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IMPROVED CLASSICAL PATH APPROXIMATION FOR THE BOLTZMANN DENSITY MATRIX*

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Abstract

A classical path approximation for diagonal matrix elements of the Botlzmann density operator, i.e., the equilibrium particle density, is derived and its properties analyzed, which is not only more accurate than an earlier result, but considerably simpler to apply to systems with many degrees of freedom. The most important simplifying feature is that it is not necessary to deal with classical trajectories with double-ended boundary conditions. The partition function , for example, is given by a phase space average over initial conditions of an exponential function of a classical action integral along the trajectory with these initial conditions.

I. INTRODUCTION.

It has recently been shown[1-2] how the semiclassical approximations now commonly used in molecular collision dynamics[3] can be carried over into statistical mechanics. This "classical path approximation" was derived by applying a steepest descent approximation to the evaluation of

Feynman's[4] path integral representation of the Boltzmann density operator, $\exp(-\beta H)$. Alternatively, one obtains the same result by beginning with the semiclassical approximation to the propagator[3a,3b], $\exp(-iHt/\hbar)$, and making the formal replacement $t = -i\hbar\beta$.

The classical path approximation for the diagonal matrix elements of $\exp(-\beta H)$, i.e., the equilibrium particle density, was seen[1-2] to be considerably more accurate than that obtained from ordinary classical statistical mechanics; i.e., many of the quantum effects are accurately contained within the classical path approximation. It was seen , for example, that a good approximation to the particle density was obtained even on the limit of zero temperature ($\beta \to \infty$), a case for which the purely classical result is meaningless. The reason the semiclassical approach goes so much further than a strictly classical treatment is that the latter incorporates an inherent short time limit for the propagator, whereas the former does not.

The primary shortcoming of the previous semiclassical results[1-2] is the difficulty in applying them to anything but one dimensional systems. This difficulty arises because it is necessary to find classical trajectories that satisfy certain double-ended boundary conditions, and since for systems with more than one degree of freedom the trajectories must in general be computed numerically, this means one must deal with a non-linear boundary value problem with many variables. The situation is further complicated by the fact that there may be several different trajectories obeying the same boundary conditions, and it is necessary to include them all.

In this paper an improved classical path approximation is presented

which is more accurate than the previous one, but more importantly, it is of a form that can be readily applied to systems with many degrees of freedom. In particular, there is no reference at all to double-ended boundary conditions in the final expressions derived in Section II; the relevant trajectories are required only as a function of a complete set of initial conditions, a problem that can be readily handled numerically. The expression for the partition function [Equation (2.11)], for example, involves the average of an exponential function of the classical action over the phase space of initial conditions.

In Section III the improved classical path approximation for the particle density [Equation (2.10)] is expanded in powers of $\hbar$ in order to compare term by term with the exact quantum corrections; this gives additional insight into the nature of the quantum effects that are contained within the classical path approximation. Section IV concludes with a discussion of the principal limitation of the classical path approximation for many-body systems, the inability to deal with exchange of identical particles in a simple manner.

II. IMPROVED CLASSICAL PATH APPROXIMATION.

A. Derivation.

The improved classical path approximation takes its particularly simple form only for diagonal matrix elements of the density operator; thus consider the diagonal elements in a coordinate representation, i.e., the particle density

$$\rho(\underset{\sim}{q}) \equiv \langle \underset{\sim}{q} | \exp(-\beta H) | \underset{\sim}{q} \rangle \quad , \tag{2.1}$$

where $\underset{\sim}{q} = (q_1, q_2, \ldots, q_N)$ is the set of Cartesian coordinates for the

N-dimensional system, and β is related to the temperature in the usual fashion, $\beta = (kT)^{-1}$. Labeling the coordinate $\underset{\sim}{q}$ in Equation (2.1) as $\underset{\sim}{q}_1$, noting that

$$\exp(-\beta H) = \exp(-\tfrac{1}{2}\beta H)\exp(-\tfrac{1}{2}\beta H) \quad ,$$

and inserting a "sum" over the complete set of coordinate states $\underset{\sim}{q}_2$ gives the following equivalent expression:

$$\rho(\underset{\sim}{q}_1) = \int d\underset{\sim}{q}_2 \langle \underset{\sim}{q}_1|\exp(-\tfrac{1}{2}\beta H)|\underset{\sim}{q}_2\rangle\langle\underset{\sim}{q}_2|\exp(-\tfrac{1}{2}\beta H)|\underset{\sim}{q}_1\rangle \quad . \tag{2.2}$$

