Energy fluctuation and discontinuity of specific heat

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Abstract. The specific heat per particle ($c_v$) of an ideal gas, on many occasions, is interpreted as energy fluctuation per particle ($\Delta \epsilon^2$) of the ideal gas through the relation $\Delta \epsilon^2 = kT^2 c_v$, where $k$ is the Boltzmann constant and $T$ is the temperature. This relationship is true only in the classical limit and deviates significantly in the quantum degenerate regime. We have analytically explored quantum to classical crossover of this relationship, in particular, for 3D free Bose and Fermi gases. We have explored the same for harmonically trapped cases. We have obtained a hump of $\Delta \epsilon^2 / kT^2 c_v^{(cl)}$ around its condensation point for 3D harmonically trapped Bose gas. We have discussed the possibility of an occurring phase transition with the discontinuity of heat capacity from the existence of such a hump for other Bose and Fermi systems.

Keywords: classical phase transitions (theory), Bose–Einstein condensation (theory), quantum gases, quantum fluids
1. Introduction

Ultracold atomic gas in an optical trap is a favorite hunting ground for theoreticians and experimentalists [1–3]. Within the last two decades numerous work has been done on this topic [1–3]. Quite a few major branches, e.g. Bose–Einstein condensation in harmonic trap [1], ultracold Fermi gas in harmonic trap [3], ultracold gas in optical lattice [2], superfluid–Mott insulator transition in optical lattice [2, 4] etc, have evolved from this single topic showing its potential. However, the thermodynamic properties of the ultracold atomic gases have always been the center of attraction. The Bose–Einstein condensation fraction [5–8], temperature dependence of energy and specific heat of ultracold Fermi gases [9–11], momentum distribution for harmonically trapped Bose gas [12], momentum distribution for harmonically trapped Fermi gas [13], temperature dependence of the chemical potential [14], temperature dependence of the critical number of particles for the collapse of attractively interacting Bose gas [15], temperature dependence of thermodynamic properties of a unitary Fermi gas [16] etc, have already been studied in this regard. As the discontinuity of specific heat (at constant volume and average particle number) confirms the occurrence of the second order phase transition, the measurement of the specific heat is very important. Surprisingly, specific heat for harmonically trapped Bose gas, as far as we know, has not yet been precisely measured, particularly around the condensation point. This is because of difficulties associated with the inhomogeneity of the trapped condensate and the corresponding difficulties in analyzing the density profiles within local density approximation [17]. If this is so difficult to measure, is there any other measurable thermodynamic variable which confirms the discontinuity of specific heat? This paper finds a possible answer to this question from a general perspective.

Specific heat is very often interpreted as energy fluctuation. Energy fluctuation, for a single particle subsystem, is nothing but the variance of energy

$$\Delta \epsilon^2 = \bar{\epsilon}^2 - \bar{\epsilon}^2,$$

where
\[
\bar{\epsilon} = \sum_i \epsilon_i p_i, \quad \bar{\epsilon}^2 = \sum_i \epsilon_i^2 p_i, \quad \epsilon_i \text{ is the energy eigenvalue of the particle at the } \text{ith eigenstate and } p_i \text{ is the thermal equilibrium probability of the } \text{ith eigenstate. As long as we take this probability to be } p_i = e^{-\epsilon_i/kT} / Z, \text{ where } Z = \sum_i e^{-\epsilon_i/kT} \text{ is the canonical partition function, we obtain the familiar relationship: } \Delta \epsilon^2 = kT^2 \epsilon_v^{(cl)} \text{ where } \epsilon_v^{(cl)} \text{ is the classical specific heat of a single particle. The same probability is eventually applicable for a single particle of an ideal classical gas and as a result, this relationship is true only for a classical gas.}
\]

For a quantum (Bose or Fermi) gas, above probability can be given (considering a grand canonical ensemble) by \( p_i = e^{-\epsilon_i/(kT)} \), where \( \tilde{n}_i \) is the average number of particles occupying the \( i \)th eigenstate and \( N(= \sum_i \tilde{n}_i) \) is the total average number of particles. The average number of particles, occupying the \( i \)th eigenstate, is, of course, given by the Bose–Einstein (–) or Fermi–Dirac (+) statistics

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

where \( \mu \) is the chemical potential of the quantum (Bose or Fermi) gas. The difference between the probabilities \( (p_i) \) of the classical and the quantum gas stems essentially from the nonzero fugacity \( (z = e^{\mu/(kT)} \) of the quantum gas.

