Chapter 9: Part B
Quantum statistics of ideal gases

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Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.2 Formulation of the statistical problem

Energy:

$$E_R = n_1\epsilon_1 + n_2\epsilon_2 + n_3\epsilon_3 + \cdots = \sum_r n_r\epsilon_r$$

restriction:

$$\sum_r n_r = N$$

Partition function:

$$Z = \sum_R e^{-\beta E_R} = \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics
9.2 Formulation of the statistical problem

Mean number in *s* state:

$$\bar{n}_s = \frac{\sum_R n_s\, e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+\cdots)}}{\sum_R e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+\cdots)}}$$

$$= \frac{1}{Z}\sum_R \left(-\frac{1}{\beta}\frac{\partial}{\partial\epsilon_s}\right) e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+\cdots)}$$

$$= -\frac{1}{\beta Z}\frac{\partial Z}{\partial\epsilon_s}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.2 Formulation of the statistical problem

Maxwell-Boltzmann statistics

$n_r = 0, 1, 2, 3, \ldots \quad$ for each r

distinguishable

$$\sum_r n_r = N$$

Bose-Einstein statistics

$n_r = 0, 1, 2, 3, \ldots \quad$ for each r

indistinguishable

$$\sum_r n_r = N$$

Fermi-Dirac statistics

$n_r = 0, 1 \quad$ for each r

indistinguishable

$$\sum_r n_r = N$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics
9.3 Quantum distribution functions

$$\bar{n}_s = \frac{\sum\limits_{n_1,n_2,\dots} n_s\, e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots+n_s\varepsilon_s+\cdots)}}{\sum\limits_{n_1,n_2,\dots} e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots+n_s\varepsilon_s+\cdots)}}$$

$$\sum_r n_r = N$$

$$\bar{n}_s = \frac{\sum\limits_{n_s} n_s\, e^{-\beta n_s\varepsilon_s} \sum\limits^{(s)}_{n_1,n_2,\dots} e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)}}{\sum\limits_{n_s} e^{-\beta n_s\varepsilon_s} \sum\limits^{(s)}_{n_1,n_2,\dots} e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\cdots)}}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.3 Quantum distribution functions

Photon statistics: BE statistics without restricted *N*

$$\bar{n}_s = \frac{\sum_{n_s} n_s e^{-\beta n_s \epsilon_s}}{\sum_{n_s} e^{-\beta n_s \epsilon_s}}$$

$$\bar{n}_s = \frac{\sum_{n_s} n_s e^{-\beta n_s \epsilon_s} \quad \sum^{(s)}_{n_1, n_2, \ldots} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)}}{\sum_{n_s} e^{-\beta n_s \epsilon_s} \quad \sum^{(s)}_{n_1, n_2, \ldots} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)}}$$

$$\bar{n}_s = \frac{(-1/\beta)(\partial/\partial\epsilon_s)\Sigma\, e^{-\beta n_s \epsilon_s}}{\Sigma\, e^{-\beta n_s \epsilon_s}}$$

$$= -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_s}\ln\left(\Sigma\, e^{-\beta n_s \epsilon_s}\right)$$

$$= \frac{1}{1 - e^{-\beta\epsilon_s}}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.3 Quantum distribution functions

Photon statistics: BE statistics without restricted *N*

$$\bar{n}_s = \frac{1}{\beta}\frac{\partial}{\partial \epsilon_s}\ln\left(1 - e^{-\beta\epsilon_s}\right) = \frac{e^{-\beta\epsilon_s}}{1 - e^{-\beta\epsilon_s}}$$

$$\bar{n}_s = \frac{1}{e^{\beta\epsilon_s} - 1}$$

Plank distribution

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.3 Quantum distribution functions

$$\sum_r n_r = N$$

Fermi-Dirac statistics $n_r = 0 \text{ and } 1$

define

$$Z_s(N) = \sum_{n_1, n_2, \ldots}^{(s)} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)}$$

$n_s = 0$ 1

$$\bar{n}_s = \frac{0 + e^{-\beta\epsilon_s} Z_s(N-1)}{Z_s(N) + e^{-\beta\epsilon_s} Z_s(N-1)}$$

$$\bar{n}_s = \frac{1}{[Z_s(N)/Z_s(N-1)]\, e^{\beta\epsilon_s} + 1}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.3 Quantum distribution functions

Fermi-Dirac statistics

$$\bar{n}_s = \frac{1}{[Z_s(N)/Z_s(N-1)]\, e^{\beta\epsilon_s} + 1}$$

define

$$\alpha = \frac{\partial \ln Z}{\partial N}$$

$$Z(N)/Z(N-1) = e^{\alpha}$$

$$\bar{n}_s = \frac{1}{e^{\alpha+\beta\epsilon_s} + 1}$$

Fermi-Dirac distribution

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.3 Quantum distribution functions

Fermi-Dirac statistics

define $$\alpha = \frac{\partial \ln Z}{\partial N}$$

$$\alpha = -\frac{1}{kT}\frac{\partial F}{\partial N} =$$

$$= -\frac{\mu}{kT} = -\beta\mu$$

$$\bar{n}_s = \frac{1}{e^{\alpha+\beta\epsilon_s}+1}$$

$$0 \le \bar{n}_s \le 1$$

$$\bar{n}_s \rightarrow 0$$

if ϵ_s becomes large enough

Chemical potential per particle

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.3 Quantum distribution functions

