Quantum Statistical Mechanics in Classical Phase Space. Test Results for Quantum Harmonic Oscillators

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The von Neumann trace form of quantum statistical mechanics is transformed to an integral over classical phase space. Formally exact expressions for the resultant position-momentum commutation function are given. A loop expansion for wave function symmetrization is also given. The method is tested for quantum harmonic oscillators. For both the boson and fermion cases, the grand potential and the average energy obtained by numerical quadrature over classical phase space are shown to agree with the known analytic results. A mean field approximation is given which is suitable for condensed matter, and which allows the quantum statistical mechanics of interacting particles to be obtained in classical phase space.

I. INTRODUCTION

Many-particle systems pose serious computational challenges for quantum mechanics. These primarily arise from the difficulty in finding the energy eigenfunctions and eigenvalues of the system, and from the difficulty in enforcing the boson and fermion occupancy rules. In addition to the technical barriers that inhibit the accurate numerical description of many-particle systems, it is the rapid increase in computational cost with system size that can be prohibitive. Common partial differential equation algorithms, for example, scale exponentially with system size.

Of course various and sophisticated attempts to ameliorate the difficulties have been made, such as an imaginary-time nonuniform mesh method, pseudo-potential and mean-field methods, density functional theory, quantum Monte Carlo methods, lattice Gaussian approach, collocation method, discrete variable representation method, and variational Gaussian wave-packet methods, as examples. It is usually the case that various approximations are introduced in these methods, such as neglecting wave function symmetrization, which can limit their individual reliability and range of application.

Despite in many cases the proven merits of these algorithms and their demonstrated improvement over partial differential equation methods, the size of quantum many body systems that can currently be treated computationally remains perhaps one or two orders of magnitude smaller than classical many body systems. For example, Hernando and Vanček found the first 50 energy eigenvalues and included symmetrization effects, but the system contained just five Lennard-Jones atoms in one dimension. Larger system sizes have been achieved, but at the cost of additional approximations or neglect of one or other quantum effect. For example, the variational treatment of up to 6500 Lennard-Jones atoms by Georgescu and Mandelshtam was restricted to the ground state, as well as neglecting wave function symmetrization.

Compared to quantum systems, classical many-particle systems scale much more favorably with system size and have considerably reduced computational demands. This suggests that an advantageous numerical approach for quantum systems could be developed by performing an expansion about the overlying classical system.

In previous work the author has presented a transformation of the von Neumann trace form for the quantum partition function and averages to classical phase space. The analysis invoked directly position and momentum states, and is a somewhat simpler formulation than the earlier method of Wigner and of Kirkwood. The author’s approach is not directly related to these earlier approaches, although they agree upon the first and second quantum corrections to classical statistical mechanics. The Wigner function has been used to explore aspects of the quantum-classical relationship, as well as the related problem of the dissipative evolution in open quantum systems and the quantum-classical transition. It has also been used for quantum optics.

In the author’s approach, quantum statistical mechanics is cast as an integral over classical phase space of the Maxwell-Boltzmann factor times the product of two formally exact series expansions, one that accounts for wave function symmetrization, and the other for the non-commutativity of position and momentum operators. The leading term is precisely classical statistical mechanics. This suggests that the approach might be both feasible and accurate for condensed matter problems, because for many terrestrial systems the quantum correction amounts to no more than a fraction of a per cent. Further, the approach represents a systematic approximation, which is an advantage because the error due to the truncation of the infinite series can be quantified term by term. Finally, since the method is cast in terms of classical averages over phase space, all of the techniques and algorithms that have been developed over the years for the computer treatment of classical many-particle systems become immediately available for quantum systems.

The present work gives a simpler and more rigorous derivation of the transformation to classical phase space than in the earlier work. It also derives new general expressions for the statistical average of an operator, and corrects several errors that appear in the earlier presen-
II. THE PARTITION FUNCTION AND THE SYMMETRIZATION FUNCTION

A. General Case of Interacting Particles

Consider a system of $N$ interacting particles. Let $|n\rangle$ be an unsymmetrized, normalized energy eigenfunction, $\hat{H}|n\rangle = E_n|n\rangle$. The position representation vector is $r = \{r_1, r_2, \ldots, r_N\}$, with $r_j = \{r_{jx}, r_{jy}, \ldots, r_{jd}\}$ in a space of $d$ dimensions. Assume that the energy state can be similarly decomposed, $n = \{n_1, n_2, \ldots, n_N\}$. For simplicity spin is not here considered, although its inclusion would not create insurmountable difficulties.

Writing the unsymmetrized wave function also as $\phi_n(r) = |n\rangle$, the symmetrized wave function formed from the orthonormal set of these is

$$\phi_n^\pm(r) = \frac{1}{\sqrt{N!}\chi_n^\pm} \sum_p (\pm 1)^p \phi_p^n(r)$$

or $|n\rangle^\pm = \frac{1}{\sqrt{N!}\chi_n^\pm} \sum_p (\pm 1)^p |\hat{P}n\rangle$. (2.1)

Here $p$ is the parity of the permutation $\hat{P}$. The upper sign is for bosons and the lower sign is for fermions.

The symmetrization factor $\chi_n^\pm$ is characteristic of the state. It is inversely proportional to the number of non-zero distinct permutations of the wave function. Specifically, normalization, $\langle \phi_n^\pm | \phi_n^\pm \rangle = 1$, gives

$$\chi_n^\pm = \sum_p (\pm 1)^p \langle n | \hat{P}n \rangle. \quad (2.2)$$

The grand partition function is the sum over distinct states$^{22,23}$

$$\Xi^\pm = \sum_{N=0}^{\infty} z^N \sum_n \langle \chi_n^\pm e^{-\beta E_n} \rangle \quad (2.3)$$

where the fugacity is $z = e^{\beta \mu}$, where $\mu$ is the chemical potential, and $\beta = 1/k_B T$ is called the inverse temperature, with $k_B$ being Boltzmann’s constant and $T$ the temperature. The sum over energy states in the final two equalities is unrestricted, since the symmetrization factor accounts for double counting of the same state, and for the cancelation of forbidden states.

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The permutation operator that transposes particles $j$ and $k$ is $\hat{P}_{jk}$. Any permutation is a sequence of such pair transpositions, the number of which gives its parity. A connected sequence is called a loop, (eg. $\hat{P}_{jk} \hat{P}_{kl}$ is a three particle loop). Any permutation may be expressed as a product of loops. Hence the symmetrization factor may be expanded as$^{22,23}$

$$\chi_n^\pm = \sum_p (\pm 1)^p \langle \hat{P}n | \hat{P}n \rangle$$

$= 1 \pm \sum_{j,k} \langle \hat{P}_{jk}n | \hat{P}_{jk}n \rangle + \sum_{j,k,l} \langle \hat{P}_{jk} \hat{P}_{kl}n | \hat{P}_{jk} \hat{P}_{kl}n \rangle + \cdots$ (2.4)

The prime indicates distinct permutations, $\sum'_{j,k} \equiv \sum_{j<k}$ etc. The comma in $\chi_{jk,lm}(n)$ etc. denotes separate loops.

