

Ideal Quantum Gases

from Statistical Physics using Mathematica

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The indistinguishability of identical particles has profound effects at low temperatures and/or high density where quantum mechanical wave packets overlap appreciably. The occupation representation is used to study the statistical mechanics and thermodynamics of ideal quantum gases satisfying Fermi-Dirac or Bose-Einstein statistics. This notebook concentrates on formal and conceptual developments, liberally quoting more technical results obtained in the auxiliary notebooks *occupy.nb*, which presents numerical methods for relating the chemical potential to density, and *fermi.nb* and *bose.nb*, which study the mathematical properties of special functions defined for Fermi-Dirac and Bose-Einstein systems. The auxiliary notebooks also contain a large number of exercises.

Indistinguishability

In classical mechanics identical particles remain distinguishable because it is possible, at least in principle, to label them according to their trajectories. Once the initial position and momentum is determined for each particle with the infinite precision available to classical mechanics, the swarm of classical phase points moves along trajectories which also can in principle be determined with absolute certainty. Hence, the identity of the particle at any classical phase point is connected by deterministic relationships to any initial condition and need not ever be confused with the label attached to another trajectory. Therefore, in classical mechanics even identical particles are distinguishable, in principle, even though we must admit that it is virtually impossible in practice to integrate the equations of motion for a many-body system with sufficient accuracy.

Conversely, in quantum mechanics identical particles are absolutely indistinguishable from one another. Since the particle labels have no dynamical significance, exchanging the coordinates or labels of two identical particles can change the wave function by no more than an overall phase factor of unit magnitude. In this chapter we analyze the sometimes quite profound consequences of permutation symmetry for systems of identical particles, but first we would like to provide a qualitative explanation for the similarities and differences between the classical and quantum pictures. Perhaps the most significant difference between these pictures is found in the inherent fuzziness of quantum trajectories. Contrary to classical ideas, it is not possible even in principle to determine both the position and momentum of a particle simultaneously with arbitrary precision. The precisions with which conjugate variables can be determined simultaneously are limited by the Heisenberg uncertainty relation $\Delta x \Delta p_x \geq \frac{\hbar}{2}$, whereby precise measurements of one variable cause the uncertainty in its conjugate variable to be quite large. Therefore, the set of classical phase points cannot be determined with absolute certainty; nor can the evolution of the system be confined to sharp trajectories through phase space. The trajectory for each particle is initially broadened by the uncertainty product and it becomes fuzzier and more diffuse as it evolves, much as a wave packet would spread as it propagates through a dispersive medium. However, a quantum wave packet spreads naturally even without a dispersive medium.

Under some circumstances these two apparently conflicting pictures can in fact become quite similar. When the wave packets are sufficiently compact and the density of the system is sufficiently small that different wave packets rarely overlap, we can again distinguish particles by the trajectories followed by their wave packets. Small corrections may be necessary for quantum effects that might occur when a pair of wave packets does overlap, but otherwise the classical description can be quite accurate under appropriate conditions. As we argued when developing semiclassical statistical mechanics, the applicability of the classical picture is governed by the thermal wavelength

$$\lambda_B = \frac{h}{p_B} = \left(\frac{2\pi\hbar^2}{m k_B T} \right)^{1/2} \quad p_B = (2\pi m k_B T)^{1/2}$$

corresponding to the de Broglie wavelength for a particle with typical thermal momentum p_B . From dimensional arguments alone it is clear that the width of the wave packet is inversely proportional to the momentum of the particle and is similar to the wavelength for the dominant component of the wave packet. The typical momentum must be proportional to the mass and to the typical velocity near the peak of the Maxwell-Boltzmann distribution. Therefore, large mass or high temperature produce small λ_B where the classical approximation becomes useful. Small mass or low temperature result in large λ_B , which increases the overlap between wave packets and requires a quantum description. Thus, the relative importance of fundamentally quantum mechanical behavior is gauged by the quantum concentration

$$n_Q = \frac{N}{gV} \lambda_B^3$$

which compares the volume occupied by wave packets to the volume available to each particle. Here we use g to represent the multiplicity factor for a point in phase space. This factor typically takes the values $2s + 1$ where s is the intrinsic angular momentum, but may be larger if there are other internal degrees of freedom. The classical picture may be appropriate when $n_Q \ll 1$, but as n_Q approaches unity nonclassical behavior is expected.

It is important to recognize that even when the classical description is useful, the quantum mechanical indistinguishability of identical particles continues to have important consequences. One must still consider indistinguishability when enumerating classical states in order to resolve the Gibbs paradox and to obtain extensive thermodynamic potentials. Similarly, the granularity of phase space is needed to establish the scale for entropy.

Permutation symmetry

An N -body system is described by a wave function of the form $\Psi[q_1, \dots, q_N]$ where q_i denotes the full set of coordinates belonging to particle i . Suppose that the N particles are identical and hence indistinguishable from one another. The Hamiltonian must then be invariant with respect to interchange of any pair of identical particles. Consider the action of the particle exchange operator $X_{i,j}$ defined by

$$X_{i,j} \Psi[\dots q_i \dots q_j \dots] = s \Psi[\dots q_j \dots q_i \dots]$$

which exchanges the coordinates of particles i and j . A second application of the exchange operator

$$X_{i,j}^2 \Psi = s^2 \Psi = \Psi$$

must restore the wave function to its original state. The symmetry of the Hamiltonian under particle exchange requires X to be unitary and hence $s^2 = 1$. Therefore, the wave function must be either symmetric ($s = 1$) or antisymmetric ($s = -1$) with respect to particle exchange.

Experimentally, the exchange symmetry of many-body systems is found to be intimately related to the intrinsic angular momentum (spin) of their constituents. Particles with half-integral spin live in antisymmetric wave functions and are called *fermions*; particles with integer spin live in wave functions symmetric under particle exchange and are called *bosons*. Although these relationships can be derived using relativistic quantum field theory, for our purposes it is sufficient to regard this distinction as an experimental fact. We shall soon find that the statistical properties of fermion and boson systems are profoundly different at low temperatures. Fermions obey Fermi-Dirac (FD) statistics, whereas bosons obey Bose-Einstein (BE) statistics. In the classical limit, both distributions reduce to the Maxwell-Boltzmann (MB) distribution.

The indistinguishability of identical particles affects the number of distinct states very strongly. Consider a system of two identical noninteracting fermions. The wave function must be antisymmetric wrt exchange of the coordinates of the two particles. Hence, the two-particle wave function takes the form

$$\Psi_{n,m}[q_1, q_2] = \frac{1}{\sqrt{2}} (\psi_n[q_1] \psi_m[q_2] - \psi_n[q_2] \psi_m[q_1])$$

where q_1 and q_2 are particle coordinates and ψ_n and ψ_m are single-particle wave functions. Notice that the two-particle wave function vanishes if one attempts to place both particles in exactly the same state. Therefore, the *Pauli exclusion principle* states that it is not possible for more than one fermion to occupy any particular state; occupancy by one fermion blocks occupancy by others.

Consider a system of 2 identical particles for which 3 single-particle states are available. If, as in classical mechanics, the particles are considered distinguishable, they may be labeled as A and B . On the other hand, both particles must have the same label, say A , if they are considered indistinguishable. The tables below enumerate all distinct states for distinguishable classical particles or for indistinguishable fermions and bosons. Classically, $3^2 = 9$ distinct microstates are available, but only 3 are available to fermions or 6 to bosons. Also notice that the ratio between the probability that the two particles occupy the same state to the probability that they occupy different states is 0.5 classically, 1.0 for bosons, and 0 for fermions. Therefore, the requirements of permutation symmetry severely limit the number of states, especially for fermions.

classical			fermions			bosons		
1	2	3	1	2	3	1	2	3
A	B					A	A	
	A							A
A		B	A	A		A		A
B		A						
	A	B				A	A	
	B	A						

N-body wave functions

Consider a system of N identical particles confined to volume V . Let $q = \{q_1, \dots, q_N\}$ represent a complete set of coordinates. The wave function for a many-body state labeled Ψ_α , where $\alpha = \{\alpha_1, \dots, \alpha_N\}$ denotes a complete set of quantum numbers, will then have the form

$$\langle q_1 \cdots q_N | \Psi_\alpha \rangle = \Psi_\alpha[q_1 \cdots q_N] = \Psi_\alpha[q]$$

Let P denote a particular permutation operator and let $s[P] = \pm 1$ represent the signature for an even (+) or odd (-) permutation. For example, $P_{213} \{q_1, q_2, q_3\} = \{q_2, q_1, q_3\}$ would be an odd permutation with $s[P_{213}] = -1$, while $P_{231} \{q_1, q_2, q_3\} = \{q_2, q_3, q_1\}$ would be an even permutation with $s[P_{231}] = +1$. Any permutation of the coordinates or labels changes the wave function by at most a phase factor; it matters not whether we choose to permute coordinates or labels. Bosons are symmetric with respect to particle exchange, such that

$$\text{bosons} \implies P \Psi_\alpha[\{q_i\}] = \Psi[P\{q_i\}] = \Psi_{P\alpha}[\{q_i\}] = \Psi_\alpha[q]$$

whereas fermions are antisymmetric with respect to particle change, such that the phase of a permutation is even or odd according to the signature of the permutation

$$\text{fermions} \implies P \Psi_\alpha[\{q_i\}] = \Psi[P\{q_i\}] = \Psi_{P\alpha}[\{q_i\}] = (-)^{s[P]} \Psi_\alpha[q]$$

It will be useful to define

$$\begin{aligned} \text{bosons} : \delta_P &= +1 \\ \text{fermions} : \delta_P &= (-)^{s[P]} \end{aligned}$$

It is useful to introduce a complete orthonormal set of single-particle wave functions $\phi_\alpha[q]$, such that $\langle \phi_\alpha | \phi_\beta \rangle = \delta_{\alpha,\beta}$. Unsymmetrized product wave functions for the N -body systems can then be defined by

$$Y_\alpha[q] = \phi_{\alpha_1}[q_1] \phi_{\alpha_2}[q_2] \cdots \phi_{\alpha_N}[q_N] = \prod_{i=1}^N \phi_{\alpha_i}[q_i]$$

Properly symmetrized N -body wave functions can now be constructed by adding all possible permutations of the product wave functions with appropriate phases, such that

$$\Phi_\alpha[q] = \frac{1}{\sqrt{N!}} \sum_P \delta_P Y_\alpha[Pq] = \frac{1}{\sqrt{N!}} \sum_P \delta_P Y_{P\alpha}[q]$$

Any Φ_α constructed from single-particle eigenfunctions ϕ_{α_i} will now represent a properly symmetrized eigenfunction for system of N noninteracting identical particles. Wave functions for interacting systems can be constructed from superpositions of product wave functions, which serve as basis vectors for the system. However, for bosons one must be careful to properly normalize the product wave functions.

Occupation representation

We begin our investigation of the thermodynamic consequences of permutation symmetry by studying ideal quantum fluids composed of identical fermions or bosons under conditions where their mutual interactions may be neglected. Under these circumstances the many-particle Hamiltonian may be expressed as a summation over N independent identical single-particle contributions

$$H = \sum_{i=1}^N h_i$$

with eigenfunctions Φ_ν represented by the set of occupation numbers $\nu = \{n_1, n_2, \dots, n_\infty\}$ such that

$$H \Phi_\nu = E_\nu \Phi_\nu \quad E_\nu = \sum_{\alpha=1}^{\infty} n_\alpha[\nu] \varepsilon_\alpha \quad N_\nu = \sum_{\alpha=1}^{\infty} n_\alpha[\nu]$$

where $n_\alpha[\nu]$ is the number of particles in the single-particle orbital ϕ_α satisfying the eigenvalue problem

$$h \phi_\alpha = \varepsilon_\alpha \phi_\alpha$$

The many-body wave function

$$\Phi_\nu = \sum_P (\pm)^P \prod_{i=1}^N \phi_i$$

may then be constructed from a properly symmetrized product of N_ν single-particle wave functions where here the index i runs over all occupied orbitals and where the summation over P includes all permutations of the particle labels with appropriate phases. Rather than specifying the coordinates or quantum numbers for each particle in the system, the occupation representation specifies how many, but not which, particles occupy each single-particle orbital. This is the most natural representation of the states for a system of identical particles and avoids the complications of enforcing the permutation symmetry and evaluating degeneracy factors.