Bose–Einstein or Fermi–Dirac statistics as expressed above are applicable only in the thermodynamic limit where microcanonical, canonical and grand canonical ensembles of statistical mechanics reproduce the same result \([8, 18]\). However, a grand canonical ensemble is convenient to work with, in particular, for the quantum (Bose and Fermi) gases.

In the following, we will see how a nonzero fugacity plays a vital role in the deviation of \( \Delta \epsilon^2 \) from \( kT^2 \epsilon_v^{(cl)} \), in particular, for 3D free \([19]\) and harmonically trapped \([20]\) ideal Bose and Fermi gases.

2. Energy fluctuations

2.1. For free Bose and Fermi gases

For a free gas, we can replace the single particle energy eigenstates \( \{i\} \) by the single particle momenta \( \{p\} \) so that \( \epsilon_i \rightarrow \epsilon_p = p^2/2m \) where \( m \) is the mass of the single particle. Degeneracy of this level, within the semiclassical approximation, is given by \( \frac{V4\pi\pi^2dp}{(2\pi\hbar)^3} \), where \( V \) is the volume of the system. In the thermodynamic limit \((N \rightarrow \infty, V \rightarrow \infty, N/V = \tilde{n} = \text{const.})\), the straightforward textbook level calculation, for the energy fluctuation \( \Delta \epsilon^2 = \sum_i \epsilon_i^2 \tilde{n}_i / N - (\sum_i \epsilon_i \tilde{n}_i / N)^2 \) results in

\[
\Delta \epsilon^2 = \begin{cases} (kT)^2 \left[ \frac{15 \zeta(7/2)}{4 \zeta(5/2)} \left( \frac{T}{T_c} \right)^{3/2} - \frac{9 c^2(5/2)}{4 \zeta(5/2)} \left( \frac{T}{T_c} \right)^3 \right] & \text{for } \frac{T}{T_c} \leq 1 \\ (kT)^2 \left[ \frac{15 \text{Li}_{7/2}(z)}{4 \text{Li}_{3/2}(z)} - \frac{9 \text{Li}_{5/2}^2(z)}{4 \text{Li}_{3/2}^2(z)} \right] & \text{for } \frac{T}{T_c} > 1 \end{cases}
\]

where \( T_c = \frac{2\pi^2 \hbar^2}{mk} \left( \frac{\tilde{n}}{\zeta(3/2)} \right)^{2/3} \) \([19]\) is the Bose–Einstein condensation temperature and \( \text{Li}_j(z) = z + \frac{z^2}{2^j} + \frac{z^3}{3^j} + ... \) is a polylog function of order \( j \). A similar straightforward
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calculation, for a 3D free Fermi gas, results in
\[ \Delta \epsilon^2 = (kT)^2 \left[ \frac{15}{4} \text{Li}_{3/2}(-z) - \frac{9}{4} \text{Li}_{3/2}^2(-z) \right] . \]  
(3)

Comparing the above results with the textbook results for \( kT^2 \) times \( c_v \) [19], one can easily check that \( \Delta \epsilon^2 \neq kT^2 c_v \) except in the classical limit (\( z \to 0 \)). To visualize how the above results deviate from their unique classical value (\( \frac{3}{2}(kT)^2 \)), we can plot the right-hand sides of equations (2) and (3) in units of \( \frac{3}{2}(kT)^2 \) for the entire range of temperature. But, the plotting of the same is not an easy job until one manages to get temperature dependence of \( z \) or of \( \mu \) from the implicit relations [19]
\[ \left( \frac{\text{Li}_{3/2}(z)}{\zeta(3/2)} \right)^{2/3} = \frac{T_c}{T} \]  
(4) for 3D free Bose gas and [19]
\[ (-\text{Li}_{3/2}(-z)\Gamma(5/2))^{2/3} = \frac{T_F}{T} \]  
(5) for 3D free Fermi gas whose Fermi temperature is given by \( T_F = \frac{k^2}{2m}(6\pi^2\bar{n})^{2/3} \).

