

High density equation of state and condensation of ideal Bose gas using Mayer's generating function

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Received: 21.06.2018

Accepted/Published Online: 20.09.2018

Final Version: 14.12.2018

Abstract: The equation of state of an ideal collection of bosons in the low-density and high-density regime are found using the method of cluster expansion with Mayer's generating function. The saturation density and the other thermodynamic properties are calculated by the application of Mayer's convergence of the partition function. By calculating the value of saturation density from the singularity of the partition function series, the differences between the Mayer series convergence and the virial series convergence for ideal bosons are also established.

Key words: Equation of state, Mayer's convergence, Bose–Einstein condensation

1. Introduction

The equation of state and hence the thermodynamic properties of the ideal quantum systems, like Bose or Fermi, show significant deviation from the ideal behavior [1]. This can be explained with the help of the quantum statistical method by considering the symmetric and antisymmetric properties of the wave functions. Bosons show a peculiar attractive spatial correlation, which can lead to a condensation [2,3] due to the symmetric nature of the wave functions, and fermions show repulsive spatial correlations due to the antisymmetric wave functions. Hence, the equation of state of these systems has the nature of the virial series [4,5]. The radius of convergence of the virial series can be calculated by using the virial coefficients, and the values are obtained from the studies of Widom [6], Fuchs [7], Yang and Lee [8], Jenson and Hemmer [9], and later by Ziff and Kincaid [10]. All the above studies are great theoretical works, giving the connection between the radius of convergence of the virial series in density of ideal bosons with the condensation phenomenon and the connection to the critical density (ρ_0). Fuchs proved that the radius of convergence ($R_0 = \rho_0 \lambda^3$) of ideal Bose gas virial series in density is $12.56 \leq R_0 \leq 27.73$, and the other above mentioned calculations also give values within the Fuchs limits. All these show that the radius of convergence of the virial equation of state in density of ideal Bose gas is far beyond quantum statistically known value of condensation point $\rho_0 \lambda^3 = \zeta\left(\frac{3}{2}\right)$ [4,5,11], where λ is the thermal wave length and $\zeta\left(\frac{3}{2}\right)$ is the Reimann zeta function. All the above studies also show that the radius of convergence of the virial equation of state in density has no relation with the saturation density at Bose–Einstein condensation. Here, we use Mayer cluster expansion and the method of Mayer's convergence of the partition function to find the thermodynamic properties and the cluster expansion equation of state of ideal bosons.

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2. Cluster theory with Mayer’s generating function

Due to the attractive spatial correlation, ideal bosons can be treated as a prototype of an imperfect gas, and in that case, the Hamiltonian H can be represented as

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i,j,i < j} U_{ij}(|\vec{r}_i - \vec{r}_j|), \tag{1}$$

where p_i are the momenta of the particles, m is the mass, and U_{ij} is the interaction potential that depends on the distance $|\vec{r}_i - \vec{r}_j|$ between the particles. The partition function can be written as [1,4,5]

$$Q_N(VT) = \sum_{m_i} \left[\prod_{l=1}^N \left(\frac{b_l V}{\lambda^3} \right)^{m_l} \frac{1}{m_l!} \right], \tag{2}$$

where b_l are the cluster integrals. The cluster integrals b_l can be represented in terms of the irreducible cluster integral β_k [1,4,5] as

$$l^2 b_l = \sum_{n_k} \prod_{k=1}^{l-1} \frac{(l \beta_k)^{n_k}}{n_k!} \tag{3}$$

with the restrictive condition $\sum_{k=1}^{l-1} k n_k = l - 1$. The reverse equation is given in [5]

$$\beta_{l-1} = \sum_{\{m_i\}} (-1)^{\sum_i m_i - 1} \frac{(l - 2 + \sum_i m_i)!}{(l-1)!} \prod_i \frac{(i b_i)^{m_i}}{m_i!}, \tag{4}$$

where the summation goes over all sets $\{m_i\}$ that conforms to the condition $\sum_{i=2}^l (i-1) m_i = l - 1; m_i = 0, 1, 2, \dots$. In Mayer’s theory of cluster expansion, the partition function can be viewed as the expansion coefficient of the generating function $F_M(z)$ [1,12], where

