Quantum Statistical Mechanics in Classical Phase Space. Expressions for the Multi-Particle Density, the Average Energy, and the Virial Pressure.

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Quantum statistical mechanics is formulated as an integral over classical phase space. Some details of the commutation function for averages are discussed, as is the factorization of the symmetrization function used for the grand potential and for the multi-particle density. Three binary choices (eight routes) for the average energy are shown to be mutually consistent. An expression for the phase space function that gives the average virial pressure is derived.

I. INTRODUCTION

For some years now I have been seeking to formulate quantum statistical mechanics as an integral over classical phase space. The motivation for this quixotic quest is not just to pursue a different research direction, but it comes also from the observed state of our physical world, and from the computational challenges posed by quantum statistical mechanics.

In the terrestrial sphere most systems are dominated by classical behavior. For example, water at standard temperature and pressure has a quantum correction on the order of one part in $10^4$, depending upon the property of interest. Hence it seems sensible to describe terrestrial condensed matter using classical statistical mechanics with added quantum corrections or perturbations.

From the computational viewpoint classical statistical mechanics is easy, whereas quantum statistical mechanics is difficult. The chief technical barriers that inhibit accurate numerical description are the need for explicit eigenvalues and eigenfunctions, and the need to either symmetrize the wave function or else to enforce the occupancy rules for bosons and fermions. In addition, it is the rapid increase in computational cost with system size that can be prohibitive. It is routine nowadays for simulations of classical systems to include tens of thousand particles in one dimension. Of course, by introducing various approximations one can treat larger systems. For example, 6,500 Lennard-Jones atoms were able to be simulated using a variational approach, approximating the eigenfunctions, restricting the calculations to the ground state, and neglecting wave function symmetrization. In pursuing exact quantitative simulation results, these examples suggest that a computationally efficient alternative would be to formulate the problem in classical terms, and to build in the quantum phenomena as systematic corrections or perturbations.

This paper summarizes the current state of the classical phase space formulation of quantum statistical mechanics with a transparent derivation and precise notation. In addition it resolves certain questions of consistency in the expressions for the average energy. Finally, an expression is derived for the phase function that is to be used to calculate the average virial pressure.

II. PARTITION FUNCTION, COMMUTATION FUNCTION, AND AVERAGE

A. Grand Partition Function

I consider $N$ spinless particles in $d$ dimensions confined to a hypercube of volume $V = L^d$. Where it is necessary I shall use the position representation, $\mathbf{r} = \{r_x, r_y, \ldots, r_N\}$, with $r_j \equiv \{r_{jx}, r_{jy}, \ldots, r_{jd}\}$. The unsymmetrized position and momentum eigenfunctions are respectively

$$|\mathbf{q}\rangle = \delta(\mathbf{r} - \mathbf{q}), \quad |\mathbf{p}\rangle = \frac{e^{-\mathbf{p} \cdot \mathbf{r}/i\hbar}}{\sqrt{V^{N/2}}}. \quad (2.1)$$

The position eigenvalues belong to the continuum. The momentum eigenvalues are discrete with spacing $\Delta_p = 2\pi\hbar/L$ per particle per dimension almost immediately the continuum limit for this will be taken. Each set of eigenfunctions is complete.

I shall now use these to transform the grand partition function to classical phase space, after which I shall discuss in detail each stage of the derivation. The grand partition function is

$$\Xi^\pm = \text{TR'}\left\{ e^{-\beta \hat{H}} \right\}$$

$$= \sum_{N=0}^{\infty} \frac{z^N}{N!} \sum_{\hat{p}} \sum_{\mathbf{p}} \left( \pm 1 \right)^p \left\langle \hat{\mathbf{p}} | e^{-\beta \hat{H}} | \mathbf{p} \right\rangle$$

$$= \sum_{N=0}^{\infty} \frac{z^N}{N!} \sum_{\hat{p}} \sum_{\mathbf{p}} \int d\mathbf{q} \left( \hat{\mathbf{p}} | \mathbf{q} \right\rangle \left\langle \mathbf{q} | e^{-\beta \hat{H}} | \mathbf{p} \right\rangle$$

$$= \sum_{N=0}^{\infty} \frac{z^N}{h^{dN}N!} \int d\Gamma \left( \frac{\left\langle \mathbf{q} | e^{-\beta \hat{H}} | \mathbf{p} \right\rangle \left\langle \mathbf{p} | \mathbf{q} \right\rangle}{(\mathbf{q} | \mathbf{p}) (\mathbf{p} | \mathbf{q})} \right\rangle (\Gamma). \quad (2.2)$$

Here $z = e^{\beta \mu}$ is the fugacity, $\beta = 1/k_B T$ is the inverse temperature, $\hbar$ is Planck’s constant, and $\Gamma = \{\mathbf{p}, \mathbf{q}\}$ is a point in classical phase space.

The first equality here has the appearance of von Neumann trace form for the partition function. It arises from the collapse of the total wave function due to entanglement of the sub-system with the reservoir upon energy
(and particle) exchange. The prime on the trace signifies that it is over unique states, which is to say that each distinct state can only appear once, or if more than once each occurrence must have appropriately reduced weight. Not all workers avert to this requirement.

The second equality writes the trace as a sum over momentum states. It also symmetrizes the eigenfunctions by summing over all particle permutations \( \hat{P} \), with the upper (plus) sign for bosons, the lower (minus) sign for fermions, according to the parity \( p \) of the permutation. The factor of \( N! \) in the denominator corrects for the double counting of the states due to this symmetrization. This formulation of particle statistics is formally exact, and carries over to the continuum where it would otherwise be impossible to enforce particle state occupancy rules.

The third equality inserts the completeness condition \( \int dq \, |q| \langle q | = \delta(r' - r'') \). Introducing this to the left of the Maxwell-Boltzmann operator as here produces an asymmetry in position and momentum that is discussed shortly.

The fourth equality transforms to the momentum continuum. The factor from the momentum volume element, \( \Delta^* \), combines with the factor of \( V^{-N} = |q(p)\langle p|q| \) that cancels the denominator introduced here to give the prefactor \( h^{-dN} \). This is now an integral over classical phase space.

The fifth equality writes the phase space integral in terms of the commutation function \( W_p \), and symmetrization function \( \eta^{\pm}_{q} \), which will be defined explicitly next. If at the third equality the completeness condition had been inserted to the right of the Maxwell-Boltzmann operator one would have ended up with position and momentum swapped in these subscripts,

\[
\Xi^{\pm} = \sum_{N=0}^{\infty} \frac{z^N}{h^{dN} N!} \int d\Gamma \, e^{-\beta H(\Gamma)} W_{q}(\Gamma) \eta^{\pm}_{p} (\Gamma). \quad (2.3)
\]

Obviously the partition function must remain unchanged.

The symmetrization functions are defined as

\[
\eta^{\pm}_{q}(p, q) \equiv \frac{1}{|q(p)|} \sum_{\hat{P}} (\pm 1)^{\hat{P}} \langle \hat{P} p |q\rangle, \quad (2.4)
\]

and

\[
\eta^{\pm}_{p}(p, q) \equiv \frac{1}{|q(p)|} \sum_{\hat{P}} (\pm 1)^{\hat{P}} \langle \hat{P} q |p\rangle. \quad (2.5)
\]

Since \( \langle \hat{P} p |q\rangle = \langle p |\hat{P} q\rangle \), it is evident that \( \eta^{\pm}_{p}(p, q) = \eta^{\mp}_{q}(p, q)^* \). Also, since \( |p| \equiv e^{-p r_i i \hbar} / V^{N/2} \), \( \eta^{\pm}_{p}(p, q)^* = \eta^{\pm}_{q}(-p, q) \). These symmetrization functions will be discussed in greater detail in \( \text{III}\).

