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A PHASE SPACE SAMPLING APPROACH TO EQUILIBRIUM SEMICLASSICAL STATISTICAL MECHANICS

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A non-perturbative semiclassical approach to statistical mechanics is reviewed and discussed in terms of the idea of phase space sampling. The approach is then used to treat quantum effects in the vibrational state distribution of HCl and in the two particle radial distribution function for He⁴ as well as in the case of a sample discontinuous potential. Although further work is indicated for hard wall potentials, the method does seem to provide a facile technique for approximating quantum corrections in situations of chemical interest.
I. Introduction

Since many problems of current chemical interest in equilibrium statistical mechanics are difficult to treat in the framework of classical mechanics, it would seem to be clear that any attempt to introduce quantum effects would probably make things even more unwieldy. The mathematical complexities of dealing with the classical N body problem are sufficiently intractable without replacing dynamical variables and phase space integrals by operators and quantum mechanical traces.

Yet if one could somehow preserve the form of classical statistical averages—that of a phase space integral over some distribution function—it is conceivable that much of the classical formalism could be extended to include at least some quantum effects. For example, one could easily extend the distribution function formulation of the theory of fluids\(^1\) if it were possible to have a semiclassical phase space distribution rather than a purely classical one. Moreover, in view of the mass and temperature regions of chemical interest, a semiclassical approach should be adequate.

In this spirit this paper investigates a semiclassical partition function and expressions for the semiclassical ensemble average energy (including all quantum effects other than nuclear spin) which can be derived from the semiclassical propagator\(^2\) in imaginary time. The highly suggestive classical phase space integral form of these expressions leads to a useful, though not strictly correct, representation of general semiclassical ensemble averages. Possibly more important however, this particular semiclassical approach lends itself readily to physical
interpretation while still retaining its ties to quantum mechanics. Thus it also permits one to at least think about the development of a self-consistent semiclassical statistical mechanics.

By way of contrast consider some of the alternative methods of including quantum mechanics in equilibrium statistical mechanics. The exact approach is to use the Boltzmann density operator \( \rho = e^{-\beta \hat{H}} \). The partition function \( Q \) and the ensemble average of any observable \( F \) are then given in terms of the quantum mechanical trace (i.e., a sum over bound states and/or an integral over continuum states).

\[
Q = \text{Tr}(e^{-\beta \hat{H}}) = \sum_n <\psi_n | e^{-\beta \hat{H}} | \psi_n > = \sum_n e^{-\beta E_n}
\]

\[
<F> = \frac{1}{Q} \text{Tr}(\hat{F} e^{-\beta \hat{H}}) = \frac{1}{Q} \sum_n <\psi_n | \hat{F} e^{-\beta \hat{H}} | \psi_n >
\]

Another exact (and therefore equivalent) representation may be obtained from the Wigner function \(^3\)

\[
\rho_W(p,q) = h^{-N} \int dq' e^{ipq'/\hbar} <q - \frac{1}{2} q' | e^{-\beta \hat{H}} | q + \frac{1}{2} q'>
\]

which leads to a phase space integral formulation

\[
Q = \frac{1}{\hbar} \int \int \rho_W(p,q) dp dq 
\]

\[
<F> = \frac{1}{Q\hbar} \int \int F(p,q) \rho_W(p,q) dp dq
\]

though Eq. (1.3) is not quantum mechanically correct if \( F \) is a coupled function of \( p \) and \( q \).
Both of these representations suffer from the fact that one must first solve the Schrödinger equation in order to evaluate the necessary matrix elements. This presents not only computational problems but formal ones as well. Further, in situations of chemical interest where quantum effects are relatively small, the unwieldiness of these expressions tends to obscure whatever physical insight might be gained from observing the onset of quantum effects.

A rather different, though still exact, approach is to express the density matrix in terms of a functional (path) integral

\[
\rho(x_0) = \int \exp \left\{ -\frac{1}{\hbar} \int_0^\beta \frac{1}{2} m \left( \frac{dx}{dt} \right)^2 + V(x(t)) \right\} dx(t)
\]

where the notation \( dx(t) \) means to integrate over all paths \( x(t) \) which start and end at the point \( x_0 \) [i.e., \( x(t=0) = x_0, x(t=\beta) = x_0 \)]. This is an intuitively appealing expression which in fact can be used to derive the results of this paper. However when directly applied to molecular problems, the need to integrate over an infinite number of functions (rather than an infinite number of points) can present grave calculational difficulties.

Finally, the traditional method of obviating these troubles with molecular statistical mechanics is to approximate the quantum effects via the Wigner-Kirkwood expansion

\[
\rho(x) = \rho_{CL}(x) \left[ 1 + \lambda A + \lambda^2 B + \ldots \right]
\]

where the classical density matrix is \( \rho_{CL} \) and
\[ \rho_{CL}(x) = (2\pi\mu/\hbar^2)^{1/2} e^{-\beta V(x)} \]

\[ \lambda = \hbar^2 \beta^2 / 2m \]

\[ A = \beta (\frac{\partial V}{\partial x})^2 / 12 - \frac{\beta^2 V}{36} \]

\[ B = \beta^2 (\frac{\partial V}{\partial x})^4 / 288 - \beta (\frac{\partial V}{\partial x})^2 (\frac{\partial^2 V}{\partial x^2}) (11/360) + \frac{\beta^2 V}{40} \]

\[ + \left( \frac{\partial V}{\partial x} \right) \left( \frac{\partial^3 V}{\partial x^3} \right) / 30 - \frac{1}{\beta} \left( \frac{\partial^4 V}{\partial x^4} \right) / 60 \]  

(1.6)

Since this is an expansion in powers of \( \hbar \), the term by term physical interpretation is clear if the series converges. Nonetheless, this is also an expansion in derivatives of the potential so that any application to hard wall (discontinuous) potentials is automatically precluded.

