Pramana – J. Phys. (2019) 92:45
https://doi.org/10.1007/s12043-018-1699-6

Mayer's convergence and thermodynamics of ideal Bose gas

T P SURESH[1], K M UDAYANANDAN[2],* and VISHNU MAYYA BANNUR[3]

[1]School of Pure and Applied Physics, Kannur University, Swami Anandatheertha Campus, Payyannur 670 327, India
[2]Nehru Arts and Science College, Kanhangad 671 314, India
[3]University of Calicut, Thenhipalam 673 635, India
*Corresponding author. E-mail: udayanandan@gmail.com

MS received 9 June 2018; revised 20 July 2018; accepted 25 July 2018; published online 4 February 2019

Abstract. The equation of state for a collection of ideal bosons in both the low-density and high-density regions is found using the method of cluster expansion with a new generating function. The importance of the radius of convergence in the cluster expansion and its connection to the Bose–Einstein condensation phenomenon are studied. The radius of convergence of the partition function is calculated and the values of critical density, fugacity and other thermodynamic properties at condensation are obtained using Mayer's convergence method.

Keywords. Cluster expansion; equation of state; Bose–Einstein condensation; radius of convergence.

PACS Nos 05.20.y; 05.70.Ce; 05.70.–a; 05.70.Fh

1. Introduction

Quantum mechanically, ideal bosons possess an attractive spatial correlation, which leads to the important phenomenon of Bose–Einstein condensation (BEC) [1,2]. Due to this attractive spatial correlation, an ideal Bose gas has been used as a prototype of an imperfect gas for the analysis of divergence of virial series in density and its connection to the condensation [3,4]. There are legendary works by Widom [3], Fuchs [4], Yang and Lee [5], Jenson and Hemmer [6] and Ziff and Kinakid [7] about the radius of convergence of virial series of ideal bosons and its relation with BEC. The radius of convergence of the virial series in density is the maximum value of the density in the series for which the series converges, and that value is considered as saturation density (ρ_0). But from the above-mentioned studies [4,7], the virial series in density is found to be converging into the mixed phase region with the densities lying between $12.56 \le \rho_0\lambda^3 \le 27.73$, which is far beyond the known value of saturation density $\rho_0\lambda^3 = 2.612375348685417$ [4–6], where λ is the thermal wavelength. These results show that, determining the saturation density at the condensation point from the value of the radius of convergence of the virial series in density, is not exact. So, in this paper, we investigate how the Mayer's convergence [8] with a new generating function for partition function [9–11] can be applied for ideal bosons to find exact saturation density and thermodynamic properties.

2. Representation of partition function with a new generating function

For any non-ideal gas, the Hamiltonian 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 m is the mass and p_i are the momenta of the particles. U_{ij} is the pair potential between the particles that depends on the distance $|\vec{r}_i - \vec{r}_j|$. Using this Hamiltonian, the partition function is obtained as [8]

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

where b_l are the cluster integrals. The cluster integrals b_l are related to the irreducible cluster integrals β_l as

$$\beta_{l-1} = \sum_{\{m_i\}} (-1)^{\sum_i m_i - 1} \frac{(l-2+\sum_i m_i)!}{(l-1)!} \prod_i \frac{(ib_i)^{m_i}}{m_i!}, \tag{3}$$

where the summation is over all sets $\{m_i\}$ that conform the condition

$$\sum_{i=2}^{l}(i-1)\,m_i = l-1, \quad m_i = 0, 1, 2, \ldots .$$

To find the equation of state and to get an idea about the condensation, Mayer's convergence method was used [8,11] based on Mayer's generating function. In Mayer's method [8], the generating function of the partition function was in terms of cluster integrals b_l and one more relation connecting the cluster integral and irreducible cluster integral was needed to get the equation of state. Ushcats [9,10] developed a new generating function for the partition function in terms of irreducible cluster integrals. With this generating function it is possible to find the equation of state not limited by the convergence radius of the density. Bannur [11] gave a rigorous proof for the generating function of partition function and arrived at the same formalism of Ushcats. These developments helped to formulate the partition function and the equation of state is not limited by the low-density condition $\sum_k k\beta_k\rho^k < 1$. The new generating function for the cluster expansion of the partition function is given by [9–11]

$$F(y) = \left(1-\sum_k k\beta_k y^k\right) \mathrm{e}^{N\left[\frac{y}{\rho\lambda^3}\left(1-\sum_k \frac{k}{k+1}\beta_k y^k\right)+\sum_k \beta_k y^k\right]} = \sum_n a_n y^n. \tag{4}$$