Although permutation symmetry can be enforced explicitly within the canonical ensemble or microcanonical ensembles, the grand canonical ensemble provides a more efficient method. This method focuses upon the occupancy of a particular orbital α as the relevant subsystem instead of treating the particles themselves as the subsystems. As a subsystem the orbital exchanges energy and particles with a reservoir comprised of the particles occupying all other orbitals. Because the number of particles occupying each orbital is indefinite, a statistical quantity, this approach naturally involves the grand canonical ensemble. The properties of the reservoir establish a temperature and chemical potential which serve as Lagrange multipliers that enforce constraints upon the energy and density of the entire system. The occupancy and its dispersion can be deduced easily.

The probability P_ν for a state $\nu = \{n_\alpha\}$ in the occupation representation can be expressed as

$$P_\nu = \mathcal{Z}^{-1} \text{Exp}[-\beta(E_\nu - \mu N_\nu)]$$

where

$$N_\nu = \sum_{\alpha=1}^{\infty} n_\alpha[\nu] \quad E_\nu = \sum_{\alpha=1}^{\infty} n_\alpha[\nu] \varepsilon_\alpha$$

are the total particle number and total energy and where

$$\mathcal{Z}[T, V, \mu] = \sum_{N_\nu=0}^{\infty} \sum'_{\nu} \prod_{\alpha} \text{Exp}[-\beta n_\alpha (\varepsilon_\alpha - \mu)]$$

is the grand partition function. The temperature and chemical potential are determined by the constraints upon energy and density. The dependence upon volume is carried implicitly by the dependence of the single-particle energy levels ε_α upon the size of the system. The separability of the energy allows the partition function for each state ν to be expressed as a product of partition functions for each orbital α . The restricted sum \sum'_{ν} indicates summation over all sets of occupation numbers $\{n_\alpha\}$ with total particle number N_ν . The grand partition function then sums over N_ν as well, weighted by the factor $\text{Exp}[\beta \mu N_\nu]$. The effect of this summation over N_ν is to remove the restriction upon sum over $\{n_\alpha\}$, such that

$$\mathcal{Z}[T, V, \mu] = \sum_{\{n_\alpha\}} \prod_{\alpha} \text{Exp}[-\beta n_\alpha (\varepsilon_\alpha - \mu)]$$

where each sum over n_α is now independent, only restricted by the Pauli exclusion principle for fermions. It is useful to define

$$\xi_\alpha \equiv \beta (\varepsilon_\alpha - \mu)$$

as the energy of orbital α relative to the chemical potential in units of the thermal energy $k_B T$, such that

$$\mathcal{Z}[T, V, \mu] = \sum_{\{n_\alpha\}} \prod_{\alpha} \text{Exp}[-n_\alpha \xi_\alpha]$$

The summation and product can now be interchanged

$$\sum_{\{n_\alpha\}} \prod_{\alpha} \text{Exp}[-n_\alpha \xi_\alpha] = \prod_{\alpha} \sum_{n_\alpha} \text{Exp}[-n_\alpha \xi_\alpha]$$

so that

$$\mathcal{Z} = \prod_{\alpha} \mathcal{Z}_\alpha \quad \mathcal{Z}_\alpha = \sum_{n_\alpha} \text{Exp}[-n_\alpha \xi_\alpha]$$

becomes a product of independent single-orbital grand partition functions. This result is quite analogous to the factorization of an N -element canonical partition function in terms of independent single-element factors, now applied to orbitals rather than to particles. Note that there will normally be an infinite number of \mathcal{Z}_α factors, but most will be unity. Similarly, the probability P_ν also factors according to

$$P_\nu = \prod_{\alpha} P_\alpha \quad P_\alpha = \mathcal{Z}_\alpha^{-1} \text{Exp}[-n_\alpha \xi_\alpha]$$

The mean particle number and total energy are now obtained as ensemble averages

$$\begin{aligned} \langle N \rangle &= \sum_{\nu} P_\nu N_\nu = \sum_{\nu} \sum_{\alpha} P_\nu n_\alpha[\nu] = \sum_{\alpha} \bar{n}_\alpha \\ \langle E \rangle &= \sum_{\nu} P_\nu E_\nu = \sum_{\nu} \sum_{\alpha} P_\nu n_\alpha[\nu] \varepsilon_\alpha = \sum_{\alpha} \bar{n}_\alpha \varepsilon_\alpha \end{aligned}$$

where

$$\bar{n}_\alpha = \sum_\nu P_\nu n_\alpha[\nu]$$

is the mean occupancy of orbital α . Recognizing that each single-orbital probability distribution is normalized, such that

$$\sum_{n_\alpha} P_\alpha[n_\alpha] = 1,$$

the mean occupancy for each orbital can be evaluated independently using

$$\bar{n}_\alpha = \sum_{n_\alpha} P_\alpha n_\alpha$$

where the relationship between the occupancies for various orbitals is governed by ε_α and μ and where the total density is governed by μ . Thus, the thermodynamic properties of the system are determined by the mean occupancies, which are obtained from the grand partition function according to

$$\bar{n}_\alpha = k_B T \frac{\partial \ln \mathcal{Z}_\alpha}{\partial \mu} = - \left(\frac{\partial \mathcal{G}_\alpha}{\partial \mu} \right)_{T,V} = - \frac{\partial \ln \mathcal{Z}_\alpha}{\partial \xi_\alpha}$$

where $\mathcal{G}_\alpha = -k_B T \ln \mathcal{Z}_\alpha$ is the single-orbital contribution to the grand potential $\mathcal{G} = \sum_\alpha \mathcal{G}_\alpha$. The variance in occupancy can also be obtained easily. Evaluating the mean square particle number in each orbital

$$\langle n_\alpha^2 \rangle = \mathcal{Z}_\alpha^{-1} \frac{\partial^2 \mathcal{Z}_\alpha}{\partial \xi_\alpha^2} = \left(\frac{\partial \mathcal{G}_\alpha}{\partial \mu} \right)^2 - k_B T \frac{\partial^2 \mathcal{G}_\alpha}{\partial \mu^2} = \bar{n}_\alpha^2 - k_B T \frac{\partial^2 \mathcal{G}_\alpha}{\partial \mu^2}$$

we find that the variance becomes

$$\sigma_{n_\alpha}^2 = \langle (n_\alpha - \bar{n}_\alpha)^2 \rangle = \frac{\partial^2 \ln \mathcal{Z}_\alpha}{\partial \xi_\alpha^2} = -k_B T \left(\frac{\partial^2 \mathcal{G}_\alpha}{\partial \mu^2} \right)_{T,V} = - \frac{\partial \bar{n}_\alpha}{\partial \xi_\alpha}$$

Therefore, the occupancy variance is related to the derivative with respect to chemical potential by

$$\sigma_{n_\alpha}^2 = - \frac{\partial \bar{n}_\alpha}{\partial \xi_\alpha}$$

Continuous approximation for uniform systems

If the system is sufficiently large and the spacing between single-particle energy levels sufficiently small, we can replace discrete sums over states by integrals over energy weighted by the density of states. Thus, the total number of particles becomes

$$N = \sum_\alpha \bar{n}_\alpha \rightarrow N = \int_0^\infty d\varepsilon \mathcal{D}[\varepsilon] \bar{n}[\varepsilon, \beta, \mu]$$

and determines the dependence of the chemical potential on the temperature and density of the system. If the particle density is specified, the chemical potential can be determined by numerical solution of this equation. However, we will find that for the Bose-Einstein distribution care must be taken with the continuous approximation whenever one or more

states develops macroscopic occupancy. Similarly, the equation of state is determined by the grand potential, which in the continuous approximation takes the form

$$\mathcal{G} = -k_B T \sum_{\alpha} \ln \mathcal{Z}_{\alpha} \longrightarrow -k_B T \int_0^{\infty} d\varepsilon \mathcal{D}[\varepsilon] \ln \mathcal{Z}[\varepsilon, \beta, \mu]$$

where

$$\mathcal{Z}[\varepsilon, \beta, \mu] = (1 \pm e^{-\beta(\varepsilon-\mu)})^{\pm 1}$$

is the single-orbital partition function. Therefore, the grand potential becomes

$$\mathcal{G} = \mp k_B T \int_0^{\infty} d\varepsilon \mathcal{D}[\varepsilon] \text{Log}[1 \pm e^{-\beta(\varepsilon-\mu)}]$$

with upper or lower signs for fermions or bosons, respectively.

The density of states for a gas confined to a simple box of volume V is related to the phase-space density by

$$\mathcal{D}[\varepsilon] d\varepsilon = \mathcal{D}[\vec{k}] d^3 k = g V \frac{d^3 k}{(2\pi)^3}$$

where g is the intrinsic degeneracy of a state in momentum space. For example, if the only degree of freedom that is needed to describe the internal state of a particle is its spin s , then $g = 2s + 1$ represents the total number spin states which are degenerate in the absence of an external magnetic field. If the system is spherically symmetric, we can use

$$\mathcal{D}[\vec{k}] d^3 k \longrightarrow g V \frac{k^2 dk}{2\pi^2}$$

Assuming that nonrelativistic kinematics are applicable, the relationship between energy and momentum representations of the density of states is given by

$$\varepsilon = \frac{(\hbar k)^2}{2m} \implies \frac{d\varepsilon}{dk} = 2 \frac{\varepsilon}{k} \implies k^2 dk = \frac{1}{2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} d\varepsilon$$

such that

$$\mathcal{D}[\varepsilon] = \frac{g V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon^{1/2}$$

Systems with lower dimensionality, or with relativistic kinematics, or with harmonic oscillator rather than square-well confinement potentials, are considered in the exercises.

Statistics of occupation numbers

The occupancy of single-particle states in a many-body system is a statistical quantity subject to thermodynamic fluctuations. Since the number of particles occupying any state is indeterminate, each orbital can be visualized as a subsystem in equilibrium with a reservoir of energy and particles. Therefore, the statistics of occupancy are susceptible to analysis using the grand canonical ensemble. The probability distribution describing the occupancy of orbital α with single-particle energy ε_{α} in an ideal quantum fluid is

$$P[n_\alpha] = \frac{e^{-n_\alpha \xi_\alpha}}{\mathcal{Z}_\alpha} \quad \mathcal{Z}_\alpha = \sum_{n_\alpha} e^{-n_\alpha \xi_\alpha}$$

where μ is the chemical potential established by the reservoir and where it is very convenient to define a reduced energy relative to the chemical potential as $\xi_\alpha = \beta(\varepsilon_\alpha - \mu)$. The grand partition function \mathcal{Z}_α sums over all possible values of the occupancy n_α for orbital α . The mean occupancy and its variance are given by

$$\bar{n}_\alpha = \sum_{n_\alpha} P_\alpha n_\alpha = -\frac{\partial \ln \mathcal{Z}_\alpha}{\partial \xi_\alpha}$$

$$\sigma_{n_\alpha}^2 = \langle (n_\alpha - \bar{n}_\alpha)^2 \rangle = -\frac{\partial \bar{n}_\alpha}{\partial \xi_\alpha}$$

■ Maxwell-Boltzmann distribution

Although the semiclassical Maxwell-Boltzmann (MB) distribution does not actually pertain to any real quantum system, it is nevertheless instructive to compare the FD and BE distributions to this classical model. Classically, the degeneracy for a state of N identical particles described by occupation numbers $\nu = \{n_\alpha\}$ would be $N! / \prod_\alpha n_\alpha!$, but we must divide by $N!$ to resolve the Gibbs paradox so that $g_\nu = (\prod_\alpha n_\alpha!)^{-1}$ becomes the proper statistical weight for the MB distribution. The grand partition function can then be factored, such that

$$\mathcal{Z}_\alpha = \sum_{n_\alpha=0}^{\infty} \frac{e^{-n_\alpha \xi_\alpha}}{n_\alpha!} = \text{Exp}[e^{-\xi_\alpha}]$$

is recognized as an exponential function with a fancy argument. Therefore, the grand potential, mean occupancy, and occupancy variance become

$$\mathcal{G}_\alpha = -k_B T e^{-\xi_\alpha} \implies \bar{n}_\alpha = e^{-\xi_\alpha} \implies \sigma_{n_\alpha}^2 = \bar{n}_\alpha$$

The single-orbital occupancy probability distribution can now be expressed in a form

$$P[n_\alpha] = \frac{1}{n_\alpha!} e^{-n_\alpha \xi_\alpha} e^{-e^{-\xi_\alpha}} = \frac{\bar{n}_\alpha^{n_\alpha}}{n_\alpha!} e^{-\bar{n}_\alpha}$$

we recognize as the Poisson distribution, which is an approximation to the binomial distribution that applies to ensembles consisting of many independent trials with low probability for success in each trial. Similarly, the MB distributions applies when the total number of particles is large but the probability that any particular single-particle orbital is occupied, and hence its mean occupancy, is small. Thus, the rms fluctuation in orbital occupancy

$$\frac{\sigma_{n_\alpha}}{\bar{n}_\alpha} = \left(\frac{1}{\bar{n}_\alpha} \right)^{1/2}$$

is characteristic of systems with statistical independence.

