

Statistical Physics

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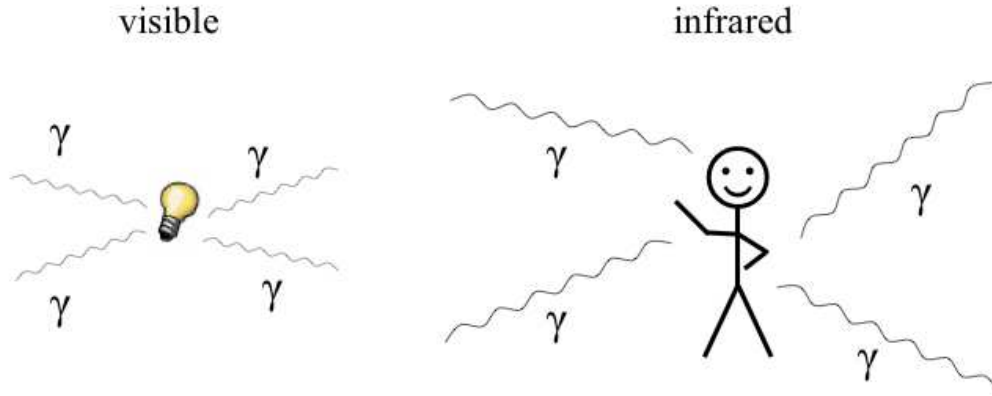


Figure 11: A light-bulb is hot and radiates energetic photons which have a visible wavelength. Humans are not so hot, so they emit less energetic photons with infrared wavelength.

8 Bose-Einstein distribution

8.1 Black-body radiation

Any body at a temperature greater than zero radiates electromagnetic waves (see Fig. 11), the quanta of which we call photons. Recall the energy of an electromagnetic wave is inversely proportional to its wavelength

$$\varepsilon = \frac{hc}{\lambda}. \quad (8.1.1)$$

Consider a box with perfectly reflecting walls which contains radiation (photons). The photons may have differing values of energy.

Into this box we put a so-called black body (Fig. 12). “Black” here means that the body absorbs any photon which hits it, reflecting no photons. But because the temperature of the body is greater than zero, it also *emits* photons. The constant absorption and emission of photons by the black body leads to thermal equilibrium between the photon and the body.

Photons have spin 1, and so they are bosons. The distribution of photon occupation number $\bar{n}(\varepsilon)$ will be a Bose-Einstein distribution with temperature T . Since photon number is not conserved, the constraint $\sum_{\varepsilon} \bar{n}(\varepsilon) = N$ does not hold. Consequently no Lagrange multiplier is needed in our derivation of the statistical distribution function in the grand canonical ensemble (6.1.6), so $\gamma = 0 = \mu$. Radiation characterised only by a temperature T is called **black-body radiation**.

We previously derived the density of states for an ideal gas of photons (4.1.15). (We can safely neglect any interactions between photons.) From the Bose-Einstein distribution (7.2.18) and (7.2.19), with $\mu = 0$, we obtain the **Planck distribution**

$$\bar{n}(\omega) = \frac{V\omega^2}{\pi^2c^3} \frac{1}{e^{\beta\hbar\omega} - 1}. \quad (8.1.2)$$

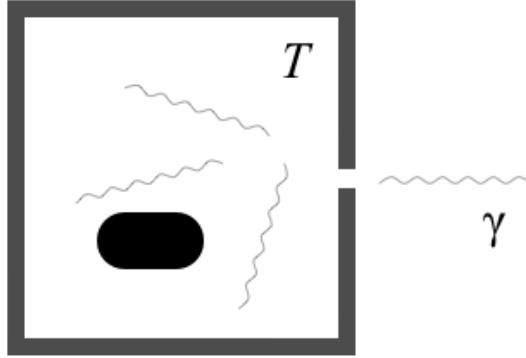


Figure 12: A black body inside an insulated box is in thermal equilibrium with the radiation in the box. We can deduce the temperature of the body by measuring the energy flux some distance away.

