.,

$$\rho_c(E) = \rho_L(E) [1 - \Theta(E - E^*)] + \rho_H(E) \Theta(E - E^*), \quad (2.98)$$

where E^* is the energy at $\rho_L(E)$ crosses $\rho_H(E)$.

The density of states in eq.(2.98) represents the density of states of porous silicon in our model then it is simply called the PS DOS. The PS DOS is shown graphically in Figure 2.4. This PS DOS will be used in our calculation for the optical absorption coefficient in next chapter.

Additionally we can conclude based on the PS DOS, the low- or the high-energy limit density of states that the density of states closed to the band edge

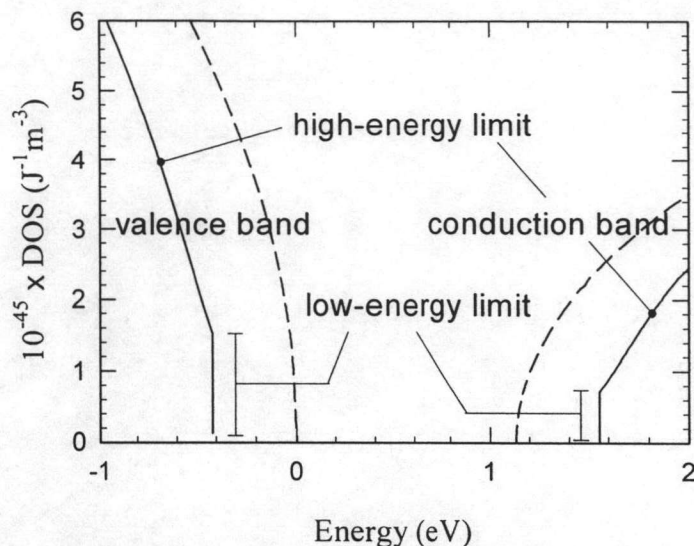


Figure 2.4: The density of states of porous silicon (PS DOS), for valence band and conduction band, consist of low-energy limit density of states and high-energy limit density of states.

of bulk crystalline silicon are clearly much less than that of parabolic density of states of bulk crystalline silicon. This is the band-gap widening from our model which is an important feature of the model in order to explain the visible photoluminescence. The band-gap widening in our model is approximately equal to the confinement energy ΔE (see also the last of Section 2.2) which is wider when porosity is increased. This trend with porosity is same as that of crystalline silicon model.

Finally, it is important to emphasize that such an expression obtained (eq.(2.98)) is the first analytical density of states which is directly extracted from the realistic structure of a whole porous silicon sample.

2.3.3 The Variational Equation

As mention earlier, the essential step of this method is to adjust the variational parameter (z or γ) which is introduced in the trial action. In doing this, we must have a rule or principle which allow us to be able to find out the appropriate value of the parameter. This is known as the Lloyd and Best variational principle (Lloyd and Best, 1975).

Lloyd and Best have shown that, the exact density of states is the function which maximizes the pressure $P(E)$ of the fermion system

$$P(E) \equiv \int_{-\infty}^E dE' \int_{-\infty}^{E'} dE'' \rho(E) = \int_{-\infty}^E dE' (E - E') \rho(E'). \quad (2.99)$$

This means that, for calculating the approximated density of states, the variational parameter should be chosen so that the pressure function reaches its maximum value. Therefore, the variational equation is obtained in the form

$$\frac{\partial}{\partial z} P(E; z) = 0, \quad (2.100)$$

or

$$\int_{-\infty}^E dE' (E - E') \frac{\partial}{\partial z} \rho(E'; z) = 0. \quad (2.101)$$

The asymptotic behavior of this variational principle is to maximize the density of states, which is so-called the Halperin and Lax's variational ansatz (1966,1967) obtained by their work relating to the band tail in heavily doped semiconductor. That is

$$\frac{\partial}{\partial z} \rho(E; z) = 0 \quad (2.102)$$

η	z from eq.(2.105)	z from eq.(2.101)
-0.01	0.039	0.040
-0.05	0.171	0.172
-0.10	0.306	0.308
-0.50	1.000	1.002
-1.00	1.562	1.572
-5.00	4.000	4.000
-10.0	5.844	5.844
-50.0	13.651	13.651

Table 2.1: Calculated variational parameter from eq.(2.105) and (2.101) at different energy

