COURSE 4

THEORY OF QUANTUM PROCESSES
IN LIQUIDS

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1. Preliminaries

During the last decade, an exciting occurrence in liquid state theory has been the discovery and development of techniques that accurately treat quantum processes in liquids. Examples include successful calculations of superfluid order parameters, calculations of electronic states for excess electrons in liquids, and calculations of tunneling as mediated by the spontaneous fluctuations in a liquid. This is what my lectures are about – how to do these calculations.

The central theme is Feynman’s space-time formulation of quantum theory. This approach is particularly well suited for treating disordered systems. Indeed, at present, if one desires computationally feasible rigorous treatments of complex materials, there are no alternatives. Other techniques (e.g., electronic density functional methods), while less rigorous, have proved useful too. But I have chosen not to discuss them in order to limit the length of presentation.

Students listening to these lectures may not yet be very familiar with Feynman’s approach. I do assume, however, a knowledge of standard textbook quantum mechanics, statistical mechanics and liquid state theory. The books by Baym [1], by Chandler [2], and by Hansen and McDonald [3], respectively, provide a bibliography in this regard. If jargon seems either undefined or unfamiliar (e.g., terms or names like “transfer matrix,” “Kramers–Krönig,” “fluctuation–dissipation theorem” etc.), information on these standard topics can be found in these three texts – as well as in many others. I have also added a few other texts and monographs as general bibliography [4,5,6]. While not necessary, they contain further background and supplementary material which can be quite helpful.

With regard to citations, I have tried to provide enough in the way of examples to give the student an accurate feeling for the literature. But the list is not a comprehensive bibliography. Students can create their own as they begin to actively participate in the field – something I hope they can do after reading these lecture notes.

As I believe appropriate for the Les Houches school, I have adopted a textbook style for my presentation. Omitted details are often discussed in the format of exercises for the reader.
To set the stage, we will consider first some elementary facts about correlation functions and observables for quantal systems. The context might be somewhat new, but presumably it is not the first time these facts have been encountered.

1.1. What to calculate

Consider a system with a time independent hamiltonian, $H$. The partition function, $Q$, is

$$ Q = \text{tr} \ e^{-\beta H}, \quad \beta^{-1} = k_B T. \quad (1.1) $$

We will see that all observables can be determined from the appropriate differentiation of $Q$ — even time dependent properties.

If $A$ is a dynamical operator, its observed value when the system is at equilibrium is the time independent

$$ \langle A \rangle = Q^{-1} \text{tr} \ e^{-\beta H} A. \quad (1.2) $$

If, however, the system at time $t = 0$, is displaced slightly from equilibrium, then the observed value is the time dependent $A(t)$ given by the fluctuation–dissipation theorem,

$$ \Delta A(t) = \bar{A}(t) - \langle A \rangle = \Delta \bar{A}(0) \int_0^{\beta h} \frac{d\tau}{\beta h} \langle \Delta A(\tau) \Delta A(t) \rangle \int_0^{\beta h} \frac{d\tau}{\beta h} \langle \Delta A(\tau) \Delta A(0) \rangle, \quad (1.3) $$

where

$$ A(t) = e^{iHt/\hbar} A e^{-iHt/\hbar} = \Delta A(t) + \langle A \rangle. \quad (1.4) $$

† Alternatively, the curious integration over imaginary time can be replaced with a commutator expression since

$$ \int_0^{\beta h} \frac{d\tau}{\beta h} \langle \Delta A(-i\tau) \Delta A(t) - \Delta A(0) \rangle = \frac{i}{\beta \hbar} \int_0^t dt' \langle [\Delta A(0), \Delta A(t')] \rangle. $$

† Text parts set in a smaller typeface, like the current paragraph, contain examples, exercises, etc. illustrating the topics of the main text.
The demonstration is left as an exercise. To carry it out you’ll need to show that due to the cyclic invariance of the trace
\[
\langle A(t)B(t') \rangle = Q^{-1} \text{tr} e^{-\beta H_0 \frac{i}{\hbar}} A e^{-iH(t-t')/\hbar} B e^{-iHt'/\hbar}
\]
satisfies
\[
\langle A(t)B(t') \rangle = \langle A(0)B(t'-t) \rangle \\
= \langle B(t'-i\beta \hbar)A(t) \rangle. \tag{1.5}
\]

So, we want to calculate things like $Q$, $\langle A \rangle$, $\langle A(t')B(t) \rangle$, etc. And the time dependent quantities should be considered for complex time.

1.2. Spatial representation

We let $r$ stand for a point or state in configuration space. Then
\[
Q = \int dr \langle r | e^{-\beta H} | r \rangle. \tag{1.6}
\]

Note that in describing many particle systems, $r$ is a high dimensional variable.

Further, if $A$ is a position dependent operator, $\langle r | A | r' \rangle = \delta(r-r')A(r)$, then
\[
\langle A \rangle = Q^{-1} \int dr A(r) \langle r | e^{-\beta H} | r \rangle. \tag{1.7}
\]

If $B$ is similarly a position dependent operator, then
\[
\langle A(t)B(t') \rangle = Q^{-1} \text{tr} e^{-\beta H_0 \frac{i}{\hbar}} A e^{-iH_0 \frac{i}{\hbar}} e^{iH(t-t')/\hbar} B e^{-iHt'/\hbar} \\
= Q^{-1} \int dr \int dr' \int dr'' \langle r | e^{-\beta H} | r'' \rangle \langle r'' | e^{iH(t-t')/\hbar} | r' \rangle \\
\times \langle r' | e^{-iH(t-t')/\hbar} | r \rangle A(r')B(r). \tag{1.8}
\]

Now we see that the central quantity is
\[
\rho(r, r'; \beta \hbar) = \langle r | e^{-\beta H} | r' \rangle = \langle r | e^{-iH_0 \frac{i}{\hbar}} | r' \rangle \tag{1.9}
\]
and its real time counterpart
\[
\rho(r, r'; it) = \langle r | e^{-iHt/\hbar} | r' \rangle = \langle r | e^{itH_0 \frac{i}{\hbar}} | r' \rangle \tag{1.10}
\]
No arrow is required on the diagram depicting the imaginary time quantity, \( \rho(r, r'; \beta \hbar) \), because it is real and symmetric.

The quantity \( \rho(r, r'; \beta \hbar) \) is a density matrix – the thermal density matrix. Its diagonal part gives the partition function

\[
Q = \int dr \rho(r, r; \beta \hbar) = \int \rho(r, r; \beta \hbar) dr
\]  

(1.11)

and the average density,

\[
\langle \delta(\hat{r} - r) \rangle = \langle \rho(r) \rangle = \frac{1}{Q} \int r \rho(r, r; \beta \hbar) dr
\]  

(1.12)

Further,

\[
\langle A(t)B(0) \rangle = Q^{-1} \int dr \int dr' \int dr'' \rho(r, r', \beta \hbar) \rho(r'', r'; -it)
\]

\[
\times A(r')B(r) \rho(r', r; it)
\]

\[
= Q^{-1} \int dr' \int dr A(r')B(r) \rho(r', r; it)
\]

(1.13)

where the blackened circle is a white circle that has been integrated over.

In imaginary time, the correlation function is

\[
C_{AB}(-it) = \langle A(-it)B(0) \rangle \equiv \tilde{C}_{AB}(t), \quad t \text{ real}.
\]  

(1.14)

This function leads to the diagram

\[
\]

where the equality follows from completeness, i.e.,

\[
\int dr'' \rho(r, r''; t) \rho(r'', r', t') = \rho(r, r'; t + t').
\]

(1.15)

In the pictures, \( t \) is a length of imaginary time. It must be positive; \( \beta \hbar - t \) must be positive too. In other words,

\[
0 \leq t \leq \beta \hbar.
\]
Due to the cyclic nature of these functions, we can continue \( t \) outside this region by employing periodicity:

\[
\tilde{C}_{AB}(t) = \tilde{C}_{AB}(t + n\beta\hbar), \quad n = \text{integer}.
\] (1.15)

This imaginary time is called Euclidean time.

Notice that for real \( t \), \( \tilde{C}_{AB}(t) = C_{AB}(-it) \) is pure real. Yet \( C_{AB}(t) \) is in general complex. In fact, as an exercise, you can show that eq. (1.5) is equivalent to

\[
C_{AB}^*(t) = C_{AB}(t \pm i\beta\hbar).
\]

This result or (1.5) is known as the KMS (Kubo–Martin–Schwinger) boundary condition. Equation (1.15) is a special case of this result.

1.3. Example: harmonic oscillator

Consider the system with hamiltonian

\[
H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2x^2.
\] (1.16)

There is only one frequency in this problem, \( \omega_0 \). The Heisenberg equations of motion give \( \frac{d^2x}{dt^2} = -\omega_0^2 x \) for real time. So, in the real time domain,

\[
\langle x(t)x(0) \rangle = a\cos\omega_0 t + b\sin\omega_0 t,
\]

with \( a \) and \( b \) constants. The first of these is fixed by the initial condition

\[
a = \langle x^2 \rangle.
\]

The virial theorem gives \( \frac{1}{2}m\omega_0^2\langle x^2 \rangle = \frac{1}{2}\langle \text{energy} \rangle \). An elementary calculation of the oscillator partition function therefore leads to

\[
\langle x^2 \rangle = \frac{\hbar}{2m\omega_0} \coth \left( \frac{\beta\hbar\omega_0}{2} \right).
\]

The constant \( b \) can be determined by noting [eq. (1.5)]

\[
\langle x(-t - i\beta\hbar)x(0) \rangle = \langle x(t)x(0) \rangle.
\]

Hence,

\[
a\cos\omega_0 t + b\sin\omega_0 t = a\cos[\omega_0(i\beta\hbar + t)] - b\sin[\omega_0(i\beta\hbar + t)].
\]
Evaluation at $t = 0$ and some algebra gives

$$b = -i(\hbar/2m\omega_0).$$

Hence, for real time

$$C(t) = \langle x(t)x(0) \rangle = \frac{\hbar}{2m\omega_0} \left[ \coth \left( \frac{\beta\hbar\omega_0}{2} \right) \cos(\omega_0 t) - i \sin(\omega_0 t) \right].$$

(1.17)

For Euclidean time, send $t \to -it$. This gives

$$\tilde{C}(t) = \langle x(-it)x(0) \rangle = \frac{\hbar}{2m\omega_0} \frac{1}{\sinh(\beta\hbar\omega_0/2)} \cosh \left[ \beta\hbar\omega_0 \left( \frac{1}{2} - \frac{t}{\beta\hbar} \right) \right].$$

(1.18)

for $0 \leq t \leq \beta\hbar$. In contrast with its real time behavior, fig. 1 shows how $\tilde{C}(t)$ looks in Euclidean time.

What we see in this figure is more general than we might suspect from considering only the harmonic oscillator. The picture illustrates ground state dominance. Specifically, for any oscillator with a discrete energy spectrum

$$\langle x(-it)x(0) \rangle = Q^{-1} \text{tr} e^{-\beta H} x e^{-tH/\hbar} x e^{tH/\hbar}$$

$$= Q^{-1} \sum_{n,m} e^{-\beta\epsilon_n^+} |x_{nm}|^2 e^{-t(\epsilon_m - \epsilon_n)/\hbar}$$

(1.19)

where $\epsilon_n$ is the energy of the $n$th state, and $x_{nm}$ denotes $\langle n|x|m \rangle$.

It is apparent from eq. (1.19) that $\langle x(-it)x(0) \rangle$ goes to zero for Euclidean time, $t$, much larger than $\hbar/\Delta \epsilon$. Here, $\Delta \epsilon$ is the energy gap between the ground state and the first excited level. Thus, if temperature is low enough
that $\beta A \varepsilon \gg 1$, then $\langle x(-it)x(0) \rangle$ will appear as illustrated for the harmonic oscillator with $\beta \hbar \omega_0 \gg 1$.

Outside the range $0 \leq t \leq \beta \hbar$, the Euclidean time correlation function is determined from the condition of periodicity. With a Fourier series, periodicity implies

$$\tilde{C}(t) = \sum_{n=-\infty}^{\infty} C_n e^{-i\Omega_n t}, \quad \Omega_n = 2\pi n / \beta \hbar$$

(1.20)

where

$$C_n = \frac{1}{\beta \hbar} \int_0^{\beta \hbar} \text{d}t \ 2 \tilde{C}(t) e^{i\Omega_n t}.$$  

(1.21)

It is a straightforward exercise to perform the Fourier transform of $\tilde{C}(t) = \langle x(-it)x(0) \rangle$ for the harmonic oscillator:

$$C_n = \frac{1}{\beta n} \left( \frac{1}{\omega_0^2 + \Omega_n^2} \right).$$

(1.22)

The Fourier series can be summed with this expression for $C_n$ and one arrives back again at the formula for $\langle x(-it)x(0) \rangle$ in Euclidean time.

As an exercise, you may perform the summation by noting the identity

$$\frac{1}{2} \sum_{n=-\infty}^{\infty} \frac{\cos \theta}{n^2 + \alpha^2} = \frac{\pi \cosh(\theta \alpha)}{\sinh(\pi \alpha)}$$

for $\alpha$ real and $0 \leq \theta \leq 2\pi$. You can also derive the identity. [Hint: write the sum as the integral of

$$\frac{e^{iz\theta}}{z^2 + \alpha^2} (e^{2\pi iz} - 1)^{-1}$$

over a suitable contour for $z$.]

After performing the summation, the Euclidean time correlation function can then be analytically continued to real time. Note, however, the Fourier series in Euclidean time must be summed before sending $t \rightarrow it$. The series diverges if the continuation to real time is attempted before completing the sum.
Finally, notice that the derivative of $\dot{C}(t)$ is not zero at $t = 0^+$. This behavior is general and not specific to the harmonic oscillator as can be established from eq. (1.19). Thus, the periodic function $\dot{C}(t)$ has singular derivatives at $t = 0$, $\pm \beta \hbar$, $\pm 2\beta \hbar$, $\ldots$.

1.4. Wick’s rotations

Due to the periodicity of $\dot{C}(t)$, the behavior of this function in one strip, e.g., $0 \leq t \leq \beta \hbar$, is sufficient to determine $\dot{C}(t)$ for all real $t$. Analytic continuation to complex $t$ leads evidently to the real time correlation function $C(t)$. Let us now consider the corresponding manipulations for the frequency dependent Fourier transforms. The manipulations passing back and forth from imaginary to real time or frequency axes are called Wick’s rotations. Baym and Mermin [7] demonstrated the remarkable fact that the results obtained from these manipulations are in principle unique provided physically relevant boundary conditions are enforced.

The Fourier series (1.20) can be written as

$$\dot{C}(t) = \sum_{n=-\infty}^{\infty} \dot{C}(\Omega_n) e^{-i\Omega_n t}, \quad (1.23)$$

where

$$\dot{C}(\Omega_n) = C_n \quad \text{for} \quad \Omega_n = 2\pi n / \beta \hbar. \quad (1.24)$$

Now consider the analytic continuation

$$\dot{C}(\omega) = \dot{C}(-i\omega), \quad (1.25)$$

performing the Fourier transform of eq. (1.19) and then sending $\Omega_n$ to $-i\omega$. The resulting expression is analytic in the upper-half $\omega$-plane. In other words, $\dot{C}(\omega)$ is the Fourier transform of a causal function. Hence, the real and imaginary parts of $\dot{C}(\omega)$ are connected by Kramers-Kronig relations.

Indeed, from the Fourier transform of a spectral representation such as eq. (1.19), one may show

$$\text{Im} \dot{C}(\omega) = \frac{1}{2\beta \hbar} (1 - e^{-\beta \hbar \omega}) \int_{-\infty}^{\infty} dt e^{i\omega t} \langle A(0) A(t) \rangle \quad (1.26)$$

and

$$\dot{C}(\omega) = -k_B T \dot{\chi}(\omega), \quad (1.27)$$
where
\[
\hat{\chi}(\omega) = (i/h) \int_0^\infty dt e^{i\omega t} \langle [A(0), A(t)] \rangle.
\] (1.28)

The explicit demonstration of eqs. (1.26) - (1.28) is left as an exercise. In carrying out the demonstration, one can also derive the connection between \( \text{Im} \hat{C}(\omega) \) and absorption, and finally the connection between \( \hat{C}(\omega) \) and the real-time Fourier transform of \( \langle \pi(t)\pi(0) \rangle \). Finally, notice that \( C(t) \) and \( \hat{C}(\omega) \) must be complex to satisfy the condition of detailed balance. For guidance, you can compare some of your steps with results in section 17.2 of Parisi’s text [5].

In summary, the exact knowledge of Euclidean time correlation functions is equivalent to the knowledge of the real time correlation functions. This fact is often useful as a formal device. For example, we will exploit it later in these lectures to show how certain dynamical quantities such as tunnel splittings can be conveniently determined from imaginary time calculations. But as a practical matter, the mapping between real and imaginary time is often illusory. The reason is that the configurations or states that are statistically most significant in determining the Euclidean time correlation functions can have little overlap with those that are most significant for the real time functions. In the case of ground state dominance, for instance, the Euclidean time quantities are determined almost entirely by the ground state while real time dynamics is associated with excitations from the ground state. Further, the statistical overlap diminishes as real time grows making the conversion from Euclidean to real time an unstable numerical procedure for long real time.

While straightforward analytical continuation is often impractical, there are alternative numerical techniques by which real time correlation functions can be successfully computed. These techniques are discussed in the last of these lectures, section 7. To get to that point, however, we need to show how in general the evaluation of a quantum correlation function can be expressed as a classical statistics problem. To do that it is most convenient to first work in purely imaginary time. Then the formal mapping to real time can be made, and finally we will address the numerical problems involved in that mapping.

2. Converting quantum calculations to classical statistical calculations

As indicated above, we now discuss a conceptual framework with which the densities and correlation functions can be computed with techniques of
classical statistical mechanics. This framework is Feynman’s path integral formulation of quantum theory. My own perspective on this approach is influenced by work Peter Wolynes and I did together ten years ago [8].

2.1. Isomorphism

Here is the basic idea. Consider the partition function represented as a trace over configurational states, \(|r\rangle\), as in eq. (1.6). The configurations, \(r\), can be a multidimensional space. Recall that \(\exp(-iHt/\hbar)|r\rangle\) is the state \(|r, t\rangle\) that has evolved at time \(t\) from the initial \(|r, 0\rangle = |r\rangle\). The calculation of \(Q\) is therefore the overlap of \(|r, -i\beta\hbar\rangle\) with the initial state, as depicted in the figures we have drawn in the previous sections.

The evolution of a state can be thought of in terms of paths – in this case, imaginary time quantum paths in real configuration space. To describe paths, we need to first analyze a step in the path. The smaller the steps the simpler they are. So we will consider quantum paths as a sequence of very small steps – ultimately a continuum of infinitesimal steps. The way to break a path into small steps is to factor the propagator into many parts,

\[
e^{-\beta H} = (e^{-(\beta/P)H})^P.
\]  

Then, by inserting complete sets of states between each of the \(P\) factors, we obtain

\[
Q = \int dr^{(1)} dr^{(2)} \cdots dr^{(P)} \langle r^{(1)}|e^{-\epsilon H}|r^{(2)}\rangle \\
\times \langle r^{(2)}|e^{-\epsilon H}|r^{(3)}\rangle \cdots \langle r^{(P)}|e^{-\epsilon H}|r^{(1)}\rangle
\]  

with \(\epsilon = \beta/P\). We will make \(P\) so large that \(\epsilon\) will be very small. Further, suppose there is a natural division of \(H\) into a reference part, \(H_0\), and a remainder, \(V\). Then

\[
e^{-\epsilon H} = e^{-\epsilon (H_0 + V)} = e^{-\epsilon H_0} e^{-\epsilon V [1 + O(\epsilon^2)]}.
\]  

As an exercise you can show that

\[
e^{-\epsilon (A + B)} = e^{-\epsilon A} e^{-\epsilon B [1 + O(\epsilon^2)]},
\]

where the correction term of the order of \(\epsilon^2\) involves the commutator \([A, B]\).
Hence, for large enough $P$, we have the asymptotic result
\[ \langle r | e^{-iH\epsilon} | r' \rangle \sim \rho_0(r, r'; \epsilon\hbar) e^{-iV(r)}, \quad \epsilon \text{ small} \tag{2.4} \]

where
\[ \rho_0(r, r'; \epsilon\hbar) = \langle r | e^{-iH_0} | r' \rangle \tag{2.5} \]
is the unperturbed density matrix, and we have assumed $V$ is a configurational energy and therefore diagonal in $r$. Therefore, we have
\[ Q = \lim_{P \to \infty} \int dr(1) \cdots \int dr(P) \left[ \prod_{\alpha=1}^{P} \rho_0(r^{(\alpha)}, r^{(\alpha+1)}; \epsilon\hbar) e^{-iV(r^{(\alpha)})} \right] \tag{2.6} \]
with the periodic or cyclic boundary condition, $r^{(P+1)} = r^{(1)}$. In the continuum limit, $P \to \infty$, the $P$-fold integrations are called “path” or “functional” integration. We’ll have more to say about this later. For now, note that
\[ Q_P = Q \text{ as given above with } P \text{ discrete points} \]

has the form of a partition function for a “ring polymer” with nearest neighbor interactions. Each site, $\alpha$, on the isomorphic polymer refers to a different “time slice” for the path of the system in a configuration space.