Thus,

$$\bar{\varepsilon}(\omega) = \hbar\omega\bar{n}(\omega) = \frac{V\hbar\omega^3}{\pi^2c^3} \frac{1}{e^{\beta\hbar\omega} - 1}. \quad (8.1.3)$$

The classical limit is the high T or low ω limit, where

$$e^{\beta\hbar\omega} - 1 \simeq \beta\hbar\omega \quad (8.1.4)$$

and

$$\begin{aligned} \bar{\varepsilon}(\omega) &\propto g(\omega)kT && \text{recovering classical equipartition} \\ &\propto \omega^2. && \end{aligned} \quad (8.1.5)$$

This classical result is the **Rayleigh-Jeans Law**, and the fact that it diverges as ω grows was called the **ultraviolet catastrophe**. Why a catastrophe? Because then the total energy inside the box with a black body at temperature T , $E(T) = \int_0^\infty \bar{\varepsilon}(\omega)d\omega$ is infinite.

Data agreed with the Rayleigh-Jeans Law at low frequencies only, but then saturated and decreased. Only by positing that light was made of individual constituents which could be treated using Boltzmann's statistical mechanics did Planck reproduce the experimental results. The 2 energy spectra are compared in Figure 13. At the time this particle picture of light was widely viewed as a mathematical convenience, with no physical significance.

Using the Planck distribution, one finds a sensible result for the energy

$$E(T) = \frac{V}{(\hbar c)^3\pi^2} \int_0^\infty \frac{(\hbar\omega)^3 d(\hbar\omega)}{e^{\beta\hbar\omega} - 1}. \quad (8.1.6)$$

Substituting $x = \beta\hbar\omega$

$$E(T) = \frac{V(kT)^4}{(\hbar c)^3\pi^2} \int_0^\infty \frac{x^3 dx}{e^x - 1}. \quad (8.1.7)$$

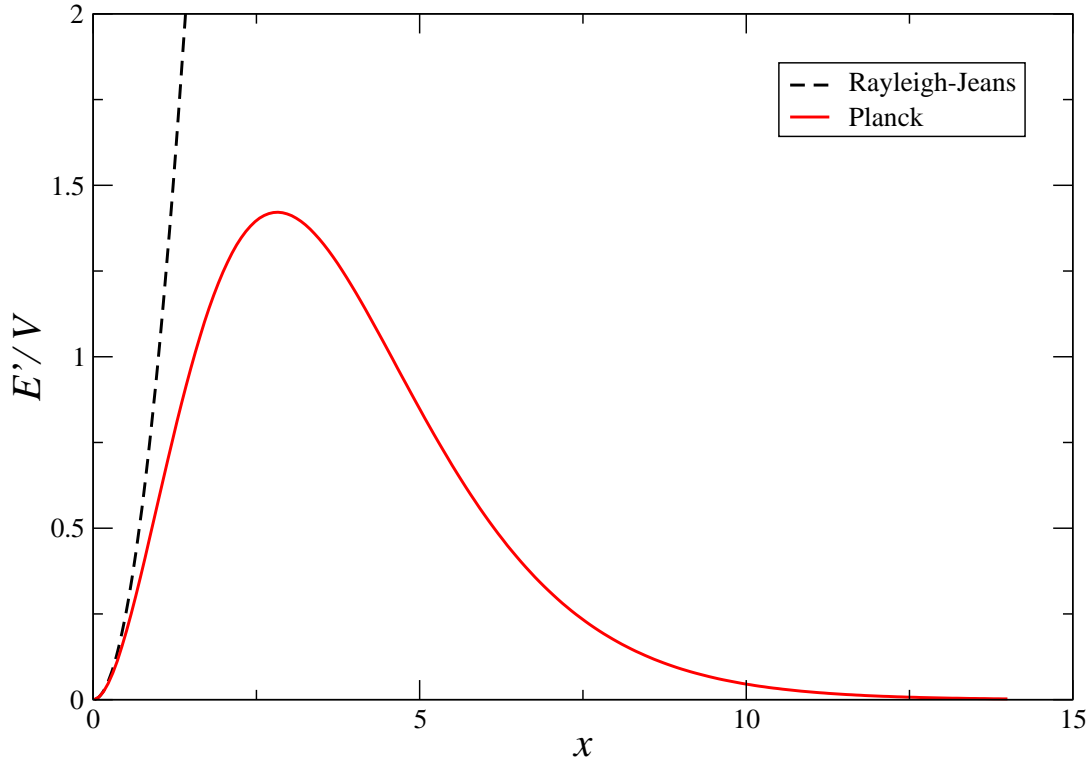


Figure 13: Energy density distribution in dimensionless units $E'/V = \pi^2(\hbar c)^3\beta^4 E/V$ as a function of $x = \beta\hbar\omega$.