Approximate analyses of the temperature dependence of the chemical potentials were done by Biswas et al from the above two equations [21]. They obtained temperature-dependent approximate formulas of \( \mu \) not only for the free Bose and Fermi gases, but for the harmonically trapped Bose and Fermi gases. Using their appropriate formulas of \( \mu \), we plot \( \Delta \epsilon^2 s \) in units of \( \frac{3}{2}(kT)^2 \) in figure 1(a) for the free Bose gas and in figure 1(b) for the free Fermi gas.

### 2.2. For harmonically trapped Bose and Fermi gases

For harmonically trapped cases, all the particles are 3D harmonic oscillators and the energy levels are given by \( \epsilon_i = (\frac{3}{2} + i)\hbar \omega \), where \( \omega \) is the angular frequency of oscillations. Although the degeneracy (\( g_i \)) of this level is \( i^2/2 + 3i/2 + 1 \) [22], yet in the thermodynamic limit (\( N \to \infty \), \( \omega \to 0 \) and \( N\omega^3 = \text{const.} \)), only the first term of the degeneracy contributes significantly. In this limit, the zero point energy can be neglected. Now, a straightforward textbook level calculation, for the energy fluctuation \( \Delta \epsilon^2 = \frac{1}{N} \int_0^\infty \epsilon^2 \bar{n}(\epsilon) g(\epsilon) d\epsilon - \frac{1}{N^2} \int_0^\infty \epsilon \bar{n}(\epsilon) g(\epsilon) d\epsilon \) where \( g(\epsilon) = \epsilon^2/2 \) in the thermodynamic limit of a 3D harmonically trapped Bose gas, results in
\[ \Delta \epsilon^2 = \begin{cases} (kT)^2 \left[ 12 \frac{\zeta(5)}{\zeta(3)} \left( \frac{T}{T_c} \right)^3 - 9 \frac{\zeta^2(4)}{\zeta^2(3)} \left( \frac{T}{T_c} \right)^6 \right] & \text{for } \frac{T}{T_c} \leq 1 \\ (kT)^2 \left[ 12 \frac{\text{Li}_5(z)}{\text{Li}_3(z)} - 9 \frac{\text{Li}_4(z)}{\text{Li}_3(z)} \right] & \text{for } \frac{T}{T_c} > 1 \end{cases} \]  
(6)

where \( T_c = \frac{\hbar \omega}{k} \left( \frac{N}{\zeta(3)} \right)^{1/3} \) [20] is the Bose–Einstein condensation temperature for the trapped system. A similar straightforward calculation, for a 3D harmonically trapped Fermi gas, results in
\[ \Delta \epsilon^2 = (kT)^2 \left[ 12 \frac{\text{Li}_5(-z)}{\text{Li}_3(-z)} - 9 \frac{\text{Li}_4(-z)}{\text{Li}_3(-z)} \right] . \]  
(7)

\[ \text{doi:10.1088/1742-5468/2015/03/P03013} \]
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Figure 1. Solid lines in (a)–(d) (corresponding to the approximate chemical potentials in [21]) respectively represent the right-hand sides of equations (2) and (3) in units of \( \frac{3}{2} (kT)^2 \) and equations (6) and (7) in units of \( 3(kT)^2 \). Dotted lines represent classical results. Points represent exact graphical solutions. (a) For free Bose gas. (b) For free Fermi gas. (c) For trapped Bose gas. (d) For trapped Fermi gas.