To be more explicit, let us take $H_0$ as the hamiltonian for a collection of $N$ free particles and $V(r) = V(r_1, r_2, \ldots, r_N)$ as the total potential energy. Then
\[ \rho_0(r, r'; \epsilon\hbar) = \prod_{i=1}^{N} E(r_i, r'_i; \epsilon) \tag{2.7} \]
Fig. 2. Quantum paths with $N = 2$ particles, one particle is light, the other is heavy. The configuration of the isomorphic necklace is a quantum path for the quantal particle.

where

$$E(r, r'; \epsilon) = \langle r | e^{-\epsilon r^2/2m} | r' \rangle$$

$$= \int \frac{dk}{(2\pi)^3} \langle r | k \rangle e^{-\epsilon k^2/2m} \langle k | r' \rangle$$

$$= \int \frac{dk}{(2\pi)^3} e^{ik(r-r')} e^{-\epsilon k^2/2m}$$

$$= (m/2\pi\hbar^2\epsilon)^{3/2} e^{-m|r-r'|^2/2\hbar^2\epsilon}$$

$$= \text{Gaussian with variance } \epsilon\hbar^2/m. \quad (2.8)$$

So,

$$Q_P = \int \left[ \prod_{i=1}^{N} \prod_{\alpha=1}^{P} dr_i^{(\alpha)} \right] \left[ \prod_{i=1}^{N} \prod_{\alpha=1}^{P} E(r_i^{(\alpha)}, r_i^{(\alpha+1)}; \epsilon) \right]$$

$$\times \exp \left[ -\epsilon \sum_{\alpha=1}^{P} V(r_1^{(\alpha)}, \ldots, r_N^{(\alpha)}) \right]. \quad (2.9)$$

Now we see that each quantum particle maps onto a ring polymer held together by Hooke's law springs. The variance of each nearest neighbor spring is $\epsilon\hbar^2/m$, and if unperturbed, the variance of the entire polymer or necklace would be $\beta\hbar^2/m$. This picture is illustrated in fig. 2.

The length $\lambda = (\beta\hbar^2/m)^{1/2}$ is the uncertainty spreading or thermal wavelength for a particle of mass $m.$

In the limit of a large mass (or a high temperature), all the points on the polymer or necklace coalesce to a single point in space. This is the classical
limit. The $E$-functions tend to localized delta functions. So

\[
Q_P \xrightarrow{\text{classical limit}} \int dr_1^{(1)} \cdots dr_N^{(1)} \left\{ \int dr_1^{(2)} \cdots dr_1^{(P)} \prod_{\alpha=1}^P E(r_1^{(\alpha)} - r_1^{(\alpha+1)}; \epsilon) \right. \\
\left. \cdots \int dr_N^{(2)} \cdots dr_N^{(P)} \prod_{\alpha=1}^P E(r_N^{(\alpha)} - r_N^{(\alpha+1)}; \epsilon) \right\} \\
\times \exp\left[ -\beta \sum_{i=1}^N V(\ldots r_i^{(1)} \ldots) \right].
\] (2.10)

Here, the “classical limit” means $\lambda$ is smaller than any important length over which $V$ changes. Thus, we have replaced $V(\ldots r_i^{(\alpha)} \ldots)$ with $V(\ldots r_i^{(1)} \ldots)$. Since $V$ does not change as $\alpha$ changes (since all the $r_i^{(\alpha)}$s coalesce to $r_i^{(1)}$), we can integrate over the coordinates $r_i^{(2)} \ldots r_i^{(P)}$ with only the $E$-functions contributing:

\[
\int dr_i^{(2)} \cdots dr_i^{(P)} E(r_i^{(1)} - r_i^{(2)}; \epsilon) \cdots E(r_i^{(P-1)} - r_i^{(P)}; \epsilon) \\
\times E(r_i^{(P)} - r_i^{(1)}; \epsilon) = \left( \frac{m}{2\pi\hbar^2\beta} \right)^{3/2}.
\] (2.11)

One way to understand this last result is to note the group property

\[
\rho_{\epsilon} \rho_{\epsilon'} = \rho_{\epsilon + \epsilon'}
\]

Here, $\rho_{\epsilon}$ denotes the $E$-function, i.e., $\rho_{\epsilon}(r, r'; \epsilon \hbar)$ for one particle. Alternatively, you can use the convolution theorem. Equations (2.10) and (2.11) combine to give

\[
Q_{\text{classical}} = Q_1 = \left( \frac{m}{2\pi\hbar^2\beta} \right)^{3N/2} \int dr_1 \cdots dr_N \exp[-\beta V(r_1 \ldots r_N)].
\] (2.12)

The $(N!)^{-1}$ factor we are accustomed to seeing in a partition function is missing because we haven’t yet accounted for indistinguishability of particles. Up to this point, we are considering only the wave-like or dispersive nature of quantum theory. Symmetry and indistinguishability are features we’ll get to later in section 3.
Thus far, we see that

\[(1 \text{ quantum particle}) \xrightarrow{\text{isomorphic mapping}} (P \rightarrow \infty \text{ classical particles})\]

which we can represent diagrammatically as

\[\text{Diagram showing isomorphic mapping between quantum and classical particles.}\]

The configuration space spanned by the \(P\) classical particles is the space spanned by a quantum particle obeying the uncertainty principle. As the mass \(m\) gets large, the uncertainty diminishes, the space is the same as that spanned by 1 classical particle. How big is the dispersion in space? Here are some numbers:

\[\lambda^2 = \frac{\beta h^2}{m} = 48\text{Å}^2(\text{amu})(\text{K})/Tm;\]  \hspace{1cm} (2.13)

thus, \(\lambda \sim 1\text{Å}\) for He at 10K, and \(\lambda \sim 17\text{Å}\) for an electron at 300K. The schematic pictures in fig. 3 are useful for qualitative considerations.

With fig. 3 in mind, the following questions are worth pondering.

**Question:** Isotope effects on equations of state are often measured. For example, \(\text{H}_2\text{O}\) and \(\text{D}_2\text{O}\) freeze at different temperatures (keeping \(p = 1\text{ atm}\)), and their density maxima appear at different temperatures too. Which substance freezes at the higher temperature and why?

**Question:** If you measure the radial distribution function, \(g(r)\), for dense supercritical fluid helium at 10K, what would it look like? Remember, \(\sigma_{\text{He}} \approx 2.5\text{Å}\) and \(\lambda \approx 1\text{Å}\) at 10K.

**Question:** Below 2 or 3K, \(\lambda \gtrsim \sigma \approx 2.5\text{Å}\) for He. What might happen? Think about paths which could exchange identity of particles. Do repulsive interactions between particles increase or decrease the temperature at which exchange might first become significant? Why is the critical temperature of an ideal Bose gas higher than the critical temperature of the superfluid transition temperature for real helium?

The last of these questions requires a significant generalization of the concepts we've discussed up to this point. You might consider it again after studying section 4.
2.2. Examples: electrons in liquids

With the isomorphism, the behavior of a solvated electron can be studied by classical simulation techniques. The closed shell atoms or ions in the liquid solvent may be treated as structureless classical particles \((P = 1)\) with these solvent particles coupled to the electron via electron–atom pseudopotentials. As we shall see in section 4.2, such a model is reasonable provided the excitation energies for electrons within an atom are large compared to the energy of the solvated electron. That separation in energy scales, corresponding to a separation in time scales too, allows one to integrate out intra-atomic fluctuations before considering explicitly the single excess electron. The determination of electron–atom pseudopotentials can be accomplished by quantum chemical electronic structure calculations [9] or by fitting parameterized potentials to empirical properties such as ionization potentials.
Fig. 4. A sequence of electron paths (isomorphic electron polymers) beginning with a non-equilibrated structure and ending with a localized electron in molten $\text{K}^+\text{Cl}^-$. The paths are projected on the $x-y$ plane, and the ions are not shown. The side length of one of the panels is approximately $10\text{Å}$. (Adopted from Parinello and Rahman, ref. [10].)

By using the isomorphism and this type of model, Parinello and Rahman [10] studied an electron in molten $\text{K}^+\text{Cl}^-$ at $T \approx 1000\text{K}$ with molecular dynamics. For the electron polymer in this system, they found that $P = 200$ was sufficient to accurately approximate the continuum limit, $P \to \infty$. The molten salt ions were treated classically, $P = 1$. Their molecular dynamics trajectory illustrated in fig. 4 shows the formation of a localized electron – a small polaron.

Notice that the polymer structure or electron path looks very rough. It is indeed a fractal object as is indicated by its spatial scaling: the variance for the polymer with $P$ beads is $P$ times the variance for the nearest neighbor separation.
Quantum processes in liquids

To quantify what is seen in this polaron formation, consider the spatial statistics of the polymer chain. The average density of sites on an isomorphic polymer is the average density of the quantum particle. This fact is arrived at by starting from eqs. (1.11) or (1.12), and discretizing the pictured path in the same way done to arrive at eq. (2.6). Similarly, by discretizing \( \rho(\mathbf{r}, \mathbf{r}'; t-t') \rho(\mathbf{r}', \mathbf{r}; \beta \hbar - t + t') \), you can show that the quantity

\[
\langle \delta(\mathbf{r}^{(\alpha)} - \mathbf{r}) \delta(\mathbf{r}^{(\alpha')} - \mathbf{r}') \rangle
\]

which describes pair correlations on the isomorphic polymer corresponds to the two-point quantum distribution function

\[
\langle \delta(\mathbf{r}(-it) - \mathbf{r}) \delta(\mathbf{r}(-it') - \mathbf{r}') \rangle
\]

for \( 0 \leq t - t' \leq \beta \hbar \) when

\[
t - t' = |\alpha - \alpha'| \beta \hbar / P. \tag{2.14}
\]

The second moment of that distribution is

\[
R^2(t - t') = \langle |\mathbf{r}(-it) - \mathbf{r}(-it')|^2 \rangle
= 2(|\mathbf{r}|^2 - \mathbf{r}(-it) \cdot \mathbf{r}(-it')). \tag{2.15}
\]

The magnitude squared notation refers to the vector dot product, not the magnitude of a complex number. Indeed \( R^2(t - t') \) is complex when analytically continued to real time.

For the free electron,

\[
R^2(t - t') = \lim_{\omega_0 \to 0^+} \sum_{n=-\infty}^{\infty} \frac{[1 - \cos \Omega_n (t - t')]^{-1}}{\beta m \Omega_n^2 + \omega_0^2},
= 3\lambda_0^2 (t - t') (\beta \hbar - t + t') / (\beta \hbar)^2, \quad 0 \leq t - t' \leq \beta \hbar. \tag{2.16}
\]

where \( \lambda_0^2 = \beta \hbar / m_e \). You can derive this result from the relations in section 1.3.

Figure 5 shows what Schmitker and Rossky [11] found when they studied the electron polymer in liquid water. The figure is an illustration of ground state dominance. In other words, hydrated electrons are trapped in deep potential wells created by arrangements of molecules. The physical basis for this phenomenon is self trapping: the localized electron biases the polar
Fig. 5. The root mean square length, $R(\tau)$, for the hydrated electron (adapted from Schnitker and Rossky, ref. [11]), and the isomorphic electronic polymer (pictured schematically on the left).

(or charged) environment to arrange in such a way to make the solvation of localized charge energetically favorable. If it were not for the entropy of the polymers (or equivalently, the electron kinetic energy), this energetic effect would cause the electronic charge to coalesce to a point.

2.3. How big is $P$?

We now consider important technical issues thus far omitted from our discussion of the examples. These issues pertain to the choice of $P$, and the most appropriate algorithms for carrying out numerical sampling of the isomorphic chains.

To see if $P$ is large enough to approximate the continuum limit (i.e., the exact result, $P \to \infty$), consider reducing its size. This reduction can be done by moving bonds as in the Migdal–Kadanoff procedure used to derive approximate renormalization group equations (see, for example, Parisi's text [5], section 7.6). Specifically, consider the diagram

representing a section of an isomorphic polymer with $P = \beta/e$. The vertical lines depict the potential energy Boltzmann factors, $\exp(-eV)$. Now consider moving every other one of these factors or bonds to an adjacent time slice or site on the isomorphic polymer. The bond moving gives
where $E$ is the error incurred by “misplacing” or moving half the potential energy bonds. Due to the completeness condition, integration over the intermediate points on the path, $\alpha - 1, \alpha + 1, \ldots$, yields an isomorphic polymer with $P/2$ beads.

Note that two Boltzmann factor bonds, each of strength $\epsilon V$, are equal to a single Boltzmann factor bond of strength $2\epsilon V$.

If $P/2$ is a large enough number of discretization points, then the bond moving error, $E$, should be of negligible size. To estimate its size, note that $|r^{(\alpha+1)} - r^{(\alpha)}|$ is of the order of $\lambda/\sqrt{P}$. Hence, by Taylor expansion

$$|E| \approx \left| \sum_{\alpha=1,3,5,\ldots} \epsilon[V(r^{(\alpha+1)}) - V(r^{(\alpha)})] \right|$$

$$\approx \beta F \frac{\lambda}{\sqrt{P}}, \quad (2.17)$$

where $F$ is the typical magnitude of the force, $-dV/dr$. The criterion for large enough $P$ is that $|E| \ll 1$; therefore, from (2.17) we see that

$$\frac{\lambda}{\sqrt{P}} \ll \text{any relevant length scale}. \quad (2.18)$$

Whether this condition is satisfied in practice can be judged by comparison with related but solvable problems. For example, Parrinello and Rahman [10] in their study of polaron formation examined first an electron in the field of a single cation. They showed that the $P = 200$ path integral calculation of the electron density well reproduced that obtained from the solution of Schrödinger’s equation with the same radially symmetrical potential. This comparison allows one to be reasonably confident that $P = 200$ is sufficient to treat the electron in the disordered liquid $K^+\text{Cl}^-$. 
Incidentally, Schrödinger wave function algorithms as opposed to path integral procedures have been used to treat single electron states in liquids [12]. Wave function procedures are limited due to finite size basis sets. Continuum states are not well treated, and there is lack of resolution at small (i.e., thermal) energy scales. These limitations may be insignificant for certain applications such as determining the qualitative structure of a solvated electron or rough locations of electronic absorption spectra. In these cases, wave function approaches can be of practical use.

When a system contains more than one type of quantal particle, decisions concerning the appropriate value of $P$ should be made separately for each component. For instance, with two particles, one of mass $m_1$ and the other of mass $m_2$, and $m_2 \gg m_1$, the paths of the heavier particle are more confined than for the lighter. As a result, it may be possible to perform more bond moving on the paths of particle 2 than those for particle 1. This idea, for example, leads to the picture of interacting isomorphic polymers shown in fig. 6. There the number of beads for particle 1, $P_1$, is more than that for particle 2, e.g. $P_2 = \frac{1}{3}P$ in the picture.

The ultimate reduction to $P = 1$ is the reduction used for the solvent in the solvated electron examples mentioned above. The $P = 1$ limit is the extreme classical or adiabatic limit. All quantal fluctuations are ignored. The disorder is static though annealed. No dynamics of the solvent remains with $P = 1$.

2.4. Avoiding $P$ too big

For many applications, extremely large values of $P$ may be required to satisfy (2.18). This necessity can present a problem for numerical work. When $P$ is very large, the nearest neighbor kinetic energy springs are very tight, so tight that the isomorphic chain possesses high frequency modes. These modes are difficult to equilibrate in a molecular dynamics trajectory.
Quantum processes in liquids

In Monte Carlo, the problem manifests itself with high rejection ratios for all but the shortest wavelength displacements.

One way to resolve the difficulties of stiff springs is to improve the quadrature used for the short time propagator. Indeed, eq. (2.4) is a primitive algorithm akin to a trapezoidal rule of integration. A number of improvements over eq. (2.4) exist based on perturbation theory [13], short time Taylor expansions [14], and interpolation procedures [15].

As an exercise, consider applying the primitive algorithm to a system with attractive Coulomb potentials. Any finite value of \( P \) is unacceptable leading to a collapse of the isomorphic polymer. The infinite negative energy is only overcome by the unfavorable entropy of localizing an infinite number of beads. An acceptable algorithm must account better for the continuum of points on the quantum path. One that does regularize the Coulomb potential is

\[
\rho(r, r', \epsilon \hbar) = \rho_0(r, r', \epsilon \hbar) \exp\left\{-\epsilon [\bar{V}_c(r) + \bar{V}_c(r')] / 2\right\},
\]

(2.19)

where

\[
\epsilon \bar{V}_c(r) = \int d\bar{r} \int_0^{\epsilon \hbar} \frac{dt}{\hbar} \rho_0(\bar{r}, \bar{r}; t)V(\bar{r})\rho_0(\bar{r}, r; \epsilon \hbar - t)
\]

(2.20)

The diagrammatic notation adopted here is self-evident. It is left as an exercise to show that eq. (2.19) follows from first-order perturbation theory of \( \rho(r, r', \epsilon \hbar) \) evaluated at \( r = r' \). Equation (2.19) is manifestly exact as \( \epsilon \to 0 \). Further, for Coulomb potentials, the integral in (2.20) can be performed analytically. For any finite \( P \), there are no divergences. Sprick et al. [16] have applied this short time propagator in their simulation of an electron in liquid ammonia.

Even with improved algorithms, the spatial extent of quantal fluctuations can be so large as to still require very large \( P \) and concomitant sampling over a multitude of length scales (or a multitude of energy scales). This case is found in the treatment of extended electrons in low temperature disordered materials. Here, the spatial extent of the electronic fluctuations can be as large as \( \lambda \), and this length can be much larger than the range of the potentials that perturb or scatter the electron throughout the material.

A form of staging can be used to efficiently sample many length scales. It corresponds to a step in a renormalization group Monte Carlo calculation. Or it can be viewed as a type of multigrid Monte Carlo method [17]. To discuss how it works, imagine dividing the isomorphic polymer into primary and secondary beads as pictured in fig. 7.
Fig. 7. Isomorphic necklace partitioned into primary and secondary beads.

The total $P$ is $P_1 \times P_2$, where $P_1$ is the number of primary beads, and $P_2 - 1$ is the number of secondary beads per link. With the beads partitioned, consider creating new configurations of the polymer in stages, long wavelength and short wavelength displacements, the former governed by the weight created by sampling over the latter. Specifically, if $W(r^{(1)}, \ldots, r^{(P)})$ is the total weight for the isomorphic polymer, then

$$W(r^{(1)} \ldots, r^{(P_{1})}) = \int d(\text{secondary coordinates})W(r^{(1)} \ldots, r^{(P)})$$

is the weight for the primary coordinates denoted by

$$(r^{(1)} \ldots, r^{(P_{1})}) \equiv r^{P_{1}}.$$

With this notation, the staging procedure is as follows:

1. Move primary beads, $r^{P_{1}} \rightarrow r^{P_{1}}$.
2. With primary beads fixed, sample secondary beads to determine

$$\tilde{W}(r^{P_{1}})/W(r^{P_{1}}).$$

Note, this sampling over the $P_1$ different subsections can be done in parallel.

3. Accept or reject $r^{P_{1}}$ according to a standard Monte Carlo rule such as the Metropolis algorithm.
4. Continue by moving the primary beads again.

This procedure is consistent with the correct rules of statistical sampling. Further, by controlling the primary beads, the staging procedure orchestrates long wavelength or collective waves. As a result, such long wavelength displacements are encountered frequently rather than serendipitously and infrequently. Hence, the staging method solves the problem
of simultaneous sampling of many length scales. Examples of its use are found in treatments of electron localization [18] and in a general sense, simulations of superfluid helium [19a] use a form of staging as well.

The analysis of superfluids involves another feature of quantum mechanics - exchange between indistinguishable particles. We turn to that issue now.

3. Indistinguishability and exchange

The cyclic structure of quantum paths or isomorphic polymers is a consequence of the trace, tr. operation that is associated with any observable. For identical particles, however, the trace does not require that each particle's path end where it itself started. It could end where another started.

For example, imagine a two particle system. The trace of the Boltzmann operator gives the paths

\[
\frac{1}{2} \int dr_1 \int dr_2 \left[ \begin{array}{c}
\text{path 1} \\
\text{path 2}
\end{array} \right]
\]

where we have noted that the symmetry number for 2 identical particles is 2. But for identical particles, we also have the paths

\[
\pm \frac{1}{2} \int dr_1 \int dr_2 \left[ \begin{array}{c}
\text{path 1} \\
\text{path 2}
\end{array} \right]
\]

corresponding to exchange of the indistinguishable objects. Since we are to sum up all possible paths, the two particle partition function is (pictured with \( P = 4 \))

\[
\begin{array}{c}
\text{path 1} \\
\text{path 2}
\end{array}
\quad \pm \quad \begin{array}{c}
\text{path 1} \\
\text{path 2}
\end{array}
\]

The "+" or "-" in the picture depends upon whether the particles are bosons or fermions, i.e., the sign of the wave function on exchange of particles. The dotted lines stand for the interparticle potentials that couple particles at equal times. Notice that if these interactions are repulsive and tend to exclude particle overlap, exchange is inhibited unless the temperature is low since then the paths can extend beyond the range of the interparticle equal time repulsions.
Fig. 8. A strong potential and its single particle energy levels.

For fermions, notice what happens if two particles end up at the same point at the same instant. Let \( \mathcal{C} \) denote that point. The sum of paths is then

\[
\begin{array}{c}
\begin{array}{c}
\infty \\
\cdots \\
\cdots \\
\cdots \\
\infty
\end{array}
\end{array}
\] - \[
\begin{array}{c}
\begin{array}{c}
\infty \\
\cdots \\
\cdots \\
\cdots \\
\infty
\end{array}
\end{array}
\] = 0
\]

This result is Pauli's exclusion principle.