The integral is not one you should be expected to memorise. It happens to be equal to the product of the Γ function and the Riemann zeta function evaluated at $n = 4$, $\Gamma(4)\zeta(4) = \pi^4/15$. See Pathria, appendix D for details.⁷ The final result

$$E(T) = 4V \frac{\sigma}{c} T^4, \quad \sigma \equiv \frac{\pi^2 k c}{60} \left(\frac{k}{\hbar c} \right)^3 \quad (8.1.9)$$

where σ is Stefan's constant (equal to $5.67 \times 10^{-8} \text{ J s}^{-1} \text{ m}^{-2} \text{ K}^{-4}$, for what it's worth).

What is usually measured in experiment or observation is not the total energy, but an energy flux, \mathcal{E} . Imagine a tiny aperture in the box which contains the black body. The rate energy leaves the box, per unit area of the hole, is the energy flux. (Assume there is no inward flux.) The speed of the photons is c . The number of photons with angular frequency in $(\omega, d\omega)$ is $\bar{n}(\omega) d\omega$. The number of photons per unit area passing through the hole per unit time which have frequency in $(\omega, d\omega)$ is

$$df(\omega) = \frac{c}{4V} \bar{n}(\omega) d\omega. \quad (8.1.10)$$

⁷The class of integrals appearing in calculations with bosons look like

$$g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1} dx}{z^{-1} e^x - 1} \quad (8.1.8)$$

with $x = \beta\varepsilon$ and $z = e^{\beta\mu}$. $g_n(1) = \zeta(n)$ for $n > 1$.

It is clear that this number should scale like the speed the photons travel. The faster particles go, the more should be emitted per unit time. The factor of $1/V$ is also clear since it is the particle number density which controls how many particles are near the aperture. The derivation of the factor of $1/4$, due to the angular integration over velocity directions, is a bit tedious, so we simply refer to Landau & Lifshitz, §63. Since the energy of a photon with frequency ω is $\hbar\omega$, the energy flux is

$$\mathcal{E} = \int df(\omega) \hbar\omega = \frac{c}{4V} \int_0^\infty d\omega \hbar\omega \bar{n}(\omega) = \frac{c}{4V} E = \sigma T^4 \quad (8.1.11)$$

This result is called the **Stefan-Boltzmann Law**.

We can also calculate the entropy of the black body. Since $\mu = 0$

$$S = k \log \mathcal{Z} + \frac{E}{T}. \quad (8.1.12)$$

In the first term, we have

$$\begin{aligned} \log \mathcal{Z} &= - \int_0^\infty d\varepsilon g(\varepsilon) \log(1 - e^{-\beta\varepsilon}) \\ &= - \int_0^\infty d\omega \frac{\omega^2 V}{\pi^2 c^3} \log(1 - e^{-\beta\hbar\omega}) \\ &= \frac{\beta}{3} \frac{V}{\hbar^3 \pi^2 c^3} \int_0^\infty \frac{(\hbar\omega)^3 d(\hbar\omega)}{e^{\beta\hbar\omega} - 1} \\ &= \frac{\beta}{3} E. \end{aligned} \quad (8.1.13)$$

Integration by parts was used to go from the second to third steps. The entropy is

$$S = \frac{E}{3T} + \frac{E}{T} = \frac{4E}{3T} = \frac{16V\sigma}{3c} T^3. \quad (8.1.14)$$

