E3010: Heat capacity of ideal Bose gas

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The problem:

Consider a volume V that contains N mass m bosons. The gas is in a thermal equilibrium at temperature T.

(1) Write an explicit expression for the condensation temperature T_c.
(2) Calculate the chemical potential, the energy and the pressure in the Boltzmann approximation $T \gg T_c$.
(3) Calculate the chemical potential, the energy and the pressure in the regime $T < T_c$.
(4) Calculate C_v for $T < T_c$.
(5) Calculate C_v for $T = T_c$.
(6) Calculate C_v for $T \gg T_c$.
(7) Express the ratio C_p/C_v using the polylogarithmic functions. Explain why $C_p \to \infty$ in the condensed phase?
(8) Find the γ in the adiabatic equation of state. Note that in general it does not equal C_p/C_v.

The solution: Note an impoved version in [ex3009].

(1) The condensation temperature:

$$T_c = \frac{2\pi}{m}\left(\frac{N}{\zeta\left(\frac{3}{2}\right)V}\right)^{\frac{2}{3}} \quad , \quad \zeta\left(\frac{3}{2}\right) \approx 2.612 \tag{1}$$

See Pathria, 2nd edition, p.161.

(2) In Boltzmann approximation $T \gg T_c$ and also $g_\nu(z) \approx z$, therefore:

$$\frac{N}{V} = \frac{1}{\lambda_T^3} z \quad , \quad z = \mathrm{e}^{\beta\mu} \quad , \quad \lambda_T = \left(\frac{2\pi}{mT}\right)^{\frac{1}{2}} \tag{2}$$

$$\frac{N}{V}\lambda_T^3 = \mathrm{e}^{\mu/T} \;\Rightarrow\; \mu = T\ln\left(\frac{N}{V}\lambda_T^3\right) \tag{3}$$

$$\frac{E}{V} = \frac{3}{2}\frac{T}{\lambda_T^3} z = \frac{3}{2}\frac{N}{V}T \;\Rightarrow\; E = \frac{3}{2}NT \tag{4}$$

$$P = \frac{2}{3}\left(\frac{E}{V}\right) = \frac{T}{\lambda_T^3} z = \frac{N}{V}T \tag{5}$$

These are the classical results for an ideal gas.

(3) For $T < T_c$:

$$\mu = 0 \quad , \quad z = 1 \tag{6}$$

$$E = \frac{3}{2}\frac{T}{\lambda_T^3} V g_{5/2}(1) = \frac{3}{2}\zeta\left(\frac{5}{2}\right)\left(\frac{m}{2\pi}\right)^{\frac{3}{2}} V T^{\frac{5}{2}} \quad , \quad \zeta\left(\frac{5}{2}\right) \approx 1.341 \tag{7}$$

$$P = \frac{2}{3}\left(\frac{E}{V}\right) = \zeta\left(\frac{5}{2}\right)\left(\frac{m}{2\pi}\right)^{\frac{3}{2}} T^{\frac{5}{2}} \tag{8}$$

(4) Heat capacity for $T < T_c$:

$$C_v = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \frac{15}{4}\zeta\left(\frac{5}{2}\right)\left(\frac{m}{2\pi}\right)^{\frac{3}{2}} V T^{\frac{3}{2}} \tag{9}$$

From now on, all dervivatives with respect to T will be calculated keeping V and N constant, unless noted otherwise.

(5) Since the expression we got for the energy in (7) is valid for $T \leq T_c$, at $T = T_c$:

$$C_v = \frac{15}{4}\zeta\left(\frac{5}{2}\right)\left(\frac{m}{2\pi}\right)^{\frac{3}{2}} V T_c^{\frac{3}{2}} = \frac{15}{4} N \frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)} \approx 1.925N \tag{10}$$

(6) For $T \gg T_c$:

$$E = \frac{3}{2}NT \Rightarrow C_v = \frac{3}{2}N \tag{11}$$

(7) Let us find C_v for $T > T_c$:

$$\frac{N}{V} = \frac{1}{\lambda_T^3} g_{3/2}(z) \quad , \quad E = \frac{3}{2}V\frac{T}{\lambda_T^3} g_{5/2}(z) = \frac{3}{2}NT\frac{g_{5/2}(z)}{g_{3/2}(z)} \tag{12}$$

$$\frac{C_v}{N} = \frac{\partial}{\partial T}\left[\frac{3}{2}T\frac{g_{5/2}(z)}{g_{3/2}(z)}\right] \tag{13}$$