The first term of unity gives the monomer term in the partition function,

$$\Xi_1 = \sum_{N=0}^{\infty} \frac{z^N}{N!} \sum_n e^{-\beta E_n}. \quad (2.5)$$

The ratio of the full to the monomer partition function is just the monomer average of the symmetrization factor,

$$\frac{\Xi^\pm}{\Xi_1} = \langle \chi^\pm \rangle_1$$

$$= \left( 1 + \sum_{j,k} \langle \chi_{jk} \rangle + \sum_{jkl} \langle \chi_{jkl} \rangle + \sum_{jklm} \langle \chi_{jklm} \rangle + \cdots \right) \frac{N!}{(N-2)!2!} \frac{N!}{(N-3)!3!} \frac{N!}{(N-4)!4!} + \cdots \quad (2.6)$$

$$= \sum_{\{m_i\}} \frac{1}{m_1!} \prod_{l=2}^{\infty} \left( \frac{N!}{(N-l)!l!} \langle \chi^{(l)} \rangle \right)^{m_l}$$

$$= \prod_{l=2}^{\infty} \sum_{m_l=0}^{\infty} \frac{1}{m_1!} \left( \frac{N!}{(N-l)!l!} \langle \chi^{(l)} \rangle \right)^{m_l}$$

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Here the present paper tests the classical phase space approach numerically for the case of the quantum harmonic oscillator, for which exact analytic results are well-known. As a concrete example, the present results clarify and validate the new formulation of quantum statistical mechanics, which should lead to a better appreciation of its utility. In addition, a mean field approach numerically for the case of the quantum harmonic oscillator, and this ought to be useful for general condensed matter, interacting particle systems.
The third and following equalities write the average of the product of loops as the product of the averages. This is exact for ideal system, because then the energy basis functions factorize into the product of single particle functions. More generally, as is discussed in the phase space derivation below, it is exact in the thermodynamic limit, since, for example, $m$ uncorrelated loops scale as $V^m$, whereas $m$ correlated loops scale as $V$, where $V$ is the volume. The combinatorial factor accounts for the number of unique loops in each term; $\chi^{(l)}$ refers to any one set of $l$ particles, since all sets give the same average. Explicitly, the $l$-loop symmetrization factor here is

$$
\chi^{(l)}(n^{(l)}) = (\pm 1)^{l-1} \langle \{n_1, n_2, \ldots, n_l\} \{n_2, n_3, \ldots, n_1\} \rangle = (\pm 1)^{l-1} (n^{(l)}) \Omega^{(l)}. \tag{2.7}
$$

This depends only on the state of the $l$ particles involved.

The grand potential is $-k_B T \ln \Xi$. The monomer grand potential is given by

$$
-\beta \Omega_1 = \ln \Xi. \tag{2.8}
$$

The full grand potential is given by

$$
-\beta \Omega^\pm = -\beta \Omega_1 + \ln \Xi^\pm \Xi = -\beta \Omega_1 + \sum_{l=2}^{\infty} \langle \frac{N!}{(N-l)!} \chi^{(l)} \rangle_1 \tag{2.9}
$$

The final equality defines the $l$-mer grand potential.

**B. Ideal System of Non-Interacting Particles**

Now this result is applied to an ideal system comprising non-interacting particles. In this case the total energy is just the sum of that of the individual particle states,

$$
E_n = \sum_{j=1}^{N} \varepsilon_{n_j}. \tag{2.10}
$$

Also, the wave function factorizes, $|n\rangle = \prod_j |n_j\rangle$, as does the loop symmetrization factor

$$
\chi^{(l)}(n^{(l)}) = (\pm 1)^{l-1} \langle n_1 | n_2 \rangle \prod_{j=1}^{l-1} \langle n_j | n_{j+1} \rangle. \tag{2.11}
$$

With these the monomer partition function becomes

$$
\Xi_1 = \sum_{N=0}^{\infty} \frac{z^N}{N!} \prod_{j=1}^{N} \sum_{n_j} e^{-\beta \varepsilon_{n_j}} \tag{2.12}
$$

Hence the monomer grand potential is given by $-\beta \Omega_1 = z \sum_{n_1} e^{-\beta \varepsilon_{n_1}}$.

The dimer grand potential is given by

$$
-\beta \Omega_2^\pm = \langle \frac{N!}{(N-2)!^2} \chi^{(2)} \rangle_1 \tag{2.13}
$$

Similarly, the trimer grand potential is given by

$$
-\beta \Omega_3^\pm = \langle \frac{N!}{(N-3)!^3} \chi^{(3)} \rangle_1 \tag{2.14}
$$

Continuing in this fashion, the full grand potential for this system of non-interacting single particle states is

$$
-\beta \Omega^\pm = -\beta \Omega_1 + \sum_{l=2}^{\infty} \frac{(\pm 1)^{l-1} l!}{N!} \sum_{n_1} e^{-l \beta \varepsilon_{n_1}} \tag{2.15}
$$
For the case of the simple harmonic oscillator in \(d\)-dimensions, the single particle energy is
\[
\varepsilon_{n_j} = \left[ \frac{d}{2} + n_{jx} + n_{jy} + \ldots + n_{jd} \right] \hbar \omega,
\] (2.16)
with \(n_{jx} = 0, 1, 2, \ldots\). In this case the grand potential is
\[
-\beta \Omega^\pm = \sum_{l=1}^\infty \frac{(\pm 1)^{l-1} z^l}{l} e^{-l\beta \hbar \omega/2} \prod_{\alpha=x \atop n_\alpha = 0}^\infty e^{-l\beta \hbar \omega n_\alpha}
\]
\[
= \sum_{l=1}^\infty \frac{(\pm 1)^{l-1} z^l}{l} \left[ e^{-l\beta \hbar \omega/2} \right] d. \quad (2.17)
\]
Note that this diverges for \(z > e^{d\beta \hbar \omega/2}\).

1. Text Book Derivation

Although superficially different, the general result derived above for non-interacting particles may be shown to agree with the standard textbook result, and it allows for a novel interpretation of the terms that occur in a series expansion of the latter.

Following \$6.2\) of Pathria\textsuperscript{45} single particle states labeled by \(\varepsilon\) can be occupied by \(N_\varepsilon = 0, 1, \ldots, N_\pm\) particles, with \(N_+ = \infty\) for bosons, and \(N_- = 1\) for fermions. The grand partition function is the weighted sum over all possible occupancies of each state,
\[
\Xi^\pm (z) = \sum_{N_0 = 0}^{N_+} \sum_{N_1 = 0}^{N_+} \ldots \sum_{N_\infty = 0}^{N_\pm} \sum_{\varepsilon}^N N_\varepsilon e^{-\beta \varepsilon} \sum_{N_\varepsilon}^{N_\pm} \varepsilon N_\varepsilon
\]
\[
= \prod_{\varepsilon = 0}^{\infty} \left\{ \sum_{N_\varepsilon = 0}^{N_\pm} z N_\varepsilon e^{-\beta \varepsilon N_\varepsilon} \right\}
\]
\[
= \prod_{\varepsilon = 0}^{\infty} \left[ 1 \mp z e^{-\beta \varepsilon} \right]^{\mp 1}
\]
\[
= \prod_{n_x = 0}^{\infty} \prod_{n_y = 0}^{\infty} \ldots \prod_{n_d = 0}^{\infty} \left[ 1 \mp z e^{-\beta \varepsilon_{n_\varepsilon}} \right]^{\mp 1}. \quad (2.18)
\]

The sums and products over energy is an abbreviated notation that visits each state once, as is explicit in the final equality. This is Pathria’s expression. The grand potential is given by the logarithm of this, a subsequent expansion of which yields
\[
-\beta \Omega^\pm = \pm \ln \left[ 1 \mp z e^{-\beta \varepsilon_{n_\varepsilon}} \right]
\]
\[
= \pm \sum_{n_\varepsilon = 0}^{\infty} \sum_{l=1}^{\infty} \frac{(\pm z)^l}{l} e^{-\beta \varepsilon_{n_\varepsilon} l}
\]
\[
= \sum_{l=1}^{\infty} \frac{(\pm 1)^{l-1} z^l}{l} \sum_{n_\varepsilon = 0}^{\infty} e^{-\beta \varepsilon_{n_\varepsilon} l}. \quad (2.19)
\]
This agrees with the above expression based on symmetrization loops, Eq. (2.11). Notice that between the two there is a one-to-one correspondence for the terms indexed by \(l\). The interpretation is that each such term arises from the cyclic permutation of the group of particles involved. For the case of the simple harmonic oscillator, the one-dimensional summation over symmetrization loops, Eq. (2.17), is a somewhat simpler expression than the conventional multi-dimensional sum over possible energy states, the first equality in Eq. (2.18).