The commutation functions, which are essentially the same as the functions introduced by Wigner and analyzed by Kirkwood, are defined by

\[
e^{-\beta H(p, q)} W_p(p, q) = \frac{\langle q |e^{-\beta \hat{H}} |p\rangle}{\langle q |p\rangle}. \quad (2.6)
\]

and

\[
e^{-\beta H(p, q)} W_q(p, q) = \frac{\langle q |e^{-\beta \hat{H}} |p\rangle}{\langle q |p\rangle}. \quad (2.7)
\]

Again one has \( W_p(p, q) = W_q(p, q)^* \), and also \( W_p(p, q)^* = W_p(-p, q) \). High temperature expansions for the commutation function have been given.

The commutation function in phase space can also be written as a series of energy eigenfunctions and eigenvalues, \( \hat{H}(n) = E_{n}(n) \). Using the completeness properties of these one obtains

\[
e^{-\beta \hat{H}(p, q)} W_p(p, q) = \frac{\langle q |e^{-\beta \hat{H}} |p\rangle}{\langle q |p\rangle}, \quad (2.8)
\]

and analogously for \( W_q \). There is reason to believe that this formulation in terms of energy (entropy) eigenvalues and eigenfunctions might be useful in computational applications.

It is clear that the grand partition function is real, because the imaginary part of \( W \) and of \( \eta^{\pm} \) is odd in momentum. Furthermore, as discussed for Eq. (2.3), the partition function is unchanged by the replacement \( W_p \eta^\pm_q \Rightarrow W_q \eta^\mp_p \). Since these are the complex conjugate of each other, this proves that the partition function is real. On occasion below I shall omit the subscripts, in which case it is implicit that whichever is used for \( W \), the opposite must be used for \( \eta^{\pm} \).

In classical statistical mechanics and in classical probability theory is is essential that the weight density be real and non-negative. But in quantum statistical mechanics there is no such requirement. Hence any problems associated with \( W \) and \( \eta^{\pm} \) being complex are practical and computational rather than fundamental and principled.

**B. Statistical Averages**

The grand canonical average of an operator is similarly

\[
\langle \hat{A}\rangle_{z, \beta, V}^{\pm} = \Xi^{\pm} \text{TR} \left\{ e^{-\beta \hat{H}} \hat{A} \right\} = \sum_{N=0}^{\infty} \frac{z^N}{h^{dN} N!} \int d\Gamma \, e^{-\beta H(\Gamma)} A(\Gamma) W_{A,p}(\Gamma) \eta^{\pm}_{q} (\Gamma), \quad (2.9)
\]

The final equality follows by swapping \( p \) and \( q \). Reversing the order of \( e^{\beta \hat{H}} \) and \( \hat{A} \) replaces \( W \) by \( W \), here and in
the defining equations next. Such a cyclic permutation of the operators leaves the trace and hence the average unchanged.

The commutation functions for the average are defined by

\[ e^{-\beta H(p,q)}A(p,q)W_{A,p}(p,q) = \frac{\langle q|e^{-\beta \hat{H}}A|p \rangle}{\langle q|p \rangle}, \] (2.10)

and

\[ e^{-\beta H(p,q)}A(p,q)W_{A,q}(p,q) = \frac{\langle p|e^{-\beta \hat{H}}A|q \rangle}{\langle p|q \rangle}. \] (2.11)

Swapping the order of the operators gives \( \hat{W} \),

\[ e^{-\beta H(p,q)}A(p,q)\hat{W}_{A,p}(p,q) = \frac{\langle q|\hat{A}e^{-\beta \hat{H}}|p \rangle}{\langle q|p \rangle}, \] (2.12)

and

\[ e^{-\beta H(p,q)}A(p,q)\hat{W}_{A,q}(p,q) = \frac{\langle p|\hat{A}e^{-\beta \hat{H}}|q \rangle}{\langle p|q \rangle}. \] (2.13)

In the simplest case the operator being averaged is an ordinary function of the momentum and position operators, \( \hat{A} = A(\hat{p}, \hat{q}) \), which leads directly to the phase space function \( A(p,q) \) appearing as more. Here generally, one should probably use the right hand side to define the product \( (AW_{A,p})(p,q) \) etc. as a single phase space function.

I assume that the operator is Hermitian, \( \hat{A} = \hat{A}^\dagger \), and so the average is real. Taking the complex conjugate of the defining equation yields

\[ e^{-\beta H(p,q)}A(p,q)W_{A,p}(p,q)^* = \frac{\langle p|\hat{A}e^{-\beta \hat{H}}|q \rangle}{\langle p|q \rangle} = e^{-\beta H(p,q)}A(p,q)\hat{W}_{A,q}(p,q). \] (2.14)

Of course if \( \hat{A} = A(\hat{H}) \), it commutes with the Maxwell-Boltzmann operator. In such a case \( \hat{W}_{A,q} = W_{A,q} \), and \( \hat{W}_{A,p} = W_{A,p} \).

In general

\[ W_{A,q}(\Gamma) \neq W_q(\Gamma) \text{ and } W_{A,p}(\Gamma) \neq W_p(\Gamma). \] (2.15)

Unlike classical statistical mechanics, for quantum statistical mechanics the phase space weight depends upon the function being averaged. However in the case of pure functions, from the definitions one can show that

if \( \hat{A} = A(\hat{p}) \) then \( W_{A,p}(\Gamma) = W_p(\Gamma) \)

and \( \hat{W}_{A,q}(\Gamma) = W_q(\Gamma). \) (2.16)

And also that

if \( \hat{A} = A(\hat{q}) \) then \( W_{A,q}(\Gamma) = W_q(\Gamma) \)

and \( \hat{W}_{A,p}(\Gamma) = W_p(\Gamma). \) (2.17)

One can see that any linear combination of pure functions of the position and momentum operators has an average that can be arranged as a linear combination of averages with the original commutation function, \( W_p \) or \( W_q \). This is now illustrated explicitly for the energy operator.

### C. Energy

The first expression for the average energy takes \( \hat{A} = \hat{H} \) and \( W_{A,p} \) or \( W_{A,q} \), giving

\[ \langle \hat{H} \rangle_{z,\beta,V}^{\pm} = \frac{1}{z^N} \sum_{N=0}^\infty \frac{z^N}{h^{2N}N!} \int d\Gamma e^{-\beta H(\Gamma)} \mathcal{H}(\Gamma)W_{A,p}(\Gamma)\eta_p^{\pm}(\Gamma) \]

\[ = \frac{1}{z^N} \sum_{N=0}^\infty \frac{z^N}{h^{2N}N!} \int d\Gamma e^{-\beta H(\Gamma)} \mathcal{H}(\Gamma)W_{A,q}(\Gamma)\eta_q^{\pm}(\Gamma). \]

Obviously because the energy operator commutes with the Maxwell-Boltzmann operator, \( W_{A,q} = W_{A,q} \) and \( \hat{W}_{A,p} = W_{A,p} \).