The coefficients a_n for $n = N$ give the partition function. So $F(y)$ can be viewed as the generating function for the partition function Q_N. Using Mayer's convergence method, which is based on the Cauchy–Hadamard theorem [8], the radius of convergence can be found as

$$R = \lim_{N\to\infty}(a_N)^{-1/N}. \tag{5}$$

In the complex plane of y, we have

$$a_N = Q_N = \frac{1}{2\pi i}\oint \frac{F(y)\,\mathrm{d}y}{y^{N+1}}. \tag{6}$$

With the values of a_N, defining a series $H(y,\beta)$ as [8,11]

$$H(y,\beta) = \sum_{N=1}^{\infty} a_N y^N = \sum_{N=1}^{\infty} Q_N y^N, \tag{7}$$

we get [8,11]

$$H(y,\beta) = \frac{1}{1-(Y/\rho\lambda^3)}. \tag{8}$$

Here Y is related to y as [11]

$$y = Y\mathrm{e}^{-\left[\frac{Y}{\rho\lambda^3}\left(1-\sum_k \frac{k}{k+1}\beta_k Y^k\right)+\sum_k \beta_k Y^k\right]}. \tag{9}$$

This series will show a singularity at $Y = \rho\lambda^3$. Substituting this value in eq. (9), the radius of convergence R_1 of the Hadamard series, which is the value of y, for which the series diverges is obtained as

$$R_1 = (\rho\lambda^3)\mathrm{e}^{-\left[1+\sum_k \frac{1}{k+1}\beta_k(\rho\lambda^3)^k\right]}. \tag{10}$$

From eq. (5), we get $\ln Q_N = -N\ln R$. Then, the Helmholtz free energy A is

$$A = NkT\ln R_1.$$

Substituting the value of R_1 from eq. (10)

$$A = NkT\left[\ln(\rho\lambda^3) - \left(1+\sum_k \frac{1}{k+1}\beta_k(\rho\lambda^3)^k\right)\right]. \tag{11}$$

From the Helmholtz energy, the pressure P is

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

This is similar to the equation of state obtained in the low-density region [8].

3. Singularity of partition function and condensation

With the use of the new generating function given by eq. (4), the low-density virial equation of state can be derived from the singularity at $Y = \rho\lambda^3$ as given in eq. (12). To get the equation of state at high density and to describe condensation, we make use of other singularities of Hadamard series. As $H(y,\beta)$ is not analytic, its derivative will give

$$\frac{\partial H(y,\beta)}{\partial y} = \frac{Y/\rho\lambda^3}{y(1-(Y/\rho\lambda^3))}\frac{1}{\left(1-\sum_k k\beta_k(Y)^k\right)}. \tag{13}$$

This series shows another singularity at $\sum_k k\beta_k(Y)^k = 1$, with $Y = Y_0$ as a constant. At the point of condensation, we get

$$\sum_k k\beta_k(\rho_0\lambda^3)^k = 1, \tag{14}$$

where ρ_0 is a constant at a particular temperature which can be taken as the saturation density for condensation. Thus, if the density of the system exceeds this constant density ρ_0, the value of the radius of convergence R_2 for this singularity can be obtained from eq. (9) and is given by

$$R_2 = (Y_0)\mathrm{e}^{-\frac{Y_0}{\rho}\left[1-\sum_k \frac{k}{k+1}\beta_k(Y_0)^k\right]-\sum_k \beta_k(Y_0)^k}. \tag{15}$$

Substituting the value of Y_0

$$R_2 = (\rho_0\lambda^3)\mathrm{e}^{-\frac{\rho_0}{\rho}\left[1-\sum_k \frac{k}{k+1}\beta_k(\rho_0\lambda^3)^k\right]-\sum_k \beta_k(\rho_0\lambda^3)^k}. \tag{16}$$