Once again, plotting \( \Delta \epsilon^2 \), for the entire range of temperature, is not an easy job until one manages to get the temperature dependence of \( z \) or of \( \mu \) from the implicit relations

\[
\left( \frac{\text{Li}_3(z)}{\zeta(3)} \right)^{1/3} = \frac{T_c}{T} \tag{8}
\]

for 3D harmonically trapped ideal Bose gas [20] and

\[
\left( -\text{Li}_3(-z)\Gamma(4) \right)^{1/3} = \frac{T_F}{T} \tag{9}
\]

for 3D harmonically trapped ideal Fermi gas whose Fermi temperature is given by \( T_F = \frac{\hbar \omega}{k} (\Gamma(4)N)^{1/3} \) [23]. Biswas et al obtained approximate temperature-dependent formulas of \( \mu \) from the above two equations [21]. Using their approximate formulas of \( \mu \), we plot \( \Delta \epsilon^2 \)'s in units of \( 3(kT)^2 \) in figure 1(c) for the harmonically trapped Bose gas and in figure 1(d) for the harmonically trapped Fermi gas.

3. Existence of ‘humps’ in Bose systems

It is interesting to note in figure 1(c) that \( \Delta \epsilon^2/kT^2c_v^{(cl)} \) of the 3D harmonically trapped ideal Bose gas is smooth unlike its \( c_v \) and has a hump just below the condensation point. The maximum in the hump physically means maximum average deviation of the energy of the system from its average energy both in units of average classical energy. The appearance of such a hump over the classical limit may indicate a discontinuity of \( c_v \) as well as a phase transition around the condensation point \( (T_c) \). Here, by the phrase ‘over the classical limit’ we mean the average deviation of energy is more than the classical average energy divided by the square root of the classical specific heat in the unit of the Boltzmann constant.

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To measure the energy fluctuation, we need to observe energy distribution for different temperatures. From this observation, both the average of the energy and the dispersion of the energy can be easily obtained. Temperature can be measured from the width of the distribution. Thus, one can have experimental data for energy fluctuation (dispersion of the energy distribution) for different temperatures. Momentum distribution for the harmonically trapped (Bose/Fermi) gas has already been observed by applying the technique of releasing the harmonic trap [12,24]. Energy for the harmonically trapped gas has been measured by applying this method [6,9,10]. Although the specific heat is very difficult to measure for the 3D harmonically trapped Bose gas [17], energy fluctuation can be easily measured from energy distribution data by applying the technique of releasing the harmonic trap.

The appearance of a hump in $\Delta \epsilon^2/kT^2 c_v^{(cl)}$ over its classical limit may indicate a discontinuity of $c_v$, is our conjecture.

Bose–Einstein condensation is possible for 3D free Bose gas. But, there is no discontinuity in its specific heat [20]. It is clear from figure 1(a) that, for 3D free Bose gas, there is no hump in $\Delta \epsilon^2/kT^2 c_v^{(cl)}$. There is no question of phase transition as well as discontinuity of $c_v$ for an ideal (or weakly interacting) Fermi gas. Obviously, there is no hump in $\Delta \epsilon^2/kT^2 c_v^{(cl)}$ as is clear in figures 1(b) and (d) for the ideal Fermi gases.

Although Bose–Einstein condensation is possible for 2D harmonically trapped ideal Bose gas, there is no discontinuity of its specific heat [20]. It is clear from figure 2 that, for the 2D harmonically trapped ideal Bose gas, although there is a hump in $\Delta \epsilon^2/kT^2 c_v^{(cl)}$, it is not over the classical limit.

For the $\lambda$ transition of $^4$He, discontinuity of specific heat was observed way back in 1935 [25]. The theoretical explanation of such discontinuity deals with phonon dispersion which effectively simplifies the interacting Bose system to a 3D harmonically trapped ideal Bose gas [26]. Considering this simplification, one can easily check that a hump over the classical limit must exist in $\Delta \epsilon^2/kT^2 c_v^{(cl)}$ for the liquid He-4 below the $\lambda$ point.