Bose-Einstein statistics $n_s = 0, 1, 2, 3, \ldots$

$n_s = \quad 0 \qquad 1 \qquad\qquad 2$

$$\bar{n}_s = \frac{0 + e^{-\beta\epsilon_s} Z_s(N-1) + 2e^{-2\beta\epsilon_s} Z_s(N-2) + \cdots}{Z_s(N) + e^{-\beta\epsilon_s} Z_s(N-1) + e^{-2\beta\epsilon_s} Z_s(N-2) + \cdots}$$

$$Z(N)/Z(N-1) = e^{\alpha}$$

$$\bar{n}_s = \frac{Z_s(N)[0 + e^{-\beta\epsilon_s} e^{-\alpha} + 2e^{-2\beta\epsilon_s} e^{-2\alpha} + \cdots]}{Z_s(N)[1 + e^{-\beta\epsilon_s} e^{-\alpha} + e^{-2\beta\epsilon_s} e^{-2\alpha} + \cdots]}$$

$$\bar{n}_s = \frac{\sum_s n_s e^{-n_s(\alpha+\beta\epsilon_s)}}{\sum_s e^{-n_s(\alpha+\beta\epsilon_s)}}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.3 Quantum distribution functions

Bose-Einstein statistics

$$\bar{n}_s = \frac{\sum_s n_s e^{-n_s(\alpha+\beta\epsilon_s)}}{\sum_s e^{-n_s(\alpha+\beta\epsilon_s)}}$$

$$\bar{n}_s = \frac{1}{e^{\alpha+\beta\epsilon_s} - 1}$$

αcan be determined by

$$\sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} - 1} = N$$

$$\alpha = -\beta\mu$$

$$\bar{n}_s = \frac{1}{e^{\beta(\epsilon_s-\mu)} - 1}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.4 Maxwell-Boltzmann statistics

Partition function:

$$Z = \sum_{R} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)}$$

for *given* values of $\{n_1, n_2, \ldots\}$

Possible way:

$$\frac{N!}{n_1!n_2!\cdots}$$

$$Z = \sum_{n_1, n_2, \ldots} \frac{N!}{n_1!n_2!\cdots} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)}$$

$$\sum_{r} n_r = N$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.4 Maxwell-Boltzmann statistics

Partition function:

$$Z = \sum_{n_1, n_2, \ldots} \frac{N!}{n_1! n_2! \cdots} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots)}$$

$$Z = \sum_{n_1, n_2, \ldots} \frac{N!}{n_1! n_2! \cdots} (e^{-\beta\varepsilon_1})^{n_1} (e^{-\beta\varepsilon_2})^{n_2} \cdots$$

$$Z = (e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2} + \cdots)^N$$

$$\boxed{\ln Z = N \ln \left(\sum_r e^{-\beta\varepsilon_r} \right)}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.4 Maxwell-Boltzmann statistics

Partition function:

$$Z = \sum_{n_1, n_2, \ldots} \frac{N!}{n_1! n_2! \cdots} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots)}$$

1	2	3
AB	...	...
...	AB	...
...	...	AB
A	B	...
B	A	...
A	...	B
B	...	A
...	A	B
...	B	A

$$Z =$$

$$\exp(-\beta \times 2\varepsilon_1) + \exp(-\beta \times 2\varepsilon_2) + \exp(-\beta \times 2\varepsilon_3)$$

$$+ \exp(-\beta \times (\varepsilon_1 + \varepsilon_2)) + \exp(-\beta \times (\varepsilon_1 + \varepsilon_2))$$

$$+ \exp(-\beta \times (\varepsilon_1 + \varepsilon_3)) + \exp(-\beta \times (\varepsilon_1 + \varepsilon_3))$$

$$+ \exp(-\beta \times (\varepsilon_2 + \varepsilon_3)) + \exp(-\beta \times (\varepsilon_2 + \varepsilon_3))$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.4 Maxwell-Boltzmann statistics

Partition function:

$$\boxed{\ln Z = N \ln \left(\sum_r e^{-\beta\epsilon_r}\right)}$$

$$\Rightarrow \quad \bar{n}_s = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \epsilon_s} = -\frac{1}{\beta} N \frac{-\beta\, e^{-\beta\epsilon_s}}{\sum_r e^{-\beta\epsilon_r}}$$

$$\Rightarrow \quad \boxed{\bar{n}_s = N \frac{e^{-\beta\epsilon_s}}{\sum_r e^{-\beta\epsilon_r}}}$$

Maxwell-Boltzmann distribution

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.5 Photon statistics

Partition function:

$$Z = \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)}$$

$$Z = \sum_{n_1, n_2, \ldots} e^{-\beta n_1 \epsilon_1} e^{-\beta n_2 \epsilon_2} e^{-\beta n_3 \epsilon_3} \cdots$$

$$Z = \left(\sum_{n_1=0}^{\infty} e^{-\beta n_1 \epsilon_1}\right)\left(\sum_{n_2=0}^{\infty} e^{-\beta n_2 \epsilon_2}\right)\left(\sum_{n_3=0}^{\infty} e^{-\beta n_3 \epsilon_3}\right) \cdots$$

$$Z = \left(\frac{1}{1 - e^{-\beta\epsilon_1}}\right)\left(\frac{1}{1 - e^{-\beta\epsilon_2}}\right)\left(\frac{1}{1 - e^{-\beta\epsilon_3}}\right) \cdots$$

$$\boxed{\ln Z = -\sum_r \ln\left(1 - e^{-\beta\epsilon_r}\right)}$$

$$\boxed{\bar{n}_s} \boxed{= -\frac{1}{\beta Z}\frac{\partial Z}{\partial \epsilon_s}}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.6 Bose-Einstein statistics

Partition function:

$$Z = \sum_{R} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)}$$

$$n_r = 0, 1, 2, \ldots \qquad \sum_r n_r = N$$

Considering Z(N').

Z(N') increases rapidly with N', but we are only interested in Z at N'=N .

Multiply $e^{-\alpha N'}$ to produce a function $Z(N')e^{-\alpha N'}$ with maximum at N'=N by a proper choice of *α*.

