Thermodynamics of quantum gases for the entire range of temperature

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Abstract
We have analytically explored the thermodynamics of free Bose and Fermi gases for the entire range of temperature, and have extended the same for harmonically trapped cases. We have obtained approximate chemical potentials for the quantum gases in closed forms of temperature so that the thermodynamic properties of the quantum gases become plausible, especially in the intermediate regime between the classical and quantum limits.

1. Introduction
In undergraduate courses on statistical physics, one has to plot the specific heats of free (ideal homogeneous) Bose and Fermi gases [1]. To plot the specific heat of a quantum gas with respect to its temperature, one has to know the temperature dependence of its chemical potential, which in general is obtained from an implicit relationship with the number density of particles [1, 2]. This relationship involves a polylog function of an exponential of the chemical potential which cannot be obtained in a closed form of temperature because an inverse of a polylog function, in general, does not exist. In spite of that, students are taught how to obtain the approximate temperature dependence of the chemical potential for the classical and quantum (degenerate) regimes [1]. However, for the intermediate regime they are advised to obtain graphical solutions. Considering the difficulty of obtaining graphical solutions, in this paper we incorporate an easy technique for obtaining the approximate chemical potentials of the quantum gases in closed forms of temperature not only for the intermediate regime but also for the entire range of temperature.

After the observation of Bose–Einstein condensation in 1995 [3–5], studying trapped quantum gases is now a topic of high experimental and theoretical interest for research [6–8]. So, it is reasonable to extend our discussion for harmonically trapped (ideal inhomogeneous) cases.

This paper’s calculations begin with the Bose–Einstein statistics. In subsection 2.1, we present a technique for obtaining an approximate chemical potential of a free Bose gas in a closed form of temperature. We do the same for a harmonically trapped Bose gas in
subsection 2.2, and for free and harmonically trapped Fermi gases in section 3. We plot approximate chemical potentials in figure 1. We also plot specific heats, equation of states and susceptibilities in figures 2 and 3 using our approximate chemical potentials.

2. Thermodynamics of Bose gases

Let us consider a 3D free Bose gas in thermodynamic equilibrium with a (heat and particle) reservoir characterized by temperature \( T \) and chemical potential \( \mu \). All the thermodynamic quantities of this system can be obtained from the Bose–Einstein statistics

\[
\bar{n}_i = \frac{1}{e^{(\epsilon_i - \mu)/kT} - 1},
\]

where \( \bar{n}_i \) is the (equilibrium) average number of particles at the \( i \)th single particle state having energy \( \epsilon_i \). From equation (1), we can see that the total average number of particles \( (N = \sum_i \bar{n}_i) \) and total average energy \( (E = \sum_i \bar{n}_i \epsilon_i) \) are functions of \( \mu \). Hence, all the thermodynamic quantities like pressure \( (p) \), average number density of particles \( (\bar{n}) \), average energy per particle \( (\bar{\epsilon}) \), specific heat per particle \( (c_v) \), etc are expected to be functions of \( \mu \).

For a free gas, we can replace the single particle energy eigenstates \{\( \epsilon_i \)\} by the single particle momenta \{\( p \)\} so that \( \epsilon_i \) essentially becomes \( \epsilon_p = p^2/2m \), where \( m \) is the mass of a single particle. Degeneracy of the level \( \epsilon_p \) in the semiclassical limit is given by \( \sqrt{2\pi \hbar^2 p^2} \), where \( V \) is the volume of the system. In the thermodynamic limit \( (N \to \infty, V \to \infty, N/V = \text{const.}) \), the standard text book result for specific heat per particle of the free Bose gas is given by [1]

\[
c_v = \begin{cases} 
\frac{15}{4} \frac{L_{1/2}(z) - 9 L_{3/2}(z)}{L_{1/2}(z)} & \text{for } T > T_c \\
\frac{15}{4} \frac{L_{5/2}(z)}{L_{1/2}(z)} \left( \frac{T}{T_c} \right)^{3/2} & \text{for } T \leq T_c
\end{cases}
\]

