Statistical Mechanics of Ideal Bose Systems

from Statistical Physics using Mathematica

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The statistical mechanics and thermodynamics of ideal Bose-Einstein systems is developed in terms of special functions defined by integrating the mean occupation number against powers of the single-particle energy. The analytical and numerical properties of these bose functions are studied in considerable detail. Here we consider primarily nonrelativistic systems in three dimensions, but other systems can be explored easily with appropriate modifications of this notebook. Particular attention is paid to the thermodynamics of Bose condensation, with an application made to liquid helium. Bose condensation in atomic traps in developed in concluding exercises.

Introduction

According to the Bose-Einstein distribution function, which is derived within the notebook occupy.nb, the mean occupancy for a single-particle orbital with energy $\varepsilon$ is

$$\bar{n}[\varepsilon] = \frac{1}{\text{Exp}(\frac{\varepsilon - \mu}{k_B T} ) - 1}$$

where chemical potential $\mu$ is a function of density and temperature. Positivity of the mean occupancy requires the chemical potential $\mu$ to be less than or equal to the energy of the lowest single-particle state; hence, since the ground-state is normally placed at $\varepsilon_0 = 0$, we require $\mu \leq 0$. However, if $\mu \to \varepsilon_0$ for a finite temperature $T_c$, the mean occupancy of the ground state appears to diverge. Under these conditions the ground state can display macroscopic occupancy, in which an appreciable fraction of the particles collect in a single state, and the phenomenon of Bose-Einstein condensation occurs; special care is required to obtain consistent results in the regime $T \leq T_c$.

The dependence of the chemical potential upon density and temperature is determined by integrating the occupation numbers to obtain the total particle number

$$N = \int_0^\infty \bar{n}[\varepsilon] D[\varepsilon] \, d\varepsilon$$

where for large systems the density of states, $D[\varepsilon]$, is approximated by a continuous function of energy. For an ordinary nonrelativistic gas in three dimensions, the single-particle energy is simply $\varepsilon = \frac{\hbar^2 k^2}{2m}$ and the density of momentum states is $D(k) \, d^3 k = g V \frac{d^3 k}{(2\pi)^3}$ where $g = 2s + 1$ is the intrinsic degeneracy for a particle with spin $s$ and $V$ is the volume of the system. Generalizations to one- or two-dimensional systems or to relativistic kinematics are developed in the problems at the end of the notebook. The chemical potential enters the above integral through $\bar{n}[\varepsilon]$ in a rather nontrivial fashion that requires numerical evaluation. Similarly, other thermodynamic properties can be expressed in terms of integrals of this type. Therefore, it is useful to define the bose function of order $n$ as
\[
\text{bose}[n, z] = \frac{1}{\Gamma[n]} \int_0^\infty \frac{x^{n-1}}{z^{-1} \text{Exp}[x] - 1} \, dx
\]

where \( z = \text{Exp}\left[ \frac{\mu}{\lambda k_B T} \right] \) is known as the fugacity. The gamma function is included to ensure a convenient normalization, namely \( \text{bose}[n, z] \to z \) for small \( z \). The properties of bose functions are investigated below in considerable detail.

In this notebook we emphasize the properties of ideal nonrelativistic Bose gases in three dimensions with particular attention to the phenomenon of Bose condensation; generalizations to lower spatial dimensionality or to relativistic systems are explored in the problems at the end. Thus, we show below that the grand potential for an ideal nonrelativistic Bose gas in three dimensions becomes

\[
\mathcal{G} = -p V = g k_B T \left( \log[1 - z] - \frac{V \text{bose}[\frac{5}{2}, z]}{\lambda^3} \right)
\]

where \( \lambda = \sqrt{\frac{2 \pi m}{k_B T}} \) is the thermal wavelength. The fugacity, or equivalently the chemical potential, is determined by the equation

\[
n_Q = \frac{N \lambda^3}{g V} = \text{bose}\left[ \frac{3}{2}, z \right]
\]

where \( n_Q \) is the quantum concentration. The phase transition for Bose-Einstein condensation occurs when the fugacity reaches its limiting value of unity for a critical concentration \( n_c \), such that

\[
n_c = \frac{N \lambda^3}{g V} = \text{bose}\left[ \frac{3}{2}, 1 \right] = \zeta\left[ \frac{3}{2} \right], \quad T_c = 3.3125 \left( \frac{N}{g V} \right)^{2/3} \frac{\hbar^2}{k_B m}
\]

For temperatures below the critical temperature, a macroscopic occupation of the ground state develops such that

\[
\tau < 1 \quad \Rightarrow \quad \frac{N_{\text{gs}}}{N} = 1 - \tau^{3/2} \quad \frac{N_{\text{exc}}}{N} = \tau^{3/2}
\]

where \( \tau = T / T_c \) is the reduced temperature expressed in units of the critical temperature. Since the ground state does not contribute to the entropy, energy, or pressure, most of the thermodynamic functions display discontinuities in either slope or value at the critical temperature.

Most textbook presentations of the thermodynamics of Bose gases employ simple box potentials because the mathematics is relatively simple, but experiments studying Bose-Einstein condensation do not use box potentials. A much better approximation to experimental conditions of ultracold atomic traps is provided by harmonic confining potentials. Although the analysis proceeds in a conceptually similar fashion, there are important modifications to the thermodynamic functions. Nevertheless, the Bose functions developed here remain useful. The thermodynamics of harmonic traps is developed in a series of problems at the end of this notebook. The student is strongly encouraged to perform a thorough investigation of these phenomena, using the problems as guidance.

There are also several closely related distributions which describe the behavior of Bose systems which are not subject to a constraint upon the total particle number. In the absence of such a constraint upon particle number, the chemical potential is identically zero. For example, electromagnetic radiation in an enclosure consists of photons, which obey Bose-Einstein statistics but are not constrained to a fixed number. The photon gas obeys the Planck distribution, which is a variation of the Bose-Einstein distribution for \( \mu = 0 \), and is developed in the notebook planck.nb. Similarly, phonons also obey Bose-Einstein statistics with \( \mu = 0 \) and are studied in the notebook debye.nb. The chemical potential, which governs the sharing of a conserved particle number between a system and a reservoir of particles, vanishes for photons or phonons because quanta of excitation are not conserved. Instead, excitation quanta represent sharing of energy between a system and a heat bath and their number is already governed by temperature.
### Glossary

- $N$ = number of particles
- $V$ = volume
- $v$ = volume/particle
- $T$ = temperature
- $k_B$ = Boltzmann constant
- $g$ = energy-level degeneracy
- $\varepsilon$ = single-particle energy
- $k$ = single-particle wave number
- $\mathcal{D}[\varepsilon]$ = density of states wrt energy
- $\mathcal{D}[k]$ = density of states wrt momentum
- $\lambda$ = thermal wavelength
- $n_Q$ = quantum concentration
- $\mu$ = chemical potential
- $z$ = fugacity
- $\mathcal{Z}_1$ = grand partition function for single orbital
- $\bar{n}$ = mean occupation number
- $T_c$ = critical temperature for Bose-Einstein condensation
- $\tau$ = reduced temperature ($T / T_c$)
- $\mathcal{G}$ = grand potential
- $U$ = internal energy
- $p$ = pressure
- $S$ = entropy
- $F$ = free energy
- $H$ = enthalpy
- $C_V$ = isochoric heat capacity
- $C_p$ = isochoric heat capacity
- $\gamma = \frac{C_p}{C_V}$ = ratio of principal heat capacities
- $\text{bose}[n, z]$ = Bose-Einstein function of order $n$
- $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_p$ = isobaric expansivity
- $\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$ = isothermal compressibility
- $\kappa_S = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_S$ = adiabatic compressibility
Initialization

- Defaults, packages, and symbols

  ClearAll["Global`*"];
  Off[General::spell, General::spell1];

  $DefaultFont = {"Times", 12};
  $TextStyle = {FontFamily → "Times", FontSize → 12, FontSlant → "Italic"};

  Needs["Utilities`Notation`"];
  Needs["Miscellaneous`PhysicalConstants`"];
  Needs["Miscellaneous`Units`"];
  Needs["Graphics`Master`"]

  Symbolize[\[ScriptCapitalN]\]

  Symbolize[kB]; Symbolize[nx_]; Symbolize[\[Lambda]x_];
  Symbolize[Tx_]; Symbolize[Cx_]; Symbolize[vx_]; Symbolize[Vx_]

  Symbolize[Nx_]; Symbolize[\[HBar]h]; Symbolize[\[Bar]h]

  Symbolize[kmax]; Symbolize[\[Kappa]x_]


  SetAttributes[{kB, \[HBar]h, g, m}, Constant];

  FundamentalConstants =
  \[\{kB \rightarrow \frac{\text{BoltzmannConstant}}{\text{Kelvin}}, \[HBar]h \rightarrow \frac{\text{PlanckConstantReduced}}{\text{Joule Second}}\}\];

- Memory management

  This notebook consumes enough memory that it becomes advantageous to run the memory conservation utility. However, we are not interested in seeing the messages reporting the actions of that process.