A sum of all N' must select only terms of interest near N

$$\boxed{\sum_{N'} Z(N')\, e^{-\alpha N'} = Z(N)\, e^{-\alpha N}\, \Delta^* N'}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics
9.6 Bose-Einstein statistics

Define Grand partition function

$$\sum_{N'} Z(N')\, e^{-\alpha N'} = Z(N)\, e^{-\alpha N} \Delta^* N'$$

$$\mathcal{Z} \equiv \sum_{N'} Z(N') e^{-\alpha N'}$$

$$\ln Z(N) = \alpha N + \ln \mathcal{Z}$$

?

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.6 Bose-Einstein statistics

Grand partition function $$Z = \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots)} e^{-\alpha(n_1 + n_2 + \cdots)}$$

$$Z = \sum_{n_1, n_2, \ldots} e^{-(\alpha+\beta\epsilon_1)n_1 - (\alpha+\beta\epsilon_2)n_2 - \cdots}$$

$$= \left(\sum_{n_1=0}^{\infty} e^{-(\alpha+\beta\epsilon_1)n_1}\right)\left(\sum_{n_2=0}^{\infty} e^{-(\alpha+\beta\epsilon_2)n_2}\right) \cdots$$

$$Z = \left(\frac{1}{1 - e^{-(\alpha+\beta\epsilon_1)}}\right)\left(\frac{1}{1 - e^{-(\alpha+\beta\epsilon_2)}}\right) \cdots$$

$$\ln Z = -\sum_r \ln\left(1 - e^{-\alpha-\beta\epsilon_r}\right)$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.6 Bose-Einstein statistics

$$\ln Z(N) = \alpha N + \ln Z$$

Grand partition function $\ln Z = -\sum_r \ln\left(1 - e^{-\alpha-\beta\epsilon_r}\right)$

$$\ln Z = \alpha N - \sum_r \ln\left(1 - e^{-\alpha-\beta\epsilon_r}\right)$$

Keep N'=N by a proper choice of α $Z(N')e^{-\alpha N'}$

$$\frac{\partial}{\partial N'}\left[\ln Z(N') - \alpha N'\right] = \frac{\partial \ln Z(N)}{\partial N} - \alpha = 0$$

$$\left[\alpha + \left(N + \frac{\partial \ln Z}{\partial \alpha}\right)\frac{\partial \alpha}{\partial N}\right] - \alpha = 0$$

$$N + \frac{\partial \ln Z}{\partial \alpha} = \frac{\partial \ln Z}{\partial \alpha} = 0$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics
9.6 Bose-Einstein statistics

$$\boxed{\ln Z = \alpha N - \sum_r \ln\left(1 - e^{-\alpha-\beta\epsilon_r}\right)}$$

$$N + \frac{\partial \ln Z}{\partial \alpha} = \frac{\partial \ln Z}{\partial \alpha} = 0$$

$$\Rightarrow \quad N - \sum_r \frac{e^{-\alpha-\beta\epsilon_r}}{1 - e^{-\alpha-\beta\epsilon_r}} = 0$$

$$\Rightarrow \quad \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} - 1} = N$$

0

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \epsilon_s} = -\frac{1}{\beta}\left[-\frac{\beta e^{-\alpha-\beta\epsilon_s}}{1 - e^{-\alpha-\beta\epsilon_s}} + \frac{\partial \ln Z}{\partial \alpha}\frac{\partial \alpha}{\partial \epsilon_s}\right]$$

$$\Rightarrow \quad \boxed{\bar{n}_s = \frac{1}{e^{\alpha+\beta\epsilon_s} - 1}}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.6 Bose-Einstein statistics

$$\boxed{\bar{n}_s = \frac{1}{e^{\alpha+\beta\epsilon_s} - 1}}$$

$$\boxed{\frac{\partial \ln Z(N)}{\partial N} - \alpha = 0}$$

$$\Rightarrow \quad \sum_r \bar{n}_r = N$$

$$\mu = \frac{\partial F}{\partial N} = -kT\frac{\partial \ln Z}{\partial N} = -kT\alpha$$

$$\boxed{\alpha = -\beta\mu}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.7 Fermi-Dirac statistics

$$n_r = 0 \text{ and } 1 \qquad \text{for each } r$$

Similar to the treatment in BE statistics

$$Z = \sum_{n_1, n_2, n_3} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \cdots) - \alpha(n_1 + n_2 + \cdots)}$$

$$= \left(\sum_{n_1=0}^{1} e^{-(\alpha+\beta\epsilon_1)n_1} \right) \left(\sum_{n_2=0}^{1} e^{-(\alpha+\beta\epsilon_2)n_2} \right) \cdots$$

$$Z = (1 + e^{-\alpha-\beta\epsilon_1})(1 + e^{-\alpha-\beta\epsilon_2}) \cdots$$

$$\ln Z = \sum_r \ln(1 + e^{-\alpha-\beta\epsilon_r})$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.7 Fermi-Dirac statistics

$$\ln Z = \sum_r \ln\left(1 + e^{-\alpha-\beta\epsilon_r}\right)$$

$$\boxed{\ln Z = \alpha N + \sum_r \ln\left(1 + e^{-\alpha-\beta\epsilon_r}\right)}$$

α is also determined by the condition

$$\frac{\partial \ln Z}{\partial \alpha} = N - \sum_r \frac{e^{-\alpha-\beta\epsilon_r}}{1 + e^{-\alpha-\beta\epsilon_r}} = 0$$

$$\boxed{\sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} + 1} = N}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.7 Fermi-Dirac statistics

$$\bar{n}_s = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \epsilon_s} = \frac{1}{\beta}\frac{\beta e^{-\alpha-\beta\epsilon_s}}{1+e^{-\alpha-\beta\epsilon_s}}$$

$$\Rightarrow \quad \boxed{\bar{n}_s = \frac{1}{e^{\alpha+\beta\epsilon_s}+1}}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

Maxwell-Boltzmann statistics

$$\bar{n}_s = N \frac{e^{-\beta \epsilon_s}}{\sum_r e^{-\beta \epsilon_r}}$$

$$\ln Z = N \ln \left(\sum_r e^{-\beta \epsilon_r} \right)$$

Bose-Einstein statistics

$$\bar{n}_s = \frac{1}{e^{\alpha + \beta \epsilon_s} - 1}$$

$$\ln Z = \alpha N - \sum_r \ln \left(1 - e^{-\alpha - \beta \epsilon_r}\right)$$