We can look at the expressions for E (8.1.9) and S (8.1.14) as functions of T , solve for T and equate them, obtaining

$$\left(\frac{E}{4V} \frac{c}{\sigma} \right) = \left(\frac{3S}{16V} \frac{c}{\sigma} \right)^{4/3} \quad (8.1.15)$$

or

$$E = 4 \left(\frac{3S}{16} \right)^{4/3} \left(\frac{c}{V\sigma} \right)^{1/3}. \quad (8.1.16)$$

The free energy is

$$F = E - TS = -\frac{E}{3}. \quad (8.1.17)$$

Since extensivity requires $F(V, T, N) = -PV + \mu N$ in general, and since $\mu = 0$ in this case, we can find the radiation pressure to be

$$P = \frac{E}{3V} = \frac{4\sigma}{3c} T^4. \quad (8.1.18)$$

A similar calculation to those we have performed shows the number density of photons is

$$\frac{N}{V} \propto T^3. \quad (8.1.19)$$

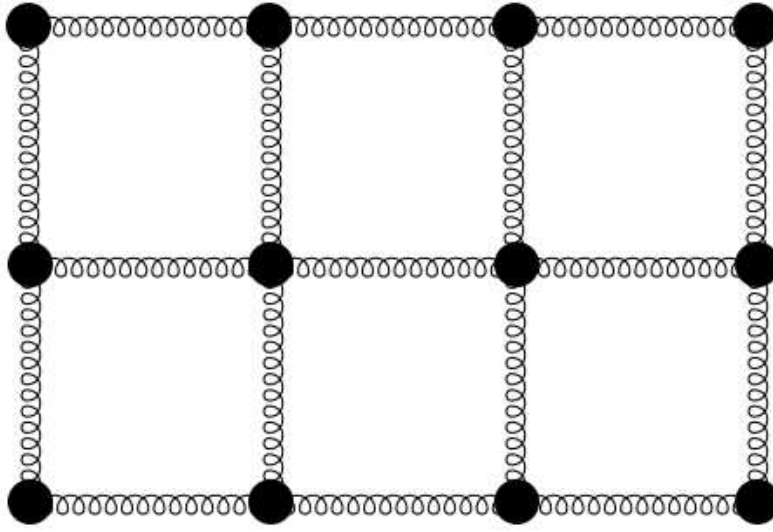


Figure 14: Schematic picture of a solid as atoms joined at lattice points by springs. Vibrations propagate through the lattice as waves of quasiparticles called phonons.

8.2 Debye model of vibrations in solids

We now discuss an example which is quite different from others in the course, the **Debye model of vibrations in solids**. Consider a crystal of atoms which make up a solid (Fig 14). The atoms themselves are not a gas of non-interacting, or even weakly interacting, particles as we have discussed before. However, we can describe the waves of vibrations in solids, *i.e.* **sound waves**, using the same statistical physics, introducing the notion of **quasiparticle**.

As a preliminary step, consider a system of harmonic oscillators. The single oscillator partition function for a harmonic oscillator of frequency ω is the sum of Boltzmann factors over all excitation numbers n

$$z(\omega) = \sum_n \exp(-\beta(n + \frac{1}{2})\hbar\omega) = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}. \quad (8.2.1)$$

The last step summed the geometric series.

The average single oscillator energy is

$$\begin{aligned} \bar{\varepsilon}(\omega) &= -\frac{\partial}{\partial\beta} \log z \\ &= \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} + \frac{1}{2}\hbar\omega \end{aligned} \quad (8.2.2)$$

$$= \left(\bar{n} + \frac{1}{2}\right)\hbar\omega \quad (8.2.3)$$

where the last step identifies the average excitation number

$$\bar{n}(\omega) = \frac{1}{e^{\beta\hbar\omega} - 1} \quad (8.2.4)$$

which is equivalent to the Planck distribution. We see that each excitation of this harmonic oscillator is equivalent to an abstract bosonic particle, or **quasiparticle**. (In quantum field theory, even real particles are described as harmonic excitations.)

[We can further point out the classical limit ($\hbar\omega \ll kT$) of (8.2.2),

$$\bar{\varepsilon} = \text{small} + \hbar\omega \left(\exp\left(\frac{\hbar\omega}{kT}\right) - 1 \right)^{-1} \approx kT = 2\left(\frac{1}{2}kT\right) \quad (8.2.5)$$

satisfies the classical equipartition theorem for a body with 2 degrees-of-freedom. The classical Hamiltonian for a harmonic oscillator is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \quad (8.2.6)$$

with p and x independent degrees-of-freedom.]

