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Thermodynamics and Statistical Mechanics

Statistical Mechanics V
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- **Stefan-Boltzmann law**
- **Blackbody radiation**
- **Bose-Einstein condensation**

CLASSICAL ARGUMENTS FOR PHOTON GAS

A number of thermodynamic properties of photon gas can be determined from purely classical arguments

① Assume photon gas is confined to rectangular box of dimensions $L_x \times L_y \times L_z$

further assume that dimensions are all expanded by a factor $\lambda^{1/3}$ ☟

that is volume is isotropically expanded by a factor of λ

Cavity modes of electromagnetic radiation have quantized wave vectors

even within classical electromagnetic theory ☛ $\vec{k} = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z}\right)$

for a given mode $\varepsilon(\vec{k}) = \hbar c|\vec{k}|$ ↴

energy changes by $\lambda^{-1/3}$ under an adiabatic volume expansion $V \to \lambda V$

It follows that ↴

$$V\left(\frac{\partial U}{\partial V}\right)_S = \lambda\left(\frac{\partial U}{\partial \lambda}\right)_S = -\frac{1}{3}U \quad \text{and} \quad P = -\left(\frac{\partial U}{\partial V}\right)_S = \frac{U}{3V}$$

Since $U = U(T,V)$ is extensive ☛ we must have $P = P(T)$ alone

MORE CLASSICAL ARGUMENTS FOR PHOTON GAS

② Since $P = P(T)$ alone ↴

using Maxwell relation ☛ $$\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial P}{\partial T}\right)_V$$

after invoking the First Law ☛ $dU = TdS - PdV$

☟

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_P = 3P$$

$$= T\left(\frac{\partial P}{\partial T}\right)_V - P$$

It follows that ☛ $$T\frac{dP}{dT} = 4P \Rightarrow P(T) = aT^4$$

☟

a ☛ constant

STEFAN-BOLTZMANN LAW

③ Given energy density U/V

differential energy flux emitted in direction θ relative to surface normal

$$dJ_{\mathcal{E}} = c\,\frac{U}{V}\,\cos\theta\,\frac{d\Omega}{4\pi}$$

$d\Omega$ ☛ differential solid angle

Power emitted per unit area

$$J_{\mathcal{E}} = \frac{d\mathcal{P}}{dA} = \frac{cU}{4\pi V}\int_0^{\pi/2} d\theta \int_0^{2\pi} d\phi \sin\theta\cos\theta = \frac{c}{4}\frac{U}{V} = \frac{3}{4}cP(T) \equiv \sigma T^4$$

$$\sigma = \frac{3}{4}ca \Rightarrow P(T) = aT^4$$

Using quantum statistical mechanical considerations we will show that ↴

Stefan's constant ☛ $$\sigma = \frac{\pi^2 k_B^4}{60c^2\hbar^3} = 5.67 \times 10^{-8}\,\frac{W}{m^2K^4}$$

SURFACE TEMPERATURE OF EARTH

We'll need three lengths: radius of sun ☛ $R_\odot = 6.96 \times 10^8 \text{m}$

radius of earth ☛ $R_\oplus = 6.38 \times 10^6 \text{ m}$

radius of earth's orbit ☛ $d_{\oplus-\odot} = 1.50 \times 10^{11} \text{ m}$

Assume that earth has achieved a steady state temperature ☛ $T_\oplus$

balance total power incident upon earth with power radiated by earth

Power incident upon earth $\mathcal{P}_{\rm incident} = \dfrac{\pi R_\oplus^2}{4\pi d_{\oplus-\odot}^2} \cdot \sigma T_\odot^4 \cdot 4\pi R_\odot^2 = \left(\dfrac{R_\oplus R_\odot}{d_{\oplus-\odot}}\right)^2 \cdot \pi \sigma T_\odot^4$

Power radiated by earth ☛ $\mathcal{P}_{\rm radiated} = \sigma T_\oplus^4 \cdot 4\pi R_\oplus^2$

Setting $\mathcal{P}_{\rm incident} = \mathcal{P}_{\rm radiated}$ ☛ $T_\oplus = \left(\dfrac{R_\odot}{2 d_{\oplus-\odot}}\right)^{1/2} T_\odot = 0.04817\ T_\odot$

$$T_\odot = 5780 \text{ K} \Rightarrow T_\oplus = 278.4 \text{ K}$$

Mean surface temperature of the earth ☛ $T_\oplus = 287 \text{ K}$

Difference is due to fact that earth is not perfect blackbody

(object which absorbs all incident radiation upon it and emits according to Stefan's law)

