7.H.1. Bose-Einstein Gases

For an ideal gas of bosons of mass $m \neq 0$ and spin $s = 0$, the grand partition function is

$$Z_{BE}(T, V, \mu') = \prod_l \left(\sum_{n_l=0}^{\infty} e^{-\beta n_l (\epsilon_l - \mu')} \right) \qquad \text{[(7.121) used.]} \qquad (7.124a)$$

The sum

$$\sum_{n_l=0}^{\infty} e^{-\beta n_l (\epsilon_l - \mu')} = \lim_{N \to \infty} \frac{1 - e^{-\beta n_l (\epsilon_l - \mu')(N+1)}}{1 - e^{-\beta(\epsilon_l - \mu')}}$$

converges only if

$$e^{-\beta(\epsilon_l - \mu')} < 1 \qquad \to \qquad \mu' < \epsilon_l \qquad (7.124b)$$

Thus,

$$Z_{BE}(T, V, \mu') = \prod_l \frac{1}{1 - e^{-\beta(\epsilon_l - \mu')}} \qquad (7.124)$$

provided (7.124b) is obeyed for all l, i.e.,

$$\mu' < \epsilon_0 \qquad (7.124c)$$

where ϵ_0 is the lowest (or ground state) energy. For free particles,

$$\epsilon_0 = 0 \qquad \to \qquad \mu' < 0 \qquad (7.124d)$$

The grand potential (7.111) becomes

$$\begin{aligned} \Omega_{BE}(T, V, \mu') &= -k_B T \ln Z_{BE}(T, V, \mu') \\ &= k_B T \sum_l \ln\left[1 - e^{-\beta(\epsilon_l - \mu')}\right] \end{aligned} \qquad (7.125)$$

From the definition

$$d\Omega = -S\,dT - P\,dV - \langle N \rangle\, d\mu'$$

we get

$$\begin{aligned} \langle N \rangle &= -\left(\frac{\partial \Omega_{BE}}{\partial \mu'} \right)_{TV} \\ &= -k_B T \sum_l \frac{-\beta e^{-\beta(\epsilon_l - \mu')}}{1 - e^{-\beta(\epsilon_l - \mu')}} \qquad \text{[(7.125) used.]} \\ &= \sum_l \frac{e^{-\beta(\epsilon_l - \mu')}}{1 - e^{-\beta(\epsilon_l - \mu')}} \\ &= \sum_l \frac{1}{e^{\beta(\epsilon_l - \mu')} - 1} \\ &= \sum_l \langle n_l \rangle \end{aligned} \qquad (7.126)$$

where

$$\langle n_l \rangle = \frac{1}{e^{\beta(\epsilon_l - \mu')} - 1} = \text{occupation number of state } l. \qquad (7.127a)$$

$$= \frac{1}{\frac{1}{z} e^{\beta(\epsilon_l - \epsilon_0)} - 1} \qquad (7.127)$$

where

$$z = e^{\beta(\mu' - \epsilon_0)} = \text{fugacity}. \qquad (7.127b)$$

Using (7.124c), we have

$0 \le z \le 1$ (7.127c)

where the lower & upper bounds are given by $\beta(\mu' - \epsilon_0) = -\infty$ & 0, respectively.

Putting (7.124d) into (7.127) gives the occupation number of the ground state as

$$\langle n_0 \rangle = \frac{z}{1-z} \quad (7.128)$$

$$\xrightarrow[z\to 1]{} \infty \quad (7.128a)$$

which means every particle can be in the same 1-particle ground state even in the thermodynamic limit if $z = 1$. In which case, the entire system is in the symmetrized ground state called a Bose condensate, while low lying excited states can be considered as the result of “evaporation” of particles from the condensate. The evaporated particles form a vapor that coexist with the (diminished but still infinite) condensate. Since $z < 1$ means only a finite number (and hence a zero fraction) of the infinite number of particles are in the condensate, $z = 1$ also marks the onset of the Bose condensation in the thermodynamic limit. Thus, the system is

an ideal gas	for $z < 1$
a mixture of vapor & condensate	for $z = 1$

This behavior of the condensate is embodied by the average density of particles in the ground state

$$n_0(V, z) \equiv \frac{\langle n_0 \rangle}{V} = \frac{1}{V}\frac{z}{1-z} \qquad [\,(7.128)\text{ used.}\,] \quad (7.128b)$$

In the thermodynamic limit where

$$\lim_{\langle N \rangle, V \to \infty} \frac{\langle N \rangle}{V} = \overline{n} = \text{average density of particles} = \text{finite} \quad (7.128c)$$

we have

$$n_0(\infty, z < 1) = 0$$
$$0 \le n_0(\infty, 1) \le \overline{n} \quad (7.128d)$$

where the exact value of $n_0(\infty, 1)$ is determined by the other thermodynamic variables such as T & P.

Plots of $n_0(V, z)$ for various values of V are shown in Fig.7.11, from which the behavior given by (7.128d) can be extrapolated.

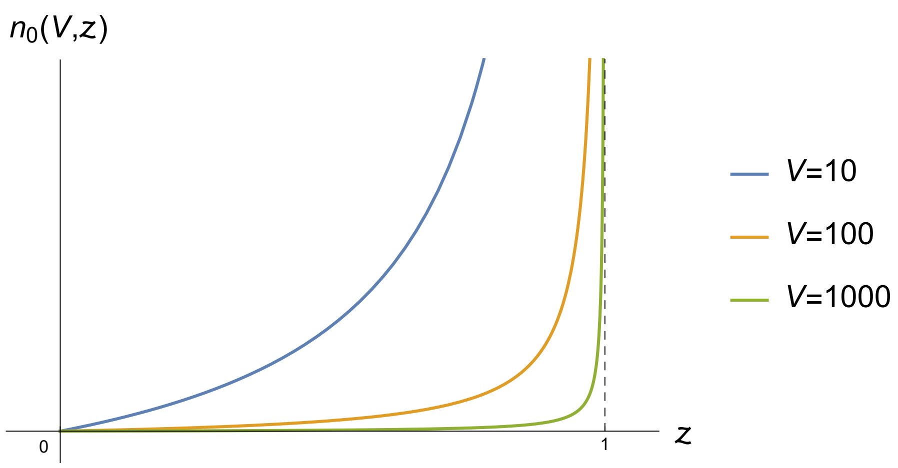

Fig.7.11. Plots of $n_0(V, z)$.

From (7.127b), we see that

$z \to 1$ if $\beta(\mu' - \epsilon_0) \to 0$ $\Rightarrow$ $T \to \infty$ or $\mu' \to \epsilon_0$

Since

$$T \to \infty \qquad \Rightarrow \qquad \beta(\mu' - \epsilon_l) \to 0 \qquad \forall\, l$$

it bears no special physical significance.

