Heat capacity and entropy in Bose-Einstein condensation

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Here we discuss the temperature dependence of the heat capacity in the vicinity of the critical temperature.

$$\frac{2}{\sqrt{\pi}}\int_0^\infty dx \frac{\sqrt{x}}{\frac{1}{z}e^x - 1} = \varsigma_{3/2}(z) = \text{PolyLog}[\frac{3}{2}, z]$$

$$\frac{2}{\sqrt{\pi}}\int_0^\infty dx \frac{x^{3/2}}{\frac{1}{z}e^x - 1} = \frac{3}{2}\varsigma_{5/2}(z) = \frac{3}{2}\text{PolyLog}[\frac{5}{2}, z]$$

$$n_Q(T) = \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}$$

1. Internal energy and heat capacity

The total energy is given by using the zeta function as

$$\begin{aligned}
U &= \int_0^\infty \varepsilon D(\varepsilon) f(\varepsilon) d\varepsilon \\
&= \frac{gV}{4\pi^2}(\frac{2m}{\hbar^2})^{3/2}\int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{\frac{1}{z}e^{\beta\varepsilon} - 1} \\
&= \frac{gV}{4\pi^2}(\frac{2m}{\hbar^2})^{3/2}\int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{\frac{1}{z}e^{\beta\varepsilon} - 1} \\
&= \frac{gV}{4\pi^2}(\frac{2m}{\hbar^2})^{3/2}(k_B T)^{5/2}\int_0^\infty dx \frac{x^{3/2}}{\frac{1}{z}e^x - 1} \\
&= gVn_Q(T)\,(k_B T)\frac{3\sqrt{\pi}}{4}\varsigma_{5/2}(z) \\
&= \frac{3k_B T}{2} gVn_Q(T)\varsigma_{5/2}(z)
\end{aligned}$$

or

$$U = \frac{3}{2} g V n_Q(T)(k_B T)\varsigma_{5/2}(z)$$

where g is the spin degeneracy; $g = 2S+1$. Since

$$N = gVn_Q(T)\varsigma_{3/2}(z) = gVn_Q(T_E)\varsigma_{3/2}(z=1)$$

we have

$$\frac{U}{Nk_BT_E} = \frac{3}{2}t^{5/2}\frac{\varsigma_{5/2}(z=1)}{\varsigma_{3/2}(z=1)} \qquad \text{for } t<1$$

or U is proportional to $t^{5/2}$, and

$$\frac{U}{Nk_BT_E} = \frac{3}{2}t\frac{\varsigma_{5/2}(z)}{\varsigma_{3/2}(z)} = \frac{3}{2}t^{5/2}\frac{\varsigma_{5/2}(z)}{\varsigma_{3/2}(z=1)} \qquad \text{for } t>1$$

where z as a function of t can be determined from the relation

$$t^{3/2} = \frac{\varsigma_{3/2}(z=1)}{\varsigma_{3/2}(z)} \qquad \text{for } t>1.$$

where t is a reduced temperature.

$$t = \frac{T}{T_E}$$

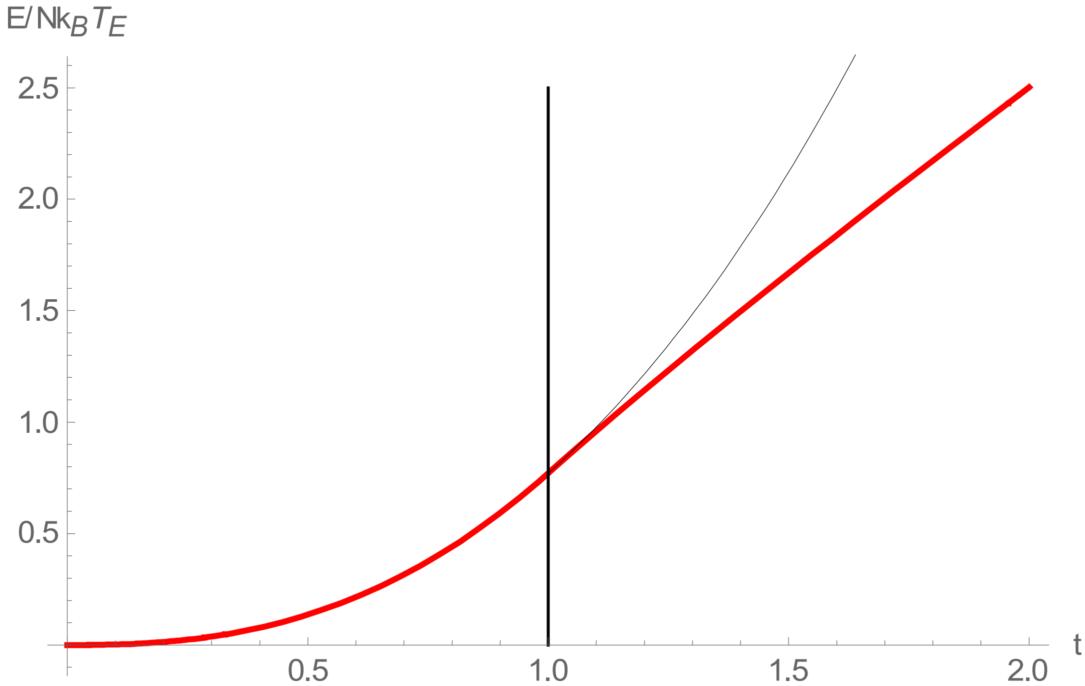


Fig. The internal energy $U/(Nk_BT_E)$ vs $t = T/T_E$. $T_E = T_E(n)$ with $n = N/V$.

Note that the Einstein temperature is given by

$$T_E(n) = \frac{2\pi\hbar^2}{mk_B}\left(\frac{n}{2.61238}\right)^{2/3}.$$

where n is the number density. Note that

$$\frac{2}{\sqrt{\pi}}\int_0^\infty dx \frac{x^{3/2}}{\frac{1}{z}e^x - 1} = \frac{3}{2}\varsigma_{5/2}(z), \qquad \frac{2}{\sqrt{\pi}}\int_0^\infty dx \frac{\sqrt{x}}{\frac{1}{z}e^x - 1} = \varsigma_{3/2}(z)$$

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

Note that there is no contribution from $\varepsilon = 0$ state to the internal energy.