$$F_M(z) = e^{N \sum_l \frac{b_l v z^l}{\lambda^3}} = \sum_n a_n z^n \tag{5}$$

and z is the fugacity. The coefficients a_n for $n=N$ give the N particle partition function. In a complex plane, this series can be represented as a Laurent series and a_N is given by

$$a_N = \frac{1}{2\pi i} \int \frac{dz'}{z'^{N+1}} F_M(z'). \tag{6}$$

Applying Mayer’s convergence method based on the Cauchy Hadamard theorem [1], the coefficient of a series expansion can be related to the radius of convergence of the series [1,12]. In the Hadamard series,

$$H_0^0(z\rho b) = \sum_{N=1}^{\infty} Q_N z^N = \sum_{N=1}^{\infty} a_N z^N. \tag{7}$$

Putting the value of a_N from Eq. (6), we get [1]

$$H_0^0(z, \rho b) = \frac{\sum_{l \geq 1} \frac{b_l y^l}{\rho \lambda^3}}{1 - \sum_{l \geq 1} \frac{b_l y^l}{\rho \lambda^3}}, \tag{8}$$

where $z = y e^{-\sum_{l \geq 1} \frac{b_l y^l}{\rho \lambda^3}}$, and ρ is the number density of particles. The radius of convergence is the value of z at the singularity of $H_0^0(z, \rho b)$, which occurs at $1 - \sum_{l \geq 1} \frac{b_l Y^l}{\rho \lambda^3} = 0$. For this case with $y = \rho \lambda^3$, the radius of convergence R_1 is given by

$$R_1 = Y e^{-\sum_{l \geq 1} \frac{b_l Y^l}{\rho \lambda^3}}. \tag{9}$$

Here,

$$Y = z = (\rho \lambda^3) e^{-\sum_{l \geq 1} k \beta_k (\rho \lambda^3)^k}. \tag{10}$$

From this, it is clear that R_1 is a function of density. Using the relationship between the radius of convergence of this series (R_1) and the partition function, we get the Helmholtz free energy $A = NkT \ln R_1$, and from this, the equation of state can be derived as shown below [1,12]. Substituting R_1 ,

$$A = NkT \left[\ln Y - \frac{1}{\rho \lambda^3} \sum_{l \geq 1} b_l Y^l \right]. \tag{11}$$

Using the equation $\sum_{l \geq 1} b_l Y^l = y \left[1 - \sum_{k=1}^{\infty} \frac{k}{k+1} \beta_k (\rho \lambda^3)^k \right]$ [1], the equation of state is obtained as

$$\frac{P}{kT} = \frac{y}{\lambda^3} \left[1 - \sum_{k=1}^{\infty} \frac{k}{k+1} \beta_k (\rho \lambda^3)^k \right]. \tag{12}$$

Since $H_0^0(z, \rho b)$ is not analytic, it has other singularity when $\sum_{l \geq 1} l^2 b_l Y^l$ is singular. From the relationship between b_l and β_l , we get [1,12,13]

$$\sum_{l \geq 1} l^2 b_l Y_2^l = \frac{y_2}{1 - \sum_{l \geq 1} k \beta_k y_2^k}. \tag{13}$$

It has a singularity at $\sum_{l \geq 1} k \beta_k y_2^k = 1$ and the corresponding radius of convergence R_2 is given by

$$R_2 = Y_2 e^{-\sum_{l \geq 1} \frac{b_l Y_2^l}{\rho \lambda^3}}. \tag{14}$$

Here, $Y_2 = y_2 e^{-\sum_{l \geq 1} \beta_k y_2^k}$, which is independent of density. From this R_2 , the equation of state is obtained as

$$\frac{P}{kT} = \frac{y_2}{\lambda^3} \left[1 - \sum_{k=1}^{\infty} \frac{k}{k+1} \beta_k (y_2)^k \right]. \tag{15}$$

Here, y_2 is the solution of the singularity condition $\sum_{l \geq 1} k \beta_k y_2^k = 1$. Hence, we have an equation of state with pressure independent of density, which may correspond to condensation with $y_2 = \rho_0 \lambda^3$ as a saturation density [1,12,13].