Returning to our solid, we treat waves of lattice vibrations as plane waves

$$\psi_{\mathbf{k}}(\mathbf{x}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{x}} \quad \mathbf{k} = \frac{2\pi}{L} \mathbf{n} \quad \mathbf{n} \in \mathbb{Z}^3 \quad (8.2.7)$$

which have a dispersion relation

$$\varepsilon = \hbar\omega = \hbar|\mathbf{k}|c_s. \quad (8.2.8)$$

We denote the speed of sound by c_s , and implicitly we have assumed c_s is the same in all directions.

The similarity between sound waves and light led people to call these bosonic quasiparticles, **phonons**. While obeying a massless dispersion relation, as quasiparticles in a crystal they are not required by Lorentz symmetry to have vanishing longitudinal polarisation. Therefore $g_s = 3$ for phonons, in contrast to $g_s = 2$ for photons. The density of states for phonons is

$$g(\omega) = \frac{3V\omega^2}{2\pi^2 c_s^3}. \quad (8.2.9)$$

If we have N atoms in the solid, with each atom free to vibrate in each of the 3 dimensions, then there are $3N$ degrees-of-freedom. When we switch to the phonon description of the vibrations, we still cannot exceed this number of degrees-of-freedom. Said another way, a string of M atoms with length L must oscillate with a minimum wavelength λ_{\min} . The distance between nodes of oscillation must be greater than the distance between atoms L/M . Therefore $\lambda_{\min} = 2L/M$. Fig. 15 gives a rough illustration.

A minimum wavelength implies a maximum frequency ω_{\max} . The constraint on the maximum oscillator degrees-of-freedom gives us a way to calculate ω_{\max} :

$$\int_0^{\omega_{\max}} d\omega g(\omega) = 3N \quad (8.2.10)$$

which implies

$$\omega_{\max} = \left(\frac{6\pi^2 N}{V} \right)^{1/3} c_s. \quad (8.2.11)$$

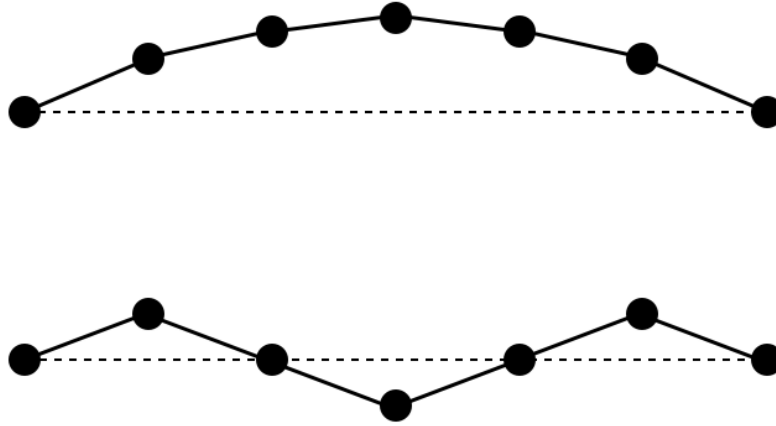


Figure 15: 7 atoms in a row vibrating with 2 nodes and 4 nodes. The important point is that the minimum separation between nodes is equal to the distance between neighbouring atoms.

The total energy is then

$$E = \int_0^{\omega_{\max}} d\omega \frac{\hbar\omega g(\omega)}{e^{\beta\hbar\omega} - 1} \quad (8.2.12)$$

relative to the zero-point energy $3N\hbar\omega/2$, which is unobservable and can be subtracted.