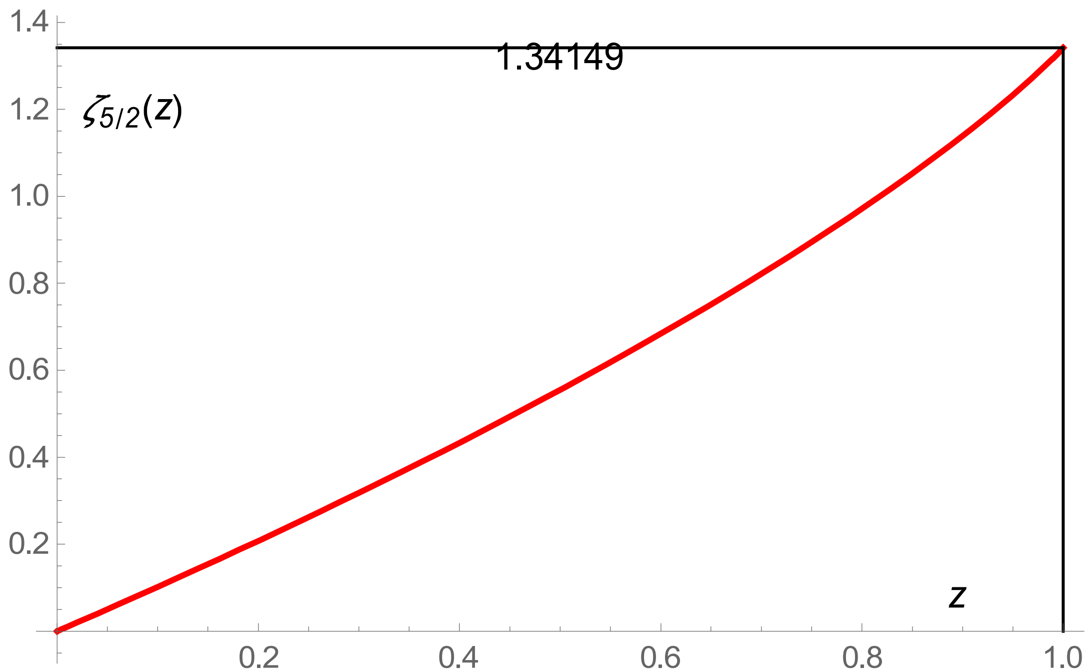


Fig. Plot of $\varsigma_{5/2}(z)$ as a function of z. $\varsigma_{5/2}(z=1) = 1.34149$.

Then the ratio is given by

$$\frac{U}{N_e(T,z)} = \frac{Vn_Q(T)\frac{3}{2}(k_B T)\varsigma_{5/2}(z)}{Vn_Q(T)\varsigma_{3/2}(z)} = \frac{3}{2}k_B T\frac{\varsigma_{5/2}(z)}{\varsigma_{3/2}(z)}$$

Here we note that

$$N = N_0 + N_e(T, z=1)$$

where N_0 is the total number of bosons occupying in the ground state.

$$N_e(T,z) = N \qquad \text{for } T>T_E,$$

$$N_e(T,z=1) = N\left(\frac{T}{T_E}\right)^{3/2} \qquad \text{for } T<T_E$$

and

$$N_0 = N[1 - \left(\frac{T}{T_E}\right)^{3/2}] \qquad \text{for } T<T_E.$$

(i) $T<T_E$,

U is given by

$$U = \frac{3}{2}k_B T N_e(T, z=1)\frac{\varsigma_{5/2}(z=1)}{\varsigma_{3/2}(z=1)} = \frac{3}{2}k_B T\left(\frac{1.34149}{2.61238}\right)N_e(T, z=1)$$
$$= \frac{3}{2}k_B T(0.513513)N_e(T, z=1)$$

Using the expression of $N_e(T, z=1)$, we get

$$U = \frac{3}{2}k_B T(0.513513)N\left(\frac{T}{T_E}\right)^{3/2},$$

The heat capacity C_V is obtained as

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= \frac{3}{2}Nk_B\frac{\varsigma_{5/2}(z=1)}{\varsigma_{3/2}(z=1)}\frac{5}{2}\left(\frac{T}{T_E}\right)^{3/2} \\ &= \frac{15}{4}Nk_B\frac{\varsigma_{5/2}(z=1)}{\varsigma_{3/2}(z=1)}\left(\frac{T}{T_E}\right)^{3/2} \\ &= \frac{15}{4}(0.513513)Nk_B\left(\frac{T}{T_E}\right)^{3/2} \\ &= \frac{3}{2}Nk_B(1.2837825)t^{3/2} \end{aligned}$$

or

$$\begin{aligned} C_V &= \frac{3}{2}Nk_B(0.513513)\frac{5}{2}t^{3/2} \\ &= \frac{3}{2}Nk_B(1.2837825)t^{3/2} \end{aligned}$$

or

$$C_V = Nk_B(1.92567375)t^{3/2}$$

for $T<T_E$, where t is the reduced temperature,

$$t = \frac{T}{T_E}.$$

The heat capacity has a peak [1.925673 Nk_B] at T_E.