Earth's atmosphere re-traps fraction of emitted radiation ☛ **greenhouse effect**

QUANTUM WAVES INSIDE A BOX

Wave function for quantum waves in one-dimensional box ☛ $\Psi = A \sin kx$

$$k = \frac{2\pi}{\lambda} = \frac{n\pi}{L} \qquad n = 1, 2, 3, \cdots \qquad (85)$$

λ ☛ de Broglie wavelength

L ☛ box dimension

substituting $c = \lambda\nu$ in (85) ☛ $n = \frac{2L}{c}\nu$

For a cube $V = L^3$ ☛

$$n = \frac{2V^{1/3}}{c}\nu \qquad (86)$$

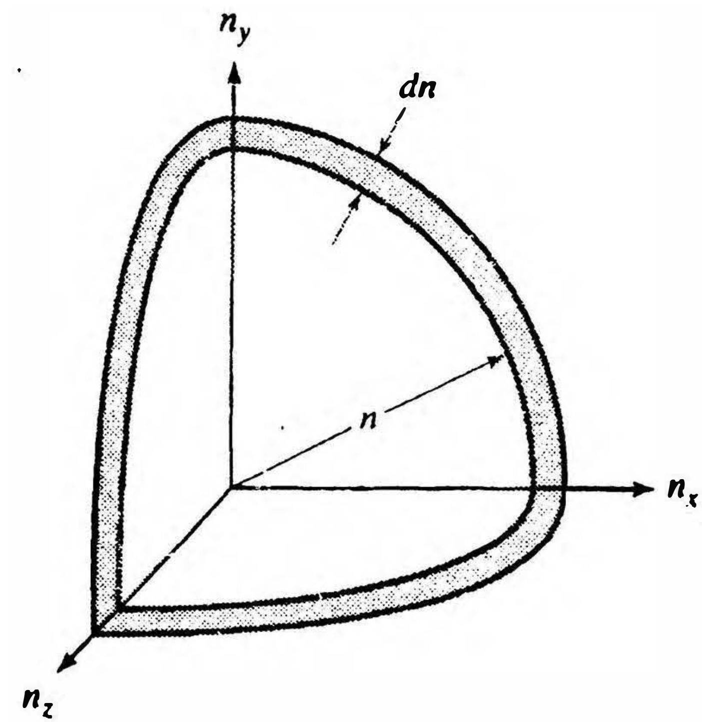
$n^2 = n_x^2 + n_y^2 + n_z^2$ ☛ $n_x, n_y, n_z \in \mathbb{Z}^+$

Possible values occupy first octant of sphere of radius $n = (n_x^2 + n_y^2 + n_z^2)^{1/2}$

DENSITY OF STATES OF QUANTUM WAVES INSIDE A BOX

$g(\nu)\ d\nu$ ☛ number of possible frequencies in range $(\nu, \nu + d\nu)$

$n \propto \nu \Rightarrow g(\nu)\ d\nu$ ☛ number of possible set of integers in $(n, n + dn)$ within shell of thickness dn of octant of sphere of radius n



$$g(\nu)d\nu = \frac{1}{8}4\pi n^2 dn = \frac{\pi}{2}n^2 dn \quad (87)$$

substituting (86) in (87) ☛ $g(\nu)d\nu = \frac{4\pi V}{c^3}\nu^2 d\nu$

PHOTON STATISTICS

Photons are bosons of spin 1 and hence obey Bose-Einstein statistics

number of photons per quantum state ☛ $$f_j = \frac{N_j}{g_j} = \frac{1}{e^{\varepsilon_j/kT} - 1}$$

for continuos distribution ☛ $$f(\varepsilon) = \frac{N(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{\varepsilon/kT} - 1}$$

photon energy is ☛ $$f(\nu) = \frac{N(\nu)}{g(\nu)} = \frac{1}{e^{h\nu/kT} - 1}$$

