F. Ideal Bose Gas ain't classical ideal gas even at high temperature

[This section is Optional]

Question: What is the behavior of Ideal Bose Gas at high temperature?

What for? All gases approach classical ideal gas at high temperatures, but any signature of bosons in high-T behavior?

Classical ideal gas $pV = NkT$ or $\frac{p}{kT} = \frac{N}{V}$

Bose Gas at high temperature $\frac{pV}{NkT} = 1 + (\text{something})$?

or $$\frac{p}{kT} = \frac{N}{V} + \underbrace{(\text{some factor})}_{\text{What is this?}}\left(\frac{N}{V}\right)^2 \qquad (15)$$

Approach

- We have Eqs. (1), (2), (3), (4)
- Eq. (4) says $pV = \frac{2}{3}E = \frac{2}{3}\underbrace{\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}}_{A}\int_0^\infty \frac{\varepsilon^{3/2}}{e^{(\varepsilon-\mu)/kT}-1}\,d\varepsilon$

[Call $x = \varepsilon/kT$, $\varepsilon^{3/2} = (kT)^{3/2}x^{3/2}$, $d\varepsilon = (kT)\,dx$, $\varepsilon^{1/2} = (kT)^{1/2}x^{1/2}$]

$$pV = \frac{2}{3}A(kT)^{5/2}\underbrace{\int_0^\infty \frac{x^{3/2}}{e^{-\mu/kT}e^{x}-1}\,dx}_{\text{after integrating over } x\text{, it is a function of } e^{-\mu/kT}} \qquad (16) \qquad (\text{Exact})$$

Similarly, Eq. (1) says

$$N = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{e^{(\varepsilon-\mu)/kT}-1}\,d\varepsilon = A(kT)^{3/2}\underbrace{\int_0^\infty \frac{x^{1/2}}{e^{-\mu/kT}e^{x}-1}\,dx}_{\text{after integrating over } x\text{, it is a function of } e^{-\mu/kT}} \qquad (17) \qquad (T>T_c\text{, exact})$$

N_0 term irrelevant for $T > T_c$

Let's call $e^{+\mu/kT} \equiv \xi$, so $e^{-\mu/kT} = \xi^{-1}$

this follows standard notation (<u>not</u> to confuse with DOS)

Define $$\int_0^\infty \frac{x^{n-1}}{\xi^{-1}e^{x}-1}\,dx = \underbrace{\Gamma(n)}_{\text{Gamma Function}^{+}} \cdot g_n(\xi) \qquad (18)$$

Note^{+}:

$\Gamma(1/2) = \sqrt{\pi}$

as $\Gamma(n) = \int_0^\infty z^{n-1} e^{-z}\,dz$

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

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

$$\frac{pV}{N} = \frac{2}{3}kT\,\frac{\displaystyle\int_0^\infty \frac{x^{3/2}}{\xi^{-1}e^{x}-1}\,dx}{\displaystyle\int_0^\infty \frac{x^{1/2}}{\xi^{-1}e^{x}-1}\,dx}$$

this is "1"

$$\frac{pV}{NkT} = \frac{2}{3}\,\frac{\Gamma(5/2)\,g_{5/2}(\xi)}{\Gamma(3/2)\,g_{3/2}(\xi)} = \cancel{\frac{2}{3}\,\frac{\frac{3}{4}\sqrt{\pi}}{\frac{1}{2}\sqrt{\pi}}}\;\frac{g_{5/2}(\xi)}{g_{3/2}(\xi)} = \frac{g_{5/2}(\xi)}{g_{3/2}(\xi)}$$

$$\Rightarrow \boxed{\frac{pV}{NkT} = \frac{g_{5/2}(\xi)}{g_{3/2}(\xi)}} \qquad (19)$$

(Exact) $(T > T_c)$

$^{+}$ See Notes on the Gamma Functions under "Essential Math Skills"

So far, all equations are exact, just rewriting Eqs.(1)-(4).

If we know ξ ($\xi \equiv e^{+\mu/kT}$ (but μ itself can be negative as in classical gas)), then Eq.(19) gives $\frac{pV}{NkT}$ (more than just "1").