Next, we need to find the derivatives of the polylogarithmic functions with respect to T:

$$\frac{\partial}{\partial T} g_{3/2}(z) = \frac{\partial}{\partial T}\left(\frac{N}{V}\lambda_T^3\right) = -\frac{3}{2}\frac{N}{V}\left(\frac{2\pi}{mT}\right)^{\frac{3}{2}} \cdot \frac{1}{T} = -\frac{3}{2T} g_{3/2}(z) \tag{14}$$

Using the recurrence relation (Pathria, 2nd edition, Appendix: D.10)

$$z\frac{\partial}{\partial z} g_\nu(z) = g_{\nu-1}(z)\,, \tag{15}$$

we get:

$$z\frac{\partial}{\partial z} g_{3/2}(z) = g_{1/2}(z) \tag{16}$$

Dividing (14) by (16):

$$\frac{\partial z}{\partial T} = -\frac{3z}{2T}\frac{g_{3/2}(z)}{g_{1/2}(z)} \quad , \quad \frac{\partial}{\partial z} = \frac{\partial}{\frac{\partial z}{\partial T}\partial T} = -\frac{2T}{3z}\frac{g_{1/2}(z)}{g_{3/2}(z)}\frac{\partial}{\partial T} \tag{17}$$

Using (15) and (17) we get:

$$z\frac{\partial}{\partial z}g_{5/2}(z) = z\left(-\frac{2T}{3z}\right)\frac{g_{1/2}(z)}{g_{3/2}(z)}\frac{\partial}{\partial T}g_{5/2}(z) = g_{3/2}(z) \tag{18}$$

$$\frac{\partial}{\partial T}g_{5/2}(z) = -\frac{3}{2T}\frac{g_{3/2}^2(z)}{g_{1/2}(z)} \tag{19}$$

Using (14) and (19) in the calculation of (13) and after some algebra we finally get:

$$\frac{C_v}{N} = \frac{15}{4}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)} \tag{20}$$

We find C_p in a similar way:

$$C_p = \left(\frac{\partial\left(E+PV\right)}{\partial T}\right)_{P,N} = \left(\frac{\partial E}{\partial T}\right)_{P,N} + P\left(\frac{\partial V}{\partial T}\right)_{P,N} \tag{21}$$

From now on all derivatives with respect to T will be calculated keeping P and N constant, meaning we cannot use the expressions we got for the derivatives of the polylogarithmic functions and we need to do the calculations again. From (12):

$$\frac{\partial E}{\partial T} = \frac{\partial}{\partial T}\left[\frac{3}{2}NT\frac{g_{5/2}(z)}{g_{3/2}(z)}\right] \tag{22}$$

$$P = \frac{T}{\lambda_T^3}g_{5/2}(z) \tag{23}$$

$$\frac{\partial}{\partial T}g_{5/2}(z) = \frac{\partial}{\partial T}\left(P\frac{\lambda_T^3}{T}\right) = -\frac{5}{2}P\left(\frac{2\pi}{mT}\right)^{\frac{3}{2}}\frac{1}{T}\cdot\frac{1}{T} = -\frac{5}{2T}g_{5/2}(z) \tag{24}$$

Recalling that

$$z\frac{\partial}{\partial z}g_{5/2}(z) = g_{3/2}(z)\,, \tag{25}$$

we divide (24) by (25) and get:

$$\frac{\partial z}{\partial T} = -\frac{5z}{2T}\frac{g_{5/2}(z)}{g_{3/2}(z)} \quad , \quad \frac{\partial}{\partial z} = \frac{\partial}{\frac{\partial z}{\partial T}\partial T} = -\frac{2T}{5z}\frac{g_{3/2}(z)}{g_{5/2}(z)}\frac{\partial}{\partial T} \tag{26}$$

Using (16) and (26) we get:

$$z\frac{\partial}{\partial z}g_{3/2}(z) = z\left(-\frac{2T}{5z}\right)\frac{g_{3/2}(z)}{g_{5/2}(z)}\frac{\partial}{\partial T}g_{3/2}(z) = g_{1/2}(z) \tag{27}$$

$$\frac{\partial}{\partial T}g_{3/2}(z) = -\frac{5}{2T}\frac{g_{5/2}(z)g_{1/2}(z)}{g_{3/2}(z)} \tag{28}$$

Using (24) and (28) in the calculation of (22) and arranging we obtain:

$$\frac{\partial E}{\partial T} = N\frac{g_{5/2}(z)}{g_{3/2}(z)}\left[-\frac{9}{4} + \frac{15}{4}\frac{g_{5/2}(z)g_{1/2}(z)}{g_{3/2}^2(z)}\right] \tag{29}$$

