The Break Down of Semiclassical Density Matrix of a Particle Moving in Barrier Potential at Temperature T

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The nonlinear barrier potential with bound states is presented. The equilibrium density matrix of a particle moving at temperature T in this nonlinear barrier potential field is determined. The exact density matrix is compared with the result of the path integral approach in the semiclassical approximation is found to be sufficient at high temperatures while at low temperatures the fluctuation paths may have a caustic depending on temperature and end points. Near the caustics, the divergence of the simple semicalssical approximation of the density matrix is removed by a nonlinear fluctuation potential. For opaque barriers, the improved semiclassical approximation is compulsory required.

1. Introduction:

The semiclassical approximation to quantum mechanical problems is useful in large field. In chemistry and physics this approach becomes more prevalent for many reasons. For instance, semiclassical methods are efficient for the calculation of highly excited states, for which direct quantum mechanical calculations become difficult. The semiclassical approach also offers conceptual insights into the dynamic of many systems that are not easily extracted directly from the quantum mechanical treatment [1]. Finally, physical quantities of systems with barrier potentials can be calculated in semiclassical limit that corresponds to a large barrier height or large barrier width [2&3] *et al*. 1995. A system with a nonlinear potential field that has a barrier and an adjacent will be discussed. For the specific potential field considered, the classical equation of motion can be solved exactly. Therefore, the model can be used to test the quality of approximation to which one has to resort for most realistic potential fields.

It has been noted already for more than 2 decades that classical path methods offer facile techniques to determine the semiclassical approximation of the equilibrium density matrix [4&5].

The semiclassical approximation for the density matrix studied in the past [6-11] for Eckart potential only, gave an exact solution at high temperature and failed to give a good explanation for low temperature.

This paper shows that simple semiclassical approximation for the density matrix of a given potential becomes exact at high temperature, however for coordinates near critical values divergence arise when the temperature is lowered. In this region, one has to improve the simple semiclassical approximation and evaluate the non-Gaussion fluctuation integrals.

A. Path Integral and Semiclassical Approximation:

The dimensionless coordinate representation of the equilibrium density matrix of a quantum particle moving in potential V(x) may be written in an imaginary time path integral, [12&13] as

$$\rho_\beta(x,x`) = \int D\ [x] e^{-S[x]} \tag{1}$$

Here, the functional integral is over all paths $x(\tau), 0 \le \tau \le \beta$ *with* $x(\tau_1 = 0) = x$ *and* $x(\tau_2 = \beta) = x`$. Each path is weighted by its Euclidean action(Berry et al ,1972;Miller ,1977).

$$S[x] = \int_0^\beta d\tau [\frac{1}{2} x^2 + V(x)] \tag{2}$$

To evaluate the path integral in semiclassical expansion one can first determine the maximum of the weighting factor that is the minimum of S[x]. This is given by the classical action S[x_{cl}], where x_{cl} is the classical path solving the classical equation of motion following from Hamilton's principle $\delta S[x] = 0$.

If there exists a set $\{X_{cl}^{\alpha}\}$of classical trajectories in V(x), this procedure must be performed for each $\{X_{cl}^{\alpha}\}$, and all contributions are summed to yield the semiclassical density matrix.

$$\rho_\beta(x,x`) = \sum_\alpha \frac{1}{\sqrt{J_\alpha}} e^{-S[x_{c1}^{\alpha}]} \tag{3}$$

where $J_\alpha = \det\{\delta^2 s[x]/\delta_x(\tau_1)\delta_x(\tau_2)\}_{x=x_{c1}^\alpha}$ is the determinant describing the Gaussian integral over the quantum fluctuations ([12). J_α is given by the product of given values $\{\Lambda_n\}$ of the second order variational operator:

$\delta^2 S[x]/\delta x(\tau_1)\delta x(\tau_2) \quad \big| x = x_{c1}^\alpha$

as

$$J_\alpha = 2\pi\beta \prod_n (N\Lambda_n^\alpha) \tag{4}$$

where N is an appropriate normalized constant. As long as the Second order variation operator is positive definite, i.e. $\Lambda_n > 0$ for all n, the Gaussion approximation gives the leading order fluctuation term. But a problem arises if one of Λ_n's eigen value tends to zero, then the quantum fluctuations of this mode become arbitrarily large and simple semiclassical approximation breaks down. Generally, the vanishing of an eigen value defines a point where new minimal action paths in the potential V(*x*) become possible. This is well-known as the problem of caustics. For this purpose, another representation equivalent to Eqn. (4) is used. One find [1&3].

$$J_\alpha = 2\pi \dot{x}_{cl}^\alpha(\beta) x_{cl}^{\cdot\alpha}(0) \int_o^\beta \frac{1}{[\dot{x}_{cl}^\alpha(\tau)]^2} d\tau \tag{5}$$

This way the semiclassical approximation is completely determined by the classical path.

B. Classical paths:

Consider the 1-dim barrier potential given by

$$V(x) = \begin{cases} \alpha^2 & |x| < 1 \\ \dfrac{\alpha^2}{x^2} & |x| > 1 \end{cases} \tag{6}$$

as shown in Fig. (1), and the classical equation of the motion for $0<\varepsilon<\alpha^2$ is

$$\varepsilon = -\frac{1}{2}\dot{x}^2 + V(x) \tag{7}$$

where ε is the Euclidean energy of the system and considererd to be equivalent to η^2

Therefore, the classical path for a given V(x) can be obtained by integrating this equation which gives $x(\tau)$ as in table (1).

Table (1): The solution of the classical equation of motion for a given V(x) and $0 < \varepsilon < \alpha^2$

$$x(\tau)=\begin{cases}
(i) & \frac{\alpha}{\eta}\cos\theta \qquad\qquad 0\le\tau\le\tau_1 \\
 & \theta_0<\theta<\theta_1 \qquad \tau_1=\frac{\alpha}{\sqrt{2}\eta^2}\left(\frac{\sqrt{\alpha^2-\eta^2}}{\alpha}-Sin\theta_o\right) \\
(ii) & 1-\sqrt{2(\alpha^2-\eta^2)}(\tau-\tau_1) \qquad \tau_2\le\tau\le\tau_1 \\
 & \qquad \tau_2=\sqrt{\frac{2}{\alpha^2-\eta^2}}+\frac{\alpha}{\sqrt{2}\eta^2}\left(\frac{\sqrt{\alpha^2-\eta^2}}{\alpha}-\sin\theta_o\right) \\
(iii) & \frac{\alpha}{\eta}\cos\theta \qquad\qquad \tau_2\le\tau\le\tau_3 \\
 & \theta_2<\theta<\theta_3 \qquad \tau_3=\sqrt{\frac{2}{\alpha^2-\eta^2}}+\frac{\alpha}{\sqrt{2}\eta^2}\left(\frac{2\sqrt{\alpha^2-\eta^2}}{\alpha}-\sin\theta_o\right) \\
(iv) & \frac{-\alpha}{\eta}\cos\theta \qquad\qquad \tau_3\le\tau\le\tau_4 \\
 & \theta_3<\theta<\theta_4 \qquad \tau_4=\sqrt{\frac{2}{\alpha^2-\eta^2}}+\frac{\alpha}{\sqrt{2}\eta^2}\left(\frac{3\sqrt{\alpha^2-\eta^2}}{\alpha}-\sin\theta_o\right) \\
(v) & -1+\sqrt{2(\alpha^2-\eta^2)}(\tau-\tau_4) \qquad \tau_4\le\tau\le\tau_5 \\
 & \qquad \tau_5=2\sqrt{\frac{2}{\alpha^2-\eta^2}}+\frac{2\alpha}{\sqrt{2}\eta^2}\left(\frac{3\sqrt{x^2-\eta^2}}{\alpha}-\sin\theta_o\right) \\
(vi) & \frac{\alpha}{\eta}\cos\theta \qquad\qquad \tau_5\le\tau\le\tau_6 \\
 & \theta_5<\theta<\theta_6 \qquad \tau_6=2\sqrt{\frac{2}{\alpha^2-\eta^2}}+\frac{2\alpha}{\sqrt{2}\eta^2}\left(\frac{2\sqrt{\alpha^2-\eta^2}}{\alpha}-\sin\theta_o\right)
\end{cases}$$