Define the Debye temperature in relation to ω_{\max}

$$T_D = \frac{\hbar\omega_{\max}}{k} \quad (8.2.13)$$

and let $x = \hbar\omega/(kT)$ so that $x_{\max} = T_D/T$. Then

$$E = \frac{3V}{2\pi^2(\hbar c_s)^3} (kT)^4 \int_0^{T_D/T} \frac{x^3 dx}{e^x - 1}. \quad (8.2.14)$$

If we define the Debye function as

$$D(z) = \frac{3}{z^3} \int_0^z \frac{x^3 dx}{e^x - 1} \quad (8.2.15)$$

and substitute for (8.2.11) then we find

$$E = 3NkT D\left(\frac{T_D}{T}\right). \quad (8.2.16)$$

We can consider 2 extremes. First, if $T \gg T_D$, then $z \ll 1$ and we Taylor expand $D(z)$ about $z = 0$ as

$$D(z) = 1 - \frac{3z}{8} + \mathcal{O}(z^2). \quad (8.2.17)$$

(For small z the denominator in (8.2.15) can be approximated as $x + \frac{x^2}{2} + \dots$) We then obtain the classical result

$$E = 3NkT \quad (8.2.18)$$

and consequently

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = 3Nk. \quad (8.2.19)$$

There is no ultraviolet catastrophe since there is a finite ω_{\max} . Note we recover the classical equipartition theorem for a system with $6N$ degrees-of-freedom, *i.e.* $3N$ classical harmonic oscillators.

In the other extreme, $T \ll T_D$ ($z \gg 1$) and the upper limit of integration goes to infinity:

$$D(z) = \frac{3}{z^3} \int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{5z^3}. \quad (8.2.20)$$

We find

$$E = \frac{3\pi^4}{5}(NkT) \left(\frac{T}{T_D} \right)^3 \quad (8.2.21)$$

and consequently

$$C_V = \frac{12\pi^4}{5}Nk \left(\frac{T}{T_D} \right)^3. \quad (8.2.22)$$

8.3 Bose-Einstein condensation

We consider a nonrelativistic gas of bosons in 3 dimensions. There the density of states is

$$g(\varepsilon) = KV\sqrt{\varepsilon} \quad \text{where } K = \frac{g_s}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2}. \quad (8.3.1)$$

Then the total particle number is given by

$$\begin{aligned} N &= \int_0^\infty \frac{g(\varepsilon) d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1} \\ &= KV \int_0^\infty \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\beta(\varepsilon-\mu)} - 1} \\ &= \frac{KV}{\beta^{3/2}} \int_0^\infty \frac{\sqrt{x} dx}{e^x e^{-\beta\mu} - 1} \\ &= KV(kT)^{3/2} \int_0^\infty \frac{\sqrt{x} dx}{z^{-1}e^x - 1} \end{aligned} \quad (8.3.2)$$

$$\begin{aligned} &= \frac{g_s V}{\pi^2 \sqrt{2}} \left(\frac{mkT}{\hbar^2} \right)^{3/2} \frac{\sqrt{\pi}}{2} g_{3/2}(z) \\ &= \frac{g_s V}{\lambda^3} g_{3/2}(z) \end{aligned} \quad (8.3.3)$$

The general integral

$$g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1} dx}{z^{-1}e^x - 1} \quad (8.3.4)$$

is discussed at length in Pathria, App. D.

Remembering the partition function (7.2.8), in order for the sum to converge to (7.2.9) for bosons, we required $\mu \leq 0$ (for $\mu = 0$ the series converges for $\varepsilon_r > 0$). If $z = e^{\beta\mu} < 1$, that is if $\beta\mu < 0$, then express the denominator in (8.3.2) as a geometric series $(1 - y)^{-1} = \sum_{\ell=0}^{\infty} y^{\ell}$ so that

$$\frac{1}{z^{-1}e^x - 1} = (ze^{-x}) \frac{1}{1 - ze^{-x}} = (ze^{-x}) \sum_{\ell=0}^{\infty} (ze^{-x})^{\ell} = \sum_{\ell=1}^{\infty} (ze^{-x})^{\ell} \quad (8.3.5)$$

and

$$\int_0^{\infty} \frac{\sqrt{x} dx}{z^{-1}e^x - 1} = \int_0^{\infty} dx \sqrt{x} \sum_{\ell=1}^{\infty} z^{\ell} e^{-\ell x}. \quad (8.3.6)$$