With the shortcomings of these methods in mind the next two sections (II, III) of this paper will review the derivation of the non-perturbative semiclassical expressions for the partition function and particle density given by Miller and discuss their interpretation and possible usage. Section IV gives some elementary examples of usage including both intra- and inter-molecular applications. The last section (V) is devoted to possible future developments.
II. Summary of Formalism

Following the work of Miller\textsuperscript{7,9} and Miller and Hornstein\textsuperscript{8} the
semiclassical partition function can be derived from the semiclassical
propagator. The basis of the derivation is the formal similarity
between the quantum mechanical propagator Eq. (2.1) and the Boltzmann
density matrix Eq. (2.2).

\[ U(t,t_0) = e^{\hat{H}(t-t_0)/i\hbar} \]  
\[ \rho(\beta) = e^{-\beta\hat{H}} \]  

If the identification of temperature with an imaginary time interval is
made

\[ \hbar\beta = i(t-t_0) \]  

then Eqs. (2.1) and (2.2) become identical. Equivalently, the quantum
mechanical propagator can be shown to be a solution to the Bloch equation

\[ \frac{\partial \rho}{\partial \beta} = -\hat{H}\rho \]

which is what defines the density matrix.

The advantage of making this purely quantum mechanical identification
is that one can then use a semiclassical approximation to the propagator
to simultaneously provide a semiclassical density matrix. In the semi-
classical limit a quantum mechanical matrix element corresponding to any
unitary transformation may be approximated\textsuperscript{2} by an expression involving
the generator of the corresponding classical canonical transformation. The relevant transformation for the propagator, evolution in time, is generated by the classical action. Hence the classical limit propagator may be written as follows:

$$\langle q | \exp\left(\hat{H}(t-t_0)/i\hbar\right) | q_0 \rangle = \left[\hbar N \left(\frac{\partial q}{\partial q_0}\right)_{q_0} \right]^{-\frac{1}{2}} \frac{i\phi}{\hbar}$$

(2.5)

where the transformation involved is the evolution of the state with coordinate $q_0$ at time $t_0$ to a state with coordinate $q$ at time $t$, all while following a classical path with action given by $\phi$

$$\phi = \int_{t_0}^{t} L dt'$$

$L = \text{Lagrangian}$

Since we are interested in the diagonal elements of the density matrix (the particle density itself)

$$\rho(q_0) = \langle q_0 | e^{-\hat{H}} | q_0 \rangle$$

it is convenient to break up the matrix into two parts each of which may be separately approximated by our semiclassical propagator. Letting $| q \rangle$ represent a complete set of states

$$\rho(q_0) = \langle q_0 | e^{-\hat{H}} | q_0 \rangle = \langle q_0 | e^{-\hat{H}/2} e^{-\hat{H}/2} | q_0 \rangle$$

$$= \int \langle q_0 | e^{-\hat{H}/2} | q \rangle \langle q | e^{-\hat{H}/2} | q_0 \rangle dq$$

$$= \int | \langle q | e^{-\hat{H}/2} | q_0 \rangle |^2 dq$$

(2.6)
Now identifying the density matrix element with the propagator matrix element and approximating that via Eq. (2.5) leaves

\[ \rho(q_0) = \hbar^{-N} \int \left( \frac{\partial p_0}{\partial q_0} \right) e^{2i\phi/h} \, dq \]

\[ \rho(q_0) = \hbar^{-N} \int e^{2i\phi/h} \, dp_0 \]  \hspace{1cm} (2.7)

where the correspondence relation equivalent to Eq. (2.3), but for the operator \( e^{-\beta \hat{H}/2} \) instead of \( e^{-\beta \hat{H}} \), is given by

\[ \hbar \beta/2 = i(t-t_0) \]  \hspace{1cm} (2.8)

Given Eq. (2.7) the partition function may then be written

\[ Q = \int \rho(q_0) dq_0 = \hbar^{-N} \int \int e^{2i\phi/h} \, dp_0 \, dq_0 \]  \hspace{1cm} (2.9)

At this point it is worthwhile to note the form of Eqs. (2.7) and (2.9). The partition function, for example, has the appearance of an integral over phase space of a probability factor for each phase space point \((q_0, p_0)\). That probability factor, in turn, depends on the action of an imaginary time classical path starting at the phase point in question and continuing for a total imaginary time of \( \hbar \beta/2 \). In other words, our formalism suggests a semiclassical phase space distribution which weights phase space points by considering them as starting points for weighting trajectories.

To complete the derivation of the partition function we need an explicit expression for the imaginary time action. From classical
mechanics the Lagrangian may be written

\[ L = p \frac{dq}{dt} - H(p, q) \quad (H = \text{Hamiltonian}) \]

thus making the substitutions \( \tau = it \) and \( \tilde{p} = -ip \) implies

\[ L = - p \frac{dq}{d\tau} - H(ip, q) \]

so that the action becomes (using Eq. (2.8) to give the imaginary time interval)

\[ \phi = i \int \frac{h^2}{2} \left[ p(\tau) \frac{dq(\tau)}{d\tau} + H(ip(\tau), q(\tau)) \right] d\tau \]  

and the equivalent of Hamilton's equations of motion needed to determine \( p(\tau) \) and \( q(\tau) \) becomes

\[ \frac{dq(\tau)}{d\tau} = - \frac{\partial H(ip, q)}{\partial \tilde{p}}, \quad \frac{dp(\tau)}{d\tau} = \frac{\partial H(ip, q)}{\partial q} \]  

If the Hamiltonian is in Cartesian form -- i.e., \( H(p, q) = \frac{1}{2m} p^2 + V(q) \), Eq. (2.10) simplifies considerably since then \( \tilde{p} = m \frac{dq(\tau)}{d\tau} \).

\[ \phi = i \int_0^{h^2/2} \left( \frac{1}{2m} \tilde{p}^2 + V(q) \right) d\tau = i \int_0^{h^2/2} H[\tilde{p}(\tau), q(\tau)] d\tau \]  

The equations of motion are also reduced.