■ Fermi-Dirac distribution

The exclusion principle restricts the occupancy n_α for fermions to either 0 or 1. Thus, the grand partition function and grand potential for the Fermi-Dirac (FD) distribution reduce to simply

$$\mathcal{Z}_\alpha = 1 + e^{-\xi_\alpha} \implies \mathcal{G}_\alpha = -k_B T \text{Log}[1 + e^{-\xi_\alpha}]$$

where $\xi_\alpha = \beta(\varepsilon_\alpha - \mu)$. Therefore, the mean occupancy becomes

$$\bar{n}_\alpha = -\frac{\partial \ln \mathcal{Z}_\alpha}{\partial \xi_\alpha} = (e^{\xi_\alpha} + 1)^{-1}$$

for the FD distribution. Using

$$e^{\xi_\alpha} = \frac{1 - \bar{n}_\alpha}{\bar{n}_\alpha} \implies \mathcal{Z}_\alpha = 1 - \bar{n}_\alpha$$

the probability distribution $P[n_\alpha]$ for occupation numbers can be expressed in the form

$$\begin{aligned} P[n_\alpha = 0] &= \mathcal{Z}_\alpha^{-1} = 1 - \bar{n}_\alpha \\ P[n_\alpha = 1] &= \mathcal{Z}_\alpha^{-1} e^{-\xi_\alpha} = \bar{n}_\alpha \end{aligned}$$

Therefore, we can interpret \bar{n}_α for the FD distribution as the probability that orbital α is occupied and $1 - \bar{n}_\alpha$ as the probability that it is empty.

Similarly, the occupancy variance is

$$\sigma_{n_\alpha}^2 = -\frac{\partial \bar{n}_\alpha}{\partial \xi_\alpha} = \frac{e^{\xi_\alpha}}{(e^{\xi_\alpha} + 1)^2} = \bar{n}_\alpha (1 - \bar{n}_\alpha)$$

so that the relative rms fluctuation in occupancy is

$$\frac{\sigma_{n_\alpha}}{\bar{n}_\alpha} = \left(\frac{1 - \bar{n}_\alpha}{\bar{n}_\alpha} \right)^{1/2}$$

Hence, the occupancy fluctuations are suppressed relative to a normal (uncorrelated) distribution by a factor of $(1 - \bar{n}_\alpha)^{1/2}$ due to the influence of quantum correlations arising from permutation symmetry.

■ Bose-Einstein distribution

For bosons the occupancy of each orbital is unrestricted so that the sum over n_α extends from zero to infinity. The grand partition function

$$\mathcal{Z}_\alpha = \sum_{n_\alpha=0}^{\infty} e^{-n_\alpha \xi_\alpha} = (1 - e^{-\xi_\alpha})^{-1}$$

is thus an infinite geometric series. The grand potential and mean occupancy are then

$$\mathcal{G}_\alpha = k_B T \text{Log}[1 - e^{-\xi_\alpha}] \implies \bar{n}_\alpha = (e^{\xi_\alpha} - 1)^{-1}$$

The requirements that the orbital occupancies be positive definite and that \mathcal{Z} converges necessitate $\mu \leq \varepsilon_0$ where ε_0 is the lowest single-particle energy. Since by convention $\varepsilon_0 = 0$, we require $-\infty \leq \mu \leq 0$ for the Bose-Einstein (BE) distribution, whereas μ is unrestricted for the FD distribution. Using

$$e^{\xi_\alpha} = \frac{1 + \bar{n}_\alpha}{\bar{n}_\alpha} \implies \mathcal{Z}_\alpha = 1 + \bar{n}_\alpha$$

we find that the occupancy probability distribution

$$P[n_\alpha] = \frac{e^{-n_\alpha \xi_\alpha}}{\mathcal{Z}_\alpha} = \frac{\bar{n}_\alpha^{-n_\alpha}}{(1 + \bar{n}_\alpha)^{n_\alpha+1}} = \bar{n}_\alpha^{-1} \left(\frac{\bar{n}_\alpha}{1 + \bar{n}_\alpha} \right)^{n_\alpha+1}$$

is a geometric distribution with constant ratio

$$\frac{P[n_\alpha + 1]}{P[n_\alpha]} = \frac{\bar{n}_\alpha}{1 + \bar{n}_\alpha}$$

between successive terms.

The occupancy variance is

$$\sigma_{n_\alpha}^2 = -\frac{\partial \bar{n}_\alpha}{\partial \xi_\alpha} = \frac{e^{\xi_\alpha}}{(e^{\xi_\alpha} - 1)^2} = \bar{n}_\alpha (1 + \bar{n}_\alpha)$$

so that the rms fluctuation

$$\frac{\sigma_{n_\alpha}}{\bar{n}_\alpha} = \left(\frac{1 + \bar{n}_\alpha}{\bar{n}_\alpha} \right)^{1/2}$$

is enhanced by a factor of $(1 + \bar{n}_\alpha)^{1/2}$ compared with a normal (classical) system. Thus, fluctuations in the FD distribution are suppressed and in the BE distribution enhanced by the occupancy of an orbital. These correlations arise from the permutation symmetry of the many-body wave function even without interactions.

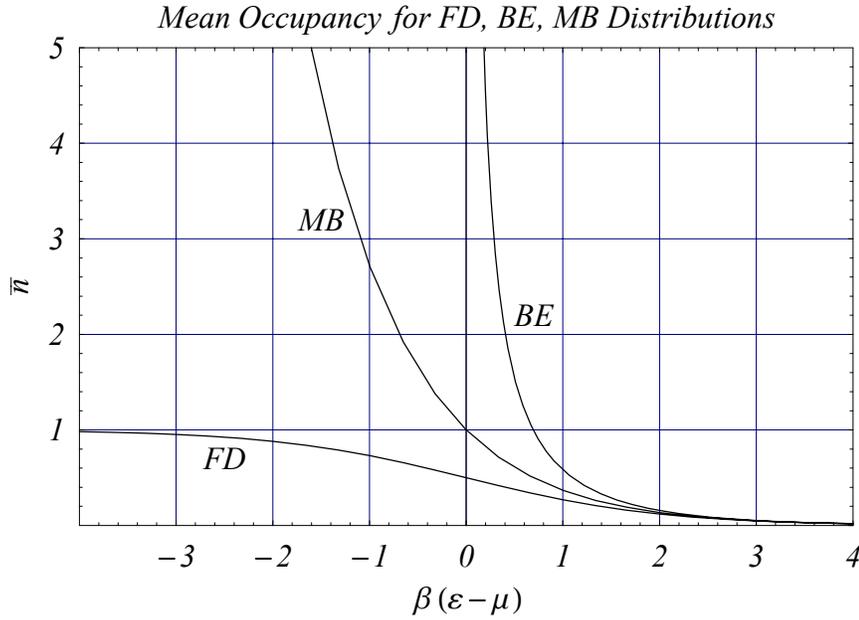
The BE occupancy distribution should be familiar from our studies of the Debye model and the Planck distribution. For these models we found that the mean number of quanta in a mode with energy ε was $\bar{n}[\varepsilon] = (e^{\beta\varepsilon} - 1)^{-1}$, which has the same form as the Bose-Einstein distribution with $\mu = 0$. Recognizing that quanta of the electromagnetic field are photons, an elementary particle with spin 1, we must treat photons with the same energy and polarization as indistinguishable bosons satisfying Bose-Einstein statistics. However, because the number of photons is truly indeterminate, the chemical potential for a photon gas vanishes. Although there is no elementary particle that corresponds to quantized lattice vibrations of a crystal, these quanta behave identical spinless particles with vanishing chemical potential. In fact, there is a wide variety of quantized excitations that are governed by BE statistics with $\mu = 0$.

■ Comparison between FD, BE, and MB occupancies

The mean occupancy $\bar{n}[\varepsilon, \beta, \mu]$ for an orbital with energy ε in a system with inverse temperature β and chemical potential μ can be expressed in the generic form

$$\bar{n}[\varepsilon, \beta, \mu] = (e^{\beta(\varepsilon - \mu)} + \gamma)^{-1} \quad \text{where} \quad \begin{array}{l} \text{FD} \implies \gamma = +1 \\ \text{MB} \implies \gamma = 0 \\ \text{BE} \implies \gamma = -1 \end{array}$$

where $\gamma = 0, \pm 1$ governs the statistical properties of the distribution. Adopting the usual convention that the single-particle energy spectrum starts at $\varepsilon_0 = 0$, such that $\varepsilon \geq 0$, the requirement that \bar{n} be positive definite requires $-\infty \leq \mu \leq 0$ for the BE distribution, but μ may assume either sign for the MB and FD distributions. These occupancy functions are compared below.



These occupancy functions converge in the limit

$$\frac{\varepsilon - \mu}{k_B T} \gg 1 \implies \bar{n}[\varepsilon, \beta, \mu] = e^{-\beta(\varepsilon - \mu)}$$

where the mean occupancy $\bar{n} \ll 1$ is very small. Ordinarily one considers the classical limit to be synonymous with high temperature, but this comparison demonstrates that a more rigorous description of the classical limit is "small single-orbital occupancy", which is needed for the Gibbs resolution of the indistinguishability problem to become accurate. It is not sufficient to require the temperature to be large, which is needed to approximate a discrete spectrum of energy states by a continuous phase space, but one must also require the density to small enough for the chemical potential to be large and negative such that

$$\text{classical limit: } \mu \ll \varepsilon - k_B T$$

As T increases, μ must become increasingly negative to fulfill this condition for any fixed ε . To gauge the accuracy of the classical approximation, we relate the chemical potential for a classical ideal gas to its density by summing the mean number of particles in each momentum state using the MB distribution.

$$\frac{N}{V} = \int \frac{d^3 p}{(2\pi\hbar)^3} \text{Exp}\left[-\beta\left(\frac{p^2}{2m} - \mu\right)\right] = \lambda_B^{-3} e^{\beta\mu} \quad \text{where } \lambda_B = \left(\frac{2\pi\hbar^2}{m k_B T}\right)^{1/2}$$

Thus, we find that the chemical potential is closely related to the quantum concentration:

$$\mu = k_B T \text{Log}\left[\frac{N}{V} \lambda_B^3\right] = k_B T \text{Log}[n_Q]$$

This result applies to a nonrelativistic gas in three spatial dimensions. Clearly,

$$\mu \ll 0 \implies n_Q \ll 1$$

a large negative chemical potential requires a small quantum concentration to minimize the overlap between wave packets associated with the characteristic thermal energy. The relationship between chemical potential and density is more complicated for the FD and BE distributions, but reduces to the MB result in the classical limit $n_Q \ll 1$.

Degenerate Fermi gas

According to the FD distribution, the mean occupancy for a single-particle state with energy ε is

$$\bar{n}[\varepsilon, \beta, \mu] = (e^{\beta(\varepsilon-\mu)} + 1)^{-1}$$

At $T = 0$ the argument of the exponential is $-\infty$ for $\varepsilon < \mu$ or is $+\infty$ for $\varepsilon > \mu$. Hence, the occupancy is unity for all states with ε below μ and is zero for states with $\varepsilon > \mu$. Therefore, the completely degenerate Fermi gas at $T = 0$ is described by a frozen distribution in which all orbitals below the chemical potential are occupied and all orbitals above μ are vacant.

For a fixed density, the chemical potential is a function of temperature alone. By convention, we define the *Fermi energy*, ε_F , to be the chemical potential the system has at $T = 0$ for a given density. Similarly, the *Fermi temperature*, T_F , is defined by

$$T = 0 \implies \mu = \varepsilon_F = k_B T_F$$

It is then useful to express ε and μ in units of ε_F and to define the reduced temperature as $\tau = T/T_F$. Also notice that

$$\varepsilon = \mu[T] \implies \bar{n} = 0.5$$

such that the chemical potential for finite temperature is equal to the energy for which the occupancy is one half.