It is an instructive exercise to use exchange paths to demonstrate that a bound pair of fermions make a boson. To carry out the demonstration you must assume that one does not resolve fluctuations on the small distance scales (or high energy scales) over which the fermions are bound.

Another important aspect of the cancellation exchange due to fermions has to do with ground states. Imagine paths for very low temperatures, i.e., \( \beta \to \infty \). The size of the necklace or polymer representing the quantal particle is then very large. Now suppose the quantal particle is trapped by a very strong potential as depicted schematically in fig. 8.

When we have this situation, the particle has excited state(s) with significantly higher energies than the ground state. Note too

\[
Q = \text{tr} e^{-\beta H} = \sum_n e^{-\beta \varepsilon_n} = e^{-\beta \varepsilon_0} \sum_{n>0} e^{-\beta \Delta \varepsilon_n},
\]

so that

\[
\lim_{\beta \to \infty} \frac{\ln Q}{\beta} = -\varepsilon_0.
\]

Now, what happens if two particles, two \emph{identical} particles, feel this strong potential, \( V(x) \)? They will both tend to be localized. The \emph{non}-exchange paths look like the paths in fig. 8 and the exchange paths look just the
same. In both cases, the chains are bunched together into a small region of space. The only differences are the boundary conditions indicating whether the tangled chains are actually two necklaces each with \( P \) beads, or one longer necklace with \( 2P \) beads. It is difficult to resolve the difference.

Thus, for fermions, the cancellation in the addition of

\[
\begin{align*}
\text{1} & \quad \text{2} \\
\text{-} & \quad \text{1} \quad \text{2}
\end{align*}
\]

and

\[
\begin{align*}
\text{1} & \quad \text{2} \\
\text{1} & \quad \text{2}
\end{align*}
\]

can be quite substantial. How much so? Consider the elementary estimate

\[
Q = Q_{\text{no ex}} - Q_{\text{ex}} \approx e^{-\beta(\Delta\varepsilon_1 + 2\varepsilon_0)}. \tag{3.4}
\]

But

\[
Q_{\text{no ex}} \approx e^{-\beta 2\varepsilon_0} \tag{3.5}
\]

and

\[
Q_{\text{ex}} \approx e^{-\beta \varepsilon_0}. \tag{3.6}
\]

So that,

\[
\frac{Q_{\text{no ex}} - Q_{\text{ex}}}{Q_{\text{no ex}}} \approx e^{-\beta \Delta\varepsilon_1}. \tag{3.7}
\]

In the Bose ground state, particles can condense to the same single particle state. But fermions cannot. The cancellation that disallows the condensation for the fermions is so extensive that straightforward calculation of its effects is impossible: \( Q_{\text{no ex}} \) and \( Q_{\text{ex}} \) agree to one part in \( \exp(\beta \Delta\varepsilon_1) \), and it's the difference we care about. The problem of computing the effects of the cancellation is known as the alternating weights or sign problem. It is a fundamental and generally unsolved problem. Alternating weights or sign oscillations also appear when treating real time quantum dynamics.
In that context, we will discuss a numerical sampling procedure that does solve the problem in section 7.

In general, the quantum partition function for \( N \) particles can be written as

\[
Q = \sum_{N_1, N_2, \ldots, N_s \text{ such that } \sum_s N_s = N} (\pm 1)^{N_s} \text{partition function for mixture with } N_1 \text{ monomers, } N_2 \text{ exchange dimers, } N_3 \text{ exchange trimers, } \ldots
\]

(3.8)

where, for example, before integrating over coordinates for time slice 1, a trimer looks like

![Diagram of a trimer](image)

The symmetry number for the partition function with \( N_1 \) monomers, \( N_2 \) dimers and so on is

\[
\prod_s \frac{1}{N_s!} \frac{1}{s^{N_s}}.
\]

Figure 9 illustrates the contributions to \( Q(N) \) when \( N = 3 \).

For fermions, it is as if, in the grand canonical ensemble, the chemical potential of the exchange \( n \)-mer is complex.

\[
\mu_n = n\mu_1 + i\pi(n - 1).
\]

(3.9)

For bosons, however, exchange paths add rather than subtract, and a rather spectacular effect can occur at low enough temperatures. The extent or length of a typical single particle path is then relatively long. As such, there can be a relatively small entropic cost for joining particles in exchange dimers, trimers, and so on. Indeed, one may identify a finite
Fig. 9. Isomorphic polymers with $N = 3$. Notice that the symmetry numbers associated with these diagrams ensure that distinct paths for the equivalent particles are not multiply counted.

but low enough temperature where in the Boltzmann weighted sum over all paths, the probability of observing an $n$-mer approaches that for an $(n - 1)$-mer. This occurrence corresponds to a Bose condensation (see, for example, ref. [8]), and Feynman argued that it is the mechanism for superfluidity. [19b] The recent Monte Carlo calculations by Ceperley and Pollock [19a] have quantified Feynman’s ideas by carrying out exactly the calculational program he prescribed. Their calculations of observables like the superfluid transition temperature for helium are in excellent agreement with experiment. Incidentally, Feynman also tried to treat superconductivity with these procedures, but he failed. He couldn’t solve the fermion sign problem!

4. Analytical considerations

Up to this point, much of our emphasis has been on numerical procedures. Now we focus on the types of things that can be derived analytically.

4.1. Continuum limit and the action functional

First, let’s imagine we can actually perform the $P 	o \infty$ or $\epsilon 	o 0$ limit. We have

$$ (r_i^{(n)} - r_i^{(n-1)}) / \epsilon \hbar \longrightarrow \dot{r}_i(t). \quad (4.1) $$

where $t = (\alpha / P) \beta \hbar$ is a Euclidean time. From this, it follows that

$$ m |r_i^{(n)} - r_i^{(n-1)}|^2 / 2 \hbar^2 \epsilon \longrightarrow \epsilon \left[ \frac{1}{2} m \dot{r}_i^2(t) \right]. \quad (4.2) $$
Furthermore,

\[
\sum_{\alpha=1}^{P} m|\vec{r}_i^{(\alpha)} - \vec{r}_i^{(\alpha-1)}|^2 / 2\hbar^2 \epsilon \rightarrow \int_0^{2\hbar} \frac{dt}{\hbar} \left[ \frac{1}{2} m \ddot{r}_i^2 (t) \right].
\]  

(4.3)

Also

\[
\epsilon \sum_{\alpha=1}^{P} V(\vec{r}_1^{(\alpha)}), \vec{r}_2^{(\alpha)}, \ldots, \vec{r}_N^{(\alpha)} \rightarrow \int_0^{2\hbar} \frac{dt}{\hbar} V[\ldots, \vec{r}_j(t), \ldots].
\]  

(4.4)

Put all this together with the “metric” convention

\[
\lim_{\hbar \rightarrow \infty} \left[ \int \left( \frac{m}{2\pi\hbar^2 \epsilon} \right)^{3/2} d\vec{r}_1^{(1)} \ldots \int \left( \frac{m}{2\pi\hbar^2 \epsilon} \right)^{3/2} d\vec{r}_P \right] \equiv \int \mathcal{D}\vec{r}_i(t)
\]  

(4.5)

and we have the path integral

\[
Q = \int \mathcal{D}r_1(t) \ldots \int \mathcal{D}r_N(t) \exp\{S[\vec{r}_1(t), \ldots, \vec{r}_N(t)]\}.
\]  

(4.6)

where

\[
S[\ldots, \vec{r}_j(t), \ldots] = -\beta \int_0^{2\hbar} \frac{dt}{\beta\hbar} \left\{ \sum_{\alpha=1}^{N} \frac{1}{2} m |\dot{r}_j(t)|^2 + V[\ldots, \vec{r}_j(t), \ldots] \right\}
\]  

(4.7)

is the action functional for imaginary time in units of \(\hbar\) with \(t\) between 0 and \(\beta\hbar\). Unless indicated otherwise, the path integrations are over all cyclic paths.

Equation (4.6) is the partition function in the absence of exchange. Inclusion of exchange and particle indistinguishability follows the same lines as described in section 3. We omit that feature now for the sake of notational simplicity.

The weight governing paths in the continuum limit is the functional \(\exp\{S[\ldots, \vec{r}_j(t), \ldots]\}\). The most probable paths are those which maximize the imaginary time action. That is

\[
\delta S / \delta \vec{r}_i(t) = 0.
\]  

(4.8)
which implies

\[ m \ddot{\mathbf{r}}_j(t) = \frac{\partial V}{\partial \mathbf{r}_j(t)}. \]  

Equation (4.9) corresponds to classical equation of motion in an "upside down" potential, i.e., Newton's laws for a system with potential energy \(-V\). It is the imaginary time that turns over the potential. Later we will see that for real time, the extremal paths correspond to classical trajectories in the actual potential.

To be consistent with the Heisenberg operator notation of section 1, paths in Euclidean time should be denoted by \( \mathbf{r}_j(-it) \) rather than \( \mathbf{r}_j(t) \). In eqs. (2.14) and (2.15), for example, we have made the effort to be consistent in this way. But such consistent notation is not standard! In the interest of notational simplicity, we therefore follow convention and omit factors of \( \sqrt{-1} \) provided the intent of working in Euclidean time is perfectly clear. When the omission might result in ambiguity, we will resort to the slightly more cumbersome notation with the factors of \( \sqrt{-1} \) inserted.

### 4.2. Influence functional

In the discrete case or the continuum limit, we are often faced with trying to understand a few quantal degrees of freedom coupled to a bath as illustrated in fig. 10.

The picture we have drawn corresponds to the partition function

\[
\int dr^{(1)} \ldots dr^{(\alpha)} \ldots dr^{(P)} \int dR^{(1)} \ldots dR^{(\alpha)} \ldots dR^{(P)} \\
\times \left[ \prod_{\alpha=1}^{P} \rho_0 \left( r^{(\alpha+1)}, r^{(\alpha)}; \epsilon \right) \right] \times \left[ \prod_{\alpha=1}^{P} \rho_B \left( R^{(\alpha+1)}, R^{(\alpha)}; \epsilon \right) \right] \\
\times \prod_{\alpha=1}^{P} \exp[-\epsilon V(r^{(\alpha)}, R^{(\alpha)})],
\]

where \( \rho_0(r, r'; \epsilon) \) stands for the unperturbed density matrix of the system of interest and \( \rho_B(R, R'; \epsilon) \) is that for the bath and both \( r \) and \( R \) can be multidimensional. If we now integrate out the bath keeping the path \( r(t) \)
fixed we get the influence functional. That is, we let

$$Q_B e^{-\beta \Delta w[r(t)]} = \int DR(t) \exp\left\{ S_B[R(t)] - \int_0^{\beta h} \frac{dt}{\hbar} V[r(t), R(t)] \right\},$$

(4.10)

so that the remaining integral is

$$Q = Q_B \int DR(t) \left\{ e^{S_0[r(t)]} e^{-\beta \Delta w[r(t)]} \right\},$$

(4.11)

where the term in curly brackets is the weight for paths $r(t)$, and

$$Q_B = \int dR^{(1)} \cdots \int dR^{(P)} \prod_{\alpha=1}^{P} \rho_B(R^{(\alpha+1)}, R^{(\alpha)}; \epsilon)$$

(4.12)

$$= \int DR(t) \exp(S_B[R(t)])$$

(4.13)

is the bath partition function. Clearly,

$$e^{-\beta \Delta w[r(t)]} = \exp\left[ -\beta \Delta w \left( r^{(1)}, r^{(2)}, \ldots, r^{(P)} \right) \right]$$

$$= \left\langle \exp\left[ -\epsilon \sum_{\alpha=1}^{P} V \left( r^{(\alpha)}, R^{(\alpha)} \right) \right] \right\rangle_B$$

$$= \left\langle \exp\left\{ -\int_0^{\beta h} \frac{dt}{\hbar} V[r(t), R(t)] \right\} \right\rangle_B.$$
where $\langle \ldots \rangle_B$ is the average in the pure bath.

From the discrete representation, we see that the calculation of the influence functional,

$$g[r(t)] = e^{-\beta \Delta w[r(t)]} \quad (4.15)$$

is the standard problem of solvation for flexible species in liquids. The influence functional arises from integrating over bath or secondary degrees of freedom – subjugating these degrees of freedom to the path of the primary variable(s). The result of these integrations, $\Delta w[r(t)]$, can be viewed as bath induced couplings between different time slices on the path $r(t)$ as illustrated in fig. 11. These couplings are therefore memory effects much like those encountered when studying the generalized Langevin equation. Here, however, the memory is in imaginary time. Analytic continuation to real time leads to the quantum generalization of friction.

In general, $\Delta w[r(t)]$ is not pair decomposable. The reason has to do with the non-linear response of the bath. This fact will become clear from the example given below and also the discussion of excess electrons in section 6.

Suppose the “tagged degrees of freedom” were the coordinates of two identical particles (e.g., a pair of electrons with the same spin). The influence functional would dress the paths for the pair of particles, both for the case of exchange paths and for the case of non-exchange paths. Does the influence functional differ for these two cases?

For a specific example, consider a solute with a fluctuating dipole in a dielectric solvent. The latter is a material with fluctuating electric fields. The coupling between the tagged dipole and the solvent is

$$V = -m\epsilon, \quad (4.16)$$

where $m$ is the dipole, and $\epsilon$ is the component of the local electric field along the dipole axis. This electric field depends upon the solvent coordinates,
and it fluctuates as the coordinates change. Accordingly, in the absence of the solute, the average local field is zero (i.e., $\langle \mathcal{E} \rangle_{B=0}$). The influence functional is

$$y[m(t)] = \left\langle \exp \left[ \int_0^{3\hbar} \frac{dt}{\hbar} m(t) \mathcal{E}(t) \right] \right\rangle_B \approx \exp \left( \frac{1}{2} \int_0^{3\hbar} \frac{dt}{\hbar} \int_0^{3\hbar} \frac{dt'}{\hbar} m(t) m(t') \langle \mathcal{E}(t) \mathcal{E}(t') \rangle_B \right). \quad (4.17)$$

The approximation in eq. (4.17) is the neglect of terms beyond second order in the cumulant series. Third and higher order cumulants would couple dipolar fluctuations at three or more points in time. The approximate form for $y[m(t)]$ would actually be exact if $\mathcal{E}(t)$ was a Gaussian variable. Gaussian statistics is obeyed rigorously only if the solvent is linear (i.e., a bath of harmonic oscillators) and if $\mathcal{E}$ is a linear combination of the oscillator variables. Nothing in nature is so simple, but the model can still be of quantitative use. The accuracy of the Gaussian model can be examined by studying deviations from linear response. A Gaussian bath has only linear response since harmonic oscillators have only linear restoring forces. Tests performed by computer simulation have demonstrated that the Gaussian model is, for example, an accurate description of aqueous solvation of localized charge distributions [20]. The model is therefore a reasonable one to adopt for a number of physical situations.

As an exercise, you can show that if $\{x_i\}$ is a set of Gaussian random variables, then

$$\left\langle \exp \left( \sum_{i=1}^n a_i x_i \right) \right\rangle = \exp \left( \sum_{i=1}^n a_i \langle x_i \rangle + \frac{1}{2} \sum_{i,j=1}^n a_i a_j \langle \delta x_i \delta x_j \rangle \right) \quad (4.18)$$

with $\delta x_i = x_i - \langle x_i \rangle$. This result can be used to generate all the moments of a Gaussian distribution. Equation (4.17) follows from (4.18).

Stability of the Gaussian bath requires that the Euclidean time correlation function $\langle \mathcal{E}(t) \mathcal{E}(t') \rangle_B$ be positive definite. That is, $\langle \mathcal{E}^{(\alpha)} \mathcal{E}^{(\gamma)} \rangle_B$ with $1 \leq \alpha, \gamma \leq P$ must be a positive definite matrix. In view of this fact, we see that $y[m(t)]$ in eq. (4.17) favors large dipoles over small dipoles. The stabilization of a dipole due to the solvation by a dielectric environment is a familiar effect. There are many consequences. For example, it leads to a condensed phase renormalization of atomic polarizability. This example is discussed below in section 4.3. In nonlinear systems, the stabilization
of dipoles can lead to broken symmetry such as the formation of dipolar atoms. Indeed, an argument along these lines was used [21] to explain the computer simulation observation [22] that a Li atom in a polar solvent possesses a permanent dipole. Another example of broken symmetry induced by dipolar solvation is the quenching of electronic tunneling. This phenomenon, a type of self trapping, is discussed at length in section 5 below.

As we will see in section 5, it is the low frequency, or slow modes of the bath that are primarily responsible for breaking symmetry of tunneling systems. Suppose, however, the dynamics of the bath is characterized by only high frequency motions. Then, the Euclidean time \( \langle \mathcal{E}(t)\mathcal{E}(t') \rangle_B \) is short ranged in \( t - t' \) so that memory effects are negligible and \( \ln y[m(t)] \) in eq. (4.17) is essentially local in time. We know from our discussion of ground state dominance in section 1 that \( \langle \mathcal{E}(t)\mathcal{E}(t') \rangle B \) is effectively local under such circumstances from our discussion of ground state dominance in section 1. Hence, when the bath is characterized by relatively high excitation frequencies, the influence of the bath is to add a pseudopotential energy to the hamiltonian. For the specific example of eq. (4.17), this potential energy function is

\[
\frac{1}{2} \text{(const)} \cdot m^2
\]

where

\[
\text{(const)} = \int_0^{\beta \hbar} \frac{dt}{\hbar} \langle \mathcal{E}(0)\mathcal{E}(t) \rangle_B.
\]

Pseudopotential models of a more complicated sort are used in treating the scattering of slow electrons from closed shell atoms and molecules. The justification for such models is that the intra-atomic excitation energies are large compared to those of the extra electron. If not, the coupling between the two would be nonlocal in time and not be describable in terms of a hamiltonian and a simple potential energy function. At short distances, of course, the form of electron–atom pseudopotentials involve electron exchange. This feature – exchange between the bath and the tagged particle – complicates and extends the picture of an influence functional from that we have described here.

4.3. Quantum theory of polarization

Now we are ready to do a path integral calculation for a specific physical problem. We treat the polarizability of atoms in a liquid. We use the model
of harmonically bound dipoles embedded in hard spheres as illustrated in fig. 12.

Each particle contains a harmonic oscillating dipole, \( m \). The action for such an oscillator—a Drude oscillator—when uncoupled to the environment is

\[
S_0 = -\frac{1}{\hbar} \int_0^{\beta \hbar} dt' \left[ |\dot{m}(t')|^2 / 2a_0 \omega_0^2 + |m(t')|^2 / 2\alpha_0 \right].
\]  

(4.19)

Here, \( 1/\alpha_0 \) is the oscillator force constant and \( (1/\omega_0^2) \) the reduced mass. The distribution of paths for the dipole when unperturbed by the environment is

\[
s^{[0]}[m(t)] \propto \exp\{S_0[m(t)]\}.
\]  

(4.20)

To perform averages with this distribution, we have to perform Gaussian path integrals. How do we do that? Consider the most general quadratic action functional

\[
S[x(t)] = \frac{1}{2} \int_0^{\beta \hbar} \frac{dt}{\beta \hbar} \int_0^{\beta \hbar} \frac{dt'}{\beta \hbar} c(t-t') x(t)x(t').
\]  

(4.21)

With Fourier components

\[
\hat{x}_n = \int_0^{\beta \hbar} \frac{dt}{\beta \hbar} x(t) e^{i\Omega_n t}, \quad \Omega_n = \frac{2\pi n}{\beta \hbar},
\]  

(4.22)

we have

\[
x(t) = \sum_{n=-\infty}^{\infty} \hat{x}_n e^{-i\Omega_n t}.
\]  

(4.23)

Hence,

\[
S[x(t)] = \frac{1}{2} \int_0^{\beta \hbar} \frac{dt}{\beta \hbar} \int_0^{\beta \hbar} \frac{dt'}{\beta \hbar} c(t-t') \sum_{n,l} \hat{x}_n \hat{x}_l e^{-i(\Omega_n t + \Omega_l t')}
\]  

\[
= -\frac{1}{2} \sum_n \hat{c}_n |\hat{x}_n|^2 = S[\{\hat{x}_n\}].
\]  

(4.24)
Quantum processes in liquids

Since the Jacobian of the transformation between \( x(t) \) and \( \{ \hat{x}_n \} \) is unity,

\[
D x(t) s_G[x(t)] = \{ d\hat{x}_n \} s_G[\{ \hat{x}_n \}].
\] (4.25)

(The subscript "G" stands for "Gaussian." ) Further, since the different \( \hat{x}_n \)'s are uncoupled, we need consider only one at a time

\[
s_G[\{ \hat{x}_n \}] = \prod_n s_G(\hat{x}_n)
\] (4.26)

with

\[
s_G(\hat{x}_n) \propto e^{-\frac{1}{2} c_n |\hat{x}_n|^2}.
\] (4.27)

Note, however, \( \hat{x}_n^* = \hat{x}_{-n} \) so for \( n \neq 0 \), the \( \hat{x}_n \)'s have two components (i.e., real and imaginary parts). Both variables must be integrated over, and often their polar coordinate representation is most convenient. More details are given in the Appendix. The result is

\[
\langle |x_n|^2 \rangle = 1/c_n
\] (4.28)

or

\[
\langle x(t)x(t') \rangle = c^{-1}(t-t').
\] (4.29)

where \( c^{-1}(t-t') \) is the inverse Fourier transform of \( 1/c_n \); it is the functional inverse of \( c(t-t') \).