  Needs["Utilities`MemoryConserve`"];
  Off[MemoryConserve::start, MemoryConserve::end];

- Error messages

  Several annoying error messages can be suppressed, if desired, but should be enabled when developing or debugging code.
Off[General::ovfl];
Off[Solve::ifun];
Off[NIntegrate::inum];
Off[NIntegrate::ncvb];
Off[NIntegrate::slwcon];
Off[NIntegrate::precw];

**Rules for changing variables**

\[
\begin{align*}
T\to\Lambda &= \left\{ T \to \frac{2\pi\hbar^2}{m_k^2\lambda^2}, \quad \beta \to \frac{1}{k_B T} \right\}; \\
\Lambda \to T &= \left\{ \lambda \to \sqrt{\frac{2\pi\hbar^2}{m_k T}} \right\}; \\
\lambda \to Z &= \left\{ \lambda \to \left( \frac{g\sqrt{\text{bose}\left[ \frac{3}{2}, z \right]} N}{\mathcal{N}} \right)^{1/3} \right\}; \\
\text{bose} \to \lambda &= \left\{ \text{bose}\left[ \frac{3}{2}, z \right] \to \frac{N\lambda^3}{g\mathcal{V}} \right\}; \\
z \to \tau &= z \to \text{fugacity}[\tau]; \\
\mu \to Z &= \mu \to k_B T \log[z] \\
z \to T &= z \to \exp\left[ \frac{\mu}{k_B T} \right];
\end{align*}
\]

**Simplification rules**

\[
\begin{align*}
\text{MyAssumptions} &= \{ m > 0, \quad V > 0, \quad g > 0, \quad k_B > 0, \quad n_\_ > 0, \quad \hbar > 0, \quad T > 0, \quad \hbar > 0, \quad \lambda > 0, \quad \beta > 0, \quad N > 0 \}; \\
\text{MySimplify} &= \text{Simplify}[#, \text{MyAssumptions}] &; \\
\text{MyFullSimplify} &= \text{FullSimplify}[#, \text{MyAssumptions}] &;
\end{align*}
\]

**Density of states**

Evaluate the density of states for nonrelativistic gas in 3 dimensions in terms of both momentum and energy.

\[
\begin{align*}
\mathcal{D}[k] &= \frac{4\pi g V k^2}{(2\pi)^3}; \\
\epsilon_k &= \frac{(\hbar k)^2}{2m}; \\
\mathcal{D}[\epsilon] &= \frac{\mathcal{D}[k]}{\partial_k \epsilon_k} \quad \text{//} \quad \left\{ k \to \frac{\sqrt{2m}\epsilon}{\hbar} \right\} \quad \text{//} \quad \text{PowerExpand} \\
g \frac{m^{3/2} \sqrt{\epsilon}}{\sqrt{2\pi} \hbar^3}
\end{align*}
\]
Bose-Einstein functions

In this section we explore some of the symbolic and numerical properties of Bose-Einstein functions and develop some simplification rules that will be useful in later sections.

Definitions

Bose-Einstein functions are also known as polylogarithm functions and are represented by Mathemtica as 
\[
\text{PolyLog}[\nu, z]
\]

\[
\text{bose}[\nu_, z_] = \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{x^{\nu-1}}{\exp(x/z) - 1}, \text{Assumptions} \rightarrow \{\text{Re}\{\nu\} > 0\}
\]

The Bose-Einstein functions for \(\nu, \frac{1}{2}, \frac{3}{2}\) are plotted as functions of \(z\). In addition, the limiting case of \(\nu \to \infty\), where \(\text{bose}[\nu, z] \to z\), is shown. Note that functions with \(\nu \leq 1\) diverge as \(z \to 1\), \(\text{bose}[\frac{3}{2}, z]\) remains finite at \(z = 1\) but with infinite slope, while functions with \(\nu > \frac{1}{2}\) have finite values and slopes at \(z = 1\). Hence, for \(\nu \leq \frac{3}{2}\) special attention is needed to handle the vicinity of \(z \to 1\).

\[
\text{Plot}\left[\text{Evaluate}\left[\text{Table}\left[\text{bose}[\nu, z], \{\nu, \frac{1}{2}, 3, \frac{1}{2}\}\right], \{z, 0, 0.999\}\right], \text{PlotRange} \rightarrow \{(0, 1), (0, 2.5)\}, \text{GridLines} \rightarrow \text{Automatic}, \text{Frame} \rightarrow \text{True}, \text{FrameLabel} \rightarrow \{"z", "g[z]"}, \text{PlotLabel} \rightarrow \text{"Bose-Einstein functions"}\right];
\]

Small z expansion

Inspection of the Taylor series around \(z \to 0\)
suggests that the general power series takes the form

\[
\text{boseZexpansion}[ν, z, k_{\text{max}}] := \sum_{k=1}^{k_{\text{max}}} \frac{z^k}{k^ν}
\]

Below we verify that the infinite series does reproduce the desired function.

\[
\text{bose}[ν, z] = \text{boseZexpansion}[ν, z, ∞]
\]

True

Thus, we recognize that Bose-Einstein functions are closely related to the \text{Zeta} function

\[
\sum_{k=1}^{∞} \frac{z^k}{k^ν}
\]

\text{PolyLog}[ν, z]

\text{bose}[ν, 1]

\text{Zeta}[ν]

It will be useful to define a rule for small \(z\) as follows.

\[
z\text{SmallRule} = \text{bose}[ν, z] \rightarrow \text{boseZexpansion}[ν, z, 3]
\]

\text{PolyLog}[ν, z] \rightarrow z + 2^{-ν} z^2 + 3^{-ν} z^3

### Asymptotic expansion for \(z\) near 1

The behavior of Bose-Einstein functions near \(z \rightarrow 1\) must be studied with more care because the integrand is singular at \(x = 0\) for \(ν ≤ 1\) and is undefined (0/0) for larger \(ν\). In the following we develop an expansion for \(z\) near unity, following the method of J.E. Robinson, Phys. Rev. 83, 678 (1951). The method is based upon the Mellin transform of the expansion in powers of \(z\) developed in the previous section. We define \(α\) by \(z = e^{-α}\) such that the Mellin transform takes the following form.

\[
\text{Clear}[α]
\]

\[
\text{mellinTransform}[ν, t] = \sum_{k=1}^{∞} \int_{0}^{∞} \frac{z^{t-1} \text{Exp}[-k α]}{k^ν} \text{d}α
\]

The inverse transform is obtained by integration in the complex \(t\)-plane along a line with positive \text{Real}[\(t\)] that is parallel to the imaginary axis. The contour is closed with an infinite semicircular arc, to the left, where it can be shown that the integrand vanishes sufficiently rapidly. The inverse transform is then

\[
\text{inverseMellinTransform} =
\]

\[
\frac{1}{2 \pi i} \int_{c-i∞}^{c+i∞} \alpha^{-t} \text{mellinTransform}[ν, t] \text{d}t = \sum_{\text{poles}} \alpha^{-t} \text{Residue}[\text{mellinTransform}[ν, \text{pole}]]
\]

\(\text{Gamma}[t]\) has simple poles at \(t = -m\), where \(m\) is a nonnegative integer, with residues \((-1)^m\). \(\text{Zeta}[t + n]\) has a simple pole with unit residue at \(t = 1 - n\). Therefore, when \(ν ≤ 0\) or \(ν\) is nonintegral the inverse transform becomes:
\[ \text{inverseMellinTransform}[\nu, \alpha, k_{\text{max}}] = \sum_{m=0}^{k_{\text{max}}} \frac{\alpha^m \text{Zeta}[\nu - m] (-1)^m}{m!} + \text{Gamma}[1 - \nu] \alpha^{\nu - 1} \]
\[ \alpha^{-1/\nu} \text{Gamma}[1 - \nu] + \sum_{m=0}^{k_{\text{max}}} \frac{\alpha^m \text{Zeta}[\nu - m] (-1)^m}{m!} \]