Thus, we can verify our conjecture for a certain class of Bose and Fermi systems.

Our conjecture linking the maximum in the hump of the scaled energy fluctuation ($\Delta \epsilon^2/kT^2 c_v^{(cl)}$) and the possible discontinuity of $c_v$ (in units of $c_v^{(cl)}$) can be justified by elaboration through a set of model specific heats as shown in figure 3 for other Bose and
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Figure 3. The dotted lines in (a)–(d) represent model specific heats in units of their respective classical values ($c_v/c_v^{(cl)}$) with respect to scaled temperature ($T/T_c$). Dashed and solid lines respectively represent scaled energy per particle ($\bar{\epsilon}/\sqrt{kT^2c_v^{(cl)}}$) and scaled energy fluctuation ($\Delta\epsilon^2/kT^2c_v^{(cl)}$) corresponding to the respective model specific heats. (a) For Bose system with a model $c_v$. (b) For Bose system with another model $c_v$. (c) For $\lambda$ transition. (d) For superconducting transition.

Fermi systems. The model specific heat per particle ($c_v$), as represented by the dotted line in figure 3(a), is appropriate for a homogeneous Bose system [19]. We represent the average energy per particle ($\bar{\epsilon}$) and approximate energy fluctuation per particle ($\Delta\epsilon^2$) in this figure by the dashed and the solid lines respectively. We obtain the average energy by integrating the model specific heat with respect to the temperature ($\bar{\epsilon} = \int c_v dT$) and the scaled energy fluctuation by simply squaring it ($\Delta\epsilon^2 = \bar{\epsilon}^2 - \bar{\epsilon}^2 \approx k\bar{\epsilon}^2/c_v^{(cl)}$) so that the approximate energy fluctuation becomes exact in the classical limit. Figure 3(a) represents a special case of Bose system with no discontinuity in specific heat at $T = T_c$. We do a similar exercise in figures 3(b)–(d) with different model specific heats with finite discontinuity (e.g. in 3D harmonically trapped Bose gas) at $T_c$ [1], with infinite (logarithmic divergence) discontinuity (e.g. in the $\lambda$ transition of $^4$He) at $T_c$ [26] and with a different finite discontinuity (e.g. in the superconducting/superfluid transition of a strongly interacting Fermi system) [16], respectively. The humps of $\Delta\epsilon^2/kT^2c_v^{(cl)}$s over their respective classical limits and the discontinuities of $c_v$s are simultaneously present only in figures 3(b) and (c) which are appropriate for Bose systems. Although there is a discontinuity of $c_v$ in figure 3(d) which is appropriate for a strongly interacting Fermi gas, there is no hump in $\Delta\epsilon^2/kT^2c_v^{(cl)}$. From these figures we can essentially verify our conjecture and say that, for any thermodynamic system, the maximum in the hump of $\Delta\epsilon^2/kT^2c_v^{(cl)}$ over its classical limit corresponds to a finite or infinite discontinuity of its specific heat $c_v$.

4. Conclusion

Here, we have analytically explored quantum to classical crossover in energy fluctuations mainly for free and harmonically trapped quantum gases. We have illustrated how specific heats differ from energy fluctuations for the entire range of temperature. In this regard, we
have conjectured about the possibility of discontinuity of specific heat in terms of scaled energy fluctuation.

It is impossible to get exact temperature-dependent formulas of chemical potentials for the four systems (3D free and harmonically trapped ideal Bose and Fermi gases), because inverses of polylog functions in equations (4), (5), (8) and (9) do not exist in closed forms. For this reason, we have used approximate temperature-dependent formulas of chemical potentials from [21]. Consequently, plots of $\Delta \epsilon^2$ in figure 1, become approximate except in the region $0 \leq T < T_c$ for the Bose gases. To show how good our approximate results are, we have compared them with their exact graphical solutions in the same figures. In the same figures, we have plotted the classical results just to show the deviations of $\Delta \epsilon^2$ from $kT^2 c_v^{(cl)}$. These deviations clearly illustrate quantum to classical crossover in energy fluctuation ($\Delta \epsilon^2$) of the four systems of our main interest.