As an alternative, you may use the discrete form

\[
S[x(t)] \rightarrow \frac{1}{2} \sum_{\alpha,\gamma=1}^{P} \frac{1}{P^2} c_{\alpha\gamma} x^{(\alpha)} x^{(\gamma)}.
\]

The \( x^{(\alpha)} \)'s are a set of Gaussian variables with variance

\[
\frac{1}{P^2} \langle x^{(\alpha)} x^{(\gamma)} \rangle = (c^{-1})_{\alpha\gamma}.
\]

where \( c^{-1} \) is the inverse of the matrix with elements \( c_{\alpha\gamma} \). To invert the matrix you might diagonalize it first. To do that, you'll use Fourier transforms so, it's the same story as above.
With the Fourier analysis, the independent Drude oscillator action can be written as

$$S_0 = -\sum_n \left[ \frac{\beta \Omega_n^2}{2\alpha_0 \omega_0^2} + \frac{\beta}{2\alpha_0} \right] |\hat{m}_n|^2. \quad (4.30)$$

where $|\hat{m}_n|^2 = m_n \cdot m_{-n}$. Now, remember that each $\hat{m}_n$ is a vector in 3D space, and each component has a real and imaginary part. Hence, from the law of Gaussian statistics,

$$\langle 3/\beta \alpha_n^{(0)} \rangle \equiv \langle |\hat{m}_n|^2 \rangle = (3/\beta) \frac{\alpha_0}{1 + \Omega_n^2/\omega_0^2}. \quad (4.31)$$

where $\alpha_n^{(0)}$ is the unperturbed oscillator polarizability at a frequency $\Omega_n$. The Lorentzian form of (4.31) is to be expected from our previous analysis of the harmonic oscillator. See eq. (1.22). Now we see where it comes from in terms of path integrals.

To place this result in a more general context, note that polarizability is defined according to

$$\langle m(t) \rangle_{\text{induced}} = \int_{-\infty}^{\infty} dt' \alpha(t-t') E(t'). \quad (4.32)$$

for real times, or equivalently, with imaginary time frequencies,

$$\langle \hat{m}_n \rangle_{\varepsilon_n} = \alpha^{(n)} \varepsilon_n. \quad (4.33)$$

Here, $E(t)$ stands for an electric field acting on a molecule with polarizability $\alpha(t)$, and $m(t)$ refers to the dipole component in the direction of $E(t)$. The standard connection between fluctuation and response then shows $\beta \langle |\hat{m}_n|^2 \rangle = \alpha_n$ in one dimension, and

$$\langle \beta/3 \rangle \langle |\hat{m}_n|^2 \rangle = \alpha_n \quad (4.34)$$

in three.

The tagged Drude oscillator is in a medium (with other Drude oscillators). The medium changes the polarizability of the molecule from $\alpha_0^{(n)}$ to a renormalized $\alpha^{(n)}$. We wish to compute this renormalization.

In the linear response approximation, the influence functional is of the form given in eq. (4.17). It is pair decomposable. From the Fourier analysis, therefore, this approximation in three dimensions leads to

$$y[m(t)] \propto \exp \left[ + \sum_n \beta |\hat{m}_n|^2 E_n \right], \quad (4.35)$$
where $E_n$ is the Euclidean time Fourier transform of $\langle \mathcal{E}(t) \cdot \mathcal{E}(t') \rangle_B$. It is a property of the medium, and it is positive.

Equations (4.30), (4.31) and (4.35) give

$$\mathcal{D}m(t) \cdot s(m(t)) \propto \prod_n [d\hat{m}_n s(\hat{m}_n)].$$

with

$$s(\hat{m}_n) \propto \exp \left\{ -\frac{\beta}{2} \left[ \frac{1}{\alpha_n^{(0)}} - 2E_n \right] |\hat{m}_n|^2 \right\}.$$  

Thus, the Gaussian average gives

$$\langle \beta/3 |m_n|^2 \rangle = \frac{\alpha_n^{(0)}}{1 - 2\alpha_n^{(0)} E_n}$$

which, according to eq. (4.34) is the desired expression for a solvent renormalized polarizability. Notice that because $E_n$ is positive, $\alpha^{(n)} > \alpha^{(0)}$. In other words, the effect of the fluctuating environment is to reduce the restoring force constant of the Drude oscillator.

Analytic continuation of eq. (4.38) leads to the Fourier transform of the electronic dipole autocorrelation function of a solvated molecule. The analytically continued expression has been used to interpret electronic spectra of molecules in liquids [23]. Generalization of the model to include fluctuating quadrupoles provides a theory for "collisionally induced" spectra [24]. Since the liquid medium surrounding the tagged solute also contains quantum fluctuating dipoles, the solvent should be treated self-consistently with the same theory as the solute. In that case, $E_n = E[|m_n|^2]$. The resulting algebraic equation for $|m_n|^2$ leads to a theory for absorption bands and also metal insulator transitions [25]. The latter has been associated with the divergence that occurs when $0 = 1 - 2\alpha_n^{(0)} E_n$ in the limit of low frequencies. This divergence occurs because at strong enough couplings between dipole oscillators, the Drude model hamiltonian will become unstable, and the dipoles will dissociate.

Equation (4.38) has the standard form of a random phase approximation. That is, fluctuations of a given frequency are renormalized by the bath modes of that same frequency only. This feature is a characteristic of a linear theory. A slight generalization of this linear theory of polarization is sometimes called the dynamical "mean spherical approximation" (MSA) [26]. The reasons behind this terminology have to do with mathematical
connections between this theory and the classical MSA integral equation for dipolar fluids. See ref. [3]. The mathematical structure of the theory is quite versatile. It can be adapted, for example, to estimate band structures for electrons in liquids [27]. In these contexts of quantal fluctuations and solvent dynamics, however, the jargon would appear confusing as the reader might ponder over what quantities are “mean” or “spherical.”

Through perturbation treatments, nonlinear effects can be incorporated into a theory like eq. (4.38) [28]. There are, however, classes of phenomena so intrinsically nonharmonic that perturbation theory alone does not provide a satisfactory treatment of nonlinearities. Tunneling is one such case. We turn to that now.

5. Tunneling systems

In this section we consider the effects of a fluctuating environment on tunneling. The discussion is relevant to many natural phenomena. Electron transfer, mixed valency and tautomerization are a few examples. We begin by discussing the physics of a two state tunneling system, first with wave functions and then by path methods. The latter are most easily adapted to examine the role of fluctuations.

5.1. Elementary ideas

Consider the static and symmetric bistable potential $V_0(x)$ pictured in fig. 13. The barrier between the stable states is very high, and so the left and right regions, $|l\rangle$ and $|r\rangle$, are weakly coupled. If uncoupled, the ground state for that potential would be doubly degenerate. Let $E_0$ denote the energy of that degenerate level. A first excited level at energy $E_0 + \Delta E$ would also be doubly degenerate. The degeneracies are removed through the interactions between the left and right regions. We use $K$ to denote the interaction or coupling; i.e., $K$ is the energy associated with resonance between $|l\rangle$ and $|r\rangle$. An elementary analysis shows that $2K$ is the splitting of the ground state degeneracy. Since this splitting is due to tunneling from $|l\rangle$ to $|r\rangle$, $2K$ is called the “tunnel splitting.”

We assume $\Delta E$ is a relatively large energy. Specifically, as illustrated in fig. 13,

$$\Delta E \gg K. \quad (5.1)$$

Further, we assume it is large compared to thermal energies, $k_B T$. In some sense, therefore, we expect that $\Delta E$ should be an unimportant energy scale, and that only the two low lying levels should be relevant.
Note that $2\pi \hbar / \Delta E$ is the period for oscillations of a quantal particle within either the left or right well. Similarly, $2\pi \hbar / 2K$ is the period for a localized wave packet to oscillate between the left and right wells. Thus, eq. (5.1) implies a separation in time scales where the movement from $|l\rangle$ to $|r\rangle$ occurs much less frequently than intra-well fluctuations. We will see that when considering the low frequency dynamics (i.e., the dynamics occurring on time scales of the order of $\hbar / K$ or more) the high frequency intra-well dynamics can be removed from explicit consideration by integrating out high frequency fluctuations. It is in this sense, when considering low frequency processes, that the higher energy states are irrelevant. To conceive of such integrations, it is useful to adopt a path or functional integral representation. We do that now.

5.2. Path ways

Figure 14 illustrates a typical path for a quantal particle with $V_0(x)$. The passages between $|l\rangle$ and $|r\rangle$ are fleeting because the barrier is assumed high. Hence, the particle will spend little Euclidean time in the barrier region. The rapid passages are sometimes referred to as "instantons," or for obvious pictorial reasons, they are also called "kinks." Due to the trace property, quantum paths contributing to partition functions must end where they begin. As a result, kinks come in pairs.

Owing to the separation in time scales, $\hbar / \Delta E \ll \hbar / K$, we can find a time $\epsilon \hbar$ such that

$$\frac{\hbar}{\Delta E} \ll \epsilon \hbar \ll \frac{\hbar}{K}.$$  \hspace{1cm} (5.2)

Suppose intra-well dynamics is not of interest, and only well-to-well dynamics is relevant. Then time $\epsilon \hbar$ can serve as the elementary or infinitesimal time scale. Figure 14 illustrates this idea. In this course grained view of time, instantons or kinks are instantaneous events.
Fig. 14. Quantum paths in the bistable potential $V_0(x)$.

To quantify the picture consider the partition function

$$Q = \int \mathcal{D}x(t) \exp\{\mathcal{S}[x(t); \beta\hbar]\}.$$  \hspace{1cm} (5.3)

We will break the integrations into sections. Specifically,

$$Q = \int \mathcal{D}x(t) \times \exp\left\{-\left(\int_0^{t \hbar} \frac{dt}{\hbar} + \int_{t \hbar}^{2t \hbar} \frac{dt}{\hbar} \ldots \int_{(P-1)t \hbar}^{Pt \hbar} \frac{dt}{\hbar}\right) \left(\frac{1}{2} m \dot{x}^2(t) + V_0(x(t))\right)\right\}$$

$$= \int_{x(0)}^{x(Pt \hbar)} \mathcal{D}x(t) \int_{x(t \hbar)}^{x(2t \hbar)} \mathcal{D}x(t) \ldots \int_{x((P-1)t \hbar)}^{x(Pt \hbar)} \mathcal{D}x(t)$$

$$\times \prod_{\alpha=0}^{P} \exp\left\{-\int_{\alpha t \hbar}^{(\alpha+1)t \hbar} \frac{dt}{\hbar} \left[\frac{1}{2} m \dot{x}^2(t) + V_0(x(t))\right]\right\}. \hspace{1cm} (5.4)$$

Now imagine doing the integration for one of the elements,

$$\int_x^{x'} \mathcal{D}x(t) e^{\mathcal{S}[x(t); \hbar]} = \langle x | e^{-\hbar H} | x' \rangle. \hspace{1cm} (5.5)$$

Since $\hbar \epsilon \gg \hbar / \Delta E$, the integral samples (essentially completely) fluctuations within a well, so,

$$\langle x | e^{-\hbar H} | x' \rangle = e^{-\hbar E_0} \phi_\sigma(x) \phi_\sigma(x')$$

$$\equiv \phi_\sigma(x) \phi_\sigma(x'), \quad x \text{ and } x' \text{ same side}. \hspace{1cm} (5.6a)$$

Here, $\phi_\sigma(x)$ is the ground state basis function localized at the left ($\sigma = -1$) or the right ($\sigma = +1$), and we have chosen $E_0$ as the zero of energy.
Similarly,

\[
\langle x | e^{-\epsilon H} | x' \rangle = T \phi_\sigma(x) \phi_{\sigma'}(x') \\
\equiv \epsilon K \phi_\sigma(x) \phi_{\sigma'}(x'), \quad x \text{ and } x' \text{ different sides, } \sigma \neq \sigma'.
\]

(5.6b)

The fact that \( T \) is linear in \( \epsilon \) (i.e., the fact that \( T \) is extensive in the time duration of the short path) can be understood from the other inequality, \( \epsilon \ll 1/K \), and the expansion of \( \exp(-\epsilon H) \) to linear order in \( \epsilon \).

With eqs. (5.4) and (5.6), the high frequency dynamics has been integrated out. The only relevant dynamics that remains is characterized by

\[
\sigma(x) = \begin{cases} 
1, & x \text{ in right well;} \\
-1, & x \text{ in left well}.
\end{cases}
\]

(5.7)

It is, in effect, a spin variable.

With it, the partition function becomes

\[
Q = \sum_{\sigma^{(1)}, \sigma^{(2)}, \ldots, \sigma^{(P)}} \prod_{\alpha=1}^{P} M_{\sigma^{(\alpha)}, \sigma^{(\alpha+1)}}.
\]

(5.8)

where

\[
M_{\sigma\sigma'} = \begin{cases} 
1, & \sigma = \sigma', \\
T, & \sigma \neq \sigma'.
\end{cases}
\]

(5.9)

and as usual, periodic boundary conditions are employed. Equivalently.

\[
Q = Tr(M)^P, \quad M = \begin{pmatrix} 
1 & \epsilon K \\
\epsilon K & 1
\end{pmatrix}.
\]

(5.10)

Equation (5.10) is the partition function of a one-dimensional Ising model. It is a somewhat abnormal Ising model, however, in the sense that the coupling strength for nearest neighbor interactions scales as \( \ln(\epsilon K) \). Nevertheless, the model can still be solved by the usual transfer matrix method. In particular,

\[
Q = \lambda_+^P + \lambda_-^P.
\]

(5.11)
where $\lambda_{\pm}$ are the eigenvalues of $M$. That is,

$$0 = \det \begin{bmatrix} 1 - \lambda_+ & \epsilon K \\ \epsilon K & 1 - \lambda_- \end{bmatrix}$$

which implies

$$\lambda_{\pm} = 1 \pm \epsilon K.$$ 

Thus,

$$Q = (1 + \epsilon K)^P + (1 - \epsilon K)^P \xrightarrow{P \to \infty} [e^{-\beta K} + e^{\beta K}].$$ \hfill (5.12)

As to be expected, we recognize eq. (5.12) as the partition function of a two level system (TLS) with energy levels $\pm K$. The derivation we have given provides a plausible basis for accepting a two-state model. It also provides a formula for the tunnel splitting,

$$\epsilon K = \frac{\int_{\sigma = -1}^{\sigma = +1} \mathcal{D} x(t) \exp\{S[x(t); \epsilon \hbar]\}}{\int_{\sigma = 1}^{\sigma = +1} \mathcal{D} x(t) \exp\{S[x(t); \epsilon \hbar]\}}$$ \hfill (5.13)

where the limits of the integrations refer to the stable regions occupied by $x(t)$ at the end points, $x(0)$ and $x(\epsilon \hbar)$. We see from eq. (5.13) that $\ln \epsilon K$ is the reversible work or free energy change (in units of $-\beta^{-1}$) to pull the end of an isomorphic chain polymer from one stable state to another so as to form one kink. Since the transfer element should be extensive in $\epsilon$ [see eq. (5.6)], an appropriate value of the coarse grained time element, $\epsilon$, is determined by finding the smallest $\epsilon$ for which $T/\epsilon = K$ is independent of $\epsilon$. As an example, Ceperley and Jacucci [29] have used this procedure to compute the tunnel splitting for collective motions in solid $^3$He. In this case, the application is more general than our derivation might suggest. Appendix 3 expands on this point.

Calculations like those of Ceperley and Jacucci employ Monte Carlo sampling to evaluate the free energy change. A useful, though approximate, alternative procedure employs a semiclassical method. In particular, the integrals in eq. (5.13) can be evaluated by steepest descent. One may determine the most probable paths contributing to the integrals. These paths, $x_{mp}(t)$, are the classical trajectories in the upside down potential discussed in section 4. See eq. (4.9). Fluctuations about these paths can be included
analytically by first expanding $S[x(t)] - S[x_{mp}(t)]$ to quadratic order and then performing the resulting Gaussian path integral. Such a procedure is sometimes called the “instanton” method. This procedure is the multidimensional generalization of WKB theory. It was pioneered by Miller [30] and has been discussed at length by Coleman [31]. Also see Chapter 14 of Parisi’s text [5], and Secs. 18 and 19 of Shulman’s text [6].

Along with the partition function, we can also compute averages and correlation functions. For example, the Euclidean time spin-spin correlation function is obtained from

$$
\frac{1}{Q} \sum_{\sigma(0,\ldots,\sigma(N-1))} \prod_{\sigma(0,\ldots,\sigma(N-1))} M_{\sigma(0,\ldots,\sigma(N-1))} \prod_{\gamma=N}^P M_{\sigma(0,\ldots,\sigma(N-1))}
$$

with $t = N/\beta \hbar / P$, $0 < N < P$. \hfill (5.14)

The first of these sums is a finite 1D Ising partition function with $N$ spins, and the second is a finite 1D Ising partition function with $P - N$ spins. After tedious algebra, and after performing the continuum limit, $P$ and $N \to \infty$ and $N/P = t/\beta \hbar$, one finds

$$
\langle \sigma(0)\sigma(-it) \rangle = \frac{1}{Q} \sum_{\sigma(0,\ldots,\sigma(N))} \left( \sigma(0,\ldots,\sigma(N)) \left( \begin{array}{c} 0 \\ ..., \ldots, \ldots, \ldots, t \end{array} \right) \right)
$$

$$
= e^{-\beta K} e^{2itK/\hbar} + e^{\beta K} e^{-2itK/\hbar} / [e^{\beta K} + e^{-\beta K}],
$$

with $0 \leq t \leq \beta \hbar$. \hfill (5.15)

It is an instructive exercise to perform the detailed steps of this calculation. In carrying it out, you must carefully account for the boundary conditions of the finite Ising systems. Notice that on analytic continuation to real time, $t \to it$, eq. (5.15) gives

$$
\langle \sigma(t)\sigma(0) \rangle = \cos(2Kt/\hbar) - i \tanh(\beta K) \sin(2Kt/\hbar). \hfill (5.16)
$$

The result exhibits the quantum coherence of a two-state system with period $\hbar / 2K$.

Equations (5.12), (5.15) and (5.16) are the results of a two state tight binding model – a two level system (TLS). If we were not concerned with
the issues of justifying such a model, we could have started immediately at that point. Indeed, with the left and right wells as the localized sites, \(|l\rangle\) and \(|r\rangle\) are the tight binding states. In this representation, the Hamiltonian is a \(2 \times 2\) matrix,

\[
H_{\text{TLS}} = \begin{bmatrix} 0 & K \\ K & 0 \end{bmatrix}
\]  

(5.17a)

and

\[
\langle \sigma | e^{-\epsilon H_{\text{TLS}}} | \sigma' \rangle = \begin{cases} 
1, & \sigma = \sigma', \\
-\epsilon K, & \sigma \neq \sigma',
\end{cases}
\]  

(5.17b)

where we have assumed \(\epsilon\) is very small. Thus, for example,

\[
Q = \sum_{\{\sigma^{(\alpha)}\}} \prod_{\alpha=1}^{P} | \langle \sigma^{(\alpha)} | \exp(-\epsilon H_{\text{TLS}}) | \sigma^{(\alpha+1)} \rangle |
\]

\[
= \sum_{\{\sigma^{(\alpha)}\}} \prod_{\alpha=1}^{P} \sqrt{\epsilon K} \exp\left[ -\sigma^{(\alpha)} \sigma^{(\alpha+1)} \ln \sqrt{\epsilon K} \right]
\]

\[
= (\epsilon K)^{P/2} \sum_{\{\sigma^{(\alpha)}\}} \exp\left\{ \sum_{\alpha=1}^{P} \sigma^{(\alpha)} \sigma^{(\alpha+1)} \left[ - \ln \sqrt{\epsilon K} \right] \right\}.
\]  

(5.18)

In the first of these equalities, only the magnitude of the matrix element is relevant because the trace requires only even powers of the off-diagonal elements. (Recall, kinks come in pairs.) The last equality demonstrates the connection between \(Q\) and the partition function of the 1D Ising model. Equation 5.12 follows immediately.

It is left as an exercise to show with matrix mechanics and Heisenberg equations of motion that the quantum correlation function \(\langle \sigma(0) \sigma(t) \rangle\) for the two-state model is exactly (5.16). Note that the representation of \(\sigma\) is the Pauli matrix

\[
\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.
\]

Notice too the connection between the transfer matrix method and the diagonalization of matrices familiar in quantum theory.

### 5.3. Spin-boson model

Now suppose the variable \(x\) (or \(\sigma\)) is associated with a dipole moment, \(m\). For example, \(x\) might specify a position of an electron that can move
back and forth between two potential wells. As \( \sigma \) changes sign so does the \( x \)-component of the dipole. A dipole–local field coupling therefore provides a simple physical model for the interaction between the tunneling system and its environment. Specifically, we use the hamiltonian

\[
H_{SB} = H_{TLS} - m\mathcal{E} + H_B(y_1, y_2, \ldots, y_N),
\]

(5.19)

where

\[
\mathcal{E} = \sum_i^N c_i y_i
\]

(5.20)

is the local electric field, \( H_{TLS} = K\sigma_x \) as in (5.17), and

\[
m = \mu \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix},
\]

(5.21)

i.e., \( m = \mu \sigma_x \). The \( y_i \)'s are the bath variables, and the hamiltonian governing their dynamics is \( H_B \).