Although the present approach and the text-book approach arrive at the same result for ideal states, the present approach proceeds from a rather different viewpoint, namely that the symmetrization of the wave function is the fundamental axiom, and that the occupancy of states (multiple for bosons, single for fermions) is a quantity derived from it. The present approach will be shown to be extremely useful when the results are transformed to the continuum that is classical phases space.

In the case of the continuum it is impossible to define unambiguously discrete states and the occupancy thereof, whereas the symmetrization of the wave function itself remains a valid concept.

III. QUANTUM PARTITION FUNCTION IN CLASSICAL PHASE SPACE

This section transform the partition function from a sum over energy states to an integral over classical phase space by invoking directly position and momentum states. This is not directly related to the formulation of Wigner\textsuperscript{22}, although the commutation function that arises here also appears in the earlier analysis. Kirkwood added the first quantum correction due to wave function symmetrization\textsuperscript{25} the infinite resummation of symmetrization loops appears unique to the author’s analysis\textsuperscript{22,23}.

The position representation for \(N\) particles in \(d\) dimensions is \(q = \{q_1, q_2, \ldots, q_N\}\), with \(q_j = \{q_{jx}, q_{jy}, \ldots, q_{jd}\}\). The momentum eigenfunctions are\textsuperscript{23,46}
\[
|p\rangle \equiv \zeta_p (q) = e^{-\hat{p} \cdot \hat{q} / \hbar} \frac{1}{\sqrt{N/2}}, \quad (3.1)
\]
where the volume of the sub-system is \(V = L^d\). The momentum eigenfunctions form a complete orthonormal set. The momentum label \(p\) is a \(dN\)-dimensional integer, and the corresponding continuum components are, \(\hat{p}_j = p_j a / L\). The spacing between momentum states is \(\Delta_p = 2\pi \hbar / L\).

It is possible to take the continuum limit of these immediately. It is also possible to introduce position eigenfunctions that are Dirac-\(\delta\) functions, which form a complete orthonormal set. In both cases the final phase space expression is the same as that which results from the present analysis.

In order to re-sum the symmetrization loops, it is convenient to work in a grand canonical system, in which the sub-system can exchange number and energy with
a reservoir. Following entanglement and collapse, the
grand canonical partition function has trace form.\(^\text{22,23}\)
Hence it can be written as a sum over the momentum states,

\[
Ξ^± = \sum_{N=0}^{\infty} \frac{z^N}{N!} \sum_{p}^\infty (\pm 1)^p \sum_{p} \langle \hat{P} p | e^{-\beta \hat{H}} | p \rangle \\
= \sum_{N=0}^{\infty} \frac{z^N}{N!} \Delta_p^{-dN} L^{-dN} \sum_{p} (\pm 1)^p \\
\times \int dq dp e^{(\hat{P} p) q/\hbar} e^{-\beta \hat{H}} e^{-q \cdot p/\hbar} \\
= \sum_{N=0}^{\infty} \frac{z^N}{h^{dN} N!} \int d\Gamma e^{-\beta \mathcal{H}(\Gamma)} W_p(\Gamma) \eta_q^±(\Gamma). 
\]

Here and below, \( \Gamma = \{p, q\} \) denotes a point in classical
phase space, and the tilde has been dropped.

Following Wigner\(^\text{24}\) the commutation function \( W \) is
defined via the action of the Hamiltonian operator on the
momentum eigenfunctions\(^\text{22,23}\)

\[
e^{-\beta \hat{H}} e^{-p \cdot q/\hbar} \equiv e^{-p \cdot q/\hbar} e^{-\beta \hat{H}(p,q)} W_p(p, q). 
\]

As for the energy states, the symmetrization function
may be expanded as\(^\text{22,23}\)

\[
\eta_q^±(\Gamma) = \sum_p (\pm 1)^p e^{-p \cdot q/\hbar} e^{(\hat{P} p) q/\hbar} \\
= 1 + \sum_{j,k}^N \eta_j^+ e^{-p \cdot q/\hbar} e^{(\hat{P} p) q/\hbar} + \ldots \\
= 1 + \sum_{j,k}^N \eta_j^+ e^{-p \cdot q/\hbar} e^{(\hat{P} p) q/\hbar} + \ldots \\
= 1 + \sum_{j,k}^N \eta_j^+ (\Gamma) + \ldots \quad (3.4)
\]

Because these terms are highly oscillatory, they average
to zero unless consecutive particles in a loop are close
together in position or momentum space.

1. Grand Potential

The series for the grand potential based on the loop expansion obtained above via energy states, Eq.\(^\text{2,9}\)
carries over essentially unchanged. The monomer grand potential is given by \( -\beta \Omega_1 = \ln \Xi_1 \), with the monomer

\[
\Xi_1 = \sum_{N=0}^{\infty} \frac{z^N}{h^{dN} N!} \int d\Gamma e^{-\beta \mathcal{H}(\Gamma)} W_p(\Gamma). 
\]

The loop grand potential is a monomer average in phase
space,

\[
-\beta \Omega_1^± = \frac{1}{N!} \int (N-l)! \eta_q^±(\Gamma)^l, \quad l \geq 2 \\
= \frac{1}{\Xi_1} \sum_{N=0}^{\infty} \frac{z^N h^{-dN}}{(N-l)!} \int d\Gamma e^{-\beta \mathcal{H}(\Gamma)} W_p(\Gamma) \eta_q^±(\Gamma)^l. 
\]

In obtaining this result the monomer average of the product
of distinct loops has been written as the product of the
average of the individual loops, which is valid because the
individual loops must be compact to avoid cancellation
by rapid oscillation.

The l-loop symmetrization function is

\[
\eta_q^±(\Gamma^l) = (\pm 1)^l e^{-q_i \cdot p_i/\hbar} \prod_{j=1}^{l-1} e^{-q_{i+j} \cdot p_{i+j}/\hbar} . \quad (3.7)
\]

The monomer term, \( \eta_q^±(1) = 1 \), is obviously the classical
one, and it is the dominant term when \( \rho \Lambda^d \ll 1 \),
which is the low density \( \rho \), small thermal wave length
\( \Lambda = [2\pi \hbar^2 /m]^{1/2} \) (or high temperature) limit.\(^\text{22,23,25}\)

The original von Neumann trace for the partition function is real. The present transformation to classical phase
space introduces an asymmetry between position and mo-
momentum, which induces an imaginary component. But
since this is odd in momentum, it integrates to zero.
One can symmetrize the expression for the grand potential with respect to position and momentum. Since \( W_\rho^* = W_q^* \) \( \text{and} \) \( \eta_q^± = \eta_p^± \), this is equivalent to making the replacement \( W_p \eta_q^± \Rightarrow \text{Re}(W_p \eta_q^±) \). It is not essential to
do this because the imaginary parts of the integrand
are odd in momentum and so they integrate to zero. (See Ref.\(^\text{5}\) for a more detailed treatment of this point.)

IV. EXPRESSIONS FOR THE COMMUTATION
FUNCTION

A. Expansion for Large \( W \)

The commutation function \( W_p \) was defined in
Eq.\(^\text{8,9}\), or equivalently \( e^{p \cdot q/\hbar} e^{-\beta \hat{H}} e^{-p \cdot q/\hbar} = e^{-\beta \hat{H}(p,q)} W_p(p, q) \). The subscript \( p \) will now be dropped.

The Hamiltonian operator is \( \hat{H} = \hat{H}(\hat{p}, \hat{q}) = U(\hat{q}) + \hat{p}^2 /2m \), and the momentum operator is \( \hat{p} = -i\hbar \nabla_q \).