The relationship between the chemical potential and temperature is determined by fixing the average density of the system. At $T = 0$, all states below ε_F have unit occupancy so that the total number of particles in a completely degenerate nonrelativistic Fermi gas is given by

$$N = \int_0^{\infty} d\varepsilon \mathcal{D}[\varepsilon] \bar{n}[\varepsilon] = \frac{g V}{4 \pi^2} \left(\frac{2 m}{\hbar^2} \right)^{3/2} \int_0^{\varepsilon_F} \varepsilon^{1/2} d\varepsilon = \frac{g V}{6 \pi^2} \left(\frac{2 m \varepsilon_F}{\hbar^2} \right)^{3/2}$$

Solving for ε_F in terms of the particle density $\rho = N/V$, we find

$$\varepsilon_F = \frac{\hbar^2}{2 m} \left(\frac{6 \pi^2}{g} \rho \right)^{2/3} = \frac{(\hbar k_F)^2}{2 m}$$

$$k_F = \left(\frac{6 \pi^2}{g} \rho \right)^{1/3}$$

The fact that the Fermi momentum k_F scales with $\rho^{1/3}$ is a consequence of the fact that the wave numbers for single-particle states scale with $V^{-1/3}$. For later purposes it will be useful to observe that the density of states can also be expressed in the forms

$$\mathcal{D}[\varepsilon] d\varepsilon = \frac{3}{2} N \frac{\varepsilon^{1/2} d\varepsilon}{\varepsilon_F^{3/2}} = N d\left(\frac{\varepsilon}{\varepsilon_F}\right)^{3/2}$$

$$\mathcal{D}[k] dk = 3 N \frac{k^2 dk}{k_F^3} = N d\left(\frac{k}{k_F}\right)^3$$

by scaling according to either ε_F or k_F , as appropriate.

The average single-particle energy is

$$\bar{\varepsilon} = \frac{\int_0^\infty d\varepsilon \mathcal{D}[\varepsilon] \bar{n}[\varepsilon, \mu, T] \varepsilon}{\int_0^\infty d\varepsilon \mathcal{D}[\varepsilon] \bar{n}[\varepsilon, \mu, T]}$$

which for a completely degenerate Fermi gas reduces to

$$T = 0 \implies \bar{\varepsilon} = \frac{\int_0^{\varepsilon_F} d\varepsilon \varepsilon^{1/2} \varepsilon}{\int_0^{\varepsilon_F} d\varepsilon \varepsilon^{1/2}} = \frac{3}{5} \varepsilon_F$$

Hence, the total internal energy for a degenerate Fermi gas with N particles is simply

$$T = 0 \implies U = \frac{3}{5} N \varepsilon_F$$

Similarly, the pressure for any nonrelativistic ideal gas, classical or quantum, is simply two-thirds of the energy density. Thus, we find that the pressure

$$T = 0 \implies p = \frac{2}{5} \rho \varepsilon_F = \frac{\hbar^2}{5m} \left(\frac{6\pi^2}{g} \right)^{2/3} \rho^{5/3}$$

is finite, scaling with $\rho^{5/3}$, even at $T = 0$.

Contrary to the behavior of a classical ideal gas, for which the pressure vanishes at $T = 0$, a Fermi gas retains substantial pressure at absolute zero. This additional pressure, which may be called *degeneracy pressure*, is due to the exclusion principle which, by preventing more than g particles from occupying the same energy level, compels fermions to occupy a distribution of energy levels above the ground state. Hence, the energy density is proportional to $\rho^{5/3}$ and the pressure seeking to reduce that energy density can be quite large. Even without explicit interactions between particles, correlations due to antisymmetrization of the wave function produce an effective repulsion between fermions. This is a purely quantum effect with no classical counterpart.

■ Example: conduction electrons

Conduction electrons in a metal move within an average potential that confines them to the volume of the material, but mutual interactions can often be neglected. The dispersion relation for electrons moving within a uniform mean field can then be expressed in the form

$$\varepsilon = \frac{(\hbar k)^2}{2m} + \mathcal{U}[k^2]$$

where $\mathcal{U}[k^2]$ is a momentum-dependent potential describing the interaction with the lattice. It is convenient to express \mathcal{U} as a function of k^2 rather than k because it must be an even function to satisfy rotational and reflection symmetries. Recognizing that momenta near the Fermi surface play a dominant role in the thermodynamics of a nearly degenerate Fermi gas, it is useful to expand the potential about the Fermi momentum k_F , such that

$$\mathcal{U}[k^2] \approx \mathcal{U}_0 + \mathcal{U}_1 \frac{\hbar^2 (k^2 - k_F^2)}{2m} + \dots$$

where

$$\mathcal{U}_0 = \mathcal{U}[k_F^2] \quad \mathcal{U}_1 = \frac{2m}{\hbar^2} \left(\frac{\partial \mathcal{U}[k^2]}{\partial k^2} \right)_{k^2=k_F^2}$$

Combining the kinetic and potential terms, the dispersion relation now takes the form

$$\varepsilon \approx \varepsilon_0 + \frac{(\hbar k)^2}{2 m_{\text{eff}}}$$

where $\varepsilon_0 = \mathcal{U}_0 - \mathcal{U}_1 \frac{k_F^2}{2m}$ is an energy shift and

$$\frac{m_{\text{eff}}}{m} = (1 + \mathcal{U}_1)^{-1}$$

is the effective mass for electrons near the Fermi surface. Therefore, the primary effect of the mean field is to shift the energy scale and alter the effective mass. In metals one usually finds that $\mathcal{U}_1 > 0 \implies m_{\text{eff}} > m$ such that the effective mass for a conduction electron with momentum near k_F appears to be increased by its attraction to the lattice.

Thus, one can treat conduction electrons as an ideal Fermi gas of particles with effective mass m_{eff} . Using $\rho = 8.5 \times 10^{22} \text{ cm}^{-3}$ and $m_{\text{eff}} = 1.39 m_e$, we obtain a Fermi energy $\varepsilon_F = 5.07 \text{ eV}$ for copper. The corresponding Fermi temperature, $T_F \approx 6 \times 10^4$ kelvin, is so large that the electron gas can be treated as almost completely degenerate at room temperature. The corresponding pressure within this gas is then $p \approx 2.7 \times 10^5$ atmospheres! This large outward pressure must be balanced by the attractive electrostatic forces binding the electrons to the lattice. The confinement of the electron gas is accomplished by a nearly uniform potential rather than by walls at the boundaries of its volume. Nevertheless, since the interactions with the lattice can be represented as a smooth mean field in which all of the electrons move more or less independently of each other, the noninteracting Fermi gas model is still appropriate.

■ Example: nuclear matter

The atomic nucleus consists of protons and neutrons, which are both spin $\frac{1}{2}$ particles of equal mass. It is useful to treat protons and neutrons as states of the same particle, the *nucleon*, differing only in an internal quantum number called *isospin*. Nuclear matter is a theoretical system consisting of equal numbers of protons and neutrons with the Coulomb interaction turned off. Thus, the intrinsic degeneracy factor for momentum states in nuclear matter is $g = 4$. The density of nuclear matter is based upon the central density of large nuclei, which is approximately constant at 0.16 fm^{-3} , where 1 femtometer (fm) is 10^{-15} m . Using these values, one obtains $\varepsilon_F = 37 \text{ MeV}$, which corresponds to an enormous pressure of 4×10^{27} atmospheres that must be balanced by the mean potential generated by the mutual interactions among nucleons. Obviously the name *strong force* for the nucleon-nucleon interaction is well deserved! It was a major accomplishment of nuclear physics in the 1950s to demonstrate that the Fermi gas model provides a reasonable starting point for studying nuclear structure despite the strength of this interaction.

Thermodynamics of nearly degenerate Fermi gases

To develop the thermodynamics of nearly degenerate Fermi gases, we must determine the relationship between chemical potential and density for arbitrary temperature. The total number of particles is obtained by integration of the mean occupancy over the density of states, such that

$$N = \int_0^\infty d\varepsilon \mathcal{D}[\varepsilon] \bar{n}[\varepsilon, \mu, T] \implies \varepsilon_F^{3/2} = \frac{3}{2} \int_0^\infty d\varepsilon \frac{\varepsilon^{1/2}}{e^{\beta(\varepsilon-\mu)} + 1}$$

provides an equation that can be used to determine μ given the temperature and ε_F , which depends only on density and fundamental constants. It is useful to express energy and temperature in dimensionless form using $\tau = T/T_F$ and to introduce the *fugacity* $z = e^{\beta\mu}$, such that

$$\int_0^{\infty} dx \frac{x^{1/2}}{z^{-1} e^x + 1} = \frac{2}{3} \tau^{-3/2}$$

provides an equation that determines the temperature dependence of the fugacity. In chemistry fugacity is often called *absolute activity*. The classical limit defined by large negative μ corresponds to small z , while large z corresponds to the low-temperature limit of a nearly degenerate Fermi gas. Recognizing that other thermodynamic functions depend upon integrals of similar form, it is customary to define a family of Fermi functions using

$$f_\nu[z] = \frac{1}{\Gamma[\nu]} \int_0^{\infty} dx \frac{x^{\nu-1}}{z^{-1} e^x + 1}$$

where the normalization factor is chosen to ensure that $f_\nu[z] \rightarrow z$ when $z \rightarrow 0$. Thus, the chemical potential is obtained from the solution of the equation

$$\Gamma\left[\frac{5}{2}\right] \tau^{3/2} f_{3/2}[z] = 1$$

or

$$f_{3/2}[z] = \frac{4}{3\sqrt{\pi}} \tau^{-3/2}.$$

It is important to recognize that $T_F \propto (N/V)^{2/3}$ is a function only of density, such that

$$\frac{N}{V} \propto T^{3/2} f_{3/2}[z]$$

represents the temperature dependence of density at constant z or the dependence of chemical potential on temperature and density. Numerical methods for solution of the density equation are developed in *fermi.nb*.

Similarly, the internal energy can be expressed in terms of Fermi functions using

$$U = N \bar{\epsilon} = \frac{\int_0^{\infty} d\epsilon \mathcal{D}[\epsilon] \bar{n}[\epsilon, \mu, T] \epsilon}{\int_0^{\infty} d\epsilon \mathcal{D}[\epsilon] \bar{n}[\epsilon, \mu, T]} = N k_B T \frac{\int_0^{\infty} dx \frac{x^{3/2}}{z^{-1} e^x + 1}}{\int_0^{\infty} dx \frac{x^{1/2}}{z^{-1} e^x + 1}} = N k_B T \frac{\Gamma[5/2]}{\Gamma[3/2]} \frac{f_{5/2}[z]}{f_{3/2}[z]}$$

such that the thermal equation of state becomes

$$\frac{U}{N k_B T} = \frac{3}{2} \frac{f_{5/2}[z]}{f_{3/2}[z]}$$

Next, the mechanical equation of state for a nonrelativistic ideal gas is simply $pV = \frac{2}{3} U$, whereby

$$\frac{pV}{N k_B T} = \frac{f_{5/2}[z]}{f_{3/2}[z]}$$

Thus, the pressure and energy density scale according to

$$p \propto \frac{U}{V} \propto T^{5/2} f_{5/2}[z]$$

Finally, the entropy

$$S = \frac{U + pV - N\mu}{T} \implies \frac{S}{N k_B} = \frac{5}{2} \frac{f_{5/2}[z]}{f_{3/2}[z]} - \text{Log}[z]$$

can be expressed in terms of z and N ; hence, isentropic processes at constant N also require constant z . Therefore, using

$$\text{constant } z, N \implies V T^{3/2} = \text{constant}, \quad p T^{-5/2} = \text{constant}$$

we find that adiabats for the nonrelativistic ideal Fermi gas take the familiar form

$$\text{constant } S, N \implies p V^{5/3} = \text{constant}$$

The numerical and analytical properties of Fermi functions are studied in detail within the notebook *fermi.nb*; here we summarize some of the results. These functions can be represented by a power series

$$f_\nu[z] = - \sum_{k=1}^{\infty} \frac{(-z)^k}{k^\nu}$$

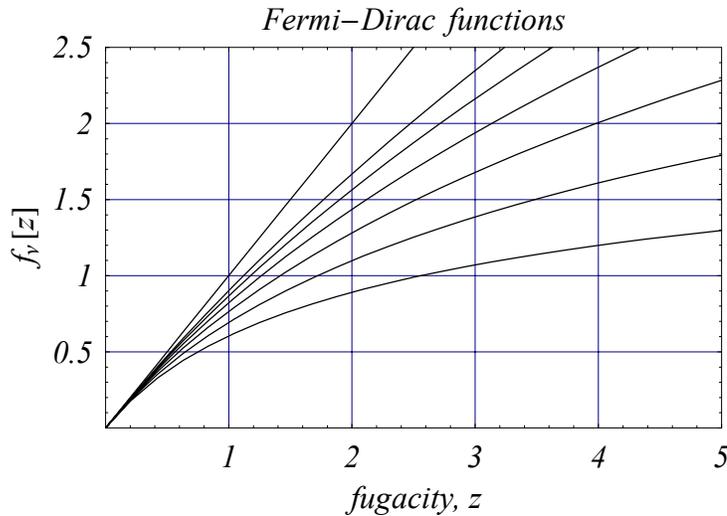
that converges for all $z > 0$, $\nu > 0$. There is a limiting value $f_\infty[z] = z$ and a useful downward recursion relation

$$f_{\nu-1}[z] = z \frac{\partial}{\partial z} f_\nu[z]$$

For large z , the asymptotic expansion known as *Sommerfeld's lemma*

$$f_\nu[e^{\beta\mu}] \simeq \frac{(\beta\mu)^\nu}{\Gamma[\nu+1]} \left(1 + \nu(\nu-1) \frac{\pi^2}{6} (\beta\mu)^{-2} + \nu(\nu-1)(\nu-2)(\nu-3) \frac{7\pi^4}{360} (\beta\mu)^{-4} + \dots \right)$$

