Equation of states for Bose-Einstein condensation Masatsugu Sei Suzuki Department of Physics, SUNY at Binghamton (Date: November 06, 2018)

Here we discuss the equation of states for the Bose-Einstein condensation. We use the following integrals.

$$\frac{2}{\sqrt{\pi}} \int_{0}^{\infty} dx \frac{\sqrt{x}}{\frac{1}{z}e^{x} - 1} = \zeta_{3/2}(z) = \text{PolyLog}[\frac{3}{2}, z]$$

$$\frac{2}{\sqrt{\pi}} \int_{0}^{\infty} dx \frac{x^{3/2}}{\frac{1}{z}e^{x} - 1} = \frac{3}{2} \zeta_{5/2}(z) = \frac{3}{2} \text{PolyLog}[\frac{5}{2}, z]$$

$$\int_{0}^{\infty} dx \frac{x^{1/2}}{\frac{1}{z}e^{x} - 1} = \frac{\sqrt{\pi}}{2} \zeta_{3/2}(z) = \frac{\sqrt{\pi}}{2} \text{PolyLog}[\frac{3}{2}, z]$$

$$\int_{0}^{\infty} dx \frac{x^{3/2}}{\frac{1}{z}e^{x} - 1} = \frac{3\sqrt{\pi}}{4} \zeta_{3/2}(z) = \frac{3\sqrt{\pi}}{4} \text{PolyLog}[\frac{3}{2}, z]$$

with z as the fugacity, and

$$P = gn_{Q}(k_{B}T)\varsigma_{5/2}(z), \qquad N(T,z) = gVn_{Q}\varsigma_{3/2}(z).$$

$$\varsigma_{5/2}(z=1) = \varsigma(\frac{5}{2}) = 1.34149, \qquad \varsigma_{3/2}(z=1) = \varsigma(\frac{3}{2}) = 2.61238$$

$$\frac{\varsigma_{5/2}(z=1)}{\varsigma_{3/2}(z=1)} = 0.513512447$$

Definition:

$$\varsigma_{5/2}(z) = \operatorname{PolyLog}[\frac{5}{2}, z], \qquad \varsigma_{3/2}(z) = \operatorname{PolyLog}[\frac{3}{2}, z]$$

((Series expansion))

$$\varsigma_{3/2}(z) = z + \frac{z^2}{2\sqrt{2}} + \frac{z^3}{3\sqrt{3}} + \frac{z^4}{8} + \frac{z^5}{5\sqrt{5}} + \dots \qquad \text{around} \ z = 0$$

$$\varsigma_{5/2}(z) = z + \frac{z^2}{4\sqrt{2}} + \frac{z^3}{9\sqrt{3}} + \frac{z^4}{32} + \frac{z^5}{25\sqrt{5}} + \dots \qquad \text{around} \ z = 0$$

((Derivative))

$$\frac{d}{dz}\varsigma_{3/2}(z) = \frac{1}{z}\varsigma_{1/2}(z), \qquad \frac{d}{dz}\varsigma_{5/2}(z) = \frac{1}{z}\varsigma_{3/2}(z)$$

((Note))

The condition for the occurrence of Bose-Einstein condensation is that

 $\lambda_{th} > (2.6138)^{1/3} d_{av} = 1.3775 d_{av}$

This form tells that the thermal de Broglie wavelength λ_{th} must exceed 1.38 times the average interatomic separation. In short, the thermal wave packets must overlap substantially. The Bose-Einstein condensation occurs below

$$T_E(n) = \frac{2\pi\hbar^2}{mk_B} \left(\frac{n}{2.612}\right)^{2/3}.$$

Since

$$n = gn_Q(T_E)\varsigma_{3/2}(z=1) = 2.61238gn_Q(T_E)$$

with g = 1.