PLANCK RADIATION FORMULA

photon gas ☛ two polarization states

$$g(\nu)d\nu = \frac{8\pi V}{c^3}\nu^2 d\nu$$

Energy $u(\nu)d\nu$ in range $(\nu, \nu + d\nu)$

number of photons in this range times energy $h\nu$ of each

☟

$$u(\nu)\ d\nu = N(\nu)d\nu \times h\nu$$

Substituting $N(\nu) = g(\nu)\ f(\nu)$ ↴

Planck's radiation formula ☛ $u(\nu)d\nu = \frac{8\pi hV}{c^3}\left[\frac{\nu^3\ d\nu}{e^{h\nu/kT} - 1}\right]$

ULTRAVIOLET CATASTROPHE

Using

$$e^{h\nu/kT} - 1 = \frac{h\nu}{kT} + \mathcal{O}(h^2)$$

take classical limit $h \to 0$

$$u_{\rm class}(\nu) = \lim_{h\to 0} u(\nu) = V\frac{8\pi kT}{c^3}\nu^2$$

In classical electromagnetic theory

total energy integrated over all frequencies **diverges**

ultraviolet catastrophe ☛ divergence comes from large ν part of integral

which in optical spectrum is ultraviolet portion

Bose-Einstein factor imposes effective ultraviolet cutoff on frequency integral

$$kT/h$$

total energy is finite ☟

$$u(T) = 3P(T) = \frac{8\pi^5 (kT)^4}{15 h^3 c^3} = 7.56464 \times 10^{-15} (T/{\rm K})^4 \ {\rm erg/cm^3}$$

$$1 \ {\rm J} \equiv 10^7 \ {\rm erg} = 6.24 \times 10^9 \ {\rm GeV}$$

SPECTRAL DENSITY

Define spectral density

$$\rho_\varepsilon(\nu, T) = \frac{u(\nu, T)}{u(T)} = \frac{15}{\pi^4}\frac{h}{kT}\frac{(h\nu/kT)^3}{e^{h\nu/kT} - 1}$$

so that → $\rho_\varepsilon(\nu, T)\, d\nu$ is fraction of electromagnetic energy between frequencies ν and $\nu + d\nu$

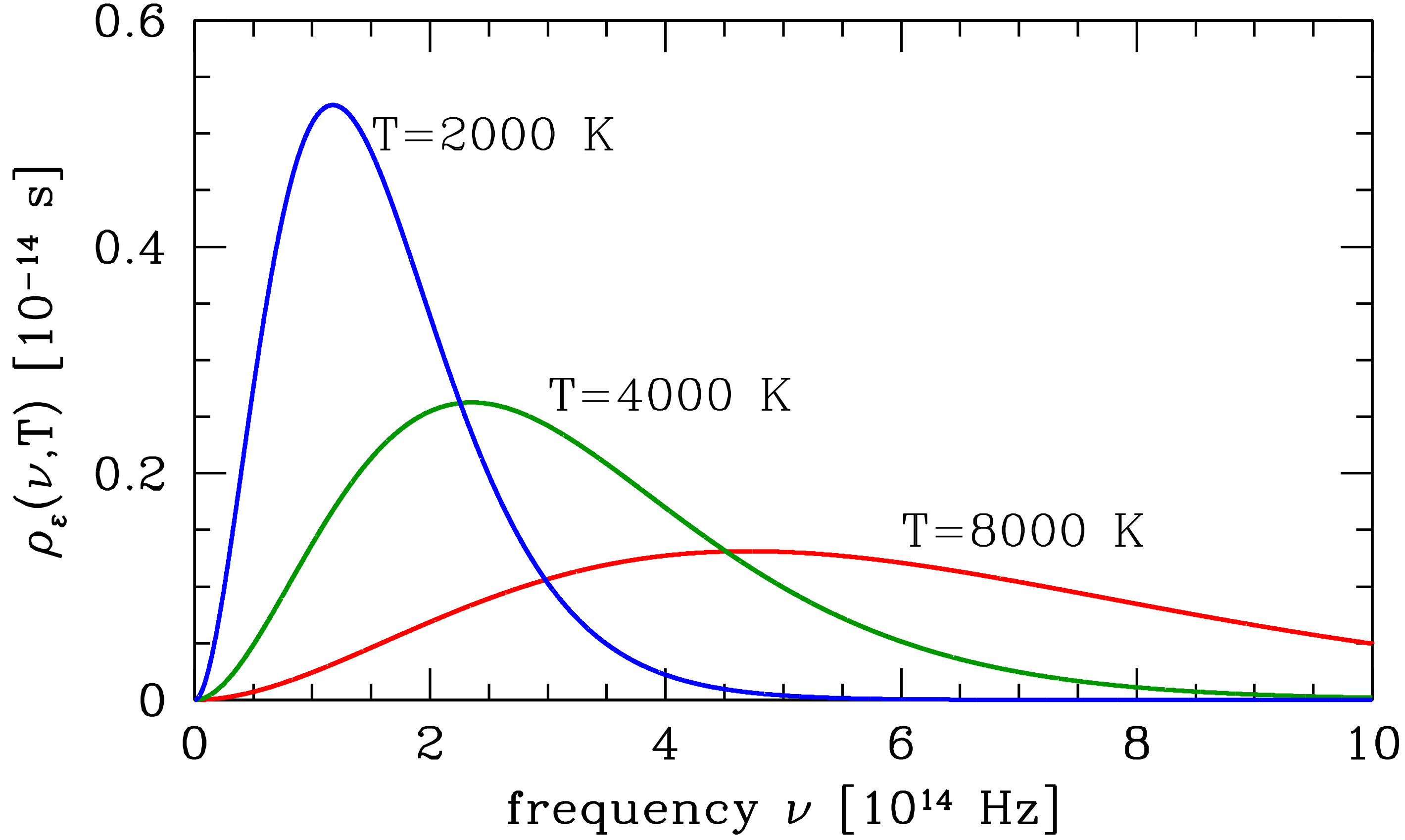
(under equilibrium conditions)