Fermi-Dirac statistics

$$\bar{n}_s = \frac{1}{e^{\alpha + \beta \epsilon_s} + 1}$$

$$\ln Z = \alpha N + \sum_r \ln \left(1 + e^{-\alpha - \beta \epsilon_r}\right)$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics
9.8 Quantum statistics in the classic limit

BE and FD distributions:

$$\bar{n}_r = \frac{1}{e^{\alpha+\beta\epsilon_r} \pm 1}$$

Total particles:

$$\sum_r \bar{n}_r = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} \pm 1} = N$$

Partition function:

$$\ln Z = \alpha N \pm \sum_r \ln\left(1 \pm e^{-\alpha-\beta\epsilon_r}\right)$$

Limiting cases:

very low concentration $\bar{n}_r \ll 1$ $\quad \exp(\alpha + \beta\epsilon_r) \gg 1$

Very high T $\beta \longrightarrow 0$ $\quad \beta\epsilon_r \ll \alpha$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics
9.8 Quantum statistics in the classic limit

Limiting cases:

very low concentration $\bar{n}_r \ll 1$ $\exp(\alpha + \beta\epsilon_r) \gg 1$

Very high T $\beta \longrightarrow 0$ $\beta\epsilon_r \ll \alpha$

$$\boxed{\sum_r \bar{n}_r = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} \pm 1} = N}$$

Number of terms contribute substantially to summation increases
Requires α must be large enough
To keep sum ==N

$\exp(\alpha + \beta\epsilon_r) \gg 1$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.8 Quantum statistics in the classic limit

Limiting cases:

very low concentration、very high T

$$e^{\alpha+\beta\epsilon_r} \gg 1 \Rightarrow \bar{n}_r \ll 1$$

$$\bar{n}_r = \frac{1}{e^{\alpha+\beta\epsilon_r} \pm 1} \Rightarrow \bar{n}_r = e^{-\alpha-\beta\epsilon_r}$$

$$\sum_r e^{-\alpha-\beta\epsilon_r} = e^{-\alpha}\sum_r e^{-\beta\epsilon_r} = N$$

$$e^{-\alpha} = N\left(\sum_r e^{-\beta\epsilon_r}\right)^{-1}$$

Limiting cases:

low concentration

high T --→MB dis.

$$\bar{n}_r = N\frac{e^{-\beta\epsilon_r}}{\sum_r e^{-\beta\epsilon_r}}$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

$$\ln Z = \alpha N \pm \sum_r \ln\left(1 \pm e^{-\alpha-\beta\varepsilon_r}\right)$$

9.8 Quantum statistics in the classic limit

Partition function:

$$\ln Z = \alpha N \pm \sum_r \left(\pm e^{-\alpha-\beta\varepsilon_r}\right) = \alpha N + N$$

$$\alpha = -\ln N + \ln\left(\sum_r e^{-\beta\varepsilon_r}\right)$$

$$\ln Z = -N\ln N + N + N\ln\left(\sum_r e^{-\beta\varepsilon_r}\right)$$

While MB gives:

????????????????

$$\ln Z = N\ln\left(\sum_r e^{-\beta\varepsilon_r}\right)$$

Maxwell-Boltzmann, Bose-Einstein, Fermi-Dirac statistics

9.8 Quantum statistics in the classic limit

Partition function:

$$\ln Z = \ln Z_{MB} - (N \ln N - N)$$

$$\ln Z = \ln Z_{MB} - \ln N!$$

$$Z = \frac{Z_{MB}}{N!}$$

<<< distinguishable

Ideal gas in the classical limit

9.9 Quantum states of a single particle

Wave function:

Consider a particle is non-relativistic and with mass m, position vector r and momentum p ;

The particle is in volume V and experiences no force;

The wave function: **amplitude**

$$\boxed{\Psi = A e^{i(\boldsymbol{\kappa}\cdot\boldsymbol{r}-\omega t)} = \psi(\boldsymbol{r})\, e^{-i\omega t}}$$

plane wave **wave vector** **frequency**

energy $\boxed{\epsilon = \hbar\omega}$ **momentum** $\boxed{\boldsymbol{p} = \hbar\boldsymbol{\kappa}}$

$$\boxed{\epsilon = \frac{\boldsymbol{p}^2}{2m} = \frac{\hbar^2\boldsymbol{\kappa}^2}{2m}}$$

Ideal gas in the classical limit

9.9 Quantum states of a single particle

Wave function 《=== Schrodinger equation

$$\boxed{i\hbar \frac{\partial \Psi}{\partial t} = \mathcal{H}\Psi}$$

One can choose the potential energy to be 0 in container
Then Hamiltonian reduces to kinetic energy only

$$\boxed{\mathcal{H} = \frac{1}{2m} p^2 = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla\right)^2 = -\frac{\hbar^2}{2m}\nabla^2}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

A testing solution

$$\boxed{\Psi = \psi e^{-i\omega t} = \psi e^{-(i/\hbar)\epsilon t}}$$

Ideal gas in the classical limit
9.9 Quantum states of a single particle

$$\mathcal{H}\psi = \epsilon\psi$$

$$\nabla^2\psi + \frac{2m\epsilon}{\hbar^2}\psi = 0$$

Time-independent Schrodinger equation

$$\vec{k} = (k_x, k_y, k_z)$$

General solution:

$$\psi = A\, e^{i(\kappa_x x + \kappa_y y + \kappa_z z)} = A\, e^{i\boldsymbol{\kappa}\cdot\mathbf{r}}$$