where \( T_c = \frac{2\pi \hbar^2}{mk} \left( \frac{\bar{n}}{\bar{n}_{(3/2)}} \right)^{2/3} \) is the Bose–Einstein condensation temperature at and below which \( \mu \) takes the highest possible value (0), \( z = e^{\mu/kT} \) is the fugacity and \( L_j(z) = z + \frac{z^2}{2} + \frac{z^3}{3} + \cdots \) is a polylog function of order \( j \). Plotting \( c_v \) for \( T \leq T_c \) is very easy. But plotting \( c_v \) for \( T > T_c \)
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Figure 2. Solid lines represent approximate specific heats per particle. Points represent their respective exact graphical solutions. Dotted lines represent classical results.

Figure 3. Solid lines in figures 3(a) and (b) represent equation of state \( p/p^{(0)} \) in units of \( p^{(0)} = \hbar k T \). Solid lines in figures 3(c) and (d) represent paramagnetic (\( \chi_{\text{Pauli}} \)) and diamagnetic (\( \chi_{\text{Landau}} \)) parts of susceptibilities of the ideal homogeneous Fermi (electron) gas in units of \( C/T_F = \mu_0 \hbar v_F^2 / k T_F \). Dotted lines represent classical results. Points represent respective exact graphical solutions.

It is not easy until one manages to obtain the temperature dependence of \( z \) or of \( \mu \) from the implicit relation [1]:

\[
\left( \frac{\text{Li}_{3/2}(z)}{\zeta(3/2)} \right)^{2/3} = \frac{1}{t},
\]

which can be obtained as a result of phase-space integration of the right-hand side of equation (1), and where \( t = T/T_c \). As an inverse of a polylog function (\( \text{Li}_j(z) \)) does not

\[
\text{Li}_{3/2}(z) = \frac{1}{z^{3/2}}.
\]
exist except for \( j = 1 \), we are not able to obtain \( \mu \) from equation (3) or \( c_i \) from equation (2) as a function of temperature without approximation, in particular for \( T > T_c \).

On the other hand, for a harmonically trapped case, all the particles are 3D harmonic oscillators, and the single particle energy levels are given by \( \epsilon_i = (i^2 + 1)\hbar\omega \), where \( \omega \) is the angular frequency of oscillations. Although the degeneracy \( (g_i) \) of this level is \( i^2/2 + 3i/2 + 1 \) [9], in the thermodynamic limit \( (N \to \infty, \omega \to 0 \text{ and } N\omega^3 = \text{const.}) \) only the first term of the degeneracy contributes significantly. Zero point energy can also be neglected in this limit. The implicit relation between the chemical potential and temperature (in the thermodynamic limit) for this case is given by (instead of equation (3))

\[
\left( \frac{\text{Li}_3(z)}{\zeta(3)} \right)^{1/3} = \frac{1}{t},
\]

where \( t = \frac{T}{T_c} \) and \( T_c = \frac{\hbar}{k}\left[ \frac{N}{\omega} \right]^{1/3} \) [2, 6, 10].

In the following, we present approximate analyses of equations (3) and (4), and obtain approximate chemical potentials for the two cases indicating suitable suffices for different temperature regimes.

2.1. For free Bose gas

The classical regime of a quantum gas is characterized by \( t \gg 1 \) (or by \( z \ll 1 \)), so that in this regime we may write \( \text{Li}_{3/2}(z) \approx z \), which along with equation (3) yields the approximate classical result

\[
\mu_{\geq 1}(t) \approx -kT \frac{2}{3}\ln(t/\zeta^2(3/2)).
\]