$$\int_0^\infty d\nu\, \rho_\varepsilon(\nu, T) = 1$$

Maximum occurs when $s \equiv h\nu/k_B T$ satisfies

$$\frac{d}{ds}\left(\frac{s^3}{e^s - 1}\right) = 0 \quad \Rightarrow \quad \frac{s}{1 - e^{-s}} = 3 \quad \Rightarrow \quad s = 2.82144$$

BLACKBODY RADIATION AT THREE TEMPERATURES



BOSE-EINSTEIN GAS

In macroscopic limit $N \to \infty$ and $V \to \infty$

so that concentration of particles $n = N/V$ is constant

energy levels of system become so finely quantized that become quasi continuous

Bose-Einstein continuum distribution is

$$f(\varepsilon) = \frac{N(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{(\varepsilon-\mu)/kT} - 1} \tag{88}$$

Initial concern is determining how chemical potential varies with temperature

Adopt convention of choosing ground state energy to be zero

At $T = 0$ all N bosons will be in the ground state

Setting $\varepsilon = 0$ in (88) we see that if $f(\varepsilon)$ is to make sense $\Rightarrow \mu < 0$

Furthermore ☛ $\mu = 0$ at temperature of absolute zero

and only slightly less than zero at non-zero temperatures

assuming N to be large number

HIGH TEMPERATURE LIMIT

At high temperatures ☛ in classical limit of dilute gas MB distribution applies

$$f(\varepsilon) = e^{-(\varepsilon-\mu)/kT}$$

$$\mu = -kT \ln\left(\frac{Z}{N}\right) \qquad \text{with} \qquad Z = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

$$\frac{\mu}{kT} = -\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{V}{N}\right]$$

For 1 kilomole of a boson gas comprising $^4\mathrm{He}$ atoms at standard T and P

$$\frac{\mu}{kT} = -\ln\left\{\left[\frac{2\pi(6.65\times10^{-27})(1.38\times10^{-23})(273)}{(6.63\times10^{-34})^2}\right]^{3/2}\left(\frac{22.4}{6.02\times10^{26}}\right)\right\}$$

$$= -12.43$$

$$\mu = -0.29 \text{ eV}$$

VALIDITY OF DILUTE GAS APPROXIMATION

Average energy of ideal monoatomic gas atom $\varepsilon = (3/2)kT = 0.035 \text{ eV}$

$$(\varepsilon - \mu)/kT = 1.5 + 12.4 = 13.9$$

substituting this value in (88)