(ii) $T>T_E$, $(t>1)$

$N_e(T,z)$ is given by

$$N = N_e(T,z) = Vn_Q(T)\varsigma_{3/2}(z)$$

At $T = T_E$,

$$N = N_e(T_E, z=1) = Vn_Q(T_E)\varsigma_{3/2}(z=1) = Vn_Q(T_E)2.61238,$$

Then we have

$$N = N_e(T, z=1) = Vn_Q(T)\varsigma_{3/2}(z) = Vn_Q(T_E)2.61238$$

or

$$\varsigma_{3/2}(z) = (\frac{T_E}{T})^{3/2}2.61238 = 2.61238t^{-3/2}$$

From the numerical calculation (ContourPlot), the parameter z can be evaluated as a function of t

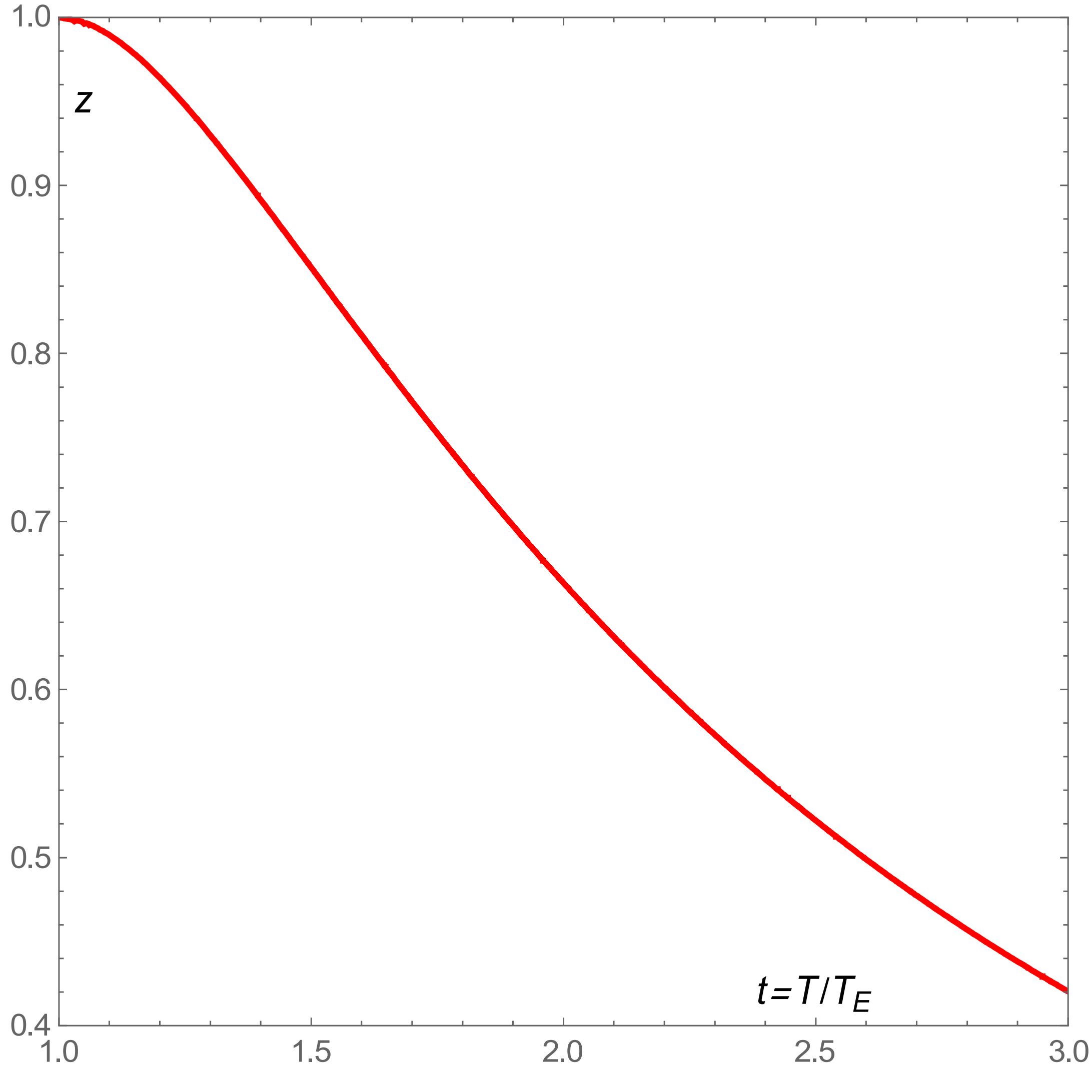
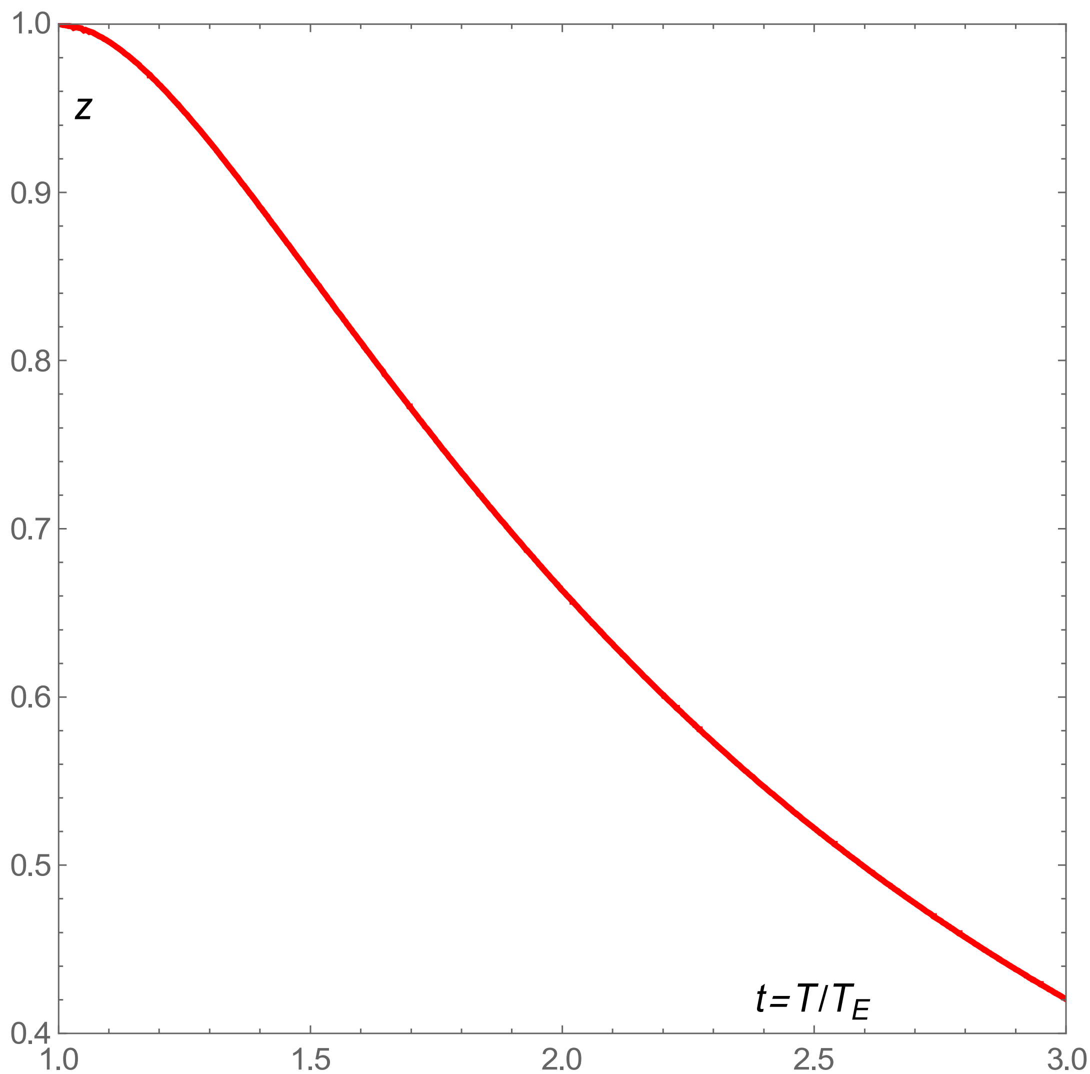