\[ \frac{dq(\tau)}{d\tau} = - \frac{\partial H(ip, q)}{\partial \tilde{p}} = \frac{1}{m} \tilde{p} \]

\[ \frac{dp(\tau)}{d\tau} = \frac{\partial H(ip, q)}{\partial q} = \frac{\partial V}{\partial q} \]
For convenience we will assume a Cartesian form for the remainder of this paper with the understanding that the action integral of Eq. (2.12) need only be replaced by Eq. (2.10) should other coordinates be desired. Accordingly, dropping the (now superfluous) bar over "p" gives the final form for the semiclassical particle density and the semiclassical partition function:

\[ \rho_{SC}(q_0) = \hbar^{-N} \int_{-\infty}^{\infty} \exp\left\{ -\frac{2}{\hbar} \int_{0}^{\hbar \beta/2} H[p(\tau), q(\tau)] d\tau \right\} dp_0 dq_0 \]  

(2.14)

\[ Q_{SC} = \hbar^{-N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left\{ -\frac{2}{\hbar} \int_{0}^{\hbar \beta/2} H[p(\tau), q(\tau)] d\tau \right\} dp_0 dq_0 \]  

(2.15)

It should be mentioned, in passing, that the correspondence relation between temperature and imaginary time (Eq. (2.8)) does not imply that the trajectory progresses from \( T \) to 0 to \( \tau = \hbar \beta/2 \), but only that the time interval is \( \hbar \beta/2 \). This means that the \( \tau \) integrals in Eqs. (2.14) and (2.15) could have limits of \( \tau_0 \) and \( \hbar \beta/2 + \tau_0 \) for some arbitrary constant, \( \tau_0 \). However, since our mechanics is still Hamiltonian in character it turns out to be possible to define a transformation in \( \tau \) as a canonical transformation (one preserving our equations of motion). Hence it will always be possible to do a time translation to get rid of any \( \tau_0 \).

Now that an expression for the partition function has been obtained it is a simple matter to obtain corresponding formulas for ensemble averages of energy to any power. From quantum statistical mechanics
Therefore by differentiating Eq. (2.15) with respect to $\beta$ we find that

$$\langle E \rangle_{SC} = \frac{1}{N_{Sch}^N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} H(\beta/2) \exp\left\{ \frac{1}{\hbar} \int_{0}^{\hbar \beta/2} H(\tau) d\tau \right\} d\xi_0 dq_0$$  \hspace{1cm} (2.16)

$$\langle E^2 \rangle_{SC} = \frac{1}{N_{Sch}^N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} H^2(\beta/2) \exp\left\{ \frac{1}{\hbar} \int_{0}^{\hbar \beta/2} H(\tau) d\tau \right\} d\xi_0 dq_0$$

$$- \frac{1}{N_{Sch}^N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left( \frac{\partial}{\partial \beta} H(\beta/2) \right) \exp\left\{ \frac{1}{\hbar} \int_{0}^{\hbar \beta/2} H(\tau) d\tau \right\} d\xi_0 dq_0$$  \hspace{1cm} (2.17)

$$\langle E^3 \rangle_{SC} = \frac{1}{N_{Sch}^N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} H^3(\beta/2) \exp\left\{ \frac{1}{\hbar} \int_{0}^{\hbar \beta/2} H(\tau) d\tau \right\} d\xi_0 dq_0$$

$$- 3 \frac{1}{N_{Sch}^N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} H(\beta/2) \left( \frac{\partial^2}{\partial \beta^2} H(\beta/2) \right) \exp\left\{ \frac{1}{\hbar} \int_{0}^{\hbar \beta/2} H(\tau) d\tau \right\} d\xi_0 dq_0$$

$$+ \frac{1}{N_{Sch}^N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left( \frac{\partial^2}{\partial \beta^2} H(\beta/2) \right) \exp\left\{ \frac{1}{\hbar} \int_{0}^{\hbar \beta/2} H(\tau) d\tau \right\} d\xi_0 dq_0$$  \hspace{1cm} (2.18)
and so on. The notation $H(h\beta/2)$ means $H[p(\tau = h\beta/2), q(\tau = h\beta/2)]$.

Observe also that in the limit that $\beta$ goes to zero (infinite temperature), $H(h\beta/2)$ goes to $H(0) = H(p_0, q_0)$ and the argument of the exponent goes to

$$-\beta \frac{2}{h\beta} \int_0^{h\beta/2} H(\tau) d\tau \longrightarrow -\beta H(0) = -\beta H(p_0, q_0).$$

Thus the semiclassical partition function and semiclassical ensemble average energy reduce to the correct classical limit.

$$Q_{SC} \longrightarrow h^{-N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\beta H(p_0, q_0)} dp_0 dq_0 = Q_{CL}$$

(2.19)

$$\langle E \rangle_{SC} \longrightarrow \frac{1}{Q_{CL}h^N} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} H(p_0, q_0) e^{-\beta H(p_0, q_0)} dp_0 dq_0 = \langle E \rangle_{CL}$$

(2.20)

Moreover since in the low $\beta$ limit $H(h\beta/2)$ becomes independent of $\beta$, the higher powers of energy also reduce correctly. The semiclassical formalism, in addition to possessing the desired phase space integral form, is therefore seen to behave in accordance with the correspondence principle.
III. Discussion

It is particularly illuminating to contrast the semiclassical form of the partition function (Eq. 2.15) with the classical form (Eq. (2.19)). The only difference between the two is that the semiclassical expression replaces $\exp\{-\beta H\} \exp\{-\frac{2}{\hbar\beta} \int_0^\beta H(\tau) d\tau\}$ -- i.e., it replaces the Hamiltonian evaluated at phase space point of interest by the time average of the Hamiltonian along some path through phase space which starts at the point of interest.

In effect this means that the semiclassical formalism is automatically weighting each phase space point not just according to its own "merits" (its own Hamiltonian) but according to the contributions (Hamiltonians) of the neighboring phase space points as well (with only those phase points which lie along the imaginary trajectory considered as neighbors). Moreover since the length of the trajectory which "samples" the neighboring phase space is proportional to $\beta$, the sampling is temperature dependent. At high temperatures (small $\beta$, the classical limit) only those regions of phase space very close to the original phase point contribute whereas at low temperatures (large $\beta$, the quantum regime) it is necessary to include the contributions of a significant number of new phase space points.

Because of this, the temperature dependence can be construed as just a manifestation of the energy/time uncertainty principle. Rewriting Eq. (2.8)

\[(1/\beta) \tau = \hbar/2\]

appears to imply that the larger the thermal energy $(1/\beta)$ the smaller the
sampling time \( t \) and vice-versa. In other words, at high temperatures the amount of quantum interference with the neighboring phase space is miniscule but at lower temperatures the effects of superposition and interference between any one phase space point and those surrounding it become important.