(i) The average interatomic separation between atoms, d

$$n = \frac{1}{d^3}$$
 or $d = \frac{1}{n^{1/3}}$

where *n* is the number density *n*:

(ii) The thermal de Broglie wave length λ_{th}

$$n_{Q}(T) = \frac{1}{\lambda_{th}^{3}} = \left(\frac{mk_{B}T}{2\pi\hbar^{2}}\right)^{3/2}$$
(quantum concentration)
$$\lambda_{th} = \left(\frac{2\pi\hbar^{2}}{mk_{B}T}\right)^{1/2}$$
(de Broglie wavelength)

1. Pressure and number for the Boson system The pressure is given by

 $P = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu}$

The grand potential Φ_G is

$$\Phi_{G} = k_{B}T \sum_{k} \ln[1 - e^{-\beta(\varepsilon_{k} - \mu)}]$$
$$= k_{B}T \frac{gV}{(2\pi)^{3}} \int d^{3}k \ln[1 - e^{-\beta(\varepsilon_{k} - \mu)}]$$
$$= k_{B}T \frac{gV}{(2\pi)^{3}} 4\pi \int_{0}^{\infty} k^{2}dk \ln(1 - ze^{-\beta\varepsilon_{k}})$$

We use the following dispersion relation

$$\varepsilon_k = \varepsilon = \frac{\hbar^2}{2m}k^2, \qquad k = \left(\frac{2m}{\hbar^2}\right)^{1/2}\sqrt{\varepsilon}, \qquad dk = \frac{1}{2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\frac{1}{\sqrt{\varepsilon}}$$

So we have

$$\Phi_{G} = -PV$$

$$= k_{B}T \frac{gV}{(2\pi)^{3}} \frac{4\pi}{2} \left(\frac{2m}{\hbar^{2}}\right)^{3/2} \int_{0}^{\infty} \sqrt{\varepsilon} d\varepsilon \ln(1 - ze^{-\beta\varepsilon})$$

$$= k_{B}T \frac{gV}{4\pi^{2}} \left(\frac{2m}{\hbar^{2}}\right)^{3/2} \int_{0}^{\infty} \sqrt{\varepsilon} d\varepsilon \ln(1 - ze^{-\beta\varepsilon})$$

The integration by parts gives

$$\begin{split} \Phi_{G} &= -\frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2\pi^{2}\hbar^{3}}} \int_{0}^{\infty} \frac{\varepsilon^{3/2}}{\frac{1}{z}e^{\beta\varepsilon} - 1} d\varepsilon \\ &= -\frac{2}{3} \frac{gVm^{3/2}}{\sqrt{2\pi^{2}\hbar^{3}}} (k_{B}T)^{5/2} \int_{0}^{\infty} \frac{x^{3/2}}{\frac{1}{z}e^{x} - 1} dx \\ &= -\frac{2}{3} \frac{gV(2\pi)^{3/2}}{\sqrt{2\pi^{2}}} (\frac{mk_{B}T}{2\pi\hbar^{2}})^{3/2} (k_{B}T) \int_{0}^{\infty} \frac{x^{3/2}}{\frac{1}{z}e^{x} - 1} dx \\ &= -\frac{2}{3} gVn_{Q}(k_{B}T) \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} \frac{x^{3/2}}{\frac{1}{z}e^{x} - 1} dx \\ &= -gVn_{Q}(k_{B}T)\varsigma_{5/2}(z) \end{split}$$

Then the pressure P is obtained as

$$P = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu} = gn_Q(k_B T)\varsigma_{5/2}(z)$$

This is valid in both the gas and the condensed phase, because particles with zero momentum do not contribute to the pressure. Since z = 1 in the condensed phase, the pressure becomes independent of number density.

$$\frac{P}{k_B T} = g n_Q(T) \varsigma_{5/2}(z=1)$$

The number is given by

$$N(T,z) = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V}$$
$$= \frac{gVm^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty \frac{\sqrt{\varepsilon}d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}$$
$$= gVn_Q \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{x}dx}{\frac{1}{z}e^x - 1}$$
$$= gVn_Q \zeta_{3/2}(z)$$

The number density is given by

$$n(T,z) = \frac{N(T,z)}{V} = gn_{\varrho}\varsigma_{3/2}(z)$$

where $n_{\rm Q}$ is the quantum concentration,

$$n_{\mathcal{Q}} = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} = \left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}$$