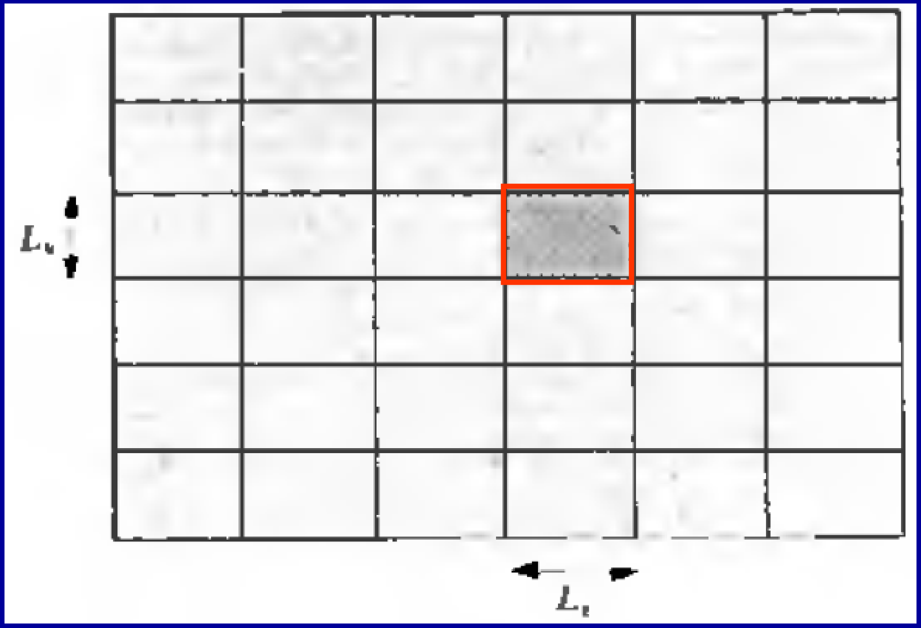
$$-(\kappa_x^2 + \kappa_y^2 + \kappa_z^2) + \frac{2m\epsilon}{\hbar^2} = 0$$

$$\epsilon = \frac{\hbar^2\kappa^2}{2m}$$

Ideal gas in the classical limit
9.9 Quantum states of a single particle
Boundary conditions and enumeration of states

Ψ must satisfy certain boundary conditions, and not all values of k, p are allowed.

Considering a rectangular cell with $L_x x L_y x L_z = V$, we can completely neglect any container walls and imagine that the cell is embedded in an infinite system



Periodical boundary

Ideal gas in the classical limit

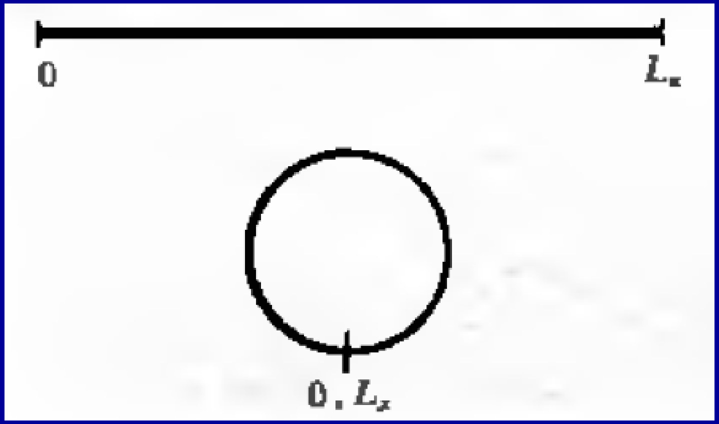
9.9 Quantum states of a single particle

Boundary conditions and enumeration of states

Periodical boundary

$$\left.\begin{aligned}\psi(x+L_x, y, z) &= \psi(x,y,z)\\ \psi(x, y+L_y, z) &= \psi(x,y,z)\\ \psi(x, y, z+L_z) &= \psi(x,y,z)\end{aligned}\right\}$$

if L>>λ, such treatment does not affect the physics



Ideal gas in the classical limit

9.9 Quantum states of a single particle

Boundary conditions and enumeration of states

Periodical boundary

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} = e^{i(\kappa_x x+\kappa_y y+\kappa_z z)}$$

$$\left.\begin{aligned}\psi(x+L_x, y, z) &= \psi(x,y,z)\\ \psi(x, y+L_y, z) &= \psi(x,y,z)\\ \psi(x, y, z+L_z) &= \psi(x,y,z)\end{aligned}\right\}$$

$$\kappa_x(x+L_x) = \kappa_x x + 2\pi n_x$$

$$\left\{\begin{aligned}\kappa_x &= \frac{2\pi}{L_x} n_x\\ \kappa_y &= \frac{2\pi}{L_y} n_y\\ \kappa_z &= \frac{2\pi}{L_z} n_z\end{aligned}\right.$$

$$\epsilon = \frac{\hbar^2}{2m}\left(\kappa_x^2+\kappa_y^2+\kappa_z^2\right) = \frac{2\pi^2\hbar^2}{m}\left(\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right)$$

n_x, n_y, n_z can be any integer

Ideal gas in the classical limit

9.9 Quantum states of a single particle

Boundary conditions and enumeration of states

Periodical boundary

Since L_x, L_y, L_z are large, the possible values of k are closely spaced.