Fig. Plot of z vs a reduced temperature t above T_E.

((**Note**)) Mathematica (ContourPlot)

$$\varsigma_{3/2}(z) = (\frac{T_E}{T})^{3/2} 2.61238 = 2.61238 t^{-3/2}$$

```
Clear["Global`*"];
f1 = PolyLog[3/2, z] - 2.61238 t^(-3/2);
g1 = ContourPlot[f1 == 0, {t, 1, 3}, {z, 0, 1},
  PlotPoints → 100, ContourStyle → {Red, Thick},
  PlotRange → {{1, 3}, {0.4, 1}}];
g2 =
 Graphics[
  {Text[Style["z", Black, 12, Italic], {1.05, 0.95}],
   Text[Style["t=T/T_E", Black, 12, Italic],
    {2.5, 0.42}]}];
Show[g1, g2]
```



Then the total energy is given by

$$U = \frac{3}{2} N k_B T \frac{\varsigma_{5/2}(z)}{\varsigma_{3/2}(z)} = \frac{3}{2} N k_B T_E t \frac{\varsigma_{5/2}(z(t))}{\varsigma_{3/2}(z(t))}$$

The heat capacity C_V is evaluated as

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= \frac{3}{2} N k_B \frac{\partial}{\partial t}[t \frac{\varsigma_{5/2}(z(t))}{\varsigma_{3/2}(z(t))}] \end{aligned}$$

or

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\ &= \frac{3}{2} N k_B \frac{\partial}{\partial t}[t^{5/2} \frac{\varsigma_{5/2}(z(t))}{\varsigma_{3/2}(z=1)}] \\ &= \frac{3}{2} \frac{N k_B}{\varsigma_{3/2}(z=1)} \frac{\partial}{\partial t}[t^{5/2} \varsigma_{5/2}(z(t))] \end{aligned}$$

We note that

$$\lim_{z \to 0} \frac{\varsigma_{5/2}(z)}{\varsigma_{3/2}(z)} = 1, \qquad \lim_{z \to 1} \frac{\varsigma_{5/2}(z)}{\varsigma_{3/2}(z)} = 0.5135124468$$

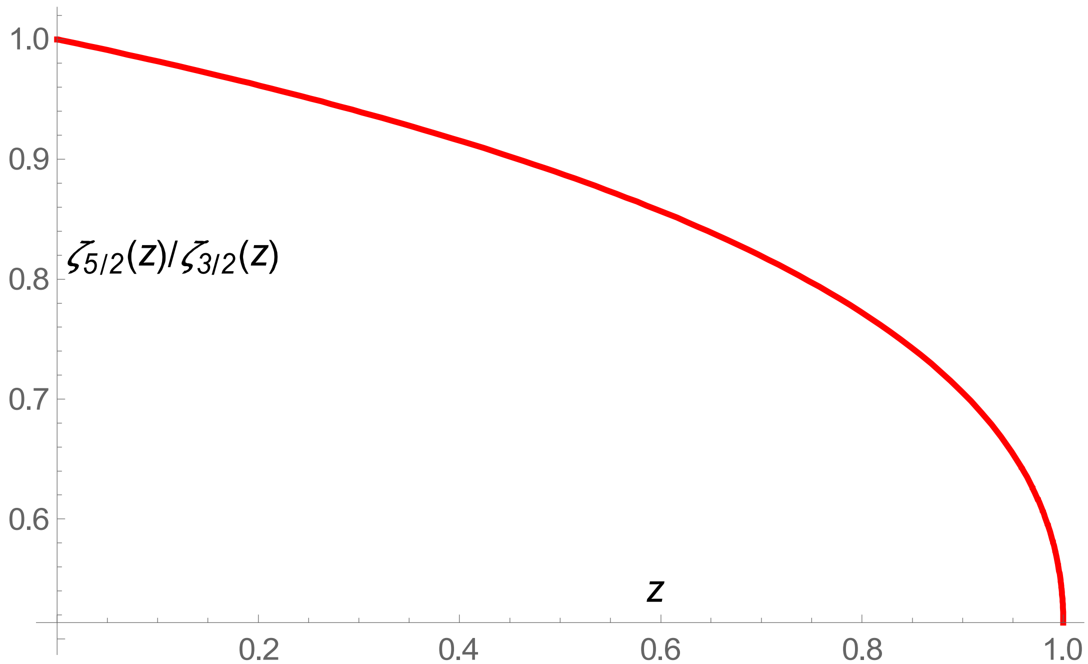


Fig. Plot of $\varsigma_{5/2}(z)/\varsigma_{3/2}(z)$ as a function of z .