A harmonic bath captures the essential physics we wish to describe. Thus, we will assume the \( y_i \)'s are harmonic variables. They might be phonons of a crystal or the polarization modes of a liquid. These variables can be constructed such that the potential of mean force for \( x \) is \( V_0(x) \) considered above. That is, we consider only the effects of bath fluctuations in altering the dynamics of the tunneling system. Since the \( y_i \)'s are harmonic, the bath is a bosonic system. Further, the two level system (TLS) is like a spin. These analogies are the origin of the name “spin–boson” (SB) model which is used to describe the hamiltonian (5.19).

To within trivial constant factors, with \( P \) very large, the partition function for the model is

\[
Q_{SB} = \int \prod_{i=1}^N \prod_{\alpha=1}^P dy^{(\alpha)}_i \sum_{\sigma^{(1)}, \ldots, \sigma^{(P)}} \exp \left( S_{TLS}[(\sigma^{(\alpha)})] \right)
\]

\[
+ \frac{1}{P} \sum_{\alpha=1}^P \beta \mu \sigma^{(\alpha)} \mathcal{E}^{(\alpha)} + S_B[(y^{(\alpha)}_i)]
\]

(5.22)

where

\[
S_{TLS}[(\sigma^{(\alpha)})] = \sum_{\alpha=1}^P \sigma^{(\alpha)} \sigma^{(\alpha+1)} (-\ln \sqrt{\epsilon K})
\]

(5.23)
is the discretized action for the TLS, see eq. (5.19), and \( S_B[\{y_1^{(a)}\}] \) denotes the discretized action for the bath. Since the bath is Gaussian, we can integrate out its fluctuations to obtain a Gaussian influence functional as done in section 4.2. The result is

\[
Q_{SB} = \lim_{P \to \infty} \sum_{\{\sigma^{(a)}\} = \pm 1} e^{S_{TLS} + S_I} Q_B,
\]

where the influence functional contribution to the action is

\[
S_I = (\mu^2 c^2 / 2) \sum_{a, \gamma = 1}^P \sigma^{(a)} \sigma^{(\gamma)} \chi_{\alpha\gamma}, \tag{5.25}
\]

with \( \chi_{\gamma\alpha} = \langle \mathcal{E}^{(a)} \mathcal{E}^{(\gamma)} \rangle_B \). In the continuum limit,

\[
S_I = (\mu^2 / 2) \int_0^{3\hbar} \frac{dt}{\hbar} \int_0^{3\hbar} \frac{dt'}{\hbar} \sigma(t) \sigma(t') \langle \mathcal{E}(t) \mathcal{E}(t') \rangle_B. \tag{5.26}
\]

Here, one should understand that the variables \( t \) and \( t' \) are Euclidean times. The bath correlation function in eq. (5.26) is therefore a correlation function of the type \( C(t - t') \) discussed in section 1.

It is seen from eqs. (5.23) - (5.25) that the evaluation of \( Q_{SB} \) is isomorphic to the calculation of the partition function for a 1D Ising system with long ranged interactions. Equivalently, we can write

\[
Q_{SB} / Q_B = \int \mathcal{D} \mathcal{E}(t) P_B[\mathcal{E}(t)] \sum_{\{\sigma^{(a)}\} = \pm 1} \exp \left( S_{TLS} + \epsilon \mu \sum_{a = 1}^P \sigma^{(a)} \mathcal{E}^{(a)} \right), \tag{5.27}
\]

where \( P_B[\mathcal{E}(t)] \) stands for the bath distribution functional for \( \mathcal{E}(t) \) - a Gaussian distribution of zero mean with variance \( \chi_{\alpha\gamma} = \langle \mathcal{E}^{(a)} \mathcal{E}^{(\gamma)} \rangle_B \). From eq. (5.27), we see that the evaluation of \( Q_{SB} \) is isomorphic to computing the partition function of the 1D Ising magnet in a random fluctuating field.

In the presence of random fields or long ranged interactions, the Ising model cannot be solved by the usual transfer matrix method. Indeed, neither the spin–boson model nor the isomorphic Ising models can be solved exactly by any known technique. This intractability is most remarkable in view of the model's apparent simplicity. The Gaussian bath is an infinite state problem, but easily treated analytically due to its linear nature. The TLS is nonlinear, but easily analyzed because it involves only two states. Their combination, however, results in a nonlinear infinite state problem.
A problem of different and often greater complexity than (5.27) is the partition function associated with an Ising model in a random quenched field,

$$Z = \int \mathcal{D}\epsilon(t)P_0[\epsilon(t)]\ln\left\{ \sum_{\{\sigma^{(\alpha)}\}=\pm 1} \exp\left( S_{\text{TLS}} + \epsilon_0 \sum_{\alpha=1}^P \sigma^{(\alpha)}\epsilon^{(\alpha)} \right) \right\}. $$

(5.28)

Instead of averaging a partition function as in eq. (5.27), the prescription here is to average the logarithm of a partition function. It is an instructive exercise to show that eq. (5.28) is the partition function that generates the spin correlation functions appropriate to the Ising magnet when the random field is fixed and cannot respond to fluctuations of the spin. In contrast, eq. (5.27) is the partition function for annealed averages where the temperature of the bath is meaningful and its fluctuating field does respond to the spin.

Not only is the spin–boson problem nontrivial mathematically, it is also nontrivial physically as it can exhibit a phase transition. To examine this possibility and its consequences for tunneling systems we consider now a special case of the model which can be solved analytically.

5.4. Solution of spin–boson model with adiabatic bath

An adiabatic bath is a sluggish bath – one that is characterized by only zero frequency fluctuations. As such,

$$\langle \epsilon(t)\epsilon(t') \rangle_B = \sum_{n} \langle |\epsilon_n|^2 \rangle_B \delta(t-t')$$

$$= \langle |\epsilon_0|^2 \rangle = \chi.$$

(5.29)

Hence,

$$Q_{\text{ASB}}/Q_B = \sum_{\{\sigma^{(\alpha)}\}=\pm 1} \exp\left\{ S_{\text{TLS}}[\{\sigma^{(\alpha)}\}] + \frac{\mu^2}{2} \chi^2 \sum_{\alpha,\gamma} \sigma^{(\alpha)}\sigma^{(\gamma)} \right\}$$

(5.30)

where “ASB” means “adiabatic spin–boson.” Notice that eq. (5.30) is also the partition function of a 1D Ising model with infinite range interactions. It is equivalent to a solvable Gaussian model as seen by uncompleting the square. That is,

$$Q_{\text{ASB}}/Q_B = \int_{-\infty}^{\infty} d\epsilon_0 \frac{e^{-\epsilon_0^2/2\chi}}{\sqrt{2\pi}\chi} \times \sum_{\{\sigma^{(\alpha)}=\pm 1\}} \exp\left\{ S_{\text{TLS}}[\sigma^{(\alpha)}] + \epsilon_0 \sum_{\alpha} \sigma^{(\alpha)} \right\}.$$ 

(5.31)
Fig. 15. Schematic of the adiabatic or “Born–Oppenheimer” surfaces for the spin–boson model.

You may check that (5.31) follows from (5.30) by completing the square and performing the Gaussian integral in eq. (5.31). This procedure is a very simple example of a standard trick for removing bilinear terms by employing linear coupling to a Gaussian random variable or field: It is often referred to as a “Hubbard–Stratonovich transformation.” In a slightly more general form, it has a number of uses as we will see in later sections of these lectures.

The summation in eq. (5.31) corresponds to a 1D Ising model with a mean field. That problem is equivalent to a two state quantum system with Hamiltonian

\[ H = \begin{bmatrix} \mu E_0 & K \\ K & -\mu E_0 \end{bmatrix}. \]

Its energy levels are \( E_{\pm} = \pm \sqrt{K^2 + \mu^2 E_0^2} \). With these eigenvalues, or equivalently, by applying the transfer matrix method to the Ising model, eq. (5.31) becomes

\[ Q_{\text{ASB}}/Q_B = \int_{-\infty}^{\infty} \frac{d\epsilon_0}{\sqrt{2\pi}\chi} \exp \left\{-\frac{\epsilon_0^2}{2\chi} + \ln 2 \cosh \left[ \beta \sqrt{K^2 + \mu^2 E_0^2} \right] \right\}. \tag{5.32} \]

The model is therefore solved (i.e., reduced to quadrature). We have been able to obtain the solution because only one degree of freedom, the spin, is quantal. There is no quantum dynamics in the bath. Therefore, the problem reduces to a classical statistics problem of low dimensionality.

To discuss the qualitative features of the solved model, we introduce the notation \( \varphi = \mu E_0 \), and \( c = \beta \mu^2 \chi \). Then, eq. (5.32) can be rewritten as

\[ Q_{\text{ASB}}/Q_B = \int_{-\infty}^{\infty} \frac{d\varphi}{\sqrt{2\pi}c/\beta} \left[ e^{-\beta F_1(\varphi)} + e^{-\beta F_2(\varphi)} \right], \tag{5.33} \]
where
\[ F_\pm(\varphi) = \frac{\phi^2}{2c} \pm \sqrt{K^2 + \phi^2} \]  \hspace{1cm} (5.34)
are the adiabatic potential energies for the field $\varphi$. That is, $F_\pm(\varphi)$ are the two Born–Oppenheimer potentials for the sluggish field, after averaging over (i.e., performed the quantum mechanics of) the quantal variable $x$. Equivalently, the logarithm of the term in the square brackets in eq. (5.32) is $-\beta$ times the free energy or reversible work function for $\varphi$ having integrated out the fluctuations of the isomorphic Ising magnet.

The adiabatic surfaces are qualitatively different depending upon the size of
\[ L = c/K. \]  \hspace{1cm} (5.35)
If $L > 1$, an elementary analysis shows that $F_-(\varphi)$ is bistable, while for $L \leq 1$ both $F_+(\varphi)$ are monostable with minima at $\varphi = 0$. This behavior is illustrated in fig. 15.

If $L > 1$, the ground state of the adiabatic spin–boson model exhibits broken symmetry. Indeed, in the low temperature limit, only $\varphi = \pm \sqrt{c^2 - K^2}$ are accessible. Correspondingly, as $\beta \to \infty$ for $L > 1$, the average spin, $\langle \sigma \rangle$, is nonzero.

To compute $\langle \sigma \rangle$, one may add a fixed external field, $\phi_{\text{ext}}$, to $\varphi$ and then use
\[ \sigma_{\phi_{\text{ext}}} = \frac{\partial}{\partial \phi_{\text{ext}}} Q_{\text{ASB}}. \]
The evaluation is left as an exercise. (See Exercises 5.26, 5.27 and 6.14 in ref. [2].)
The result of the calculation is drawn in fig. 16.

This particular example of broken symmetry is a type of self trapping. To understand this terminology in the current context, consider the physics of the phenomenon. If the two state system were not to tunnel, i.e., if $K = 0$, then the dipole would be solvated with the favorable energy of a classical dipole in a polarizable medium. That classical solvation energy is $c = \beta \mu^2 \chi$. See fig. 15. The reason is that a dipole of size $\mu$ polarizes the environment. According to linear response, the induced average local electric field is $\beta \mu \chi$. This induced field couples with the inducing moment giving an energy $-\beta \mu^2 \chi$. It is the standard reaction field argument. Notice, however, that this favorable energy is lost for any section of time during which the dipole resonates. During that time, the average dipole is zero, and the sluggish field cannot adjust to the changing dipole. Thus, the localized or trapped dipole is favored over the resonating dipole.
Whether the trapping occurs involves a competition between the solvation energy, \( c \), and the resonance energy, \( K \), since the latter is lost when resonance stops. In the isomorphic Ising systems, the resonance corresponds to a favorable entropy of a disordered chain of spins. Long range order of the spins corresponds to a self trapped state and quenched tunneling. The competition is explicitly evident in that \( L \) is the control parameter for the transition between the two states, and \( L_c = 1 \) is the critical point.

Notice that the symmetry breaking or localization of the dipole is a kind of fluctuation induced transition. In other words, coupling to a slowly fluctuating field impedes tunneling and can cause it to stop. Indeed, if the bath did not fluctuate spontaneously, it could not be polarized by a dipole. If spontaneous fluctuations were absent, i.e., if \( \chi = 0 \), then \( L = 0 \) always.

5.5. Spin–boson model with dynamical bath

While the general model cannot be solved exactly, we can still say much about the model based on what we’ve found in the adiabatic case. First, let us contrast the general and adiabatic cases by comparing the fluctuation induced interactions of the two models. Figure 17 illustrates the bath-TLS coupling and the resulting influence functional bonds.

Slow modes in the bath give rise to long ranged influence functional bonds, while fast modes give short ranged bonds. This fact is understood by introducing the spectral density,

\[
\Phi(\omega) = \sum_{i=1}^{N} \pi \delta(\omega - \omega_i)c_i^2/m_i\omega_i
\]  

(5.36)
where $\omega_i$ and $m_i$ are the fundamental frequency and mass, respectively, for normal mode $g_i$. With that notation, as discussed in Appendix 2, the strength of the influence functional bonds can be expressed as a superposition of imaginary time harmonic oscillator correlation functions. That is,

$$\langle \mathcal{E}(t)\mathcal{E}(t') \rangle_B = \int_0^\infty d\omega \Phi(\omega) \left\{ \frac{\hbar}{2\pi} \frac{\cosh[(\omega/2)(\beta\hbar - 2t + 2t')]}{\sinh(\beta\hbar\omega/2)} \right\}$$

(5.37)

where $t$ and $t'$ are points in Euclidean time, $0 < t - t' < \beta\hbar$. See eq. (1.18).

We see that the larger $\omega$ is, the faster the components decay. It is the long ranged components that force distant spins to align. The short ranged components are not effective this way.

Alternatively, note that a fast mode can respond quickly to a change in dipole. Therefore, the loss in solvation energy from a fast mode is not substantial when resonance or tunneling occurs.

In effect, therefore, fast bath modes couple less strongly to transitions of the tunneling particle than do slow modes. We can quantify this observation by creating an effective adiabatic theory for the dynamical spin–boson model. The idea is to minimize the effects of bath dynamics through an adiabatic field that couples to the spin with a renormalized coupling strength. The procedure is the Euclidean time analog of a mean field theory. See fig. 17 where an effective zero frequency field is drawn schematically along with the time varying field. To put this picture into equations, we write the total action as

$$S = S_{TLS}(K) + \frac{1}{2} \mu^2 \int_0^{3\hbar} \frac{dt}{\hbar} \int_0^{3\hbar} \frac{dr'}{\hbar} \sigma(t)\sigma(t')\langle \mathcal{E}(t)\mathcal{E}(t') \rangle_B$$

$$= \left\{ S_{TLS}(K') + \frac{1}{2} \left( \frac{c'}{\beta} \right)^2 \left[ \int_0^{3\hbar} \frac{dt}{\hbar} \sigma(t) \right]^2 \right\} + \Delta S,$$

(5.38)

where the second equality defines $\Delta S$. The term in curly brackets is the action of an adiabatic spin–boson model with resonance energy $K'$ and solvation energy $c'$. The effects of fluctuations are contained in $\Delta S$ and/or the parameters $K'$ and $c'$ which are not equal to $K$ and $c$. By adjusting $K'$ and $c'$, one can try to minimize the effects of $\Delta S$. It is important, however, that the reference system still possesses adiabatic fluctuations – long wavelength fluctuations in the Ising chain. These are fluctuations that can create localization. If they are omitted from the reference system, no finite perturbative treatment could successfully describe their effects.
Fig. 17. Paths and couplings in the spin–boson model before and after integration over the Gaussian bath.

A method to choose the renormalized parameters $K'$ and $c'$ exploits the Gibbs–Bogoliubov–Feynman variational principle. In particular, for a partition function of the form $Q = \int D\sigma(t) \exp\{S[\sigma(t)]\}$, factorization of $S$ into a reference and difference yields

$$Q = \int D\sigma(t) e^{S_{\text{ref}}[\sigma(t)] + \Delta S[\sigma(t)]}$$

$$= Q_{\text{ref}} \exp\{\Delta S[\sigma(t)]\}_{\text{ref}}$$ (5.39)

where $\langle \ldots \rangle_{\text{ref}}$ indicates the average with $S_{\text{ref}}$. Due to the convexity of the exponential, we therefore have,

$$Q \geq Q_{\text{ref}} \exp\{\Delta S\}_{\text{ref}}.$$ (5.40)

This inequality is the above mentioned bound.

To exploit this inequality, one may adjust the reference system so as to optimize this first order perturbation theory bound. Carmeli and I used
this scheme to choose $K'$ and $c'$ in the effective adiabatic reference system [32]. The results of this method were shown to be very accurate. According to this theory, $K' \leq K$ where the equality holds only in the adiabatic case. Physically this result means that the dynamics of the bath produces a loss of coherence in the tunneling system. Further, according to the theory, $c' \leq c$, implying that a dynamical bath solvates less strongly than a slow bath. Finally, it is interesting to note that $K'$ and $c'$ still exhibit localization, and the exponents for the transition calculated from the optimized effective adiabatic theory are in agreement with those computed by renormalization group procedures [33]. The reason for the agreement is that the essential features of the phase transition in this model are contained in the adiabatic model.

The variationally optimized first order perturbation treatment we have sketched is an accurate theory for equilibrium properties and renormalized parameters of the spin–boson model. It is not, however, the complete theory for real time correlation functions. The correlation functions of an effective adiabatic model do not exhibit dissipation. The demonstration is left as an exercise. Specifically, you can compute the effective adiabatic correlation function, $(\sigma(t)\sigma(0))_{EA}$, as follows: 1) Determine the Euclidean time correlation function by averaging $\sigma(0)\sigma(t)$ with the effective adiabatic weight functional [i.e., the weight $\exp(\delta_{EA})$ where $\delta_{EA}$ is the action surrounded by curly brackets in eq. (5.38)]. When performing this calculation, it is useful to uncomplete the square. 2) Analytically continue $t \rightarrow it$ to obtain the real time correlation function. The result is

$$
\langle \sigma(t)\sigma(0) \rangle_{EA} = \frac{1}{Q_{EA}} \int_{-\infty}^{\infty} d\phi e^{-\beta\phi^2/2c'} J(\phi, t) \tag{5.41}
$$

where

$$
Q_{EA} = \int_{-\infty}^{\infty} d\phi e^{-\beta\phi^2/2c'} 2\cosh\beta\epsilon(\phi), \tag{5.41a}
$$

$$
\epsilon(\phi) = \frac{(K'^2 + \phi^2)^{\frac{1}{2}}}{2}, \tag{5.41b}
$$

$$
J(\phi, t) = \frac{[\phi/\epsilon(\phi)]^2 \cosh\beta\epsilon(\phi)}{\cosh(\beta\epsilon(\phi))}
+ [K'/\epsilon(\phi)]^2 \{\cosh(\beta\epsilon(\phi)) \cos[2t\epsilon(\phi)/\hbar] - \sinh(\beta\epsilon(\phi)) \sin[2t\epsilon(\phi)/\hbar]\}. \tag{5.41c}
$$

This result is the two level system correlation function, eq. (5.15), inhomogeneously broadened by the adiabatic field fluctuations. Due to the time independent part of $J(\phi, t)$, it does not decay to zero at large times.

The qualitative features of spin–boson dynamics can be discussed in terms of the two extreme limits of weak and strong coupling. In the first, $L \ll 1$, the adiabatic surfaces are two nearly harmonic potentials separated
by approximately $2K$. See fig. 15. Dynamical fluctuations and anharmonic terms in the adiabatic potentials cause dephasing and infrequent transitions between surfaces. These effects can be treated straightforwardly by second order time dependent perturbation theory. The small parameter in the perturbation theory is either $L$ or $\beta KL \approx \beta^2 \mu^2 \langle E^2 \rangle_B$. This procedure leads to Bloch equations or Redfield equations of the sort familiar in the theory of nuclear magnetic resonance [34].

The strong coupling limit $L \gg 1$, is quite different. Electron transfer in polar liquids is an important example of this case. In view of fig. 15, we see that the left–right kinetics involves an activated process. At finite temperatures, tunneling still occurs, but in an incoherent fashion. That is, left–right transitions are statistically independent processes which occur essentially only at the infrequent times where the bath variables are arranged such that $\phi \approx 0$. Away from $\phi \approx 0$, the left and right states are not degenerate, and transitions or resonance between them will not happen. Thus, the rate constant for transitions has the Arrhenius form

$$k = Ae^{-\beta E^*}$$  \hspace{1cm} (5.42)

where $E^*$ is the activation energy such that $\exp(-\beta E^*)$ is the relative probability that $\phi = 0$. The prefactor or frequency, $A$, depends upon the details of the dynamics in the transition region.