The condition for $z = 1$ is therefore taken to be

$$\mu' = \epsilon_0 \tag{7.128e}$$

Owing to the possibility of condensation, the ground state $\boldsymbol{l} = \mathbf{0}$ must be treated separately. Thus, for an arbitrary function f,

$$\sum_{\boldsymbol{l}} f(\boldsymbol{l}) = f(\mathbf{0}) + \sum_{\boldsymbol{l} \neq 0} f(\boldsymbol{l})$$

$$\xrightarrow[V \to \infty]{} f(\mathbf{0}) + \frac{V}{(2\pi)^3} \int_{\boldsymbol{k} \neq \mathbf{0}} d^3 k\, f(\boldsymbol{k}) \qquad \text{[Periodic boundary conditions assumed.]}$$

$$= f(\mathbf{0}) + \frac{V}{(2\pi)^3} \int d\Omega \int_{k_0}^{\infty} dk\, k^2\, f(\boldsymbol{k}) \tag{7.131a}$$

where Ω is the solid angle and

$$\frac{4\pi}{3} k_0^3 = \frac{(2\pi)^3}{V} = \boldsymbol{k}\text{-space volume occupied by 1 state.}$$

$$\to \quad k_0 = \left(\frac{6}{\pi}\right)^{1/3} \frac{\pi}{L} \tag{7.131b}$$

(7.126) then becomes

$$\langle N \rangle = \langle n_{\mathbf{0}} \rangle + \frac{V}{(2\pi)^3} \int d\Omega \int_{k_0}^{\infty} dk\, k^2 \frac{1}{e^{\beta(\epsilon_{\boldsymbol{k}} - \mu')} - 1} \qquad \left[\ \epsilon_{\boldsymbol{k}} = \frac{\hbar^2 k^2}{2m}\ \right]$$

$$= \frac{z}{1-z} + \frac{4\pi V}{(2\pi)^3} \int_{k_0}^{\infty} dk\, k^2 \frac{1}{\frac{1}{z} e^{\beta \hbar^2 k^2 / 2m} - 1} \qquad \text{[(7.127 \& b) used.]} \tag{7.131}$$

Similarly, (7.125) gives

$$\Omega_{\text{BE}}(T, V, \mu') = k_B T \ln\left[1 - e^{-\beta(\epsilon_{\mathbf{0}} - \mu')}\right] + \frac{4\pi k_B T V}{(2\pi)^3} \int_{k_0}^{\infty} dk\, k^2 \ln\left[1 - e^{-\beta(\epsilon_{\boldsymbol{k}} - \mu')}\right]$$

$$= k_B T \ln(1 - z) + \frac{4\pi k_B T V}{(2\pi)^3} \int_{k_0}^{\infty} dk\, k^2 \ln\left(1 - z\, e^{-\beta \hbar^2 k^2 / 2m}\right) \tag{7.132}$$

Using

$$x = \sqrt{\frac{\beta}{2m}}\, \hbar k \qquad\qquad x_0 = \sqrt{\frac{\beta}{2m}}\, \hbar k_0 \tag{7.132a}$$

(7.131) becomes

$$\langle N \rangle = \frac{z}{1-z} + \frac{4\pi V}{(2\pi)^3 \hbar^3} \left(\frac{\beta}{2m}\right)^{3/2} \int_{x_0}^{\infty} dx\, x^2 \frac{1}{\frac{1}{z} e^{x^2} - 1}$$

$$= \frac{z}{1-z} + \frac{4V}{\lambda_T^3 \sqrt{\pi}} \int_{x_0}^{\infty} dx\, x^2 \frac{1}{\frac{1}{z} e^{x^2} - 1} \tag{7.134}$$

where

$$\lambda_T = \sqrt{\frac{2\pi \hbar^2 \beta}{m}} = \text{thermal wavelength} \tag{7.135}$$

$$\to \quad x_0 = \frac{\lambda_T}{2\sqrt{\pi}} k_0 = \frac{\lambda_T}{2\sqrt{\pi}} \left(\frac{6}{\pi}\right)^{1/3} \frac{\pi}{L} = \lambda_T \left(\frac{3}{4\pi}\right)^{1/3} \frac{\sqrt{\pi}}{L} \tag{7.135a}$$

Similarly, (7.132) becomes

$$\Omega_{BE}(T, V, \mu') = k_B T \ln(1-z) + \frac{4 k_B T V}{\lambda_T^3 \sqrt{\pi}} \int_{x_0}^{\infty} dx\, x^2 \ln\left(1 - z e^{-x^2}\right) \qquad (7.133)$$

Consider the integral

$$-\int_0^{\infty} dx\, x^2 \ln\left(1 - z e^{-x^2}\right) = \sum_{n=1}^{\infty} \frac{z^n}{n} \int_0^{\infty} dx\, x^2\, e^{-n x^2}$$

$$= \sum_{n=1}^{\infty} \frac{z^n}{2 n^{5/2}} \int_0^{\infty} dy \sqrt{y}\, e^{-y} \qquad y = n x^2 \quad \to \quad dx = \frac{dy}{2 n x}$$

$$= \sum_{n=1}^{\infty} \frac{z^n}{2 n^{5/2}} \Gamma\left(\frac{3}{2}\right)$$

$$= \frac{\sqrt{\pi}}{4} g_{5/2}(z) \qquad \Gamma\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2} \qquad (7.133a)$$

where Γ is the Gamma function and

$$g_j(z) \equiv \sum_{n=1}^{\infty} \frac{z^n}{n^j} = \text{polylogarithm function of order } j. \qquad (7.137a)$$

$$\to \quad g_{5/2}(z) = -\frac{4}{\sqrt{\pi}} \int_0^{\infty} dx\, x^2 \ln\left(1 - z e^{-x^2}\right) \qquad (7.137)$$

(7.133) can therefore be written as

$$\Omega_{BE}(T, V, \mu') = k_B T \ln(1-z) + \frac{k_B T V}{\lambda_T^3} \left[g_{5/2}(z) - I_{5/2}(z, x_0) \right] \qquad (7.133b)$$

where

$$I_{5/2}(z, x_0) = -\frac{4}{\sqrt{\pi}} \int_0^{x_0} dx\, x^2 \ln\left(1 - z e^{-x^2}\right) \qquad (7.138)$$

Using (2.122) of §2.F.5, we have

$$P = -\frac{\Omega_{BE}}{V} = -\frac{k_B T}{V} \ln(1-z) + \frac{k_B T}{\lambda_T^3} \left[g_{5/2}(z) - I_{5/2}(z, x_0) \right] \qquad (7.136)$$