Recall $\mu(T)$ (thus $\xi = e^{\mu/kT}$) is fixed by the "N-equation" (Eq.(1)), i.e.

$$N = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}(kT)^{3/2}\,\underbrace{\Gamma(3/2)}_{\frac{\sqrt{\pi}}{2}}\,g_{3/2}(\xi) \qquad (T>T_c)$$

$$= \frac{V}{4\pi^2}\left(\frac{\sqrt{2mkT}}{\hbar}\right)^3 \cdot \frac{\sqrt{\pi}}{2}\, g_{3/2}(\xi)$$

$$= V\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3 g_{3/2}(\xi) = \frac{V}{\lambda_{th}(T)^3}\, g_{3/2}(\xi)$$

$$\boxed{N = \frac{V}{\lambda_{th}^3}\, g_{3/2}(\xi)} \quad (20)$$

can be used to fix ξ for $T>T_c$

Back to our goal, what is behavior in approach the classical gas limit?

Recall: Obtained for classical ideal gas [See Application CE-(C7)]

$$\mu = -kT\ln\left[\frac{V}{N}\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3\right]$$

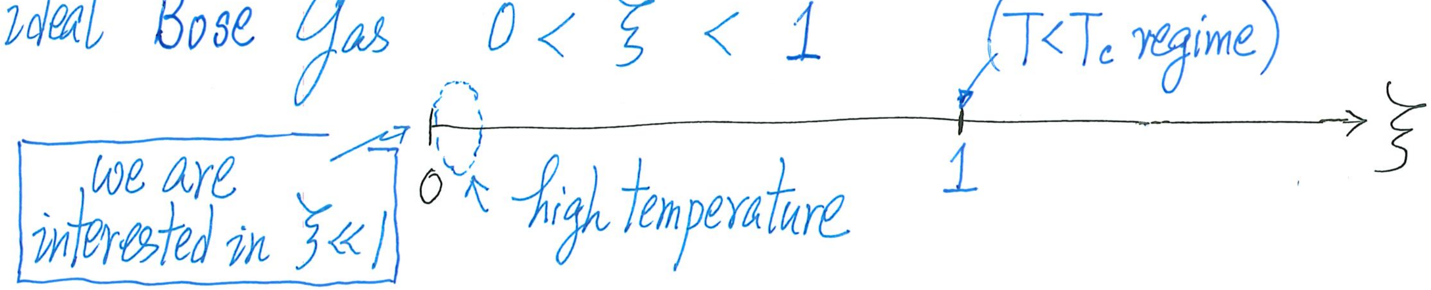
$$= \underset{\text{negative}}{-}kT\ln\left[\underbrace{\left(\frac{V}{N}\right)\frac{1}{\lambda_{th}^3}}_{\text{large } \left(\frac{V}{N}\right)^{1/3} >> \lambda_{th}^3 \text{ (ideal gas)}}\right]$$

$$\therefore \xi_{classical} = e^{\mu/kT} = e^{-\ln\left[\frac{V}{N}\frac{1}{\lambda_{th}^3}\right]} = \frac{\lambda_{th}^3}{\left(\frac{V}{N}\right)} \ll 1$$

As we want to study ideal Bose Gas as it approaches the classical gas limit, we expect $\xi \approx \xi_{classical} \ll 1$

Formally, $\mu(T<T_c) = 0$, $\xi_{(T<T_c)} = e^{0/kT} \to \overset{\text{bounded by 1}}{\downarrow} 1$

i.e. for ideal Bose Gas $0 < \xi < 1$



Strategy Update: Study $g_{5/2}(\xi)$ and $g_{3/2}(\xi)$ for $\xi \ll 1$

$$\int_0^\infty \frac{x^{n-1}}{\xi^{-1}e^{x}-1}\,dx = \int_0^\infty \frac{\xi\, x^{n-1}\, e^{-x}}{1-\xi e^{-x}}\,dx \qquad (\text{Exact})$$

$$\approx \int_0^\infty \xi\, x^{n-1} e^{-x}\left[1+\xi e^{-x}+(\xi^{2}\text{ and higher terms})\right]dx$$

$$= \xi\int_0^\infty x^{n-1}e^{-x}\,dx + \xi^{2}\int_0^\infty x^{n-1}e^{-2x}\,dx \qquad \left(\begin{array}{l} y=2x \\ \text{in 2nd term}\end{array}\right)$$

$$= \xi\,\Gamma(n) + \xi^{2}\int_0^\infty \frac{y^{n-1}}{2^{n-1}}\,e^{-y}\,\frac{dy}{2}$$

$$= \xi\,\Gamma(n) + \frac{\xi^{2}}{2^{n}}\Gamma(n) = \Gamma(n)\underbrace{\left[\xi+\frac{\xi^{2}}{2^{n}}\right]}_{\text{this is } g_n(\xi) \text{ for } \xi \ll 1} = \Gamma(n)\overbrace{g_n(\xi)}^{\text{for } \xi \ll 1}$$

$$\therefore\ \boxed{g_n(\xi) = \xi + \frac{\xi^{2}}{2^{n}}} \qquad \text{for}^{+}\ \xi \ll 1 \qquad (21)$$