Notice that when $L \gg 1$, the energy $K$ is nearly negligible compared to the solvation energy, $c$, and the adiabatic curves in fig. 15 can be viewed in terms of two intersecting parabolas. The parabolas are then the adiabatic energy functions for diabatic states (“diabatic” states are the eigenstates when $K = 0$). Also note that in this case

$$E^* = \frac{1}{2}c.$$  \hspace{1cm} (5.43)

While $L \gg 1$, one may still have $\beta K \gg 1$. In this case, passage through the transition region is a classical barrier crossing. As such, the frequency factor is

$$A \sim \omega_b,$$  \hspace{1cm} (5.44)

where $\omega_b$ is a bath frequency, either the unstable mode frequency at the barrier top or an effective stable state well frequency, whichever is smaller. On the other hand, if $\beta K$ is not large, the bath dynamics in the crossing region will cause transitions between the two adiabatic surfaces. For $\beta K$ very small, this effect can be analyzed with the golden rule (see section 7 and appendix 4). In this case,

$$A \sim K^2/\hbar \sqrt{2c/\beta \pi}.$$  \hspace{1cm} (5.45)
For either situation, eq. (5.44) or (5.45), the exponential Arrhenius factor is the dominant contributor to the rate.

In the case of activated electron transfer, the left and right states (the diabatic states) are redox sites – i.e., two different locations for the electron. The asymmetry of the localized charge distribution couples to the electric field of the environment, say liquid water, giving the energy $\varphi$. Electrons can resonate between the two redox sites only when the solvent reorganizes such that $\phi \approx 0$. These configurations are unstable, however, as we see from fig. 15. If $\varphi$ falls to the stable state that is not the initial one, then the electron will be trapped at a new site and the electron will then be transferred.

Notice that there are two bistable potentials. One is the potential energy in Figs. 13 and 14 which in effect limits the electron to the two redox sites. The other bistable potential is the ground state potential energy for the bath, fig. 15. The latter results from the strong coupling of the former (i.e., the redox system) to the harmonic bath.

The scenario of electron transfer described here is Marcus’ theory for such processes [35]. Equation (5.43) corresponds to one of Marcus’ relationships that connects the solvation energy or chemical potential of a stable redox pair to the activation energy for the transfer rate.

As an exercise you can generalize this treatment of electron transfer to the asymmetric case where the two redox states are solvated with different energies. In so doing you will discover that $E^*$ and therefore the rate of transfer is not in general a monotonic function of stable state solvation energies. The region where the rate is predicted to decrease with an increasing thermodynamic driving force is referred to as the Marcus inverted region.

6. Excess electrons in liquids

In the previous section, we considered localization relevant to mixed valence systems. Now we consider localization of a different sort, that associated with excess electrons in liquids.

Perhaps the most striking experimental probe of this phenomenon is the widely varying behavior of the self diffusion constants or mobilities for electrons in different liquids [36]. We will set this as our task: to show that large variation of mobilities is connected with precipitous transitions from localized to delocalized electronic states, and to develop a theory which describes both types of behavior and the transition between them.

As noted by earlier examples in these lectures, there have been several
simulation studies of excess electrons employing relatively realistic hamiltonians of the type

\[ H = H_{\text{solute}}(R_1, R_2, \ldots, R_N) + \frac{p^2}{2m_e} + V(\mathbf{r}; R_1, R_2, \ldots, R_N), \]  

(6.1)

where

\[ V = \sum_{i=1}^{N} v_{pe}(|\mathbf{r} - \mathbf{R}_i|) + \text{polarization energies} \]  

(6.2)

and \( v_{pe}(r) \) denotes the atom–electron pseudopotential. Some interesting results have been obtained in this way, but it’s not what we stress here. Rather we consider an analytical theory.

6.1. Influence functional

For a single \( e^- \) in a liquid, the Euclidean time distribution of paths is

\[ s[\mathbf{r}(t)] \propto s_o[\mathbf{r}(t)]g[\mathbf{r}(t)] \]  

(6.3)

where \( g[\mathbf{r}(t)] \) is the influence functional, and

\[ s_o[\mathbf{r}(t)] \propto \exp \left[ - \int_0^{\beta \hbar} \frac{dt}{\hbar} \frac{1}{2} m \dot{r}^2(t) \right] \]

\[ \times \prod_{\alpha=1}^{P} \exp \left[ -m |\mathbf{r}^{(\alpha)} - \mathbf{r}^{(\alpha+1)}|^2 / 2\epsilon h^2 \right], \quad \mathbf{r}^{(P+1)} = \mathbf{r}^{(1)} \]  

(6.4)
is the distribution of the unperturbed $e^-$. It is the distribution of a Gaussian necklace as made clear by the discretized form in the second proportionality. The influence functional describes how the environment changes the statistics of the isomorphic polymer. That is, $-\beta^{-1} \ln y[r(t)]$ is the sum of solvent induced interactions as depicted in fig. 18. In pictorial terms, the interactions dress the bare electron.

Notice that the fluctuations integrated out in this picture are spatial fluctuations in the solvent density. So this influence functional is a generalization of the one considered in Sections 4 and 5. In the previous case, the influence functional arose from correlations in the bath at different points in Euclidean time. In the present case, the self interactions on the electron path arise because the $e^-$ at time slice $\alpha$ couples to the solvent at a point in space; then through spatial correlations, the solvent can indirectly couple slice $\alpha$ with slice $\gamma$ provided $\gamma$ is not farther away in space than a solvent correlation length from $\alpha$. To analyze this behavior in detail, it is useful to extend the concept of a Gaussian bath to spatially dependent fluctuations — a Gaussian field theory.

6.2. Field theory estimate of influence functional bonds

One can specify points in configuration space with atomic coordinates $R_1, R_2, \ldots, R_N$. For our purposes, however, the equivalent representation in terms of density fields is more convenient. Let $\rho_s(r)$ denote the density field for the solvent. For each point in space, $\rho_s(r)$ is a different variable. The statistical weight of solvent configurations in this representation is therefore

$$\mathcal{D}\rho_s(r)P[\rho_s(r)]$$

where $\mathcal{D}\rho_s(r)$ denotes the differentials $d\rho_s(1)d\rho_s(2)\cdots d\rho_s(r)\cdots$ for all the points in space, and $P[\rho_s(r)]$ is the distribution functional. We use $P[\rho_s(r)]$ to denote the distribution for the pure solvent. To include the effects of the solute, we need to introduce the electron solvent coupling (in units of $-k_B T$)

$$\int_0^{\beta \hbar} \frac{dt}{\beta \hbar} \int d\mathcal{X}_{es}(|r(t) - r|) \rho_s(r) = \frac{1}{P} \sum_{\alpha=1}^P \int d\mathcal{X}_{es}(|r^{(\alpha)} - r|) \rho_s(r).$$

(6.5)

The coupling, $c_{es}(r)$, is still to be determined. In general, it can be a functional of the solvent density. We, however, limit ourselves to the simplified
class of models where $c_{cs}(r)$ is independent of the instantaneous fields, and
depends upon solvent density only through its average.

$$\langle \rho_s(r) \rangle = \rho_s.$$ (6.6)

With this notation,

$$y[r(t)] = \int D\rho_s(r)P[\rho_s(r)]\exp\left\{ \int_0^{\beta\hbar} \frac{dt}{\beta\hbar} \int dr c_{cs}(|r(t) - r|)\rho_s(r) \right\}$$

$$\approx \exp\left\{ \int_0^{\beta\hbar} \frac{dt}{\beta\hbar} \int dr \rho_s(r)c_{cs}(|r(t) - r|)$$

$$+ \frac{1}{2} \int_0^{\beta\hbar} \frac{dt}{\beta\hbar} \int_0^{\beta\hbar} \frac{dt'}{\beta\hbar} \int dr \int dr' c_{cs}(|r(t) - r|)$$

$$\times (\delta\rho_s(r)\delta\rho_s(r'))c_{cs}(|r' - r'(t')|) \right\}$$ (6.7)

where the approximation assumes that $P[\rho_s(r)]$ is Gaussian. The average
for this Gaussian bath is eq. (6.6), and the variance is the density density
correlation function.

$$\langle \delta\rho_s(r)\delta\rho_s(r') \rangle = \chi_{ss}(|r - r'|).$$ (6.8)

Thus, due to the isotropic symmetry of the liquid, eq. (6.7) becomes

$$y[r(t)] = \exp\left\{ \rho_s \frac{1}{P} \sum_\alpha \hat{c}_{\alpha s}(0) + \frac{1}{2} \frac{1}{P^2} \sum_{\alpha, \gamma} v(|r^{(\alpha)} - r^{(\gamma)}|) \right\}.$$ (6.9)

where

$$v(|r^{(\alpha)} - r^{(\gamma)}|) = \int dr \int dr' c_{\alpha s}(|r^{(\alpha)} - r|)\chi_{ss}(|r - r'|)c_{\gamma s}(|r' - r^{(\gamma)}|)$$

(6.10)

or in an obvious diagrammatic notation

$$v(|r^{(\alpha)} - r^{(\gamma)}|) =$$

(6.10')

This function $v(r)$ is the intrapolymer interaction due to solvent fluctuations or disorder.

In this analysis, we have assumed the solvent is adiabatic and one-component.
The generalization to a dynamical and/or multicomponent bath is left as an
exercise. Specifically, you will need to consider a time dependent field, $\rho_s(r, t)$.  

where $s$ is now a species label. For an isotropic stationary system, $(\rho_s(\mathbf{r}, t)) = \rho_s$, and the variance is the Euclidean time response function $\langle \delta \rho_s(\mathbf{r}, t) \delta \rho_s(\mathbf{r}', t') \rangle = \chi_{ss'}(\mathbf{r}, t; \mathbf{r}', t')$. In essence, the generalization simply adds an assortment of subscripts and superscripts to the equations already listed.

### 6.3. RISM

To complete the model, we must estimate $c_{es}(\mathbf{r})$. To do this, consider the electron-solvent pair correlation function. The radial distribution function is

$$\rho_s g_{es}(r) = \langle N_s \delta[\mathbf{r}(t) - \mathbf{R}_1 + \mathbf{r}] \rangle = \langle \rho_s(\mathbf{r}) \rangle \big|_{\mathbf{r}(t) \text{ at origin}}. \quad (6.11)$$

Thus,

$$\rho_s g_{es}(|\mathbf{r} - \mathbf{r}'|) = \text{const} \int \mathcal{D}\mathbf{r}(t) \int \mathcal{D}\mathbf{r}_s(\mathbf{r}) s_0[\mathbf{r}(t)] \delta[\mathbf{r}(t) - \mathbf{r}] \rho_s(\mathbf{r}')$$

$$\times P[\rho_s(\mathbf{r})] \exp \left\{ \int_0^{\frac{3\hbar}{\beta}} dt \int d\mathbf{r} \ c_{es}[|\mathbf{r}(t) - \mathbf{r}|] \rho_s(\mathbf{r}) \right\}$$

$$= \rho_s + \int d\mathbf{r}'' \int d\mathbf{r}''' \int_0^{\frac{3\hbar}{\beta}} dt'' \omega(|\mathbf{r} - \mathbf{r}''; t - t'')$$

$$\times c_{es}(|\mathbf{r}''' - \mathbf{r}''|) \chi_{ss}(|\mathbf{r}''' - \mathbf{r}'|) \quad (6.12)$$

with

$$\omega(|\mathbf{r} - \mathbf{r}'|; t - t') = \langle \delta[\mathbf{r}(t) - \mathbf{r}(t') - \mathbf{r} + \mathbf{r}'] \rangle. \quad (6.13)$$

The second equality in eq. (6.12) follows from a few steps of algebra after performing the Gaussian averages. The $\omega$-function is the intrapolymer pair correlation function or electron self correlation function (in Euclidean time). We can represent it diagrammatically with the picture

```
\begin{tikzpicture}
    % Pictograph of the correlation function
    % (adapt as needed)
    % End of Pictograph
\end{tikzpicture}
```

As such, eq. (6.12) becomes

$$\rho_s g_{es}(|\mathbf{r} - \mathbf{r}'|) - 1 = \begin{tikzpicture}
    % Pictograph of the correlation function
    % (adapt as needed)
    % End of Pictograph
\end{tikzpicture} \quad (6.14)$$

One may recognize (6.14) as the Chandler–Andersen equation of the reference interaction site model (RISM) [37]. In that context, it is a generalization of the Ornstein–Zernike (OZ) equation sometimes referred to as
the site-site OZ (i.e., SSOZ) equation. See Ch. 12 of ref. [3] as well as I. R. McDonald’s lectures in this Les Houches school. In these cases, \( c_{ss}(r) \) is known as the site-site direct correlation function.

Notice that eq. (6.14) depends on the zero frequency part of the electron self-correlation function

\[
\omega_0(r - r') = \int_0^{\beta \hbar} \frac{d(t - t')}{\beta \hbar} \omega(|r - r'|; t - t')
\]  

(6.15)

and that nonzero frequency components do not contribute. This feature would change if the solvent was treated non-adiabatically, i.e., if the \( \chi \)-function was time dependent. The generalization to a time dependent \( \chi \) is left as an exercise.

A standard closure of eq. (6.14) is

\[
g_{ss}(r) = 0, \quad r < d.
\]
\[
c_{ss}(r) = 0, \quad r > d.
\]  

(6.16)

which is appropriate for the hard sphere \( e^- \)-solvent pseudopotential. Equations (6.14) and (6.16) combined are a RISM equation. They can be solved in this way: The function \( c_{ss}(r) \) is constructed and adjusted numerically until it is found that \( g_{ss}(r) \) computed from (6.14) is zero for \( r < d \). This adjustment determines \( c_{ss}(r) \) for \( r \leq d \), and eq. (6.16) says it is zero for \( r > d \). Then \( g_{ss}(r) \) is computed for \( r \geq d \) by inserting \( c_{ss}(r) \) into (6.14). Solutions to the RISM equation will generally yield

\[
c_{ss}(r) = c_{ss}[r; \omega_0(r)].
\]  

(6.17)

That is, the polymer-solvent coupling depends on average polymer pair structure. Nonlinear effects are therefore treated in this model with self consistent mean pairs (not mean fields). This point is perhaps made clear on pondering fig. 19.

If the solvated electron problem was treated entirely as a mean field approximation, we would miss the localization phenomenon. Specifically, the self interactions, \( v(r) \), vanish in the absence of solvent disorder. For this reason, the simplest acceptable approximations must be made at the pair level, and not the traditional mean field or single particle level.

Incidentally, all these ideas including the RISM equation for isomorphic electron polymers can also be applied to real polymers [38].

6.4. *Feynman's polaron theory*

The problem we have now to solve is the computation of

\[
Q = \int \mathcal{D}r(t) \exp\left\{ S_0[r(t)] + \frac{1}{2} \int_0^{\beta\hbar} \frac{dt}{\beta\hbar} \int_0^{\beta\hbar} \frac{dt'}{\beta\hbar} v(|r(t) - r(t')|) \right\}
\]

(6.18)

with \( v(|r - r'|) \) given by eq. (6.9) or (6.10), and \( S_0[r(t)] \) is the free electron action [see eqs. (6.3) and (6.4)]. We have omitted constant factors as they have no effect in the electronic structure. Equation (6.18) is the partition function for an \( e^- \) in a random material as is evident from the equivalent representation

\[
Q = \int \mathcal{D}\varphi(r) P[\varphi(r)] \int \mathcal{D}r(t) \exp\left\{ S_0[r(t)] \pm \int_0^{\beta\hbar} \frac{dt}{\beta\hbar} \varphi(r(t)) \right\}.
\]

(6.19)

Here, \( P[\varphi(r)] \) is a Gaussian distribution functional with zero mean and variance \( \langle \varphi(r) \varphi(r') \rangle = v(|r - r'|) \). One may verify that (6.19) is the same as (6.18) by performing the Gaussian average in (6.19). The averaging over the disorder is an annealed average, not quenched. The latter might be appropriate for a glass, but not a fluid.

As an aside, we note that at nonzero electron temperature there would seem to be no difference between annealed and quenched averages provided the latter is performed with a frozen solvent configuration taken from the thermal equilibrium state of the pure solvent. The reason is that the frozen macroscopic solvent can be divided into a macroscopic number of cells, each one with side lengths larger than the correlation length of the actual solvent and also larger than the electron's length, \( \lambda \). With enough time or enough averaging, the electron will visit many of these cells and thus effectively sample from the annealed ensemble.

Note the sign of the coupling in this problem. Specifically,

\[
\hat{v}(0) = [\hat{c}_{es}(0)]^2 \tilde{\chi}_{ss}(0) \geq 0.
\]

(6.20)
This means that \( v(\|r - r'\|) \) favors localization — a folding or crumpling of the polymer into a volume of size \( \sim \xi^3 \), where \( \xi \) is the correlation length of the solvent. (We assume that \( \lambda \gg \xi \), which is usually the case.) The opposite effect — a swelling of the polymer — could only arise if \( \varphi(r) \) were complex. To solve the polymer statistics problem with these interactions, we will adapt the variational method Feynman used to study a similar polaron problem — the theory of slow moving electrons in harmonic crystals [39]. To begin, we note that a problem we can solve is the partition function with the quadratic action

\[
S_{\text{ref}} = S_0[r(t)] - \frac{1}{2} \int_0^{\beta \hbar} \frac{dt}{\beta \hbar} \int_0^{\beta \hbar} \frac{dt'}{\beta \hbar} \Gamma(t - t')|r(t) - r(t')|^2.
\]

(6.21)

The analysis is straightforward following the methods mapped out in section 4 and appendix 1. We find that \( \omega(|r - r'|; t - t') \) is Gaussian with second moment

\[
R^2(t - t') = \langle |r(t) - r(t')|^2 \rangle = \sum_{n=-\infty}^{\infty} [1 - \cos \Omega_n(t - t')] \frac{6}{\beta n \Omega_n^2 + \gamma_n}.
\]

(6.22)

where

\[
\gamma_n = 2(\Gamma_n - \Gamma_0)
\]

(6.23)

and \( \Gamma_n \) is the Fourier component of \( \Gamma(t - t') \) with frequency \( \Omega_n \).

Next, we use variational perturbation theory as we discussed earlier in the context of the spin boson problem:

\[
Q = Q_{\text{ref}} e^{(S - S_{\text{ref}})} \geq Q_1 = Q_{\text{ref}} e^{(S_1 - S_{\text{ref}})}.
\]

(6.24)

Optimization demands

\[
0 = \frac{\delta}{\delta \gamma_n} \ln Q_1
\]

(6.25)

and the analysis of this derivative gives

\[
\gamma_n = \frac{1}{6\pi^2 \beta \hbar} \int_0^{\beta \hbar} dt [1 - \cos \Omega_n t] \int_0^\infty dk k^4 \hat{e}(k) e^{-k^2 R^2(t)/6}.
\]

(6.26)
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Analytic continuation gives, \( z = \omega + i\epsilon \),

\[
\hat{\gamma}(z) = -\frac{1}{3\pi^2\beta\hbar} \int_0^\infty \, dt [1 - e^{i \text{sgn(Im}\, z)}] \times \int_0^\infty \, dk k^4 \hat{h}(k) \text{Im} e^{-k^2 C_>(t)}
\]

with

\[
C_>(t) = R^2(it)/6.
\]

The derivations of (6.26) from (6.25) and of (6.27) from (6.26) are left as exercises. For guidance, the reader might refer to refs. 40.

To clarify what we have done, it is helpful to carry out another calculation. In particular, one may evaluate \( R^2(t - t') \) for a particle linearly coupled to a bath of oscillators. The analysis of this linear problem yields

\[
R^2(t - t') = \sum_n \left[ 1 - \cos \Omega_n(t - t') \right] \frac{6}{\beta m \Omega_n^2 + \Omega_n \xi(\Omega_n)}
\]

where \( \Omega_n \xi(\Omega_n) \) is the response function of the harmonic bath.

The derivation of (6.29) is left as an exercise. The analysis can follow the same methods illustrated in section 4 for performing calculations with quadratic action functionals.

We have written the response function as \( \Omega_n \xi(\Omega_n) \) since then \( \xi(\Omega_n) \) is recognized as the frequency dependent friction or memory function. Thus, eq. (6.27) is a self consistent equation for the memory function. It has the form of equations encountered in mode coupling theory. (See, for example, Professor Götze's lectures in this same school.) The diffusion constant is given by the reciprocal of the low frequency friction constant,

\[
D = \lim_{\omega \to 0^+} \frac{1}{\xi(-i\omega)} = \lim_{\omega \to 0^+} \frac{i\omega}{\hat{\gamma}(\omega)}.
\]

6.5. Results

The RISM-polaron theory, eqs. (6.16), (6.26) and (6.27), has been solved for the model of an electron in a fluid of hard spheres [41]. It is like a
quantum Lorentz gas, but with nontrivial solvent pair correlations. (The terminology “quantum Lorentz gas” is often used for the simplified model in which the hard spheres are distributed randomly without pair correlations.) This model serves as a caricature of $e^-$ in fluid helium. The same model has also been studied in Euclidean time by staging quantum Monte Carlo. A comparison is shown in fig. 20. We see that localization does occur in this system. Specifically, for temperature corresponding to $\lambda = (\beta h^2/m)^{\frac{1}{2}} = 6\sigma$, as solvent density is increased beyond $\rho \sigma \approx 0.2$, the electron passes from an extended state to a self-trapped state (i.e., one dominated by the ground state). The transition is found to be more sudden by the simulation than predicted by the RISM-polaron theory. This difference is to be expected since the theory approximates the effects of fluctuations while the simulation treats them essentially exactly, and it is the spatial fluctuations or disorder that leads to the localization.