On the other hand, the quantum regime for the Bose gas is characterized by \( t \lesssim 1 \) (or by \( z \approx 1 \)). For \( t \ll 1 \), we have \( \mu = 0 \) [2], and for \( t > 1 \) \( \mu \) is obtained from equation (3). In the following we extend a standard (but not very familiar) result [11] for \( t \gg 1 \) up to the second lowest order. From equations (1) and (3) we can redefine the polylog function \( \text{Li}_{3/2}(z) \) as

\[
\text{Li}_{3/2}(z) = \frac{2}{\sqrt{\pi}} \int_0^\infty \left[ \frac{1}{e^{\epsilon/\pi} - 1} - \frac{1}{e^{\epsilon} - 1} \right] e^{1/2}d\epsilon,
\]

in an integral form where \( v = |\mu|/kT \). One can check that \( \text{Li}_{3/2}(z) \) is not an analytic function of \( z \), particularly about \( z = 1 \). To know even the approximate values of chemical potential for \( t \gg 1 \) is thus difficult. Let us adopt the trick of Landau and Lifshitz for this purpose [12]. Subtracting \( \text{Li}_{3/2}(1) \) from \( \text{Li}_{3/2}(z) \) we can recast the above equation as [12]

\[
\text{Li}_{3/2}(z) - \zeta \left( \frac{3}{2} \right) = \frac{2}{\sqrt{\pi}} \int_0^\infty \left[ \frac{1}{e^{\epsilon/\pi} - 1} - \frac{1}{e^{\epsilon} - 1} \right] e^{1/2}d\epsilon.
\]

It is clear from equation (7) that, for \( t \gg 1 \) (or for \( v \ll 1 \)), the integrand will contribute only for smaller values of \( \epsilon \), so that up to the second lowest order we can have

\[
\text{Li}_{3/2}(z) \approx \zeta \left( \frac{3}{2} \right) - \frac{2}{\sqrt{\pi}} \int_0^\infty \left[ \frac{(1 + \epsilon + \frac{\epsilon^2}{2})(v + \frac{\epsilon}{2})\epsilon^{1/2}}{((\epsilon + v) + (\epsilon + v)[(\epsilon + v)]^2)(\epsilon + \frac{\epsilon^2}{2})} \right] d\epsilon
\]

\[
\approx \zeta \left( \frac{3}{2} \right) - 2\sqrt{\pi} v^{1/2} \left[ 1 + \frac{v^{1/2}}{2\sqrt{\pi}} + O(v^{1/2}) \right].
\]

Let us use this result at the left-hand side of equation (3). In its right-hand side, we may have the Taylor expansion about \( t = 1 \) as

\[
1/t = 1 - (t - 1) + (t - 1)^2 + \cdots.
\]
Plugging the above two expansions into equation (3) we obtain
\[ \mu_\approx(t) \approx -kT_e \frac{9 \zeta(3)}{16\pi} (\delta t)^2 \left[ 1 - \left( \frac{1}{4} + \frac{3 \zeta(\frac{1}{2})}{8\sqrt{2\pi}} \right) \delta t \right] \]

up to the second lowest order in \( \delta t = t - 1 \). It should be mentioned that the lowest order term in equation (10) was previously obtained by Bhattacharjee, adopting the same trick of Landau and Lifshitz [11, 12].

The intermediate regime is an overlap of the classical and quantum regimes, and can be characterized by \( t \gtrsim 1 \). For this case, our approximation is made considering only the first three terms of \( \text{Li}_3(z) \) instead of all its terms in equation (3). Thus, solving the cubic equation of \( z \) we have
\[ \mu_\approx(t) \approx t \ln \left[ -\frac{3}{8} - \frac{432\sqrt{3} - 162t}{36 \cdot 2^4 \cdot 3^5 f_1(t)} + \frac{t^{-2} f_1(t)}{2 \cdot 2^7 \cdot 3^9} \right], \]

where \( f_1(t) = \left[ 136\sqrt{6} - 9\sqrt{2} \right] \right] \theta(1.711 - t) + \mu_\approx(t) \theta(t - 1.711), \]

where \( \theta \) is a unit step function. Now it is time to verify how good our approximate chemical potential is. We can verify it comparing with the (exact) graphical solutions of the chemical potential.