$^{+}$c.f. Fermi Gas, $f_n(\xi) = \xi - \frac{\xi^{2}}{2^{n}}$

Recall: μ (or ξ now) is fixed by Eq. (1).

$$N = \frac{V}{\lambda_{th}^3(T)} g_{3/2}(\xi) \approx \frac{V}{\lambda_{th}^3}\left(\xi + \frac{\xi^2}{2^{3/2}}\right)$$

$$\Rightarrow \xi \approx \underbrace{\left(\frac{N}{V}\frac{\lambda_{th}^3}{2}\right)}_{\text{this is } \left(\frac{1}{2}\xi_{\text{classical}}\right) \ll 1 \text{, this is the leading term}} - \frac{\xi^2}{2^{3/2}}$$

$$\approx \left(\frac{N}{V}\frac{\lambda_{th}^3}{2}\right) - \underbrace{\frac{1}{2^{3/2}}\left(\frac{N}{V}\frac{\lambda_{th}^3}{2}\right)^2}_{\text{Even smaller!}}$$

$$\approx \underbrace{\left(\frac{N}{V}\frac{\lambda_{th}^3}{2}\right)}_{\text{just the classical ideal gas value}} \quad (22) \text{ sufficient for our purpose}$$

(temperature T inside $\lambda_{th} = \frac{h}{\sqrt{2\pi mkT}}$)

$$\frac{pV}{NkT} = \frac{g_{5/2}(\xi)}{g_{3/2}(\xi)} \quad \text{(exact)} \quad \approx \frac{\xi + \frac{\xi^2}{2^{5/2}}}{\xi + \frac{\xi^2}{2^{3/2}}}$$

($\xi \ll 1$, approaching classical gas limit)

$$\approx \left(1 + \frac{\xi}{2^{5/2}}\right)\left(1 - \frac{\xi}{2^{3/2}}\right) \approx 1 - \xi\left(\frac{1}{2^{3/2}} - \frac{1}{2^{5/2}}\right) + \text{ignored}\,(\xi^2, \xi^3 \ldots)$$

$$= 1 - \frac{1}{4\sqrt{2}}\,\xi$$

$$= 1 - \underbrace{\frac{1}{4\sqrt{2}}\,\frac{\lambda_{th}^3}{2}\left(\frac{N}{V}\right)}_{\text{something!}} \qquad (23)$$

$$\therefore \boxed{\frac{p}{kT} = \frac{N}{V} - \underbrace{\frac{1}{4\sqrt{2}}\,\frac{\lambda_{th}^3}{2}}\left(\frac{N}{V}\right)^2 = \frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2} \qquad (24)$$

Ideal (Non-interacting) Bose Gas behaves as $\frac{p}{kT} = n + B_2(T)n^2$ with a Negative Second Virial Coefficient $B_2(T) = \frac{-1}{4\sqrt{2}}\,\frac{\lambda_{th}^3}{2}$

Negative $B_2(T)$ implies some effective attraction between bosons, even though they don't interact!

Aside: We saw in Van der Waals Gas $\left(P+\frac{n^2 a}{V^2}\right)(V-nb)=nRT$

attractive

repulsive

\# moles

then

$$\frac{p}{kT} = n + \underbrace{B_2(T)}_{\left[+\frac{b}{N_A}-\frac{a}{N_A^2 kT}\right]} n^2$$

attractive part contributes negative term to B_2

repulsive part of particle-particle interaction contributes positive term to B_2

Summary

- Even when ideal Bose Gas approaches the classical ideal gas limit, the first correction term indicates the quantum nature of the bosons with a negative B_2, as if they have an effective attractive interaction.

References

- Pathria, "Statistical Mechanics" Ch.7 [more mathematical treatment]
- Greiner, Neise, Stöcker, "Thermodynamics and Statistical Mechanics" Ch.13
- Yoshioka, "Statistical Physics: An Introduction" Ch.10 [simpler treatment]