$$f(\varepsilon) = 9 \times 10^{-7}$$

confirming validity of approximation

In classical limit

$$e^{-\mu/kT} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{V}{N}$$

positive number that increases with temperature

and decreases with particle density N/V

It turns out that below some temperature T_B

ideal Bose-Einstein gas undergoes **Bose-Einstein condensation**

A macroscopic number of particles $N_0 \sim N$ falls into ground state

These particles are called **Bose-Einstein condensate**

LOW-TEMPERATURE LIMIT

Setting energy of ground state to zero ☛ $N_0 = \frac{1}{e^{-\beta\mu} - 1}$

Resolving this for μ

$$\mu = -k_B T \ln\left(1 + \frac{1}{N_0}\right) \cong -\frac{k_B T}{N_0}$$

Since N_0 is very large ☛ $\mu = 0$ below Bose condensation temperature

For $\mu = 0$ ☛ easy to calculate number of particles in excited states $N_{\rm ex}$

$$N_{\rm ex} = \int_0^\infty d\varepsilon \, \frac{\rho(\varepsilon)}{e^{\beta\varepsilon} - 1}$$

Total number of particles ☛ $N = N_0 + N_{\rm ex}$

In three dimensions ☛ using density of states $\rho(\varepsilon)$ given by (39)

$$N_{\rm ex} = \frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty d\varepsilon \, \frac{\sqrt{\varepsilon}}{e^{\beta\varepsilon} - 1} = \frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{1}{\beta^{3/2}} \int_0^\infty dx \, \frac{\sqrt{x}}{e^x - 1} \qquad (89)$$

MATHEMATICAL INTERLUDE

$$\int_0^\infty dx \, \frac{x^{s-1}}{e^x - 1} = \Gamma(s)\,\zeta(s)$$

$\Gamma(s)$ ☛ gamma-function satisfying

$$\Gamma(n+1) = n\Gamma(n) = n!$$

$$\Gamma(1/2) = \sqrt{\pi}, \quad \Gamma(3/2) = \sqrt{\pi/2}$$

$\zeta(s)$ ☛ Riemann zeta function

$$\zeta(s) = \sum_{k=1}^{\infty} k^{-s}$$

$$\zeta(1) = \infty, \quad \zeta(3/2) = 2.612 \quad \zeta(5/2) = 1.341$$

$$\frac{\zeta(5/2)}{\zeta(3/2)} = 0.5134$$

BOSE-EINSTEIN CONDENSATE

(89) yields ☛ $$N_{\rm ex} = \frac{V}{(2\pi)^2} \left(\frac{2mk_BT}{\hbar^2}\right)^{3/2} \Gamma(3/2)\,\zeta(3/2)$$

(increasing with temperature)

At $T = T_B$ one has $N_{\rm ex} = N$ that is ↴

$$N = \frac{V}{(2\pi)^2} \left(\frac{2mk_BT_B}{\hbar^2}\right)^{3/2} \Gamma(3/2)\,\zeta(3/2) \qquad (90)$$

