Finite Temperature Path Integral Method for Fermions and Bosons: a Grand Canonical Approach

M. Skorobogatiy, J. Joannopoulos

Department of Physics, MIT, Cambridge, USA

(March 24, 2022)

Abstract

The calculation of the density matrix for fermions and bosons in the Grand Canonical Ensemble allows an efficient way for the inclusion of fermionic and bosonic statistics at all temperatures. It is shown that in a Path Integral Formulation fermionic density matrix can be expressed via an integration over a novel representation of the universal temperature dependent functional. While several representations for the universal functional have already been developed, they are usually presented in a form inconvenient for computer calculations. In this work we discuss a new representation for the universal functional in terms of Hankel functions which is advantageous for computational applications. Temperature scaling for the universal functional and its derivatives are also introduced thus allowing an efficient rescaling rather than recalculation of the functional at different temperatures. A simple illustration of the method of calculation of density profiles in Grand Canonical ensemble is presented using a system of noninteracting electrons in a finite confining potential.
I. INTRODUCTION

The standard treatment of fermionic and bosonic systems in canonical ensemble using Path Integral Formalism is based on the isomorphism between a system of interacting quantum particles and a set of interacting classical polymer rings [1]. For a system of bosons all the ring contributions to the density matrix come with the same sign thus allowing an effective Monte-Carlo sampling of the relevant terms [2]. However, for the case of fermions situation is more complicated as different ring contributions to the density matrix come with alternating signs thus making statistical fluctuations so big that an unreasonably long averages are required to provide for the meaningful results. While several promising attempts were made to circumvent the sign problem [3,4] there is still much to be done before this problem will be solved.

However, instead of operating in a canonical ensemble for fermionic and bosonic systems it might be more advantageous to work in the Grand Canonical Ensemble. To see why, as soon as one knows the normal excitations \( E_i \) of the system the grand canonical partition function is then

\[
\Xi(\beta) = \pm \sum_{i=1}^{\infty} \log(1 \pm Z\exp(-\beta E_i))
\]  

(1)

where \( Z = \exp(\beta \mu) \). The density matrix can then be expressed as

\[
\rho(r, r'; \beta, \mu) = <r|\frac{1}{Z^{-1}\exp(\beta H)\pm 1}|r'>
\]  

(2)

where \( H \) is the Hamiltonian. By reformulating the problem in this fashion, one need not worry about the explicit antisymmetrization or symmetrization of \(|r>\) and \(|r'>\) states. The problem of finding \( \Xi(\beta) \) and \( \rho(r, r'; \beta, \mu) \) is re-expressed in terms of the normal excitations of a system. Thus if in the canonical formulation we had \( N \) interacting fermionic or bosonic particles with a density matrix \( \exp(-\beta H_0) \) and a properly symmetrized wave function, in the grand canonical formulation we can in principle reduce the problem to a system of non interacting particles described by the density matrix \( \frac{1}{Z^{-1}\exp(\beta H)\pm 1} \). This appears much
simpler than the problem in a canonical formulation but there is one problem. The question is how to find a spectrum of normal excitations. For fermionic systems the problem is solved in principle in the Kohn Sham (KS) density functional formalism [5]. According to (KS) the problem of $N$ interacting fermions with a Hamiltonian $H_0$ can be mapped into a problem of $N$ noninteracting particles described by a modified Hamiltonian $H$ which is, in turn, the functional of the density (see the review [3])

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V_{ion}(r) + V_H(r) + V_{XC}(r)$$ (3)

where $V_{ion}(r)$ is an electron-ion interaction potential,

$$V_H(r) = e^2 \int \frac{\rho(r', r'; \beta)}{|r - r'|} d^3r'$$ (4)

is the Hartree potential of the electrons and finally,

$$V_{XC}(r) = \frac{\delta E_{XC}(\rho(r, r; \beta))}{\delta \rho(r, r; \beta)}$$ (5)

is a universal exchange correlation electron density functional.

