Bose-Einstein condensation in real space

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Abstract

We illustrate how Bose-Einstein condensation occurs not only in momentum space but also in coordinate (or real) space. Analogies between the isotherms of a van der Waals gas of extended (or finite-diameter) identical atoms and the point (or zero-diameter) particles of an ideal Bose gas allow one to conclude that, in contrast to the van der Waals case, the volume per particle can go to zero in the pure Bose condensate phase precisely because the particle diameter is zero.

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1 Introduction

It is sometimes said that the Bose-Einstein condensation (BEC) in a perfect or ideal (i.e., without interactions) boson gas is a condensation in momentum space, but not in coordinate or real space like the condensation of vapor into liquid. For example: F. London [1] claims that “...one may say that there is actually a condensation, but only in momentum space, and not in ordinary space, ...[where] no separation of phases is to be noticed.” [2]. The same author speaks of bosons that “...settle in some kind of order in momentum space even at the expense of order in ordinary space.” Landau & Lifshitz [3] state that: “The effect of concentrating the particles in the state $\epsilon = 0$ is often called ‘BEC’. We must emphasize that at best one might perhaps talk about ‘condensation in momentum space.’ Actual condensation certainly does not take place in the gas.” T.L. Hill [4] asserts that “...As it is usually stated, the condensation occurs in momentum space rather than in coordinate space: the condensed phase consists of molecules with zero energy and momentum, and macroscopic de Broglie wavelength.” Fetter & Walecka [5] say this: “…The assembly is ordered in momentum space and not in coordinate space; this phenomenon is called BEC.” B. Maraviglia [6] writes (freely translated) that “…Superfluidity results from the fact that the $^4$He atoms, since they obey BE statistics, can condense not in position but in momentum space....” F. Mandl [7] says “…It differs from the condensation of a vapour into a liquid in that no spatial separation into phases with different properties occurs in BEC.” Finally, D.A. McQuarrie [8] p. 176 concludes “…Therefore the BEC is a first-order process. This is a very unusual first-order transition, however, since the condensed phase has no volume, and the system therefore has a uniform macroscopic density rather than the two different densities that are usually associated with first-order phase transitions. This is often interpreted by saying that the condensation occurs in momentum space rather than coordinate space,.....”

We argue here that Bose-Einstein condensation is a phase transition that occurs in
real space too, which substantiates assertions made by other authors, e.g., R. Becker [9], D. ter Haar [10], K. Huang [11] and D.L. Goodstein [12].

2 Van der Waals gas

The van der Waals equation of state for a classical monatomic gas is

\[ P + a \left( \frac{N}{V} \right)^2 (V - Nb) = Nk_BT, \]

where \( P \) is the pressure, \( V \) the volume, \( T \) the absolute temperature, \( N \) the number of atoms and \( k_B \) Boltzmann’s constant. The effective “excluded volume” per particle [13] is

\[ b = \frac{14}{27} \pi (\sigma)^3 = \frac{2}{3} \pi \sigma^3; \]

where \( \sigma \) is the diameter of each particle, thought of as a hard sphere. It is the reduction in the original volume per particle \( V/N \) due to finite-sized atoms, and was proposed by Clausius for an imperfect gas [13]. In 1873 van der Waals introduced a second correction term (see e.g., Ref. [13]) to the equation of state \( PV = Nk_BT \) of an ideal gas to account for the attractive forces between molecules. In (1) the parameter \( a \) is given by

\[ a \equiv -\frac{4\pi}{2} \int_{\sigma}^{\infty} u(r)r^2dr, \]

where \( u(r) \leq 0 \) is the attractive interaction potential between two atoms whose center-to-center separation is \( r \).

On a \( P-V \) phase diagram (1) exhibits the well-known isotherm loops signaling a vapor to liquid phase transition. One such loop (at a given \( T \)) is shown in Fig. 1 (left panel), where the horizontal plateau connecting points D and B is called the “Maxwell construction.” Loops occur only for isotherms with \( T < T_c \), where \( T_c \) is the critical point where both \( (dP/dV)_T = 0 \) (zero slope) and \( (d^2P/dV^2)_T = 0 \) (change of curvature). These two conditions along with (1) give

\[ P_c = \frac{a}{27b^2}; \quad V_c = 3Nb; \quad T_c = \frac{8a}{27k_Bb} \]
for the critical pressure, volume and temperature.