and thus condensate disappears ☛ $N_0 = 0$

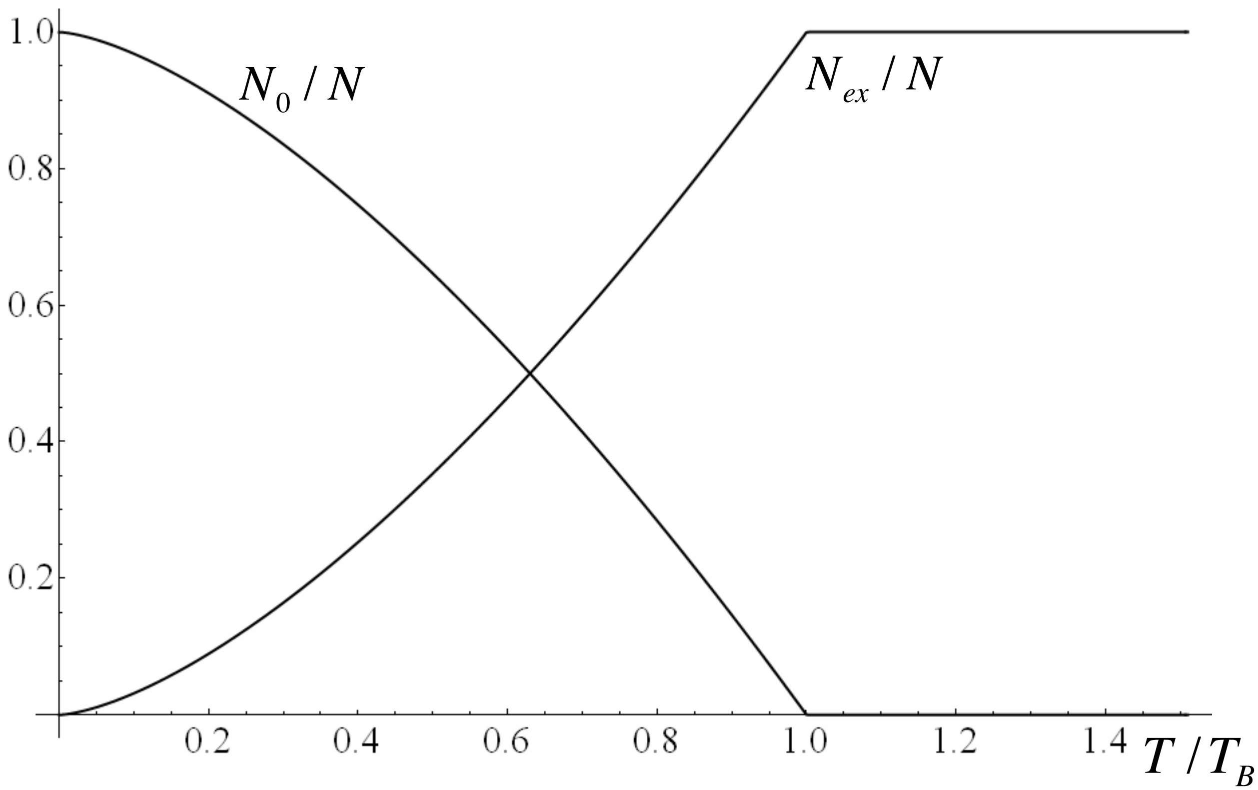
From equation above follows ↴

$$k_BT_B = \frac{\hbar^2}{2m} \left(\frac{(2\pi)^2\, n}{\Gamma(3/2)\,\zeta(3/2)}\right)^{2/3} \qquad n = \frac{N}{V} \qquad (91)$$