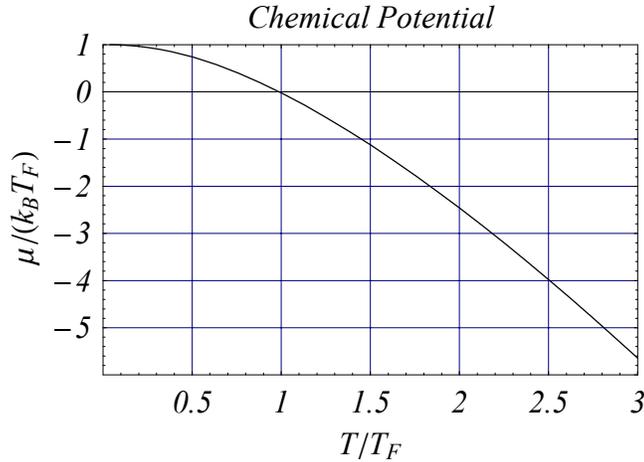
can be derived by exploiting the fact that the mean occupancy for nearly degenerate systems has a sharp edge at the Fermi energy. Representative Fermi functions are shown below for $\nu = \{\frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, 3, \infty\}$ with $f_{1/2}$ lowest and f_∞ highest.



The temperature dependence of the chemical potential can be obtained by numerical solution of the equation

$$f_{3/2}[z] = \frac{4}{3\sqrt{\pi}} \tau^{-3/2}$$

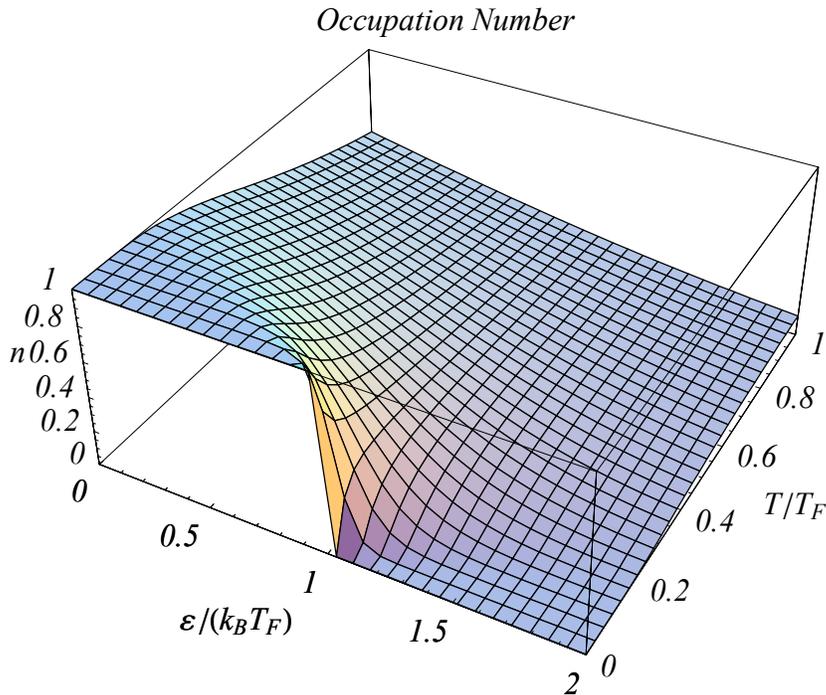
with the result plotted below.



The chemical potential is defined as the Fermi energy at $T = 0$, vanishes at the Fermi temperature, and is large and negative for high temperatures where the classical limit applies. For low temperatures we can approximate the chemical potential as

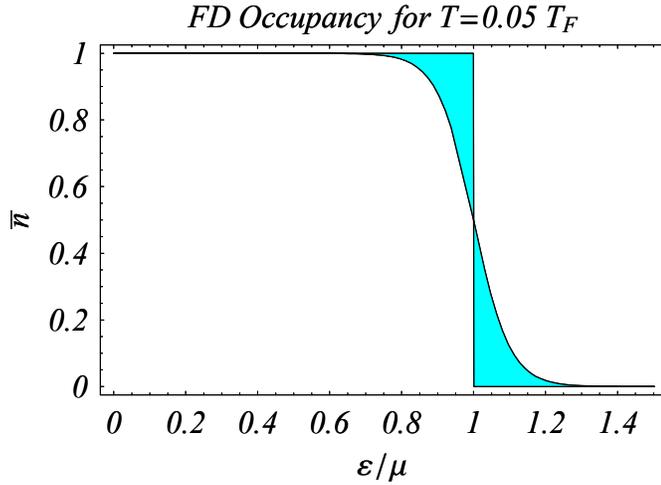
$$T \ll T_F \implies \mu \approx \varepsilon_F \left(1 - \frac{\pi^2 \tau^2}{12} - \frac{\pi^4 \tau^4}{80} \right)$$

The temperature and energy dependence of the occupation probability are illustrated below. For very low temperatures one finds that states with $\varepsilon < \varepsilon_F$ are filled while states above ε_F are empty. As the temperature increases, the Fermi surface becomes more diffuse as the population of energy levels above ε_F are populated at the expense of states below ε_F .



The thermal response of a nearly degenerate Fermi gas with small T/T_F is largely determined by orbitals in the immediate vicinity of the Fermi energy. Particles lying deeper in the energy distribution cannot absorb small amounts of energy because all nearby orbitals are already occupied by other particles and are blocked by the exclusion principle. Only particles in the approximate energy range $\varepsilon \pm k_B T$ can participate strongly in thermal processes. The shaded region in the

figure below illustrates the fraction the of system that can be considered thermodynamically active, which is a rather small fraction at low temperatures.



Thus, we might estimate the heat capacity for a nearly degenerate Fermi gas using

$$T \ll T_F \implies C_V \sim \mathcal{D}[\varepsilon_F] (2 k_B T) \left(\frac{3}{2} k_B \right) = \frac{9}{2} N k_B \frac{T}{T_F}$$

where $\mathcal{D}[\varepsilon_F]$ is the density of states near the Fermi surface, the next factor is the width of the active energy interval, and the final factor is the heat capacity per participating particle. Therefore, we expect the heat capacity to be linear for low temperature and to approach the classical limit from below. A more rigorous analysis based upon the large- z expansion of Fermi function gives the similar result

$$T \ll T_F \implies \frac{U}{N \varepsilon_F} \approx \frac{3}{5} + \frac{\pi^2 \tau^2}{4} - \frac{3 \pi^4 \tau^4}{80} + \dots \implies \frac{C_V}{N k_B} \approx \frac{\pi^2}{2} \tau - \frac{3 \pi^4}{20} \tau^3 + \dots$$

except that the coefficient $\frac{9}{2}$ is replaced by $\frac{\pi^2}{2}$. In fact, one does find that the contribution made by conduction electrons to the heat capacity of metals for $T \ll T_F$ is linear in temperature and that this model provides a good prediction for the slope.

It is probably worthwhile to evaluate C_V explicitly in order to practice manipulation of fermi functions. Using the chain rule, one obtains

$$U = \frac{3}{2} N k_B T \frac{f_{5/2}[z]}{f_{3/2}[z]} \implies C_V = \frac{3}{2} N k_B \left(\frac{f_{5/2}[z]}{f_{3/2}[z]} + T \left(\frac{\partial z}{\partial T} \right)_{V,N} \left(\frac{\partial}{\partial z} \frac{f_{5/2}[z]}{f_{3/2}[z]} \right) \right)$$

Then using the recursion relation $z \partial_z f_\nu[z] = f_{\nu-1}[z]$, one soon finds

$$C_V = \frac{3}{2} N k_B \left(\frac{f_{5/2}[z]}{f_{3/2}[z]} + \frac{T}{z} \left(\frac{\partial z}{\partial T} \right)_V \left(1 - \frac{f_{5/2}[z] f_{1/2}[z]}{f_{3/2}[z]^2} \right) \right)$$

The isochoric temperature dependence of z is obtained by dimensional analysis of the density equation

$$\Gamma\left[\frac{5}{2}\right] \left(\frac{k_B T}{\varepsilon_F} \right)^{3/2} f_{3/2}[z] = 1 \implies \frac{N}{V} \propto T^{3/2} f_{3/2}[z]$$

Thus, constant V , N requires $T^{3/2} f_{3/2}[z]$ to remain constant, such that

$$T^{3/2} f_{3/2}[z] = \text{constant} \implies \frac{3}{2} T^{1/2} f_{3/2}[z] + T^{3/2} z^{-1} f_{1/2}[z] \left(\frac{\partial z}{\partial T} \right)_{V,N} = 0$$

Therefore,

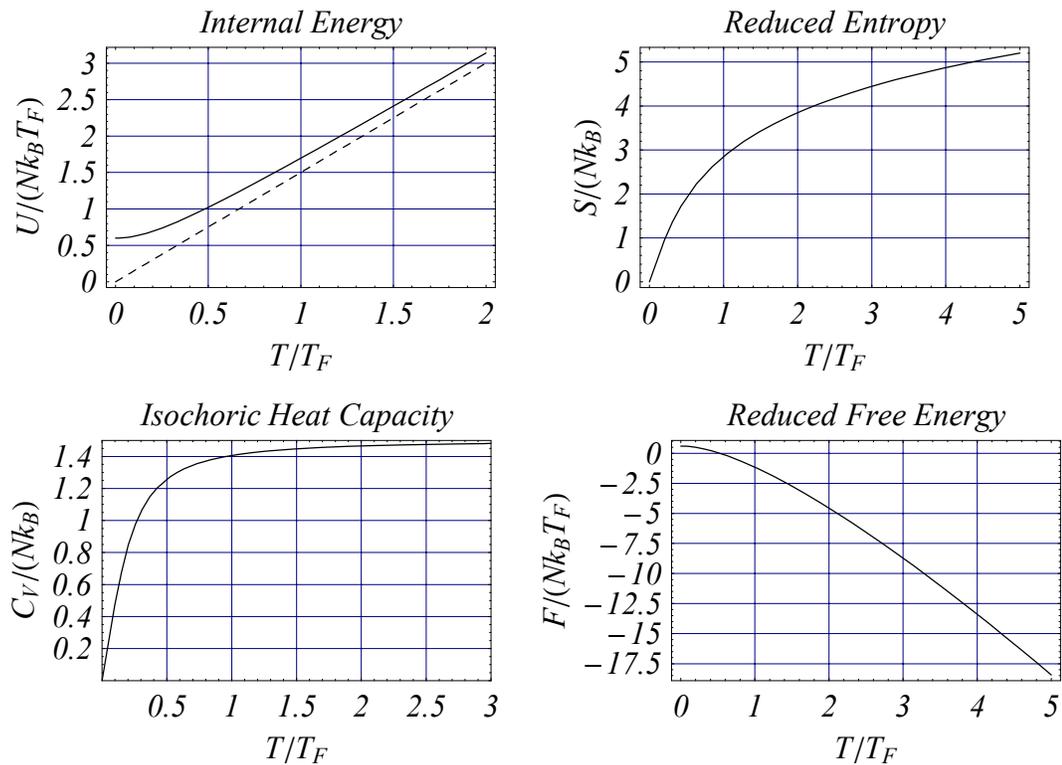
$$\left(\frac{\partial z}{\partial T}\right)_{V,N} = -\frac{3}{2} \frac{z}{T} \frac{f_{3/2}[z]}{f_{1/2}[z]}$$

Finally, substituting this result, we obtain

$$\frac{C_V}{N k_B} = \frac{15}{4} \frac{f_{5/2}[z]}{f_{3/2}[z]} - \frac{9}{4} \frac{f_{3/2}[z]}{f_{1/2}[z]}$$

This result reduces to the classical limit for $z \rightarrow 0$ or to the nearly degenerate result quoted above for large z or, equivalently, $T \ll T_F$. Although it is often useful to express formal results in terms of the reduced temperature, $\tau = T/T_F = k_B T/\varepsilon_F$, we must always remember that ε_F depends upon density.