Although the approximate values of $\Delta \epsilon^2$, for the Bose and Fermi systems, match well with their exact graphical solutions, it should be mentioned that, for the Fermi systems, the plotting of $\Delta \epsilon^2$ had difficulties, particularly in the low-temperature regime, because of the rapidly oscillatory nature of their polylog functions. For this reason, we have plotted the Sommerfeld’s asymptotic forms in figures 1(b) and (d) only for $T/T_F \leq 0.2$ [19].

It is interesting to note that the scaled energy fluctuation ($\Delta \epsilon^2/kT^2 c_v^{(cl)}$) of the 3D harmonically trapped Bose gas has a hump just below $T_c$. The appearance of such a hump over the classical limit may indicate a discontinuity of $c_v$ as well as a phase transition around the condensation point. The appearance of a hump in $\Delta \epsilon^2/kT^2 c_v^{(cl)}$ over its classical limit which might point to a discontinuity of $c_v$, is our conjecture for any thermodynamic system. We have already verified this conjecture for a number of Bose systems. For ideal Fermi gases, as shown in figures 1(b) and (d), the existence of the hump and discontinuity of specific heat is impossible. In contrast, such possibilities exist for a number of interacting or noninteracting Bose gases. Although the specific heat is very difficult to observe for the 3D harmonically trapped Bose gas [17], energy fluctuation can be easily measured apparently by applying the technique of releasing the harmonic trap [12,27]. Thus, one can predict the discontinuity of specific heat from the existence of the hump over the classical limit.

By $c_v$, we not only mean specific heat at constant (effective [28] or exact) volume $(V)$ but at a constant (average or exact) number of particles $N$.\footnote{Sommerfeld’s asymptotic forms of $\Delta \epsilon^2$s in units of $(kT)^2$ are $\frac{12}{175} \pi^2 + \frac{\pi^2}{2} (T/T_F)^2 + \ldots$ for the free Fermi gas and $\frac{3}{\pi} + \frac{3}{2} (T/T_F)^2 + \ldots$ for the harmonically trapped Fermi gas. See [19] for Sommerfeld expansion.} It should be mentioned that the volume of a harmonically trapped system cannot be precisely defined, although it can be effectively defined for an ultracold situation as $V_{\text{eff}} \sim (\hbar/m\omega)^3/2$ [28]. For this reason, $c_v$, for a trapped system, is very often denoted by $c_N$.

In reality, harmonic traps are not isotropic. In that case, the angular frequency ($\omega$) in all our results should be replaced by the geometric mean of $\omega_x$, $\omega_y$, and $\omega_z$. We have not considered spin degeneracy of particles. Consideration of the same would not change any of our results, because they are intensive variables.

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microcanonical, canonical and grand canonical ensembles of statistical mechanics only in the thermodynamic limit, which has been taken into consideration for the entire calculation of this paper [18]. That is why we have expressed both the energy fluctuation and the specific heat in per-particle form. For a finite system, this relationship must be different for different ensembles [18]. An extension of our result for a finite system of different statistical ensembles would be an interesting problem.

To conclude, this paper illustrates quantum to classical crossover in energy fluctuations for a number of Bose and Fermi systems. The appearance of the hump in the scaled energy fluctuation ($\Delta \epsilon^2 / kT^2 c_v^{(cl)}$) over its classical limit which may indicate a discontinuity of $c_v$, is our conjecture for any (Bose or Fermi) system. The inverse of this statement may not always be true as depicted in figure 3(d). All the calculations in this article have been done keeping in mind the scope of general science readers. The extension of our calculations for other spatial dimensions and interacting cases is pretty straightforward and can be taken up by interested readers. They can verify our conjecture for those cases. Proving our conjecture, of course, is an entirely nontrivial and open problem.

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