At sufficiently high temperatures

$$C_V = \frac{3}{2} N k_B \frac{\partial}{\partial t} t = \frac{3}{2} N k_B$$

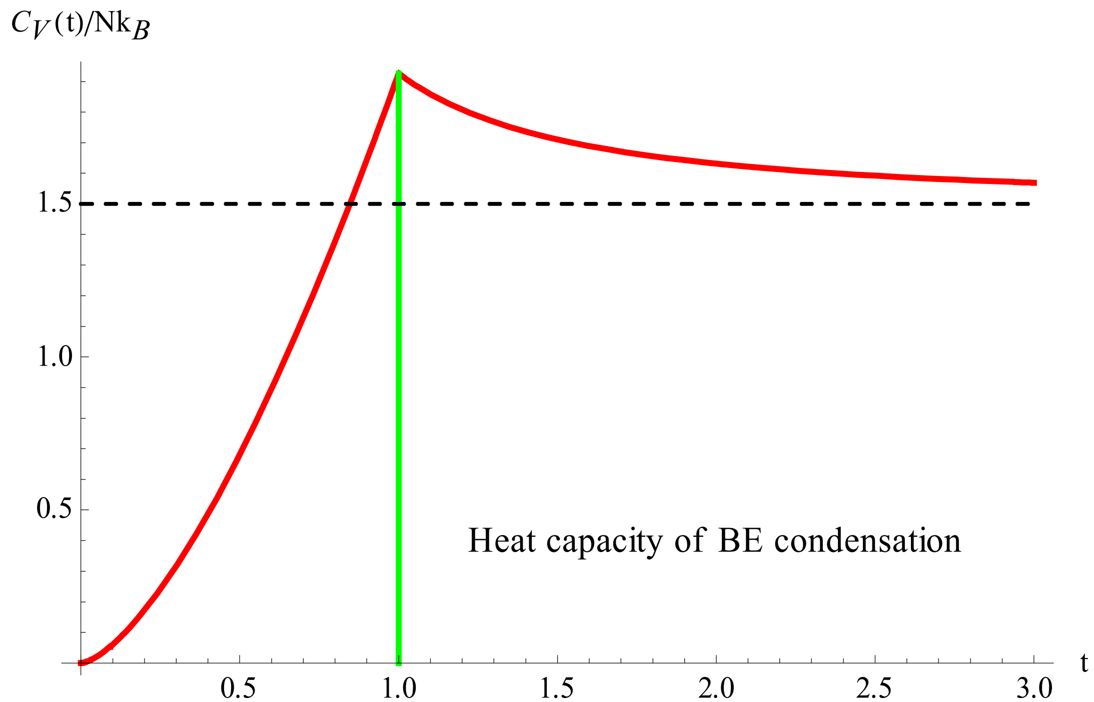


Fig. Normalized heat capacity vs a reduced temperature t (= T/T_E). $C_V / Nk_B \propto t^{3/2}$ for t<1. C_V has a peak at t = 1 (C_V / Nk_B = 1.925). For t>>1, C_V / Nk_B = 1.5. The heat capacity shows a cusp-like behavior at $T = T_E$.

((**Mathematica**))

Heat capacity of the Bose-Einstein condensation

```
Clear["Global`*"];
```

$$\text{k1}[t\_] := \text{PolyLog}\left[\frac{3}{2}, z\right] - \frac{\text{PolyLog}\left[\frac{3}{2}, 1\right]}{t^{3/2}};$$

```
Lamda[t_] := Module[{eq1, eq2, z1},
   eq1 = FindRoot[k1[t] == 0, {z, 0.1, 1}];
   z1 = z /. eq1[[1]]];
```

Interpolation and its derivative

$$\text{E1}[t\_] := \frac{3}{2} t \frac{\text{PolyLog}\left[\frac{5}{2}, \text{Lamda}[t]\right]}{\text{PolyLog}\left[\frac{3}{2}, \text{Lamda}[t]\right]};$$

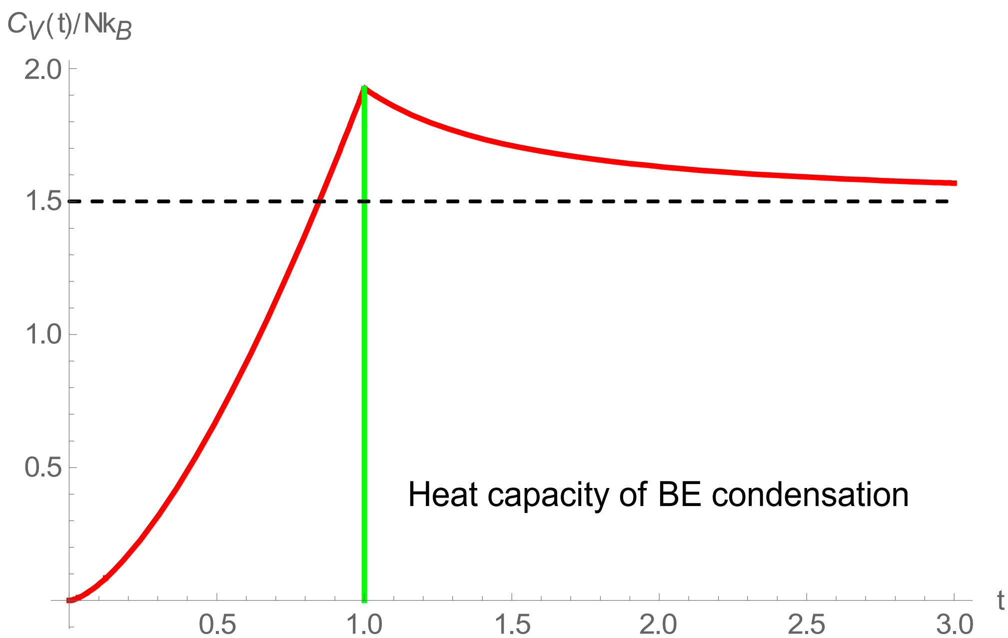
```
g1 = Table[{t, E1[t]}, {t, 1, 10, 0.01}];
g11 = Interpolation[g1];
CU = g11';
```