3. Equation of state and Bose–Einstein condensation

To find the saturation density for the Bose–Einstein condensation, we use the singularity condition

$$\sum_{k \geq 1} k \beta_k y_2^k = 1. \tag{16}$$

The values of β_k for ideal bosons can be calculated using Eq. (4) by using the values of reducible cluster integrals, $b_l = \frac{1}{l^{\frac{5}{2}}}$ [4–11]. The calculated values of the irreducible cluster integrals are shown in Table. Substituting these values into the singularity condition Eq. (16), we get

$$y_2 = \rho_0 \lambda^3 = 2.6123753486863197. \tag{17}$$

This is in exact agreement with the quantum statistical calculations [4,5]. In the high-density region, $> \rho_0$, the equation of state can be obtained from R_2 and is given by

$$\frac{P}{kT} = \rho_0 \left[1 - \sum_{k=1}^{\infty} \frac{k}{k+1} \beta_k (\rho_0 \lambda^3)^k \right], \tag{18}$$

where ρ_0 can be considered as the saturation density.

Table. Values of irreducible cluster integrals.

β_1	$3.535533905932738 \times 10^{-1}$
β_2	$4.950089729875255 \times 10^{-3}$
β_3	$1.483857712887233 \times 10^{-4}$
β_4	$4.425630118996707 \times 10^{-6}$
β_5	$1.006361644748311 \times 10^{-7}$
β_6	$4.272405418573282 \times 10^{-10}$
β_7	$-1.174926531930948 \times 10^{-10}$
β_8	$-7.936985074019214 \times 10^{-12}$
β_9	$-2.984404389769838 \times 10^{-13}$
β_{10}	$-4.462901839886734 \times 10^{-15}$
β_{11}	$3.051320702281767 \times 10^{-16}$
β_{12}	$3.074464622622820 \times 10^{-17}$
β_{13}	$1.506932077279162 \times 10^{-18}$
β_{14}	$3.889612806544511 \times 10^{-20}$

Taking the difference in specific volume between two phases as $\Delta v_s = v_0$ [4], we have

$$\frac{dP_0}{dT} = \frac{L}{T \Delta v_s}, \tag{19}$$

where L is the latent heat given by

$$L = \frac{5kT}{2} 0.5135124467952001, \tag{20}$$

which proves the first order phase transition nature of Bose–Einstein condensation. Fugacity can be calculated at the beginning of phase transition and is obtained as $z = 0.999999999999998 \approx 1$ at critical density so that the value of chemical potential and Gibbs free energy are zero. The dependence of fugacity to the number density is plotted and is shown in Figure 1. When the density increases, the value of radius of convergence R_1 also increases. At the saturation density, the radius of convergence R_1 becomes equal to R_2 . After the saturation density, the radius of convergence can be calculated by Eq. (14). The numerical value of the radius of convergence at the saturation density is obtained as

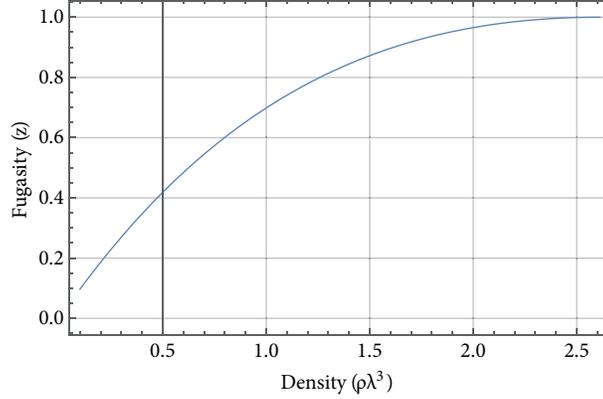


Figure 1. Variation of fugacity with density.

$$R_2 = 0.59839006994955. \tag{21}$$

The value of Helmholtz free energy at saturation density is given by

$$A = NkT \ln(0.59839006994955). \tag{22}$$

Simplifying,

$$A = -NkT(0.5135124467952). \tag{23}$$

When density increases, after the saturation density, the radius of convergence reaches 1 (one) as shown in Figure 2. This shows that the value of Helmholtz free energy is a minimum at maximum density of Bose–Einstein condensation. The variation of R_1 and R_2 with density are also shown in Figure 2. The equations of states given by Eqs. (12) and (18) in the low- and high-density regions are shown in Figure 3. The horizontal portions in the isotherms, where the pressure is independent of volume, is the region of condensation. The other thermodynamic quantities like internal energy U , specific heat C_V , and entropy S are also obtained and are given below.