Then the Helmholtz free energy is given by

$$A = NkT \ln(\rho_0\lambda^3) + NkT\left[-\frac{\rho_0}{\rho}\left(1-\sum_k \frac{k}{k+1}\beta_k(\rho_0\lambda^3)^k\right) - \sum_k \beta_k(\rho_0\lambda^3)^k\right]. \tag{17}$$

3.1 *Calculation of thermodynamic properties at condensation*

From the value of the Helmholtz free energy given by eq. (17), the pressure is

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

This shows that the pressure is independent of density or volume, which is a characteristic of first-order phase transition. Thus, from eqs (12) and (18), the cluster expansion equation of state acquires a piecewise form

$$P = \begin{cases} \rho kT\left[1-\sum_k \frac{k}{k+1}\beta_k(\rho\lambda^3)^k\right], & \rho \le \rho_0, \\ \rho_0 kT\left[1-\sum_k \frac{k}{k+1}\beta_k(\rho_0\lambda^3)^k\right], & \rho \ge \rho_0 \end{cases} \tag{19}$$

and these equations are exactly the same as those obtained in [9–11] for imperfect gases. To calculate the saturation density and other thermodynamic properties at the condensation region of ideal Bose gas using this new formalism, irreducible cluster integrals β_k are calculated (table 1) using eq. (3) and using the known values of the reducible cluster integrals b_l for bosons [4–7,12–14], where b_l are given by

$$b_l = \frac{1}{l^{5/2}}. \tag{20}$$

Substituting these values of β_k into the singularity condition given by eq. (14), we get

$$\rho_0\lambda^3 = 2.612375348685417. \tag{21}$$

This saturation density value matches with the quantum statistical calculations using the Bose–Einstein distribution function. Thus, this Mayer's convergence model predicts the exact value of saturation density of BEC, while the virial series convergence model failed to do so. Substituting the values of β_k and $\rho_0\lambda^3$, the value of pressure at condensation is obtained from eq. (18) as

Table 1. 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}	$3.889612806544511 \times 10^{-20}$

$$P_0 = 1.3414872572509124 \times \frac{kT}{\lambda^3}. \tag{22}$$

This value can be treated as a saturation vapour pressure. When two phases coexist during the phase transition of ideal bosons, the gas phase has a specific volume v_s and the condensed phase has specific volume zero [12]. Then the difference in specific volume between two phases is Δv_s. Then, for a first-order phase transition, we have

$$\frac{\mathrm{d}P_0}{\mathrm{d}T} = \frac{L}{T\Delta v_\mathrm{s}}, \tag{23}$$

where L gives the value of latent heat during the phase transition. Latent heat L is obtained as

$$L = \frac{5kT}{2} \times 0.5135124467952001. \tag{24}$$

This also establishes the first-order phase transition character of BEC, obeying exactly the Clausius–Clapeyron equation [12,13]. The equations of chemical potential μ and fugacity z are obtained as

$$\mu = kT\left[\ln(\rho_0\lambda^3) - \sum_k \beta_k(\rho_0\lambda^3)^k\right], \tag{25}$$

$$z = (\rho_0\lambda^3)\mathrm{e}^{-\sum_k \beta_k(\rho_0\lambda^3)^k}. \tag{26}$$

The same results have been obtained in a different manner [15–17] by considering the virial expansions in powers of fugacity. Substituting the values of $\rho_0\lambda^3$ and β_k, we get fugacity, $z = 0.999999999999998 \approx 1$, which is the expected value based on the conventional method and it shows that the value of chemical potential is zero and hence the Gibbs free energy is also zero.