Following Kirkwood\(^\text{26}\) differentiation with respect to
inverse temperature gives\(^\text{22,23}\)

\[
\frac{\partial W}{\partial \beta} = -\frac{\beta \hbar^2}{2m} (\nabla^2 U) W - \frac{\beta \hbar^2}{m} (\nabla U) \cdot (\nabla W)
\]
\[ + \frac{\beta^2 h^2}{2m} (\nabla U) \cdot (\nabla U) W + \frac{h^2}{2m} \nabla^2 W 
+ \frac{i\hbar}{m} p \cdot (\nabla W) - \frac{i\hbar \beta}{m} p \cdot (\nabla U) W. \] (4.1)

Here and below \( \nabla \equiv \nabla_q \).

Expand the commutation function in powers of inverse temperature,

\[ W = \sum_{n=0}^{\infty} W_n \beta^n. \] (4.2)

One has \( W_0 = 1 \), which is the classical limit, and \( W_1 = 0 \), since there are no terms of order \( \beta^0 \) on the right hand side of the temperature derivative. Terms of order \( \beta^1 \) yields

\[ W_2 = -\frac{h^2}{4m} \nabla^2 U - \frac{i\hbar}{2m} p \cdot \nabla U, \] (4.3)

and those of order \( \beta^2 \) give

\[ W_3 = \frac{h^2}{6m} \nabla U \cdot \nabla U - \frac{h^4}{24m^2} \nabla^2 \nabla^2 U - \frac{i\hbar^3}{6m^2} p \cdot \nabla^2 U 
+ \frac{h^2}{6m^2} pp \cdot \nabla U. \] (4.4)

Equating terms of order \( \beta^n \) yields the recursion relation

\[ W_{n+1} = \frac{-\hbar^2}{2(n+1)m} (\nabla^2 U) W_{n-1} - \frac{h^2}{(n+1)m} \nabla U \cdot \nabla W_n 
+ \frac{h^2}{2(n+1)m} \nabla U \cdot \nabla W_{n-2} 
+ \frac{h^2}{2(n+1)m} \nabla^2 W_n + \frac{i\hbar}{(n+1)m} p \cdot \nabla W_n 
- \frac{i\hbar}{(n+1)m} p \cdot (\nabla U) W_{n-1}. \] (4.5)

### B. Expansion for Small \( w \)

Also defined has been a ‘small \( w \)’ commutation function, \( W(\Gamma) = e^{w\Gamma} \), in the hope that its expansion might have better convergence properties. An expansion of this in powers of Planck’s constant,

\[ w \equiv \sum_{n=1}^{\infty} w_n \beta^n, \] (4.6)

and temperature differentiation leads to the recursion relation

\[ \frac{\partial w_n}{\partial \beta} = \frac{i}{m} p \cdot \nabla w_{n-1} + \frac{1}{2m} \sum_{j=1}^{n-2} \nabla w_{n-2-j} \cdot \nabla w_j 
- \frac{\beta}{m} \nabla w_{n-2} \cdot \nabla U + \frac{1}{2m} \nabla^2 w_{n-2}. \] (4.7)

The first several terms may be obtained explicitly. One has for \( n = 0 \), \( w_0 = 0 \), for \( n = 1 \),

\[ w_1 = -\frac{i\beta^2}{2m} p \cdot \nabla U, \] (4.8)

for \( n = 2 \),

\[ w_2 = \frac{\beta^3}{6m^2} pp : \nabla \nabla U + \frac{1}{2m} \left\{ \frac{\beta^3}{3} \nabla U \cdot \nabla U - \frac{\beta^2}{2} \nabla^2 U \right\}, \] (4.9)

for \( n = 3 \),

\[ w_3 = \frac{i\beta^4}{24m^3} ppp \cdot \nabla \nabla \nabla U + \frac{5i\beta^4}{24m^2} p(U) : \nabla \nabla U 
- \frac{i\beta^3}{6m^2} p \cdot \nabla^2 U, \] (4.10)

and for \( n = 4 \),

\[ w_4 = \frac{-\beta^5}{5m^4} (p \cdot \nabla)^4 U + \frac{\beta^4}{16m^2} (p \cdot \nabla)^2 \nabla^2 U 
- \frac{\beta^5}{15m^3} \left(p \cdot \nabla \nabla U \right) \cdot \left(p \cdot \nabla \nabla U \right) 
- \frac{3\beta^5}{40m^3} pp p p \nabla \nabla \nabla \nabla U - \frac{\beta^3}{24m^2} \nabla^2 \nabla^2 U 
+ \frac{5\beta^4}{48m^2} \nabla U \cdot \nabla \nabla U + \frac{\beta^4}{24m^2} \nabla U \cdot \nabla U 
- \frac{\beta^5}{15m^2} \nabla \nabla \nabla \nabla U : \nabla \nabla \nabla \nabla U. \] (4.11)

This result for \( w_4 \) corrects Eq. (7.112) of Ref. 23. Unfortunately published numerical results are vitiated by that error. 24

1. Simple Harmonic Oscillator

Using \( \hbar \omega \) as the unit of energy, and dimensionless momentum and position operators, \( \hat{P} = \hat{\rho}/\sqrt{m\hbar \omega} \) and \( \hat{Q} = \sqrt{m\omega}/\hbar q \), the Hamiltonian operator for the simple harmonic oscillator may be written\(^\text{26}\)

\[ \hat{H} = \frac{1}{2} \left\{ \hat{P}^2 + \hat{Q}^2 \right\}. \] (4.12)

In these dimensionless units, \( \hbar = m = 1 \).

For one particle in \( d \) dimensions, \( \nabla U = Q \) and \( \nabla^2 U = d \). Hence with \( P^2 \equiv P \cdot P \), \( Q^2 \equiv Q \cdot Q \), and \( R \equiv P \cdot Q \), the ‘big \( W \)’ recursion relation for the temperature expansion coefficients of the simple harmonic oscillator is

\[ W_{n+1} = -\frac{d}{2(n+1)} W_{n-1} - \frac{1}{n+1} Q \cdot \nabla W_{n-1} 
+ \frac{Q^2}{2(n+1)} W_{n-2} + \frac{1}{2(n+1)} \nabla^2 W_n 
+ \frac{i}{n+1} P \cdot \nabla W_n - \frac{iR}{n+1} W_{n-1}. \] (4.13)
The first several expansion coefficients are explicitly 
\[ W_0 = 1, \quad W_1 = 0, \quad \text{and} \]
\[ W_2 = \frac{-d^2 + iR}{4}, \quad W_3 = \frac{1}{6} P^2 + \frac{1}{6} Q^2, \quad W_4 = \frac{3d^2 + 4d + 9}{24} iR - \frac{1}{8} R^2, \quad W_5 = \frac{-5d + 3}{120} P^2 - \frac{5d + 5}{120} Q^2 - \frac{1}{12} iRQ^2 - \frac{1}{12} iR^2. \]

Each of these is symmetric in \( P \) and \( Q \), which is a useful check.

The first several 'small \( w \)' coefficients in its expansion in powers of Planck's constant for the simple harmonic oscillator for one particle in \( d \) dimensions are explicitly (with \( \beta \) dimensionless)
\[ w_1 = \frac{-i\beta^2}{2} R, \quad w_2 = \frac{3\beta^2}{6} P^2 + \frac{\beta^3}{6} Q^2 - \frac{d\beta^2}{4}, \quad w_3 = \frac{5i\beta^4}{24} R, \quad w_4 = \frac{-\beta^5}{15} P^2 + \frac{d\beta^4}{24} - \frac{\beta^5}{15} Q^2. \] (4.15)

C. Series in Energy States

Now the commutation function will be expressed in energy eigenfunctions, which will give a formally exact phase space representation.