Although the present formulation is indeterminate when \( \nu \) is a positive integer, Robinson used analytic continuation to demonstrate that the result above is, in fact, valid for all \( \nu \) because the singularities cancel. Below we evaluate the first few terms numerically for several \( n \).

\[ \text{boseAlphaExpansion}[\nu, \alpha, k_{\text{max}} : \_] = \text{inverseMellinTransform}[\nu, \alpha, k_{\text{max}}] \]
\[ \alpha^{-1/\nu} \text{Gamma}[1 - \nu] + \sum_{m=0}^{k_{\text{max}}} \frac{\alpha^m \text{Zeta}[\nu - m] (-1)^m}{m!} \]

\[ \text{boseAlphaExpansion}[\nu, \alpha, 3] \]
\[ \alpha^{-1/\nu} \text{Gamma}[1 - \nu] - \frac{1}{6} \alpha^3 \text{Zeta}[-3 + \nu] + \frac{1}{2} \alpha^2 \text{Zeta}[-2 + \nu] - \alpha \text{Zeta}[-1 + \nu] + \text{Zeta}[\nu] \]

\[ N[\text{boseAlphaExpansion}\left[\frac{1}{2}, \alpha, 3\right]] \]
\[ -1.46035 + \frac{1.77245}{\sqrt{\alpha}} + 0.207886 \alpha - 0.0127426 \alpha^2 - 0.00141949 \alpha^3 \]

\[ N[\text{boseAlphaExpansion}\left[\frac{3}{2}, \alpha, 3\right]] \]
\[ 2.61238 - 3.54491 \sqrt{\alpha} + 1.46035 \alpha - 0.103943 \alpha^2 + 0.00424753 \alpha^3 \]

\[ N[\text{boseAlphaExpansion}\left[\frac{5}{2}, \alpha, 3\right]] \]
\[ 1.34149 - 2.61238 \alpha + 2.36327 \alpha^{3/2} - 0.730177 \alpha^2 + 0.0346477 \alpha^3 \]

\[ N\left[\frac{\text{boseAlphaExpansion}\left[\frac{3}{2}, \alpha, 3\right]}{\text{bose}\left[\frac{3}{2}, z\right]} \right] / . \{\alpha \to 0.9, z \to \text{Exp}[-\alpha]\} \]
\[ 0.999567 \]

It will be useful to define an expansion rule for \( z \to 1 \) as follows.

\[ \text{zLargeRule}[mm_] = \text{bose}[\nu, z] \to \text{boseAlphaExpansion}[\nu, -\text{Log}[z], mm] \]

\[ \text{PolyLog}[\nu, z] \to \text{Gamma}[1 - \nu] (-\text{Log}[z])^{-1/\nu} + \sum_{m=0}^{\infty} \frac{(-\text{Log}[z])^m \text{Zeta}[\nu - m] (-1)^m}{m!} \]

\section*{Recursion relations for symbolic derivatives}

It is also useful to note the following downward recursion relation for derivatives.

\[ \frac{\partial_z \text{bose}[\nu, z]}{z} \]
\[ \text{PolyLog}[-1 + \nu, z] \]
\[ z \partial_z \text{bose}[v, z] = \text{bose}[v - 1, z] \]

True

### Rules for manipulation of Bose-Einstein integrals

Unfortunately, the Mathematica Integrate function still fails to recognize several simple variants of the Bose-Einstein integral. Furthermore, we would like to employ symbolic integrals without needing to specify the parameters. Therefore, in order to guide Mathematica toward proper evaluation of these integrals, we need to temporarily unprotect the Integrate routine so that we may install our own rules for the relevant types of integrals. It is necessary to provide some rather redundant rules to ensure that all equivalent variations are recognized.

\begin{align*}
\text{Unprotect}[\text{Integrate}];
\int_0^\infty \frac{A\ x\ x^n}{\text{Exp}[\beta\ .\ x_] - 1} \ dx_\_ &= A \frac{\Gamma[n + 1] \eta[n + 1]}{\beta^{n + 1}} \\
\int_0^\infty \frac{A\ \text{Exp}[-\beta\ .\ x_] \ x\ x^n}{1 - \text{Exp}[-\beta\ .\ x_]} \ dx_\_ &= A \frac{\Gamma[n + 1] \eta[n + 1]}{\beta^{n + 1}} \\
\int_0^\infty \frac{A\ x\ x^n}{\text{Exp}[\beta\ .\ x_] - 1} \ dx_\_ &= A \frac{\Gamma[n + 1] \text{bose}[n + 1, z]}{\beta^{n + 1}} \\
\int_0^\infty \frac{A\ \text{Exp}[-\beta\ .\ x_] \ x\ x^n}{1 - z \text{Exp}[-\beta\ .\ x_]} \ dx_\_ &= A \frac{\Gamma[n + 1] \text{bose}[n + 1, z]}{z \beta^{n + 1}}
\end{align*}

\text{sumRule} = \int_0^\infty (a\ +\ b\ .\ ) \ dx_\_ \Rightarrow \int_0^\infty a\ dx + \int_0^\infty b\ dx; \\
\text{partsRule1} = \int_0^\infty x\ x^n - y\ dx_\_ \Rightarrow \int_0^\infty -mx^{n - 1} \int y\ dx\ dx; \\
\text{partsRule2} = \int_0^\infty x\ x^n - y\ dx_\_ \Rightarrow \int_0^\infty -\frac{x^{n + 1}}{m + 1} \partial_x y\ dx;

\text{Protect}[\text{Integrate}];
\text{gammaRule} = n\ .\ \Gamma[n\ .\ ] \rightarrow \Gamma[n + 1];
Occupation numbers and chemical potential

Mean occupation number

The mean occupation number, as a function of energy and chemical potential, is determined from the grand partition function. In addition, the total number of particles in excited states is obtained by integrating the density of states against the occupation number distribution. However, this method does not determine the ground state occupancy because the density of states is inaccurate for low energies, giving no weight to the ground state.

\[
Z_1^{BE} = \sum_{n=0}^{\infty} \exp \left[ -n \beta (\varepsilon - \mu) \right] \\
\frac{e^{\beta (\varepsilon - \mu)}}{1 + e^{\beta (\varepsilon - \mu)}}
\]

\[
\bar{N}_{BE} = k_B T \partial_{\mu} \left( \text{Log}[Z_1^{BE}] / \{ \beta \rightarrow \frac{1}{k_B T} \} \right) // \text{FullSimplify}
\]

\[
\frac{1}{1 + e^{\frac{\mu}{k_B T}}}
\]

\[
\bar{N}_{BE} /. \text{muToZ} // \text{FullSimplify}
\]

\[
\frac{Z}{e^{\frac{\mu}{k_B T}} - 1}
\]

The fugacity, for the Bose-Einstein distribution must be limited to the range \(0 \leq z \leq 1\) so that the mean occupation number is nonnegative.

Evaluate the total number of particles in excited states

Although direct summation of the mean occupancy for all single-particle states should give the total number of particles in the system, for practical reasons we normally replace the sum by an integration over a continuous density of states. However, the density of states formula for a nonrelativistic three-dimensional gas gives no weight to the ground state because the analytic density of states is proportional to \(\sqrt{\varepsilon}\) and approaches zero. Therefore, integration of the mean occupancy against the density of states only gives the total number of particles, \(N_{exc}\), that occupy excited single-particle states. The number of particles in the ground state, \(N_{gs}\), can then be obtained directly from the mean occupancy as

\[
N_{gs} = N - N_{exc} = \frac{1}{1-z}
\]

Therefore, as \(z \rightarrow 1\) the occupancy of the ground state becomes macroscopic.

\[
N_{exc}[z_] = \\
\text{Integrate}\left[ D[\varepsilon] \bar{N}_{BE} / . \text{muToZ}, \{\varepsilon, 0, \infty\}, \text{Assumptions} \rightarrow \{\text{Re}\left[\frac{1}{k_B T}\right] > 0\} \right] / . \text{TtoLambda} // \text{PowerExpand} // \text{Simplify}
\]

\[
\frac{g V \text{PolyLog}\left[\frac{1}{3}, z\right]}{\lambda^3}
\]

This expression shows that the total number of particles found in excited states depends upon temperature, volume, chemical potential, and the particle type (mass, spin degeneracy). However, the chemical potential is itself a function of temperature and density that is required to be nonpositive. Hence, if the chemical potential reaches zero for a finite critical temperature, \(T_c\), the number of particles in excited states has an explicit value that depends only on temperature.
and volume (and particle type). Therefore, any additional particles that are added to the system must enter the ground state because there is no room for them in excited states. The ground state then develops a macroscopic occupancy that is described as Bose-Einstein condensation.