From eq. (14), the value of chemical potential is obtained as

$$\mu = kT\left(\ln(\rho\lambda^3) - \sum_k \beta_k(\rho\lambda^3)\right) \tag{27}$$

and fugacity z is

$$z = \rho\lambda^3 \mathrm{e}^{-\sum_k \beta_k(\rho\lambda^3)^k}. \tag{28}$$

This equation shows that the fugacity is a function of number density and temperature. The variation of fugacity with the number density is plotted in figure 1. The value of fugacity reaches 1 when the density becomes $\rho\lambda^3 = 2.612375348685417$. It is interesting to note that when the density increases, the value of radius of convergence R_1 also increases. When the density reaches $Y_0 = \rho_0\lambda^3 = 2.612375348685417$, which is the saturation density for the beginning of BEC, the radius of convergence is $R_1 = R_2$. When the density of the system exceeds the saturation density, the radius of convergence is given by eq. (16). Using eq. (16) and irreducible cluster integrals, we can calculate the numerical value of radius of convergence at the density 2.612375348685417 and we get

$$R_2 = 0.59839006994955. \tag{29}$$

Then the value of the Helmholtz free energy at $\rho_0\lambda^3$ is given by

$$A = NkT \ln 0.59839006994955, \tag{30}$$

which is

$$A = -NkT(0.5135124467952). \tag{31}$$

When the density is very large compared to $\rho_0\lambda^3$, figure 2 shows the radius of convergence reaching towards a constant value of 1 and this proves that the Helmholtz free energy goes to a minimum at maximum density of Bose–Einstein condensation. The variation of R_1 with density up to the saturation density and the variation of R_2 after the saturation density are also shown in figure 2. Isotherms of ideal Bose gas are plotted according to eq. (19) and are shown in figure 3. The nature of isotherms with the pressure keeps a constant value after saturation density, which show the region of phase transition. The values of internal energy U, specific heat C_V and entropy S are also obtained and are given below:

$$U = \frac{3}{2}\frac{NkT}{\rho\lambda^3} \times 1.3414872572509124. \tag{32}$$

The specific heat is given by

$$C_V = \frac{15Nk}{4\rho\lambda^3} Y_0 \left(1 - \sum_k \frac{k}{k+1}\beta_k Y_0^k\right) \tag{33}$$

and the entropy

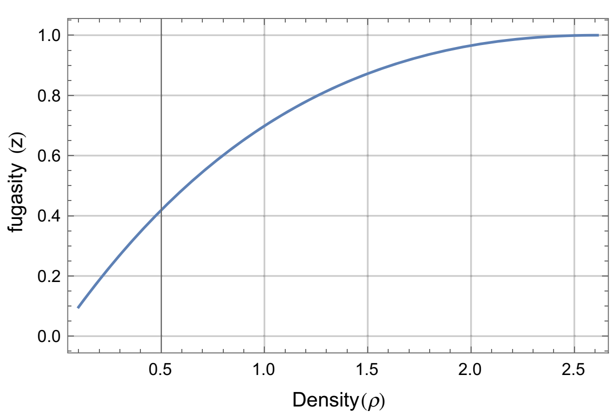

Figure 1. Variation of fugacity of ideal Bose gas with density.

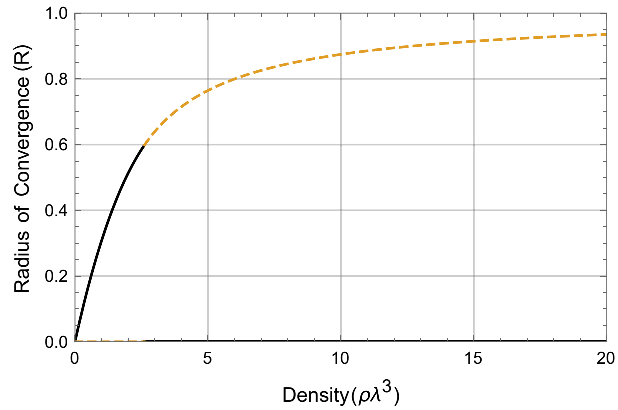

Figure 2. Variation of radius of convergence with density (the solid line shows the variation of R_1 and dashed line shows the variation of R_2 with density).

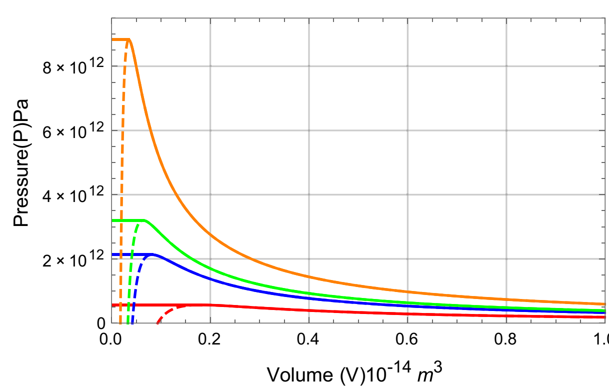

Figure 3. Isotherms for ideal Bose gas. Dashed line shows Mayer's virial relation and solid lines show high-density condensation regime for temperatures 100 nK (red line), 170 nK (blue line), 200 nK (green line) and 300 nK (orange line).