All of this conceptual framework is more than a little reminiscent of Feynman's path integral approach to quantum mechanics\(^\text{12}\) in which the probability of traveling from one point to another is expressed in terms of a sum over every possible connecting path of a probability for that path. As in our semiclassical statistical mechanics the probability of any particular time propagation (phase space point) would depend not only on the classical trajectory (original phase space point) but on the interference with the neighboring trajectories (phase space points) as well.

The similarity with the path integral representation even goes beyond this. For one thing it is possible to derive this semiclassical formalism from expressions such as Eq. (1.4)\(^\text{13}\) by replacing the integral over all paths with an integral over simply the classical path. More directly, as pointed out by Miller,\(^\text{9}\) the device of breaking up the diagonal density matrix element into two parts (Eq. (2.6)) can be extended to a division into an infinite number of parts.

\[
\rho(q_0) = \langle q_0 | e^{-\hat{H}t} | q_0 \rangle = \int \cdots \int <q_0 | e^{-\hat{H}/(N+1)} | q_1 > <q_1 | e^{-\hat{H}/(N+1)} | q_2 > \cdots <q_N | e^{-\hat{H}/(N+1)} | q_0 > dq_1 dq_2 \cdots dq_N
\]

Even though each part would still be evaluated via a classical path approximation, the end result would be a quantum mechanically exact path integral form.
Based on this similarity of our formalism to that of the (exact) path integral formalism and in view of its physically appealing interpretation it is certainly tempting to consider the integrand of Eqs. (2.14) and (2.15) as a bona fide semiclassical phase space distribution. Given such an ansatz one could then write a general expression for a semiclassical ensemble average of any quantity $A(p,q)$.

$$\langle A \rangle_{SC} = \frac{1}{Q_{SC}} \left\langle \int \int A(p_0, q_0) \exp\left\{- \frac{2}{\hbar} \int_0^\beta \int_0^\beta H(\tau) d\tau\right\} dp_0 dq_0 \right\rangle$$  \hspace{1cm} (3.1)

However while this may be a useful conceptual (and even computational) tool it is clearly not strictly correct—even in the semiclassical limit. One only has to compare Eq. (3.1) with the expressions for energy to various powers (Eqs. (2.17) and (2.18)) to realize this.

Further, the very meaning of a phase space average for a general function of $p$ and $q$ is ambiguous due to noncommutativity of the $\hat{p}$ and $\hat{q}$ operators. Consequently it would not be totally unexpected if quantum mechanical averages of any function which is coupled in $p$ and $q$ classically (such as $E^n$) failed to satisfy an equation such as (3.1). On the other hand, Eq. (3.1) is certainly correct, within our formalism if $A$ is a function of $q$ alone. That follows from Eq. (2.14). In addition the formulas for $\langle E^2 \rangle$ and $\langle E^3 \rangle$ suggest that Eq. (3.1) might be at least approximately correct for other functions since it may be the leading term in the "correct" answer. This is illustrated for the harmonic oscillator in the next section of the paper.

Before concluding this section it would be worthwhile to make one further point concerning the semiclassical statistical mechanics formalism.
Namely, even though the Hamiltonian used in computing the partition function (e.g.,) may be separable in kinetic energy and potential energy (p and q) the resulting action integral in general will not be separable into \( p_0 \) and \( q_0 \) segments. Mathematically this is simply because classical mechanics itself does not preserve such a separation when a mechanical quantity is expressed in terms of initial coordinates.\(^\text{14}\) Note however that this implies that it will not be possible to express N-body semi-classical expressions in terms of configuration integrals alone (as is done with the corresponding classical formulas). Despite the added computational labor this engenders, it is interesting to observe its occurrence as a direct result of including quantum effects in statistical mechanics.
IV. Examples of Usage

With all of the examples discussed below overall procedure is
1) first solve the imaginary time equations of motion (Eq. 2.13) to
obtain $p(\tau)$ and $q(\tau)$ as a function of the initial coordinates, $p_0$ and $q_0$;
2) then substitute these into $H(p, q)$ to get $H(\tau)$ as a function of $p_0$ and $q_0$;
3) integrate this (Eq. 2.12) to get the action and therefore the phase space
weight as a function of $p_0$ and $q_0$, and finally, 4) do the phase space
integrations as in Eqs. (2.15) and (2.16).

A. Simple Harmonic Oscillator

The harmonic oscillator is one of the few examples for which the
semiclassical formalism, the classical statistical mechanics, and the
exact quantum statistical mechanics can all be computed analytically
so it serves as a useful starting point. For the classical Hamiltonian

$$H = \frac{1}{2m} p^2 + \frac{1}{2} \hbar \omega q^2$$

the classical partition function and average energy are given by

$$Q_{CL} = (\hbar \omega \beta)^{-1}$$

$$\langle E \rangle_{CL} = 1/\beta$$

(4.1)

while the corresponding quantum results are

$$Q_{QM} = (2 \sinh (\hbar \omega \beta / 2))^{-1}$$

$$\langle E \rangle_{QM} = \frac{\hbar \omega}{2} \coth (\hbar \omega \beta / 2)$$

(4.2)
However proceeding semiclassically: the imaginary time equations of motion become

\[ \frac{dq}{d\tau} = \frac{1}{m} p, \quad \frac{dp}{d\tau} = m\omega^2 q \]

Solving these yields

\[ q(\tau) = q_0 \cosh \omega \tau + \frac{p_0}{m\omega} \sinh \omega \tau \]
\[ p(\tau) = p_0 \cosh \omega \tau + m\omega q_0 \sinh \omega \tau \]

which implies that the Hamiltonian is

\[ H(\tau) = H(p(\tau), q(\tau)) \]
\[ = \left( \frac{1}{2m} p_0^2 + \frac{1}{2} m\omega^2 q_0^2 \right) \cosh 2\omega \tau + (\omega p_0 q_0) \sinh 2\omega \tau \]

and therefore that the action can be written

\[ \int_0^{\beta/2} \frac{2}{\hbar} H(\tau) d\tau = \]
\[ \frac{1}{\hbar \omega} \left( \frac{1}{2m} p_0^2 + \frac{1}{2} m\omega^2 q_0^2 \right) \sinh \hbar \omega \beta + \frac{1}{\hbar \omega} (\omega p_0 q_0) (\cosh \hbar \omega \beta - 1) \]