But

$$\langle\underset{\sim}{q}_1|\exp(-\tfrac{1}{2}\beta H)|\underset{\sim}{q}_2\rangle = \langle\underset{\sim}{q}_2|\exp(-\tfrac{1}{2}\beta H)|\underset{\sim}{q}_1\rangle^* \quad ,$$

so that Equation (2.2) becomes

$$\rho(\underset{\sim}{q}_1) = \int d\underset{\sim}{q}_2 \left|\langle \underset{\sim}{q}_2|\exp(-\tfrac{1}{2}\beta H)|\underset{\sim}{q}_1\rangle\right|^2 \quad . \tag{2.3}$$

Equation (2.3) is still an exact quantum mechanical expression, but the classical path approximation[1] is now introduced for the matrix element in the integrand of Equation (2.3), namely

$$\langle \underset{\sim}{q}_2|\exp(-\tfrac{1}{2}\beta H)|\underset{\sim}{q}_1\rangle \simeq \left[(2\pi\hbar)^N\left(\frac{\partial \underset{\sim}{q}_2}{\partial \underset{\sim}{p}_1}\right)_{\underset{\sim}{q}_1}\right]^{-\frac{1}{2}}$$

$$\times \exp[-\phi(\underset{\sim}{q}_2,\underset{\sim}{q}_1;\ \hbar\beta/2)/\hbar] \quad , \tag{2.4}$$

where ϕ is the action-like integral

$$\phi(\underset{\sim}{q}_2,\underset{\sim}{q}_1;\ \hbar\beta/2) = \int_0^{\hbar\beta/2} d\tau\ H(\tau) \tag{2.5}$$

along the "classical trajectory" $\underset{\sim}{q}(\tau)$ determined by the Newton-like

equations (but note the sign difference)

$$m_i \ddot{q}_i(\tau) = + \frac{\partial V(\underset{\sim}{q})}{\partial q_i} \quad , \tag{2.6}$$

with double-ended boundary conditions

$$\underset{\sim}{q}(0) = \underset{\sim}{q}_1 \tag{2.7a}$$

$$\underset{\sim}{q}(\hbar\beta/2) = \underset{\sim}{q}_2 \quad . \tag{2.7b}$$

The Hamiltonian H in the integrand of Equation (2.5) has the usual Cartesian form

$$H(\tau) = \sum_{i=1}^{N} p_i(\tau)^2/2m_i + V(\underset{\sim}{q}(\tau)) \quad , \tag{2.8}$$

where $p_i(\tau) \equiv m_i \dot{q}_i(\tau)$; $(\partial \underset{\sim}{q}_2/\partial \underset{\sim}{p}_1)\underset{\sim}{q}_1$ in Equation (2.4) is an N-dimensional Jacobian determinant relating the final coordinates $\underset{\sim}{q}_2$ to the initial "momenta" $\underset{\sim}{p}_1 \equiv \underset{\sim}{p}(o)$. As has been discussen before[1], the classical path approximation summarized in Equations (2.4)-(2.8) takes advantage of the fact that the classical equations of motion for Cartesian coordinates in the imaginary time variable τ are equivalent to those in real time with the negative potential energy function. Consequently, it is not the Hamiltonian H that is constant with τ , but rather the Hamiltonian with the negative potential, i.e., the Lagrangian.