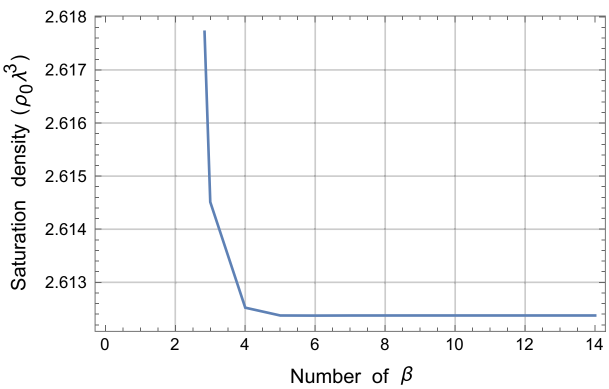

Figure 4. Variation of saturation density with number of irreducible integrals (β_k) used.

$$S = \frac{5Nk}{2\rho\lambda^3} Y_0 \left(1 - \sum_k \frac{k}{k+1} \beta_k Y_0^k\right). \tag{34}$$

Substituting the values of Y_0 and β_k we get

$$C_V = \frac{15Nk}{4\rho\lambda^3} \times 1.3414872572509124 \tag{35}$$

and

$$S = \frac{5Nk}{2\rho\lambda^3} \times 1.3414872572509124. \tag{36}$$

All these calculations show that the equations of internal energy, specific heat and entropy of ideal Bose gas in the condensed region obtained using the new method of cluster expansion match exactly with the quantum statistical calculations.

In order to get an idea about how the saturation density depends on the number of irreducible cluster integrals used for the calculations, we plotted the variation of saturation density with the number of irreducible cluster integrals used and is shown in figure 4. This figure shows that the saturation density keeps an almost constant value when the number of irreducible integrals used increases. From this it is clear that there is a fast convergence of the results with the addition of higher power terms of β_k.

4. Discussion

According to the Cauchy–Hadamard theorem and Mayer's convergence, the coefficients of a series expansion are related to the radius of convergence of the series and the partition function can be calculated from it. As explained in §3, the singularity point of the Hadamard series provides the value of the saturation density as in eq. (21) and the corresponding radius of convergence of the series can be calculated using eq. (16). In this theory, R_2 gives the value of thermodynamic properties at condensation point. This shows that the Mayer's series converges with a radius of convergence which is different from the virial series convergence. In Mayer's cluster expansion series, the derivative of the logarithm of the partition function diverges much faster, so that the logarithm of the partition function actually does not diverge [15–17]. Jenssen and Hemmer [6] found the radius of convergence of the virial series in the density. But here in this analysis, the radius of convergence is associated with the series of the partition function itself. Thus, our study gives an alternative proof for the first-order character of BEC and its thermodynamic properties using the Mayer's convergence method.

5. Conclusions

The Bose–Einstein condensation, which is purely a quantum mechanical phenomenon, is discussed using the cluster expansion and Mayer's convergence method with a new generating function. The equation of state for bosons in the high-density and low-density regions is obtained using this new generating function which is not possible with the conventional virial expansion due to the low-density approximation. The differences between Mayer's series convergence and virial series convergence for ideal bosons are also established. The saturation number density for the Bose–Einstein condensation and other thermodynamic quantities is calculated from the properties of Hadamard series and Mayer's convergence, which matches well with the quantum statistical calculations. The nature of the isotherms clearly shows a phase transition as the pressure takes a constant value when the density exceeds the saturation density. The variation in the saturation density value with the number of irreducible integrals used is also discussed. Our analysis provides a new way of investigating the Bose–Einstein condensation, using Mayer's convergence and cluster expansion methods.

Acknowledgements

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

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