The energy eigenfunctions and eigenvalues are \( \tilde{\mathcal{H}}(\mathbf{n}) = E_n(\mathbf{n}) \). At this stage there is no need to be specific about the dimensionality or the number of particles. Formally the commutation function can be written as
\[ e^{-\beta \tilde{\mathcal{H}}(\mathbf{p}, \mathbf{q})} W_{\mathcal{E}}(\mathbf{p}, \mathbf{q}) = e^{\mathbf{p} \cdot \mathbf{i} \mathbf{h}} e^{-\beta \tilde{\mathcal{H}}(\mathbf{p}, \mathbf{q})} \]
\[ = e^{\mathbf{p} \cdot \mathbf{i} \mathbf{h}} L^{d/2} \sum_n e^{-\beta \tilde{\mathcal{H}}(\mathbf{n})} \langle \mathbf{n} | \mathbf{p} \rangle \]
\[ = e^{\mathbf{p} \cdot \mathbf{i} \mathbf{h}} L^{d/2} \sum_n e^{-\beta E_n} \langle \mathbf{n} | \mathbf{p} \rangle \phi_n(\mathbf{q}). \] (4.16)

This expression is general and is not restricted to ideal systems or to the simple harmonic oscillator. In the summand appear in essence the energy eigenfunctions and their Fourier transform,
\[ \langle \mathbf{n} | \mathbf{p} \rangle = L^{-d/2} \int d\mathbf{q} e^{-\mathbf{p} \cdot \mathbf{i} \mathbf{h}} \phi_n(\mathbf{q}) \]
\[ = L^{-d/2} \phi_n(\mathbf{p}), \] (4.17)

With this the weighted commutation function may be written
\[ e^{-\beta \tilde{\mathcal{H}}(\mathbf{p}, \mathbf{q})} W_{\mathcal{E}}(\mathbf{p}, \mathbf{q}) = e^{\mathbf{p} \cdot \mathbf{i} \mathbf{h}} \sum_n e^{-\beta E_n} \phi_n(\mathbf{p}) \phi_n(\mathbf{q}). \] (4.18)

The imaginary part of this is odd in \( p \). This result is formally exact.

For an interacting system, one can imagine evaluating this expression for the commutation function by approximating the energy eigenvalues and eigenfunctions, and then using it in addition to the symmetrization function to weight the points of classical phase space. (Alternatively, see [41]).

1. Simple Harmonic Oscillator Commutation Function

This form for the commutation function can be given explicitly for the simple harmonic oscillator. In dimensionless units, the energy eigenvalues are \( E_n = \sum_{j,\alpha} [n_{j,\alpha} + 1/2] \), and the energy eigenfunctions are the Hermite functions,\[ \phi_n(Q) = \prod_{j,\alpha} \frac{1}{\sqrt{2^{n_{j,\alpha}} n_{j,\alpha}!}} e^{-Q_{j,\alpha}^2/2} H_{n_{j,\alpha}}(Q_{j,\alpha}), \] (4.19)

where \( H_n(Q) \) is the Hermite polynomial of degree \( n \). The Hermite function is essentially its own Fourier transform,
\[ \tilde{\phi}_n(P) = \prod_{j,\alpha} \frac{\sqrt{2^{n_{j,\alpha}} n_{j,\alpha}!}}{\sqrt{2^{n_{j,\alpha}} n_{j,\alpha}!}} e^{-P_{j,\alpha}^2/2} H_{n_{j,\alpha}}(P_{j,\alpha}). \] (4.20)

Figure [sharp] shows the simple harmonic oscillator commutation function for one particle in one dimension at \( P = Q = 0 \). One can see that the phase space weight is increasingly reduced from the classical Maxwell-Boltzmann weight as the temperature is decreased. At higher temperatures, \( \beta \lesssim 1 \), there is good agreement between the exact series form and the six (up to \( W_5 \)) and five (up to \( w_4 \)) term high temperature expansions for \( W \) and \( w \).
respective. The exact series used up to \( n = 54 \) terms for high temperatures, \( \beta \to 0 \). As the temperature is reduced the number of necessary terms declines: at \( \beta = 1 \) the tenth term was \( O(10^{-10}) \), and at \( \beta = 2 \) the fifth term was \( O(10^{-10}) \). The commutation function can differ significantly from unity at lower temperatures; at \( \beta = 2 \) and \( P = Q = 0 \), it reduces the phase space weight by about 50% from its classical value.

Figure 2 shows the real part of the weighted commutation function, \( \text{Re} e^{-\beta H(P,Q)} W(P,Q) \), as a function of phase space along the line \( P = Q \) at a fixed temperature \( \beta = 2 \). The inset compares results for \( \beta = 1 \) with \( \beta = 2 \). The commutation function generally decreases the phase space weight from that given by the classical Maxwell-Boltzmann factor alone. The effect is most significant in the region of the potential minimum, in this case \( P = Q \lesssim 1 \), or, equivalently, \( H \lesssim 1 \). It can be seen in the main figure that the high temperature expansions remain relatively accurate at \( \beta = 1 \). Fewer terms need be retained in the exact series as the temperature is decreased; at \( \beta = 2 \) results with \( n = 4 \) terms were indistinguishable from those with \( n = 5 \to 10 \).

Some oscillatory behavior was observed at larger energies, which depended upon the number of terms retained in the series. One would like a probability density to be non-negative, but there seems to be no fundamental requirement that the transformation of quantum statistical mechanics to classical phase space should yield an actual probability density. In any case, the numerical problems (i.e. the sensitivity to the number of retained terms) with the exact series for the commutation function at large energies and high temperatures are likely moot because the Maxwell-Boltzmann factor makes the total phase space weight negligible in this regime.

Figure 3 compares the grand potential obtained as a phase space integral, Eq. (3.6), with the exact analytic result, Eq. (2.17). The imaginary parts of the phase space expressions integrate to zero. As expected, the energy series expressions with a small number of terms works well at low temperatures, and the two high temperature expansions work well in the opposite regime. The purpose of the figure is to show that it is quite feasible to obtain computationally the quantum grand potential from an integral over classical phase space.

Because the grand potential diverges in the classical limit, \( \beta \to 0 \), it can be more challenging to obtain accurate numerical results in the high temperature regime. At \( \beta = 0.2 \), for the monomer grand potential \( -z^{-1} \beta \Omega_1 \), the exact analytic result is 4.99, using the energy series with \( n = 4 \) terms it is 3.16, and with \( n = 8 \) terms it is 4.17. Again at \( \beta = 0.2 \), for the dimer grand potential \( +z^{-2} \beta \Omega^2_2 \), the exact analytic result is 1.24, using the energy series with \( n = 4 \) terms it is 1.07 and with \( n = 8 \) terms it is 1.21. At high temperatures, the high temperature expansions are more sensitive to the limits used for the phase space integrals than is the energy series form.

The dimer grand potential is typically about 5–10 times smaller than the monomer grand potential at the same temperature. For the loop grand potential, the symmetrization factor induces an effective interaction between the adjacent particles around the loop, typically of the form \( \cos(Q_{j,j+1} P_{j,j+1}) \) or \( \sin(Q_{j,j+1} P_{j,j+1}) \). Since rapidly oscillating terms tend to cancel, it was found efficacious to introduce a cut-off \( R^p_{\text{cut}} \) and to neglect configurations unless both \( |Q_{j,j+1}| \leq R^q_{\text{cut}} \) and \( |P_{j,j+1}| \leq R^p_{\text{cut}} \). For the present simple harmonic oscillator, a value of \( R^p_{\text{cut}} = 4 \) was found to change the results by about 2% at \( \beta = 0.1 \) and by less than 1% at \( \beta = 1 \), while substan-
D. Commutation Function and Averages

The focus above has been on the grand potential, and the commutation function was treated with that in mind. In the case of the statistical average of an operator, the specific commutation function can depend on the particular operator. (The following analysis differs from that given in Ref. 54.)