Similarly, using

$$\frac{4}{\sqrt{\pi}} \int_0^{\infty} dx\, x^2 \frac{1}{\frac{1}{z} e^{x^2} - 1} = \frac{4}{\sqrt{\pi}} \int_0^{\infty} dx\, x^2 \frac{z\, e^{-x^2}}{1 - z e^{-x^2}}$$

$$= -\frac{4}{\sqrt{\pi}} z \frac{\partial}{\partial z} \int_0^{\infty} dx\, x^2 \ln\left(1 - z e^{-x^2}\right)$$

$$= z \frac{\partial}{\partial z} g_{5/2}(z)$$

$$= \sum_{n=1}^{\infty} \frac{z^n}{n^{3/2}} \qquad \text{[(7.137a) used.]}$$

$$= g_{3/2}(z) \qquad \text{[See (7.137a).]} \qquad (7.140)$$

turns (7.134) into

$$\bar{n} = \frac{\langle N \rangle}{V} = \frac{1}{V} \frac{z}{1-z} + \frac{1}{\lambda_T^3} \left[g_{3/2}(z) - I_{3/2}(z, x_0) \right] \qquad (7.139)$$

where

$$I_{3/2}(z, x_0) = \frac{4}{\sqrt{\pi}} \int_0^{x_0} dx\, x^2 \frac{1}{\frac{1}{z} e^{x^2} - 1} \qquad (7.141)$$

For $x_0 \to 0$, (7.138) gives

$$I_{5/2}(z, x_0) \xrightarrow[x_0 \to 0]{} -\frac{4}{\sqrt{\pi}} \int_0^{x_0} d x\, x^2 \ln\left[1 - z\left(1 - x^2 + \ldots\right)\right]$$
$$= \frac{4}{\sqrt{\pi}} \int_0^{x_0} d x\, x^2\; z\left(1 - x^2 + \ldots\right)$$
$$= O\left(x_0^3\right)$$
$$= 0 \qquad (7.141a)$$

Similarly, (7.141) gives

$$I_{3/2}(z, x_0) \xrightarrow[x_0 \to 0]{} \frac{4}{\sqrt{\pi}} \int_0^{x_0} d x\, x^2 \frac{1}{\frac{1}{z}\left(1 + x^2 + \ldots\right) - 1}$$
$$= \begin{cases} O\left(x_0^3\right) & \text{for } z < 1 \\ O(x_0) & \text{for } z = 1 \end{cases} = 0 \qquad (7.141b)$$

In the thermodynamic limit,

$$L \to \infty \qquad \Rightarrow \qquad x_0 \to 0$$

so that (7.136 & 9) simplify to

$$P = -\lim_{V \to \infty} \frac{k_B T}{V} \ln(1 - z) + \frac{k_B T}{\lambda_T^3} g_{5/2}(z) \qquad (7.141c)$$

$$\overline{n} = \lim_{V \to \infty} \frac{1}{V} \frac{z}{1 - z} + \frac{1}{\lambda_T^3} g_{3/2}(z)$$
$$= n_0(\infty, z) + \frac{1}{\lambda_T^3} g_{3/2}(z) \qquad \text{[(7.128b) used.]}$$
$$= \begin{cases} \frac{1}{\lambda_T^3} g_{3/2}(z) & \text{for } z < 1 \\ n_0(\infty, 1) + \frac{1}{\lambda_T^3} g_{3/2}(1) & \text{for } z = 1 \end{cases} \qquad \text{[(7.128d) used.]} \qquad (7.145)$$

Note that $n_0(\infty, 1)$, with values lying between 0 & $\overline{n}$, is itself a function of T & P.

Plots of $g_{3/2}(z)$ & $g_{5/2}(z)$ are shown in Fig.7.10, where

$$g_j(0) = 0 \qquad \forall\ j \qquad \text{[See (7.137a).]}$$
$$g_{3/2}(1) = \sum_{n=1}^{\infty} \frac{1}{n^{3/2}} = \zeta\left(\frac{3}{2}\right) \approx 2.61238$$
$$g_{5/2}(1) = \sum_{n=1}^{\infty} \frac{1}{n^{5/2}} = \zeta\left(\frac{5}{2}\right) \approx 1.34149$$

and ζ is the Riemann-Zeta function.

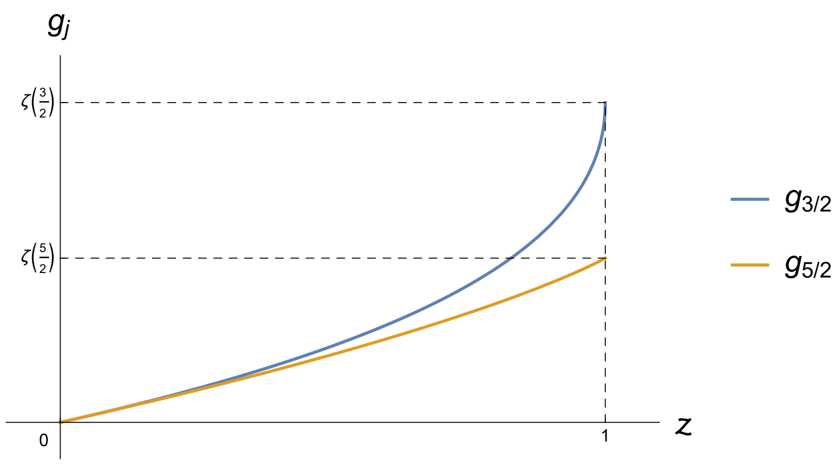

Fig.7.10. Plots of $g_{3/2}(z)$ & $g_{5/2}(z)$.

(7.128b) can be inverted to give,

$$z = \frac{n_0 V}{1 + n_0 V} = \left(1 + \frac{1}{n_0 V}\right)^{-1}$$

$$\xrightarrow[V\to\infty]{} 1 - \frac{1}{n_0 V} + \ldots \qquad [\, z \approx 1\,] \qquad (7.141f)$$

Hence,

$$-\frac{1}{V}\ln(1-z) \xrightarrow[V\to\infty]{} \begin{cases} 0 & \text{for } z < 1 \\ \frac{1}{V}\ln(n_0 V) = 0 & \text{for } z \approx 1 \end{cases} \qquad [\text{ Density } n_0 \text{ is always finite. }]$$

which means (7.141c) becomes, in the thermodynamic limit,

$$P = \frac{k_B T}{\lambda_T^3} g_{5/2}(z) \qquad (7.144)$$

In other word, the condensate does not contribute to the pressure of the gas.

The plot of $\overline{n}\lambda_T^3$ as given by(7.145) is shown in Fig.7.12. The case for $V = 100$ is also shown for comparison [see also Figs.7.10 -1].