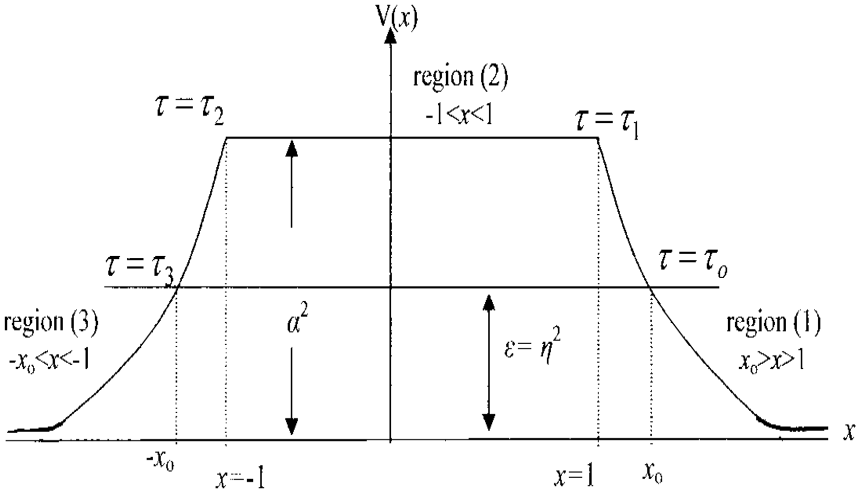

Fig. (1): The variation of V(x) versus x.

The parameter η^2 of the solution are determined by the boundary condition: $x(0) = x(\beta)$,where β is a time required to complete one cycle; One expects that there are may be more than one trajectory connecting the end points for a given inverse temperature and "time" β. These trajectories contribute to the semiclassical approximate of the equibrium density matrix. One can find β for this solution:

$$\beta = \frac{2\sqrt{2}}{\sqrt{\alpha^2 - \eta^2}} + \frac{\alpha}{\sqrt{2}}\,\frac{1}{\eta^2}(4\sin\theta_1 - 2\sin\theta_0) \qquad (8)$$

i.e,

$$\beta = \frac{2\sqrt{2}}{\sqrt{\alpha^2 - \eta^2}} + \frac{\sqrt{2}}{\eta^2}\,\alpha\left[\frac{2\sqrt{\alpha^2 - \eta^2}}{\alpha} - \sin\theta_0\right] \qquad (9)$$

where θ_o is an arbitrary angle corresponds to $\tau_o = 0$ and θ is an angle of motion.

However, β is required for at least one solution (named β_c)

C. Calculation of β_c:

(i) For $\theta_o = \theta_1$ i.e, $x = x` = 1$
From eq.(9)

$$\beta_c = \frac{\sqrt{2}}{\sqrt{\alpha^2 - \eta^2}}\left[2 + (\frac{\alpha^2}{\eta^2} - 1)\right] \tag{10}$$

i.e,

$$\beta_c = \frac{\sqrt{2}}{\sqrt{\alpha^2 - \eta^2}}\left[1 + \frac{\alpha^2}{\eta^2}\right] \tag{11}$$

(ii) For $\theta_o = 0$
In this case $\beta = \beta_c$ if $\sin\theta_o = 0$

i.e,

$$\therefore \beta_c = \frac{\sqrt{2}}{\sqrt{\alpha^2 - \eta^2}}\left[1 + \frac{1}{\eta^2}(\alpha^2 - \eta^2)\right] \tag{12}$$

let $k = \frac{\alpha^2}{\eta^2}$ then eq. (12) will be

$$\beta^2\alpha^2 = \frac{2k^3}{(k-1)} \tag{13}$$

then

$$C^2 = \frac{1}{2}\beta^2\alpha^2$$

i.e,

$$C^2 = \frac{k^3}{(k-1)}$$

$$C^2(k-1) = k^3 \tag{14}$$

let

$$F(k) = k^3 - c^2(k-1) \tag{15}$$

then

$$F`(k) = 3k^2 - c^2$$
$$= 0 \qquad at \qquad k = \pm\frac{c}{\sqrt{3}}$$

see Fig.(2)