Thus, a self-consistent algorithm for finding the density matrix in the Grand Canonical Formulation would be implemented as following

a) Use $\rho(r, r; \beta)$ to find a new effective Hamiltonian $H$

b) Given $H$ calculate a new $\rho(r, r; \beta)$ from

$$\rho(r, r'; \beta, \mu) = \langle r | \frac{1}{Z^{-1} exp(\beta H) \pm 1} | r' >$$ (6)

c) Update the chemical potential $\mu$ (which comes via $Z = exp(\beta \mu)$)

d) If self-consistency is not achieved go to a)

Up to this point the algorithm is rather general and can be implemented in many ways. One of the implementations of this algorithm for fermions is originally due to S. Goedecker [7] and lately extended by Baer [8]. The most important step is to implement part b). So that
\[ \rho(r, r'; \beta, \mu) = \langle r | \frac{1}{Z^{-1} \exp(\beta H) + 1} | r' \rangle = \sum_{k=1}^{\infty} \sum_{k'=1}^{\infty} \langle r | k \rangle \frac{1}{Z^{-1} \exp(\beta H) + 1} \langle k' | r' \rangle \]

(7)

where \( \langle r | k \rangle \) is any convenient basis set. By approximating \( \frac{1}{Z^{-1} \exp(\beta H) + 1} \) using Chebyshev Polynomials Goedecker et al obtained an efficient way of calculating the density matrix using \( Pol(H; \beta) \) as a propagator.

An alternative and potentially more beneficial method for implementation of step b) is to use the Path Integral approach \[9,10\]. In the Path Integral Formalism to evaluate the density matrix one would insert \( P \) auxiliary states thus reducing the problem to the evaluation of \( \langle r | (1 \exp(\beta(H - \mu))^{\pm 1}) \hat{P} | r' \rangle \). At high temperature

\[
\langle r | (\frac{1}{\exp(\beta(H - \mu))} + 1) \hat{P} | r' \rangle \sim \langle r | \exp(-\beta \frac{P}{P} (H - \mu)) | r' \rangle \sim
\]

\[
\langle r | \exp(-\beta \frac{P}{P} T_{kin}) | r' \rangle \exp(-\beta \frac{P}{P} V(r'))
\]

so the conventional use of the Trotter approximation for the splitting of the Hamiltonian into kinetic and potential energy is applicable. At low temperatures \( \beta \to 0 \) in the case of fermion statistics

\[
\langle r | (\frac{1}{\exp(\beta(H - \mu))}) \hat{P}^{\pm 1} | r' \rangle \sim \theta(\mu - H)
\]

(9)

where \( \theta(x) \) is a step function and the propagator becomes invariant with respect to \( P \). So the major difference between using the grand canonical approach in the Path Integral Formulation is the approximation of the intermediate propagator. As a function of \( P \), propagator

\( \langle r | (\frac{1}{\exp(\beta(H - \mu))}^{\pm 1}) \hat{P} | r' \rangle \) is very easy to estimate at high temperature by factoring out the kinetic and potential term. At low temperatures the propagator becomes \( P \)-independent thus substantially hindering its use in calculations and thus new methods need to be implemented for the evaluation of this propagator. In this work we present a tractable solution valid at all temperatures.
II. ALL TEMPERATURE SOLUTION

The problem of evaluation of the fermionic density matrix at zero temperature allows an exact solution in the Path Integral Formulation in terms of Bessel functions [11]. For the case of non-zero temperatures the problem has also been solved with the fermionic density matrix represented in integral form [12].

Here we will show that there exists a more computationally convenient representation for the fermionic and bosonic density matrix in terms of the Hankel functions of the first kind.