We note that

$$n(T, z = 1) = 2.61238 \ n_Q(T)$$

The total particle number is a sum of $n(T, z = 1) + n_0$, where n_0 is the number density in the ground state.

$$n = n_0 + n(T, z = 1)$$



The Bose-Einstein condensation temperature (Einstein temperature) is defined as

$$n = n(T_E(n), z = 1) = 2.61238n_O(T = T_E(n))$$

So $T_E(n)$ depends on the number density as



Fig. Plot of
$$\tilde{T}_E(n) = T_E(n) \frac{mk_B (2.61238)^{3/2}}{2\pi\hbar^2}$$
 as a function of the number density *n*.

The number density n_0 in the BE condensed phase is expressed by

$$n_{0}(n,T) = n - n(T, z = 1)$$

= $n[1 - \frac{n(T, z = 1)}{n(T_{E}(n), z = 1)}]$
= $n[1 - \frac{n_{Q}(T)}{n_{Q}(T_{E}(n))}]$
= $n[1 - \left(\frac{T}{T_{E}(n)}\right)^{3/2}]$

In the vicinity of $T_E(n)$, $n_0(n,T)$ can be approximated by

$$n_0(n,T) \approx -\frac{3n}{2T_E(n)} [T - T_E(n)] = \frac{3n}{2T_E(n)} [T_E(n) - T] \qquad (\text{critical behavior})$$

((Note)) Taylor expansion

$$n_0(n,T = T_E(n)) = 0$$
, , $\frac{d}{dT}n_0(n,T = T_E(n)) = -\frac{3}{2}\frac{n}{T_E(n)}$

3. Calculation of the internal energy U

$$U = \sum_{k} \varepsilon_{k} \langle n_{k} \rangle$$

= $\frac{gV}{(2\pi)^{3}} 4\pi \int_{0}^{\infty} k^{2} dk \frac{\varepsilon_{k}}{e^{\beta(\varepsilon_{k}-\mu)} - 1}$
= $\frac{gV}{4\pi^{2}} \left(\frac{2m}{\hbar^{2}}\right)^{3/2} \int_{0}^{\infty} \frac{\varepsilon^{3/2} d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}$
= $\frac{gVm^{3/2}}{\sqrt{2}\pi^{2}\hbar^{3}} \int_{0}^{\infty} \frac{\varepsilon^{3/2} d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1}$

or

$$\frac{U}{V} = \frac{3}{2} gn_{Q}(k_{B}T)\varsigma_{5/2}(z)$$

$$u = \frac{U}{V} = \begin{cases} \frac{3}{2} k_{B}T \frac{\varsigma_{5/2}(z)}{\varsigma_{3/2}(z)} & (T \ge T_{E}) \\ \frac{3}{2} k_{B}T \frac{\varsigma_{5/2}(z=1)}{\varsigma_{3/2}(z=1)} \left(\frac{T}{T_{c}}\right)^{3/2} & (T \le T_{E}) \end{cases}$$

So U is related to the grand potential as

$$U = -\frac{3}{2}\Phi_{G} = \frac{3}{2}gVn_{Q}(k_{B}T)\varsigma_{5/2}(z).$$

We get the relation

$$PV = \frac{2}{3}U.$$

4. Equation of state for BE condensation (I)

We consider the variation of the pressure P of the Bose gas with its volume V, keeping the temperature T fixed. The pressure P is given by

$$P(T,z) = -\left(\frac{\partial \Phi_G}{\partial V}\right)_{T,\mu} = gk_B T n_Q \zeta_{5/2}(z)$$

where g = 1. and

$$n(T,z) = \frac{N(T,z)}{V} = gn_{\varrho}\varsigma_{3/2}(z).$$

For z = 1 ($\mu = 0$), the pressure P is given by

$$P(T, z=1) = gk_B T n_Q \zeta(\frac{5}{2}) = 1.34149 \ gk_B T \ n_Q$$

vanishes as $T^{5/2}$ and is *independent of density*. This is because only the excited fraction N(T, z = 1) has finite momentum and contributes to the pressure. Alternatively, Bose condensation

can be achieved at a fixed temperature by increasing density (reducing volume). The transition occurs at a specific volume.