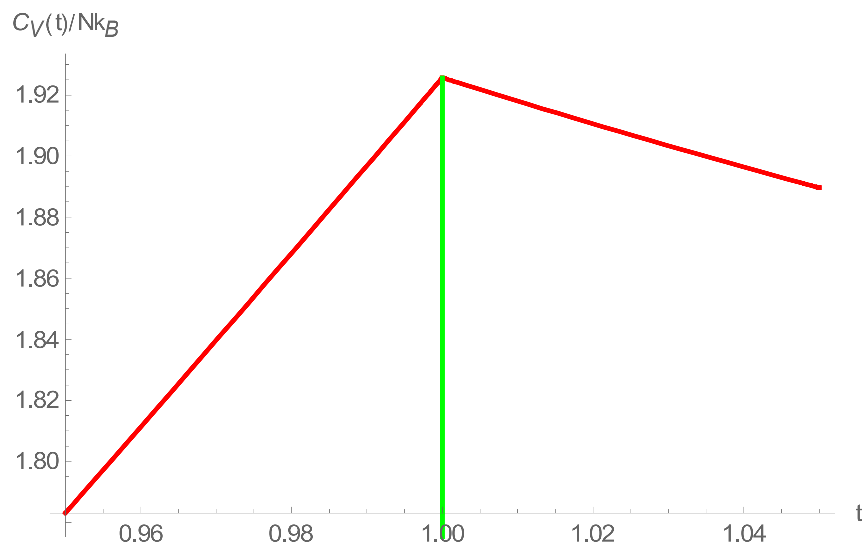
CU :heat capacity normalized by $\frac{3}{2}$ Nk_B for T>TE

CD: heat capacity normalized by $\frac{3}{2}$ Nk_B for T<TE

$$\text{CD}[t\_] := \frac{3}{2}\ 1.2837825\, t^{3/2};$$

```
CDU = Which[0 < t < 1, CD[t], t > 1, CU[t]];
p1 = Plot[CDU, {t, 0, 3}, PlotStyle → {Red, Thick},
  AxesLabel → {"t", "C_V(t)/Nk_B"}];
p2 =
 Graphics[
  {Text[Style["Heat capacity of BE condensation", Black, 12],
    {2.0, 0.4}], Green, Thick, Line[{{1, 0}, {1, CD[1]}}],
   Dashed, Thin, Black, Line[{{0, 1.5}, {3, 1.5}}] }];
Show[p1, p2]
```





((**Note**)) Calculation of the heat capacity above T_E

$$\frac{U}{Nk_B T_E} = \frac{3}{2} t \frac{\zeta_{5/2}(z)}{\zeta_{3/2}(z)}$$

with the condition

$$t^{3/2}\varsigma_{3/2}(z) = \varsigma_{3/2}(z=1)$$

Heat capacity:

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial t}{\partial T}\frac{\partial U}{\partial t} = \frac{1}{T_E}\frac{\partial U}{\partial t}$$

or

$$C_V = \frac{3}{2}\frac{Nk_B}{\varsigma_{3/2}(z=1)}\frac{\partial}{\partial t}[t^{5/2}\varsigma_{5/2}(z(t))]$$

or

$$C_V = \frac{3Nk_B}{2\varsigma_{3/2}(z=1)}\{\frac{5}{2}t^{3/2}\varsigma_{5/2}(z) + t^{5/2}\varsigma_{5/2}'(z)z'(T)\}$$
$$= \frac{3Nk_B t^{3/2}}{2\varsigma_{3/2}(z=1)}\{\frac{5}{2}\varsigma_{5/2}(z) + t\varsigma_{5/2}'(z)z'(T)\}$$

We take a derivative of $t^{3/2}\varsigma_{3/2}(z) = \varsigma_{3/2}(z=1)$ with respect to *t*.

$$\frac{3}{2}t^{1/2}\varsigma_{3/2}(z) + t^{3/2}\varsigma_{3/2}'(z)z'(T) = 0$$

or

$$z'(T) = -\frac{3}{2t}\frac{\varsigma_{3/2}(z)}{\varsigma_{3/2}'(z)}$$

Using this relation, the heat capacity can be rewritten as

$$C_V = \frac{3Nk_B t^{3/2}}{2\varsigma_{3/2}(z=1)}\{\frac{5}{2}\varsigma_{5/2}(z) - \frac{3}{2}\frac{\varsigma_{5/2}'(z)\varsigma_{3/2}(z)}{\varsigma_{3/2}'(z)}\}$$
$$= \frac{3Nk_B t^{3/2}}{2\varsigma_{3/2}(z=1)}\{\frac{5}{2}\varsigma_{5/2}(z) - \frac{3}{2}\frac{[\varsigma_{3/2}(z)]^2}{\varsigma_{1/2}(z)}\}$$

where we use the formula

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

The form of the specific heat for $t > 1$ is

$$\frac{C_V}{Nk_B} = \frac{3t^{3/2}}{4\varsigma_{3/2}(z=1)}\{5\varsigma_{5/2}(z) - 3\frac{[\varsigma_{3/2}(z)]^2}{\varsigma_{1/2}(z)}\}$$

When $t \to 1$ from the high temperature side, z tends to 1 from lower side.

$$\lim_{z\to 1-0}\varsigma_{1/2}(z) = \infty$$

So we have

$$\frac{C_V}{Nk_B} = \frac{15}{4}\frac{\varsigma_{5/2}(z=1)}{\varsigma_{3/2}(z=1)} = 1.92567$$

which agrees with the expression of the heat capacity from the low temperature side

$$\frac{C_V}{Nk_B} = \frac{15}{4}\frac{\varsigma_{5/2}(z=1)}{\varsigma_{3/2}(z=1)} t^{3/2} \qquad \text{for } t < 1$$

((**Mathematica**))

Heat capacity of the Bose-Einstein condensation

```
Clear["Global`*"];
```

$$\text{k1}[t\_] := \text{PolyLog}\left[\frac{3}{2}, z\right] - \frac{\text{PolyLog}\left[\frac{3}{2}, 1\right]}{t^{3/2}};$$

```
Lamda[t_] := Module[{eq1, eq2, z1},
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   z1 = z /. eq1[[1]]];
```