2.1 BEC as a condensation in real space

For a quantum ideal gas in three dimensions

\[ PV = \frac{2}{3} U, \]

(5)

where \( U \) is the internal energy, if [14] a quadratic energy-momentum (or dispersion) relation holds for each particle. If \( T_c \) is the BEC transition temperature below which there is macroscopic occupation in a given single quantum state (not mix up with critical temperature for a van der Waals gas), the internal energy for the ideal Bose gas for \( T \leq T_c \) (or alternatively \( V \leq V_c \) where \( V \) is the bosonic system volume and \( V_c \) the transition volume) is given in Ref. [11], Eq. (12.62). If we substitute Eqs. (12.55) into (12.62) of Ref. [11] we obtain

\[ \frac{U(V, T)}{N k_B T} = \frac{3}{2} g_{5/2}(1) \left( \frac{T}{T_c} \right)^{3/2} \quad \text{for all } V \leq V_c. \]

(6)

Here \( g_\sigma(z) \) are the so-called Bose functions defined (see p. 506 of Ref. [15]) as

\[ g_\sigma(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty dx \frac{x^{\nu-1}}{z^{-\nu}e^x - 1} = \sum_{l=1}^{\infty} \frac{z^l}{l^\sigma}, \]

(7)

where the “fugacity” \( z \equiv e^{\mu/k_B T} \), with \( \mu \) the boson chemical potential. It is well-known that the series

\[ g_1(1) = \sum_{l=1}^{\infty} \frac{1}{l} \rightarrow \infty \quad \text{when } \sigma \leq 1, \]

since for \( \sigma = 1 \) we have \( g_1(1) = 1 + \frac{1}{2} + \frac{1}{3} + \ldots \), the familiar harmonic series which diverges. On the other hand, for \( \sigma > 1 \)

\[ g_\sigma(1) = \sum_{l=1}^{\infty} \frac{1}{l^\sigma} = \zeta(\sigma), \quad (\sigma > 1), \]

(8)

the Riemann-Zeta function. Thus, (5) and (6) give

\[ P = \frac{2}{3} \frac{U}{V} = \frac{\zeta(5/2)}{\zeta(3/2)} \frac{N k_B T}{V} \left( \frac{T}{T_c} \right)^{3/2} \quad \text{for } V \leq V_c. \]

(9)
If we use for the thermal wavelength $\Lambda \equiv \hbar / \sqrt{2\pi mk_B T}$ and Eq. (10.58) of Ref. [8], the condensate fraction for $T \leq T_c$ is
\[
\frac{N_0(T)}{N} = 1 - \frac{\zeta(3/2)}{8\pi^{3/2}(\hbar^2/2m_B k_B T)^{3/2}(N/V)},
\] (10)
where $N_0(T)$ is the condensate particle number and $N$ the total particle number.

Using the fact that $N_0(T)$ is negligible compared with $N$ when $T \geq T_c$, (10) leads to the well-known BEC $T_c$ formula
\[
T_c = \frac{\hbar^2}{2mk_B} \left[ \frac{8\pi^{3/2}N/V}{\zeta(3/2)} \right]^{2/3} \simeq 3.313 \frac{\hbar^2}{m_B k_B} \left( \frac{N}{V} \right)^{2/3},
\] (11)
since $\zeta(3/2) \simeq 2.612$. Alternatively, from (10) the critical volume $V_c$ below which the BEC appears at any temperature $T$ is
\[
V_c = \frac{(\hbar^2/2m_B k_B T)^{3/2}8\pi^{3/2}N}{\zeta(3/2)}.
\] (12)
Combining (11) with (9) leaves
\[
P = \frac{2}{3} \frac{U}{V} = \frac{\zeta(5/2)}{\sqrt{(2\pi)^3}} \left( \frac{\sqrt{m_B}}{\hbar} \right)^3 (k_B T)^{5/2} \simeq 0.0851 \left( \frac{\sqrt{m_B}}{\hbar} \right)^3 (k_B T)^{5/2},
\] for all $V \leq V_c$, (13)
since $\zeta(5/2) \simeq 1.341$. So, at constant temperature $T$ if we reduce the volume below the value $V_c$ given by (12), the pressure stays constant. This corresponds to the portion BCD of the isotherm depicted in the left panel of Fig. 2. The condensate fraction given by (10), combined with (12), simplifies to
\[
\frac{N_0(T)}{N} = 1 - V/V_c \quad \text{for all} \quad V \leq V_c.
\] (14)