### Critical temperature

The importance of quantum properties of the system is governed by the quantum concentration, \( n_Q \), defined by the product of the density and the volume corresponding to the thermal de Broglie wave length, \( \lambda \). It is also useful to include the intrinsic degeneracy of single-particle states, \( g \). Bose concentration occurs when the chemical potential \( \mu \) reaches zero and it is no longer possible to accommodate the particle number \( N \) among the excited states. At this point, the occupation of the ground state must become macroscopic and hence diverges for \( N \to \infty \).

\[
\begin{align*}
  n_Q &= \frac{N \lambda^3}{g V}; \\
  n_c &= \frac{n_Q N_{\text{exc}}[1]}{N} \zeta \left[ \frac{3}{2} \right] \\
  n_Q / \lambda &/. \text{lambdaToT} \\
  T_c &= T / \lambda /. \text{Solve}[n_Q = n_c / \lambda /. \text{lambdaToT}, T][1] \\
  \lambda_c &= \lambda / \lambda /. \text{Solve}[n_Q = n_c, \lambda][1] \\
  \{n_c, \lambda_c, T_c\} &/. N \\
  \{2.61238, 1.37725 g^{1/3} V^{1/3}, 3.3125 N^{2/3} / g^{2/3} k_B m V^{2/3} \}
\end{align*}
\]

As expected, the critical concentration for nonrelativistic Bose gases in three dimensions is of order unity. The critical temperature is then determined by the mass and density. However, it is also important to note that Bose condensation does not occur for relativistic systems or for smaller spatial dimensionality because with \( N_{\text{exc}} \) proportional to \( \text{bose}[\nu, z] \), a smaller \( \nu \) allows \( N_{\text{exc}} \) to diverge at \( z = 1 \) so that the excited states can accommodate essentially infinite particle number.

### Ground state occupation

Now it is clear that below the critical temperature, where \( z \) is constant, the fraction of the total number of particles that are found in excited states must scale with \( \tau^{3/2} \), where \( \tau = T / T_c \), with the remainder in the ground state.

\[
\begin{align*}
  N_{gs}[\tau_- /; \tau < 1] &= N (1 - \tau^{3/2}) \\
  N_{gs}[\tau_- /; \tau \geq 1] &= 0
\end{align*}
\]
We can now determine the actual value of \( z \) for \( T < T_c \) more precisely.

\[
z_{\text{sol}} = \text{Solve}\left[N_{\text{gs}}(\tau) = \frac{g}{1 - z} \cdot z \right][1]\n\]

\[
\{ z \rightarrow \frac{N_{\text{gs}}(\tau)}{g + N_{\text{gs}}(\tau)} \}\n\]

\[
\text{Series}[z / . z_{\text{sol}}, \{N_{\text{gs}}[\tau], \infty, 1\}]
\]

\[
1 - \frac{g}{N_{\text{gs}}(\tau)} + O\left[\frac{1}{N_{\text{gs}}(\tau)}\right]^2
\]

In the immediate vicinity of the phase transition we can expand about \( \tau = 1 \), but must be careful interpreting this result because \( N \) is usually extremely large.

\[
\text{(Series}[z / . z_{\text{sol}}, \{N_{\text{gs}}[\tau], \infty, 1\}] / . N_{\text{gs}}[\tau] \rightarrow N (1 - \tau^{3/2}) \} // \text{Normal} //
\]

\[
\text{Series}[, \{\tau, 1, 2\}] & // \text{Collect}[#, \{N\}] &
\]

\[
1 + \frac{-\frac{g}{g} + \frac{2 g}{3 (1 - \tau^2)} + \frac{5}{12} g (1 + \tau)}{N} - \frac{\frac{5}{144} g (1 + \tau)^2}{N}
\]

### Temperature dependence of chemical potential and occupancy

In this section we construct an interpolation function to represent the chemical potential as a function of reduced temperature. This interpolation function can then be used to display the temperature dependence of thermodynamic functions. Note that we approximate \( z \) by unity for \( T < T_c \), which is appropriate for large systems.

Here we express energy and chemical potential in units of \( k_B T_c \) and temperature as \( \tau = T / T_c \).
\[
eq 1 \triangleq \frac{\text{Ne}_N}{\lambda \text{T} \rightarrow T} \quad \text{/ PowerExpand}
\]
\[
1 = \frac{N}{z} \quad \text{/ PolyLog}
\]
\[
z \text{Solution} = z / \text{FindRoot}[\text{Evaluate}[\text{eq1}[z, \tau]], \{z, 0.9, 0.85\}]
\]
\[
\text{pointsNearTc} = \text{Prepend}[\text{Evaluate}[\text{Table}[[\tau, \tau \text{Log}[z \text{Solution}[\tau]]], \{\tau, 1.2, 1.5, 0.1\}]], \{1., 0.\}];
\]
\[
\text{pointsAtLargerT} = \text{Table}[[\tau, \tau \text{Log}[z \text{Solution}[\tau]]], \{\tau, 2, 10, 0.5\}];
\]
\[
\text{points} = \text{Join}[\text{pointsNearTc}, \text{pointsAtLargerT}];
\]
\[
\text{Clear[chemicalPotential]}
\]
\[
\text{chem} = \text{Interpolation}[\text{points}, \text{InterpolationOrder} \rightarrow 5];
\]
\[
\text{chemicalPotential}[\tau_\_ \land; \tau > 1] = \text{chem}[[\tau]]
\]
\[
\text{chemicalPotential}[\tau_\_ \land; \tau \leq 1] = 0;
\]
\[
\text{DisplayTogether}[\text{Plot}[\text{chemicalPotential}[\tau], \{\tau, 0, 5\}],
\quad \text{ListPlot}[\text{points}, \text{PlotStyle} \rightarrow \text{AbsolutePointSize}[4]],
\quad \text{PlotRange} \rightarrow \{\{0, 5\}, \{-8, 1\}\}, \text{PlotLabel} \rightarrow \text{"Chemical Potential"},
\quad \text{GridLines} \rightarrow \text{Automatic}, \text{Frame} \rightarrow \text{True}, \text{FrameLabel} \rightarrow \{\text{"T/T}_c\", \text{"$/mu$/\text{(kBT}_c)\"}\}];
\]
\[
\text{fugacity}[\tau_\_ \land; \tau > 1] = \text{Exp}[[\text{chemicalPotential}[\tau] \land \tau / \tau]]
\]
\[
\text{fugacity}[\tau_\_ \land; \tau \leq 1] = 1
Display mean occupation numbers for several temperatures

Clear[temp];

\[ \text{temp}[\tau_] := \frac{\text{h}_{\text{BE}}}{k_B} \cdot (k_B \rightarrow 1, T \rightarrow \tau, \mu \rightarrow \text{chemicalPotential}[\tau]); \]

nBEplot[\tau_] := Plot[temp[\tau], \{\epsilon, 0, 2\}, PlotRange \rightarrow \{0, 2\}, \{0, 5\}],
PlotLabel \rightarrow "Occupation Number", GridLines \rightarrow \text{None}, Frame \rightarrow \text{True},
FrameLabel \rightarrow \{"\epsilon/(k_B T_c)" \"\hbar"\}, DisplayFunction \rightarrow \text{Identity};
Show[{nBEplot[1.1], nBEplot[2], nBEplot[5]},
DisplayFunction -> $DisplayFunction];

Occupation Number

\[ \bar{\eta} \]