Thus, there is many states corresponding to any small dk

$$\left\{\begin{aligned} k_x &= \frac{2\pi}{L_x} n_x \\ k_y &= \frac{2\pi}{L_y} n_y \\ k_z &= \frac{2\pi}{L_z} n_z \end{aligned}\right.$$

For given values of k_y and k_z, number Δn_x of possible integer n_x for k_x in the range $[k_x, k_x+dk_x]$

$$\Delta n_x = \frac{L_x}{2\pi} dk_x$$

Ideal gas in the classical limit

9.9 Quantum states of a single particle

Boundary conditions and enumeration of states

Periodical boundary

$$\kappa_x = \frac{2\pi}{L_x} n_x$$
$$\kappa_y = \frac{2\pi}{L_y} n_y$$
$$\kappa_z = \frac{2\pi}{L_z} n_z$$

Number of translational states ρ(k)dk for *k* in the range [k, k+dk]

$$\begin{aligned}\rho d^3\kappa &= \Delta n_x \, \Delta n_y \, \Delta n_z \\ &= \left(\frac{L_x}{2\pi} d\kappa_x\right)\left(\frac{L_y}{2\pi} d\kappa_y\right)\left(\frac{L_z}{2\pi} d\kappa_z\right) \\ &= \frac{L_x L_y L_z}{(2\pi)^3} d\kappa_x \, d\kappa_y \, d\kappa_z\end{aligned}$$

$$\rho \, d^3\kappa = \frac{V}{(2\pi)^3} d^3\kappa$$

$$d^3\kappa = d\kappa_x \, d\kappa_y \, d\kappa_z$$

Element of volume in k space

Ideal gas in the classical limit

9.9 Quantum states of a single particle

Boundary conditions and enumeration of states

Periodical boundary

range [p, p+dp]

$$\rho_p\, d^3\mathbf{p} = \rho\, d^3\boldsymbol{\kappa} = \frac{V}{(2\pi)^3}\frac{d^3\mathbf{p}}{\hbar^3} = V\frac{d^3\mathbf{p}}{h^3}$$

range [*k*, *k*+d*k*]

$$\rho_\kappa\, d\kappa = \frac{V}{(2\pi)^3}(4\pi\kappa^2\, d\kappa) = \frac{V}{2\pi^2}\kappa^2\, d\kappa$$

range [ε,ε+dε]

$$|\rho_\epsilon\, d\epsilon| = |\rho_\kappa\, d\kappa| = \rho_\kappa\left|\frac{d\kappa}{d\epsilon}\right| d\epsilon = \rho_\kappa\left|\frac{d\epsilon}{d\kappa}\right|^{-1} d\epsilon$$

$$\epsilon = \frac{p^2}{2m} = \frac{\hbar^2\kappa^2}{2m}$$

$$\rho_\epsilon\, d\epsilon = \frac{V}{2\pi^2}\kappa^2\left|\frac{d\kappa}{d\epsilon}\right| d\epsilon = \frac{V}{4\pi^2}\frac{(2m)^{\frac{3}{2}}}{\hbar^3}\epsilon^{\frac{1}{2}}\, d\epsilon$$

Ideal gas in the classical limit
9.10 Evaluation of the partition function

Partition function of a monatomic ideal gas in classical limit

$$\ln Z = N(\ln \zeta - \ln N + 1)$$

$$\zeta \equiv \sum_r e^{-\beta \epsilon_r}$$

Sum over all states of a single particle

$$Z = \frac{\zeta^N}{N!}$$

$$\zeta = \sum_{\kappa_x, \kappa_y, \kappa_z} \exp\left[-\frac{\beta \hbar^2}{2m}(\kappa_x{}^2 + \kappa_y{}^2 + \kappa_z{}^2)\right]$$

$$\zeta = \left(\sum_{\kappa_x} e^{-(\beta\hbar^2/2m)\kappa_x{}^2}\right)\left(\sum_{\kappa_y} e^{-(\beta\hbar^2/2m)\kappa_y{}^2}\right)\left(\sum_{\kappa_z} e^{-(\beta\hbar^2/2m)\kappa_z{}^2}\right)$$

Ideal gas in the classical limit
9.10 Evaluation of the partition function

Partition function of a monatomic ideal gas in classical limit

$$\boxed{\zeta = \Big(\underbrace{\sum_{\kappa_x}}_{k_x \leftrightarrow n_x} e^{-(\beta\hbar^2/2m)\kappa_x^2}\Big)\Big(\underbrace{\sum_{\kappa_y}}_{k_y \leftrightarrow n_y} e^{-(\beta\hbar^2/2m)\kappa_y^2}\Big)\Big(\underbrace{\sum_{\kappa_z}}_{k_z \leftrightarrow n_z} e^{-(\beta\hbar^2/2m)\kappa_z^2}\Big)}$$

$$\kappa_x = \frac{2\pi}{L_x} n_x$$

$\Delta k_x = 2\pi / L_x$ is very small

$$\underbrace{\left|\frac{\partial}{\partial\kappa_x}\left[e^{-(\beta\hbar^2/2m)\kappa_x^2}\right]\left(\frac{2\pi}{L_x}\right)\right|}_{\text{Change of function versus unit change of } k_x} \ll e^{-(\beta\hbar^2/2m)\kappa_x^2}$$

Change of function versus unit change of k_x

Since L>>1, the condition can be satisfied, and ...

Ideal gas in the classical limit

$$\ln Z = N(\ln \zeta - \ln N + 1)$$

9.10 Evaluation of the partition function

$$\sum_{\kappa_x=-\infty}^{\infty} e^{-(\beta\hbar^2/2m)\kappa_x^2} \approx \int_{-\infty}^{\infty} e^{-(\beta\hbar^2/2m)\kappa_x^2}\left(\frac{L_x}{2\pi}\,d\kappa_x\right)$$

$$= \frac{L_x}{2\pi}\left(\frac{2\pi m}{\beta\hbar^2}\right)^{\frac{1}{2}} = \frac{L_x}{2\pi\hbar}\left(\frac{2\pi m}{\beta}\right)^{\frac{1}{2}}$$

$$\zeta = \frac{V}{(2\pi\hbar)^3}\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} = \frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}$$

$$\ln Z = N\left(\ln\frac{V}{N} - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\frac{2\pi m}{h^2} + 1\right)$$