The localization is a fluctuation induced transition in much the same fashion as the self trapping in the spin–boson model and also much like the polaron formation illustrated in section 3. But here, the effect is due to excluded volume rather than polarization. The electron pushes on the solvent to make space for itself. The larger the space the lower the electron kinetic energy. Large space in a sea of spheres, however, is costly in terms of solvent free energy, so the solvent pushes back. The strength of that back reaction is proportional to the solvent response, the $\chi$-function. See
eq. (6.10). If the solvent could not fluctuate, i.e., if it had no spatial disorder, then the $\chi$-function would be zero. $\tilde{\chi}_{xx}(k)$ is a compressibility for the wavelength $2\pi/k$. The balance between the electron kinetic energy and the solvent compressibility results in the stable structure. The localized electron is in a cavity with energy spacings larger than $k_B T$ – thus the phenomenon of ground state dominance. These cavities are sometimes referred to as “Lifshitz traps.”

In fig. 21, we show the RISM-polaron results for the diffusion constant. (There are no simulation results for this real time quantity.) As the system passes from an extended to a localized or self trapped state, the diffusion constant drops precipitously. Notice also the switch in temperature dependence. At low solvent densities, increasing temperature [i.e., decreasing $\lambda = (\beta \hbar^2/m)^{1/2}$] lowers the diffusion constant. This is metallic-like behavior. At high densities, however, the opposite trend is observed. Indeed, to diffuse, electrons must be in excited states, and the population of excited states goes as $\exp(-\beta \Delta \epsilon)$ where $\Delta \epsilon$ is the energy gap from the ground state. We know a gap exists because the localized equilibrium structure exhibits ground state dominance. Thus, the self trapped state is akin to a semiconductor. The precipitous drop in diffusion constant is much like a phase transition where small changes in external parameters can cause an enormous change in an observed property. The fact that this transition
occurs can be used to rationalize much of the large variability of electron
mobilities in liquids.

As the energy gap from the ground state grows, the electron mobility
diminishes exponentially. Eventually, an alternative mechanism becomes
the dominant mode for the mobility – the electrons diffuse because the
solvent molecules around them diffuse. This mechanism for very slow elec-
tron motion is easy to visualize and can be studied numerically in terms of
electronically adiabatic classical mechanics for the solvent [42]. The mech-
anism is not, however, included in the theory described above since the
solvent is treated in the extreme adiabatic approximation which contains
no solvent dynamics, only solvent disorder.

7. Quantum dynamics and two aspects of Monte Carlo sampling

Let us now discuss the problem of sampling real time quantum dynamics
by Monte Carlo. It is one of both principle and practice. If the sampling
is done unintelligently, computed averages will be meaningless. A form
of importance sampling is required. But the alternating signs of the com-
plex real time propagators invalidate the traditional scheme for importance
sampling.

To discuss the nature of the problem, consider the spin–boson model
introduced in section 5. Imagine studying the dynamics for the case of \( L \gg 1 \). The adiabatic or Born–Oppenheimer potentials for the bath variables,
\( \varphi \), are sketched schematically in fig. 15. A classical trajectory algorithm
might be satisfactory until the transition region, \( \phi \approx 0 \), is approached.
Near \( \varphi = 0 \), where interconversion between states becomes probable, the
two adiabatic surfaces are sufficiently close that the kinetic energy of the
bath may induce transitions between the surfaces. These are nonadiabatic
transitions. The two surfaces have very different forces, so the distinction
between them is significant. The fact that transitions between them are
possible means that the forces acting on the bath are undefined, hence
deterministic classical dynamics is not possible.

Approximate schemes to treat the dynamics are of two types. In one,
the idea is to simply average the forces from the two surfaces. Through
the evolution of the classical bath, the coupling of the bath to the two level
system is viewed as a time varying disturbance governing the evolution of
the latter. This approach is referred to as “time dependent self consistent
field” (TDSCF). Unfortunately, it is generally a poor approximation since
nonadiabatic transitions lead to a branching of trajectories, not a single
self consistent trajectory.
Branching can be incorporated with stochastic hopping from one surface to the other [43]. The approximation inherent with this approach, however, neglects the coherence of quantum motion. If that coherence is important over significant lengths of time, the evolution must be followed according to the rule of probability amplitudes, not simply probabilities.

The surface hopping model for dynamics also neglects the possibility that the bath dynamics itself can be intrinsically quantum mechanical. For example, passage from left to right might occur not so much by \( \varphi \) passing over the barrier at \( \varphi = 0 \), but instead by tunneling through it.

Thus, there are important dynamical issues that can be resolved only with exact quantum dynamics. For low dimensional systems, exact calculations can be done with standard Schrödinger mechanics. But for complex high dimensional systems, some form of Monte Carlo with importance sampling is required. In this section we describe how one might perform such calculations by sampling Feynman paths.

The difficulty that must be addressed in this approach is evident by examining one of the elements

\[
\begin{align*}
\langle r' | e^{-iHt/\hbar} | r \rangle &= \int_{r}^{r'} C r(t) \exp \{ S[r(t); it] \} .
\end{align*}
\]

\[ (7.1) \]

For imaginary time,

\[ S[r(t); \tau] = - \int_{0}^{\tau} \frac{df}{\hbar} \left\{ \frac{1}{2} m \dot{r}^2(t) + V[r(t)] \right\} . \]

\[ (7.2) \]

Going to real time, \( \tau \to it \),

\[ S[r(t); it] = i \int_{0}^{t} \frac{d\tilde{t}}{\hbar} \left\{ \frac{1}{2} m \dot{r}^2(\tilde{t}) - V[r(\tilde{t})] \right\} . \]

\[ (7.3) \]

We see from (7.1) and (7.3), that the basic elements in the calculation are oscillating functionals of the path \( r(t) \). To sample such paths effectively, one needs to develop principles of importance sampling from distributions that alternate in sign. Standard Monte Carlo procedures by themselves do not provide the answer since those procedures are designed for positive weights.

Incidentally, wave interference is not confined to single elements or probability amplitudes. The different elements contributing to the correlation functions as shown in section 1 interfere with each other too. This fact
gives rise to the issue of quantum coherence raised above when discussing surface hopping models.

One might consider searching for stationary phase paths since regions of stationary phase should be the primary contributors to integrals with oscillating integrands. Such paths satisfy

\[
0 = \frac{\delta}{\delta r(t)} S[r(t); it] .
\]

(7.4)

Analysis of this expression leads to

\[
m\ddot{r}(t) = -\frac{dV}{dr(t)} ,
\]

(7.5)

i.e., classical mechanics.

As an exercise, it is instructive to use these path integral methods to show that in the classical limit, $\hbar \to 0$, the correlation function

\[
C(t) = Q^{-1} \text{tr} e^{-\beta H} A e^{iHt/\hbar} A e^{-iHt/\hbar}
\]

reduces to

\[
C(t) = Q^{-1} \int dr \int dp \, e^{-\beta H} A(r) A[r(t; p, r)]
\]

where $r(t; r, p)$ is $r(t)$ evolved from $t = 0$ by classical dynamics with initial phase space point $r, p$, and $Q^{-1}$ is the normalization constant.

But not all processes can occur by classical paths in real space and time. For example, tunneling and diffraction cannot occur if evolution follows eq. (7.5) and if both $t$ and $r(t)$ are real. Thus, straightforward application of stationary phase ideas will not be useful when such intrinsically quantum processes are important to the dynamics.

To a large extent, the spin–boson model and the natural systems it mimics evolve by tunneling. So the analysis of this model requires a sampling technique that can explicitly account for the effects of alternating weights. 7.1. Rate constants

Rates of transitions in the spin–boson model can be discussed in terms of the population operator

\[
h_A = \frac{\sigma_z + 1}{2} = 1 - h_B .
\]

(7.6)
The nonequilibrium average of that population is

$$\bar{h}_A(t) = \Delta \frac{\partial \bar{h}_A}{\partial \Delta A} + x_A. \tag{7.7}$$

where $x_A = \langle h_A \rangle$. From section 1, we know that the rate of change of the population when close to equilibrium is

$$k(t) = -\frac{\Delta \frac{\partial \bar{h}_A}{\partial \Delta A}}{\Delta \bar{h}_A(0)} = -\frac{1}{i \beta} \frac{1}{\bar{h}_A x_B} \langle [h_A(-i\beta h) - h_A(0)]h_A(t) \rangle. \tag{7.8}$$

In general, $k(t)$ can be quite complicated. But if after a short transition time, $k(t)$ reaches a plateau, then there is exponential relaxation with rate constants [44].

$$k = k(t_{pl}) = \frac{1}{\tau} = k_{A \to B} + k_{B \to A}. \tag{7.9}$$

Here $t_{pl}$ is the plateau time - large compared to any transient relaxation time but not so large as to permit more than one completed activated process. With eqs. (7.8) and (7.9) and the KMS boundary conditions, one may show

$$k_{A \to B} = -\frac{1}{i \beta h x_A} \langle [h_A(t_{pl}), h_A(0)] \rangle$$

$$= \frac{2}{\beta h x_A} \text{Im} \langle h_A(0)h_A(t_{pl}) \rangle. \tag{7.10}$$

As an exercise, you can use this correlation function expression to derive the golden-rule formula for rates. For example, consider the system with

$$H = H_0 + V \tag{7.11}$$

where $H_0 |i\rangle = \epsilon_i |i\rangle$, and $V = (1 - \delta_{ij})V_{ij}$. Further, in this example,

$$h_A = |1\rangle \langle 1| = 1 - h_B = 1 - \sum_{f \neq 1} |f\rangle \langle f|.$$

Then, by inserting this state representation into the correlation function you will find

$$k_{A \to B} = \sum_f k_{1 \to f}$$

$$= \frac{2\pi \epsilon_{1f}}{\hbar} \sum_f |V_{1f}|^2 \delta(\epsilon_1 - \epsilon_f) + O(V^4) \tag{7.13}$$
which is one example of the golden rule of time dependent perturbation theory. The delta function arises from the assumption that $\tau_{pl}$ can be taken to be very large, i.e., larger than any possible value of $\hbar / |\epsilon_1 - \epsilon_f|$.

7.2. Statistical object

To compute $k_{A-B}$ or more generally $k(t)$, we must evaluate the imaginary part of $\langle h_A(0) h_A(t) \rangle$. In terms of paths, this correlation function is

\[
\langle h_A(0) h_A(t) \rangle = \int \beta \pi
\]

\begin{equation}
(7.14)
\end{equation}

The statistical object governing real time correlation functions is pictured in fig. 22. The Euclidean time portion is discretized with $P$ points, and both real time elements use $M$ points; i.e., real time is discretized between

\[
0 < j \Delta t \leq T, \quad j = 1, 2, \ldots, M.
\]

We can compute real time correlations from this object for all discretized times $t \leq T$. This fact follows from

\[
\int \beta \pi = \int \beta \pi, \quad t \leq T.
\]

\begin{equation}
(7.16)
\end{equation}

which is the result of completeness.
Thus, to apply discretized path methods, one must perform averages with the complex "weight"

\[
W_c(r^{(1)}, \ldots, r^{(P+2M)}) \propto \exp\left\{ S(r^{(1)}, \ldots, r^{(P+1)}; \beta \hbar) + S(r^{(P+1)}, \ldots, r^{(P+M+1)}; it) \\
+ S(r^{(P+M+1)}, \ldots, r^{(1)}; -it) \right\}.
\]

(7.17)

The first of the three actions in curly brackets is pure real, while the second and third are pure imaginary. In general, the structure of the weight is

\[
W_c = \exp\left[ g(r) + if(r) \right],
\]

(7.18)

where \(g(r)\) and \(f(r)\) are pure real functions of a multidimensional variable \(r\); i.e., \(r\) stands for the set of variables \(r^{(\alpha)}, 1 \leq \alpha \leq P + 2M\). To perform Monte Carlo averages with the complex weight, one might sample from the positive distribution \(\exp[g(r)]\). The equations governing the procedure are

\[
\langle A \rangle_c = \int dr \ e^{g(r)}[e^{if(r)} A] = \langle e^{if(r)} A \rangle_g \int dr \ e^{g(r)}.
\]

(7.19)

This approach, however, is a bad idea. The importance sampling guided by \(\exp[g(r)]\) does not account for the importance of stationary phase regions. Successful procedures must be guided, at least in part, to search for such regions. Regions distant from those of stationary phase will have quickly oscillating integrands. Due to the resulting cancellation they will not contribute to the integral and therefore should be avoided.
7.3. Stationary phase Monte Carlo and generalization

A method that does focus on the stationary phase regions has been developed by Doll [45] and others [46]. It is a Monte Carlo importance sampling employing the distribution

\[ W_f(r) \propto D_0(r)e^{i\eta(r)}. \]  \hspace{1cm} (7.20)

where for one dimension

\[ D_0(r) = \exp\left\{-\frac{1}{2} \varepsilon^2 (df/dr)^2 \right\}. \]  \hspace{1cm} (7.21)

The damping function, \( D_0(r) \), emphasizes regions where \( df/dr \) is small. This emphasis seems to be precisely what is needed. The equations that justify it are as follows: First note,

\[
\int d\epsilon e^{i\eta(r)+i\epsilon} = \int d\epsilon e^{i\eta(r)+i\epsilon} \int dy P_\epsilon(y) \\
= \int d\epsilon e^{i\eta(r)+i\epsilon} D(r).
\]  \hspace{1cm} (7.22)

Here, \( P_\epsilon(y) \) is a normalized distribution of width \( \epsilon \). If we assume \( \epsilon \) is small, the integral over \( y \) can be estimated by expanding \( f(r-y) - f(r) \approx -f'(r)y \), and also assuming \( g(r) \) is much less slowly varying than \( f(r) \). (The latter assumption is justified in the troublesome regions of rapid phase oscillations.) For small \( \epsilon \), we therefore obtain the estimate

\[ D(r) \approx D_0(r). \]  \hspace{1cm} (7.23)

From this analysis, an algorithm emerges. (1) Averages can be performed by importance sampling from the distribution \( W_f(r) \). (2) For representative configurations in this sampling, the correction \( D(r) - D_0(r) \) is estimated by performing a nested Monte Carlo evaluation of the integral over \( y \) in eq. (7.22). This latter integration must evaluate the alternating weight explicitly. Therefore, one hopes to perform this second step only infrequently.

The success of this procedure hinges on whether a compromise for \( \epsilon \) can be found. Large \( \epsilon \) filters out rapid phase oscillations, but \( \epsilon \) too large makes \( D(r) - D_0(r) \) too large, and the alternating weights problem reappears in the necessity to frequently evaluate the correction, \( D(r) - D_0(r) \). For \( \epsilon \) not too large, however, the effects of \( D(r) - D_0(r) \) can be shown to be small, and frequent evaluation is not required. One must adjust \( \epsilon \) empirically to simultaneously minimize the correction and enhance the statistics.
Quantum processes in liquids

Unfortunately, the straightforward application of this stationary phase Monte Carlo method can be problematic if $\exp[g(r)]$ emphasizes regions far from those where $f'(r)$ is small. Figure 23 illustrates the problem. Behavior like this is generally encountered when studying systems where dynamics is highly nonclassical. For example, the equilibrium Euclidean time distributions of a bistable tunneling system will emphasize the regions of stability, while the real time dynamical processes will involve the unstable barrier region. When this behavior is encountered, no value of the empirically chosen width, $\epsilon$, would seem to work as a satisfactory compromise.

The problem can be resolved, however, by generalizing the stationary phase Monte Carlo procedure. In this regard we might note that while no tunneling or diffraction solutions exist for eq. (7.4) when $r(t)$ is real, these solution can exist for complex $r(t)$. This observation is the basis of techniques in semiclassical quantum theory [47], and it is the basis for a Monte Carlo procedure we will describe shortly. First, however, it should be understood that integrals over $r$ need not pass along the real axis. They can be deformed to pass into the complex plane provided they still formally extend to $\infty$ where boundaries are irrelevant. Hence, integrations can, for example, employ rotated coordinates,

$$r^{(\alpha)} \to s^{(\alpha)} e^{i\theta^{(\alpha)}}, \quad (7.24)$$

where one samples $s^{(\alpha)}$ rather than $r^{(\alpha)}$.

The generalized stationary phase Monte Carlo procedure uses these rotated coordinates. The choices of the $\theta^{(\alpha)}$ are made by locating the vicinity of stationary phase paths in the complex plane. In general there are several such paths, i.e., there are several $\{s^{(\alpha)}, \theta^{(\alpha)}\}$ which extremize $W_c$. They can be located numerically by the method of simulated annealing [48]. Having
identified these choices of $\{\theta^{(\alpha)}\}$, one can then sample as before employing the filtering procedure, i.e., using the weight $D_0(s) \exp[g(s)]$.

Remarkably, this procedure works. It focuses on the regions important to the integral, and it filters out the irrelevant oscillatory parts. It gives good statistics with finite computational effort as we now illustrate with the spin–boson model.

### 7.4. Quantum dynamics with the spin–boson model

In this case, the partition function for the complex statistical object is

$$
O = \sum_{\{\sigma^{(\alpha)}\}} \text{(const)} \exp \left( \frac{1}{2} \sum \sigma^{(\alpha)} K_{\alpha \gamma} \sigma^{(\gamma)} \right)
$$

where

$$
K_{\alpha \gamma} = K'_{\alpha \gamma} + i K''_{\alpha \gamma} + I_{\alpha \gamma} = K_{\alpha \gamma}.
$$

(7.25)

We use $O$ rather than $Q$ to distinguish the complex partition function from its equilibrium counterpart. Here, $K'$ and $K''$ are the real and imaginary parts of the matrix of two level system nearest neighbor couplings, and $I$ is the matrix of influence functional couplings. That is,

\begin{align}
K'_{\alpha \gamma} &= \begin{cases} 
- \ln \sqrt{\kappa} \delta_{\alpha, \gamma-1}, & 1 \leq \alpha < \gamma \leq P, \\
- \ln \sqrt{\Delta t} / \delta_{\alpha, \gamma-1}, & P + 1 \leq \alpha < \gamma \leq P + 2M.
\end{cases} \\
K''_{\alpha \gamma} &= \begin{cases} 
(\pi/4) \delta_{\alpha, \gamma-1}, & P + 1 \leq \alpha < \gamma \leq P + M, \\
-(\pi/4) \delta_{\alpha, \gamma-1}, & P + M + 1 \leq \alpha < \gamma \leq P + 2M, \\
0 & \text{otherwise}.
\end{cases}
\end{align}

(7.27a) (7.27b)

and

$$I_{\alpha \gamma} = \mu^2 \Delta t_{\alpha} \Delta t_{\gamma} \frac{\hbar}{2\pi} \int_0^\infty d\omega \Phi(\omega) \frac{\cosh[\omega(\Delta t_{\alpha \gamma} - \Delta t_{\alpha \gamma})/2]}{\sinh(\beta \hbar \omega/2)}. $$

(7.27c)
where \( \Phi(\omega) \) is the spectral density and the complex time difference \( \Delta t_\alpha \) and \( \Delta t_{\alpha\gamma} \) are defined by

\[
\Delta t_\alpha = \begin{cases} 
ch. & 1 \leq \alpha \leq P, \\
i\Delta t. & P < \alpha \leq P + M, \\
-i\Delta t. & P + M < \alpha \leq P + 2M.
\end{cases}
\] (7.27d)

and

\[
\Delta t_{\alpha\gamma} = \sum_{\beta=1}^{\gamma-1} \Delta t_\beta.
\] (7.27e)

The derivation of eqs. (7.25) (7.27) for the statistical object of the spin boson model is left as an exercise. It uses the methods discussed in section 5.

To within a factor of an irrelevant constant, one may also write

\[
\mathcal{O} = (\text{const}') \sum_{\{s^{(\gamma)}\}} \exp\left[ \frac{1}{2} \sum_{\alpha,\gamma} \sigma^{(\alpha)} M_{\alpha\gamma}^{-1} \sigma^{(\gamma)} \right]
\] (7.28)

where

\[
M = K + P_0 I.
\]

and \( P_0 \) is a complex constant chosen to make \( M \) positive definite (i.e., simply lift lowest eigenvalue above zero). With \( P_0 \) so chosen, we can use the Hubbard Stratonovich trick to write

\[
\mathcal{O} = (\text{const}'') \int d\phi^{(1)} \int d\phi^{(2)} \ldots \int d\phi^{(P+2M)}
\times \sum_{\{s^{(\gamma)}\}} \exp\left\{ -\frac{1}{2} \sum_{\alpha,\gamma} \phi^{(\alpha)} M_{\alpha\gamma}^{-1} \phi^{(\gamma)} + \sum_{\alpha} \sigma^{(\alpha)} \phi^{(\alpha)} \right\}.
\] (7.29)

Performing the discrete sums of the \( \sigma^{(\alpha)} \)'s gives

\[
\mathcal{O} = (\text{const}''') \int \mathcal{D}\varphi \exp\left\{ -\frac{1}{2} \sum_{\alpha,\gamma} \phi^{(\alpha)} M_{\alpha\gamma}^{-1} \phi^{(\gamma)} + \sum_{\alpha} \ln 2 \cosh(\phi^{(\alpha)}) \right\}
\] (7.30)
Fig. 24. $k(t)$ computed by generalized stationary phase Monte Carlo.

and averages involving $\sigma^{(\alpha)}$ are computed from the association

$$
\sigma^{(\alpha)} \longrightarrow \tanh(\phi^{(\alpha)}).
$$

The derivation of this fact follows the same procedure used to compute $\langle \sigma \rangle$ as suggested in an exercise in section 5.4.