3 Zero volume a sign of real-space condensation

Imagine the ideal Bose gas to be in a cylinder with a movable piston. According to (13), if we push the piston in, decreasing the available volume below $V_c$, given by (12), at constant
temperature $T$, the pressure remains constant. The piston can be pushed in at constant pressure until the two-phase region BCD of Fig. 2 vanishes, i.e., until the condensate particle number $N_0$ equals the total number of particles $N$. Thus, at B the condensate just begins to appear and at D there is 100% condensate.

So, to have BEC in coordinate space the gas must be condensed in momentum space, i.e., a macroscopic number of bosons must be in the ground state. The whole gas occupies zero volume only if the bosons are not moving with different speeds and directions. In the two-phase region, where $N \neq N_0 \neq 0$ the condensed phase consisting of several zero-diameter “droplets” with different particle numbers do not occupy any volume at all. Fig. 2 shows how the volume becomes zero when the bosonic system is entirely condensed at point D; see also (14) when $N = N_0$. However, for a van der Waals fluid when the vapor is entirely condensed into liquid at D, Fig. 1, the volume cannot be zero because of finite particle sizes, and the pressure rises steeply to points E and beyond as the particles are further compressed against each other.

We have apparently fallen into a contradiction since $N = N_0$ usually applies to an ideal bosonic system at $T = 0$, and not to a system along a finite $T$ isotherm. However, we note that in keeping with $N \to N_0$ for some $T \neq 0$, we approach the endpoint of the two-phase region where all the isotherms merge together, in particular the $T_c$ isotherm with which we began as well as the $T = 0$ isotherm.

4 Conclusions

By analogy with a van der Waals gas of zero-diameter atoms we have illustrated how Bose-Einstein Condensation (BEC) occurs not only in momentum space, i.e., $N = N_0$, but also in real space if we applied a external potential. This vindicates the following claims:
• R. Becker [9] p. 120, freely translated: “...the number of atoms in the condensate phase, \( N_0 \), exhibits null volume....”

• D. ter Haar [10] “...one can also consider Einstein condensation to be a condensation in coordinate space.”

• K. Huang [11] p. 290 “...If we examine the equation of state alone, we discern no difference between the BEC and an ordinary gas-liquid condensation....”

• D.L. Goodstein [12] p. 132 “...condensation takes place in real as well as momentum space....”

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Figure 1: **Left:** Schematic sketch of a typical van der Waals isotherm below the critical temperature $T_c$ in the pressure-volume plane (in arbitrary units) for a classical monatomic fluid of finite-sized atoms. The horizontal plateau DCB corresponds to Maxwell’s construction, which separates “stable” from “metastable” states, the latter being separated by an “unstable” portion as shown. **Right:** illustration of how, as the volume of the system is reduced from points A to B to C and D along the chosen isotherm on the left, the vapor condenses first into several “droplets” of different sizes and finally into a single “self-bound” drop, D and E. All points such as E correspond to a sharp rise in pressure because the single drop at D is being compressed as volume is reduced.
Figure 2: **Left:** schematic isotherm in the $P - V$ plane (in arbitrary units) for an ideal Bose gas at some fixed $T = T_c$ as given by (11). Being ideal, the gas consists of zero-diameter particles, i.e. with zero-range interparticle repulsions. **Right:** illustration of how system behaves at different volumes marked as A, B, C and D on the isotherm, with circled dots of varying sizes denoting different sized condensates of zero volume (since the bosons are point particles). 

\[ P \]
\[ \begin{array}{c}
\text{D} \\
\text{C} \\
\text{B} \\
\text{T}_c \\
\text{A} \\
\end{array} \]
\[ V \]
\[ \begin{array}{c}
\text{A} \\
\text{B} \\
\text{C} \\
\text{D} \\
\end{array} \]

- single bosons
- condensate of zero volume