The Hamiltonian is the sum of the kinetic and potential energies, which is indeed a linear combination of pure functions,

\[ \mathcal{H} = K(\hat{p}) + U(\hat{q}). \] (2.19)

Hence one can also write

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

\[ = \frac{1}{z^N} \sum_{N=0}^\infty \frac{z^N}{h^{2N}N!} \int d\Gamma e^{-\beta H(\Gamma)} \left\{ \mathcal{K}(\Gamma)W_p(\Gamma)\eta_p^{\pm}(\Gamma) + U(\Gamma)W_q(\Gamma)\eta_q^{\pm}(\Gamma) \right\} \]

\[ = \frac{1}{z^N} \sum_{N=0}^\infty \frac{z^N}{h^{2N}N!} \int d\Gamma e^{-\beta H(\Gamma)} \mathcal{H}(\Gamma)W_p(\Gamma)\eta_p^{\pm}(\Gamma) \]

\[ = \frac{1}{z^N} \sum_{N=0}^\infty \frac{z^N}{h^{2N}N!} \int d\Gamma e^{-\beta H(\Gamma)} \mathcal{H}(\Gamma)W_q(\Gamma)\eta_q^{\pm}(\Gamma). \]

The penultimate equality follows by taking the complex conjugate of the average potential energy in the second equality. The final equality follows by taking the complex conjugate of the average kinetic energy in the second equality. One sees from these that one can obtain the average energy using the same commutation function as for the partition function.

Differentiating with respect to \( -\beta \) the defining equation for \( W_p \), Eq. (2.10), one obtains

\[ \mathcal{H}(\Gamma)e^{-\beta H(\Gamma)}W_p(\Gamma) - e^{-\beta H(\Gamma)}\frac{\partial W_p(\Gamma)}{\partial \beta} \]
\[ e^{-\beta \mathcal{H}(\Gamma)} \mathcal{H}(\Gamma) W_{\mathcal{H},p}(\Gamma), \quad (2.21) \]

since \( W_{\mathcal{H},p} = W_{\mathcal{H},p} \). Hence \( W_{\mathcal{H},p} = W_{p} - \mathcal{H}^{-1} \partial W_{p}/\partial \beta \).

Inserting the left hand side into Eq. (2.18), and comparing this with Eq. (2.20) one sees that in order for the two expressions for the average energy to be equal one must have

\[ \sum_{N=0}^{\infty} \frac{z^N}{h^{2N} N!} \int d\Gamma e^{-\beta \mathcal{H}(\Gamma)} \frac{\partial W_{\mathcal{H},p}(\Gamma)}{\partial \beta} \eta^\pm_q(\Gamma) = 0. \tag{2.22} \]

An analogous result holds for \( \partial W_q(\Gamma)/\partial \beta \).

1. A Useful Result

I now prove that this vanishes individually for each particle number \( N \) and for each permutation \( \hat{P} \). This turns out to be necessary for thermodynamic consistency, as will be explained below.

With \( |p\rangle = V^{-N/2} e^{-p \cdot r/\hbar} \), one has that \( \hat{\mathcal{H}}|p\rangle = \mathcal{H}(p, r)|p\rangle \).

Also since the permutations are between identical particles, \( \mathcal{H}(p, q) = \mathcal{H}(\hat{P} p, q) = \mathcal{H}(p, \hat{P} q) \), for any permutation \( \hat{P} \). (This assumes that there are no velocity dependent forces, which is the usual case. Lorentz forces need thought.) Hence

\[ \mathcal{H}(p, q)\langle \hat{P} p|q\rangle = \langle \hat{P} p|\hat{\mathcal{H}} q\rangle. \tag{2.23} \]

With this one has

\[ \sum_{N=0}^{\infty} \frac{z^N}{h^{2N} N!} \int d\Gamma e^{-\beta \mathcal{H}(\Gamma)} \frac{\partial W_{\mathcal{H},p}(\Gamma)}{\partial \beta} \eta^\pm_q(\Gamma) \]

\[ = \sum_{N=0}^{\infty} \frac{z^N}{h^{2N} N!} \int d\Gamma e^{-\beta \mathcal{H}(\Gamma)} \eta^\pm_q(\Gamma) \]

\[ \times \{ \mathcal{H}(\Gamma) W_{\mathcal{H},p}(\Gamma) - \mathcal{H}(\Gamma) W_{p}(\Gamma) \} \]

\[ = \sum_{N=0}^{\infty} \frac{z^N V^N}{h^{2N} N!} \sum_{\hat{P}} \langle \hat{P} p|q\rangle \]

\[ \times \{ (q|e^{\beta \hat{\mathcal{H}}}|p) - \mathcal{H}(p, q)|q|e^{\beta \hat{\mathcal{H}}}|p) \} \]

\[ = \sum_{N=0}^{\infty} \frac{z^N V^N}{h^{2N} N!} \sum_{\hat{P}} \langle \hat{P} p|q\rangle \]

\[ \times \{ (q|e^{\beta \hat{\mathcal{H}}}|p) - \mathcal{H}(p, q)|q|e^{\beta \hat{\mathcal{H}}}|p) \} \]

\[ = 0. \tag{2.24} \]

The term in braces vanishes for each \( N \) and for each permutation \( \hat{P} \), as was to be shown. This result will prove important shortly. It also vanishes for each momentum configuration \( p \), which will not be required.

III. LOOP EXPANSION, GRAND POTENTIAL, AND AVERAGE ENERGY

A. Symmetrization Loops

The symmetrization function can be written in terms of loops. Any particular particle permutation operator can be factored into loop permutation operators. A loop is a connected series of pair transpositions. Hence the sum over all permutation operators can be written as the sum over all possible factors of loop permutations,

\[ \sum_{i,j} (\pm 1)^{i-j} \hat{P}_{ij} + \sum_{i,j,k} (\pm 1)^{i-j} \hat{P}_{ij} \hat{P}_{jk} \]

\[ + \sum_{i,j,k,l} (\pm 1)^{i-j} \hat{P}_{ij} \hat{P}_{kl} \ldots \]

(3.1)

Here \( \hat{P}_{jk} \) is the transpose of particles \( j \) and \( k \). The prime on the sums restrict them to unique loops, with each index being different. The first term is just the identity. The second term is a dimer loop, the third term is a trimer loop, and the fourth term shown is the product of two different dimers.

With this, the symmetrization function, \( \eta_q^+(\Gamma) = \sum_p (\pm 1)^p \langle \hat{P} p|q\rangle/\langle p|q\rangle \), is the sum of the expectation values of these loops. The monomer symmetrization function is obviously unity, \( \eta_q^{(1)} \equiv \langle p|q\rangle/\langle p|q\rangle = 1 \).

The dimer symmetrization factor in the microstate \( \Gamma \) for particles \( j \) and \( k \) is

\[ \eta_q^{(2)} = \pm \langle \hat{P}_{jk} p|q\rangle/\langle p|q\rangle \]

\[ = \pm \langle p_k|q_j\rangle/\langle p_j|q_k\rangle \]

\[ = \pm e^{(q_k-q_j)/\hbar} e^{(q_j-q_k)/\hbar}/\langle p_j|q_k\rangle \]

(3.2)

Recall that \( |p\rangle \equiv e^{-p \cdot r/\hbar}/V^{N/2} \). Note that since the basis functions are the product of single particle functions, the expectation value factorizes leaving only the permuted particles to contribute.