$$U = -NkT^2 \frac{\partial \ln R_2}{\partial T}. \tag{24}$$

Substituting R_2 , we get

$$U = \frac{3 NkT}{2 \rho \lambda^3} 1.3414872572509124. \tag{25}$$

The specific heat is given by

$$C_V = \frac{15Nk}{4\rho\lambda^3} y_2 \left(1 - \sum_k \frac{k}{k+1} \beta_k y_2^k \right). \tag{26}$$

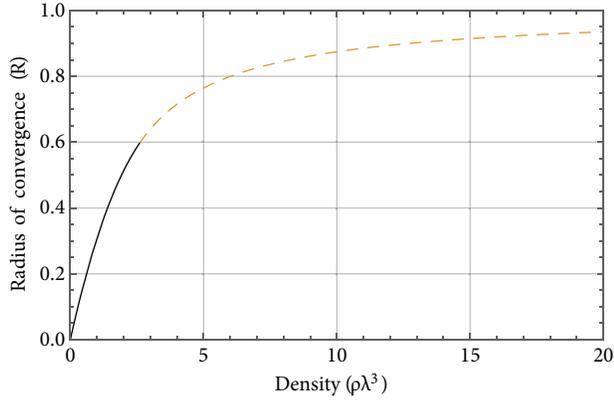


Figure 2. Variation of radius of convergence with density.

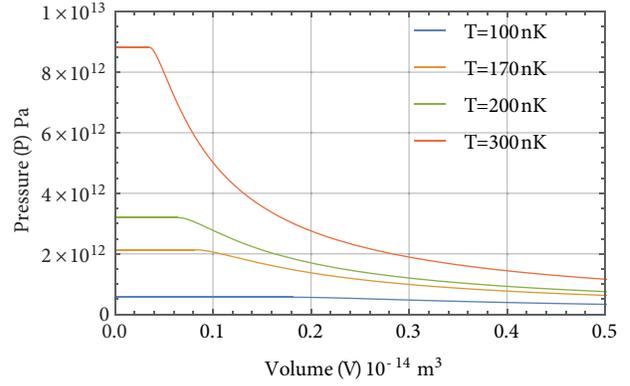


Figure 3. Isotherms of ideal Bose gas.

Substituting the values, we get

$$C_V = \frac{15Nk}{4\rho\lambda^3} 1.3414872572509124 \quad (27)$$

and entropy

$$S = \frac{5Nk}{2\rho\lambda^3} y_2 \left(1 - \sum_k \frac{k}{k+1} \beta_k y_2^k \right). \quad (28)$$

Substituting the values,

$$S = \frac{5Nk}{2\rho\lambda^3} 1.3414872572509124. \quad (29)$$

Thus, by the use of the generating function given by Mayer and studying the radius of convergence of the series, all the thermodynamic properties of the ideal bosons in the region of condensation are calculated, and the results show an exact agreement with the quantum statistical calculations. In Yang and Lee's theory [14], the first order phase transition occurs when the saturation density corresponds to the singularity of the partition function series. Our analysis gives proof for the first order character of Bose–Einstein condensation by following Lee and Yang's theory.

4. Discussion and conclusions

Bose–Einstein condensation phenomenon was discussed using cluster expansion and Mayer's convergence method using the generating function provided by Mayer. It was shown that Mayer's series converges with a radius of convergence which is different from the virial series convergence, and the condensation occurs in a region where the series of the partition function diverges and the value of saturation density can be found from the singularity condition of the Hadamard series. The equations of states for ideal bosons in the high-density and low-density regions were obtained. The saturation number density and other thermodynamic properties were also calculated, and the results matched well with the quantum statistical calculations. The isotherms for this first order phase transition were drawn and the horizontal region of the isotherm where pressure was independent of volume showed the region of phase transition. Our analysis proves that cluster expansion and Mayer's convergence with Mayer's generating function can be effectively used to calculate the thermodynamic properties of ideal Bose system at condensation.

Acknowledgment

Suresh Thelakkadan Puthiyaveetil wishes to acknowledge the University Grants Commission for the assistance given under the Faculty Development Programme.

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