The average of an operator is

$$\langle A \rangle_{z,T}^\pm = \frac{1}{\Xi^\pm} \text{TR} e^{-\beta \hat{H} \hat{A}}$$

(4.21)

$$= \frac{1}{\Xi^\pm} \sum_{N=0}^\infty \frac{z^N}{N!} \sum_n \lambda_n e^{-\beta E_n} A_{nn}$$

$$= \frac{1}{\Xi^\pm} \sum_{N=0}^\infty \frac{z^N}{N!} \sum_{n,p} (1)^n (n|e^{-\beta \hat{H}} \hat{A}|p).$$

Suppose that the operator to be averaged is an ordinary function of the position and momentum operators, \( \hat{A} = A(p, q) \). The analysis proceeds as in the text, with \( e^{-\beta \hat{H}} \Rightarrow e^{-\beta \hat{H}} \hat{A} \). One ends up with

$$\langle A \rangle_{z,T}^\pm = \frac{1}{\Xi^\pm} \sum_{N=0}^\infty \frac{z^N}{h^d N!} \int \text{dq dp} \langle q|e^{-\beta \hat{H}} \hat{A}|p \rangle \langle \hat{P} p | q \rangle$$

$$= \frac{1}{\Xi^\pm} \sum_{N=0}^\infty \frac{z^N}{h^d N!} \int \text{dq dp} e^{-\beta \hat{H}(p,q)} A(p, q) W_{A,p}(p, q) \eta_q^+(p, q).$$

(4.22)

Here the weight function for the average has been defined, which, as in the text, can be written as

$$e^{-\beta \hat{H}(p,q)} A(p, q) W_{A,p}(p, q)$$

$$= \frac{\langle q|e^{-\beta \hat{H}} \hat{A}|p \rangle}{\langle q|p \rangle}$$

$$= \frac{1}{\langle q|p \rangle} \sum_n \langle q|e^{-\beta \hat{H}} |n \rangle \langle n| \hat{A}|p \rangle$$

$$= \frac{1}{\langle q|p \rangle} \sum_n e^{-\beta E_n} \langle q|n \rangle \langle n| \hat{A}|p \rangle.$$  

(4.23)

Conversely, since the original trace form for the statistical average is unchanged by the cyclic permutation of the operators, the statistical average can also be obtained from

$$e^{-\beta \hat{H}(p,q)} A(p, q) W_{A,q}(p, q)$$

$$= \frac{\langle p|e^{-\beta \hat{H}} \hat{A}|q \rangle}{\langle p|q \rangle}$$

$$= \frac{1}{\langle p|q \rangle} \sum_n e^{-\beta E_n} \langle p|n \rangle \langle n| \hat{A}|q \rangle.$$  

(4.24)

With this the statistical average is equally well written

$$\langle A \rangle_{z,T}^\pm = \frac{1}{\Xi^\pm} \sum_{N=0}^\infty \frac{z^N}{h^d N!} \int \text{dq dp} e^{-\beta \hat{H}(p,q)} A(p, q) W_{A,q}(p, q) \eta_q^+(p, q).$$

(4.25)

One should not assume that \( W_{A,p} = W_{A,q} \). If one swaps the order of the Maxwell-Boltzmann operator and the operator to be averaged, then these are replaced by \( W_{A,p} \) and \( W_{A,q} \), with \( W_{A,p} = W_{A,q}^* \).

If the operator is only a function of position then the second form becomes

$$e^{-\beta \hat{H}(p,q)} W_{A,p}(p, q) A(p) = \frac{A(p)}{\langle q|p \rangle} \sum_n e^{-\beta E_n} \langle q|n \rangle \langle n| p \rangle.$$  

(4.26)

Hence if \( \hat{A} = A(q) \), then \( W_{A,q}(p, q) = W_{q,p}(q, p) \). If the operator is only a function of momentum, then the first form becomes

$$e^{-\beta \hat{H}(p,q)} W_{A,p}(p, q) A(p) = \frac{A(p)}{\langle q|p \rangle} \sum_n e^{-\beta E_n} \langle q|n \rangle \langle n| p \rangle.$$  

(4.27)

Hence if \( \hat{A} = A(p) \), then \( W_{A,p}(p, q) = W_{p,q}(p, q) \).

These mean that in these two cases (or their linear combination) one can use the original commutation function \( W_n(\Gamma) \) or \( W_q(\Gamma) \), and it would therefore be legitimate to regard it as a weight function for classical phase space.

If the operator is a function of the energy operator then one also has a relatively simple form,

$$e^{-\beta \hat{H}(p,q)} W_{A,p}(p, q) A(\hat{H}(p,q))$$

$$= \frac{1}{\langle q|p \rangle} \sum_n e^{-\beta E_n} A(E_n) \langle q|n \rangle \langle n| p \rangle.$$  

(4.28)

Hence if \( \hat{A} = \hat{H} \), one sees that \( W_{A,p} = W_{A,p} \), and that \( W_{A,p} = W_{A,q} \).

This result is instructive in the linear case, where \( A \) is the energy function itself, \( \hat{H} = U(q) + \hat{p}^2/2m \). In this case

$$e^{-\beta \hat{H}(p,q)} \hat{H}(p,q) W_{H,p}(p, q)$$

$$= \frac{1}{\langle q|p \rangle} \sum_n e^{-\beta E_n} E_n \langle q|n \rangle \langle n| p \rangle.$$  

(4.29)

But from the earlier analysis one also has that

$$e^{-\beta \hat{H}(p,q)} \{ W_{K,p}(p,q) K(p) + W_{U,q}(p,q) U(q) \}$$

$$= \hat{H}(p,q) \sum_n e^{-\beta E_n} \langle q|n \rangle \langle n| p \rangle$$

$$= e^{-\beta \hat{H}(p,q)} \hat{H}(p,q) W_{p}(p, q).$$  

(4.30)
Note that $W_{x,p} = W_p$ and $W_{l,q} = W_q$. Hence the average energy can also be written

$$\langle \hat{H} \rangle_{z,\beta,V}^{\pm} = \langle K \rangle_{z,\beta,V}^{\pm} + \langle U \rangle_{z,\beta,V}^{\pm}$$

$$= \frac{1}{Z} \sum_{N=0}^{\infty} \frac{z^N}{h^N N!} \int d\Gamma \ e^{-\beta \hat{H}(\Gamma)} \ {\langle K(p)W_p(\Gamma)\eta_q^\pm(\Gamma) \rangle} + \{U(q)W_q(\Gamma)\eta_p^\pm(\Gamma) \}$$

$$= \frac{1}{Z} \sum_{N=0}^{\infty} \frac{z^N}{h^N N!} \int d\Gamma \ e^{-\beta \hat{H}(\Gamma)} \hat{H}(p)W_p(\Gamma)\eta_q^\pm(\Gamma).$$

The final equality follows by taking the complex conjugate of the potential energy average. Alternatively using the complex conjugate of the average kinetic energy corresponds to the replacement $W_p\eta_q^{\pm} \Rightarrow W_q\eta_p^{\pm}$.

This result means that the average energy can be equally taken with either $W_{x,p}$ or with $W_p$ but it does not mean that $W_{x,p} = W_p$. In fact, one can confirm directly from the definitions that $W_{x,p} = W_p - \hat{H}/\partial\beta$. One must therefore have that $\sum_{N=0}^{\infty} \frac{z^N}{h^N N!} \int d\Gamma \ e^{-\beta \hat{H}(\Gamma)} \eta_q^\pm(\Gamma)\partial W_p(\Gamma)/\partial\beta = 0$. In fact one can show that this holds individually for each term $N$ and each permutation $P$. This is necessary for thermodynamic consistency, since the most likely energy is the temperature derivative of the grand potential, $\bar{E} = \partial(\beta\Omega)/\partial\beta$. (See Ref. 52 for a more detailed treatment of averages.)