We can evaluate the ℓ^{th} integral

$$\int_0^{\infty} dx \sqrt{x} e^{-\ell x} = \frac{\sqrt{\pi}}{2\ell^{3/2}} \quad (8.3.7)$$

yielding

$$N = KV(kT)^{3/2} \frac{\sqrt{\pi}}{2} \sum_{\ell=1}^{\infty} \frac{z^{\ell}}{\ell^{3/2}}. \quad (8.3.8)$$

This series converges for $0 < z \leq 1$ ($-\infty < \mu < 0$), and N is largest when $z = 1$ ($\mu = 0$)

$$g_{\frac{3}{2}}(z) \leq g_{\frac{3}{2}}(1) = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \dots = \zeta(\frac{3}{2}) \simeq 2.612\dots \quad (8.3.9)$$

This implies N is bounded beneath some N_{max} (at fixed V, T).

In fact $N = N_{\text{max}}$ occurs when $\mu = 0$ and decreases monotonically as $\mu \rightarrow -\infty$. This is strange. Consider a gas with fixed density N'/V and decrease T . With fixed density $g_{\frac{3}{2}}(z)$ should vary like $T^{-3/2}$ to compensate the explicit factor $(kT)^{3/2}$. However $g_{\frac{3}{2}}(z)$ can increase only until it reaches $g_{\frac{3}{2}}(1)$ which occurs at a temperature we will call T_c . At T_c

$$\frac{N}{V} = K(kT_c)^{3/2} \frac{\sqrt{\pi}}{2} \zeta(\frac{3}{2}). \quad (8.3.10)$$

This signals a phase transition to a **Bose-Einstein condensate**. Note we found a $T_c > 0$ because the sum (8.3.9) converged for all z of interest. Bose-Einstein condensation would not occur if we had an unbounded series (*e.g.* in 2 dimensions, as you should verify).

Below T_c , then μ is strictly zero and we define a number

$$N' \equiv KV(kT)^{3/2} \frac{\sqrt{\pi}}{2} \zeta(\frac{3}{2}). \quad (8.3.11)$$

This is the number of particles which contribute to (8.3.2):

$$\int_0^{\infty} \frac{g(\varepsilon) d\varepsilon}{e^{\beta\varepsilon} - 1} = N' \leq N \text{ for } T \leq T_c. \quad (8.3.12)$$

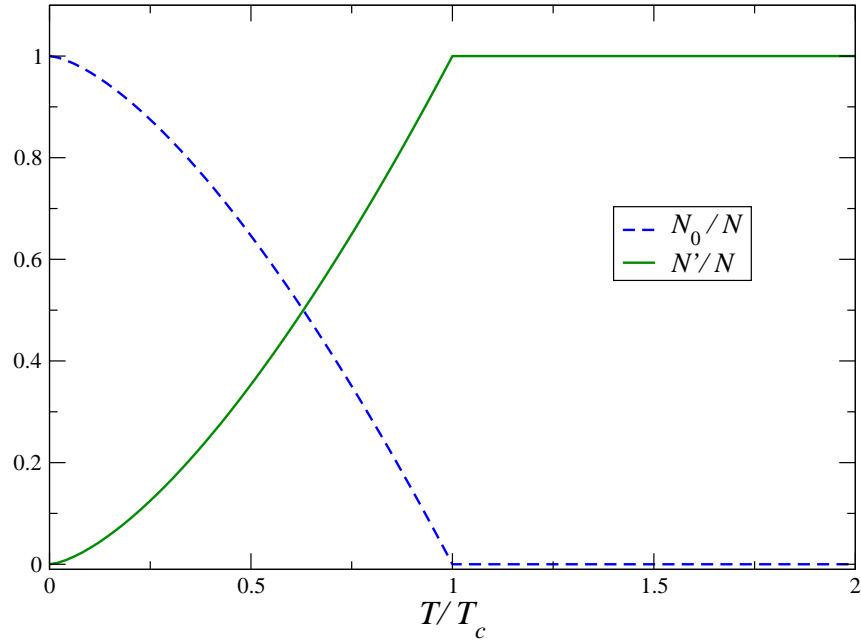


Figure 16: Fraction of bosons in ground state N_0/N and those in states with $\varepsilon > 0$, N'/N . Below the critical temperature, N_0 becomes macroscopic.