Similarly the trimer symmetrization factor for particles \( j, k, \) and \( l \) is

\[ \eta_q^{(3)} = \pm \langle \hat{P}_{jk} \hat{P}_{kl} p|q\rangle/\langle p|q\rangle \]

\[ = \pm \langle p_k|q_j\rangle/p_j|q_k\rangle \]

\[ = \pm \langle p_l|q_j\rangle/p_j|q_l\rangle \]

\[ = e^{(q_j-q_k)/\hbar} e^{(q_k-q_j)/\hbar}/\langle p_j|q_k\rangle \]

(3.3)

In general the \( l \)-loop symmetrization factor is

\[ \eta_q^{(l)} = (\pm 1)^{l-i} e^{(q_j-q_k)/\hbar} p_j|q_l\rangle/\langle p_k|q_j\rangle \]

(3.4)

where \( q_{jk} \equiv q_j - q_k \). Recall that \( \eta_p = \eta_q^{*} \).
The product of Fourier exponentials that occurs here makes each specific \( l \)-loop symmetrization factor highly oscillatory unless successive particles around the loop are close together in both momentum and position space. This means that the only non-zero contributions to phase space integrals come from such compact loops, since otherwise their oscillations would average to zero. (See Eq. (3.12) below for an explicit example.)

With these symmetrization factors, the symmetrization function can be written as a series of loop products,

\[
\eta^\pm_q(\Gamma) = 1 + \sum_{ij} \eta^{\pm(2)}_{q;ij} + \sum_{ijk} \eta^{\pm(3)}_{q;ijk} + \sum_{ijkl} \eta^{\pm(4)}_{q;ijkl} + \cdots
\]

Here the superscript is the order of the loop, and the subscripts are the atoms involved in the loop. The prime signifies that the sum is over unique loops (i.e., each configuration of particles in loops occurs once only) with each index different (i.e., no particle may belong to more than one loop).

In this one can identify the terms with only a single loop, and define the single loop symmetrization function,

\[
\eta^\pm_q(\Gamma) = \sum_j \eta^{\pm(2)}_{q;jk} + \sum_{jkm} \eta^{\pm(3)}_{q;jkm} + \sum_{jkmn} \eta^{\pm(4)}_{q;jkmn} + \cdots
\]

This gives the single \( l \)-loop symmetrization function \( \eta^\pm_q(\Gamma) \) as the sum over the \( N!/(N-l)!l \) distinct arrangements of the \( l \) particle labels. In taking the average of each single loop symmetrization function, since the particles are identical, all the terms in the sum over particles gives the same average value. Therefore, what will be shown next to be the loop grand potential can be obtained by evaluating any one arrangement, say particles \( 1, 2, \ldots, l \),

\[
-\beta \Omega^\pm_q(W_p^\pm) = \left\langle \eta^\pm_q(\Gamma) \right\rangle_{W_p^\pm} = \left\langle \sum_{j_1 \ldots j_l} \eta^\pm_q(j_1 \ldots j_l) \right\rangle_{W_p^\pm} = \frac{N!}{(N-l)!l} \left\langle \eta^\pm_q(\Gamma) \right\rangle_{W_p^\pm}.
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\]

\[
\Xi_{W_p^\pm,1} = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int dp dq e^{-\beta H(p,q)} W_p(p, q). \tag{3.8}
\]

Recall that the imaginary part of \( W_p \) is odd in momentum, and that \( W_p^p = W_q \), and so the subscript \( p \) or \( q \) (and also the superscript \( \pm \)) is redundant in the monomer case. Nevertheless it seems best to signify explicitly which of these commutation function is being used.

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

\[
\frac{\Xi_{W_p^\pm}}{\Xi_{W_p^\pm,1}} = \left\langle \eta^\pm_q \right\rangle_{W_p^\pm,1} = \left\langle \eta^\pm_q \right\rangle_{W_p^\pm,1} = 1 + \sum_{ij} \eta^{\pm(2)}_{q;ij} + \sum_{ijk} \eta^{\pm(3)}_{q;ijk} + \sum_{ijkl} \eta^{\pm(4)}_{q;ijkl} + \cdots
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\]

The third and following equalities write the average of the product as the product of the averages. This is valid
in the thermodynamic limit, since the product of the average of two loops scales as \( V^2 \), whereas the correlated interaction of two loops scales as \( V \), and similarly for all the other products. As mentioned above, only compact loops contribute to the integral; see also \( \text{III.B} \) below. The combinatorial factor accounts for the number of unique loops in each term.

The grand potential is the logarithm of the partition function \( \Omega^\pm = -k_B T \ln \Xi^\pm \). The monomer grand potential is given by \(-\beta \Omega^\pm_{W_p,1} = \ln \Xi^\pm_{W_p,1}\). For the monomer term the superscript \( \pm \) is redundant and will usually be dropped.

The difference between the full grand potential and the monomer grand potential is just the series of loop grand potentials,

\[
-\beta [\Omega^\pm_{W_p} - \Omega^\pm_{W_p,1}] = \ln \Xi^\pm_{W_p,1} = \sum_{l=2}^{\infty} \left\langle \frac{N!}{(N-l)!} \eta_{q_1 \ldots q_l}^{\pm(l)} \right\rangle W_p,1 = -\beta \sum_{l=2}^{\infty} \Omega^\pm_{W_p}(l). \tag{3.10}
\]

Here \( \eta_q \) is paired with \( W_p \); one could alternatively pair \( \eta_p \) and \( W_q \). Since these give the same, real, value for the grand potential, it is redundant and somewhat pedantic to attach the \( W_p \) subscript.

### 1. Excess Dimer Correlation

Above, the product of two dimers was written as

\[
\left\langle \sum_{jk} \eta_{q_3 q_4}^{\pm(2)} \eta_{q_5 q_6}^{\pm(2)} \right\rangle_{W_p,1} = \frac{1}{2} \left\langle \frac{N!}{(N-2)!} \eta_{q_3 q_4}^{\pm(2)} \right\rangle_{W_p,1}^2. \tag{3.11}
\]

The prime indicates that each configuration of loops occurs only once, and that no two indices are equal.

With \( \eta_{q;3;4}^{\pm(2)} = e^{-\beta \mu_q \cdot \rho_{q;3;4}/ \hbar} \), in the case of a classical average (ie. \( \langle \ldots \rangle_{1,1} \)), one can perform the momentum integrals by completing the square,

\[
\left\langle \eta_{q;3;4}^{\pm(2)} \right\rangle_{1,1} = \pm \frac{Z^{-1}}{h^{3N} N!} \int \mathcal{D} \Gamma e^{-\beta \mathcal{H}(\Gamma)} e^{-\beta \mu_q \cdot \rho_{q;3;4}/ \hbar} = \pm \frac{Z^{-1}}{V^{N} N!} \int dq \, e^{-\beta U(q)} e^{-\beta \mu_q \cdot \rho_{q;3;4}/ \hbar} = \pm \frac{Z^{-1}}{V^{N} N!} \int dq \, e^{-\beta U(q)} e^{-\beta \mu_q \cdot \rho_{q;3;4}/ \hbar} = \pm \frac{Z^{-1}}{V^{N} N!} \int dq \, e^{-\beta U(q)} e^{-\beta \mu_q \cdot \rho_{q;3;4}/ \hbar}, \tag{3.12}
\]

where the thermal wavelength is \( \Lambda = \sqrt{2\pi \hbar^2 / \beta m} \). The integrand is zero except for separations less than the thermal wavelength, \( q_{ij} \ll \Lambda \). This means that effectively particle \( j \) is tied to particle \( k \), which means that a volume integral is lost, so that \( \left\langle \eta_{q;3;4}^{\pm(2)} \right\rangle_{1,1} \sim \mathcal{O}(V^{-1}) \).