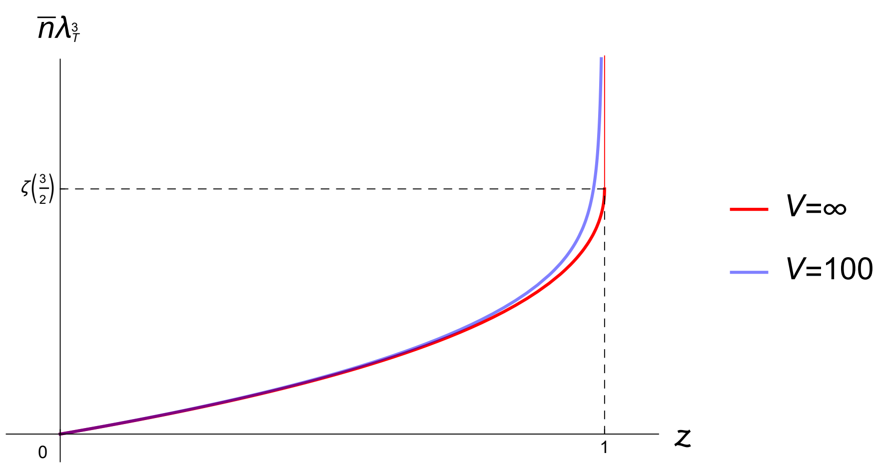

Fig.7.12. Plots of $\overline{n}\lambda_T^3$ for $V = \infty$ & $V = 100$.

At the threshold of condensation,

$$n_0(\infty, 1) = 0$$

so that (7.145) becomes

$$\overline{n} = \frac{1}{\lambda_{T_C}^3} g_{3/2}(1) \approx \frac{2.612}{\lambda_{T_C}^3} \tag{7.147}$$

$$= \left(\frac{m\,k_B\,T_C}{2\,\pi\,\hbar^2}\right)^{3/2} g_{3/2}(1) \qquad \text{[(7.135) used.]}$$

where the subscript C denotes values at the transition point of the condensation. Solving for the transition temperature, we get

$$T_C = \frac{2\,\pi\,\hbar^2}{m\,k_B}\left(\frac{\overline{n}}{g_{3/2}(1)}\right)^{2/3} \approx \frac{2\,\pi\,\hbar^2}{m\,k_B}\left(\frac{\overline{n}}{2.612}\right)^{2/3} \tag{7.148}$$

Using (7.128d), the average density of the gas/vapor is given by

$$\langle n\rangle = \begin{cases} \overline{n} & \text{for } T \geq T_C \\ \overline{n} - n_0(\infty, 1) = \dfrac{1}{\lambda_T^3} g_{3/2}(1) \approx \dfrac{2.612}{\lambda_T^3} & \text{for } T \leq T_C \end{cases} \tag{7.147}$$

$$= \frac{1}{\lambda_T^3} g_{3/2}(z) \qquad \text{[(7.145) used.]} \tag{7.147a}$$

Thus, $z = 1$ if $T \leq T_C$. For $T > T_C$, z is the solution of

$$\overline{n} = \frac{1}{\lambda_T^3} g_{3/2}(z) = \frac{1}{\lambda_{T_C}^3} g_{3/2}(1)$$

or

$$g_{3/2}(z) = \left(\frac{T_C}{T}\right)^{3/2} g_{3/2}(1) \tag{7.147b}$$

Solution of (7.147b) is given in Fig.7.12a.

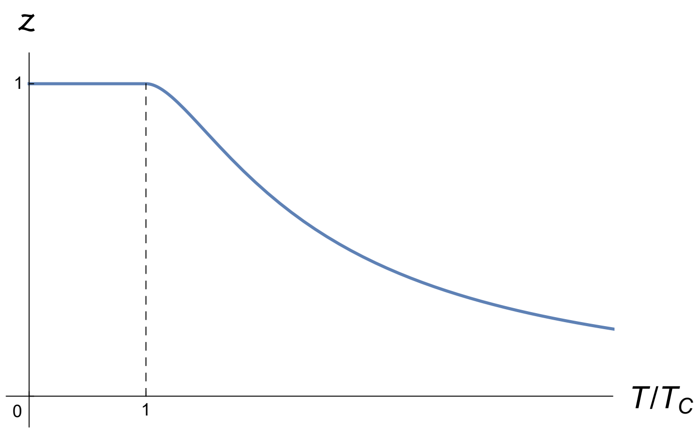

Fig.7.12a. Temperature dependence of the fugacity z obtained by solving (7.150b).

(7.147) corresponds to an average volume per particle in the gas/vapor phase

$$\langle v\rangle = \begin{cases} \dfrac{1}{\overline{n}} & \text{for } T \geq T_C \\ \dfrac{1}{\overline{n} - n_0(\infty, 1)} = \dfrac{\lambda_T^3}{g_{3/2}(1)} & \text{for } T \leq T_C \end{cases} \tag{7.147c}$$

$$= \frac{\lambda_T^3}{g_{3/2}(z)} \tag{7.147d}$$

The order parameter of the condensation is obviously

$$\eta = \frac{n_0(\infty, z)}{\overline{n}} = \begin{cases} 0 & \text{for } T \geq T_C \\ \dfrac{n_0(\infty, 1)}{\overline{n}} & \text{for } T \leq T_C \end{cases} \qquad \text{[(7.128d) used.]}$$

$$= \begin{cases} 0 & \text{for } T \geq T_C \\ 1 - \left(\frac{T}{T_C}\right)^3 & \text{for } T \leq T_C \end{cases} \tag{7.149}$$

where we have used (7.145) to write

$$\frac{n_0(\infty, 1)}{\overline{n}} = 1 - \frac{1}{\overline{n}\,\lambda_T^3}\,g_{3/2}(1) = 1 - \left(\frac{\lambda_{T_C}}{\lambda_T}\right)^3 = 1 - \left(\frac{T}{T_C}\right)^3$$

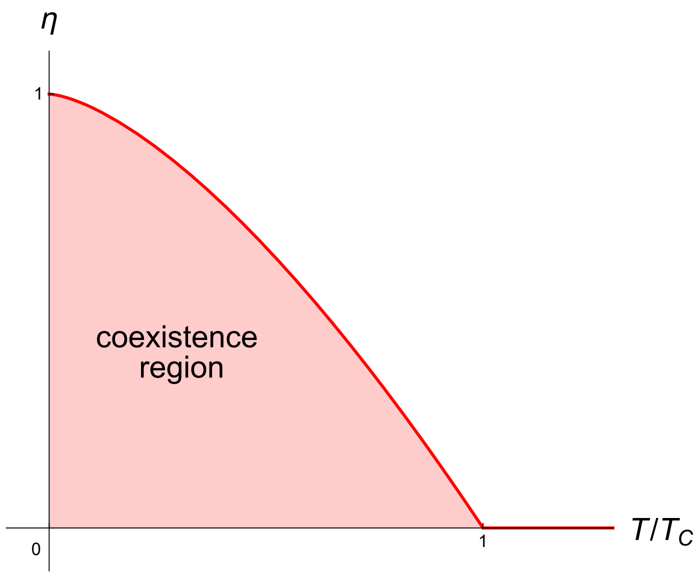

Fig.7.13. Plot of the order parameter η vs the reduced temperature T/T_C.