The temperature dependencies of the principal thermodynamic functions are illustrated below and are studied in more detail in the notebook *fermi.nb*. The internal energy is greater than that of a classical ideal gas, shown by the dashed line, because the Pauli exclusion principle forces particles into higher energy levels. Thus, the internal energy is $\frac{3}{5} N \varepsilon_F$ at $T \rightarrow 0$ and approaches the classical limit from above. The corresponding degeneracy pressure produced by the effective repulsion between identical fermions is much larger than the kinetic pressure would be for distinguishable particles. The heat capacity is small at low temperatures because only the relatively small number of particles within about $k_B T$ of the Fermi surface can participate in the thermodynamics. Similarly, the entropy is reduced at low temperature because a nearly degenerate Fermi gas is highly ordered; permutation symmetry strongly reduces the number of states available to fermions.



Thermodynamics of nearly degenerate Bose gases

The relationship between chemical potential and density for an ideal Bose gas

$$N = \sum_{\alpha} \frac{1}{z^{-1} \text{Exp}[\beta \varepsilon_{\alpha}] - 1}$$

requires more care at low temperature because it is possible for the occupancy of the ground state to become an appreciable fraction of the total number of particles, but the continuous approximation to the density of states for a uniform nonrelativistic system, $\mathcal{D}[\varepsilon] \propto \varepsilon^{1/2}$, gives no weight at all to the ground state. Under these conditions one cannot simply replace the sum by an integral because it would be impossible to account for all the particles. A simple solution to this problem is to separate the sum into two contributions, $N = N_{\text{gs}} + N_{\text{exc}}$, where the mean number of particles in the ground state with energy ε_0 is given by

$$N_{\text{gs}} = g \frac{z_0}{1 - z_0}$$

where $z_0 = \text{Exp}[\beta(\mu - \varepsilon_0)]$, while the mean number of particles found in excited states is approximated by the integral

$$N_{\text{exc}} = \int_0^{\infty} d\varepsilon \mathcal{D}[\varepsilon] \bar{n}[\varepsilon, \mu, T] = \frac{g V}{4 \pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\infty} d\varepsilon \frac{\varepsilon^{1/2}}{z^{-1} e^{\beta \varepsilon} - 1}$$

The requirement that the number of particles in excited states be positive limits the fugacity for Bose gases to the range $0 \leq z \leq 1$ and the chemical potential to the range $\mu \leq \varepsilon_0$. However, if z approaches unity the ground-state occupancy becomes macroscopically large. The accumulation of bosons in the ground state is a phenomenon, known as *Bose-Einstein condensation*, that has profound consequences for the properties of an ideal Bose gas. Expressing z_0 in terms of N_{gs} ,

$$z_0 = \frac{N_{\text{gs}}}{g + N_{\text{gs}}} \approx 1 - \frac{g}{N_{\text{gs}}}$$

where the intrinsic degeneracy g is a number of order unity, one finds that z_0 is extremely close to unity whenever N_{gs} reaches macroscopic size; in fact, z_0 is very close to unity even for as few as a thousand particles in the ground state and is extremely close to unity if N_{gs} becomes a nonnegligible fraction of a total particle number of order 10^{23} . Thus, the critical temperature T_c for Bose-Einstein condensation is determined by the condition $\mu[T_c] = \varepsilon_0$ at the specified density. Ordinarily one shifts the energy scale so that $\varepsilon_0 \rightarrow 0$ and in the continuous approximation ignores the slight dependence of the ground-state energy upon volume.

It is useful to define a family of Bose functions using

$$g_{\nu}[z] = \frac{1}{\Gamma[\nu]} \int_0^{\infty} dx \frac{x^{\nu-1}}{z^{-1} e^x - 1}$$

where the normalization factor was chosen to ensure that $g_{\nu} \rightarrow z$ as $z \rightarrow 0$. Do not confuse the Bose function, g_{ν} , with the intrinsic degeneracy of momentum states g ; the notational similarity is unfortunate but traditional. The detailed analytical and numerical properties of Bose functions are studied in *bose.nb* and here we summarize the salient results. The Bose functions increase monotonically with z . For small z , power-series expansion of the integrand produces a series representation

$$\nu > 1 \implies g_\nu[z] = \sum_{k=1}^{\infty} \frac{z^k}{k^\nu} \quad g_\nu[1] = \zeta[\nu] \quad g_{\nu-1}[z] = z \frac{\partial}{\partial z} g_\nu[z]$$

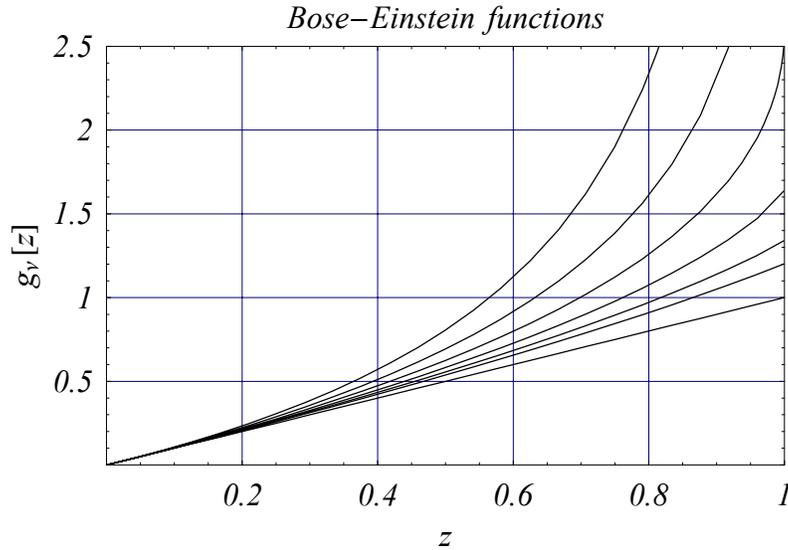
that is convergent over the entire physical range $0 \leq z \leq 1$ provided that $\nu > 1$. Thus, Bose functions with $\nu > 1$ are closely related to the Riemann zeta function $\zeta[\nu]$. More care is needed for $\nu \leq 1$ because the integrand for $z = 1$ is singular at $x = 0$. Although a simple result with logarithmic divergence is obtained for $\nu = 1$,

$$g_1[z] = -\text{Log}[1 - z]$$

more general methods are needed for arbitrary ν . The derivation of an asymptotic expansion due to Robinson (Phys. Rev. 83, 678 (1951))

$$z \rightarrow 1 \implies g_\nu[z] \simeq (-\ln z)^{\nu-1} \Gamma[1 - \nu] + \sum_{m=0}^{\infty} \frac{(\ln z)^m \zeta[\nu - m]}{m!}$$

is outlined in *bose.nb*. Note that this expansion can be used for all ν because the singularities for positive integers cancel to all orders. Representative Bose functions are shown below for $\nu = \{\frac{1}{2}, 1, \frac{3}{2}, 2, \frac{5}{2}, 3, \infty\}$ with $g_{1/2}$ highest and $g_\infty[z] = z$ lowest. Thus, we find that $g_\nu[z \rightarrow 1]$ diverges for $\nu \leq 1$, converges with finite slope for $\nu > \frac{3}{2}$, while for $\nu = \frac{3}{2}$ the limiting value is finite even though the slope is infinite at $z = 1$.



After this mathematical interlude, we are now ready to determine the density dependence of the critical temperature. The number of excited particles in a three-dimensional nonrelativistic Bose gas can be expressed in terms of Bose functions as

$$n_Q = \frac{N_{\text{exc}} \lambda^3}{g V} = g_{3/2}[z]$$

where λ is the thermal wavelength. Recognizing that $g_{3/2}[1] = \zeta[\frac{3}{2}]$ is finite, the maximum number of particles that can be placed in excited states is limited to

$$N_{\text{exc}} \leq \frac{g V}{\lambda^3} \zeta\left[\frac{3}{2}\right]$$

where $\zeta[\frac{3}{2}] \approx 2.61238$. Any additional particles must be found in the ground-state. Therefore, the temperature

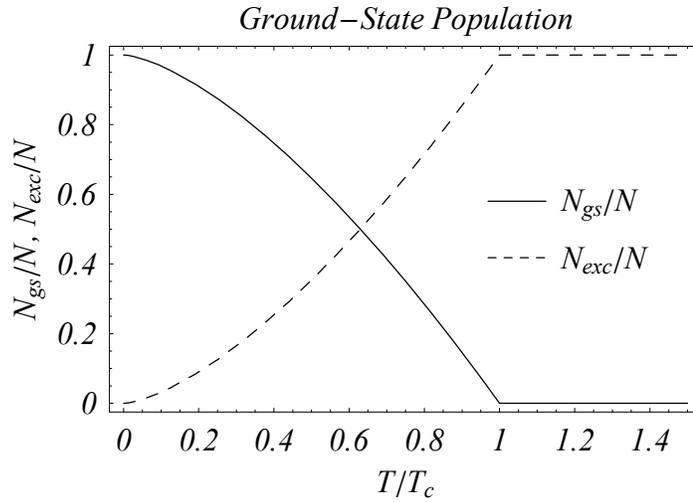
$$T_c = \frac{2\pi}{\zeta\left[\frac{3}{2}\right]^{2/3}} \left(\frac{N}{gV}\right)^{2/3} \frac{\hbar^2}{m k_B} \approx 3.3125 \left(\frac{N}{gV}\right)^{2/3} \frac{\hbar^2}{m k_B}$$

at which the maximum number of particles in excited states becomes equal to the total number of particles represents a *critical temperature* below which the ground-state begins to receive macroscopic occupancy. Below the critical temperature the occupation of the ground state becomes

$$T \leq T_c \implies \frac{N_{\text{gs}}}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2}$$

whereas for higher temperatures the fraction of the total number of particles found exactly at the ground-state energy is negligible. Although all particles occupy the same volume, below T_c it is useful to describe the system in terms of coexistence between two phases, the *normal phase* consisting of particles in excited states and a *condensed phase* consisting of particles in the ground state. For this system the condensation occurs in momentum space rather than configuration space, so that the two phases coexist in the same volume but have distinctly different properties. Most notably, we will find that the energy and pressure contributed by the condensed phase are negligible. Nor does the highly ordered condensed phase contribute to entropy. Therefore, the thermodynamic functions are determined by the fraction that is in the normal phase.

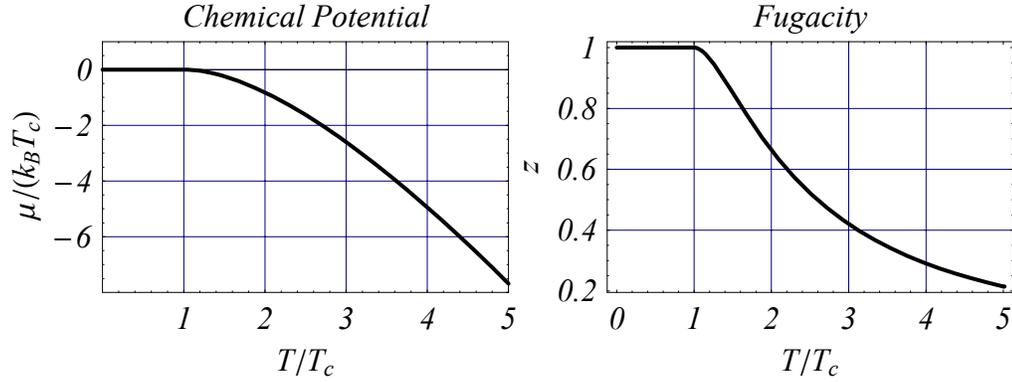
The ground-state fraction N_{gs}/N , illustrated below, serves as the order parameter characterizing the phase transition.