It is clear from this that \( \langle \sum_{jk} \eta_{q;3;4}^{\pm(2)} \eta_{q;5;6}^{\pm(2)} \rangle_{W_p,1} \) involves an integral over position space of the two particle density \( \rho^{(2)} \). Recall that in classical statistical mechanics, \( \rho^{(2)} \) at large separations goes asymptotically as the square of the singlet densities. Similarly, \( \langle \sum_{jk} \eta_{q;3;4}^{\pm(2)} \eta_{q;5;6}^{\pm(2)} \rangle_{W_p,1} \) involves an integral of the four particle density \( \rho^{(4)} \), which for large separations between the pairs goes like \( \rho^{(4)} \sim \rho^{(2)} \). Hence in the thermodynamic limit, the relative error in the factorization of the dimer product vanishes

\[
\frac{1}{2} \left\langle \sum_{jk} \eta_{q;3;4}^{\pm(2)} \eta_{q;5;6}^{\pm(2)} \right\rangle_{W_p,1}^2 \rightarrow 0 \quad \text{as} \quad z, \ T = \text{const.}, \ V \rightarrow \infty. \tag{3.13}
\]

The denominator goes like \( \mathcal{O}(V^{-2}) \). The numerator goes like \( \mathcal{O}(V^{-3}) \), because three volume integrals are lost when all four particles are correlated, which is required for the difference to be non-zero. An analogous argument holds for the arbitrary product of arbitrary loops. This justifies the factorization of the symmetrization function in the thermodynamic limit.

### C. Energy

The most likely energy can be written as the temperature derivative of the grand potential. As above the latter can be written as a series of loop derivatives. One has

\[
E_{W_p} = \frac{\partial \beta \Omega_{W_p}}{\partial \beta} = \sum_{l=1}^{\infty} E_{W_p,l}. \tag{3.14}
\]

The monomer term is

\[
E_{W_p,1} = \frac{\partial \beta \Omega_{W_p,1}}{\partial \beta} = -\frac{\partial \ln \Xi_{W_p,1}}{\partial \beta} = \frac{1}{\Xi_{W_p,1}} \sum_{N=0}^{\infty} \frac{z^N}{h^{3N} N!} \int d\Gamma \, e^{-\beta \mathcal{H}(\Gamma)} \left\{ \mathcal{H}(\Gamma) W_p(\Gamma) - \frac{\partial W_p(\Gamma)}{\partial \beta} \right\} = \langle \mathcal{H} \rangle_{W_p,1} = \langle \mathcal{H} \rangle_{W_{\mathcal{H},p,1}}. \tag{3.15}
\]

In and about Eq. (2.21) above, it was shown that \( W_{\mathcal{H},p} = W_p - \mathcal{H}^{-1} \partial W_p/\partial \beta \). It was also shown in Eq. (2.21) that the integral of the second part must vanish for each \( N \) and for each permutation \( \mathcal{P} \). One can therefore interchange \( W_{\mathcal{H},p} \) and \( W_p \) in the present monomer integrals, including \( \Xi_{W_p,1} = \Xi_{W_{\mathcal{H},p,1}} \). This says that
\[ \overline{E}_{W_p,1} = \overline{E}_{W_{N,p},1}, \text{ so that the commutation function in the subscript is redundant.} \]

For the loops \( l \geq 2 \) one has

\[ \overline{E}_{W_p,l} = \frac{\partial \beta \Omega^{+\downarrow(l)}_{W_p}}{\partial \beta} \]

\[ = -\frac{\partial}{\partial \beta} \left\langle \frac{N!}{(N-l)!} \eta_{q_{l+1}}^{(l)} \right\rangle_{W_p,1} \]

\[ = -\beta \Omega^{+\downarrow(l)}_{W_p} \frac{1}{\Xi_{W_p,1}} \frac{\partial \Xi_{W_p,1}}{\partial \beta} \]

\[ + \frac{1}{\Xi_{W_p,1}} \sum_{N=1}^{\infty} \frac{z^{N} h^{-dN}}{(N-l)!} \int d\Gamma \ e^{-\beta \mathcal{H}(\Gamma)} \]

\[ \times \left\{ \mathcal{H}(\Gamma) W_p(\Gamma) - \frac{\partial W_p(\Gamma)}{\partial \beta} \right\} \eta_{q_{l+1}}^{(l)} \]

\[ = \beta \Omega^{+\downarrow(l)}_{W_p} \overline{E}_{W_p,1} + \left\langle \mathcal{H} \eta_{q}^{(l)} \right\rangle_{W_p,1} \]

\[ = \beta \Omega^{+\downarrow(l)}_{W_p} \overline{E}_{W_{N,p},1} + \left\langle \mathcal{H} \eta_{q}^{(l)} \right\rangle_{W_{N,p,1}}. \tag{3.16} \]

Recall that \( \eta_{q}^{(l)}(\Gamma) = \sum_{j_1 \ldots j_l} \eta_{q_{j_{l+1}} \ldots j_l}^{(l)} \). Again, Eq. (2.24) has been applied here, showing that one can equally use \( W_{N,p} \) or \( W_p \). This expression has the form of the average of a fluctuation,

\[ \overline{E}_{W_p,l} = \left\langle \left[ \mathcal{H} - \mathcal{E}_{W_p,1} \right] \left[ \eta_{q}^{\downarrow(l)} - \langle \eta_{q}^{\downarrow(l)} \rangle_{W_p,1} \right] \right\rangle_{W_p,1}, \tag{3.17} \]

where \( l \geq 2 \), and where either commutation function may be used. This result will be derived by a different route in \( \text{[V]} \) below.

1. Heat Capacity

The heat capacity at constant volume and fugacity is

\[ C_V = \frac{\partial \overline{E}_1}{\partial T} \]

\[ = -k_B \beta^2 \frac{\partial \overline{E}_1}{\partial \beta} \]

\[ = -k_B \beta^2 \sum_{l=1}^{\infty} \frac{\partial \overline{E}_1}{\partial \beta}. \tag{3.18} \]

The monomer contribution comes from \( (W_p \text{ is not constant}) \)

\[ \overline{E}_1 = \frac{\partial}{\partial \beta} \frac{1}{\Xi(W_p,1)} \sum_{N=0}^{\infty} \frac{z^N h^{-dN} N!}{N!} \int d\Gamma \ e^{-\beta \mathcal{H}(\Gamma)} \]

\[ \times \mathcal{H}(\Gamma) W_p(\Gamma) \]

\[ = \left\langle \mathcal{H} - \frac{\partial \ln W_p}{\partial \beta} \right\rangle_{W_p,1} \]

\[ - \left\langle \mathcal{H}^2 - \mathcal{H} \frac{\partial \ln W_p}{\partial \beta} \right\rangle_{W_p,1}. \tag{3.19} \]