that is ☛ $T_B \propto n^{2/3}$

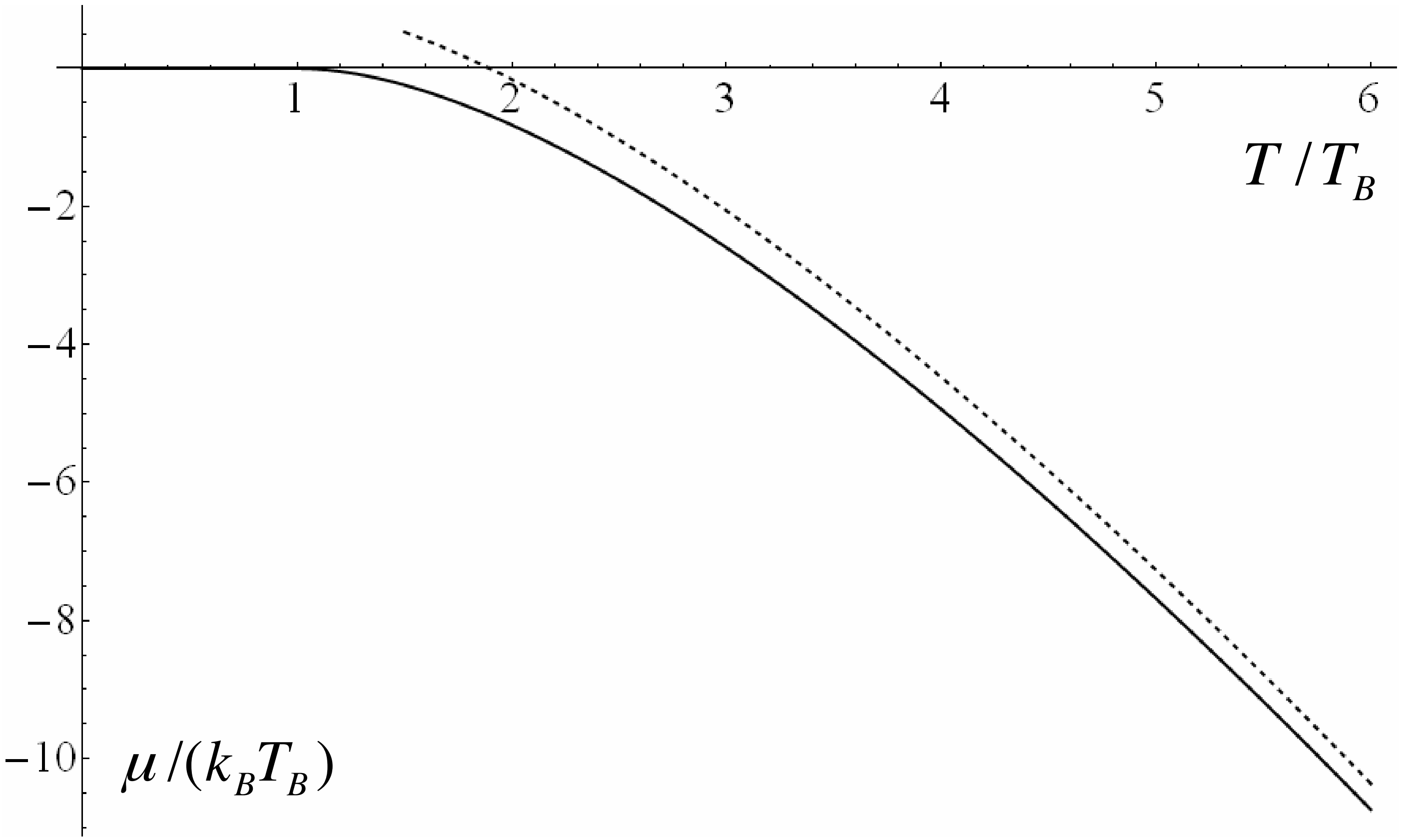
In typical situations ☛ $T_B < 0.1$

TEMPERATURE EVOLUTION



Condensate fraction $N_0(T)/N$ and fraction of excited particles $N_{\rm ex}(T)/N$

CHEMICAL POTENTIAL



Dashed line: High-temperature asymptote corresponding to Boltzmann statistics

INTERNAL ENERGY

Since energy of condensate is zero

$$U = \int_0^\infty d\varepsilon \, \frac{\varepsilon \rho(\varepsilon)}{e^{\beta(\varepsilon-\mu)} - 1}$$

For $T \gg T_B$ ☛ Boltzmann distribution applies ➢ U is given by (71)

and heat capacity is constant $C = (3/2)\, N k_B$

For $T < T_B$ ☛ $\mu = 0$ ➢ $U = \int_0^\infty d\varepsilon \, \frac{\varepsilon \rho(\varepsilon)}{e^{\beta\varepsilon} - 1}$

in three dimensions ↴

$$U = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty d\varepsilon \, \frac{\varepsilon^{3/2}}{e^{\beta\varepsilon} - 1} = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \Gamma(5/2)\, \zeta(5/2)\, (k_B T)^{5/2}$$

using (90) this can be rewritten as

$$U = N k_B T \left(\frac{T}{T_B}\right)^{3/2} \frac{\Gamma(5/2)\, \zeta(5/2)}{\Gamma(3/2)\, \zeta(3/2)} = N k_B T \left(\frac{T}{T_B}\right)^{3/2} \frac{3}{2} \, \frac{\zeta(5/2)}{\zeta(3/2)} \qquad T \leq T_B$$