With the classical path approximation of Equation (2.4) the particle density in Equation (2.3) becomes

$$\rho(\underset{\sim}{q}_1) = h^{-N} \int d\underset{\sim}{q}_2 \left[\left(\frac{\partial \underset{\sim}{q}_2}{\partial \underset{\sim}{p}_1}\right)_{\underset{\sim}{q}_1}\right]^{-1} \exp\left[-\frac{2}{\hbar}\int_0^{\hbar\beta/2} d\tau\, H(\tau)\right] \quad ; \tag{2.9}$$

holding $\underset{\sim}{q}_1$ fixed, the integration variables in Equation (2.9) can be

changed from $\underset{\sim}{q}_2$ to $\underset{\sim}{p}_1$, giving

$$\rho(\underset{\sim}{q}_1) = h^{-N}\int d\underset{\sim}{p}_1 \exp\left[-\frac{2}{\hbar}\int_0^{\hbar\beta/2} d\tau H(\tau)\right] \quad . \tag{2.10}$$

The corresponding approximation for the partition function $Z(\beta)$,

$$Z(\beta) \equiv \int d\underset{\sim}{q}_1 \; \rho(\underset{\sim}{q}_1) \quad ,$$

is thus a phase space average over initial conditions:

$$Z(\beta) = h^{-N}\int d\underset{\sim}{p}_1 \int d\underset{\sim}{q}_1 \exp\left[-\frac{2}{\hbar}\int_0^{\hbar\beta/2} d\tau \; H(\tau)\right] \quad , \tag{2.11}$$

where $H(\tau)$ in Equations (2.10) and (2.11) is given by Equation (2.8) with the trajectory $\underset{\sim}{q}(\tau)$ determined by Equation (2.6) with the initial conditions $\underset{\sim}{q}(0) = \underset{\sim}{q}_1$, $\dot{\underset{\sim}{q}}(0) = \underset{\sim}{p}_1/m$.

B. Discussion of the Results.

Equations (2.10) and (2.11) are the primary results of the paper. It is clear that this classical path approximation is more accurate than that obtained previously[1], for the semiclassical approximation in Equation (2.4) pertains to the time interval $\hbar\beta/2$, whereas the earlier classical path approximation related to the total time interval $\hbar\beta$. Insertion of the sum over states in Equation (2.2), with the subsequent semiclassical approximation of the individual matrix elements in the integrand, may in fact be viewed as a first crude step toward evaluation of the path integral[4] itself. Thus the exact quantum mechanical result could be obtained if one further sub-divided the time interval by introducing additional "sums" over states,

$$\rho(\underset{\sim}{q}_1) = \int d\underset{\sim}{q}_2 \int d\underset{\sim}{q}_3 \ldots \int d\underset{\sim}{q}_L \; \langle \underset{\sim}{q}_1 | \exp(-\beta H/L) | \underset{\sim}{q}_2 \rangle$$
$$\times \langle \underset{\sim}{q}_2 | \exp(-\beta H/L) | \underset{\sim}{q}_3 \rangle \ldots \langle \underset{\sim}{q}_L | \exp(-\beta H/L) | \underset{\sim}{q}_1 \rangle \tag{2.12}$$

and then used the classical path approximation of Equation (2.4) for each individual matrix element in Equation (2.12), letting $L \to \infty$. (Feynman actually uses a free particle approximation for each matrix element in Equation (2.12), but use of the classical path approximation would make the procedure converge faster; the two are formally equivalent since the classical path approximation gives the exact quantum result for free particle dynamics.) The results obtained in Section IIA correspond to Equation (2.12) with $L = 2$; the particularly simplifying features of Equations (2.10) and (2.11) - i.e., elimination of the double-ended boundary conditions and the Jacobian determinant - unfortunately do not occur for any choice other than $L = 2$.

Much more important than this increased accuracy, however, is the dradtically increased ease with which Equations (2.10) and (2.11) can be applied to multidimensional systems. The previous classical path approximation[1] required one to deal explicitly with the double-ended boundary conditions in Equation (2.7), a difficulty perhaps insurmountable for many dimensional systems. The change of integration variables involved in going from Equation (2.9) to Equation (2.10), however, eliminates all reference to the final coordinates and to the Jacobian factor as well.