From (12) we get an expression for V:

$$V = N\frac{\lambda_T^3}{g_{3/2}(z)} \tag{30}$$

To make the calculation of the derivative of V with respect to T easier:

$$\frac{\partial}{\partial T}\lambda_T^3 = -\frac{3}{2}\left(\frac{2\pi}{mT}\right)^{\frac{3}{2}} \cdot \frac{1}{T} = -\frac{3}{2T}\lambda_T^3 \tag{31}$$

Using (28) and (31) we calculate the derivative and get:

$$\frac{\partial V}{\partial T} = N\left[-\frac{3}{2T}\lambda_T^3\frac{1}{g_{3/2}(z)} + \frac{5}{2T}\lambda_T^3\frac{g_{5/2}(z)g_{1/2}(z)}{g_{3/2}^3(z)}\right] \tag{32}$$

Recalling that $P = \frac{T}{\lambda_T^3}g_{5/2}(z)$:

$$P\left(\frac{\partial V}{\partial T}\right) = N\frac{g_{5/2}(z)}{g_{3/2}(z)}\left[-\frac{3}{2} + \frac{5}{2}\frac{g_{5/2}(z)g_{1/2}(z)}{g_{3/2}^2(z)}\right] \tag{33}$$

Using (29) and (33) in (21) we get:

$$\frac{C_p}{N} = \frac{g_{5/2}(z)}{g_{3/2}(z)}\left[-\frac{15}{4} + \frac{25}{4}\frac{g_{5/2}(z)g_{1/2}(z)}{g_{3/2}^2(z)}\right] \tag{34}$$

Finally:

$$\frac{C_p}{C_v} = \frac{\frac{C_p}{N}}{\frac{C_v}{N}} = \frac{5}{3}\frac{g_{5/2}(z)g_{1/2}(z)}{g_{3/2}^2(z)} \tag{35}$$

In condensation $C_p \to \infty$ ($g_{1/2}(z=1)$ diverges). We look at the definition of C_p:

$$C_p \equiv T\left(\frac{\partial S}{\partial T}\right)_{P,N} = \left(\frac{đQ}{dT}\right)_{P,N} \tag{36}$$

In condensed state $P = \text{const} \cdot T^{\frac{5}{2}}$, so by keeping P constant $\Rightarrow dT = 0$. The temperature will not change, no matter how much heat will enter the system, meaning the volume will grow.

(8) We need to find the entropy. Let us look at:

$$E - TS + PV \equiv \mu N \Rightarrow \frac{S}{N} = \frac{E + PV}{NT} - \frac{\mu}{T} \tag{37}$$

For $T \leq T_c$, $\mu = 0$ and from (7) and (8):

$$E = \frac{3}{2}\frac{T}{\lambda_T^3}V\zeta\left(\frac{5}{2}\right) \quad , \quad P = \frac{T}{\lambda_T^3}\zeta\left(\frac{5}{2}\right) \tag{38}$$

Hence

$$\frac{S}{N} = \frac{5}{2}\frac{1}{\lambda_T^3}\frac{V}{N}\zeta\left(\frac{5}{2}\right) \tag{39}$$

For $T > T_c$:

$$z = \mathrm{e}^{\mu/T} \Rightarrow \mu = T\ln z \tag{40}$$

$$E = \frac{3}{2}\frac{T}{\lambda_T^3}V g_{5/2}(z) \quad , \quad P = \frac{T}{\lambda_T^3}g_{5/2}(z) \tag{41}$$

Putting it all together we get:

$$\frac{S}{N} = \frac{5}{2}\frac{V}{N}\frac{g_{5/2}(z)}{\lambda_T^3} - \ln z \tag{42}$$

Using (12) we get a final expression:

$$\frac{S}{N} = \frac{5}{2}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \ln z \tag{43}$$

A reversible adiabatic process implies that S and N are constants. For the last expression it implies that z is constant, Therefore $g_{3/2}(z)$ is constant and

$$g_{3/2}(z) = \lambda_T^3\frac{N}{V} = \text{const} \tag{44}$$

Equation (39) implies the same. Now,

$$\left(\frac{2\pi}{mT}\right)^{\frac{3}{2}}\frac{N}{V} = \text{const} \Rightarrow T^{\frac{3}{2}}V = \text{const} \tag{45}$$

For both regions, using the expressions for P we get:

$$\frac{P}{T^{\frac{5}{2}}} = \text{const} \tag{46}$$

From (45):

$$T = \text{const}\cdot\frac{1}{V^{2/3}} \tag{47}$$

$$\frac{P}{\left(V^{-\frac{2}{3}}\right)^{\frac{5}{2}}} = \text{const} \Rightarrow PV^{\frac{5}{3}} = \text{const} \tag{48}$$

Hence $\gamma = \frac{5}{3}$.