The above analysis reveals that in the case of the average of an operator that is a linear combination of ‘pure’ functions (a pure function depends only on the position operator or only on the momentum operator), then the original commutation function $W$ suffices to obtain the statistical average. This is rather useful from the computational viewpoint.

For a Hermitian operator $A(\hat{p}, \hat{q})$, the quantum statistical average is real, as is $A(\hat{p}, \hat{q})$. Since $\eta_q^\pm(\hat{p}, \hat{q}) = \eta_p^\pm(-\hat{p}, \hat{q})$, it is sufficient that $A(\hat{p}, \hat{q})W_{A,x}(\hat{p}, \hat{q}) = A(-\hat{p}, \hat{q})W_{A,x}(-\hat{p}, \hat{q})$, $x = p, q$, in order for the imaginary part to integrate to zero.

In any case, the average must be real, and so the imaginary part of the integrand must always integrate to zero no matter how one formulates the integrand. Nevertheless, it may be more efficient computationally to write it in the most symmetric fashion using the fact that the trace operation is insensitive to the order of the operators or of the position and momentum eigenfunctions. Hence one can use the symmetric integrand

$$e^{-\beta \hat{H}(\Gamma)} A(\Gamma)\Pi_{A}(\Gamma)\eta_{q}^{\pm}(\Gamma)$$

$$= \frac{1}{4} \left\{ \langle q | e^{-\beta \hat{H}} \hat{A} + \hat{A} e^{-\beta \hat{H}} | p \rangle \langle p | q \rangle \eta_{q}^{\pm}(\Gamma) \right\}$$

$$= \frac{1}{4} \left\{ \langle q | e^{-\beta \hat{H}} \hat{A} + \hat{A} e^{-\beta \hat{H}} | p \rangle \langle p | q \rangle \eta_{q}^{\pm}(\Gamma) \right\}$$

$$= \frac{1}{4} \left\{ \langle q | e^{-\beta \hat{H}} \hat{A} + \hat{A} e^{-\beta \hat{H}} | p \rangle \langle p | q \rangle \eta_{q}^{\pm}(\Gamma) \right\}$$

FIG. 4: Average energy in units of $\hbar\omega$ at $z = 1$ for ideal simple harmonic oscillators in one dimension using monomer and dimer loops (curves), or else all loops up to 50-mers (symbols). The upper data are for bosons and the lower data are for fermions. The solid curves and the symbols are the exact analytic result, Eq. (4.33), and the dashed curves result from numerical quadrature over phase space, Eq. (4.34), using the commutation function with $n = 8$ energy states, and without a cut-off for the dimers.

1. Simple Harmonic Oscillator

From thermodynamics, the most likely energy is given by the temperature derivative of the grand potential, $\bar{E} = \partial(\beta\Omega)/\partial\beta$. Applying this to the exact analytic expression for the simple harmonic oscillator, Eq. (2.17), yields

$$\bar{E}^{\pm} = \sum_{l=1}^{\infty} (\pm 1)^{l-1} z^l \left( \frac{e^{-\beta \hbar \omega/2}}{1 - e^{-\beta \hbar \omega}} \right)^{d-1}$$

$$\times e^{-\beta \hbar \omega/2} + e^{-3\beta \hbar \omega/2} \frac{1}{1 - e^{-3\beta \hbar \omega}}$$

$$\equiv \bar{E}_1 \pm \bar{E}_2 + \ldots$$

(4.33)

For the present phase space formulation, the individual terms in the loop expansion yield

$$\langle H \rangle_{z,\beta}^{\pm,\pm} = \frac{z^l}{h^l} \int d\Gamma’ e^{-\beta \hat{H}(\Gamma’)} \eta_{q}^{\pm}(\Gamma’) W_{l}(\Gamma’) \hat{H}(\Gamma’)$$
\[ \frac{1}{\hbar} \int d\Gamma \prod_{j=1}^{l} \left\{ e^{-\beta \mathcal{H}^{(1)}(\Gamma_j)} W^{(1)}(\Gamma_j) \right\} \times e^{-(q_j - q_{j+1})p_j/\hbar} \sum_{k=1}^{l} \mathcal{H}^{(1)}(\Gamma_k). \] (4.34)

(These are either \( \overline{W}_q \) and \( \eta^+ \), or else \( \overline{W}_q \) and \( \eta^- \).) These are for an ideal system. The average can be given in terms of \( \overline{W}_\mathcal{H} \) by making the replacement in the integrand

\[ \prod_{j=1}^{l} \left( \sum_{k=1}^{l} \mathcal{H}^{(1)}(\Gamma_k) \right) \prod_{j \neq k}^{l} W^{(1)}(\Gamma_j). \] (4.35)

The above result has been confirmed by deriving it both from the temperature derivative, and from the original trace form for the statistical average (not shown).

The average energy for the simple harmonic oscillator is shown in Fig. 4 as either the sum of the monomer and dimer terms in these expressions, or else the exact analytic expression (up to 50-mers). It can be seen that bosons have a higher energy than fermions at a given temperature. Presumably Fermi exclusion gives rise to an effective repulsion that leads to fewer fermions than bosons for a given fugacity. It can be seen that at the present fugacity, \( z = 1 \), dimers account for most of the difference between the two types of particles. The separation between the two cases would increase with increased fugacity, as would the contribution from higher order loops. It can be seen that the phase space expression for the average energy is quite accurate. The error at high temperatures could be ameliorated by including more terms in the energy series for the commutation function, or else by using the high temperature expansions. Imposing a cut-off of 4 changed the results by less than 0.03% at \( \beta = 0.2 \). The results using the commutation function \( W \) were indistinguishable (to at least six significant figures at all temperatures) from those using \( \overline{W}_\mathcal{H} \), which confirms the analysis earlier in this sub-section.

V. HARMONIC APPROXIMATION FOR INTERACTING PARTICLES

One can use the above results to approximate the commutation function of an interacting system by casting each configuration as a collection of non-interacting harmonic oscillators. The interacting Hamiltonian consists of the usual kinetic and potential energies,

\[ \mathcal{H}(p, q) = K(p) + U(q), \] (5.1)

with the latter containing many-body terms,

\[ U(q) = \sum_{j=1}^{N} u^{(1)}(q_j) + \sum_{j<k}^{N} u^{(2)}(q_j, q_k) + \sum_{j<k<l}^{N} u^{(3)}(q_j, q_k, q_l) + \ldots \] (5.2)

Distributing the energy equally, the energy of particle \( j \) can be defined as

\[ U_j(q) = u^{(1)}(q_j) + \frac{1}{2} \sum_{k=1}^{N} (k \neq j) u^{(2)}(q_j, q_k) + \frac{1}{3} \sum_{k<l}^{N} (k, l \neq j) u^{(3)}(q_j, q_k, q_l) + \ldots \] (5.3)

The total potential energy is just \( U(q) = \sum_{j=1}^{N} U_j(q) \).

For a given configuration \( q \), define the test energy for particle \( j \), \( U_j(r; q) \equiv \overline{U}_j(q)_{q_j=r} \). Here the \( j \)th particle has been moved to \( r \), all other particles remaining fixed in their positions for the current configuration. The location of the nearest local minimum for particle \( j \), \( \overline{T}_j(q) \), satisfies \( \nabla U_j(r; q)_{q_j=\overline{T}_j} = 0 \). Define the \( d \times d \) second derivative matrix for particle \( j \) at this local minimum as

\[ \nabla_r \nabla U_j(r; q)_{q_j=\overline{T}_j} = \overline{\mathcal{D}}_j. \] (5.4)

Newton’s method for finding \( \overline{T}_j(q) \) is discussed below.