The chemical potential and fugacity obtained by numerical solution of the equation

$$\tau^{3/2} g_{3/2}[z] = \zeta\left[\frac{3}{2}\right]$$

for $T > T_c$ are shown below; both are constant below the critical temperature. Details of the numerical solution of this equation are provided in *bose.nb*.



The grand potential can be separated into ground-state and excited-state contributions using

$$\frac{\mathcal{G}}{k_B T} = g \text{Log}[1 - z] + \int_0^\infty d\varepsilon \mathcal{D}[\varepsilon] \text{Log}[1 - z e^{-\beta\varepsilon}]$$

The second term can be integrated by parts, whereby

$$\frac{g V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty d\varepsilon \varepsilon^{1/2} \text{Log}[1 - z e^{-\beta\varepsilon}] = -\frac{g V}{6\pi^2} \left(\frac{2m k_B T}{\hbar^2}\right)^{3/2} \int_0^\infty dx \frac{x^{3/2}}{z^{-1} e^x - 1}$$

Recognizing the coefficient from the equation for z in terms of N , we find

$$T \geq T_c \implies \frac{\mathcal{G}}{k_B T} = g \text{Log}[1 - z] - N \frac{g_{5/2}[z]}{g_{3/2}[z]}$$

above the critical temperature. Next, using the relationship between z and N_{gs} ,

$$z = \frac{N_{\text{gs}}}{g + N_{\text{gs}}} \implies \text{Log}[1 - z] = \text{Log}\left[\frac{g}{g + N_{\text{gs}}}\right] \sim -\text{Log}[N_{\text{gs}}]$$

we find that for large N the first term is negligible in comparison with the second and may be omitted except perhaps for very small systems. Hence, in this approximation the energy, pressure, and entropy contributed by the ground state are negligible compared with the contributions of excited states. Therefore, the equation of state becomes

$$T \geq T_c \implies \frac{p V}{N k_B T} = \frac{g_{5/2}[z]}{g_{3/2}[z]}$$

for temperatures above the phase transition. Below the phase transition we require $z = 1$ such that the contribution of the normal phase reduces to

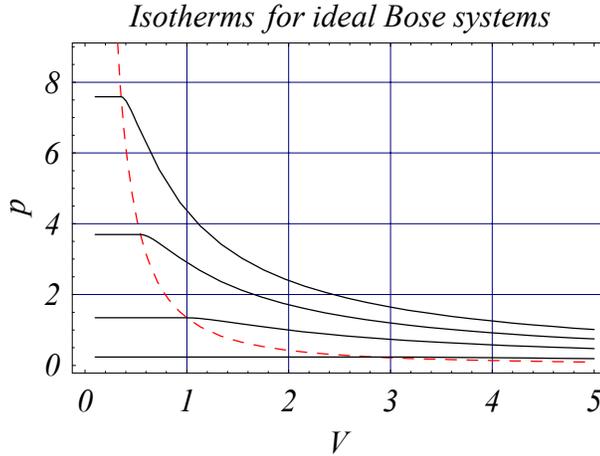
$$T \leq T_c \implies \frac{p V}{N k_B T} = \left(\frac{T}{T_c}\right)^{3/2} \frac{\zeta[\frac{5}{2}]}{\zeta[\frac{3}{2}]}$$

while the condensed phase is neglected because $\text{Log}[N_{\text{gs}}] \ll N$. Therefore, the pressure on an isotherm is actually independent of density for $T \leq T_c$ because $T_c \propto (N/V)^{2/3}$. Thus, upon evaluation of the numerical factors, the *transition line*

$$T = T_c \implies p_c \left(\frac{V_c}{N}\right)^{5/3} = \frac{2\pi \hbar^2}{m g^{2/3}} \frac{\zeta[\frac{5}{2}]}{\zeta[\frac{3}{2}]^{5/3}} \approx 3.402 \frac{\hbar^2}{m g^{2/3}}$$

relates the critical pressure to the critical density. Notice that the equation for the transition line, $p_c \propto (N/V_c)^{5/3}$, has the same form as isentropes for an ideal gas; indeed, the entropy reaches its minimum value and is constant on the transition line.

The figure below shows isotherms for a nonrelativistic ideal Bose gas, where both condensed and normal phases coexist under the dashed transition line.



In the coexistence region wavepackets with dimensions characterized by the thermal wavelength overlap sufficiently strongly for quantum correlations to strongly enhance the population of the ground state. As the temperature increases this phase transition requires increasing density (decreasing V for fixed N) to compensate for the decreasing thermal wavelength. Recognizing that the density of the normal phase in the coexistence region depends only upon temperature,

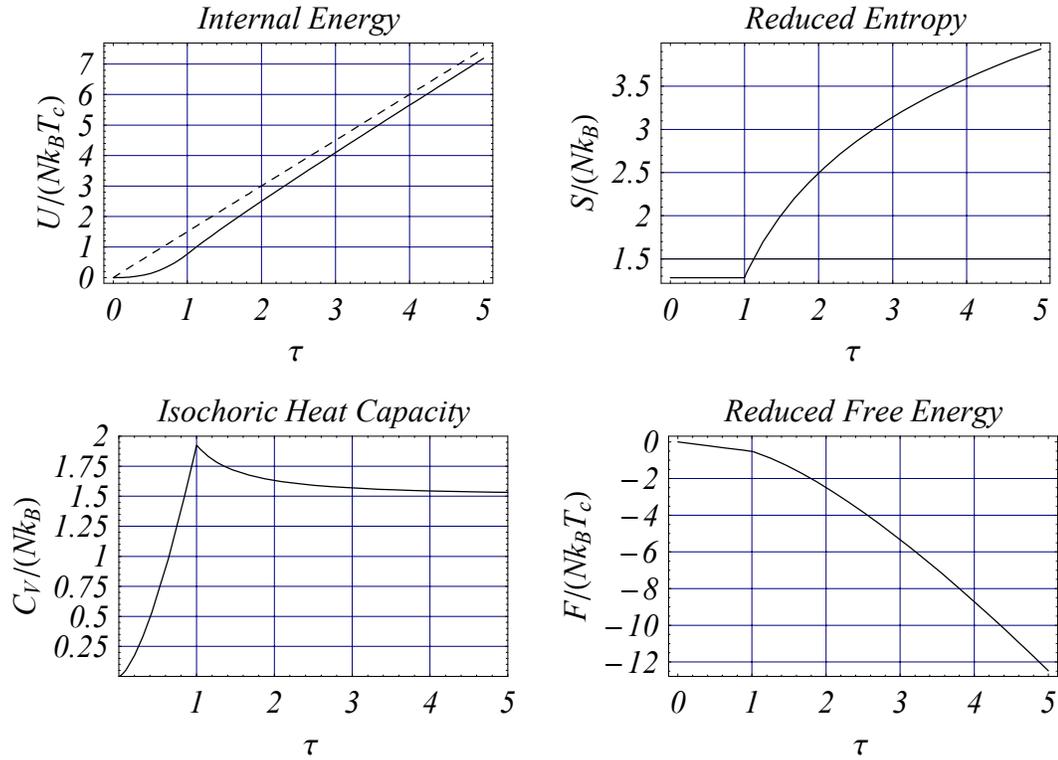
$$T \leq T_c \implies \frac{N_{\text{exc}}}{V} = \frac{N}{V} \left(\frac{T}{T_c} \right)^{3/2} = g \left(\frac{m k_B T}{2\pi\hbar^2} \right)^{3/2} \zeta \left[\frac{3}{2} \right]$$

we find that the energy density and pressure for the normal phase remain constant during isothermal compression. Therefore, the primary effect of isothermal compression is to push more particles into the condensed phase for which the energy density and pressure are negligible.

The temperature dependencies of the principal thermodynamic functions, derived in the notebook *bose.nb*, are tabulated below assuming that $\varepsilon_0 = 0$.

	$T \leq T_c$	$T \geq T_c$
N_{exc}	$\left(\frac{T}{T_c} \right)^{3/2} N$	N
U	$N_{\text{exc}} k_B T \frac{3}{2} \frac{\zeta[\frac{5}{2}]}{\zeta[\frac{3}{2}]}$	$N k_B T \frac{3}{2} \frac{g_{5/2}[z]}{g_{3/2}[z]}$
C_V	$N_{\text{exc}} k_B \frac{15}{4} \frac{\zeta[\frac{5}{2}]}{\zeta[\frac{3}{2}]}$	$N k_B \left(\frac{15}{4} \frac{g_{5/2}[z]}{g_{3/2}[z]} - \frac{9}{4} \frac{g_{3/2}[z]}{g_{1/2}[z]} \right)$
S	$N_{\text{exc}} k_B \frac{5}{2} \frac{\zeta[\frac{5}{2}]}{\zeta[\frac{3}{2}]}$	$N k_B \left(\frac{5}{2} \frac{g_{5/2}[z]}{g_{3/2}[z]} - \ln z \right)$
F	$-N_{\text{exc}} k_B T \frac{\zeta[\frac{5}{2}]}{\zeta[\frac{3}{2}]}$	$-N k_B T \left(\frac{g_{5/2}[z]}{g_{3/2}[z]} + \ln z \right)$

These functions are plotted in reduced form below using $\tau = T/T_c$.



The energy, entropy, and free energy for the condensed phase are negligible, leaving the normal phase to carry the burden of thermodynamic activity. Thus, the internal energy approaches the classical limit from below because quantum correlations between bosons enhance the relative population of the ground state and low-lying excited states relative to classical expectations based upon statistical independence. Similarly, the difference in the entropy per particle in the normal and condensed phases demonstrates that the latent heat for this first-order phase transition is

$$\frac{T_c \Delta S}{N} = k_B T_c \frac{5 \zeta[\frac{5}{2}]}{2 \zeta[\frac{3}{2}]} \approx 1.284 k_B T_c$$

Furthermore, although the isochoric heat capacity is continuous at the phase transition, its slope is not. However, the isobaric heat capacity is undefined for $T < T_c$ because one cannot vary the temperature without also varying the pressure which in the transition region depends only upon temperature.

Many presentations of Bose-Einstein condensation claim that the energy and pressure vanish for the condensed phase, often saying that the ground state has no kinetic energy. However, this is not exactly true because the energy of a particle does depend upon the volume to which it is confined, even in the ground state. Nevertheless, because the ground-state contribution to the grand potential scales with $\text{Log}[N_{\text{gs}}] = \text{Log}[N(1 - \tau^{3/2})]$ while the contribution of excited states scales with $N_{\text{exc}} = N \tau^{3/2}$, dominance of the normal phase is ensured by the condition

$$\frac{\text{Log}[N(1 - \tau^{3/2})]}{N \tau^{3/2}} \approx \frac{\text{Log}[N]}{N \tau^{3/2}} \ll 1 \implies \tau \gg \left(\frac{\text{Log}[N]}{N} \right)^{2/3}$$

Provided that this condition is satisfied, we may safely neglect the ground-state energy density and pressure. Even for a system as small as 10^4 particles, this condition is satisfied well for $T > 0.1 T_c$, while for a system with 10^{20} particles we need only require $T > 10^{-11} T_c$, which is hardly very restrictive. Furthermore, the present analysis is based upon a uniform system in which particles are confined by a square-well potential. Recent experiments that have finally achieved Bose-Einstein condensation are better described in terms of confinement by a harmonic-oscillator potential and usually contain

relatively small numbers of trapped particles, typically of order $10^6 - 10^{10}$. Continuous approximations to the density of states for harmonic potentials are developed in the exercises, but for a small number of particles one should also consider the ground-state contribution and the discreteness of the energy spectrum more carefully. These technical developments provide better accuracy, but the essential features of the thermodynamic behavior of ideal systems are unchanged. Current research is investigating the effects of additional correlations produced by interactions.