Setting

$$\langle v \rangle_c = \langle v \rangle \Big|_{z=1} = \frac{\lambda_T^3}{g_{3/2}(1)} = \frac{\lambda_T^3}{\zeta(3/2)} \tag{7.149a}$$

(7.147d) becomes

$$\langle v \rangle = \frac{\langle v \rangle_c\, \zeta(3/2)}{g_{3/2}(z)} \tag{7.149b}$$

which gives z as a function of $\langle v \rangle$.

Now,

$$\max[\,g_{3/2}(z)\,] = g_{3/2}(1) \qquad \rightarrow \qquad \langle v \rangle_c = \min[\,\langle v \rangle\,]$$

Thus,

$$\begin{aligned} &\text{for } \langle v \rangle > \langle v \rangle_c, && z \text{ is determined by (7.149b)} \\ &\text{for } \langle v \rangle \leq \langle v \rangle_c, && z = 1 \end{aligned} \tag{7.149c}$$

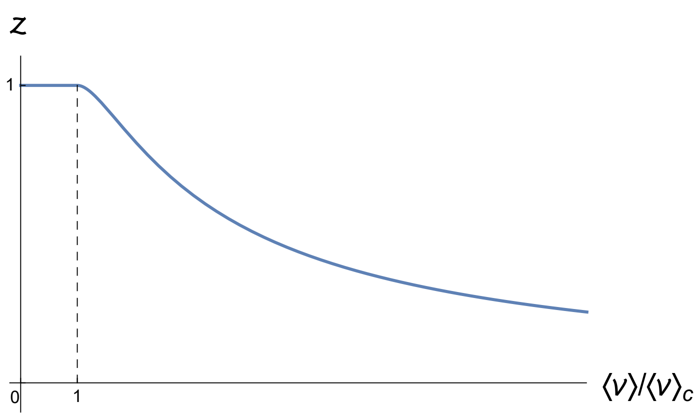

Fig.7.12b. Particle volume dependence of the fugacity z obtained by solving (7.149b).

Using (7.147c) to eliminate λ_T^3 turns (7.144) into

$$P = \frac{k_B T}{\langle v \rangle} \frac{g_{5/2}(z)}{g_{3/2}(z)} = \begin{cases} \dfrac{k_B T}{\langle v \rangle_c} \dfrac{g_{5/2}(z)}{\zeta(3/2)} & \text{for } \langle v \rangle > \langle v \rangle_c \\ \dfrac{k_B T}{\langle v \rangle_c} \dfrac{\zeta(5/2)}{\zeta(3/2)} & \text{for } \langle v \rangle \leq \langle v \rangle_c \end{cases} \qquad [\text{ (7.149c) used. }] \qquad (7.150a)$$

(7.149a) gives

$$\langle v \rangle_c = \frac{1}{\zeta(3/2)} \left(\frac{2 \pi \hbar^2}{m k_B T} \right)^{3/2}$$

$$\rightarrow \quad k_B T = \frac{2 \pi \hbar^2}{m} \left(\frac{1}{\langle v \rangle_c \zeta(3/2)} \right)^{2/3} \qquad (7.150b)$$

The transition (or coexistence) curve in the P-$\langle v \rangle$ plane is therefore

$$P_c = \frac{k_B T}{\langle v \rangle_c} \frac{\zeta(5/2)}{\zeta(3/2)}$$

$$= \frac{2 \pi \hbar^2}{m} \frac{\zeta(5/2)}{\zeta(3/2)^{5/3}} \frac{1}{\langle v \rangle_c^{5/3}} \qquad [\text{ (7.150b) used. }] \qquad (7.150)$$

$$= \frac{\alpha}{\langle v \rangle_c^{5/3}} \qquad (7.150c)$$

where

$$\alpha = \frac{2 \pi \hbar^2}{m} \frac{\zeta(5/2)}{\zeta(3/2)^{5/3}} \qquad (7.150d)$$

is a constant.

(7.150a) can also be thrown into the form

$$P = \frac{2 \pi \hbar^2}{m} \frac{\zeta(5/2)}{\zeta(3/2)^{5/3} \langle v \rangle_c^{5/3}} \begin{cases} \dfrac{g_{5/2}(z)}{\zeta(5/2)} & \text{for } \langle v \rangle > \langle v \rangle_c \\ 1 & \text{for } \langle v \rangle \leq \langle v \rangle_c \end{cases}$$

$$= P_c \begin{cases} \dfrac{g_{5/2}(z)}{\zeta(5/2)} & \text{for } \langle v \rangle > \langle v \rangle_c \\ 1 & \text{for } \langle v \rangle \leq \langle v \rangle_c \end{cases}$$

$$= \frac{\alpha}{\langle v \rangle_c^{5/3}} \begin{cases} \dfrac{g_{5/2}(z)}{\zeta(5/2)} & \text{for } \langle v \rangle > \langle v \rangle_c \\ 1 & \text{for } \langle v \rangle \leq \langle v \rangle_c \end{cases} \qquad (7.150e)$$

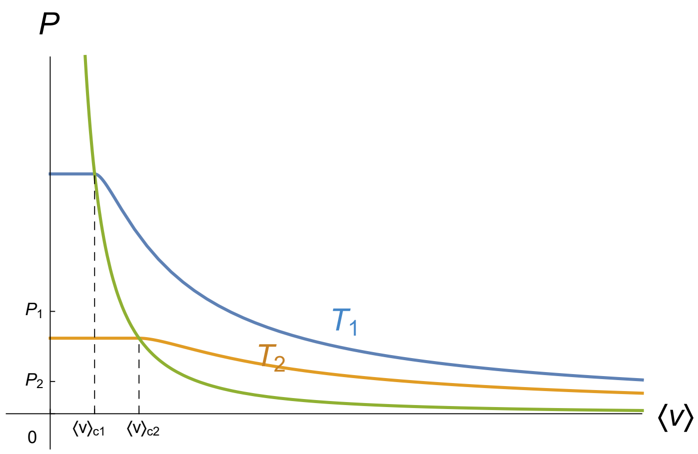

Fig.7.14. Two isotherms ($T_2 < T_1$) in the P-$\langle v \rangle$ plane.
Green curve is the coexistence (or transition) curve.

In order to calculate the heat capacity, we need to find the entropy first.