Let us now outline how to obtain the graphical solutions. In a figure, we plot the left-hand side of equation (3) with respect to \( z \), and the right-hand side of equation (3) for \( t = t_1, t_2, t_3 \) etc. Intersecting points of these plots are the solutions \( \{z(t)\} \) of \( z \) for \( t = t_1, t_2, t_3 \) etc. Thus we can have a number of graphical solutions \( \{\mu_\approx = kT_e \ln(z(t))\} \) for given values of \( t \), and plot them in figure 1(a). In the same figure, we also plot our approximate chemical potential in equation (12), and see that it matches reasonably well with the exact graphical solutions. Hence, we can approximately plot other thermodynamic variables using our approximate chemical potential in equation (12). As an example, we plot specific heat per particle (from equation (2)) in figure 2(a), and compare with its exact graphical solutions.

The fact that the approximate \( c_v \) matches well with the exact graphical solutions gives us confidence to adopt our approximation technique for application to harmonically trapped ideal Bose gas, free Fermi gas and harmonically trapped ideal Fermi gas.

2.2. For trapped Bose gas

The chemical potential of the harmonically trapped Bose gas is obtained from equation (4). The classical result \( \mu_\approx(t) \approx kT \ln \left( t/\sqrt{\pi} \right) \) for this case can be improved for the intermediate regime considering only the first three terms of \( \text{Li}_3(z) \) in equation (4), and it results in
\[ \mu_\approx(t) \approx t \ln \left[ -\frac{9}{8} \frac{165t^3}{8f_2(t)} + \frac{3 f_2(t)}{8r^3} \right], \]

where \( f_2(t) = \left[ 261t^6 + 256t^5 \zeta(3) + 16\sqrt{2}(458t^{18} + 261t^{15} \zeta(3) + 128t^{12} \zeta^2(3))^{1/3} \right] \). On the other hand, in the quantum regime and in particular for \( t \gtrsim 1 \), we should expand \( \text{Li}_3(z) \) and \( 1/t \) in equation (4) about \( z = 1 \) and \( t = 1 \), respectively. While the expansion of \( \text{Li}_3(z) \)
can be obtained (using \( \text{Li}_3(z) - \zeta(3) = \int_1^z \frac{\text{Li}_2(x)}{x} \, dx \)) and expanding \( \text{Li}_2(x) \) in the manner used to obtain equation (8)) as

\[
\text{Li}_3(z) = \zeta(3) - \zeta(2) \left[ 1 + \frac{z}{\zeta(2)} \left( \frac{3}{4} \ln \zeta - \frac{3}{4} \right) + \cdots \right],
\]

(14)

that of \( 1/t \) has already been obtained in equation (9). The presence of the logarithmic term in the above expansion says that \( \text{Li}_3(z) \) is nonanalytic about \( z = 1 \). However, plugging the expansions in equations (9) and (14) into equation (4), we obtain

\[
\mu \approx -\frac{3}{2} \zeta(3) \zeta(2) (t - 1)\]

(15)

up to the lowest order in \( t - 1 \). Once again for \( t > 1 \) we have two independent approximate results in equations (13) and (15). These two results intersect at \( t \approx 1.065 \). Combining these two, we obtain our desired result for \( t > 1 \) as

\[
\mu \approx \mu \approx (t \theta(1.065 - t) + \mu \approx (t - 1.065)).
\]

(16)

We plot this approximate chemical potential in figure 1(b) and compare it with its exact graphical solutions.

In the following section, we extend our discussions to the Fermi systems. Although in the classical regime the behaviour of a Fermi gas is identical to that of a Bose gas, in the quantum regime they are quite different. This difference requires that special care be taken when extending our approximation technique for application to Fermi systems.