Rules for derivatives with respect to temperature

\[ \frac{3}{2} z \text{bose}\left[\frac{3}{2}, z\right] \]
\[ \frac{2}{T} \text{bose}\left[\frac{1}{2}, z\right] \];

\[ d\lambda = dt[\lambda, T, \text{Constants} \rightarrow \{N, V\}] \rightarrow \frac{\lambda}{2 T} ; \]
\[ dz_{\text{thigh}} = dt[z, T, \text{Constants} \rightarrow \{N, V\}] \rightarrow dzdT; \]
\[ dz_{\text{tlow}} = dt[z, T, \text{Constants} \rightarrow \{N, V\}] \rightarrow 0; \]

\[ eq2 = \frac{N \lambda^3}{g V} = \text{bose}\left[\frac{3}{2}, z\right] \]
\[ \frac{N \lambda^3}{g V} = \text{PolyLog}\left[\frac{3}{2}, z\right] \]

\[ dz_{\text{rules}} = \text{Flatten}\left[\right. \right. \]
\[ \left. \left. \{\text{Solve}[dt[eq2, V, \text{Constants} \rightarrow \{N, T, \lambda\}], dt[z, V, \text{Constants} \rightarrow \{N, T, \lambda\}], \right. \right. \]
\[ \left. \left. \text{Solve}[dt[eq2, T, \text{Constants} \rightarrow \{N, V\}], \right. \right. \]
\[ \left. \left. \text{Dt}[z, T, \text{Constants} \rightarrow \{N, V\}]\} / d\lambda \right] \left. \right. \]
\[ \text{Dt}[z, V, \text{Constants} \rightarrow \{T, N, \lambda\}] \rightarrow -\frac{z N \lambda^3}{g V^2 \text{PolyLog}\left[\frac{1}{2}, z\right]} ; \]
\[ \text{Dt}[z, T, \text{Constants} \rightarrow \{V, N\}] \rightarrow -\frac{3 N \lambda^3}{2 g T V \text{PolyLog}\left[\frac{1}{2}, z\right]} \]}
Thermodynamic functions

■ Grand potential

The contribution of the ground state is treated separately because the ground state plays an important role at low temperatures, but the use of an approximate density of states would have given it zero weight. However, because some of the thermodynamic functions become singular at the critical temperature, we insert a parameter, \( \delta \), to manipulate the ground-state contributions.

It is convenient to express the grand potential in terms of the so-called \( q \) potential defined as

\[
q = -\left( \int_0^\infty \mathcal{D}[\varepsilon] \log[1 - z \exp(-\beta \varepsilon)] \, d\varepsilon + \delta \log[1 - z] / \text{partsRule2} \right) / k_B T q.
\]

\[
T \to \Lambda / \text{PowerExpand} / \text{. lambdaToZ}
\]

\[
-q \delta \log[1 - z] + \frac{N \text{PolyLog}[\frac{1}{2}, z]}{\text{PolyLog}[\frac{1}{2}, z]}
\]

\( \mathcal{G} = -k_B T q / \text{Simplify} \)

\[
k_B T \left( -q \delta \log[1 - z] - \frac{N \text{PolyLog}[\frac{1}{2}, z]}{\text{PolyLog}[\frac{1}{2}, z]} \right)
\]

Recognizing that \( 1 - z \approx \frac{1}{N_\text{eff}} \) below the critical temperature, it is clear that the term proportional to \( \delta \) cannot compete with the term proportional to \( N \) for macroscopic systems (\( N \sim 10^{24} \)) and may be omitted safely. Thus, we can set \( \delta \to 0 \) when evaluating the thermodynamic functions. Furthermore, above the critical temperature we can express \( \lambda \) in terms of \( \text{bose}[\frac{1}{2}, z] \). However, that replacement is not valid below the critical temperature because \( z \) reduces to unity whereas \( \lambda \propto T^{-\lambda^2} \).

\[
\mathcal{G} / \text{. lambdaToZ} / \delta \to 0
\]

\[
-\frac{k_B T N \text{PolyLog}[\frac{1}{2}, z]}{\text{PolyLog}[\frac{1}{2}, z]}
\]

■ Mechanical equation of state

Degeneracy pressure

The mechanical equation of state is obtained directly from the grand potential, \( \mathcal{G} = -p V \), omitting the ground-state contribution because without any kinetic energy it does not produce pressure. It is useful to express the mechanical equation of state in the form \( \frac{p V}{N k_B T} = B[\tau] \), where \( B \) is sometimes called the compressibility factor.
\[ p = -\frac{\Theta}{V} / . \delta \to 0 \]
\[ \frac{k_B TN \text{PolyLog}[\frac{3}{2}, z]}{V \text{PolyLog}[\frac{3}{2}, z]} \]
\[ B = \frac{pV}{N k_B T} \]
\[ \frac{\text{PolyLog}[\frac{3}{2}, z]}{\text{PolyLog}[\frac{3}{2}, z]} \]

Limit \[ p, z \to 0 \]
\[ \frac{k_B TN}{V} \]

Note that in these expressions the dependence upon density is implicit in \( z \). Therefore, care must be exercised in using these functions to distinguish between the behaviors above and below the transition temperature for a given density. Recognizing that only those particles occupying excited states contribute to the pressure and that \( N_{\text{exc}} = N \tau^{3/2} \) below the critical temperature, we find that the pressure of the system is proportional to \( T^{3/2} \) and is independent of density.

\[ p / . \text{boseToLambda} / . \lambda \to T / . z \to 1 / \text{PowerExpand} \]
\[ g k_B^{5/2} m^{3/2} T^{5/2} \text{Zeta}[\frac{3}{2}] \]
\[ 2 \sqrt{2} \pi^{3/2} h^3 \]

Therefore, the compressibility factor must scale with \( \tau^{3/2} \) for temperatures below the critical temperature. The function \( \tilde{B} \) is designed to handle temperatures both above and below the critical temperature in a form suitable for numerical evaluation.

\[ \tilde{B}[\tau_] = B / . \lambda \to T / . z \to \tau; \]
\[ \tilde{B}[	au_] = \text{If}[\tau > 1, \text{Bhigh}[\tau], \text{Blow}[\tau]]; \]

\[ \text{plot[compressibility]} = \]
\[ \text{Plot}[\tilde{B}[\tau], \{\tau, 0, 5\}, \text{PlotPoints} \to 50, \text{GridLines} \to \text{Automatic}, \text{Frame} \to \text{True}, \]
\[ \text{FrameLabel} \to \{"\tau", "pV/(Nk_B T)"}, \text{PlotLabel} \to "\text{Compressibility Factor}"]; \]

The compressibility factor for an ideal Bose gas approaches the classical limit from below at high temperatures. The tendency for bosons to collect in occupied states reduces the pressure for given density and temperature compared to classical expectations. This pressure reduction should be compared with the corresponding pressure increase in ideal Fermi gases that arises from the "quantum repulsion" due to the Pauli exclusion principle. The pressure increase for
Fermi gases is often called the degeneracy pressure. Hence, the analogous degeneracy pressure for Bose gases is negative. As $z \to 1$, the degeneracy of the Bose gas reduces the pressure for given density and temperature relative to classical expectations.

\[
B / . \ z \to 1 / / N
0.513512
\]

**Transition line**

For temperatures below the condensation temperature, the pressure becomes independent of both volume and particle number, becoming simply a function of temperature. If any additional particles are added to the system, they enter the ground state without changing the pressure or volume of the system. In that sense the volume per particle is associated entirely with excited states, with the volume contributed by the condensed phase vanishing. Thus, the specific volume scales with $r^{3/2}$ in the transition region. Since the critical temperature itself scales with $(\frac{N}{V})^{2/3}$, the transition line between normal and condensed behavior has the form $p(\frac{V}{N})^{5/3} = \text{constant}$. Therefore, the transition line which delineates the onset of Bose condensation satisfies $p V^{5/3} = \text{constant}$. Let $v_c(T)$ be the specific volume as a function of temperature along the transition line.

\[
v_c[T] = \frac{\lambda^3}{g \text{bose}[\frac{5}{2}, 1]}
\]

\[
p[T] = p / . \text{boseToLambda} / . \lambdaToT / . z \to 1 // \text{PowerExpand}
\]

\[
\text{PowerExpand}[p[T] v_c[T]^{5/3}]
\]

\[
\delta_Tp[T] \propto v_c[T] // N
1.28378 k_B T
\]

Therefore, Bose condensation can be described as a first-order phase transition.