The loop contribution \( l \geq 2 \) comes from the derivative of Eq. (3.16), with \( W_{N,p} \Rightarrow W_p \),

\[ \frac{\partial \overline{E}_l}{\partial \beta} = \frac{\partial}{\partial \beta} \left\{ \beta \Omega_l \overline{E}_1 + \frac{1}{\Xi_{l+1}} \sum_{N=0}^{\infty} \frac{z^N h^{-dN} N!}{N!} \int d\Gamma \ e^{-\beta \mathcal{H}(\Gamma)} \right\} \]

\[ \times \mathcal{E}_1 \overline{E}_{l+1} + \beta \Omega_l \frac{\partial \overline{E}_1}{\partial \beta} + \overline{E}_1 \left[ \mathcal{E}_1 - \beta \Omega_l \overline{E}_1 \right] \]

\[ - \left\langle \mathcal{H}^2 - \mathcal{H} \frac{\partial \ln W_p}{\partial \beta} \right\rangle_{W_p,0} \eta_{q_l}^{(l)}. \tag{3.20} \]

IV. MULTI-PARTICLE DENSITY

Consider a position configuration of \( n \) particles, \( Q^n = \{ Q_1, Q_2, \ldots, Q_n \} \). The distinct \( n \)-particle density quantum operator for this is

\[ \hat{\rho}^{(n)}(Q^n; q) = \sum_{k_1, \ldots, k_n} \prod_{j=1}^{n} \delta(Q_j - r_{k_j}). \tag{4.1} \]

The sum is over the particle indexes, and the double prime indicates that in any term no two indexes are equal. If there are \( N \) particles in the system, there are \( N!/(N-n)! \) terms in the sum. This says any particle is at \( Q_1 \), any different particle is at \( Q_2 \) etc. The density operator is evidently unchanged by a permutation of the \( Q_j \) or of the particle labels.

Since this is only a function of the position operator, the commutation function \( W_q \) or \( W_p \) may be used for its average. The average \( n \)-particle density is

\[ \rho_{W_p}^{(n)}(Q^n) \]

\[ = \langle \hat{\rho}^{(n)}(Q^n; q) \rangle_{W_p, \eta_{q}^{\pm}} \]

\[ = \frac{1}{\Xi_{W_p, \eta_{q}^{\pm}}} \sum_{N=0}^{\infty} \frac{z^N h^{-dN} N!}{N!} \int d\Gamma \ e^{-\beta \mathcal{H}(\Gamma)} W_p(\Gamma) \eta_{q}^{\pm}(\Gamma) \]

\[ \times \sum_{k_1, \ldots, k_n} \prod_{j=1}^{n} \delta(Q_j - q_{k_j}). \tag{4.2} \]

It is worth including the subscript \( W_p \) on the density because there may be occasion when one requires a density defined with respect to a commutation function that is specific for a particular quantity that is to be averaged. The subscript on the average, \( W_p, \eta_{q}^{\pm} \), could be replaced by, or augmented with, the subscript \( z, V, T \).

It is worth mentioning that one does not actually have to define the quantum operator density, \( \hat{\rho}^{(n)}(Q^n; q) \), but that instead one can introduce the phase function
\[ \rho^{(n)}_W(Q^n) \] directly via the phase space integral. More generally one can define the \( n \)-particle density for positions and momenta in phase space as

\[ \rho^{(n)}(\gamma^n; \Gamma) = \sum_{k_1, \ldots, k_n}^N \prod_{j=1}^n \delta(\gamma_j - \Gamma_{kj}), \quad (4.3) \]

and its average as

\[ \rho^{(n)}_{W_p}(\gamma^n) \]

\[ = \frac{1}{\Xi_{W_p}^n} \sum_{N=0}^{\infty} \frac{z^N}{N^N} \int \mathcal{D} \Gamma e^{-\beta H(\Gamma)} W_p(\Gamma) \eta^+_{q}(\Gamma) \]

\[ \times \sum_{k_1, \ldots, k_n}^N \prod_{j=1}^n \delta(\gamma_j - \Gamma_{kj}). \quad (4.4) \]

I shall use this below for the average energy.

The \( n \)-particle density for positions is evidently normalized as

\[ \int dQ^n \rho^{(n)}_{W_p}(Q^n) = \left\langle \frac{N!}{(N-n)!} \right\rangle_{z,V,T}, \quad (4.5) \]

which is in agreement with the classical convention. One also has the reduction condition

\[ \int dQ^n \rho^{(n)}_{W_p}(Q^n) \]

\[ = \left\langle \frac{N!}{(N-n)!} \right\rangle_{z,V,T} \left\langle \frac{N!}{(N-n+1)!} \right\rangle_{z,V,T} \rho^{(n-1)}_{W_p}(Q^{n-1}) \]

\[ \approx \langle N - n + 1 \rangle \rho^{(n-1)}_{W_p}(Q^{n-1}). \quad (4.6) \]

This \( n \)-particle density can be used for the average of any operator that is a function of the position operator. For example, suppose that the potential energy is the sum of pair potentials,

\[ U(q) = \frac{1}{2} \sum_{j,k} u(q_j, q_k) = \sum_{j,k} u(q_j, q_k). \quad (4.7) \]

The double prime again indicates that \( j \neq k \), and the single prime indicates that the sum is over unique pairs, \( j < k \). The average potential energy in this case is

\[ \left\langle \hat{U} \right\rangle_{z,V,T} = \frac{1}{2} \int dQ_1 dQ_2 \rho^{(2)}_{W_p}(Q_1, Q_2) u(Q_1, Q_2), \quad (4.8) \]

as can be confirmed by substituting in the definition of the pair density and interchanging the order of integrations. The factor of one half again corrects for double counting of each particle pair.

Define the density fluctuation

\[ \Delta \hat{\rho}^{(n)}(Q^n; q) \equiv \hat{\rho}^{(n)}(Q^n; q) - \langle \hat{\rho}^{(n)}(Q^n; q) \rangle_{W_p,1} \]

\[ \equiv \hat{\rho}^{(n)}(Q^n; q) - \rho^{(n)}_{W_p,1}(Q^n), \quad (4.9) \]

and similarly for the symmetrization function. With these the average density may be written

\[ \rho^{(n)}_{W_p}(Q^n) \equiv \left\langle \hat{\rho}^{(n)}(Q^n; q) \right\rangle_{W_p,1} \]

\[ = \frac{\Xi_{W_p,1}}{\Xi_{W_p,1}^n} \left\langle \hat{\rho}^{(n)}(Q^n; q) \right\rangle_{W_p,1} \]

\[ = \left\langle \eta^+_{q}(\Gamma) \right\rangle_{W_p,1}^{-1} \left\{ \left\langle \hat{\rho}^{(n)}(Q^n; q) \right\rangle_{W_p,1} \left( \eta^+_{q}(\Gamma) \right)_{W_p,1} \right\} \]

\[ - \left\langle \Delta \hat{\rho}^{(n)}(Q^n; q) \Delta \eta^+_{q}(\Gamma) \right\rangle_{W_p,1}. \quad (4.10) \]