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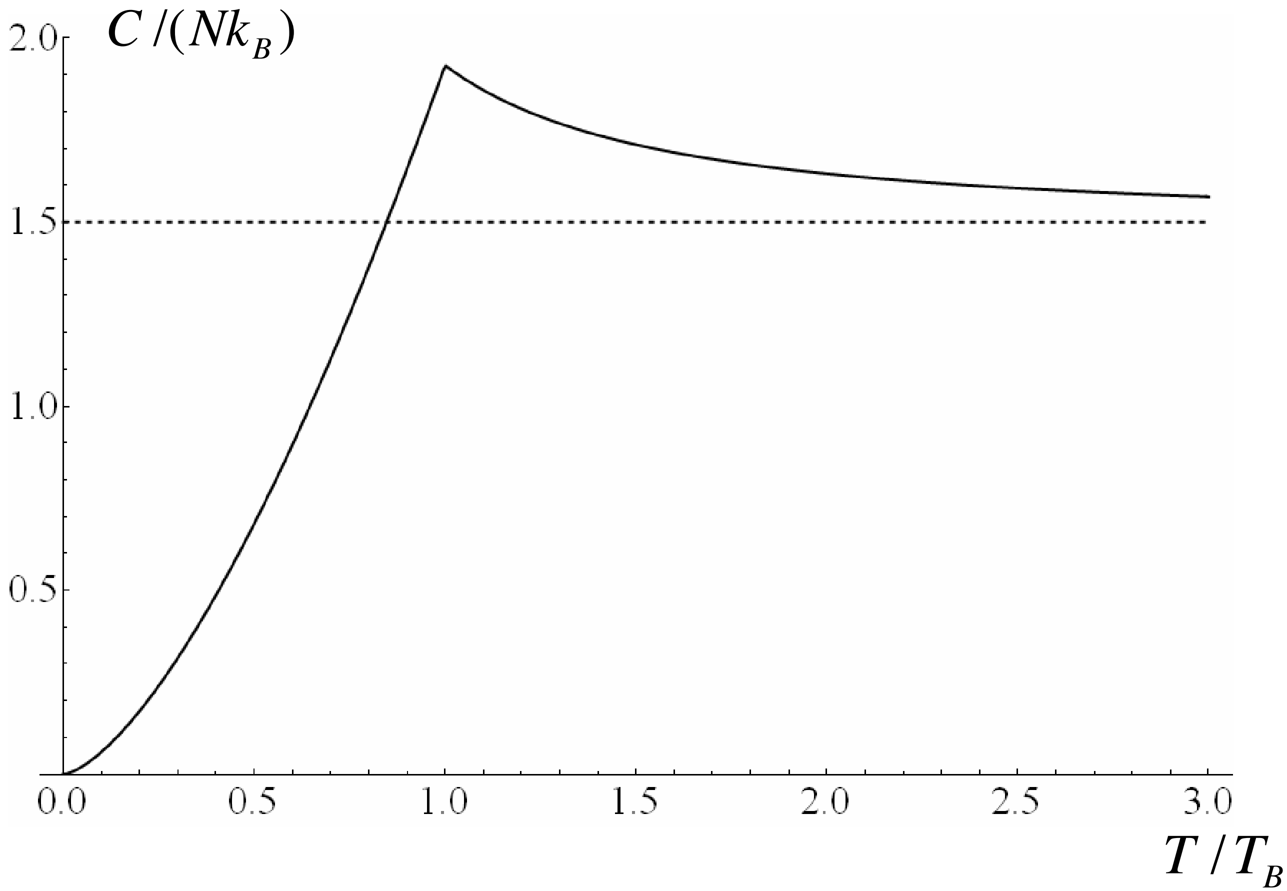
HEAT CAPACITY OF IDEAL BOSE-EINSTEIN GAS

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = N k_B \left(\frac{T}{T_B}\right)^{3/2} \frac{15}{4} \frac{\zeta(5/2)}{\zeta(3/2)} \quad T \leq T_B$$



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EQUATION OF STATE

entropy

$$S = \int_0^T dT' \, \frac{C_V(T')}{T'} = \frac{2}{3} C_V = N k_B \left(\frac{T}{T_B}\right)^{3/2} \frac{5}{2} \frac{\zeta(5/2)}{\zeta(3/2)} \qquad T \leq T_B$$

free energy

$$F = U - TS = -N k_B T \left(\frac{T}{T_B}\right)^{3/2} \frac{\zeta(5/2)}{\zeta(3/2)} \qquad T \leq T_B$$

pressure

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial F}{\partial T_B}\right)_T \left(\frac{\partial T_B}{\partial V}\right)_T = -\left(-\frac{3}{2}\frac{F}{T_B}\right)\left(-\frac{2}{3}\frac{T_B}{V}\right) = -\frac{F}{V}$$

equation of state $$PV = N k_B T \left(\frac{T}{T_B}\right)^{3/2} \frac{\zeta(5/2)}{\zeta(3/2)} \qquad T \leq T_B$$

compared to $PV = N k_B T$ at high temperatures

P of ideal Bose gas with condensate contains additional factor $(T/T_B)^{3/2} < 1$

This is because particles in condensate are not thermally agitated and thus they do not contribute into pressure