3. Thermodynamics of Fermi gases

For an ideal Fermi gas, the average number of particles occupying \( i \)th single particle state is given by the Fermi–Dirac statistics

\[
\bar{n}_i = \frac{1}{e^{(\epsilon_i - \mu)/kT} + 1}.
\]

(17)

While for a Bose gas we have defined \( t \) as \( T/T_c \), henceforth for a Fermi gas let us redefine \( t \) to be \( T/T_F \), where \( T_F \) is the Fermi temperature. Integrations of the right-hand side of equation (17) result in [1]

\[
\left(-\text{Li}_3(-z) \Gamma(5/2)\right)^{2/3} = \frac{1}{t}
\]

(18)

for a free Fermi gas with \( T_F = \frac{\hbar^2}{2m} (6\pi^2 \bar{n})^{2/3} \) [1] and

\[
\left(-\text{Li}_3(-z) \Gamma(4)\right)^{1/3} = \frac{1}{t}
\]

(19)

for a harmonically trapped Fermi gas with \( T_F = \frac{\hbar \omega}{2} (\Gamma(4) N)^{1/3} \) [13].

In the following, we present approximate analyses of equations (18) and (19) and obtain approximate chemical potentials for the two cases, indicating that they are sufficient for different temperature regimes.

3.1. For free Fermi gas

Adopting the previous approach, we obtain the classical result for the free Fermi gas to be

\[
\mu \approx (t) \approx -\frac{3}{2} kT \ln [\Gamma^2(5/2)],
\]

and improve it considering only the first three terms of \( -\text{Li}_{3/2}(-z) \) to obtain the approximate result for the intermediate regime \( (t \approx 1) \) as

\[
\mu \approx (t) \approx t \ln \left[ \frac{\sqrt{3}}{8} + \frac{(432\sqrt{3} - 162) \pi^{1/2}}{36 \cdot 2^4 \cdot 3^2} \frac{t^{1/2}}{f_3(t)} \right] + \frac{t^{-1/2} f_3(t)}{2\pi^{1/2} \cdot 2^2 \cdot 3^{3/2}}.
\]

(20)
where \( f_3(t) = \left[ 192^3 - 36^3 \sqrt{3} \right] t^{9/2} + \sqrt{3} \left( 12288 \pi^2 \rho^4 + \left( 1152 \sqrt{3} - 4608 \right) \frac{\pi^5}{12} l^{15/2} - \left( 864 - 3072 \sqrt{3} \pi^3 \rho^2 \right) l^{11/2} \right] l^{1/2} \). On the other hand, for the quantum regime \( \mu \leq \mu_0 \) as well as for \( \epsilon \gg 1 \), we expand \(-L_{3/2}(-z)\) in equation (18) according to Sommerfeld’s asymptotic formula [1]:

\[
-L_{3/2}(-z) \approx \left[ \frac{\mu(t)/kT}{\Gamma(j+1)} \right] \left[ 1 + \sum_{n=1}^{\infty} \left( 2 \zeta(2n)(1 - 2^{-2n}) \frac{j(j-1) \cdots (j-(2n-1))}{\mu(t)/kT} \right) \right].
\]

(21)

Plugging the above expansion for \( j = 3/2 \) in to equation (18), we obtain [14]

\[
\mu_\mu(t) = kT \left[ 1 - \frac{\pi^2}{12} r^2 - \frac{\pi^4}{80} r^4 + O(r^6) \right].
\]

(22)

For the entire range of temperature, we have two independent approximate results in equations (20) and (22). These two results intersect at \( t \approx 0.723 \). Their combination in the form

\[
\mu(t) \approx \mu_\mu(t) \theta(0.723 - t) + \mu_\mu(t) \theta(t - 0.723)
\]

(23)

gives us our desired approximate chemical potential. We plot this approximate chemical potential in figure 1(c) and compare it with its exact graphical solutions.