**Dimensionless forms**

The dependence is displayed in a dimensionless form. The transition line, $p V^{5/3} = \text{constant}$, marks the onset of Bose condensation and defines the scale for a particular system.

\[
p_{\text{Reduced}}[T_-, V_] =
\]

\[
p / . \text{boseToLambda} / . zToTau / . \{g \to 1, k_B \to 1, \lambda \to \frac{1}{\sqrt{T}}, \tau \to T V^{2/3}\}
\]

\[
T^{5/2} \text{PolyLog}\left[\frac{5}{2}, \text{fugacity}[T V^{2/3}]\right]
\]
transitionLine[V_] = pReduced[1, 1] V^{5/3}

\[
\frac{\text{Zeta}\left[\frac{5}{2}\right]}{V^{5/3}}
\]

Plot[
    Evaluate[{transitionLine[V], Table[pReduced[T, V], {T, 0.5, 2, 0.5}]}],
    {V, 0.1, 5}, PlotStyle ->
    {{RGBColor[1, 0, 0], Dashing[{0.02, 0.02}]}, {}, {}, {}, {}, {}},
    GridLines -> Automatic, Frame -> True, FrameLabel -> {"V", "p"},
    PlotLabel -> "Isotherms for ideal Bose systems"];

Isotherms for ideal Bose systems

Compressibility and expansivity

\(\kappa_T = -\frac{1}{V \text{Dt}[p, V, \text{Constants} \to \{N, T, \lambda\}] / . \text{dzHighTrules} / . \text{dLambdaDT} / . \text{lambdaToZ} // \text{Simplify}}\)

\[
\frac{V \text{PolyLog}\left[\frac{1}{2}, z\right]}{k_B T N \text{PolyLog}\left[\frac{1}{2}, z\right]}
\]

\(\alpha = \kappa_T \text{Dt}[p, T, \text{Constants} \to \{N, V\}] / . \text{dzHighTrules} / . \text{dLambdaDT} / . \text{lambdaToZ} / . \text{Simplify} / . \text{Apart} \)

\[-\frac{3}{2 T} + \frac{5 \text{PolyLog}\left[\frac{1}{2}, z\right] \text{PolyLog}\left[\frac{5}{2}, z\right]}{2 T \text{PolyLog}\left[\frac{1}{2}, z\right]^3} \]

Virial expansion

When \(T \gg T_c\), \(z\) is small and an expansion about the classical limit shows

\[
\text{Series}[B, \{z, 0, 3\}]
\]

\[
1 - \frac{z}{4 \sqrt{2}} + \left(\frac{1}{16} - \frac{2}{9 \sqrt{3}}\right) z^2 + \left(-\frac{3}{32} + \frac{1}{9 \sqrt{6}} - \frac{1}{4 \sqrt{2}} - \frac{\lambda^2}{2 \mu V}\right) z^3 + O[z]^4
\]

Alternatively, it is useful to develop an expansion for \(B\) in terms of the quantum concentration, \(x = \frac{N \lambda^2}{2 \mu V}\). First we expand \(x\) in terms of \(z\) and invert that result to determine the dependence of fugacity upon \(x\) for small density. Then
we develop the virial expansion itself. Since it is important to maintain all terms of the same order, we truncate all expressions at $z^2$.

$$zToX = \text{Solve}[x = \text{Normal}[	ext{Series[bose} \left[ \frac{3}{2}, z \right], \{z, 0, 2\}]], z][[1]]$$

$$\{z \rightarrow \sqrt{2} \left( -1 + \sqrt{1 + \sqrt{2} x} \right) \}$$

$$\text{virialExpansion} = \text{Series}[(\text{Normal}[	ext{Series}[B, \{z, 0, 2\}]) / . zToX], \{x, 0, 2\}]$$

$$1 - \frac{x}{4\sqrt{2}} + \left( \frac{1}{8} - \frac{2}{9\sqrt{3}} \right) x^2 + O[x]^3$$

$$\text{virialExpansion} // \text{N} // \text{Chop}$$

1. $-0.176777 x - 0.00330006 x^2 + O[x]^3$

- **Thermal equation of state**

The thermal equation of state for a nonrelativistic three-dimensional gas is obtained directly from the scaling relation $U = \frac{3}{2} p V$; other systems display similar scaling relations with different coefficients.

$$U = \frac{3}{2} p V$$

$$\frac{3 k_B T \text{N PolyLog}[\frac{3}{2}, z]}{2 \text{PolyLog}[\frac{3}{2}, z]}$$

Recognizing the relationship between $B$ and $U$, a form suitable for numerical evaluation over a wide range of temperatures is given below.

$$U_{\text{high}}[\tau_] = \frac{3}{2} \tau B_{\text{high}}[\tau]$$

$$U_{\text{low}}[\tau_] = \frac{3}{2} \tau B_{\text{low}}[\tau]$$

$$\tilde{U}[\tau_] = \text{If}[\tau > 1, U_{\text{high}}[\tau], U_{\text{low}}[\tau]]$$

$$\text{plot}[U] =$$

$$\text{Plot}[\left\{ \frac{3 \tau}{2}, \tilde{U}[\tau] \right\}, \{\tau, 0, 5\}, \text{PlotStyle} \to \{\text{Dashing}[[0.02, 0.02]], \}$$

$$\text{PlotPoints} \to 50, \text{GridLines} \to \text{Automatic}, \text{Frame} \to \text{True}, \text{FrameLabel} \to \{"\tau", \text{"U/(Nk_B T_c)"} \}, \text{PlotLabel} \to \text{"Internal Energy"}]$$
The internal energy for an ideal Bose gas is approaches the classical limit from below, and below the transition temperature is substantially lower than the classical prediction. At the transition temperature the internal energy is only about half the classical prediction.

**Isochoric Heat Capacity**

It is easy to evaluate the isochoric heat capacity above the critical temperature

\[
C_V = \frac{dU}{dT} / \frac{d\lambda}{dT} / \lambda \to Z
\]

\[
k_B N \left( -9 \text{PolyLog}\left[\frac{3}{2}, z\right] + \frac{15}{4} \text{PolyLog}\left[\frac{3}{2}, z\right] + \frac{9}{4} \text{PolyLog}\left[\frac{3}{2}, \lambda\right] + \frac{15}{4} \text{PolyLog}\left[\frac{3}{2}, \lambda\right] \right)
\]

\[
C_{V\text{high}}[\tau_] = C_V / \lambda \to \tau
\]

but below the critical temperature we must take care to recognize that only particles in excited states contribute to the heat capacity. The simplest procedure uses the low-temperature form of the energy per particle as follows

\[
C_{V\text{low}}[\tau_] = \frac{N k_B D[U_{\text{low}}[\tau], \tau]}{15 k_B N \tau^{3/2} \text{Zeta}\left[\frac{3}{2}\right]} + \frac{4}{\text{Zeta}\left[\frac{3}{2}\right]}
\]

Hence, we combine these results into a single function and display the temperature dependence of the isochoric heat capacity below.

\[
\tilde{C}_V[\tau_] = \text{If}[\tau > 1, C_{V\text{high}}[\tau], C_{V\text{low}}[\tau]];
\]

\[
\text{plot}[C_V] = \text{Plot}\left[\frac{\tilde{C}_V[\tau]}{N k_B}, \{\tau, 0, 5\}, \right.
\]

\[
\text{PlotRange} \to \{(0, 5), \{0, 2\}\}, \text{GridLines} \to \text{Automatic}, \text{Frame} \to \text{True}, \text{FrameLabel} \to \{"\tau", "C_V/(N k_B)"\}, \text{PlotLabel} \to \text{"Isochoric Heat Capacity"};
\]
Isobaric Heat Capacity

The isobaric heat capacity is defined as the derivative of enthalpy with respect to temperature for constant pressure. The enthalpy, $U + pV$, for an ideal nonrelativistic gas is quite simple, reducing to $\frac{5pV}{3}$, which allows the isobaric heat capacity to be obtained easily. Alternatively, it can also be obtained using a more general approach which relates difference between $C_p$ and $C_V$ to the isobaric expansivity and the isothermal compressibility of the system. The latter approach is more appropriate here. However, since the pressure in the transition region depends only on temperature, the isobaric heat capacity becomes meaningless below the transition temperature. Furthermore, both the isothermal compressibility and the isobaric expansivity diverge in the transition region.

\[
C_p = C_V + \frac{VT \alpha^2}{\kappa T} \quad // \text{Simplify}
\]

\[
\bar{C}_p[\tau_\_] = C_p / . \text{zToTau};
\]

\[
\text{plot}[C_p] = \text{Plot}[\frac{\bar{C}_p[\tau]}{Nk\_s}, \{\tau, 1, 5\},
\text{PlotRange} \to \{(1, 5), \{0, 5\}\}, \text{GridLines} \to \text{Automatic}, \text{Frame} \to \text{True},
\text{FrameLabel} \to \{"T/T_c", "C_p/(Nk_s)"}, \text{PlotLabel} \to \"Isobaric Heat Capacity\"];
\]