Ideal gas in the classical limit $\ln Z = N(\ln \zeta - \ln N + 1)$

9.10 Evaluation of the partition function

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2}\frac{N}{\beta} = \frac{3}{2}NkT$$

$$S = k(\ln Z + \beta\bar{E}) = Nk\left(\ln\frac{V}{N} + \frac{3}{2}\ln T + \sigma_0\right)$$

$$\sigma_0 \equiv \frac{3}{2}\ln\frac{2\pi mk}{h^2} + \frac{5}{2}$$

Difference: in (7.3.5), h_0 is an arbitrary parameter; here, h is Plank constant

$$S = kN\left[\ln\frac{V}{N} + \frac{3}{2}\ln T + \sigma_0\right]$$

$$\sigma \equiv \frac{3}{2}\ln\left(\frac{2\pi mk}{h_0^2}\right) + \frac{3}{2}$$

7.3.5

Ideal gas in the classical limit

$$\ln Z = N(\ln \zeta - \ln N + 1)$$

9.11 Physical implications of quantum mechanical enumeration of states

Two points to be noted:

1, N! is automatically involved, and Gibbs paradox does not arise;

2, No arbitrary parameters in Z, and Plank constant is automatically involved

$$Z = \frac{\zeta^N}{N!}$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -kT\left(\frac{\partial \ln Z}{\partial N}\right)_{V,T}$$

$$\mu = -kT \ln \frac{\zeta}{N}$$

Ideal gas in the classical limit
9.11 Physical implications of quantum mechanical enumeration of states: examples

Thermal ionization of hydrogen atoms

Suppose H atom is in a container with V at high T

$$\boxed{H \rightleftarrows H^+ + e^-}$$

ε_0 is the energy for ionizing the atom

means that H atom has energy of $-\varepsilon_0$

$$-H + H^+ + e^- = 0$$ Chemical equilibrium

Law of mass action: (8.10.21)

$$\boxed{\frac{N_+ N_-}{N_H} = K_N}$$ Equilibrium constant

Ideal gas in the classical limit
9.11 Physical implications of quantum mechanical enumeration of states: examples

$$\boxed{\frac{N_+ N_-}{N_H} = K_N}$$

$$\boxed{K_N = \frac{\zeta_+ \zeta_-}{\zeta_H}}$$

Electron: (9.10.7)

$$\zeta_- = 2\frac{V}{h^3}(2\pi mkT)^{3/2}$$

spin up and down

Proton:

$$\zeta_+ = 2\frac{V}{h^3}(2\pi MkT)^{3/2}$$

spin up and down

H atom:

$$\zeta_H = 4\frac{V}{h^3}(2\pi MkT)^{3/2} e^{\epsilon_0/kT}$$

two spin up and down

$$\boxed{\zeta = \frac{V}{(2\pi\hbar)^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} = \frac{V}{h^3}(2\pi mkT)^{3/2}}$$

Ground state

Ideal gas in the classical limit
9.11 Physical implications of quantum mechanical enumeration of states: examples

$$K_N = \frac{\zeta_+ \zeta_-}{\zeta_H} \Rightarrow K_N = \frac{V}{h^3}(2\pi m k T)^{3/2}\, e^{-\epsilon_0/kT}$$

Equilibrium by energy and entropy.
Energy: larger ε_0 favors H atom; T→0;
While entropy favors ionization; T→ ∞

Equilibrium ← free energy minimization

Estimate the fraction of dissociation

$$\xi \equiv \frac{N_+}{N_0}$$

Ideal gas in the classical limit
9.11 Physical implications of quantum mechanical enumeration of states: examples

$$\xi \equiv \frac{N_+}{N_0}$$

$$N_+ = N_- = N_0\xi$$

$$N_H = N_0 - N_0\xi = N_0(1-\xi) \approx N_0$$

Suppose that concentration of H+ is small

Law of mass action gives

$$\xi^2 = \left(\frac{V}{N_0}\right)\left(\frac{2\pi mkT}{h^2}\right)^{3/2} e^{-\epsilon_0/kT}$$

$$\xi N_0 * \xi N_0 / N_0 = K_N$$

$$K_N = \frac{V}{h^3}(2\pi mkT)^{3/2}\, e^{-\epsilon_0/kT}$$

Ideal gas in the classical limit
9.11 Physical implications of quantum mechanical enumeration of states: examples

Vapor pressure of a solid

Considering solid Argon in equilibrium in its gas

$$\mu = -kT \ln \frac{\zeta}{N}$$

$$\zeta = \frac{V}{(2\pi\hbar)^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} = \frac{V}{h^3}(2\pi m kT)^{3/2}$$

$$\mu_1 = \mu_2$$

gas solid

$$\mu_1 = -kT \ln\left[\frac{V_1}{N_1}\left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right]$$

$$\mu_2 = \left(\frac{\partial F}{\partial N_2}\right)_{T,V_2} = -kT\left(\frac{\partial \ln Z}{\partial N_2}\right)_{T,V_2}$$

Solid: N_2 atoms in V_2

Ideal gas in the classical limit

9.11 Physical implications of quantum mechanical enumeration of states: examples

$$\mu_2 = \left(\frac{\partial F}{\partial N_2}\right)_{T,V_2} = -kT\left(\frac{\partial \ln Z}{\partial N_2}\right)_{T,V_2}$$

$$\bar{E}(T) = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_V = kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V$$

$$\ln Z(T) - \ln Z(T_0) = \int_{T_0}^{T} \frac{\bar{E}(T')}{kT'^2}\, dT'$$

V_2 is nearly a constant; $c(T)$ is the specific heat per atom

$$(\partial \bar{E}/\partial T)_V = N_2 c$$

Ideal gas in the classical limit
9.11 Physical implications of quantum mechanical enumeration of states: examples

$$\ln Z(T) - \ln Z(T_0) = \int_{T_0}^{T} \frac{\bar{E}(T')}{kT'^2}$$

$$(\partial \bar{E}/\partial T)_V = N_2 c,$$

$$\bar{E}(T) = -N_2\eta + N_2 \int_0^T c(T'')\, dT''$$

$$\underbrace{\bar{E}(0) \equiv -N_2\eta}$$

As T->0,

$$Z = \Sigma\, e^{-\beta E_r} \longrightarrow \Omega_0\, e^{-\beta(-N_2\eta)}$$

$$\ln Z(T_0) = \frac{N_2\eta}{kT_0} \qquad \text{as } T_0 \to 0$$

$$\ln Z(T) = \frac{N_2\eta}{kT} + N_2 \int_0^T \frac{dT'}{kT'^2} \int_0^{T'} c(T'')\, dT''$$