This holds in the thermodynamic limit, \( V \to \infty \), \( z,T = \text{const.} \). Recall that \( \eta^+_{q} \), is the series of single loop symmetrization functions defined in Eq. (3.6). From Eq. (3.10), the prefactor in the second equality is \( \Xi_{W_p,1} / \Xi_{W_p,1}^n = \left\langle \eta^+_{q}(\Gamma) \right\rangle_{W_p,1} = e^{-\langle \eta^+_{q}(\Gamma) \rangle_{W_p,1}} \). Also, since \( \langle \Delta \hat{\rho}^{(n)}(Q^n) \rangle_{W_p,1} = 0 \), one can write successively

\[ \langle \Delta \hat{\rho}^{(n)}(Q^n) \rangle_{W_p,1} = \langle \Delta \hat{\rho}^{(n)}(\eta^+_{q}) \rangle_{W_p,1} \]

\[ = \langle \Delta \hat{\rho}^{(n)}(\eta^+_{q}) \rangle_{W_p,1} e^{\langle \eta^+_{q} \rangle_{W_p,1}} \]

\[ = \langle \Delta \hat{\rho}^{(n)}(\Delta \eta^+_{q}) \rangle_{W_p,1} e^{\langle \eta^+_{q} \rangle_{W_p,1}}. \quad (4.11) \]

The final equality in Eq. (4.11) is justified by the passage from the second to the third equality here. The average of the density fluctuation without loops vanishes, \( \langle \Delta \hat{\rho}^{(n)}(Q^n) \rangle_{W_p,1} = 0 \). Hence the only configurations that contribute to the average in the second equality in Eq. (4.11) are those with at least one loop in the vicinity of \( Q^n \). This means that in any product of loops in the symmetrization function \( \eta^+_{q}(\Gamma) \), one loop must be tied to \( Q^n \), and the rest are free to wander throughout the volume. Hence just as in the factorization of the grand partition function in the average of the density fluctuation times such a product can be written as the product of the average of the density fluctuation times the tied loop, times the product of the averages of each of the free loops. The symmetry number reflects the number and type of the free loops, because these are equivalent and distinct from the tied loop. Hence just as in they sum to the exponential, \( e^{\langle \eta^+_{q} \rangle_{W_p,1}} \), which gives the third equality in Eq. (4.11). The final equality in that equation, combined with the prefactor \( \langle \eta^+_{q}(\Gamma) \rangle_{W_p,1} = e^{-\langle \eta^+_{q}(\Gamma) \rangle_{W_p,1}} \) from the penultimate equality in Eq. (4.10), gives the final equality in Eq. (4.11).

The result Eq. (4.11) for the multi-particle position density holds analogously for the multi-particle phase density, Eq. (4.3). It follows that the average of any phase function can be written in terms that involve only the single loop symmetrization function, as is now shown for the energy.
I. Average Energy Factorized

Suppose that the Hamiltonian consists of many-body potentials \( \mathcal{H}(\Gamma) = \sum_n \mathcal{H}^{(n)}(\Gamma) \), with

\[
\mathcal{H}^{(n)}(\Gamma) = \frac{1}{n!} \sum_{k_1, \ldots, k_n} \mathcal{H}^{(n)}(\Gamma_{k_1}, \ldots, \Gamma_{k_n}).
\] (4.12)

The kinetic energy is included in the one-body term.

In terms of the position and momentum \( n \)-body density, Eq. [4.3], the average Hamiltonian energy may be written

\[
\langle \hat{\mathcal{H}} \rangle_{z,V,T} = \sum_n \frac{1}{n!} \int d\gamma^n \rho^{(n)}(\gamma^n) \mathcal{H}^{(n)}(\gamma^n)
\]

\[= \sum_n \frac{1}{n!} \int d\gamma^n \mathcal{H}^{(n)}(\gamma^n)
\]

\[\times \left\{ \rho^{(n)}_{W_p}(\gamma^n) + \left[ \Delta \rho^{(n)}(\gamma^n; \Gamma) \Delta \eta^\pm_q(\Gamma) \right]_{W_p,1} \right\}
\]

\[= \langle \mathcal{H}(\Gamma) \rangle_{W_p,1} + \langle \Delta \mathcal{H}(\Gamma) \Delta \eta^\pm_q(\Gamma) \rangle_{W_p,1}
\]

\[= \langle \mathcal{H}(\Gamma) \rangle_{W_p,1} + \sum_{l=2}^\infty \langle \Delta \mathcal{H}(\Gamma) \Delta \eta^\pm_q(l) \rangle_{W_p,1}.
\] (4.13)

This agrees with the expression obtained from the temperature derivative of the grand potential, \( \mathcal{H} \), where the loop contributions were given by Eq. (3.17).

\[
\mathcal{E}_{W_p,1} = \left\langle \left[ \mathcal{H} - \mathcal{E}_{W_p,1} \right] \left[ \eta^\pm_q(l) - \langle \eta^\pm_q(l) \rangle_{W_p,1} \right] \right\rangle_{W_p,1},
\] (4.14)

for \( l \geq 2 \).

V. VIRIAL PRESSURE

The thermodynamic pressure is the volume derivative of the grand potential \( \mathcal{H} \),

\[
\mathcal{P}^\pm = -\frac{\partial \Omega^\pm}{\partial V} = \sum_{l=1}^\infty -\frac{\partial \Omega^\pm_l}{\partial V}.
\] (5.1)

Perform the usual trick of scaling the position and momentum coordinates by the edge length \( L \), \( \mathbf{q}' = \mathbf{q}/L \), so that \( d\mathbf{q} = \mathbf{q}L^{-1} dL \). Recalling that the spacing between momentum states is \( \Delta_p = 2\pi\hbar/L \), and so \( dp = -pL^{-1} dL \). These give the change in a phase function as

\[
df(\Gamma) = \nabla_p f \cdot dp + \nabla_q f \cdot dq
\]

\[= \left\{ \mathbf{q} \cdot \nabla_q f - \mathbf{p} \cdot \nabla_p f \right\} L^{-1} dL.
\] (5.2)

In terms of the partition function, the pressure is

\[
\beta \mathcal{P}^\pm = \frac{\partial \ln \Xi^\pm}{\partial V}
\]

\[= \frac{L}{dV} \sum_{N=0}^\infty \frac{z^N}{h^{2N} N!} \int d\Gamma \times \frac{d}{dL} \left\{ e^{-\beta \mathcal{H}(\Gamma)} W_p(\Gamma) \eta^\pm_q(\Gamma) \right\}.
\] (5.3)

One has

\[
\frac{dV N^2 (\mathcal{P} p | q)}{dL} = \frac{d}{dL} \left\langle e^{(\mathcal{P} p) q / i\hbar} \right\rangle
\]

\[= \frac{1}{i\hbar} \left\{ \mathbf{q} \cdot (\mathcal{P} \mathbf{p}) - (\mathcal{P} \mathbf{p}) \cdot \mathbf{q} \right\} e^{(\mathcal{P} \mathbf{p}) q / i\hbar} = 0.
\] (5.4)

It follows that \( d\eta^\pm_q(\Gamma)/dL = 0 \), and that therefore

\[
L \frac{d}{dL} \left\{ e^{-\beta \mathcal{H}(\Gamma)} W_p(\Gamma) \eta^\pm_q(\Gamma) \right\}
\]

\[= \eta^\pm_q(\Gamma) \left\{ \mathbf{q} \cdot \nabla_q - \mathbf{p} \cdot \nabla_p \right\} \left\{ e^{-\beta \mathcal{H}(\Gamma)} W_p(\Gamma) \right\}.
\] (5.5)