The transition temperature $T_E(n)$ depends on the number density n as

$$v(n) = \frac{1}{n} = 0.38279 \frac{1}{n_Q[T_E(n)]} = 0.38279 \left[\frac{2\pi\hbar^2}{mk_B T_E(n)}\right]^{3/2}$$

or

$$T_{E}(n) = \frac{2\pi\hbar^{2}}{mk_{B}} [2.61238v(n)]^{-2/3} = \frac{2\pi\hbar^{2}}{mk_{B}} (2.61238)^{-2/3} [v(n)]^{-2/3}$$

Fig.
$$\tilde{T}_E(n) = \frac{mk_B}{2\pi\hbar^2} T_E(n) (2.61238)^{3/2}$$
 vs $v = 1/n$.

(i) The normal phase $(z \neq 0)$ $[T > T_E(n)]$ The pressure of the gas changes as

$$P(T,z) = gk_BT n_Q \zeta_{5/2}(z) \,.$$

(ii) The BE phase
$$(z = 1)$$
 $[T < T_E(n)]$

An appreciable number of particles falls down to the lowest level, this may be called condensation in momentum space, or Bose condensation.

$$\frac{P(T,n,z=1)}{P(T_E(n),n,z=1)} = \frac{gk_B T n_Q(T) \varsigma(\frac{5}{2})}{gk_B T_E(n) n_Q[T_E(n)] \varsigma(\frac{5}{2})} = \left[\frac{T}{T_E(n)}\right]^{5/2} \qquad (\propto T^{5/2})$$

which is independent of the volume v = 1/n of the system. Since

$$T_E(n) = \frac{2\pi\hbar^2}{mk_B} \left[\frac{\nu(n)}{0.38279}\right]^{-2/3}$$

Using this relation, we have

$$P(n, T_E(n), z = 1) = gk_B T_E(n) n_Q [T_E(n)] \varsigma_{5/2}(z = 1)$$

= 1.34149 gk_B $(\frac{mk_B}{2\pi\hbar^2})^{3/2} [T_E(n)]^{5/2}$

or

$$P(n, T_E(n), z = 1) = gk_B T_E(n) n_Q [T_E(n)] \zeta_{5/2} (z = 1)$$

= 1.34149 gk_B $(\frac{mk_B}{2\pi\hbar^2})^{3/2} [T_E(n)]^{5/2}$

or

$$P(n, T_E(n), z=1) = 0.270721gk_B(\frac{mk_B}{2\pi\hbar^2})^{-1}v(n)^{-5/2}$$



Fig. Isotherms of the ideal Bose gas. The BE condensation shows up as a first-order phase transition. $T_1 > T_2$. For $v > v_c$, Pv = const.

For v < v(n), the pressure–volume isotherm is flat, since $\frac{\partial P}{\partial v} = 0$. The flat portion of isotherms is reminiscent of coexisting liquid and gas phases. We can similarly regard Bose condensation as the coexistence of a "normal gas" of specific volume v_c , and a "liquid" of volume 0. The vanishing of the "liquid" volume is an unrealistic feature due to the absence of any interaction potential between the particles.

5. Equation of state for BE condensation (II)

For t(n) > 1

$$P(n,T,z) = gk_BT \ n_O(T)\varsigma_{5/2}(z)$$

with

$$(t(n))^{3/2} \frac{\zeta_{3/2}(z)}{\zeta_{3/2}(z=1)} = 1$$

where

$$t(n) = \frac{T}{T_E(n)}$$

The pressure can be rewritten as

$$P = P(n, T, z) = nk_B T \frac{\zeta_{5/2}(z)}{\zeta_{3/2}(z)}$$

or

$$\frac{PV}{Nk_BT_E(n)} = t(n)\frac{\zeta_{5/2}(z)}{\zeta_{3/2}(z)}$$

where $n = \frac{N}{V}$. We note that

$$PV = \frac{2}{3}U = Nk_{B}T \frac{\zeta_{5/2}(z)}{\zeta_{3/2}(z)}$$
$$\frac{PV}{Nk_{B}T_{E}(n)} = \frac{2}{3}\frac{U}{Nk_{B}T_{E}(n)}$$
$$= t(n)^{5/2} \frac{\zeta_{5/2}(z=1)}{\zeta_{3/2}(z=1)}$$
for $t(n) < 1$
$$= 0.513512 \ t(n)^{5/2}$$

As shown the figure below, the actual $PV / [Nk_BT_E(n)] = 2U / [3Nk_BT_E(n)]$ vs t(n) curve follows the red line from t(n) = 0 up to t(n) = 1 and thereafter departs, tending asymptotically to the classical limit.