In Halperin and Lax' work, this equation has been reduced to a more simple one by taking the prefactor of the exponential slowly varies with respect to the exponential term. The left-hand side of eq.(2.102) then becomes a partial derivative of the exponent of the density of states. In symbol,

$$\frac{\partial}{\partial z} b(E; z) = 0. \quad (2.103)$$

Applying eq.(2.91) to (2.103), we obtain

$$z^2 + z - 4\eta = 0. \quad (2.104)$$

Since z is the ratio of the energy associated with the harmonic oscillator and the energy of the fluctuation, it definitely must be positive. Thus keeping only the positive root,

$$z = \frac{1}{2} \left[(1 + 16\eta)^{1/2} - 1 \right]. \quad (2.105)$$

As shown in Table 2.1, there are just a little bit different between the value of variational parameters which are determined from eq.(2.101) and eq.(2.105), is existed. Thus we use eq.(2.105) to determine the variational parameter in the calculation of optical absorption coefficient, which involve with the density of

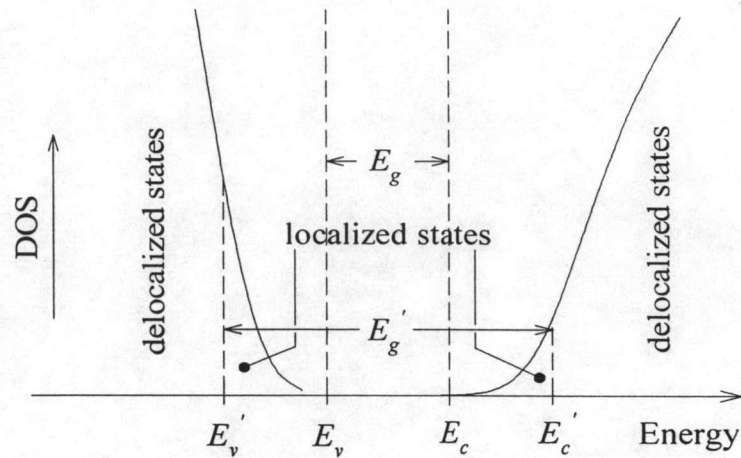


Figure 2.5: Schematic representation of density of states of porous silicon showing localized states between E'_c and E'_v with delocalized states outside this range.

states, in next Chapter.

2.4 Band Gap of Porous Silicon

Usually, a band gap is defined by the energy difference between conduction and valence band edges but this definition cannot be applied to porous silicon due to existence of band tails. We believe that it may not be meaningful to extract the band gap of porous silicon by this definition.

Consequently from our model, according to Anderson's theory of localization (Anderson, 1958), the states in a band tail near each band edge become localized due to potential fluctuation from the scatterer randomness as well the localized states and delocalized states are separated by a conventional energy level called "mobility edge" which is denoted as E'_c for conduction band and E'_v for valence band. These are depicted in Figure.2.5.

The energy difference between conduction- and valence-band mobility

edges is called "mobility gap". In a periodic system or ordered system, the mobility gap is obviously equal to the energy gap. Therefore, we can determine the mobility gap of porous silicon, E'_g , as

$$E'_g = E'_c - E'_v \quad (2.106)$$

which can be related to the band gap of crystalline silicon, E_g , as

$$E'_g = E_g + (E'_c - E_c) + (E_v - E'_v). \quad (2.107)$$

Since justification to choose mobility edges is not clear, it is reasonable to take them roughly at the value of mean potential energy E_0 due to all scatterers (Sritrakool, Sa-yakanit and Glyde, 1985). Since E_0 is measured from the band edge, then

$$E'_c - E_c = E_v - E'_v = E_0. \quad (2.108)$$

From eq.(2.20), we see that E_0 is dependent only on the number density of scatterer n_1 and the strength of scatterer v_0 . Thus the band gap of porous silicon becomes

$$E'_g = E_g + 2E_0 = E_g + 2n_1v_0 \left(\frac{\pi a_0^2}{4 \ln 2} \right)^{3/2} \quad (2.109)$$

In our model, the density of scatterers can be related to the porosity p defined in eq.(1.1)

$$p = \frac{\text{mass of Si wafer} - \text{mass of PS}}{\text{mass of Si wafer}} \times 100$$

then

$$p = \frac{\text{volume of all vacancies}}{\text{total volume}} \times 100 = \frac{n_1}{n_0} \times 100 \quad (2.110)$$

By combining eqs.(2.109) and (2.110), we obtain the approximated mobility gap of porous silicon as

$$E'_g = E_g + 2v_0n_0 \left(\frac{p}{100} \right) \left(\frac{\pi a_0^2}{4 \ln 2} \right)^{3/2} \quad (2.111)$$

i.e., for porous silicon with 72% porosity together with scatterer strength assumed to be 0.7 eV, the calculated mobility gap is about 1.8 eV. It is clear that there is an energy-gap widening from our model. However, we cannot get the mobility gap numerically because the scatterer strength v_0 cannot be obtained from our model.