This gives us the desired phase space "weighing function" (which, it might be noted, is coupled in \( p_0 \) and \( q_0 \))

\[ \rho_{SC} = \exp\left\{ -\frac{1}{\hbar \omega} \left( \frac{1}{2m} p_0^2 + \frac{1}{2} m\omega^2 q_0^2 \right) \sinh \hbar \omega \beta \right. \]
\[ \left. - \frac{1}{\hbar \omega} (\omega p_0 q_0) (\cosh \hbar \omega \beta - 1) \right\} \tag{4.3} \]

We can now compute the partition function and ensemble average energy via Eqs. (2.15) and (2.16).
Comparing the results with Eq. (4.2) reveals that the semiclassical formalism gives the exact quantum answers. Similarly with the energy squared [Eq. (2.17)]

\[
\langle E \rangle_{SC} = \frac{1}{Q_{SC}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} H(\hbar \beta/2) \rho_{SC} d\rho d\theta = \frac{\hbar \omega}{2} \coth (\hbar \omega \beta/2)
\]

Equation (2.14), for the position distribution function, also turns out to give the correct quantum answer

\[
\rho_{SC}(q_0) = \frac{1}{\hbar} \int \rho_{SC} d\rho
\]

\[
= \frac{\hbar \omega \beta}{\sinh \hbar \omega \beta} \left( \frac{2 \pi m}{\hbar^2} \right)^{\frac{1}{2}} \exp \left\{ \frac{2}{\hbar \omega} \left( \frac{1}{2} \hbar \omega q_0^2 \right) \tanh \left( \hbar \omega \beta/2 \right) \right\} \tag{4.4}
\]

If one were willing to accept that Eq. (4.3) defines a true phase space distribution function (and not just something which integrates out correctly) we could define a momentum distribution function with form analogous to Eq. (2.14). This also happens to provide the exact result.
Observe that, taken together, Eqs. (4.4) and (4.5) imply that we can use Eq. (3.1) to analytically calculate the correct ensemble average of any function of \( p \) and \( q \) (which is not coupled in \( p \) and \( q \)) for the harmonic oscillator.

Nevertheless the restriction of no coupling is a significant one.

For example, Eq. (3.1) would predict for the average of \( A = pq \) that

\[
\langle pq \rangle_{SC} = -\frac{h}{2}
\]

whereas

\[
\langle pq \rangle_{CL} = 0
\]

\[
\langle \hat{p}\hat{q} \rangle_{QM} = i\hbar/2 , \quad \langle \hat{q}\hat{p} \rangle_{QM} = -i\hbar/2
\]

and for \( A = p^2q^2 \) Eq. (3.1) would imply that

\[
\langle p^2q^2 \rangle_{SC} = \frac{\hbar^2}{4}(\coth^2 (\hbar\omega/2) + 2)
\]

whereas

\[
\langle p^2q^2 \rangle_{CL} = 1/\beta^2\omega^2
\]

\[
\langle \hat{p}^2\hat{q}^2 \rangle_{QM} = \langle \hat{q}^2\hat{p}^2 \rangle_{QM} = \frac{\hbar^2}{4}(\coth^2 (\hbar\omega/2) - 2)
\]
Coincidentally the semiclassical answer for $<p^2q^2>$ happens to be the exact quantum answer for $<\hat{p}\hat{q}^2> = <\hat{q}\hat{p}^2>$. To obtain a true semiclassical expression for $<p^2q^2>$ the result for $<E^2>_{SC}$ can be combined with those of $<p^4>_{SC}$ and $<q^4>_{SC}$ (from Eqs. (4.4) and (4.5)) to give a result in which Eq. (3.1) defines the leading term.

$$\text{true } <p^2q^2>_{SC} = \frac{1}{Q_{SC}^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} p_0^2 q_0^2 \rho_{SC} \, dp_0 dq_0$$

$$- \frac{1}{Q_{SC}^2 h^2 \omega^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \frac{3}{\hbar} \frac{\partial}{\partial \beta} (H(h\beta/2)) \rho_{SC} \, dp_0 dq_0$$

$$= <p^2q^2>_{QM}$$

B. Particle in a Box

Even though this example is not of great interest in itself, it does act as a prototype for systems with hard wall potentials which are of interest--e.g., hard sphere and Sutherland potential models of fluids. Moreover, since (as mentioned in the Introduction) the Wigner-Kirkwood expansion automatically fails for such systems, having an easily applicable semiclassical method might be of some value.

One approach for dealing with hard walls within the semiclassical framework of this paper would be to realize that any phase space sampling trajectory which crosses an infinite potential discontinuity would have infinite action. Therefore such a trajectory would have zero weight. Equivalently, only those regions of phase space $(p_0, q_0)$ which are not the starting points of trajectories which cross the hard wall would be permitted. In physical terms we would be excluding not only those particle positions which lie outside the box (the classical approach) but also those positions
which would quantum mechanically interfere with positions outside the box—those positions with "neighbors" outside the box.