To calculate the density matrix in the Grand Canonical Ensemble we will exploit the property of a meromorphic function been equal to a summation over its poles and residues at those poles.

\[
\frac{1}{\exp(\beta(H - \mu))} = \pm \frac{1}{2} \pm \sum_{n=-\infty}^{+\infty} \frac{1}{iw_n - \beta(H - \mu)}
\]

(10)

where \(w_n = \pi(2n + 1)\) for fermions and \(w_n = 2\pi n\) for bosons. The density matrix now can be written as

\[
<r| \frac{1}{\exp(\beta(H - \mu))} |r'> = \pm \frac{\delta(r - r')}{2} \pm \sum_{n=-\infty}^{+\infty} <r| \frac{1}{iw_n - \beta(H - \mu)} |r'>
\]

(11)

In this form it is still difficult to make a transition to a Path Integral Formalism. We notice, however, that for \(w_n > 0\)

\[
\frac{1}{iw_n - \beta(H - \mu)} = -i \int_0^{+\infty} dt \exp(-tw_n - it\beta(H - \mu))
\]

(12)

and for \(-w_n\)

\[
\frac{1}{-iw_n - \beta(H - \mu)} = i \int_0^{+\infty} dt \exp(-tw_n + it\beta(H - \mu))
\]

(13)

Thus, evaluation of \(<r| \frac{1}{iw_n - \beta(H - \mu)} |r'>\) is now substantially simplified and we can change to a Path Integral Formulation.

\[
<r| \frac{1}{iw_n - \beta(H - \mu)} |r'> = -i \int_0^{+\infty} dt \exp(-tw_n) <r| \exp(-it\beta(H - \mu)) |r'>
\]

(14)
Element $< r|\exp(-it\beta(H-\mu))|r' >$ is nothing else but a real time propagator. Its evaluation in a Path Integral Formalism is trivial and leads to

$$< r|\exp(-it\beta(H-\mu))|r' > = \lim_{t-i\eta \to t} \left( -imP \frac{mP^2}{2\hbar t\beta} \exp(i(\frac{mP^2}{2\hbar t} + \frac{\hbar k^2 t}{2m})) \right)$$

(15)

where

$$\frac{-imP}{2\hbar t\beta} \left( \right) \frac{mP^2}{2\hbar t\beta} \exp(i(\frac{mP^2}{2\hbar t} + \frac{\hbar k^2 t}{2m}))$$

(16)

$$i^2 P = \frac{P}{\beta} \left( \right) \frac{mP^2}{2\hbar t\beta} \exp(i(\frac{mP^2}{2\hbar t} + \frac{\hbar k^2 t}{2m}))$$

(17)

Finally, for $w_n > 0$

$$< r|\frac{1}{iw_n - \beta(H-\mu)}|r' > = -i \int_{0-i\eta}^{+\infty-i\eta} d\eta \exp(-t\eta) \left( -imP \frac{mP^2}{2\hbar t\beta}\left( \right) \frac{mP^2}{2\hbar t\beta} \exp(i(\frac{mP^2}{2\hbar t} + \frac{\hbar k^2 t}{2m})) \right)$$

(18)

and for $-w_n$

$$< r|\frac{1}{-iw_n - \beta(H-\mu)}|r' > = i \int_{0+i\eta}^{+\infty+i\eta} d\eta \exp(-t\eta) \left( -imP \frac{mP^2}{2\hbar t\beta}\left( \right) \frac{mP^2}{2\hbar t\beta} \exp(i(\frac{mP^2}{2\hbar t} + \frac{\hbar k^2 t}{2m})) \right)$$

(19)

Using the integral representation of the Hankel’s functions [13]

$$H_n^{(1)}(z) = -i \exp(-\frac{1}{2}i\pi)n! \int_0^{+\infty} dt e^{i(t+z^2/t)}$$

(20)

and summing over all frequencies, it is easy to show that the expression for the density matrix can be then rewritten as following,

$$\rho(r, r'; \beta, \mu) = \frac{\delta(r-r')}{2} + \int d^3r \frac{P}{2\pi} \left( \right) \frac{mP^2}{2\hbar t\beta}\left( \right) \frac{mP^2}{2\hbar t\beta} \exp(i(\frac{mP^2}{2\hbar t} + \frac{\hbar k^2 t}{2m}))$$