According to electrical transport properties of disordered systems, it is well known that the activation energy, E_a , of the extended state conductivity is comparable to the energy difference between the mobility edge and Fermi level, E_F (Mott and Davis, 1971). Consequently, a following relation is reasonably employed

$$E_a \cong E_F - E'_v. \quad (2.112)$$

It is worth to calculate using crystalline band edge, E_v , as a reference, then

$$E_a \cong (E_F - E_v) + (E_v - E'_v). \quad (2.113)$$

Using eqs.(2.108), (2.20), (2.110) and the fact that the Fermi level lines at the mid gap. we then obtain

$$E_a \cong \frac{E_g}{2} + v_0 \left(\frac{n_0 p}{100} \right) \left(\frac{\pi a_0^2}{4 \ln 2} \right)^{3/2}. \quad (2.114)$$

So,

$$v_0 \cong \left(E_a - \frac{E_g}{2} \right) \left(\frac{100}{n_0 p} \right) \left(\frac{\pi a_0^2}{4 \ln 2} \right)^{-3/2}. \quad (2.115)$$

Afterward, the scatterer strength, which is obtained from eq.(2.115) in various porosity using the experimental results of activation energy of Lee et al. (1996), are shown in Table 2.2. The experimental results are obtained from the slope of Arrhenius plot which is plotted between reciprocal of absolute temperature and logarithm of dark conductivity. Such results of Lee et al. (1996) are confirmed

Porosity (%)	Activation energy : E_a (eV)	Scatterer strength : v_0 (eV)
40	0.30	-0.910
55	0.51	-0.170
60	0.60	0.032
65	0.73	0.285
71	0.98	0.711
80	1.01	0.679

Table 2.2: Activation energy and calculated scatterer strength from eq.(2.115) at various porosity (Lee, Lee and Jang, 1996).

by the work of Lubianiker and Balberg (1997) that they are associated with extended conduction. The plot of scatterer strength as a function of porosity is shown in Figure 2.6 as well. Such a plot is interesting due to two aspects. First, the scatterer strength which is proportional to porosity contradicts our constant model potential [Appendix A]. It is believed that this contrast implies the perfection of potential wells in the model. Second, it appears that the scatterer strength is negative when porosity below 60%, indicating that our model is reliable at porosity above 60%. However, more detail are discussed later in Chapter 4.

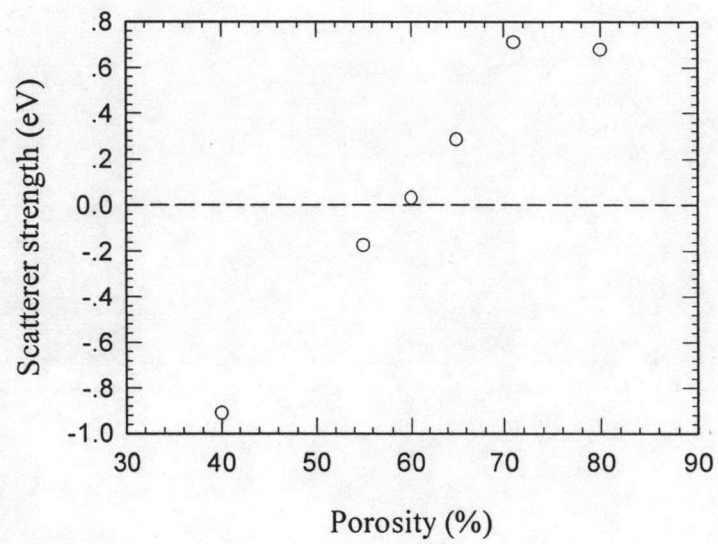


Figure 2.6: The calculated scatterer strength as a function of porosity (opened circle).