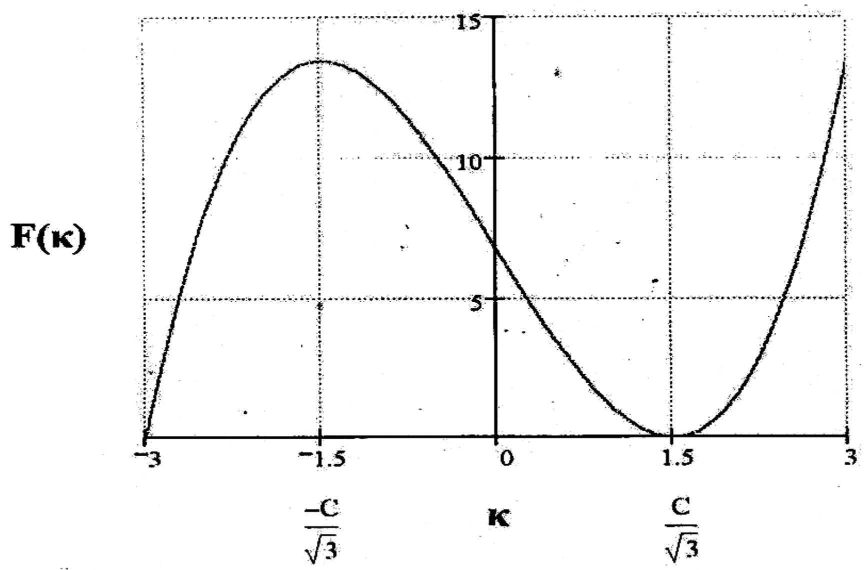

Fig. (2): The value of k in the case of θ = 0

Subs. in eq. (14), one can get

$$C = \pm\frac{3\sqrt{3}}{2} \tag{16}$$

and therefore,

$$\frac{\beta\alpha}{2\sqrt{2}} = \frac{3\sqrt{3}}{2} \tag{17}$$

corresponds to one solution.

(iii) The general value of *β* *($\theta_o \neq 0$)*

From eq. (9) one can write *β* as

$$\beta = \frac{2\sqrt{2}}{\sqrt{\alpha^2-\eta^2}} + \frac{\alpha\sqrt{2}}{\eta^2}\left[\frac{2}{\alpha}\sqrt{\alpha^2-\eta^2} - \sin\theta_o\right]$$

write $k = \frac{\alpha^2}{\eta^2}$ *i.e*, $\eta^2 = \frac{1}{k}\alpha^2$

Where *k* should be grater than 1, thus *β* can takes a form:

$$\beta = \frac{2\sqrt{2k}}{\alpha\sqrt{k-1}} + \frac{2k}{\alpha}\left\{\frac{2}{\sqrt{k}}\sqrt{k-1} - 2\gamma\right\} \tag{18}$$

i.e,

$$\frac{\beta\alpha}{2\sqrt{2}} = \sqrt{\frac{k}{k-1}} + \sqrt{k(k-1)} - \gamma k \tag{19}$$

where $\gamma = \frac{\sin\theta_o}{2}$ and γ has the boundary condition that $0 < \gamma < \frac{1}{2}$

Now, let $\beta\frac{\alpha}{2\sqrt{2}} = \Gamma > 0$ (20)

One can define Eqn. (19) as a function of *k*

$$F(k) = \left(\frac{k}{k-1}\right)^{\frac{1}{2}} + k^{\frac{1}{2}}(k-1)^{\frac{1}{2}} - \gamma k - \Gamma \tag{21}$$

Then, the single solution of *F(k)* should satisfies both:

$F(k) = 0$ and $F'(k) = 0$

i.e,

$$k^{\frac{1}{2}}\left[(k-1)^{\frac{-1}{2}} + (k-1)^{\frac{1}{2}}\right] - \gamma\ k - \Gamma = 0 \tag{22}$$

and

$$k^{\frac{1}{2}}(2k-3) = 2\gamma\ (k-1)^{\frac{3}{2}} \tag{23}$$

as k ~ ∞,

$$F(k) = k - \gamma\ k = (1-\gamma)k \quad \to \infty \tag{24}$$

since $1-\gamma > 0$ for $0 < \gamma < \frac{1}{2}$

see Fig.(3)

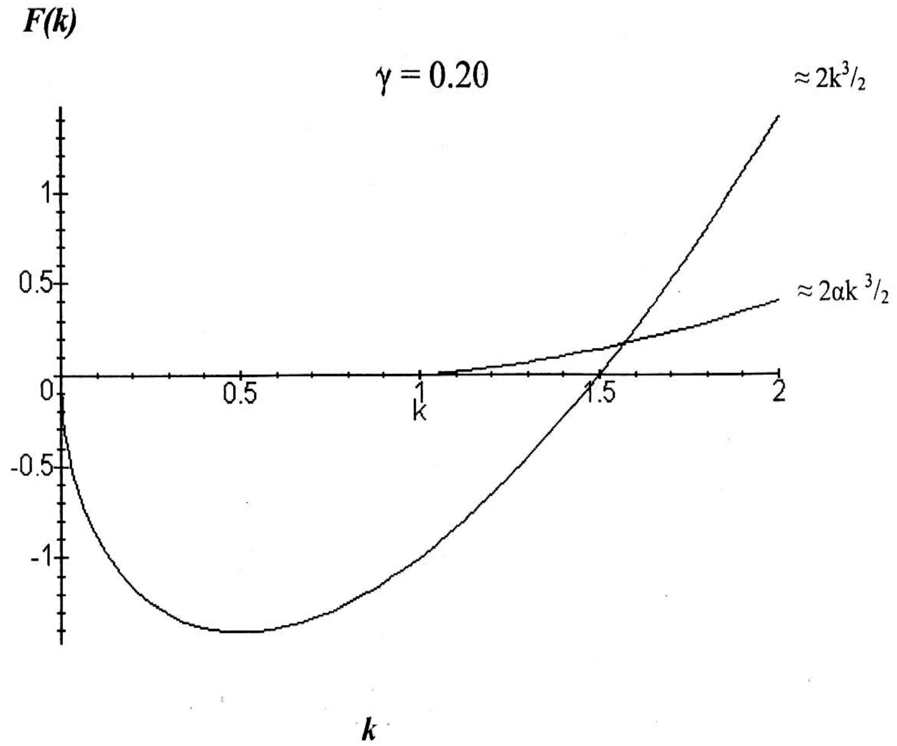

Fig. (3): The relation between the F(k) and k. One solution corresponding to $\varepsilon=2\alpha^2/3$

From above, one can determine the *k* values as

$$k = \frac{3\Gamma}{(2\Gamma - \gamma)} \tag{25}$$

On Substituting the value of *k* in Eqn. (23), one can find

$$\gamma = \left(\frac{27}{4}\right)^{\frac{1}{3}} \Gamma^{\frac{1}{3}} - \Gamma \tag{26}$$

Now, let $$F = F(\Gamma) = \Gamma + \gamma - \left(\frac{27}{4}\right)^{\frac{1}{3}} \Gamma^{\frac{1}{3}} \quad , F(0) = \gamma \tag{27}$$

both solutions $\Gamma_1, \Gamma_2 > 0$ should satisfy

$$\Gamma > ½$$

and

$$\gamma = \left(\frac{27}{4}\right)^{\frac{1}{3}} \Gamma^{\frac{1}{3}} - \Gamma \tag{28}$$

These imply

$$\Gamma \geq \frac{1}{2}$$

Therefore, one of them is excluded and the other is a unique one. i.e., there is only one solution at $\Gamma = \Gamma_2$, and this solution tends to the previous values as $\gamma \rightarrow 0$:

$$\Gamma \rightarrow \Gamma_o = \frac{3\sqrt{3}}{2} = \left(\frac{27}{4}\right)^{\frac{1}{2}} \tag{29}$$