(21)

for fermions

$$\rho(r, r'; \beta, \mu) = -\frac{\delta(r-r')}{2} - \int d^3r \frac{P}{2\pi} \left( \right) \frac{mP^2}{2\hbar t\beta}\left( \right) \frac{mP^2}{2\hbar t\beta} \exp(i(\frac{mP^2}{2\hbar t} + \frac{\hbar k^2 t}{2m}))$$

(22)

$$\lim_{w_0 \to +0} \left( \right) \frac{mP^2}{2\hbar t\beta}\left( \right) \frac{mP^2}{2\hbar t\beta} \exp(i(\frac{mP^2}{2\hbar t} + \frac{\hbar k^2 t}{2m}))$$

for bosons, where
\[ z_n = \left( \left( K^2_P + i^2 \frac{w_n}{\beta} \right) P_L^2 \right)^{\frac{1}{2}} \; ; \; w_n^{\text{ferm}} = \pi (2n + 1) ; \; w_n^{\text{bos}} = 2\pi n \]  

(23)

and

\[ \frac{\hbar^2 K^2_P}{2m} = \mu - \frac{1}{P} \left( \frac{V(r) + V(r')}{2} + \sum_{i=1}^{P-1} V(r^{(i)}) \right) \]  

(24)

\[ L^2_P = P((r - r^{(1)})^2 + \sum_{i=1}^{P-2} (r^{(i)} - r^{(i+1)})^2 + (r^{(P-1)} - r')^2) \]  

(25)

In the case of bosons, a term in the summation corresponding to zero frequency \( w_0 \) should be calculated in a limit \( w_0 \to +0 \).

**III. INTEGRAL REPRESENTATION**

It is also of interest to show how an integral representation of the universal functional appears in this formalism. We will outline the major steps on the example of fermions. We notice, that for \( w_n > 0 \) equations (12,13) can be written as

\[ \frac{1}{iw_n - \beta(H - \mu)} = -i \int_{-\infty}^{0} dt \exp(\int tw_n + it \beta(H - \mu)) \]  

(26)

and for \(-w_n\)

\[ \frac{1}{-iw_n - \beta(H - \mu)} = i \int_{0}^{+\infty} dt \exp(-tw_n + it \beta(H - \mu)) \]  

(27)

Correspondent propagators are For \( w_n > 0 \)

\[ <r| \frac{1}{iw_n - \beta(H - \mu)} |r'> = -i \int_{-\infty}^{0+i\eta} dt \exp(\int tw_n + it \beta(H - \mu)) \left( \frac{imP}{2\pi \hbar \beta} \right)^{\frac{3P}{2}} \exp\left(-i\left( \frac{ml_p^2}{2\hbar} + \frac{h\hbar^2 t}{2m} \right) \right) \]  

(28)

and for \(-w_n\)

\[ <r| \frac{1}{-iw_n - \beta(H - \mu)} |r'> = i \int_{0+i\eta}^{+\infty+i\eta} dt \exp(-tw_n + it \beta(H - \mu)) \left( \frac{imP}{2\pi \hbar \beta} \right)^{\frac{3P}{2}} \exp\left(-i\left( \frac{ml_p^2}{2\hbar} + \frac{h\hbar^2 t}{2m} \right) \right) \]  

(29)

Now summation over frequencies can be implemented. For the case of fermions

\[ \sum_{n=0}^{+\infty} <r| \frac{1}{iw_n - \beta(H - \mu)} |r'> = -i \int_{-\infty}^{0} dt \left( \sum_{n=0}^{+\infty} \exp(tw_n) \right) <r| \exp(it \beta(H - \mu)) |r'> \]  