(ii) Extension of the boson line valid for t(n) < 1 to that for t > 1 (purple line).

(iii) Classic (blue line): $PV / [Nk_BT_E(n)] = t(n)$.



Fig. *P-T* diagram of the ideal Bose gas. Note that the space above the transition curve does not correspond to anything. The condensed phase lies on the transition line itself.



Fig. *P-T* curve as the number density *n* is changed as parameter. (M. Kardar, Statistical Physics of Particles, Cambridge, 2008).

APPENDIX-I Gamma and zeta functions

$$\int_{0}^{\infty} \frac{x^{y} dx}{e^{x} - 1} = \int_{0}^{\infty} \frac{x^{y} e^{-x} dx}{1 - e^{-x}}$$
$$= \sum_{k=0}^{\infty} \int_{0}^{\infty} x^{y} e^{-(k+1)x} dx$$
$$= \Gamma(1+y) \sum_{k=0}^{\infty} (1+k)^{-(y+1)}$$
$$= \Gamma(1+y) \sum_{k=1}^{\infty} k^{-(y+1)}$$
$$= \Gamma(1+y) \zeta(y+1)$$

with

$$\int_{0}^{\infty} \frac{x^{3/2} dx}{e^{x} - 1} = \Gamma(\frac{5}{2})\varsigma(\frac{5}{2})$$

$$= \frac{3\sqrt{\pi}}{4} \times 1.34149$$

$$= 1.7833$$

$$\int_{0}^{\infty} \frac{x^{1/2} dx}{e^{x} - 1} = \Gamma(\frac{3}{2})\varsigma(\frac{3}{2})$$

$$= \frac{\sqrt{\pi}}{2} \times 2.61238$$

((Note))

$$\frac{2}{\sqrt{\pi}} \int_{0}^{\infty} dx \frac{x^{3/2}}{\frac{1}{z}e^{x} - 1} = \frac{3}{2} \zeta_{5/2}(z)$$
$$\frac{2}{\sqrt{\pi}} \int_{0}^{\infty} dx \frac{\sqrt{x}}{\frac{1}{z}e^{x} - 1} = \zeta_{3/2}(z)$$

$$\varsigma_{5/2}(z=1) = \varsigma(\frac{5}{2}) = 1.34149, \qquad \qquad \varsigma_{3/2}(z=1) = \varsigma(\frac{3}{2}) = 2.61238$$

(i) Zeta function

 $\varsigma(x)$ is the zeta function defined by

$$\zeta(x) = \sum_{k=1}^{\infty} k^{-x}$$

with

$$\varsigma(\frac{3}{2}) = 2.61238$$
, $\varsigma(\frac{5}{2}) = 1.34149$, $\varsigma(\frac{7}{2}) = 1.12673$

(ii) Gamma function

 $\Gamma(x)$ is the gamma function

$$\Gamma(1+x) = x\Gamma(x), \qquad \Gamma(1-x) = -x\Gamma(-x)$$

$$\Gamma(\frac{1}{2}) = \sqrt{\pi}, \qquad \Gamma(\frac{3}{2}) = \frac{1}{2}\sqrt{\pi},$$

$$\Gamma(\frac{5}{2}) = \frac{3}{2}\Gamma(\frac{3}{2}) = \frac{3}{4}\sqrt{\pi}$$

$$\Gamma(\frac{7}{2}) = \frac{5}{2}\Gamma(\frac{5}{2}) = \frac{15}{8}\sqrt{\pi}$$

APPENDIX II PolyLog (mathematica)

PolyLog

PolyLog[n, z]

gives the polylogarithm function $\operatorname{Li}_n(z)$.