3.2. For trapped Fermi gas

Adopting a similar treatment to that used for obtaining approximate results of the free Fermi gas, we obtain the classical and improved classical results for the trapped Fermi gas, respectively, as \( \mu_\mu_0(t) \approx -3kT \ln[I^0(4\Gamma^4)] \) and [15]

\[
\mu_\mu_0(t) \approx kT \ln \left[ \frac{9}{8} - \frac{165 \times 3^{1/3} f_0(t)}{8} + \frac{3^{2/3}}{8 f_0(t)} \right].
\]

(24)

where \( f_0(t) = t/[128 - 783 r^3 + 16(64 - 783 r^3 + 8244 r^6)]^{1/2} \). For the quantum regime, using the asymptotic formula for \( j = 3 \) we obtain [13]

\[
\mu_\mu(t) = kT \left[ 1 - \frac{\pi^2}{3} l^2 + O(l^6) \right].
\]

(25)

Once again, for the entire range of temperature, we have two independent approximate results in equations (24) and (25). These two results intersect at \( t \approx 0.468 \). Their combination in the form [15]

\[
\mu(t) \approx \mu_\mu(t) \theta(0.468 - t) + \mu_\mu(t) \theta(t - 0.468)
\]

(26)

gives us our desired approximate chemical potential. We plot this approximate chemical potential in figure 1(d) and compare it with its exact graphical solutions.

4. Conclusion

Although it is impossible to obtain chemical potentials of the quantum gases in exact closed forms of temperature, we have obtained them in approximate closed forms. The closed forms give plausibility to reproduction of the thermodynamics of the quantum gases for the entire range of temperature. To advance plausibility we have plotted specific heats for all the quantum gases in figure 2, and equations of states (pressures) of the free quantum gases in figures 3(a) and (b), with paramagnetic and diamagnetic parts of the susceptibilities of the ideal homogeneous
Fermi gas of spin-1/2 in figures 3(c) and (d) using the respective approximate chemical potentials in figure 1.

We have not shown relationships between specific heats and fugacities for the plots in figures 2(b)–(d). These are easily derivable and available in [10], [1] and [13], respectively. We have also not shown the derivation of equations of states and the susceptibilities in figure 3. These are available in standard textbooks [1, 11].

For harmonically trapped systems, we have considered oscillations to be isotropic. Otherwise, the angular frequency ($\omega$) in our results has be replaced by the geometric mean of $\omega_x$, $\omega_y$, and $\omega_z$ [2, 6].

It should have been mentioned that an approximate form of the specific heat of the free Bose gas was previously obtained for $T \gtrapprox T_c$ by Wang using Robinson’s method, which involves Mellin transform as well as analytic continuation of $Li_j(z)$ [16, 17], and for $T \lessapprox T_c$ by London using the virial expansion method [18, 1]. These methods (or techniques) can also be used for the harmonically trapped Bose gas. On the other hand, the approximate form of thermodynamic variables of the free and harmonically trapped Fermi gases can be obtained for $T \lesssim T_F$ using Sommerfeld’s asymptotic expansion of $-Li_j(-z)$, and for $T \gtrsim T_F$ using the virial expansion method [1, 8]. While none of the above methods/techniques covers the entire range of temperature, our approximation technique covers the entire range not only for Bose but also for Fermi gases. However, it would be an interesting problem for undergraduate and graduate students to obtain a temperature-dependent form of the specific heat for the trapped Bose gas for $T \gtrsim T_c$ in the way we have obtained approximate chemical potentials using the trick of Landau and Lifshitz [12]. Students can also generalize the virial expansion to obtain the approximate temperature dependence of specific heats of the trapped Bose and Fermi gases.

To conclude, this paper illustrates approximate analyses of polylog functions in demonstrating the temperature dependence of thermodynamic quantities of ideal quantum gases for the entire range of temperature in an easy and plausible manner. We have applied our approximation technique to only a few thermodynamic properties of ideal quantum gases. Our technique can also be applied to other thermodynamic properties (e.g. the temperature dependence of entropy, energy, etc) of ideal and weakly interacting quantum gases [15]. All the calculations in this paper were performed within the scope of undergraduate and graduate students. They can extend our approximation technique to obtain better results, including higher order corrections, and generalize our approximation technique to other spatial dimensions.

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