Interpolation and its derivative

$$\text{E1}[t\_] := \frac{3}{4}\, t^{3/2}\, \frac{5\,\text{PolyLog}\left[\frac{5}{2}, \text{Lamda}[t]\right] - \frac{3\left(\text{PolyLog}\left[\frac{3}{2},\text{Lamda}[t]\right]\right)^2}{\text{PolyLog}\left[\frac{1}{2},\text{Lamda}[t]\right]}}{\text{PolyLog}\left[\frac{3}{2}, 1\right]};$$

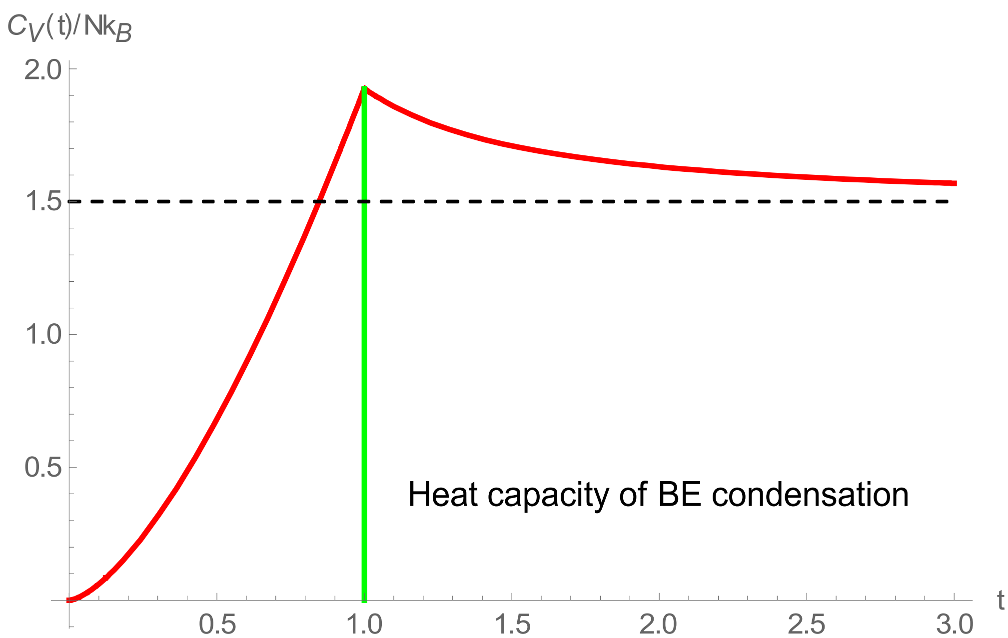
```
g1 = Table[{t, E1[t]}, {t, 1, 10, 0.01}];
g11 = Interpolation[g1];
CU = g11;
```

CU :heat capacity normalized by $\frac{3}{2}\ Nk_B$ for T>TE

CD: heat capacity normalized by $\frac{3}{2}\ Nk_B$ for T<TE

```
CD[t_] := 3/2 1.2837825 t^(3/2);

CDU = Which[0 < t < 1, CD[t], t > 1, CU[t]];
p1 = Plot[CDU, {t, 0, 3}, PlotStyle → {Red, Thick},
  AxesLabel → {"t", "C_V(t)/Nk_B"}];
p2 =
 Graphics[
  {Text[Style["Heat capacity of BE condensation", Black, 12],
    {2.0, 0.4}], Green, Thick, Line[{{1, 0}, {1, CD[1]}}],
   Dashed, Thin, Black, Line[{{0, 1.5}, {3, 1.5}}] }];
Show[p1, p2]
```



2. Entropy

From the thermodynamics, we have

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

The grand potential:

$$\Phi_G = -PV = F - \mu N = U - ST - \mu N = -\frac{2}{3}U$$

since $\mu = 0$ (which is only true below the critical temperature).

Entropy:

$$S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu} = \frac{2}{3}\frac{\partial U}{\partial T} = \frac{2}{3}C_V$$

The entropy continuously changes at $T = T_E$, being indicative of the second-order transition. The entropy becomes zero at $T = 0$ K (Thermodynamics third law).

((**Comment**))

$$\frac{C_V}{U} = \frac{\frac{5}{2}T^{3/2}}{T^{5/2}} = \frac{5}{2T}$$

Because of $\mu = 0$, we have

$$F - G = F - \mu N = F ,$$

or

$$\Phi_G = -PV = F - \mu N = U - ST = -\frac{2}{3}U$$

leading to

$$ST = \frac{5}{3}U$$

Since $S = \frac{2}{3}C_V$,

$$\frac{C_V}{U} = \frac{\frac{3}{2}S}{\frac{3}{5}ST} = \frac{5}{2T}.$$

3. Experimental results

The behavior of the specific heat of a Bose-Einstein gas around T_c is rather similar to the behavior of liquid ^{4}He near T_λ (= 2.17 K). Because of the mutual forces between particles, liquid ^{4}He is certainly not an ideal gas, but perhaps part of the explanation of the lambda transition involves Bose condensation.