Compare $C_p$ and $C_V$

For a classical ideal gas we would find $C_V = \frac{3}{2} Nk_B$, $C_p = \frac{5}{2} Nk_B$, and $\frac{C_p}{C_V} = \frac{5}{3}$ where $pV^\gamma$ is constant for adiabats with $\gamma = \frac{5}{3}$. For the Bose gas we find a somewhat more complicated expression for $\gamma$ in terms of Bose functions, but simple expansions can be developed for the degenerate or the dilute limits.

\[
\gamma = \frac{C_p}{C_V} \quad // \text{Simplify}
\]

\[
\frac{5 \text{PolyLog}[\frac{3}{2}, z] \text{PolyLog}[\frac{5}{2}, z]}{3 \text{PolyLog}[\frac{3}{2}, z]^2}
\]
plot[γ] = Plot[Evaluate[γ /. zToTau], {τ, 1, 5},
PlotRange -> {{1, 5}, {0, 3}}, GridLines -> Automatic, Frame -> True,
FrameLabel -> {"T/T_c", "C_p/C_V"}, PlotLabel -> "Ratio of Heat Capacities"];


\[
\gamma /. \text{zToTau} /. \tau \rightarrow 10
\]

1.69182

**Entropy, free energy, and free enthalpy**

**Symbolic forms**

\[
S = \frac{U + pV - N\mu}{T} /. \muToZ // \text{Simplify} // \text{Collect}[\#1, \{N, k_B\}] &
\]

\[k_B N \left( -\log(z) + \frac{5 \text{PolyLog}\left(\frac{5}{2}, z\right)}{2 \text{PolyLog}\left(\frac{3}{2}, z\right)} \right)\]

\[
F = U - TS // \text{Simplify} // \text{Collect}[\#1, \{N, k_B\}] &
\]

\[k_B T N \left( \log(z) - \frac{\text{PolyLog}\left(\frac{3}{2}, z\right)}{\text{PolyLog}\left(\frac{5}{2}, z\right)} \right)\]

\[
G = F + pV // \text{Simplify} // \text{Collect}[\#1, \{N, k_B\}] &
\]

\[k_B T N \log(z)\]

**Plot reduced forms**

We plot the entropy, free energy, and free enthalpy in dimensionless form. Note that the behaviors above and below the transition temperature must be handled differently, but the proper scaling is clear from the results above. When \( T < T_c \), we must handle the condensation phenomenon explicitly. Recognizing that only those particles occupying excited states contribute to the entropy and that \( N_{\text{exc}} = N T^{3/2} \) below the critical temperature, we find that the entropy of the system is also proportional to \( N T^{3/2} \). Similarly, the Helmholtz free energy is proportional to \( N T^{3/2} \) while the Gibbs free enthalpy vanishes (recall that \( 1 - z \) is of order \( N^{-1} \)) in the thermodynamic limit.
\[ S_{\text{high}}[\tau_] = \frac{S}{N k_B} \text{// zToTau} \text{// Collect[#1, \{N, k_B\}] \&} \]

\[ S_{\text{low}}[\tau_] = \frac{S}{N k_B} \text{// z \to 1} \]

\[ S[\tau_] = \text{If}[\tau > 1, S_{\text{high}}[\tau], S_{\text{low}}[\tau]] \]

\[ F_{\text{high}}[\tau_] = \frac{\tau F}{N k_B T} \text{// zToTau} \text{// Collect[#1, \{N, k_B\}] \&} \]

\[ F_{\text{low}}[\tau_] = \frac{\tau F}{N k_B T} \text{// z \to 1} \]

\[ F[\tau_] = \text{If}[\tau > 1, F_{\text{high}}[\tau], F_{\text{low}}[\tau]] \]

\[ G_{\text{high}}[\tau_] = \frac{\tau G}{N k_B T} \text{// zToTau} \text{// Collect[#1, \{N, k_B\}] \&} \]

\[ G_{\text{low}}[\tau_] = \frac{\tau G}{N k_B T} \text{// z \to 1} \]

\[ G[\tau_] = \text{If}[\tau > 1, G_{\text{high}}[\tau], G_{\text{low}}[\tau]] \]

plot[S] =

\[ \text{Plot}[S[\tau], \{\tau, 0, 5\}, \text{PlotLabel} \to "Reduced Entropy", \text{GridLines} \to \text{Automatic}, \text{Frame} \to \text{True}, \text{FrameLabel} \to \{"\tau", \"S/(Nk_B)\"\}, \text{DisplayFunction} \to \text{Identity}] \]

plot[F] = plot[F[\tau], \{\tau, 0, 5\},

\[ \text{PlotLabel} \to "Reduced Free Energy", \text{GridLines} \to \text{Automatic}, \text{Frame} \to \text{True}, \text{FrameLabel} \to \{"\tau", \"F/(Nk_B T_c)\"\}, \text{DisplayFunction} \to \text{Identity}] \]

plot[G] = plot[G[\tau], \{\tau, 0, 5\},

\[ \text{PlotLabel} \to "Reduced Free Enthalpy", \text{GridLines} \to \text{Automatic}, \text{Frame} \to \text{True}, \text{FrameLabel} \to \{"\tau", \"G/(Nk_B T_c)\"\}, \text{DisplayFunction} \to \text{Identity}] \]
Latent heat of condensation

Since the entropy of the condensed phase vanishes, the entropy in the transition region is due entirely to the particles in excited states. Furthermore, since the fraction of the particles in excited states scales with $\tau^{3/2}$, the reduced entropy for the gas (uncondensed) phase is constant in the transition region. Hence, the latent heat of transition is simply $T$ times the entropy per particle at the critical temperature.

$$\text{latentHeat} = \frac{T S}{N} \big/ \lambda \text{ToZ} / \cdot \ z \rightarrow 1 \big/ N$$

$$\begin{align*}
1.28378 \text{ kBT}
\end{align*}$$

Therefore, as expected, we obtain the same result from the entropy as we did previously from the Clausius-Clapeyron equation.
Examples

Liquid helium

Although liquid helium is not an ideal fluid, the superfluid transition occurs at a temperature close to the Bose condensation temperature and the superfluid state exhibits many properties which are similar to the condensed phase of an ideal Bose fluid. The following numerical calculations employ SI units, with tags removed, unless stated otherwise. The volume is converted to molar volume. The experimental value of the liquid helium density is used to estimate the theoretical critical temperature at atmospheric pressure.

```math
values = Join[
{g \rightarrow 1, N \rightarrow \text{AvogadroConstant} \text{ Mole}, \text{ density} \rightarrow \frac{146}{m}},
{m \rightarrow \frac{4 \text{ Convert[AtomicMassUnit, Kilogram]}}{\text{Kilogram}}}, \text{ FundamentalConstants}];

\text{liqHeDensity} = V \rightarrow \frac{N}{\text{density}};

\{V_{\text{He}}, T_{\text{He}}\} = \{V, T_c\} / . \text{liqHeDensity} / . \text{values}

\{0.0000273973, 3.15218\}
```

Thus, the Bose-Einstein critical temperature is intriguingly close to the superfluid transition temperature, 2.17 kelvins, for liquid $^4\text{He}$. However, the thermodynamic properties of liquid helium do not conform to those of an ideal Bose fluid. For example, the isochoric heat capacity displays a marked discontinuity at the superfluid transition whereas $C_v[T]$ for an ideal Bose fluid would be continuous (despite its kink). Nevertheless, the similarities suggest that Bose-Einstein condensation plays an important role in the superfluid transition and that deviations from ideality can be attributed to interatomic interactions.

```math
p_{\text{He}}[T_, V_] =

\frac{p}{. \text{boseToLambda} / . \text{lambdaToT} / . \text{zToTau} / . \tau \rightarrow \frac{T}{T_{\text{He}}} \left(\frac{V}{V_{\text{He}}}\right)^{2/3}} / . \text{values} / / \text{PowerExpand} / / \text{Simplify};

\text{HeTransitionLine}[V_] = p_{\text{He}}[T_{\text{He}}, V] \left(\frac{V_{\text{He}}}{V}\right)^{5/3};
```
Although this model correctly describes many of the qualitative features of the state diagram for liquid helium, it is not very accurate. For example, the pressure computed below for the critical temperature at the experimental density for atmospheric pressure is actually much larger than one atmosphere. This increased pressure is partly due to the difference between the theoretical and experimental transition temperatures. Furthermore, part of the discrepancy also reflects the repulsive core of the interatomic interaction; the importance of this effect can be gauged by comparing the molar volume to the van der Waals volume parameter.

\[
\text{pHe}[T_{\text{He}}, V_{\text{He}}] \text{ Convert[Pascal, Atmosphere]}
\]

\[
4.84811 \text{ Atmosphere}
\]

\[
\text{pHe}[2.17, V_{\text{He}}] \text{ Convert[Pascal, Atmosphere]}
\]

\[
1.90631 \text{ Atmosphere}
\]

\[
\text{vdWaals} = \{a \to 0.003457, b \to 23.7 \times 10^{-6}\};
\]

\[
\frac{V_{\text{He}}}{b} /. \text{vdWaals}
\]

\[
1.156
\]
Problems

▼ Fugacity versus quantum concentration

Plot fugacity as a function of quantum concentration.