From the fundamental equation

$$d\Omega = -S\, dT - P\, dV - N\, d\mu'$$

we get the Maxwell relation

$$s \equiv \left(\frac{\partial S}{\partial V}\right)_{T,\mu'} = \left(\frac{\partial P}{\partial T}\right)_{V,\mu'} = \left(\frac{\partial^2 \Omega}{\partial V \partial T}\right)_{\mu'}$$

Since the entropy is an extensive variable, $S \propto V$ so that

$$s = \frac{S}{V} = \text{entropy per unit volume}$$

Derivative of (7.144) gives

$$\left(\frac{\partial P}{\partial T}\right)_{V,\mu'} = \frac{k_B}{\lambda_T^3} g_{5/2}(z) - \frac{3 k_B T}{\lambda_T^4} \frac{d\lambda_T}{dT} g_{5/2}(z) + \frac{k_B T}{\lambda_T^3} \left(\frac{\partial z}{\partial T}\right)_{\mu'} g_{5/2}'(z)$$

Using

$$\frac{d\lambda_T}{dT} = -\frac{1}{2T}\lambda_T \qquad \left(\frac{\partial z}{\partial T}\right)_{\mu'} = \left(\frac{\partial e^{\beta\mu'}}{\partial T}\right)_{\mu'} = -\frac{\mu' z}{k_B T^2} = -\frac{z \ln z}{T}$$

$$g_j'(z) = \frac{d}{dz} \sum_{n=1}^{\infty} \frac{z^n}{n^j} = \sum_{n=1}^{\infty} \frac{z^{n-1}}{n^{j-1}} = \frac{1}{z} g_{j-1}(z) \qquad (7.151a)$$

we get

$$s = \left(\frac{\partial P}{\partial T}\right)_{V,\mu'} = \frac{k_B}{\lambda_T^3} g_{5/2}(z) + \frac{3 k_B}{2\lambda_T^3} g_{5/2}(z) - \frac{k_B}{\lambda_T^3} g_{3/2}(z) \ln z$$

$$= \frac{5 k_B}{2\lambda_T^3} g_{5/2}(z) - k_B \langle n \rangle \ln z \qquad \text{[(7.147a) used.]}$$

$$= \begin{cases} \dfrac{5 k_B}{2\lambda_T^3} g_{5/2}(z) - k_B \bar{n} \ln z & \text{for } z < 1 \\ \dfrac{5 k_B}{2\lambda_T^3} g_{5/2}(1) & \text{for } z = 1 \end{cases} \qquad (7.151)$$

Thus, for $T < T_C$,

$$s \propto T^{3/2} \qquad \Rightarrow \qquad \lim_{T\to 0} S = 0$$

in agreement with the 3rd law.

Owing to the assumption $V \to \infty$, the quantity closest to C_V is the heat capacity per unit volume at constant particle density defined as

$$c_{\bar{n}} = T\left(\frac{\partial s}{\partial T}\right)_{\bar{n}}$$
$$= T \begin{cases} -\frac{15\,k_B}{2\,\lambda_T^4}\frac{d\lambda_T}{dT}\,g_{5/2}(z) + \frac{5\,k_B}{2\,\lambda_T^3}\left(\frac{\partial z}{\partial T}\right)_{\bar{n}} g_{5/2}'(z) - k_B\,\frac{\bar{n}}{z}\left(\frac{\partial z}{\partial T}\right)_{\bar{n}} & \text{for } z < 1 \\ -\frac{15\,k_B}{2\,\lambda_T^4}\frac{d\lambda_T}{dT}\,g_{5/2}(1) & \text{for } z = 1 \end{cases} \qquad (7.153a)$$

From (7.147a), we have

$$0 = -\frac{3}{\lambda_T^4}\frac{d\lambda_T}{dT}\,g_{3/2}(z) + \frac{1}{\lambda_T^3}\left(\frac{\partial z}{\partial T}\right)_{\bar{n}} g_{3/2}'(z)$$
$$= \frac{3}{2\,T\,\lambda_T^3}\,g_{3/2}(z) + \frac{1}{\lambda_T^3}\left(\frac{\partial z}{\partial T}\right)_{\bar{n}}\frac{1}{z}\,g_{1/2}(z) \qquad \text{[(7.151a) used.]}$$
$$\to \quad \left(\frac{\partial z}{\partial T}\right)_{\bar{n}} = -\frac{3\,z}{2\,T}\,\frac{g_{3/2}(z)}{g_{1/2}(z)} \qquad (7.152)$$

Putting (7.151a) & (7.152) into (7.153a) gives

$$c_{\bar{n}} = \begin{cases} \frac{15\,k_B}{4\,\lambda_T^3}\,g_{5/2}(z) - \frac{3}{2}\,k_B\,\frac{g_{3/2}(z)}{g_{1/2}(z)}\left[\frac{5}{2\,\lambda_T^3}\,g_{3/2}(z) - \bar{n}\right] & \text{for } z < 1 \\ \frac{15\,k_B}{4\,\lambda_T^3}\,g_{5/2}(1) & \text{for } z = 1 \end{cases} \qquad (7.153)$$

Caution: Using (7.147a), we can turn (7.153) into Reichl's (7.153).
However, that would be a mistake since we have assumed $\bar{n} = \text{const}$.

Using $g_{1/2}(1) = \infty$, we can write (7.153) as

$$c_{\bar{n}} = \frac{15\,k_B}{4\,\lambda_T^3}\left\{g_{5/2}(z) - \frac{g_{3/2}(z)}{g_{1/2}(z)}\left[g_{3/2}(z) - \frac{2}{5}\,\lambda_T^3\,\bar{n}\right]\right\} \qquad (7.153b)$$

which also implies $c_{\bar{n}}$ is continuous at the transition point $T = T_C$. The transition is therefore continuous and of 3rd order. This means the ^4He superfluid λ-point is not a simple Bose condensation. The difference can be traced to the interactions between particles in a fluid.

Since $\bar{n}$ is kept constant, we use (7.147a) to write

$$\bar{n} = \frac{g_{3/2}(1)}{\lambda_{T_C}^3} = \frac{g_{3/2}(1)}{\lambda_T^3}\left(\frac{T_C}{T}\right)^{3/2}$$

so that (7.153b) becomes

$$c_{\bar{n}} = \frac{15\,k_B\,\lambda_{T_C}^3}{4}\left(\frac{T}{T_C}\right)^{3/2}\left\{g_{5/2}(z) - \frac{g_{3/2}(z)}{g_{1/2}(z)}\left[g_{3/2}(z) - \frac{2}{5}\left(\frac{T_C}{T}\right)^{3/2} g_{3/2}(1)\right]\right\} \qquad (7.153c)$$

where z is the solution to (7.147b) for a given T.

At $T = T_C$, (7.153c) simplifies to

$$c_{\bar{n}}(T_C) = \frac{15\,k_B\,g_{3/2}(1)}{4\,\bar{n}}\left\{g_{5/2}(1) - \frac{3}{5}\,\frac{g_{3/2}(1)^2}{g_{1/2}(1)}\right\}$$
$$= \frac{15\,k_B\,\zeta(3/2)}{4\,\bar{n}}\,\zeta(5/2)$$
$$\approx 13.14\,\frac{k_B}{\bar{n}}$$

Caution: $g_{1/2}(1) \neq \zeta(1/2)$.