To evaluate the partition function from Equation (2.11), for example, one must simply carry out an integral over the phase space of initial conditions; for systems with many degrees of freedom this integral would most conveniently be carried out by a Monte Carlo procedure. Having thus chosen a set of initial conditions $(\underset{\sim}{p}_1, \underset{\sim}{q}_1)$, one integrates the equations of motion with the negative potential [Equation (2.6)] from $\tau = 0$ to $\tau = \hbar\beta/2$,

the time integral of $H(\tau)$ being computed in the process; the exponential of this action integral is then Monte Carlo averaged over the initial conditions.

Equations (2.10) and (2.11) can be written in various equivalent forms by using the fact that the quantity

$$\sum_{i=1}^{N} \underset{\sim}{p}_i(\tau)^2/2m_i - V(\underset{\sim}{q}(\tau))$$

is conserved in time and thus equal to its value at $\tau = 0$. The particle density [Equation (2.10)], for example, can be expressed as

$$\rho(\underset{\sim}{q}_1) = \exp[-\beta V(\underset{\sim}{q}_1)]\, h^{-N} \int d\underset{\sim}{p}_1 \exp[\tfrac{1}{2}\beta \underset{\sim}{p}_1 \cdot \dot{\underset{\sim}{q}}_1 - \tfrac{2}{\hbar}\int_0^{\hbar\beta/2} d\tau\, \underset{\sim}{p}(\tau)\cdot\dot{\underset{\sim}{q}}(\tau)] \quad (2.13)$$

Finally, it is a simple matter to see how the purely classical expressions are recovered if one makes a short time approximation to the dynamics. For small $\hbar\beta$ (i.e., high temperature) one has

$$\frac{2}{\hbar}\int_0^{\hbar\beta/2} d\tau H(\tau) \simeq (\frac{2}{\hbar})(\frac{\hbar\beta}{2})\, H(0) = \beta H(\underset{\sim}{p}_1, \underset{\sim}{q}_1) \quad , \qquad (2.14)$$

so that Equation (2.10), for example, becomes

$$\rho(\underset{\sim}{q}_1) \simeq h^{-N} \int d\underset{\sim}{p}_1 \exp[-\beta H(\underset{\sim}{p}_1, \underset{\sim}{q}_1)] \quad , \qquad (2.15)$$

the standard expression of classical statistical mechanics.

III. QUANTUM CORRECTION EXPANSION.

A quantitative measure of the degree that quantum mechanical effects are contained in the classical path approximation can be obtained by expanding Equation (2.10) in powers of $\hbar$ and comparing term for term with the known[5] quantum mechanical "quantum corrections". This quantum

correction expansion is carried out only for purposes of comparison with the exact quantum correction terms, and one would not wish to use it in practice - for the classical path approximation contains a large fraction of the quantum effects to <u>infinite</u> order, a feature that is lost, of course, if one expands in powers of $\hbar$.

For simplicity the notation in this section applies to a one dimensional system, and as before[2] the goal is to express the particle density of Equation (2.10) in the form

$$\rho(x) = \rho_{CL}(x)\ [1 + \lambda C_1(x,\beta) + \lambda^2 C_2(x,\beta) + \ldots] \quad , \tag{3.1}$$

where

$$\rho_{CL}(x) = (2m/4\pi\hbar^2\beta)^{\frac{1}{2}} \exp[-\beta V(x)] \tag{3.2}$$

$$\lambda = \hbar^2\beta^2/2m \quad ; \tag{3.3}$$

i.e., one seeks the quantum correction functions $C_K(x,\beta)$ that result from Equation (2.10).