For liquids and solids, a local minimum is well defined, since each molecule is instantaneously caged by surrounding molecules. Since the distance to the local minimum is likely to be small, a second order expansion of the potential will be accurate. As shown in Fig. 2, the commutation function departs most from unity close to the minimum in the potential. For those unlikely configurations where a particle is not close to a local minimum, the commutation function can be taken to be unity; in such cases the Maxwell-Boltzmann factor will mean these configurations have little weight in the overall average.

The potential energy of particle \( j \) may be expanded to second order about the local minimum,

\[ U_j(q) = \overline{U}_j(q) + \frac{1}{2} \overline{T}_j(q_j - \overline{T}_j) : \overline{\mathcal{D}}_j : \overline{T}_j(q_j - \overline{T}_j) + \ldots \] (5.5)

where \( \overline{U}_j(q) \equiv U_j(\overline{T}_j; q) \). The total potential energy is just the sum of these.

The second derivative \( d \times d \) matrix is positive definite with eigenvalues \( \lambda_{ja}(q) > 0 \), and orthonormal eigenvectors \( \overline{T}_j X_{ja} = \lambda_{ja} X_{ja} \), \( \alpha = x, y, \ldots, d \). As \( d \) is typically 1, 2, or 3, it is trivial numerically to find these eigenvalues and eigenvectors. The orthogonal matrix \( \overline{X}_j = \{ X_{jx}, X_{jy}, \ldots, X_{jd} \} \) gives \( \overline{U}_j = \overline{X}_j^T \overline{\mathcal{D}}_j \overline{X}_j = \overline{D}_j \), where \( \overline{D}_j \) is a diagonal matrix. For molecule \( j \) in configuration \( q \) the eigenvalues define the frequencies

\[ \omega_{ja}(q) = \sqrt{\lambda_{ja}(q)/m} \quad \alpha = x, y, \ldots, d. \] (5.6)

With this the potential energy is

\[ U(q) = \sum_{j=1}^{N} \overline{U}_j + \frac{1}{2} \sum_{j=1}^{N} \sum_{\alpha=1}^{N} (q_j - \overline{T}_j)(q_j - \overline{T}_j) : \overline{\mathcal{D}}_j : (q_j - \overline{T}_j) + \ldots \]

\[ = \sum_{j=1}^{N} \overline{U}_j + \frac{1}{2} \sum_{j, \alpha}^{N} \hbar \omega_{ja}(q_j)_{j, \alpha}^{2}. \] (5.7)
Here \( Q_{ja} \equiv \sqrt{m \omega_{ja} / h} Q^j_{ja} \), and \( Q^j = \sum_j |q_j - \bar{q}_j| \). Also define \( \bar{q}_{ja} \equiv \sqrt{h/m \omega_{ja}} Q_{ja} \).

With this harmonic approximation for the potential energy, the Hamiltonian in a particular configuration can be written

\[
H(p, q) = \frac{N}{2} \sum_{j,a} \hbar \omega_{ja} \left[ p^2_{ja} + Q^2_{ja} \right],
\]

where \( P_{ja} = p_{ja} / \sqrt{m \hbar \omega_{ja}} \). This represents \( dN \) independent oscillators. Hence the commutation function for the interacting system for a particular configuration can be approximated as the product of commutation functions for effective non-interacting harmonic oscillators,

\[
e^{-\beta H(p, q)} W_p(p, q) = \prod_{k=1}^N e^{-\beta \hbar \omega_{ja} [p^2_{ja} + Q^2_{ja}] / 2} W_{p_{ja}}(p, q),
\]

with the single particle, one-dimensional commutation function being given by

\[
e^{-\beta \hbar \omega_{ja} [p^2_{ja} + Q^2_{ja}] / 2} W_{p_{ja}}(p, q)
\]

\[
e^{-\beta \hbar \omega_{ja} [p^2_{ja} + Q^2_{ja}] / 2} W_{p_{ja}}(p, q)
\]

\[
= e^{q_{ja} / \hbar / i} \sum_{n_{ja} = 0}^\infty e^{-\beta \hbar \omega_{ja} [n_{ja} + \frac{1}{2}]} \phi_{n_{ja}}(p_{ja}) \phi_{n_{ja}}(\bar{q}_{ja})
\]

\[
= e^{q_{ja} / \hbar / i} e^{-\beta \hbar \omega_{ja} / 2} e^{-\beta Q^2_{ja} / 2} e^{-\beta \hbar \omega_{ja} / 2} \times \sqrt{2} \sum_{n_{ja} = 0}^\infty \frac{\hbar}{2} n_{ja} e^{-\beta \hbar \omega_{ja} n_{ja}} H_{n_{ja}}(P_{ja}) H_{n_{ja}}(Q_{ja}).
\]

The imaginary terms here are odd in momentum. Note that the prefactor \( e^{q_{ja} / \hbar / i} \) comes from the phase space transformation factor \( 1 / (q^j | p) \), which is independent of the simple harmonic oscillator approximation. Based on the numerical results presented in the preceding section, one only needs to keep a few terms in this series and to evaluate it for particles that are close to their local potential minimum.

1. **Newton’s Method**

One can approximate the location of the local minimum for particle \( j \) in configuration \( q \) as follows. Take the second derivative matrix to be

\[
\nabla'' \approx \nabla'' = \nabla \nabla U_j(q).
\]

Then with

\[
U_j(q) = U_j(r) |q_j - \bar{q}_j| \cdot \nabla U_j(r) |q_j - \bar{q}_j| \quad (5.12)
\]

\[
+ \frac{1}{2} |q_j - \bar{q}_j| |q_j - \bar{q}_j| : \nabla \nabla U_j(r) |q_j - \bar{q}_j|,
\]

the derivative is,

\[
\nabla U_j(q) = \nabla U_j(r) |q_j| + \nabla \nabla U_j(r) |q_j| (q_j - \bar{q}_j)
\]

\[
\approx \nabla U_j(q) + U''(q_j) (q_j - \bar{q}_j).
\]

VI. **CONCLUSION**

In this paper a formally exact transformation has been given that expresses quantum statistical mechanics as an integral over classical phase space. Two phase functions that reflect specific quantum effects result: a commutation function that accounts for the non-commutativity of position and momentum operators, and a symmetrization function that accounts for wave function symmetrization (bosons) or anti-symmetrization (fermions). The latter is more computationally tractable than conventional methods of treating occupation states, such as Slater determinants. To leading order (high temperatures, low densities), the phase functions are unity and the theory reduces exactly to classical statistical mechanics. The magnitude of the quantum effects can be estimated by truncating the respective series expansions for the commutation and symmetrization functions, which provides a systematic and quantifiably approximate solution for quantum systems.

The present phase space method was illustrated and tested for non-interacting quantum harmonic oscillators, for which system exact analytic results are known. It was demonstrated that the quantum grand potential and the average quantum energy could be obtained accurately from an integral over classical phase space. Both the high temperature expansion and the energy series for the commutation function were tested and found to have overlapping regimes of reliability. Surprisingly few terms were required to get accurate results with the energy series at low temperatures. It was also demonstrated that the dimer term in the symmetrization function suffices for bosons and for fermions at intermediate and low temperatures at a fugacity of \( z = 1 \).

Numerical results for the commutation function for the quantum harmonic oscillator showed that it only departed from unity near a minimum in the potential. This suggests that a mean field theory based upon an expansion about local potential minima together with the analytic oscillator results should be accurate for quantum condensed matter, interacting particle systems. It remains to explore the computational feasibility of such a mean field approach and to test it against, for example, the high temperature expansion for the commutation function that has previously been applied to interacting Lennard-Jones liquids.23,49,50
Notes Added

(1.) An improved generic treatment of the factorization of the symmetrization function for averages, and a demonstration of the internal consistency of the approach, are given in Ref. [52].

(2.) Because of the compact nature of contributing permutation loops, in general the symmetrization function only has to be calculated for permutation loops consisting of consecutive nearest neighbors, whence appropriate neighbor tables should further ameliorate the computational burden.