PolyLog[n, p, z]

gives the Nielsen generalized polylogarithm function $\mathcal{S}_{n,p}(\boldsymbol{z})$.

Details

- Mathematical function, suitable for both symbolic and numerical manipulation.
- = $\operatorname{Li}_{n}(z) = \sum_{k=1}^{\infty} z^{k} / k^{n}$.
- = $S_{n,p}(z) = (-1)^{n+p-1} / ((n-1)! p!) \int_0^1 \log^{n-1} (t) \log^p (1-zt) / t dt$,
- $S_{n-1,1}(z) = Li_n(z)$
- PolyLog[n, z] has a branch cut discontinuity in the complex z plane running from 1 to ...
- = For certain special arguments, PolyLog automatically evaluates to exact values.
- PolyLog can be evaluated to arbitrary numerical precision.
- PolyLog automatically threads over lists.

$$\frac{2}{\sqrt{\pi}}\int_{0}^{\infty}dx\frac{\sqrt{x}}{\frac{1}{z}e^{x}-1} = \zeta_{3/2}(z) = \operatorname{PolyLog}[\frac{3}{2}, z]$$

$$\frac{2}{\sqrt{\pi}} \int_{0}^{\infty} dx \frac{x^{3/2}}{\frac{1}{z}e^{x} - 1} = \frac{3}{2} \zeta_{5/2}(z) = \frac{3}{2} \operatorname{PolyLog}[\frac{5}{2}, z]$$
$$\zeta_{3/2}(z) = \operatorname{PolyLog}[\frac{3}{2}, z]$$
$$\zeta_{3/2}(z) = \operatorname{PolyLog}[\frac{3}{2}, z]$$

Clear["Global`*"]; f1 =
$$\frac{\sqrt{x}}{\frac{pxp[x]}{z} - 1}$$
; f2 = $\frac{x^{3/2}}{\frac{pxp[x]}{z} - 1}$;
g1 = Integrate[f1, {x, 0, ∞}]
 $\frac{1}{2}\sqrt{\pi}$ PolyLog[$\frac{3}{2}$, z]
g2 = Integrate[f2, {x, 0, ∞}]
 $\frac{3}{4}\sqrt{\pi}$ PolyLog[$\frac{5}{2}$, z]
Series[PolyLog[$\frac{3}{2}$, z], {z, 0, 5}]
z + $\frac{z^2}{2\sqrt{2}}$ + $\frac{z^3}{3\sqrt{3}}$ + $\frac{z^4}{8}$ + $\frac{z^5}{5\sqrt{5}}$ + 0[z]⁶
Series[PolyLog[$\frac{5}{2}$, z], {z, 0, 5}]
z + $\frac{z^2}{4\sqrt{2}}$ + $\frac{z^3}{9\sqrt{3}}$ + $\frac{z^4}{32}$ + $\frac{z^5}{25\sqrt{5}}$ + 0[z]⁶



APPENDIX

I taught Phys.411 (511) in 2016 by using the textbook of K. Huang; Introduction to Statistical Mechanics. I found the following nice figures.



Fig. Isotherms of the Bose gas at two temperatures (M. Kardar, Statistical Physics of Particles, Cambridge, 2007).



Fig. Phase diagram of Bose-Einstein condensation in the density temperature plane.; $n \propto T^{3/2}$ (K. Huang, Introduction to Statistical Physics).



Fig. Qualitative isotherms of the ideal Bose gas. The Bose-Einstein condensation shows up as a first-order phase transition. (K. Huang, Introduction to Statistical Physics).



Fig. Isotherms of the ideal Bose gas

REFERENCES

M.Kardar, Statistical Physics of Particles (Cambridge, 2007).

K. Huang, Statistical Mechanics, second edition (John Wiley & Sons, 1987).

K. Huang, Introduction to Statistical Mechanics, second edition (Taylor and Francis, 2010).

R.K. Pathria and P.D. Beale, Statistical Mechanics, 3rd edition (Elsevier, 2011).