The systematics of carrying out the expansion in powers of $\hbar$ is somewhat simpler with the present expressions than before[2]. For a one dimensional system Equation (2.10) becomes

$$\rho(x) = h^{-1} \int_{-\infty}^{\infty} dp\ \exp\left[-\frac{2}{\hbar}\int_0^{\hbar\beta/2} d\tau\ H(\tau)\right] \quad , \tag{3.4}$$

and to expand in powers of $\hbar$ one simply expands $H(\tau)$ in the integral of Equation (3.4) in a Taylor 's series about $\tau = 0$, integrating term by term. Equation (3.4) thus becomes

$$\rho(x) = h^{-1} \int_{-\infty}^{\infty} dp\ \exp\left[-\beta \sum_{n=0}^{\infty} \left(\frac{\hbar\beta}{2}\right)^n \frac{H^{[n]}(0)}{(n+1)!}\right] \quad , \tag{3.5}$$

where $H^{[n]}(0)$ is the nth derivative of $H(\tau) \equiv H(p(\tau), x(\tau))$ evaluated at $\tau = 0$. These derivatives are easily evaluated by making use of the equation of motion [Equation (2.6)], and the first few are

$$H^{[o]}(0) = p^2/2m + V(x)$$

$$H^{[1]}(0) = 2p\, V'(x)/m$$

$$H^{[2]}(0) = 2V'(x)^2/m + 2\, p^2 V''(x)/m^2 \tag{3.6}$$

$$H^{[3]}(0) = 8p\, V'(x)\, V''(x)/m^2 + 2\, p^3 V'''(x)/m^3$$

$$H^{[4]}(0) = 8V'(x)^2\, V''(x)/m^2 + 8\, p^2\, V''(x)^2/m^3 + 14\, p^2\, V'(x)\, V'''(x)/m^3 + 2\, p^4 V''''(x)/m^4 \quad .$$

Substituting these expressions into Equation (3.5), expanding the exponential in powers of $\hbar$, and carrying out the momentum integral gives the result in Equation (3.1) with the quantum correction functions identified as

$$C_1(x,\beta) = \frac{1}{12}\beta\, V'(x)^2 - \frac{1}{6} V''(x) \tag{3.7}$$

$$C_2(x,\beta) = \frac{1}{288}\beta^2\, V'(x)^4 - \frac{11}{360}\beta\, V'(x)^2\, V''(x) + \frac{1}{40} V''(x)^2 + \frac{1}{30} V'(x)\, V'''(x) - \frac{1}{80}\beta^{-1}\, V''''(x) \quad . \tag{3.8}$$

Just as before[2], the first quantum correction [Equation (3.7)] is identical to the exact quantum mechanical result[5]. The exact quantum expression[5] for $C_2(x,\beta)$ is the same as Equation (3.8) but with the coefficient of the fourth derivative term being -1/60 rather than -1/80. The improved classical path approximation thus makes a 25% error in the

coefficient of the fourth derivative term, whereas this term was completely absent in the earlier semiclassical result[2]; this is a manifestation of the point discussed in Section IIA, that the new expression must be more accurate than the earlier one. The fact that the semiclassical approximation does not include the higher derivatives exactly correctly is understandable on the basis, as discussed before[2], that semiclassical approximations relie on slowly varying potential energy functions.

IV. CONCLUDING REMARKS.

The expressions in Equations (2.10) and (2.11) are of a form that can be readily applied to multi-dimensional systems, and much of the effect of quantum dynamics is contained within this classical path approximation. As has been discussed before[1-2], for example, the quantum effects associated with the linear and harmonic part of the potential are treated exactly, to infinite order in $\hbar$.

The most important quantum feature of many body systems that is not included in the present classical path approximation is that of exchange of identical particles. For a system of identical bosons, for example, the particle density is not just the diagonal matrix element of the Boltzmann operator, but in addition a sum of all off-diagonal elements that correspond to the exchange of identical particles[6]:

$$\rho(\underset{\sim}{q}) = (N!)^{-1} \sum_{P} \langle P\underset{\sim}{q} | \exp(-\beta H) | \underset{\sim}{q} \rangle \quad ,$$

where P is one of the N! permutations of the N identical particles and $P\underset{\sim}{q}$ is a 3N-dimensional coordinate vector that differs from $\underset{\sim}{q}$ by the corresponding exchange of coordinates of the identical particles. To obtain such terms within the classical path approximation is would be necessary

to use Equations (2.4)-(2.8) and actually find the trajectories that result in identical particles exchanging their positions. Thus it does not appear at present that it is possible to include exchange in the classical path approximation without dealing explicitly with trajectories with double-ended boundary conditions.

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