▼ Discontinuity in slope of $C_V$

Derive an explicit formula for the discontinuity in the slope of the isochoric heat capacity.

▼ Nonrelativistic Bose gases in one or two dimensions

Consider an ideal nonrelativistic Bose gas in one or two spatial dimensions.

a) Demonstrate that Bose condensation does not occur in one- or two-dimensional systems.

b) Plot $\mu[T]$ for a two-dimensional Bose gas. What is the relevant temperature scale? Compare your result with the corresponding solution for a three-dimensional system.

▼ Bose gas with $\varepsilon \propto k^s$ in $d$ dimensions

Consider an ideal Bose gas with single-particle energy spectrum $\varepsilon \propto k^s$ in $d$ spatial dimensions.

a) Find expressions for the major thermodynamic functions in terms of Bose functions of appropriate order and check that the familiar results for a three-dimensional nonrelativistic Bose gas are recovered.

b) Evaluate $C_V$ and $C_p$ in terms of Bose functions.

c) Show that adiabats satisfy $p V^\gamma$ and evaluate $\gamma$ in terms of $d$ and $s$.

▼ Debye model with $\omega \propto k^n$

Suppose that excitations of a three-dimensional solid, with $N$ atoms per volume $V$, satisfy a dispersion relation of the form $\omega \propto k^n$ for $k \leq k_{\text{max}}$ and that these excitations satisfy Bose-Einstein statistics.

a) Determine the density of states, $\rho[\omega]$, normalized to $3N$ normal modes.

b) Show that at low temperatures, $k_B T \ll \hbar \omega_{\text{max}}$, the internal energy has the form $U[T] \propto T^m$ and determine the exponent and the constant of proportionality. Compare your result with the Debye model for phonons with $n = 1$.

c) Evaluate the heat capacity when $n = 2$. 
**Internal excitations**

a) Consider an ideal Bose gas consisting of molecules with internal degrees of freedom. Assuming that only the first internal excited state, with excitation energy $\epsilon_1$ relative to the ground state, need be included, determine the condensation temperature, $T_c[\epsilon_1]$, as a function of the excitation energy. In particular, show that

$$k_B T_c^0 \ll \epsilon_1 \implies \frac{T_c}{T_c^0} \approx 1 - \frac{2}{3 \zeta[\frac{3}{2}]} \exp\left[ -\frac{\epsilon_1}{k_B T_c^0} \right]$$

$$k_B T_c^0 \gg \epsilon_1 \implies \frac{T_c}{T_c^0} \approx \left( 1 + \frac{2^{4/3}}{3 \zeta[\frac{3}{2}]} \left( \frac{\pi \epsilon_1}{k_B T_c^0} \right)^{1/2} \right)$$

where $T_c^0$ is the condensation temperature in the absence of internal modes.

b) Show that a finite number of excited states can be enumerated with the ground state in the form of a discrete summation while the remainder of the excitation spectrum is evaluated using the usual integration over a continuous density of states without substantially affecting the critical temperature for Bose-Einstein condensation. Determine the occupancies of low-lying excited states relative to the ground state. To be more specific, evaluate the temperature dependence of the mean occupancies of the lowest few states for liquid $^4$He.

**Sound velocity**

Recall that the velocity of sound in a fluid is

$$v = \sqrt{\left( \frac{\partial p}{\partial \rho} \right)_s}$$

where here $\rho$ is the mass density of the fluid. Show that

$$v^2 = \frac{5}{3} \frac{k_B T}{m \text{bose}_{ \frac{5}{2}, \frac{3}{2} } \zeta[\frac{3}{2}]} = \frac{5}{9} \bar{u}^2$$

where $\bar{u}^2$ is the mean square speed of the particles in the gas. Evaluate in the low and high temperature limits.

**Adiabatic compressibility**

Find an expression for the adiabatic compressibility of an ideal Bose gas in terms of bose functions. Discuss the dependence upon $z$.

**Effect of gravitational field on critical temperature**

Evaluate the effect of a uniform gravitational field upon the critical temperature of an ideal Bose gas. Furthermore, show that there is a finite discontinuity in the isochoric heat capacity that is proportional to $\sqrt{\frac{m g L}{k_B T}}$ and determine the coefficient of proportionality.

**Harmonic confinement (numerical summation)**

Consider an ideal Bose gas confined by an isotropic harmonic potential, $U_{\text{ext}}[r] = \frac{1}{2} m \omega^2 r^2$, instead of the simple box potential employed above.
a) Evaluate the degeneracy $g_n$ for a single-particle energy level $\epsilon_n = (n + \frac{1}{2}) \hbar \omega$.

b) Determine by numerical summation the critical temperature as a function of particle number for $N \approx 10^6$ and display using LogLogPlot. Assuming that $T_c \propto N^\eta$, estimate $\eta$ for large $N$. Compare with the box model.

c) A typical experiment uses spin-polarized $^7$Li atoms ($g = 1$) in a trap with $v \approx 150$ Hz. Evaluate $T_c$ as a function of $N$ for this experiment. [Reference: C.C. Bradley et al., Phys. Rev. Lett, 75 (1995) 1687.]

d) A useful method for comparing the oscillator and box models is to employ the semi-classical argument, $\bar{\epsilon} \approx \frac{1}{2} k_B T \approx \frac{1}{4} m \omega^2 \bar{r}^2$ where we now interpret the mean oscillation amplitude $\bar{r}$ as the size of an equivalent box, such that $V = \frac{1}{2} \pi \bar{r}^3$. Use this argument to compare the dependencies of critical temperatures upon particle number for these two potentials and provide a physical explanation for your findings.

\section*{Harmonic confinement (continuous approximation)}

Consider an ideal Bose gas confined by an isotropic harmonic potential, $U_{\text{conf}}(r) = \frac{1}{2} m \omega^2 r^2$.

a) Show that when $k_B T \gg \hbar \omega$, a continuous approximation to the density of states takes the form $\rho(\epsilon) \propto \epsilon^2$ and evaluate the constant of proportionality. Study the accuracy of this approximation.

b) Using this approximate density of states, express the number of particles in excited states in terms of an appropriate Bose function.

c) Evaluate the critical temperature for Bose-Einstein condensation as a function of $N$ and $\epsilon$. Compare with the critical temperature for a box whose dimensions are similar to the spatial extent of the gas in a harmonic well. [Hint: use an equipartition argument to relate $\omega$ and $T$ to an effective volume $V$.]

d) A typical experiment uses spin-polarized $^7$Li atoms ($g = 1$) in a trap with $v \approx 150$ Hz. Evaluate $T_c$ as a function of $N$ for this experiment. [Reference: C.C. Bradley et al., Phys. Rev. Lett, 75 (1995) 1687.]

e) Evaluate and plot the temperature dependence of the chemical potential, internal energy, and heat capacity for a nonrelativistic ideal gas of bosons in a harmonic trap, with special care to discontinuities across the critical temperature. For this purpose the heat capacity is defined as $C = (\frac{\partial U}{\partial T})_N$.

\section*{Anisotropic harmonic confinement}

Consider an ideal Bose gas confined by an anisotropic harmonic potential with single-particle energy levels of the form $\epsilon[n_1, n_2, n_3] = \sum_{i=1}^{3} (n_i + \frac{1}{2}) \hbar \omega_i$.

a) Show that a continuous approximation to the density of states takes the form $\rho(\epsilon) \propto \epsilon^2$ and evaluate the constant of proportionality. Under what conditions is this approximation accurate?

b) Evaluate the critical temperature for Bose-Einstein condensation as a function of $N$ and the parameters of the confining potential.

c) Suppose that $\omega_1 \sim \omega_2$ but that $\omega_3 \gg \omega_{1,2}$. Use this system to provide a physical explanation for the oft-quoted theorem that Bose-Einstein condensation does not occur in two-dimensional systems.