Specifying to a particle of mass m in a box of length a we may write a semiclassical partition function as follows (keeping in mind the imaginary time trajectory reductions discussed above)

\[
Q_{SC} = \frac{1}{h} \int_0^{am(2/h\beta)} \int_{-a/2}^{a/2} -\frac{p_0}{m} (h\beta/2) e^{-\frac{p_0^2}{2m}} dx_0 dp_0
\]

\[
+ \frac{1}{h} \int_{-am(2/h\beta)}^{0} \int_{-a/2}^{a/2} -\frac{p_0}{m} (h\beta/2) e^{-\frac{p_0^2}{2m}} dx_0 dp_0
\]

\[
Q_{SC} = a\left(\frac{2\pi m}{h^2 \beta}\right)^{1/2} \text{erf}\left[\frac{a}{h}\left(\frac{2m}{\beta}\right)^{1/2}\right] + \frac{1}{2\pi} \left(\frac{2m}{\beta}\right)^{1/2}
\]

Although Eq. (2.16) cannot be used directly because its derivation neglected the possibility of temperature dependence in the limits of integration, the semiclassical ensemble average energy can still be calculated by differentiating \(Q_{SC}\) with respect to \(\beta\).

\[
\langle E \rangle_{SC} = \frac{1}{Q_{SC}} (1/2\beta) \frac{1}{2\pi} \left[\frac{a}{h}\left(\frac{2m}{\beta}\right)^{1/2}\right] \text{erf}\left[\frac{a}{h}\left(\frac{2m}{\beta}\right)^{1/2}\right]
\]

For comparison the corresponding classical and quantum mechanical results

\[
Q_{CL} = a\left(\frac{2\pi m}{h^2 \beta}\right)^{1/2}
\]
\[ <E>_{\text{CL}} = \frac{1}{2\beta} \]

\[ Q_{\text{QM}} = \sum_{n=1}^{\infty} \exp\left\{-\pi n^2 \left[ \frac{a}{\hbar} \left( \frac{2m}{\beta} \right)^{1/2} \right]^2 \right\} \]

\[ <E>_{\text{QM}} = \frac{1}{2\beta} \left( \sum_{n=1}^{\infty} \frac{2\pi n^2}{Q_{\text{QM}}} \right) \exp\left\{-\pi n^2 \left[ \frac{a}{\hbar} \left( \frac{2m}{\beta} \right)^{1/2} \right]^2 \right\} \]

are plotted along with the semiclassical answers as a function of the dimensionless parameter \( \theta = \frac{a}{\hbar} \left( \frac{2m}{\beta} \right)^{1/2} \) (Figures 1 and 2) and as is plain from the graphs the semiclassical approximations do not fare that well. In spite of the obvious improvement over the classical predictions in terms of general trends, the agreement with quantum mechanics is far from quantitative.

One possible explanation of this might be that the procedure used to treat the hard wall semiclassically is just not the best one. Perhaps some sort of limiting approach to the discontinuous potential will be needed in order to do better. Even more likely, however, is that hard walls are just too quantum mechanical to deal with accurately via the formalism developed in this paper. For example, it has been argued\(^8\) that the stationary phase approximation used in deriving the semiclassical propagator\(^2\) automatically inserts the assumption of a slowly varying potential.

In any case further investigation is indicated.

C. Vibrational State Distribution

The vibrational state statistical mechanics of a Morse potential was chosen as an illustration of the applicability of the semiclassical approach

\[ \text{\ldots} \]
to intramolecular problems. As in any realistic case (with a tabulated potential (from RKR or ab initio studies) or with a semiempirical functional form) the computations had to be performed numerically. In addition, to render the system as quantum mechanical as possible and therefore provide a good test, HCl-like potential parameters were used (a characteristic vibrational temperature of 4184°K).

The actual calculations consisted of numerically solving the equations of motion (Eq. (2.13)) for each phase point \((p_0, q_0)\) in the integration grid via an Adams Moulton predictor-corrector algorithm and then doing the double integration over phase space by repeated Gauss Hermite quadrature. Just as in the corresponding classical calculation the computation must be rerun for every new temperature but the partition function and ensemble average energy may be computed simultaneously in each run. In fact the only numerical difference between the classical and semiclassical formalisms is that the semiclassical one requires that a trajectory be run for each phase point (i.e., that a set of linear ordinary differential equations be solved) instead of just evaluating a Hamiltonian.

The results plotted as a function of temperature (Figures 3, 4) show excellent agreement between the semiclassical and exact quantum answers. For both the partition function and the energy, the difference is less than half a percent through the entire temperature range studied—even when the temperature is down to almost a tenth of the characteristic temperature. Note further that the semiclassical method predicts the correct zero point energy in spite of convergence difficulties below 500°K.
Of course the Morse oscillator was chosen because it is an exactly soluble quantum mechanical problem. Yet there is no reason why the semiclassical formalism could not be tried on more complicated multidimensional systems involving vibration-rotation coupling, (e.g.). With such cases the quantum mechanics would clearly be far more difficult than the semiclassical approach.

D. Intermolecular Distribution Functions

In order to apply the formalism of this paper to the statistical mechanics of fluids it is convenient to define semiclassical position distribution functions analogous to those commonly employed in classical mechanics. For example, the classical two particle (i.e., density independent) radial distribution function is given by

\[ W_2^{CL}(r) = \exp(-\beta V(r)) \]  

(4.6)

whereas the corresponding quantum mechanical expression (excluding indistinguishability)—for the two particle Slater sum—may be written.

\[ W_2^{QM} = 2!(2\pi \hbar \beta/m)^{3/2} \sum_n \psi^*_{n}(r_1,r_2) e^{-\beta \hat{H}} \psi_{n}(r_1,r_2) \]  

(4.7)

Semiclassically one may proceed formally from the two particle partition function

\[ Q_2^{SC} = (2! \hbar^6) \int \cdots \int e^{-\beta \overline{H}} d^3 r_0 d^3 p_0 d^3 r_2 d^3 p_2 \]

\[ (\beta \overline{H} = \frac{2}{\hbar} \int_0^{\beta \hbar/2} H(\tau) d\tau) \]

and define a "configuration" integral \( Z_2 \) just as in the classical approach.
where \( V \) is the volume and \( Q_1 \) is the 1 particle partition function, \( V(\mu/\beta m^2)^{3/2} \). Accordingly, after making a center of mass transformation to internal coordinates \((\mathbf{p} \text{ and } \mathbf{r})\) we then have

\[
Z_2^{SC} = (\beta/2\pi\mu)^{3/2} \sqrt[2]{\frac{2}{12}} \int \int e^{-\beta \bar{H}} d^3 p_0 d^3 r_0
\]

Finally, since the desired radial distribution function is defined in terms of the configuration integral by

\[
Z_2 = V \int W_2 d^3 r
\]

we may write

\[
W_2^{SC}(r_0) = (\beta/2\pi\mu)^{3/2} \int e^{-\beta \bar{H}} d^3 p_0
\]