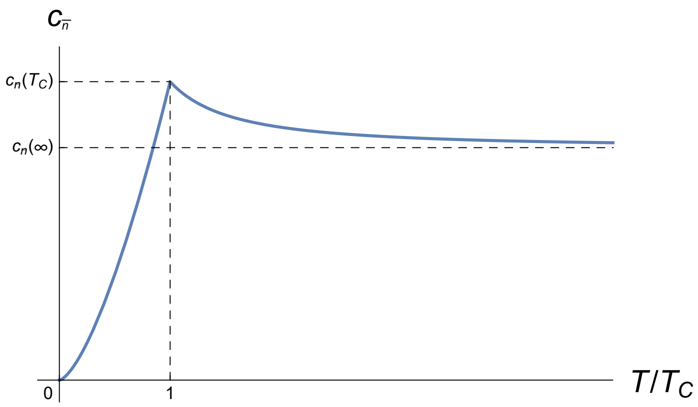

Fig.7.15. Plot of $c_{\overline{n}}$ vs T/T_C.

At high temperatures, $z \to 0$. Using

$$g_j(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^j} \approx z \qquad \forall\ j \tag{7.154a}$$

(7.145) simplifies to

$$\overline{n} \approx \frac{z}{\lambda_T^3} = \left(\frac{m\, k_B\, T}{2\, \pi\, \hbar^2}\right)^{3/2} e^{\beta \mu'} \qquad \text{for} \quad T \gg T_C \tag{7.154}$$

Similarly, (7.144) reduces to

$$P \approx \frac{k_B\, T}{\lambda_T^3} z \approx \overline{n}\, k_B\, T \qquad [\,(7.154)\text{ used.}\,]$$

$$= \frac{\langle N \rangle}{V} k_B\, T \tag{7.155}$$

which is simply the ideal gas law.

Finally, (7.153c) gives

$$c_{\overline{n}} \approx \frac{15\, k_B\, \lambda_{T_C}^3}{4} \left(\frac{T}{T_C}\right)^{3/2} \left\{ z - \left[z - \frac{2}{5} \left(\frac{T_C}{T}\right)^{3/2} \zeta(3/2) \right] \right\}$$

$$= \frac{3\, k_B\, \lambda_{T_C}^3}{2} \zeta(3/2)$$

$$= \frac{3\, k_B}{2} \overline{n} \qquad [\,(7.147b)\text{ used.}\,]$$

$$= \frac{3\, k_B}{2} \frac{\langle N \rangle}{V} \tag{7.156}$$

which is just $\frac{C_V}{V}$ of the ideal gas.

In conclusion, the ideal Bose gas reduces to the classical ideal gas at high temperatures.

Ex.7.7.

Compute $\text{var}(N)$ of an ideal Bose gas for $T \approx 0$.

Answer

For a PVT system, (7.115) of §7.G gives

$$\text{var}(N) = \left\langle \left(N - \langle N \rangle \right)^2 \right\rangle = \frac{1}{\beta} \left(\frac{\partial \langle N \rangle}{\partial \mu'} \right)_{T,V} \tag{1}$$

$$\rightarrow \quad \text{var}\left(\frac{N}{V}\right) = \left\langle \left(\frac{N}{V} - \frac{\langle N \rangle}{V} \right)^2 \right\rangle = \frac{1}{V^2 \beta} \left(\frac{\partial \langle N \rangle}{\partial \mu'} \right)_{T,V} = \frac{1}{V^2} \text{var}(N) \qquad \text{(1a)}$$

For $T < T_C$, (7.145) gives

$$\frac{\langle N \rangle}{V} = \lim_{z \to 1} \left[\frac{1}{V} \frac{z}{1-z} + \frac{1}{\lambda_T^3} g_{3/2}(z) \right] \qquad \text{(2)}$$

Using (7.151a) and

$$\frac{1}{\beta} \left(\frac{\partial z}{\partial \mu'} \right)_{T,V} = \frac{1}{\beta} \left(\frac{\partial e^{\beta \mu'}}{\partial \mu'} \right)_{T,V} = e^{\beta \mu'} = z$$

(2) gives

$$\begin{aligned} \text{var}\left(\frac{N}{V}\right) &= \lim_{z \to 1} \frac{1}{V^2} \left[\left(\frac{1}{1-z} + \frac{z}{(1-z)^2} \right) + \frac{V}{\lambda_T^3 z} g_{1/2}(z) \right] z \\ &= \lim_{z \to 1} \left[\frac{1}{V^2} \frac{z}{(1-z)^2} + \frac{1}{V \lambda_T^3} g_{1/2}(z) \right] \\ &= \left[\frac{\langle N \rangle}{V} - \frac{1}{\lambda_T^3} g_{3/2}(1) \right]^2 + \lim_{z \to 1} \frac{1}{V \lambda_T^3} g_{1/2}(z) \qquad \text{[(2) used.]} \\ &= \left(\overline{n} - \langle n \rangle \right)^2 + \lim_{z \to 1} \frac{1}{V \lambda_T^3} g_{1/2}(z) \qquad \text{[(7.147) used.]} \qquad \text{(3)} \end{aligned}$$

Since $g_{1/2}(1) = \infty$, we can avoid the singularity at finite V by invoking the condition that $z = 1$ only if $V = \infty$. However,

$$\lim_{z \to 1, V \to \infty} \frac{1}{V \lambda_T^3} g_{1/2}(z)$$

is still indefinite.

However, at $T = 0$, all particles are in the condensate so that

$$\overline{n} = \langle n \rangle$$

and (3) becomes

$$\begin{aligned} \text{var}\left(\frac{N}{V}\right) &= \lim_{z \to 1, V \to \infty} \frac{1}{V \lambda_T^3} g_{1/2}(z) \bigg|_{T=0} \\ &= 0 \end{aligned}$$

if

$$\lim_{z \to 1, V \to \infty} \frac{1}{V} g_{1/2}(z) = \text{finite} \qquad \text{(4)}$$

Since we expect $\text{var}\left(\frac{N}{V}\right) = 0$ at $T = 0$, (4) holds so that $\text{var}\left(\frac{N}{V}\right)$ as given by (3) is finite.