The statistical object, the integrand of eq. (7.30), is now a function of continuous Hubbard fields, the $\phi^{(\alpha)}$'s. In this form, the spin-boson problem is now amenable to treatment by the generalized stationary phase method. Figure 24 shows the results obtained for $k(t)$ computed with this method. Here, we have considered the model where $\Phi(\omega)/\omega$ is a Lorentzian with half width $2/\beta\hbar$.

Notice that error estimates increase as $t \to T$. This is an end-point effect akin to that encountered in ordinary molecular dynamics when one attempts to compute time correlation functions for times approaching that of the total trajectory. In the present case, we see from eq. (7.16) that until $t \to T$, there is a multitude of independent statistical samples for a given $t$ and $T$. When $t \to T$, however, the statistical object gives only one set of data for the correlation function.
Fig. 25. Representative quantum paths for the field $\varphi(t)$ when $L = 0$ and $L = 2.5$.

Also note that in the case examined here, as the localization parameter $L$ passes from 5 to 7, plateau behavior appears. Hence, for this case when $L \geq 7$, relaxation in the model is exponential, characterized by one relaxation time.

7.5. Sampling infrequent events

The generalized stationary phase Monte Carlo procedure does solve the alternating weights problem for the spin–boson model. It can be improved, however, with supplementary schemes much like non-Boltzmann sampling procedures used to enhance statistics in classical simulations. Methods of sampling infrequent events serve as an illustrative and important example [49].
Tunneling is an infrequent process for the spin boson model when \( L \) is very large. Figure 25 shows a pair of representative paths for the Hubbard field, \( \varphi(t) \). One is taken from the Monte Carlo samples generated from the discretized statistical object with \( L = 0 \), and the other from samples with \( L = 2.5 \). The kinks or instantons are associated with the tunneling as \( \varphi(t) \) reflects the behavior of \( \sigma(t) \). See eq. (7.31). We see from the diminished concentration of kinks that tunneling is indeed a rare event for \( L \gg 1 \).

These rare events are the processes that contribute to \( k(t) \). Without them, \( k(t) = 0 \). Hence, for large \( L \), the efficiency of computing this rate would be greatly enhanced if one could filter out irrelevant paths that contain no transitions. The procedure used in classical simulations initiates trajectories at an unstable transition state [49]. An analogous procedure for quantum systems can be developed with an approach suggested by Gillan [50]. The connection between this approach and a rigorous method for treating the real time dynamics of infrequent events was derived by Voth et al. [51].

To discuss their method, let us return to eq. (7.8). After a few algebraic steps, this expression can be rewritten to give

\[
k_{A \to B} = \frac{1}{Q_{A}} \text{Im} \left( \frac{2}{\beta h} \right) \int dq \int dq' \int dq'' h_{A}(q)h_{B}(q')h_{B}(q'') \times \rho(q, q'; \beta h)\rho(q', q''; -it_{pq})\rho(q'', q; it_{pq})
\]

(7.32)

where

\[
Q_{A} = \int dq h_{A}(q)\rho(q, q; \beta h)
\]

(7.33)

and \( t_{pq} \) denotes the time for \( k(t) \) to reach its plateau value. The interesting feature of eq. (7.32) is that there are three population operators as opposed to two. Using \( q^{*} \) to denote the surface which divides \( A \) from \( B \) (i.e., left states from right states in the spin–boson model or more generally reactants from products), eq. (7.32) can be represented pictorially as

\[
(\beta h/2)Q_{A}k_{A \to B} = \text{Im} \begin{array}{cc}
  & b_{B} \\
A & \cdots & b_{A} \\
  & q^{*}
\end{array}
\]

(7.34)

As is evident from the picture, only paths with two or more crossings contribute.
One can induce these crossings by controlling the center-of-mass or centroid for the thermal part of the cycle. Let

$$\tilde{q}_0 = \frac{1}{\beta \hbar} \int_0^{\beta \hbar} \text{d}t q(t)$$

(7.35)

denote this centroid. Its probability distribution is

$$p(q_x) = \langle b(\tilde{q}_0 - q_x) \rangle,$$

(7.36)

where the average over the complex statistical weight is independent of the real time section. That is, $p(q_x)$ is an equilibrium Euclidean time quantity.

Now notice, in eq. (7.34), that the geometry of relevant configurations can be created by forcing the centroid to lie close to the transition surface at $q^*$. Hence, we are motivated to use the identity,

$$(\beta \hbar/2) Q_A k_{A-B} = \int dq_x p(q_x) \text{Im} \left\{ \begin{array}{c} h_A \\ h_B \\ h_R \end{array} \right\}$$

(7.37)

The term in curly brackets represents the average over all structures of the indicated statistical object but with $\tilde{q}_0$ constrained to position $q_x$.

The analyses provided in refs. 50 and 51 suggest that the imaginary part of this constrained average gives no significant contribution to the integral over $q_x$ for $t \sim t_{eq}$ unless $q_x \approx q^*$ where $q^*$ is the bottleneck for $\tilde{q}_0$ [i.e., where $p(q)$ is minimum]. This situation is akin to the issue of choosing the location of the transition state in classical systems: If trajectories are not initiated at the unstable bottleneck, then the transmission coefficient will be small and difficult to compute. Thus, in the quantum case, $p(q^*)$ is the quantum Arrhenius exponential factor, and the integral in eq. (7.37) gives the quantum analog of the Arrhenius pre-exponential factor. In the classical limit, of course, it is easily verified that $p(q^*)$ is precisely the Arrhenius exponential factor.

To make these points concrete for a specific case, Appendix 4 provides a discussion of the golden rule rate constant for the spin-boson model. But these observations are quite general, and they make it practical to perform quantum dynamical calculations of activated processes in liquids. This ability is important as many chemical events involve strong quantum effects. For example, electron transfer in room temperature aqueous environments are dominated by quantum rotations of the water molecules.
permitting substantial proton tunneling [52]. This subject is worthy itself of extensive discussion, but for these lectures, this is The End.

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Appendix 1. Details for doing path integrals with Fourier components

Note that with an action

$$S = - \sum_{n=-\infty}^{\infty} \frac{1}{2} A_n |\hat{x}_n|^2$$

where

$$\hat{x}_n = \int_0^{\theta h} \frac{df}{\beta h} x(t)e^{i\Omega_n t}, \quad \Omega_n = \frac{2\pi n}{\beta h},$$

the variables $\hat{x}_n$ and $\hat{x}_{-n}$ are not statistically uncorrelated since

$$\hat{x}_n = \hat{x}_{-n}^*.$$

Therefore, to analyze $\langle |\hat{x}_n|^2 \rangle$, we do the following:

$$\langle |\hat{x}_n|^2 \rangle = \frac{\int Dx(t) |\hat{x}_n|^2 e^S}{\int Dx(t) e^S}$$
\[
\int \cdots \int \left( \prod_{m=\infty}^{\infty} d\hat{x}_m \right) |\hat{x}_n|^2 \prod_{\ell} e^{S_\ell} \frac{\int \cdots \int \left( \prod_{m=\infty}^{\infty} d\hat{x}_m \right) \prod_{\ell} e^{S_\ell}}{\int \cdots \int \left( \prod_{m=\infty}^{\infty} d\hat{x}_m \right) \prod_{\ell} e^{S_\ell}}
\]

and take

\[
\prod_{\ell} e^{S_\ell} = e^{S_0} \prod_{\ell>0} e^{2S_\ell}.
\]

For \( n = 0 \) (zero frequency fluctuations)

\[
\langle |\hat{x}_0|^2 \rangle = \frac{\int_{-\infty}^{\infty} d\hat{x}_0 \hat{x}_0^2 e^{-\frac{1}{2} A_0 |\hat{x}_0|^2}}{\int_{-\infty}^{\infty} d\hat{x}_0 e^{-\frac{1}{2} A_0 |\hat{x}_0|^2}} = \frac{1}{A_0}.
\]

For \( n \neq 0 \), however, we have

\[
\langle |\hat{x}_n|^2 \rangle = \frac{\int_{-\infty}^{\infty} d(\text{Re} \hat{x}_n) \int_{-\infty}^{\infty} d(\text{Im} \hat{x}_n) |\hat{x}_n|^2 e^{-A_n |\hat{x}_n|^2}}{\int_{-\infty}^{\infty} d(\text{Re} \hat{x}_n) \int_{-\infty}^{\infty} d(\text{Im} \hat{x}_n) e^{-A_n |\hat{x}_n|^2}}
\]

\[
= \int_0^\infty dr r^2 e^{-A_n r^2} \int_0^\infty dr r e^{-A_n r^2} \int_0^\infty du e^{-A_n u} \int_0^\infty du e^{-A_n u} = \frac{1}{A_n}.
\]

Thus,

\[
\langle |\hat{x}_n|^2 \rangle = \frac{1}{A_n} \text{ for all } n.
\]

Exercise: Evaluate \( Z = \langle e^{-c |\hat{x}_n|^2} \rangle \) where \( \hat{x}_n \) are Gaussian with variance \( \langle |\hat{x}_n|^2 \rangle = \frac{1}{A_n} \) and \( \langle \hat{x}_n \rangle = 0 \). [Hint: Note that \( d \ln Z / dc = -\langle |\hat{x}_n|^2 \rangle' \) where \( (\ldots)' \) is the
Appendix 2. Gaussian bath influence functional

The Gaussian bath influence functional exhibited in eq. (4.17) can be written in many equivalent ways, some of which have already been discussed in the main text. Here, we provide some more elaboration. The Gaussian influence functional contributes $S_I$ to the action, where

$$S_I = \frac{1}{2} \int_0^{\beta \hbar} \frac{dt}{\hbar} \int_0^{\beta \hbar} \frac{dt'}{\hbar} m(t)m(t') \langle E(t)E(t') \rangle_B.$$  

Since $E(t)$ is a linear combination of normal modes, eq. (5.20), the Euclidean time correlation function can be expressed as

$$\langle E(t)E(t') \rangle_B = \sum_{i,j=1}^N c_i c_j \langle y_i(t)y_j(t') \rangle_B$$

$$= \sum_{i=1}^N c_i^2 \langle y_i(t)y_i(t') \rangle_B$$

$$= \sum_{i=1}^N c_i^2 \frac{\hbar}{2m_i \omega_i} \frac{\cosh[(\omega_i/2)(\beta \hbar - 2t + 2t')] \sinh(\beta \hbar \omega_i/2)}{\sinh(\beta \hbar \omega_i/2)}.$$  

The second equality follows because different normal modes are uncorrelated, and the third employs (1.18) for the harmonic oscillator correlation function. Equation (5.37) follows directly from the last equality. According to that equation, the classical limit ($\hbar \to 0$) gives for real time $t$,

$$C_B(t) = \langle E(0)E(t) \rangle_B = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi \beta} \frac{\Phi(\omega)}{\omega} \cos(\omega t).$$

In other words, the spectral density of eq. (5.36) can be obtained from the real time Fourier transform of the classical $C_B(t)$. This observation provides a means of estimating quantum influence functionals from real time classical molecular dynamics of a realistic model bath.

The periodicity of paths and the Euclidean time correlation function also allow $S_I$ to be rewritten as

$$S_I = \frac{1}{2\hbar} \int_{-\infty}^{\infty} dt' \int_0^{\beta \hbar} dt \alpha(|t - t'|)m(t)m(t').$$
where

\[ \alpha(|t - t'|) = \int_0^\infty \Phi(\omega)e^{-\omega|t - t'|} \, d\omega. \]

This result follows from the identity

\[ \int_{-\infty}^\infty dx' e^{-|x - x'|} f(x') = \int_0^u dx' \frac{\cosh \left( |x - x'| - \frac{1}{2}u \right)}{\sinh(u/2)} f(x') \]

where \( f(x) \) is periodic with period \( u \). The demonstration is left as an exercise. [Hint: partition the infinite domain integral into an infinite sum of finite domain integrals, each of length \( u \).]

**Appendix 3. Tunnel splitting**

Our discussion of the two state model employs a tight binding approximation. Without approximation, however, a tunnel splitting formula like (5.13) can still be derived. Consider again a bistable potential like that drawn in fig. 13. The object is to compute \( K \) by path integration. Independent of basis set approximation, we may write

\[ \langle x | e^{-\epsilon H} | x' \rangle = \psi_g(x)\psi_g(x')e^{-\epsilon E_g} + \psi_u(x)\psi_u(x')e^{-\epsilon E_u} + \ldots \]

where the neglected terms in the expansion are negligible for \( \epsilon \Delta E \gg 1 \). Here, \( E_g \) and \( E_u \) are the ground and first excited state energies (\( E_u - E_g = 2K \)), and \( \psi_g(x) \) and \( \psi_u(x) \) are the corresponding wave functions.

Assume a plane of symmetry can be identified such that with \( x \) and \( x' \) in the two different stable regions

\[ \psi_g(x) = \psi_g(x'), \quad \psi_u(x) = -\psi_u(x'). \]

In principle, these points can be identified precisely. In practice, a small error in their location will introduce a small percentage error in the calculation of \( K \) described below.

With this choice for \( x \) and \( x' \), straightforward algebraic manipulations show that

\[ R \equiv \frac{\langle x | e^{-\epsilon H} | x' \rangle}{\langle x | e^{-\epsilon H} | x \rangle} \]
is given by
\[ R = \tanh[\epsilon K - z(x)] \]
or
\[ \epsilon K = \frac{1}{2} \ln \left( \frac{1 + R}{1 - R} \right) + z(x) \]
where
\[ z(x) = \ln[\psi_u(x)/\psi_g(x)]. \]

The ratio, $R$, is a small number because the barrier is high, and $x$ and $x'$ are located in the opposite stable states. As a result, the logarithm can be expanded to give
\[ \epsilon K = R + z(x) \]
in almost perfect agreement with eq. (5.13). The difference, $z(x)$, is small but in general nonzero. The difference does vanish in the tight binding approximation,

\[ \psi_g \text{ or } u(x) \approx \frac{1}{\sqrt{2}} [\phi_1(x) \pm \phi_{-1}(x)]. \]

Independent of that approximation, however, $K$ can be computed exactly from $R$ since $K$ is the slope of $R$ as a function of $\epsilon$. With tight binding, one imagines that virtually no time is spent outside the stable states. The actual instanton time is $\hbar z(x)/K$.

As an exercise, consider the case where the symmetric pair, $x$ and $x'$, can be located only approximately. Show that the tunnel splitting can still be computed exactly through
\[ \epsilon K = (RR')^{1/2} + z'(x, x') \]
where
\[ R' = \frac{\langle x' | e^{-\epsilon H} | x \rangle}{\langle x' | e^{-\epsilon H} | x' \rangle} \]
and $z'(x, x')$ is independent of $\epsilon$. 

Appendix 4. Golden-rule rate constant for the spin–boson model

Consider the case in which coupling parameter, $K$, is very small. If it is zero, the eigenstates are known as diabatic states, and no transitions between left and right are possible. The rate of transitions for small $K$ can be computed by ordering contributions to the rate constants in powers of $K$. Such a procedure was already done in the text as an exercise leading to eq. (7.13). In the present case, the reactants are the manifold of vibrational states with the spin on the left, $\sigma = -1$. We will call this species $A$. Similarly, the product $B$ has the manifold of vibrational states with $\sigma = +1$.

The direct expansion of the propagators in eq. (7.10) yields

\[
k_{A \rightarrow B} = \frac{2\pi}{\hbar} K^2 \sum_{f,i} \frac{\delta(E_i^{(A)} - E_f^{(B)})}{\sum_i e^{-\beta E_i^{(A)}}} + O(K^4)
\]

\[
= \frac{2\pi}{\hbar} K^2 \int_{-\infty}^{\infty} \frac{dt}{2\pi\hbar} C(t),
\]

where

\[C(t) = Q_A^{-1} \text{tr} e^{-(\beta \hbar - it)H_A/\hbar} e^{-itH_B/\hbar}.\]

Here $E_i^{(A)}$ and $E_f^{(B)}$ are the eigenenergies for the diabatic hamiltonians, $H_A$ and $H_B$, and $Q_A = \text{tr} \exp(-\beta H_A)$.

In the second equality and in what remains, we ignore the terms of higher order than $K^2$. It is the golden rule approximation for the rate. In view of fig. 15, the approximation is applicable when the two adiabatic surfaces are very close – appearing as two intersecting parabolas (the diabatic potentials) – and non-adiabatic transitions occur frequently. As a rough estimate of $k_{A \rightarrow B}$, consider neglecting the non-commutation of $H_A$ and $H_B$. With this approximation, the integral over $t$ yields

\[
k_{A \rightarrow B} = (2\pi/\hbar) K^2 \langle \delta(V_A - V_B) \rangle_A
\]

\[
= (2\pi/\hbar)(K^2/F) \langle \delta(q - q^*) \rangle_A
\]

where $q^*$ denotes the configuration of the bath where the two potential energy surfaces are equal, i.e., $V_A(q^*) = V_B(q^*)$, and $F^{-1}$ is the average of $|d(V_A - V_B)/dq|^{-1}$ given that the bath is at $q = q^*$. The value of the rate constant is dominated by the Arrhenius exponential factor which in this case is the probability density for $q = q^*$. 
If the bath is treated quantum mechanically, however, the actual density is replaced by the centroid density. We have argued that this is the case in section 7. Below, we illustrate the fact with an explicit calculation. Note that the distinction between density and centroid density is significant. Paths contributing to the rate must pass completely from one stable state to the other, i.e., they must tunnel through the barrier in fig. 15. Paths that tunnel only halfway through a barrier cannot contribute to the rate. The *incomplete* circuits are the dominant contributions to the density, but the complete tunneling paths dominate the centroid density.

To evaluate the integral over $C(t)$ for a quantal bath, note that $C(t)$ is generally highly oscillatory. Hence, an accurate estimate can be obtained by deforming the contour of integration to pass through a point $t^*$ where the phase of $C(t)$ is stationary. The method of steepest descents can then be applied: Write $C(t)$ as $\exp[\ln C(t^*) + (t - t^*)^2 C''(t^*)/2 + \cdots]$. truncate the expansion at quadratic order and do the Gaussian integral. This gives

$$k_{A\rightarrow B} = \frac{K^2}{\hbar^2} \left[ \frac{2\pi}{C''(t^*)} \right]^{\frac{1}{2}} C(t^*)^\frac{1}{2}.$$

Anticipating that $t^*$ will be pure imaginary, we evaluate $C(t)$ at Euclidean time $\tau$ between 0 and $\beta\hbar$:

$$\tilde{C}(\tau) = \left[ \frac{\int \mathcal{D}\mathcal{E}(t)e^{S_{\mathcal{E}}} \exp \left[ \int_0^{\beta\hbar} \frac{d\tau'}{\hbar} \mu \sigma(\tau' + \tau)\mathcal{E}(\tau') \right]}{\int \mathcal{D}\mathcal{E}(t)e^{S_{\mathcal{E}}} \exp \left[ -\int_0^{\beta\hbar} \frac{d\tau'}{\hbar} \mu \mathcal{E}(\tau') \right]} \right]$$

$$= \exp \left\{ \frac{\mu^2}{2} \int_0^{\beta\hbar} \frac{d\tau_1}{\hbar} \int_0^{\beta\hbar} \frac{d\tau_2}{\hbar} \sigma(\tau_1 + \tau)\sigma(\tau_2 + \tau) - 1][\mathcal{E}(\tau_1)\mathcal{E}(\tau_2)]_{B} \right\}$$

$$= \exp \left\{ -2\mu^2 \int_0^{\tau} d\tau_1 \int_0^{\tau} d\tau_2 [\mathcal{E}(\tau_1)\mathcal{E}(\tau_2)]_{B} \right\}$$

where $\sigma(\tau) = \text{sgn}(\tau - \beta\hbar)$, i.e., the spin changes from left to right at Euclidean time $\beta\hbar - \tau$, and $\mathcal{E}(t)$ is the Gaussian local field of the spin–boson model. Now using the autocorrelation function eq. (5.37) and integrating we find

$$\tilde{C}(\tau) = \exp \left( -4\mu^2 \int_0^\infty \frac{d\omega}{2\pi\hbar} \frac{\Phi(\omega)}{\omega^2} \frac{1}{\sinh(\beta\hbar\omega/2)} \right) \times \left\{ \cosh \left( \frac{\beta\hbar\omega}{2} \right) - \cosh \left[ \omega \left( \frac{\beta\hbar}{2} - \tau \right) \right] \right\}.$$
We see that the stationary phase point occurs at $\tau^* = \frac{1}{2} \beta \hbar$, the expected result for a symmetric system. (For an asymmetric case, an extremum would still lie on the Euclidean time axis, but displaced from the midpoint, $\frac{1}{2} \beta \hbar$.) The Arrhenius exponential factor corresponds to the centroid density at the saddlepoint between the two stable states. The evaluation of $\tilde{C}(\frac{1}{2} \beta \hbar)$ and $\tilde{C}''(\frac{1}{2} \beta \hbar)$ yields

$$k_{A \rightarrow B} = \frac{K^2}{\hbar^2} \left[ \mu^2 \int_0^\infty \frac{d\omega}{\pi^2} \frac{\Phi(\omega)}{\hbar \sinh(\beta \hbar \omega/2)} \right]^{-\frac{1}{2}} \times \exp \left\{ -2 \mu^2 \int_0^\infty \frac{d\omega}{\pi \hbar} \frac{\Phi(\omega)}{\omega^2} \tanh(\beta \hbar \omega/4) \right\}.$$

References

D. Chandler


Quantum processes in liquids