Although this is as far as one may go for a general potential it is often possible to make Eq. (4.9) more amenable to computation by transforming from the Cartesian internal momenta \( p_x, p_y, p_z \) to a set of variables including the radial momentum \( p^r \) and the angular momentum \( L \). For spherically symmetric potentials this makes the imaginary time equations of motion effectively one dimensional

\[
W_2^{SC}(r_0) = (\beta/2\pi\mu)^{3/2} (2\pi/r_0^2) \int_0^\infty \int_0^\infty Le^{-\beta \bar{H}} dL_0 dp_0
\]

where

\[
\bar{H} = \frac{2}{\hbar^2} \int_0^\infty \left[ \frac{\mathbf{p}^2}{2\mu} + V(r) + \frac{1}{2\mu r^2} \right] d\tau
\]
and the equations of motion are

$$\vec{p}_r = \mu \vec{r} \tag{4.10c}$$

$$\frac{\dot{\vec{r}}}{\mu r^3} = \frac{\partial V(r)}{\partial r} + \frac{L^2}{\mu r^3}$$

Since our coordinates are no longer Cartesian, this transformation also implies that Eqs. (2.10) and (2.11) become the relevant equations—not Eq. (2.12) and (2.13). However, because the new Hamiltonian \(\frac{\vec{p}_r^2}{2\mu} + V(r) + \frac{L^2}{2\mu r^2}\) is still quadratic in the momenta the action remains simply the time integral of the Hamiltonian while the equations of motion themselves change slightly. The time derivative of the momentum does not equal the gradient of effective potential as might be expected from Eq. (2.13) because \(L\) itself is a momentum variable.

Clearly, by following a similar procedure it is possible to derive semiclassical expressions for higher order distribution functions. Thus to find the \(N\) body distribution function one would start with the semiclassical \(N\) body partition function, calculate the \(N\) body configuration integral, and then use it in turn to provide the desired distribution function. Moreover since by using the grand canonical ensemble it is possible to formulate virial coefficients in terms of configuration integrals without assuming classical statistics, this method can also supply the semiclassical virial form of the equation of state. By way of example, the second virial coefficient can be written

$$B_2 = \frac{1}{2V} (V^2 - Z_2)$$

so that the semiclassical second virial coefficient becomes
with \(W_2^{SC}(r_0)\) given by Eq. (4.9).

It should be noted that, up to this point, all of the equations derived in this section are completely classical in form except for the fact that the so-called semiclassical configuration integral is not only a position integral but a momentum integral as well. This, as previously alluded to, arises from the nonseparability of position and momentum in the semiclassical formalism and can be made to disappear by taking the classical limit.

Specifically, replacing \(\bar{H}\) by the classical Hamiltonian always enables one to perform the momentum integrations immediately—turning equations (4.9) and (4.10) into Eq. (4.6).

However, for the particular case of the two particle radial distribution function (hereafter referred to just as the radial distribution function) the classical expression can be easily improved by making its form more quantum-like. We know beforehand that the orbital angular momentum of the two particles (L) is quantized in units of \(\hbar\). It therefore seems reasonable to replace \(L\) by \(\hbar \ell\) and sum, rather than integrate, over integer values of \(\ell\). This in turn means that \(L\) no longer acts as a momentum in the imaginary time equations of motion so that the problem becomes in fact one dimensional (and Cartesian). As a consequence this substitution also suggests that usual one dimensional semiclassical replacement of \(\ell\) by \((\ell + \frac{1}{2})\). If we make these changes, Eq. (4.10) becomes
\[ W_{SC}^{\text{direct}}(r_0) = \left( \frac{\beta}{2\pi \mu} \right)^{3/2} \left( \frac{\hbar^2}{r_0^2} \right) \sum_{\ell} (2\ell + 1) \int_{-\infty}^{\infty} e^{-\frac{\beta H_{\ell}}{\hbar}} dp_0 \] (4.12a)

where
\[ H_{\ell} = \frac{\hbar^2}{2\mu} \int_{0}^{r^2} \left[ \frac{\mathbf{p}^2}{2\mu} + V(r) + \frac{\hbar^2 (\ell + \frac{1}{2})^2}{2\mu r^2} \right] dr \] (4.12b)

and the equations of motion become
\[ \mathbf{p} \cdot \mathbf{r} = \mu \mathbf{r} \] (4.12c)
\[ \mathbf{p} \cdot \mathbf{r} = 3V(r) - \frac{\hbar^2 (\ell + \frac{1}{2})^2}{\mu r^3} \]

Still further, since the corresponding quantum mechanical expression (Eq. 4.7) can be written in similar terms, including indistinguishability, by making the standard substitution
\[ \psi_{n,\ell,m}(r_1, r_2) = \frac{u_{n,\ell}(r)}{r} Y_{\ell,m}(\hat{r}) \]
\[ W_{QM, \text{direct}}(r) = \left( \frac{\beta}{2\pi \mu} \right)^{3/2} \left( \frac{\hbar^2}{r^2} \right) \sum_{\ell} (2\ell + 1) \sum_{n} u_{n,\ell}(r) e^{-\beta E_{n,\ell}} \]
\[ W_{QM, \text{exchange}}(r) = \left( \frac{\beta}{2\pi \mu} \right)^{3/2} \left( \frac{\hbar^2}{r^2} \right) \sum_{\ell} (2\ell + 1)(-1)^\ell \sum_{n} u_{n,\ell}(r) e^{-\beta E_{n,\ell}} \]

one can include indistinguishability into the semiclassical formalism by defining
\[ W_{SC, \text{direct}}^{\text{direct}}(r_0) = \left( \frac{\beta}{2\pi \mu} \right)^{3/2} \left( \frac{\hbar^2}{r_0^2} \right) \sum_{\ell} (2\ell + 1) \int_{-\infty}^{\infty} e^{-\frac{\beta H_{\ell}}{\hbar}} dp_0 \]
\[ W_{SC, \text{exchange}}^{\text{direct}}(r_0) = \left( \frac{\beta}{2\pi \mu} \right)^{3/2} \left( \frac{\hbar^2}{r_0^2} \right) \sum_{\ell} (2\ell + 1)(-1)^\ell \int_{-\infty}^{\infty} e^{-\frac{\beta H_{\ell}}{\hbar}} dp_0 \]
Thus the final semiclassical radial distribution functions for Bose-Einstein and Fermi-Dirac statistics (respectively) are

\[
\begin{align*}
\hat{w}_{2,SC,BE}(r_0) &= \hat{w}_{2,SC,D} + \hat{w}_{2,SC,E} \\
&= (\beta/2\pi\mu)^{3/2} \left(2\pi\hbar^2/\tau_0^2\right) \sum_{\ell=0,2,4,\ldots} (2\ell+1) \int_{-\infty}^{\infty} e^{-\beta\hbar \ell} d\rho_0^r \\
\end{align*}
\]