Code

In[ ]:=
```
(* Fig.7.10 *)
Plot[{PolyLog[3/2, z], PolyLog[5/2, z]}, {z, 0, 1},
        PlotRange → {{-.1, 1.1}, {-.3, 3}},
        AxesLabel → { "z", "gj" },
        Ticks → {{0, 1}, {Zeta[3/2], Zeta[5/2]}},
        PlotLegends → {"g3/2", "g5/2"},
        Epilog → {Text["0", -.03 {1, 5}],
                Dashed, Line[{{1, 0}, {1, Zeta[3/2]}}],
                        Line[{{0, Zeta[3/2]}, {1, Zeta[3/2]}}],
                        Line[{{0, Zeta[5/2]}, {1, Zeta[5/2]}}]
                }
]
```

In[ ]:=
```
{Zeta[3/2], Zeta[5/2]} // N
```

Out[ ]= {2.61238, 1.34149}

In[ ]:=
```
(* Fig.7.11 *)
pl = 1/# z/(1 - z) & /@ {10, 100, 1000};
Plot[pl, {z, 0, 1},
        PlotRange → {{-.1, 1.1}, {-.03, .35}},
        AxesLabel → { "z", "n0(V,z)" },
        Ticks → {{0, 1}, None},
        PlotLegends → {"V=10", "V=100", "V=1000"},
        Epilog → {Text["0", -.03 {1, .5}],
                Dashed, Line[{{1, 0}, {1, .35}}]}
]
```

In[ ]:=
```
Solve[1/V z/(1 - z) == n0, z]
```

Out[ ]= $\left\{\left\{z \to \frac{V\, n_0}{1 + V\, n_0}\right\}\right\}$

In[ ]:=
```
(* Fig.7.12 *)
Plot[{PolyLog[3/2, z], PolyLog[3/2, z] + 1/100 z/(1 - z)}, {z, 0, 1},
        PlotRange → {{-.1, 1.1}, {-.3, 4}},
        PlotStyle → {Red, {Opacity[.5], Blue}},
        AxesLabel → { "z", "n̅λ_T^3" },
        Ticks → {{0, 1}, {Zeta[3/2]}},
     PlotLegends → {"V=∞", "V=100"},
        Epilog → {Text["0", -.04 {.8, 5}],
                 {Red, Line[{{1, Zeta[3/2]}, {1, 5}}]},
                 Dashed, Line[{{1, 0}, {1, Zeta[3/2]}}],
                 Line[{{0, Zeta[3/2]}, {1, Zeta[3/2]}}]
                 }
]
```

In[ ]:=
```
zs[T_] := { z /. FindRoot[PolyLog[3/2, z] == T^(-3/2) PolyLog[3/2, 1], {z, T}] // Chop   T > 1
            1                                                                        T ≤ 1
```

In[ ]:=
```
zv[v_, vc_] := { z /. FindRoot[PolyLog[3/2, z] v == vc Zeta[3/2], {z, v}] // Chop   v > vc
                 1                                                                v ≤ vc
```

In[ ]:=
```
(* Fig.7.12a *)
Plot[zs[T], {T, 0, 5},
     PlotRange → {{-.2, 5}, {-.1, 1.1}},
        AxesLabel → { "T/T_C", "z" },
        Ticks → {{0, 1}, {0, 1}},
        Epilog → {Text["0", -.05 {2, 1}],
                 Dashed, Line[{{1, 0}, {1, 1}}]
                 }
]
```

In[ ]:=
```
(* Fig.7.12b *)
Plot[zv[v, 1], {v, 0, 10},
     PlotRange → {{-.2, 10}, {-.1, 1.1}},
        AxesLabel → { "〈v〉/〈v〉_c", "z" },
        Ticks → {{0, 1}, {0, 1}},
        Epilog → {Text["0", -.05 {2, 1}],
                 Dashed, Line[{{1, 0}, {1, 1}}]
                 }
]
```

In[ ]:=
```
η[T_] := { 0          T > 1
           1 - T^(3/2)  T ≤ 1
```

In[∘]:=
```
(* Fig.7.13 *)
Plot[η[T], {T, 0, 2},
        PlotRange → {{-.1, 1.3}, {-.1, 1.1}},
        PlotStyle → Red, AspectRatio → Automatic,
        AxesLabel → { "T/T_C", "η" },
        Ticks → {{0, 1}, {0, 1}},
        Filling → Axis,
        Epilog → {Text["0", -.05 {.6, 1}],
                Text["coexistence \n region", {.3, .4}]}
]
```

In[∘]:=
```
P[v_, vc_] := Zeta[5/2] / (vc^(5/3) Zeta[3/2]^(5/3)) {  1/Zeta[5/2] PolyLog[5/2, zv[v, vc]]   v > vc
                                                       1                                    v ≤ vc
```

In[∘]:=
```
(* Fig.7.14 *)
{vc1, vc2, vm} = {.3, .6, 4};
Plot[{P[v, vc1], P[v, vc2], Zeta[5/2] / (v^(5/3) Zeta[3/2]^(5/3))}, {v, 0, vm},
        PlotRange → {{-.3, vm}, {-.3, 3}},
        AxesLabel → { "⟨v⟩", "P" },
        Ticks → {{0, {vc1, "⟨v⟩c1  "}, {vc2, "  ⟨v⟩c2"}},
              {0, {P[0, .5], "P1"}, {P[0, 1], "P2"}}},
        Epilog → {Text["0", -.2 {.6, 1}],
                Text["T1", {2, .8}], Text["T2", {1.5, .5}],
                Dashed, Line[{{vc1, 0}, {vc1, P[0, vc1]}}],
                Line[{{vc2, 0}, {vc2, P[0, vc2]}}]
  }
]
```

$$c_{\bar{n}} = \frac{15\, k_B\, \lambda^3_{T_C}}{4} \left(\frac{T_C}{T}\right)^{3/2} \left\{ g_{5/2}(z) - \frac{g_{3/2}(z)}{g_{1/2}(z)} \left[g_{3/2}(z) - \frac{2}{5} \left(\frac{T_C}{T}\right)^{3/2} g_{3/2}(1) \right] \right\}$$

In[∘]:=
```
cn[T_] :=
  (z = zs[T]; T^(3/2) (PolyLog[5/2, z] - (PolyLog[3/2, z] - 2/(5 T^(3/2)) PolyLog[3/2, 1]) PolyLog[3/2, z] / PolyLog[1/2, z]))
```

In[∘]:=
```
(* Fig.7.15 *)
Plot[cn[T], {T, 0, 5},
     PlotRange → {{-.2, 5}, {-.1, 1.5}},
        AxesLabel → { "T/T_C", "c_n̄" },
        Ticks → {{0, 1}, {0, {cn[1000], "c_n(∞)"}, {cn[1], "c_n(T_C)"}}},
        Epilog → {Text["0", -.02 {5, 3}],
                Dashed, Line[{{1, 0}, {1, cn[1]}}],
                Line[{{0, cn[1000]}, {5, cn[1000]}}],
                Line[{{0, cn[1]}, {1, cn[1]}}]
                }
]
```

In[∘]:=
```
15/4 Zeta[3/2] Zeta[5/2] // N
```

Out[∘]= 13.1418

In[ ]:= $\frac{15}{4}$ Zeta$\left[\frac{3}{2}\right]$ cn[1] // N

Out[ ]= 13.1418