But notice that since $g(\varepsilon) \propto \sqrt{\varepsilon}$, the particles with $\varepsilon = 0$ do not contribute to (8.3.2). Requiring the density to remain constant as we lower T below T_c means that a growing number of particles N_0 move to the $\varepsilon = 0$ state so that

$$N = N_0 + N'. \quad (8.3.13)$$

Below T_c , then

$$\frac{N'}{N} = \left(\frac{T}{T_c}\right)^{3/2} \quad (8.3.14)$$

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2}. \quad (8.3.15)$$

See Figure 16. Particles **condense** into the $\varepsilon = 0$ state, a **macroscopic** number of particles are in a single quantum state.

In the $T < T_c$ phase

$$\begin{aligned} E &= KV \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{\beta\varepsilon} - 1} \\ &= KV(kT)^{5/2} \Gamma\left(\frac{5}{2}\right)\zeta\left(\frac{5}{2}\right) \\ &= \frac{3}{2}(kT)\frac{V}{\lambda^3} \zeta\left(\frac{5}{2}\right). \end{aligned} \quad (8.3.16)$$

Solving for similar pre-factors in (8.3.10) We find

$$E = \frac{3}{2} \frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})} NkT \left(\frac{T}{T_c}\right)^{3/2} \quad (8.3.17)$$

$$= ANkT \left(\frac{T}{T_c}\right)^{3/2} \quad (8.3.18)$$

$$= AN'kT \quad (8.3.19)$$

The constant A is defined implicitly, and $\zeta(\frac{5}{2}) \simeq 1.341$.

The heat capacity

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = \frac{5}{2} ANk \left(\frac{T}{T_c}\right)^{3/2} = \frac{5}{2} \frac{E}{T}. \quad (8.3.20)$$

From $C_V = T(\partial S/\partial T)_V$, we can calculate the entropy

$$S = \int dT \frac{C_V}{T} = \frac{5}{3} \frac{E}{T} \propto T^{3/2} \quad (8.3.21)$$

We note $S \rightarrow 0$ as $T \rightarrow 0$. The free energy

$$F = E - TS = E - \frac{5}{3} E = -\frac{2}{3} E \quad (8.3.22)$$

which implies through extensivity ($F = -PV$) that

$$P = \frac{2}{3} \frac{E}{V}. \quad (8.3.23)$$

We state without proof that there is a discontinuity in the derivative of C_V at $T = T_c$ originating from a discontinuity in the 2nd derivative in μ

$$-\mu \propto \begin{cases} (T - T_c)^2 & \text{for } 0 < \frac{T - T_c}{T_c} \ll 1 \\ 0 & \text{for } T \leq T_c \end{cases} \quad (8.3.24)$$

Therefore $(\partial C_V/\partial T)_{V,N}$ has a term proportional to $(\partial^2 \mu/\partial T^2)_{V,N}$ and is discontinuous. This is a common feature of phase transitions.

Superfluidity in liquid helium-4 is a consequence of Bose-Einstein condensation, but in a dense, interacting system instead of a weakly interacting gas. Bose-Einstein condensation of *pairs* of fermions, which are therefore composite bosons, is an important phenomenon in nuclei and compact stars (like neutron stars). In 1995 trapped alkali atoms were finally cooled to temperatures below which they formed a Bose-Einstein condensate. The leaders of the experiments – E Cornell and C Wieman (JILA, Colorado), and W Ketterle (MIT) – were awarded the Nobel prize in 2001.

Further reading

1. F Mandl, *Statistical Physics*, (Wiley & Sons, 1988), Chapter 10, §11.6.
2. L D Landau and E M Lifshitz, *Statistical Physics*, (Pergamon Press, 1980), §63.
3. R K Pathria, *Statistical Mechanics*, (Pergamon, 1991), §§7.2-3, Appendix D.
4. F Reif, *Fundamentals of Thermal and Statistical Physics*, (McGraw-Hill, 1965), §§10.1-2.