(4.13)

\[
\begin{align*}
\hat{w}_{2,SC,FD}(r_0) &= \hat{w}_{2,SC,D} - \hat{w}_{2,SC,E} \\
&= (\beta/2\pi\mu)^{3/2} \left(2\pi\hbar^2/\tau_0^2\right) \sum_{\ell=1,3,5,\ldots} (2\ell+1) \int_{-\infty}^{\infty} e^{-\beta\hbar \ell} d\rho_0^r \\
\end{align*}
\]

(4.14)

with \(\bar{H}_\ell\) and the imaginary time equations of motion given by Eq. (4.12).

As an illustration, the low temperature two particle radial distribution function for He\(^4\) was computed from Eq. (4.13) assuming a Lennard-Jones potential with standard parameters.\(^16\)

\[
V(r) = 4\varepsilon \left[ (\sigma/r)^{12} - (\sigma/r)^6 \right]
\]

\(\sigma = 2.556 \text{ Å} \quad \varepsilon = 10.22^\circ\text{K}
\]

The numerical results (obtained by the same approach as that employed in the last section) are plotted in figures 5 and 6 along with the classical (Eq. 4.6) and the quantum mechanical curves.\(^17\) That the translational motion of helium is quantum mechanical in nature is amply evidenced by the difference between the classical and quantum distributions, yet for the most part the semiclassical predictions match the quantum values quite
accurately. Even at 10^oK (when the thermal wavelength is slightly larger than \( \sigma \)) the semiclassical distribution clearly displays the broadening, relative to the classical distribution, which is characteristic of the development of a significant quantum uncertainty in position.

In the helium example the semiclassical approach performs reasonably well in spite of the quantum mechanical character of the system. What is just as significant in this regard, though, is that the Wigner-Kirkwood expansion is useless in this case. For the Lennard-Jones potential\(^\text{17}\) the expansion is worse than classical for large \( r \) and fails to converge at all for \( r \) less than \( \sigma \). Evidently the semiclassical formalism is not inherently limited by the difficulties found in using the Wigner-Kirkwood series.
V. Conclusions and Future Work

The very form of the expressions developed in this paper guarantees that one can calculate a semiclassical partition function and a semiclassical ensemble average energy for any system for which the same quantities can be obtained classically. Of course this same form also means that at best such a calculation would have all the difficulties of a classical calculation—the need to adequately sample the phase space and the problem of evaluating the weighting function at each point sampled.

Still, if the semiclassical procedure does not simplify matters, at least it is no more restrictive than classical mechanics in its variety of possible applications. In particular the existence of a semiclassical weighting function (even one that is not a true distribution function) implies that one can generalize classical Monte Carlo calculations\textsuperscript{18} to include quantum effects by simply substituting the semiclassical weight for the classical one in the importance sampling of phase space. Some of our current research includes using just such technique to do semiclassical Markov chain phase space integration.

On the more theoretical side it seems apparent from the radial distribution function example discussed in Section IV that virial coefficients and even distribution functions can be written in semiclassical terms without undue hardship. Equivalently it may be possible to reformulate the graph theoretic version of the theory of fluids by merely changing the bond function. Whether or not this is a worthwhile pursuit is also under study.

Finally, and perhaps most significantly, the general nature and workings of the formalism are still being investigated. There are obviously a great
many unanswered questions not the least of which are: why it works as well as it does, where it's region of validity is, if it accurately treats hard wall potentials, and whether it really does imply some sort of phase space distribution. The latter question will be partially answered in an upcoming publication which will describe a recently developed procedure for obtaining a correct semiclassical ensemble average for any function of p and q. In any case, it does seem that the major value of the formalism is the physical insight it provides--the concept of the onset of quantum effects being pictured in terms of phase space sampling.
References and Notes

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11. We have temporarily reverted to a one dimensional case in order to simplify the notations but the extension to higher dimensions is straightforward.


14. This will also be illustrated by the harmonic oscillator example.


17. The quantum curves were calculated by Fosdick via a path integral calculation (along with the Wigner-Kirkwood and classical curves).

Figure Captions

Figure 1. Partition function for a particle in a box. \( \Theta = \frac{a}{\hbar} \left( \frac{2m}{\beta} \right)^{1/2} \).

Figure 2. Ensemble average energy for a particle in a box relative to the classical value (dashed line).

Figure 3. Partition function for a Morse oscillator \( (T_{\text{char}} = 4184^\circ\text{K}) \).

Figure 4. Ensemble average energy for a Morse oscillator in atomic units \( (1\ \text{m}h = 4.3594 \times 10^{-14} \text{ erg}) \).

Figure 5. Two particle radial distribution function for \( \text{He}^4 \) in a Lennard-Jones potential. Distance is in atomic units \( (\sigma = 4.83 \text{ A.U.}) \).

Figure 6. Two particle radial distribution function for \( \text{He}^4 \) in a Lennard-Jones potential.
Fig. 1
Fig. 2

Quantum

Semiclassical

$\frac{\langle E \rangle}{\langle E \rangle_{CL}}$

$\log_{10} \theta$

XBL 777-9633
Fig. 3

- Semiclassical
- Classical
- Quantum

Temperature (°K)
Fig. 4
Fig. 5
Fig. 6

(a) Classical vs. Semiclassical for $T = 50.0^\circ K$

(b) Quantum vs. Classical Semiclassical for $T = 75.0^\circ K$
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