(30)
\[
\sum_{n=-\infty}^{-1} < r \left| -i \omega_n - \beta (H - \mu) \right| r' > = i \int_0^{+\infty} dt \left( \sum_{n=-\infty}^{-1} \exp(-t \omega_n) \right) < r |\exp(it \beta (H - \mu))| r' >
\]

Making an explicit summation over frequencies and substituting the above equations into (11) we get

\[
\rho(r, r'; \beta, \mu) = \frac{\delta(r - r')}{2} + \int d^3p \int_{-\infty}^{+\infty} dt W(\beta, t) \left( \frac{im_P}{2\pi \hbar t \beta} \right) \exp\left(-i\left(\frac{m_P^2}{2\hbar t} + \frac{\hbar k_P^2 t}{2m} \right)\right) \] (32)

where

\[
W(\beta, t) = \text{sign}(t) \frac{1}{\beta} \frac{\exp(-\frac{\pi |t|}{\beta})}{1 - \exp(-2\pi \frac{|t|}{\beta})} (33)
\]

It is straightforward to check that in the limit of \( \beta \rightarrow \infty \) the above expression coincides with that of Ref. [11].

## IV. SCALING OF THE UNIVERSAL FUNCTIONAL

Above we showed that the density matrix for fermions and bosons can be expressed via a universal functional \( F_{\text{bos, ferm}}(\beta, P, L_P^2, K_P^2) \) as

\[
\rho(r, r'; \beta, \mu) = \pm \frac{\delta(r - r')}{2} \pm \int d^3p F(\beta, P, L_P^2, K_P^2) \] (34)

From the explicit form of the universal functional derived above one can easily derive a scaling law

\[
F(\beta, P, L_P^2, K_P^2) = \beta^{-\frac{2P}{2}} F(1, P, L_P^2, \beta^{\frac{1}{2}}, K_P^2, \beta^{\frac{1}{2}}) \] (35)

This scaling law can be useful if we consider that the integral over the universal functional can be rewritten as

\[
\int d^3p F(\beta, P, L_P^2, K_P^2) = \int dL_P^2 dK_P^2 P(L_P^2, K_P^2) F(\beta, P, L_P^2, \mu + K_P^2) \] (36)

where
\[
\frac{\hbar^2 K_{P_o}^2}{2m} = -\frac{1}{P} \left( \frac{V(r) + V(r')}{2} + \sum_{i=1}^{P-1} V(r^{(i)}) \right) \tag{37}
\]

and \(P(L_P^2, K_{P_o}^2)\) is the distribution of pairs of variables \((L_P^2, K_{P_o}^2)\). So, in principle, it is enough to calculate the universal functional once for say \(\beta = 1.0\) and the value of the functional at all other temperatures can be evaluated using the scaling law. The integration process can be implemented by first calculating the distribution \(P(L_P^2, K_{P_o}^2)\) (which actually depends upon \(r\) and \(r'\)) and then multiplying this distribution on the values of the universal functional calculated on a 2D grid shifted by \(-\mu\) along the \(K_{P_o}^2\) axis.

The averages and thermodynamical derivatives of the generic operator \(U(r, r')\) can now be determined from

\[
< U(r, r') >_\beta = \int d\mathbf{r} d\mathbf{r}' \rho(r, r'; \beta, \mu)U(r, r') \tag{38}
\]

and derivatives from

\[
\frac{\partial < U(r, r') >_\beta}{\partial \beta} = \int d\mathbf{r} d\mathbf{r}' \frac{\partial \rho(r, r'; \beta, \mu)}{\partial \beta} \tag{39}
\]

\[
\frac{\partial < U(r, r') >_\beta}{\partial \mu} = \int d\mathbf{r} d\mathbf{r}' \frac{\partial \rho(r, r'; \beta, \mu)}{\partial \mu} \tag{40}
\]

where the thermodynamic derivatives of the density matrix can be calculated using the scaling relation for the universal functional giving