Problems

▼ White dwarf star

The electrons in a white dwarf star form a completely degenerate Fermi gas whose pressure opposes further gravitational collapse of the star. Under what conditions is this pressure sufficient to arrest the collapse and stabilize the system? To answer this question, we must extend our treatment of the Fermi gas to the relativistic regime.

a) Evaluate the density of energy states, $\mathcal{D}[\varepsilon]$, for an ultrarelativistic gas for which $\varepsilon = \hbar k c$.

b) Calculate the Fermi energy, ε_F , and the mean single-particle energy, $\bar{\varepsilon}$.

c) The simplest model of a white dwarf stipulates that all of the hydrogen has been converted into helium and that the helium is completely ionized, such that there are 0.5 free electrons per nucleon. If we assume that the star has uniform density within radius R , the gravitational potential energy is $U_g = -\frac{3}{5} \frac{GM^2}{R}$ where $M = N m_p$ is the mass of N nucleons of mass m_p and G is the gravitational constant. By combining the internal energy, U_e , of the degenerate electron gas with the gravitational energy, estimate the mass for which $U = U_e + U_g$ vanishes. Compare with the solar mass of approximately 2×10^{30} kg. If the mass is larger, the gain in gravitational potential energy due to a decrease in stellar radius overcomes the electron pressure and the star will continue to collapse. More accurate calculations yield the Chandrasekhar limit of 1.44 solar masses beyond which degeneracy pressure is insufficient to arrest gravitational collapse. [What are some of the refinements of the present model that are needed?]

▼ Ratio of principal heat capacities

Show that

$$\gamma = \frac{C_p}{C_V} = \frac{(\partial z / \partial T)_p}{(\partial z / \partial T)_v}$$

where $v = V/N$ and evaluate γ for a nonrelativistic ideal Fermi gas. [Hint: express S as a function of z and N .]

▼ Two-dimensional Fermi gas

The phenomenon of high-temperature superconductivity in copper oxides of the perovskite type is related to the confinement of electron motion to sheets within the planar crystal structure. Hence, consider a degenerate Fermi gas in two dimensions.

- Find expressions for the density of states, Fermi energy, and Fermi temperature for a two-dimensional Fermi gas. Estimate the Fermi temperature for conduction electrons in a typical perovskite.
- Under what conditions does it make good physical sense to neglect the third spatial dimension?
- Develop an expression that relates the chemical potential to the density and temperature of a two-dimensional Fermi gas and plot $\mu[T/T_F]$. Compare your result with the corresponding solution for a three-dimensional system.

▼ Ideal Fermi gas with $\varepsilon \propto p^s$ in d dimensions

Consider an ideal Fermi gas with single-particle energy spectrum $\varepsilon \propto p^s$ in d spatial dimensions. Let V represent the "volume" in d dimensions and define an index $r = d/s$.

- Use dimensional analysis to demonstrate that $pV = U/r$.
- Express the Fermi momentum k_F and energy ε_F in terms of particle density. Then show that $\mathcal{D}[k] \propto k^{d-1}/k_F^d$ and $\mathcal{D}[\varepsilon] \propto \varepsilon^{r-1}/\varepsilon_F^r$ and determine the constants of proportionality. Finally, show that $z[\tau]$ at finite temperature is determined by

$$\Gamma[r+1] \tau^r f_r[z] = 1$$

where $\tau = k_B T / \varepsilon_F$ and $f_r[z]$ is a fermi function of order r .

- Find expressions for U , p , and S in terms of fermi functions of appropriate order and check that the familiar results for a three-dimensional nonrelativistic Fermi gas are recovered.
- Show that adiabats satisfy pV^x and evaluate x in terms of d and s .
- Evaluate C_V , C_p , and $\gamma = C_p/C_V$ in terms of fermi functions and check that familiar results are obtained for a three-dimensional nonrelativistic system.
- Find an expansion for C_p/C_V for low temperatures up to order $(T/T_F)^2$.

▼ Intrinsic semiconductor

The states available to electrons in a perfect crystal are organized into energy bands separated by gaps in which no states exist. For an intrinsic semiconductor, all possible states within the valence band are occupied at absolute zero temperature whereas all states in the conduction band are empty. Let E_G represent the energy gap between the top of the valence band and the bottom of the conduction band. At finite temperature there will be an equilibrium concentration, n_e , of conduction electrons and an equal concentration, n_h , of holes in the valence band. The holes may be considered to be quasiparticles with positive charge. Since both the conduction electrons and the holes are free to move in response to an applied electric field, the semiconductor has a finite temperature-dependent electrical conductivity at finite temperature. Hence, we describe the conduction electrons and the holes in the valence band as current carriers. Assume that both electrons and holes move as free particles with effective masses m_e and m_h , respectively, and that $k_B T_F \gg E_G \gg k_B T$.

a) Show that the carrier densities are approximately

$$n_e = n_h = 2 \left(\frac{\sqrt{m_e m_h} k_B T}{2 \pi \hbar^2} \right)^{3/2} \text{Exp} \left[-\frac{E_G}{2 k_B T} \right]$$

Compare the carrier density in a semiconductor with that of a typical metal.

b) Show that the chemical potential is given by

$$\mu = \frac{1}{2} E_G + \frac{3}{4} k_B T \text{Log} \left[\frac{m_h}{m_e} \right]$$

relative to the top of the valence band. Indicate the position of the chemical potential on an energy-level diagram (energy vs. momentum for valence and conduction electrons).

c) The states available to electrons in the conduction band can be represented by a sphere in momentum space. Similarly, the states available to holes can also be represented by a momentum sphere. In the absence of an applied electric field, both of these spheres are centered upon zero momentum, but an electric field acting for time t imparts a finite net momentum to the center of each momentum distribution. The electrons in the valence band are bound to the lattice and do not acquire a drift velocity. Assuming that the drift velocities remain small and that collisions between current carriers and the lattice randomize the momentum distribution, the net drift reaches a steady state determined by the average time between collisions. Use this model to estimate the electrical conductivity of an intrinsic semiconductor.

d) Assuming that the band gap for silicon is approximately 1.14 eV, estimate the electrical conductivity of pure (intrinsic) silicon at room temperature. Compare with the electrical conductivity of a typical metal. Assume that t is similar for both materials and that $m_e \approx m_h$.

▼ Magnetic susceptibility of Fermi gas

a) Suppose that N electrons are confined to a box of volume V and are subject to an external magnetic field B . Evaluate the magnetization in the low-temperature limit assuming that $\mu B \ll \epsilon_F$. You may neglect interactions between electrons and the magnetic field produced by them. [Hint: spin-up and spin-down electrons can be treated as two Fermi gases in equilibrium with each other.]

b) Evaluate the magnetization of N spin- $\frac{1}{2}$ particles arranged on a lattice subject to an external magnetic field in the low-temperature limit. Compare this result with that for an electron gas and provide a physical explanation for any differences.

▼ Magnetization for systems with up to 2 electrons per site

Suppose that a system contains N noninteracting sites which can each bind $0 \leq n \leq 2$ electrons in the same orbital state. This system can exchange electrons with a reservoir with chemical potential μ . Let $\bar{n}[T, \mu, B]$ represent the average number of bound electrons per site and $\bar{\varepsilon}[T, \mu, B]$ represent the average energy per site. In the absence of a magnetic field, the energy is ε_1 for one electron in a site, ε_2 for two electrons, or zero for an empty site. The electrons, with magnetic moment m , also interact with an external magnetic field B , such that the average magnetic moment per site is \bar{m} .

a) Write general expressions for the average electron number, energy, and magnetic moment per site.

b) Evaluate $\bar{n}[T, \mu, 0]$ for the special case $B = 0$ and $\varepsilon_2 = 2\varepsilon_1$. Sketch and explain the dependence of \bar{n} on μ for both low and high temperatures.

c) Express \bar{m} in terms of \bar{n} and T assuming $mB \ll \varepsilon_1 \ll k_B T$ and $\varepsilon_2 = 2\varepsilon_1$. Sketch this function and explain its important features.

▼ Absence of Bose condensation in 1 or 2 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-Einstein condensation for $\varepsilon \propto k^s$ in d dimensions

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

a) Under what conditions (a relationship between s and d) does one expect Bose condensation?

b) Show that if Bose condensation does occur the critical temperature is proportional to a power of density, such that $T_c \propto \left(\frac{N}{V}\right)^\alpha$, and deduce the exponent in terms of s and d .

c) Show that if Bose condensation does occur then $C_V \propto \left(\frac{T}{T_c}\right)^\gamma$ for $T < T_c$ and deduce the exponent in terms of s and d .

▼ Bose condensation in harmonic trap

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

- a) Show that when $k_B T \gg \hbar\omega$, a continuous approximation to the density of states takes the form $\mathcal{D}[\varepsilon] \propto \varepsilon^2$ 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 ω . 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 a virial theorem argument to relate ω and T to an effective volume V .]
- d) A typical experiment uses spin-polarized ${}^7\text{Li}$ atoms ($g = 1$) in a trap with $\nu \approx 150$ 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 $C = (\frac{\partial U}{\partial T})_{N,\omega}$. [Hint: modification of the numerical techniques developed in *bose.nb* will be helpful.]

▼ Bose condensation in anisotropic trap

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

- a) Show that a continuous approximation to the density of states takes the form $\mathcal{D}[\varepsilon] \propto \frac{\varepsilon^2}{\omega_1 \omega_2 \omega_3}$ 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.

▼ Roton contribution using Bose-Einstein statistics

The Landau theory of superfluid helium includes a class of excitations, known as *rotons*, satisfying the dispersion relation

$$\varepsilon = \Delta + \frac{(p - p_0)^2}{2m_0}$$

where ε and p are the energy and momentum of a single roton and where Δ , m_0 , and p_0 are positive constants. Assume that rotons obey Bose-Einstein statistics. [Notes: p is the magnitude of the momentum vector in three dimensions and both p and p_0 are scalars.]

- a) Determine the average number of rotons per unit volume as a function of temperature assuming that $k_B T \ll \frac{p_0^2}{2m_0}$. Justify your approximations.
- b) Compute the roton contribution to the heat capacity for low temperatures and explain the temperature dependence.

▼ Quark-gluon plasma

Scientists working at CERN recently announced that they believe a new state of matter, known as a *quark-gluon plasma* (QGP), has been observed. Although the evidence remains controversial, the search for QGP is a very hot topic. The basic idea is that nucleons consist of quarks bound together by the exchange of gluons. If sufficiently high density and temperature can be achieved by colliding energetic beams of nuclei, it might be possible to recreate a state of the early universe, immediately after the Big Bang, in which quarks and gluons form a plasma. As this system expands and cools, the quarks condense into nucleons with 3 quarks each. Here we develop a simple model of the phase boundary between QGP and ordinary nuclear matter. Quarks are fermions with degeneracy factor g_Q , while gluons are massless bosons (like photons) with degeneracy factor $g_G = 16$. Near the phase boundary we can assume that heavy quarks do not participate and, hence, use $g_Q = 12$ for u and d quarks.

a) Show that the chemical potential for an ultrarelativistic Fermi gas is related to density by

$$\frac{N}{V} \approx \frac{g_Q T^3}{6} \left(\frac{\mu}{T} + \frac{1}{\pi^2} \left(\frac{\mu}{T} \right)^3 \right)$$

where g_Q is the quark degeneracy factor. Note that we use *natural units* in which temperature is measured in energy units and $\hbar = c = 1$. More familiar units can be obtained using $\hbar c \approx 200 \text{ MeV fm}$, where a femtometer (fm) is 10^{-15} m. [Hint: although the temperature is high, the density is also large; hence, the quark gas is highly degenerate. You can use the approximation for large z developed in *fermi.nb*.]

b) Show that the equation of state for an ultrarelativistic quark gas can be expressed in the form

$$p_Q \approx \frac{1}{3} \frac{U_Q}{V} = \frac{g_Q}{3} T^4 \left(\frac{7\pi^2}{120} + \frac{1}{4} \left(\frac{\mu}{T} \right)^2 + \frac{1}{8\pi^2} \left(\frac{\mu}{T} \right)^4 \right)$$

while the equation of state for massless gluons with degeneracy factor g_G is

$$p_G = \frac{1}{3} \frac{U_G}{V} = g_G \frac{\pi^2}{90} T^4$$

c) A nucleon can be visualized as a bubble containing 3 quarks whose surface is subject to a pressure B exerted by the quantum-mechanical vacuum. Thus, balancing the internal and external pressures requires $B = p_Q + p_G$. Use these results to produce a plot of temperature versus density along the phase boundary given that $B^{1/4} \approx 0.7 \text{ fm}^{-1}$.