The commutation function is given by

\[
e^{-\beta \mathcal{H}(\Gamma)} W_p(\Gamma) = \left\langle \frac{\mathbf{q} e^{-\beta \mathcal{H}} | \mathbf{p} \rangle}{\langle \mathbf{q} | \mathbf{p} \rangle} \right\rangle
\]

\[= e^{p q / i\hbar} \int dr \delta(r - \mathbf{q}) e^{-\beta \mathcal{H}(r)} e^{-\mathbf{p} \cdot r / i\hbar}.
\] (5.6)

The prefactor is a constant with respect to \( L \), and so one has

\[
L \frac{d}{dL} e^{-\beta \mathcal{H}(\Gamma)} W_p(\Gamma)
\]

\[= \mathbf{q} \cdot \nabla_q \left\{ e^{-\beta \mathcal{H}(\Gamma)} W_p(\Gamma) \right\} - \mathbf{p} \cdot \nabla_p \left\{ e^{-\beta \mathcal{H}(\Gamma)} W_p(\Gamma) \right\}
\]

\[= e^{p q / i\hbar} \int dr \left\{ \mathbf{q} \cdot \delta(r - \mathbf{q}) e^{-\beta \mathcal{H}(r)} e^{-\mathbf{p} \cdot r / i\hbar}
\]

\[+ (i\hbar)^{-1} \delta(r - \mathbf{q}) e^{-\beta \mathcal{H}(r)} e^{-\mathbf{p} \cdot r / i\hbar} \mathbf{p} \cdot \mathbf{r} \right\}
\]

\[= -e^{p q / i\hbar} \int dr \left\{ \delta(r - \mathbf{q}) \mathbf{q} \cdot \nabla_r \left[ e^{-\beta \mathcal{H}(r)} e^{-\mathbf{p} \cdot r / i\hbar} \right]
\]

\[= -(i\hbar)^{-1} \delta(r - \mathbf{q}) e^{-\beta \mathcal{H}(r)} e^{-\mathbf{p} \cdot r / i\hbar} \mathbf{p} \cdot \mathbf{r} \right\}
\]

\[= \left\langle \frac{\mathbf{q} e^{-\beta \mathcal{H}} \mathbf{p} \cdot \mathbf{r} | \mathbf{p} \rangle}{\langle \mathbf{q} | \mathbf{p} \rangle} \right\rangle
\]

\[= e^{-\beta \mathcal{H}(\Gamma)} W_p(\Gamma) \mathcal{V}_p(\Gamma).
\] (5.7)

The final equality defines what might be called the quantum phase space virial. Note that the \( \mathbf{p} \) that appears explicitly in the middle of the first term to the right of the penultimate equality is the momentum variable, not the momentum operator, and that the gradient operator \( \nabla_r \) that appears explicitly in the second term acts on everything to its right.

With this the pressure is given by

\[
dV \beta \mathcal{P}^\pm = \frac{1}{\Xi^\pm} \sum_{N=0}^\infty \frac{z^N}{h^{2N} N!} \int d\Gamma \times e^{-\beta \mathcal{H}(\Gamma)} W_p(\Gamma) \mathcal{V}_p(\Gamma) \eta^\pm_q(\Gamma).
\] (5.8)
or, equivalently,
\[ dV \beta p^\pm = \langle V_p(\Gamma) \rangle_{W_{p,1}} + \langle \Delta V_p(\Gamma) \Delta \eta^\pm_q(\Gamma) \rangle_{W_{p,1}} \tag{5.9} \]
\[ = \langle V_p(\Gamma) \rangle_{W_{p,1}} + \sum_{l=2}^\infty \langle \Delta V_p(\Gamma) \Delta \eta^\pm_{l(q)}(\Gamma) \rangle_{W_{p,1}}. \]

In practice possibly the simplest way to obtain the quantum phase space virial will turn out to be from the right hand side of the first equality,
\[ e^{-\beta H(\Gamma)} W_p(\Gamma) \langle V_p(\Gamma) \rangle = q \cdot \nabla_q \left\{ e^{-\beta H(\Gamma)} W_p(\Gamma) \right\} - p \cdot \nabla_p \left\{ e^{-\beta H(\Gamma)} W_p(\Gamma) \right\} \]
\[ = -\beta W_p(\Gamma) e^{-\beta H(\Gamma)} \left\{ q \cdot \nabla_q U(q) - p \cdot \nabla_p K(p) \right\} + e^{-\beta H(\Gamma)} \left\{ q \cdot \nabla_q W_p(\Gamma) - p \cdot \nabla_p W_p(\Gamma) \right\}. \tag{5.10} \]

This is useful when the ‘bare’ commutation function \( W_p \) can be otherwise obtained and differentiated.

In the classical limit of the present expression, \( W_p(\Gamma) = 1 \), and assuming only an internal potential, this reduces to
\[ e^{-\beta H(\Gamma)} \langle V_q^\pm(\Gamma) \rangle = \left\{ q \cdot \nabla_q e^{-\beta H(\Gamma)} - p \cdot \nabla_p e^{-\beta H(\Gamma)} \right\} e^{-\beta H(\Gamma)} \]
\[ = \left\{ -\beta q \cdot \nabla_q U^\text{int}(q) + \frac{\beta p^2}{m} \right\} e^{-\beta H(\Gamma)} \]
\[ = \left\{ \beta V_q^\text{cl,int}(q) + \frac{\beta p^2}{m} \right\} e^{-\beta H(\Gamma)}. \tag{5.11} \]

Therefore, in the classical limit \( W_p(\Gamma) = \eta^\pm_q = 1 \), the pressure is given by
\[ \beta p^\pm = \frac{1}{dV} \sum_{N=0}^\infty \frac{z^N}{h^{2N} N!} \int d\Gamma e^{-\beta H(\Gamma)} \langle V_p^\pm(\Gamma) \rangle \]
\[ = \frac{1}{dV} \left\langle \beta V_q^\text{cl,int}(q) + \frac{\beta p^2}{m} \right\rangle_{z,T}. \tag{5.12} \]

This agrees with the known classical expression for the virial pressure.\(^{10,14}\)

\section{VI. CONCLUSION}

This paper has formulated quantum statistical mechanics as an integral over classical phase space. Two quantum phase functions appeared: the commutation function, which accounted for the non-commutativity and lack of simultaneity of the position and momentum operators, and the symmetrization function, which accounted for the full symmetrization of the wave function and the consequent statistics of bosons and fermions.

In general a specific commutation function was required for each operator being averaged. However in some circumstances this could be replaced by the ‘bare’ commutation function from the grand partition function.

It was also shown that in the thermodynamic limit, \( V \to \infty, z, T = \text{const.} \), the symmetrization function involved in the partition function and the statistical averages could be factored and exponentially re-summed. This is extremely convenient computationally and analytically. The factorization and resummation was shown to be rather general, since it held for multi-particle phase space densities.\(^{11,12}\)

Eight distinct expressions for the average energy were discussed that depended on three binary choices: either \( W_p \eta^\pm_q \) or \( W_q \eta^\pm_p \), either \( W_q \) or \( W_p \), and either the trace form for a statistical average, Eqs (2.18) and (2.20), or else the derivative of the grand potential with factorization ansatz, Eqs (3.15) and (3.17). The analysis in \( \S IV \) showed the consistency of the first two binary choices, and that in \( \S IV \) showed the consistency of the latter choice.

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