\[
\frac{\partial \rho(r, r'; \beta, \mu)}{\partial \mu} = \pm \frac{1}{\beta^{3\beta+1}} \int dL_P^2 dK_{P_o}^2 P(L_P^2, K_{P_o}^2) \frac{\partial F(1, P, L_P^{2\beta-\frac{1}{2}}, K_{P_o}^{2\beta+\frac{1}{2}})}{\partial K_{P_o}^2} \tag{41}
\]

and

\[
\frac{\partial \rho(r, r'; \beta, \mu)}{\partial \beta} = \pm \frac{1}{2\beta^{3\beta+1}} \int dL_P^2 dK_{P_o}^2 P(L_P^2, K_{P_o}^2) \frac{\partial F(1, P, L_P^{2\beta-\frac{1}{2}}, K_{P_o}^{2\beta+\frac{1}{2}})}{\partial L_P^2} - \frac{3P}{\beta^{3\beta+1}} F(1, P, L_P^{2\beta-\frac{1}{2}}, K_{P_o}^{2\beta+\frac{1}{2}}) \tag{42}
\]
V. A SIMPLE NUMERICAL STUDY

To investigate the possible usefulness of this method we have performed a study of a simple model system consisting of noninteracting fermions in a confining potential of the form

$$V(r) = \frac{10.0}{\cosh^2(r)}$$  \hspace{1cm} (43)

Here we assume to work in units $m = \hbar = 1$. This potential allows 5 discrete levels and analytical solution for the $\Psi$ functions. \[14\]. The calculations of the density profiles were implemented as follows. First, a universal functional was generated for $\beta = 1.0$, $\mu = 0.0$, and $P = 20$ (Fig. \[\text{1}\]). One can see a strong oscillatory nature of the potential signifying the fermionic nature of the system under consideration. Next step was to generate the distribution of $P(L_P^2, K_{P_0}^2)$ which is actually the most time consuming part of the calculations. So, to find $\rho(r, r)$ for each value of $r$ a proper $P(L_P^2, K_{P_0}^2)$ distribution was generated using Monte-Carlo sampling. The final step of our calculations was in computing the product of the universal potential and the $P(L_P^2, K_{P_0}^2)$ distribution. By increasing the chemical potential one moves the $P(L_P^2, K_{P_0}^2)$ distribution profile to the right thus coupling to more and more oscillations of the universal functional henceforth introducing more particles in a system. Thus calculated density profiles for different values of the chemical potential are plotted on Fig. \[\text{2}\]. For the sake of comparison density profiles obtained from the exact solution of Schroedinger equation are also plotted on Fig. \[\text{3}\]. Comparing two figures one can notice that even for such a small number of subdivisions $P = 20$ the overall structure of the density profiles is the same in both cases.

VI. CONCLUSIONS

Grand Canonical formulation of Path Integral Formalism allows an exact treatment of fermionic and bosonic systems at any temperature without encountering a complicated problem of antisymmetrization or symmetrization of coordinate eigen states. In this formulation
density matrix is expressed as an integral over the universal functional $F_{\text{bos,ferm}}(\beta, P, L^2_P, K^2_P)$ while particular properties of a system come through the variables $L^2_P, K^2_P$. Computationally convenient representation of the universal functional is possible in terms of Hankel functions of the first kind so one can, in principle, precalculate the $F_{\text{bos,ferm}}(\beta, P, L^2_P, K^2_P)$ and the density itself will be determined by a distribution of the non-universal variables $L^2_P, K^2_P$. 
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FIGURES

FIG. 1. $F_{\text{ferm}}(\beta = 1.0, P = 20, L_P^2, K_{P_0}^2)$. One can easily notice strong oscillations due to the nature of fermionic statistics.

FIG. 2. Density profiles for different values of the chemical potential calculated using Grand Canonical Path Integral Method.

FIG. 3. Density profiles for different values of the chemical potential calculated using the exact solution of Schroedinger equation.
Calculated Density

Chemical Potential

Calculated Density

Chemical Potential