This solution $\Gamma = \Gamma(\gamma)$ may be obtained explicitly as a power series in γ (note $\gamma < ½$).

$$\Gamma(\gamma) = \frac{3\sqrt{3}}{2} - \frac{3}{2}\gamma + ... \tag{30}$$

Thus,

$$\frac{\beta_c \alpha}{2\sqrt{2}} = \frac{3\sqrt{3}}{2} - \frac{3}{4}\sin\theta_o - \frac{1}{16\sqrt{3}}\sin\theta_o + ... \tag{31}$$

This determination of β_c for any θ_o: $\theta_1 \geq \theta_o \geq 0$.

For short times, i.e, high temperatures there exists only the constant solution $x(\tau) = 1$, but when the temperature is lowered a new solutions arise for $\beta \geq \beta_c$. For this solutions, two new branches emerge describing an oscillation to the other side of the well in the inverted potential. The constant path which is stable for high temperature becomes unstable for times $\beta > \beta_c$. The solution of smaller amplitude is unstable while the other one stable [8 & 9].

D. Classical action and fluctuation determinant:

Fortunately, not all extremely action paths has to be taken into account in semiclassical approximation [Eqn.(3)] for a given temperature since the corresponding classical actions are not always minima of S[x]. One gains from Eqn. (2) and Table (1) for the action of the classical paths

$$S_{c1} = -\varepsilon\beta + \left\{ \frac{8\alpha}{\sqrt{2}} \log\left(\frac{\alpha}{\eta} + \sqrt{\frac{\alpha^2}{\eta^2} - 1} \right) + 4\sqrt{2}\alpha / \sqrt{\frac{\alpha^2}{\eta^2} - 1} \right\} \tag{32}$$

for the case $\beta > \beta_c$ only the trivial solution with action.

$$S_{c1}[1] = -\varepsilon\,\beta \tag{33}$$

and for $\beta > \beta_c$ the action will be smaller than $S_{c1}[1]$. Therefore, as mentioned above, one has bifurcations at $\beta = \beta_c$.
Now, the finite part of determinant J using Eqn.(5) is:

$$J^{(finit)} = -4\tan^2\theta_o \frac{k}{\sqrt{2\alpha}}\left[\left(\frac{1}{\sin\theta_o} + \sin\theta_o\right) - 2\left(\frac{1}{\sin\theta_1} + \sin\theta_1\right) + \frac{2k^{-\frac{1}{2}}}{(k-1)^{\frac{3}{2}}}\right] \tag{34}$$

for a general case, $\theta_o \neq 0$:

$$J = \begin{cases} < 0 & for \quad 1 \le k < k_o = 1.78 \\ > 0 & for \quad k > k_o = 1.78 \end{cases} \tag{35}$$

but if $\theta_o = \theta_1$ at $x(\tau) = 1$ in the limit of $\eta \rightarrow \alpha$, J cannot be evaluated according to Eqn.(5) and the semiclassical approximation breaks down.

2. Conclusion:

Now, for high temperatures, $\beta \le \beta_c$ and given end points $(x, x`)$, there is only one classical path with amplitude x_m which is obtained from Eqn.(7) by choosing ε and β_o according to the boundary conditions. In practice ε and β_o have to be determined numerically. By virtue Eqn. (17) and (30) the semiclassical density matrix for high temperatures $\beta < \beta_c$ is given by

$$\rho(x, x`) = \frac{1}{\sqrt{J}}\, e^{-S(x_m)} \tag{36}$$

For $\beta < \beta_c$ new classical paths may emerge, first for coordinate near the critical coordinate, determined by the solution of β. A part from a narrow region about the critical temperature, these trajectories are well separated in function space and the sum of Eqn.(3) contains the contribution of pathes.

As it is shown above the simple semiclassical approximation breaks down in a narrow region around the barrier top near the critical x_c and inverse temperature β. Only there, the semiclassical determination has to be improved due to the fact that the relevant classical paths are not well separated in function space. Furthermore, this analysis also gives the precise conditions for the validity of the Eqn. (33). The author suggests that further research work needed in order to improve this.

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