A more exact description of the behavior of liquid ^{4}He near T_λ is given by

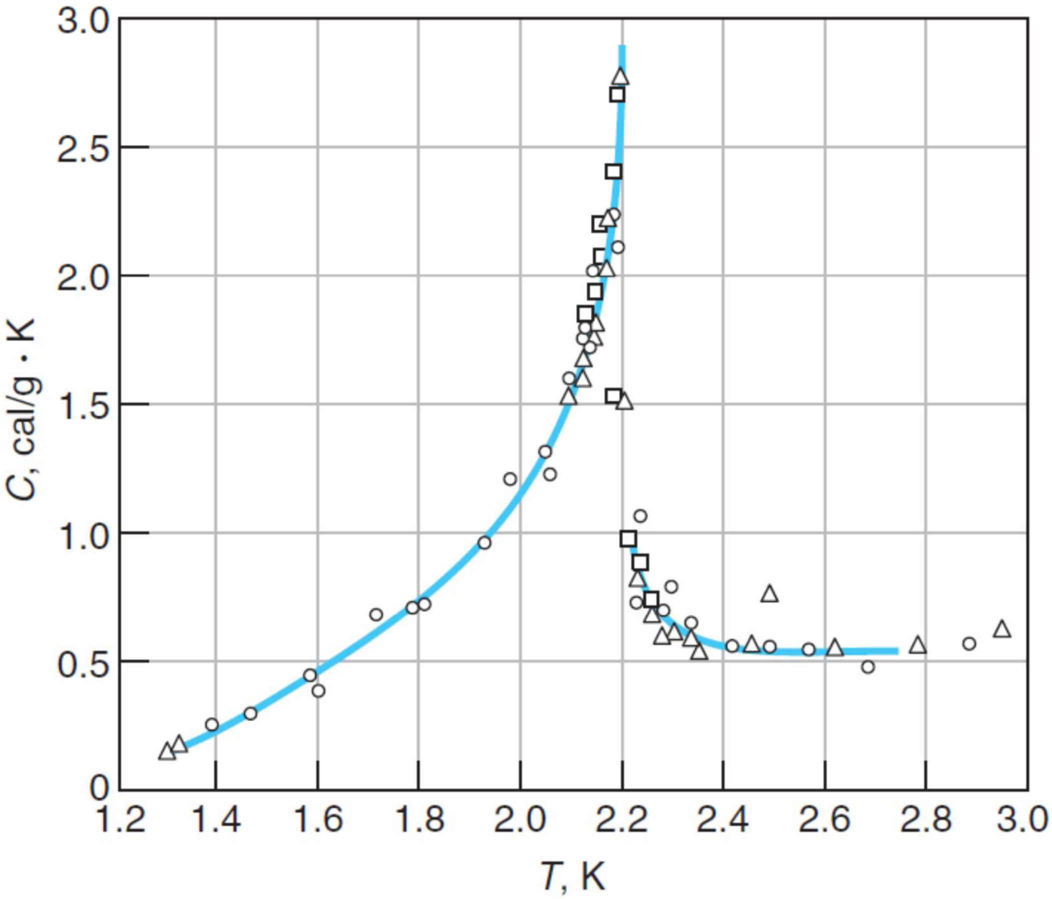
$$C_V = a + b\ln|T - T_\lambda| \qquad \text{for } T<T_\lambda$$

$$C_V = a' + b'\ln|T - T_\lambda| \qquad \text{for } T>T_\lambda$$

((**Experimental result**))

Buckingham, M. J. and Fairbank, W. M., "The Nature of the Lambda Transition", in Progress in Low Temperature Physics III, 1961.

Specific heat of liquid ^{4}He



3.0
2.5
2.0
1.5
1.0
0.5
0
C, cal/g · K
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
T, K

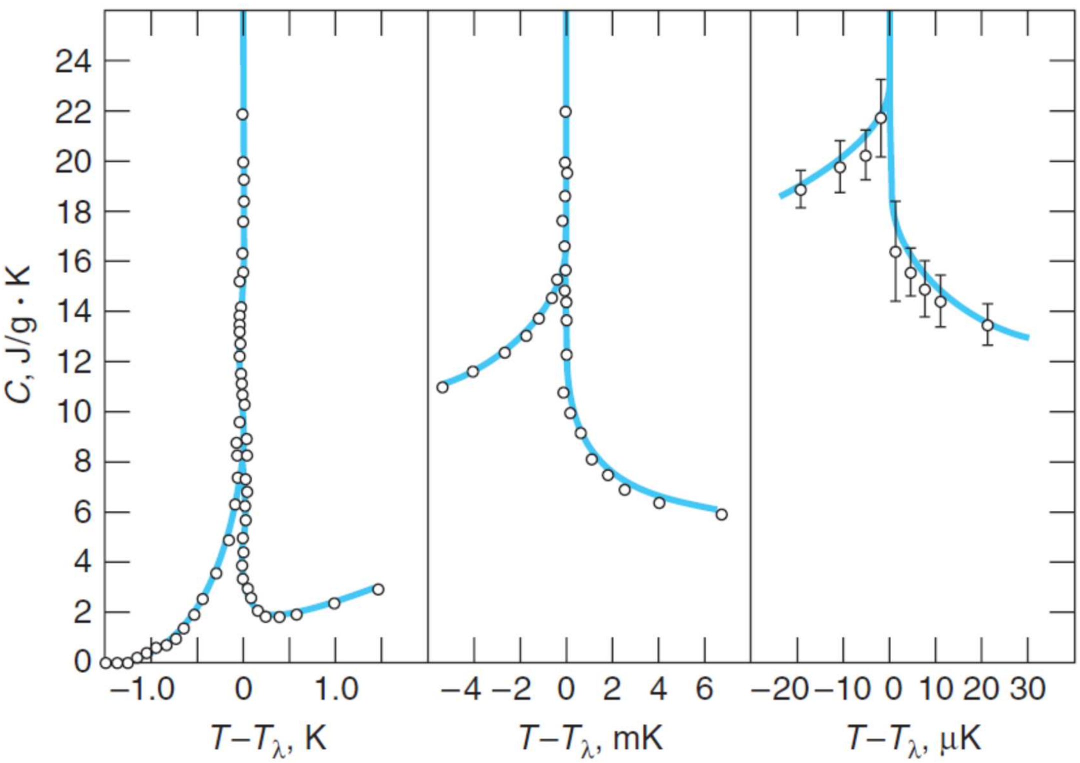


Fig. Specific heat of liquid ^{4}He as a function of T.

APPENDIX

Thermodynamics

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

The grand potential:

$$\Phi_G = -PV = F - \mu N = U - ST - \mu N = -\frac{2}{3}U$$

Entropy:

$$S = -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu} = \frac{2}{3}\frac{\partial U}{\partial T} = \frac{2}{3}C_V \,.$$

So the entropy has a peak at $T = T_E$. The peak value is 1.28333 R.

$$G = F + PV = U - ST + PV = \Phi_G + \mu N + PV = \mu N$$