Ideal gas in the classical limit
9.11 Physical implications of quantum mechanical enumeration of states: examples

$$\ln Z(T) = \frac{N_2\eta}{kT} + N_2 \int_0^{T} \frac{dT'}{kT'^2} \int_0^{T'} c(T'')\, dT''$$

$$\mu_2(T) = -\eta - T \int_0^{T'} \frac{dT'}{T'^2} \int_0^{T'} c(T'')\, dT''$$

equilibrium

$$\ln\left[\frac{V_1}{N_1}\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}}\right] = -\frac{\mu_2(T)}{kT}$$

$$\ln\left[\frac{kT}{\bar{p}}\left(\frac{2\pi m k T}{h^2}\right)^{\frac{3}{2}}\right] = -\frac{\mu_2}{kT}$$

Ideal gas in the classical limit
9.11 Physical implications of quantum mechanical enumeration of states: examples

$$\ln \bar{p} = \ln \left[\frac{(2\pi m)^{3/2}}{h^3} (kT)^{5/2} \right] + \frac{\mu_2}{kT}$$

$$\bar{p}(T) = \frac{(2\pi m)^{3/2}}{h^3} (kT)^{5/2} \exp \left[-\frac{\eta}{kT} - \frac{1}{k} \int_0^T \frac{dT'}{T'^2} \int_0^{T'} c(T'')\, dT'' \right]$$

Can be estimated by Einstein model etc

Ideal gas in the classical limit
9.13 Electromagnetic radiation in thermal equilibrium inside enclosure

Electromagnetic radiation in equilibrium inside an closure V whose walls are maintained at T

Photons are continuously absorbed and reemitted by walls;
Radiation ←----→ a collection of photons

The state s of each photon can be specified by
magnitude, direction of momentum, and direction of polarization of electric field

Mean number of photon is given by the Planck distribution

$$\bar{n}_s = \frac{1}{e^{\beta\epsilon_s} - 1}$$

Ideal gas in the classical limit
9.13 Electromagnetic radiation in thermal equilibrium inside enclosure

The electric field E satisfy the wave equation

$$\boxed{\nabla^2 \mathbf{\mathcal{E}} = \frac{1}{c^2}\frac{\partial^2 \mathbf{\mathcal{E}}}{\partial t^2}}$$

This is satisfied by plane wave solution of form

$$\boxed{\mathbf{\mathcal{E}} = \mathbf{A}\, e^{i(\boldsymbol{\kappa}\cdot\mathbf{r}-\omega t)} = \mathbf{\mathcal{E}}_0(\mathbf{r})\, e^{-i\omega t}}$$

This is satisfied by plane wave solution of form

$$\boxed{\kappa = \frac{\omega}{c}, \qquad \kappa \equiv |\boldsymbol{\kappa}|}$$

Ideal gas in the classical limit
9.13 Electromagnetic radiation in thermal equilibrium inside enclosure

If the electromagnetic wave is regarded as quantized, then

$$\boxed{\left.\begin{aligned} \epsilon &= \hbar\omega \\ \boldsymbol{p} &= \hbar\boldsymbol{\kappa} \end{aligned}\right\}}$$

$$\boxed{|\boldsymbol{p}| = \frac{\hbar\omega}{c}}$$

E satisfies the Maxwell equation

$$\nabla \cdot \boldsymbol{\mathcal{E}} = 0,$$

$$\boldsymbol{\mathcal{E}} = \boldsymbol{A}\, e^{i(\boldsymbol{\kappa}\cdot\boldsymbol{r}-\omega t)} = \boldsymbol{\mathcal{E}}_0(\boldsymbol{r})\, e^{-i\omega t} \Rightarrow \boxed{\boldsymbol{\kappa}\cdot\boldsymbol{\mathcal{E}} = 0}$$

E is perpendicular to k;

for each k, there are two direction of E

Ideal gas in the classical limit
9.13 Electromagnetic radiation in thermal equilibrium inside enclosure

$$\kappa_x = \frac{2\pi}{L_x} n_x$$

$$\kappa_y = \frac{2\pi}{L_y} n_y$$

$$\kappa_z = \frac{2\pi}{L_z} n_z$$

Not all possible values of k are allowed

Suppose L>>λ

Let $f(\boldsymbol{\kappa})\, d^3\boldsymbol{\kappa}$ = the mean number of photons per unit volume, with *one* specified direction of polarization, whose wave vector lies between $\boldsymbol{\kappa}$ and $\boldsymbol{\kappa} + d\boldsymbol{\kappa}$.

$$f(\boldsymbol{\kappa})\, d^3\boldsymbol{\kappa} = \frac{1}{e^{\beta\hbar\omega} - 1} \frac{d^3\boldsymbol{\kappa}}{(2\pi)^3}$$

f(k) is only function of |k|

Ideal gas in the classical limit

9.13 Electromagnetic radiation in thermal equilibrium inside enclosure

$$\kappa_x = \frac{2\pi}{L_x} n_x$$
$$\kappa_y = \frac{2\pi}{L_y} n_y$$
$$\kappa_z = \frac{2\pi}{L_z} n_z$$

k=ω/c and k=(ω+d ω)/c;
including two polarization directions

$$2f(\kappa)(4\pi\kappa^2\, d\kappa) = \frac{8\pi}{(2\pi c)^3} \frac{\omega^2\, d\omega}{e^{\beta\hbar\omega} - 1}$$

$u(\omega, T)d\omega$ denote the mean energy per unit volume

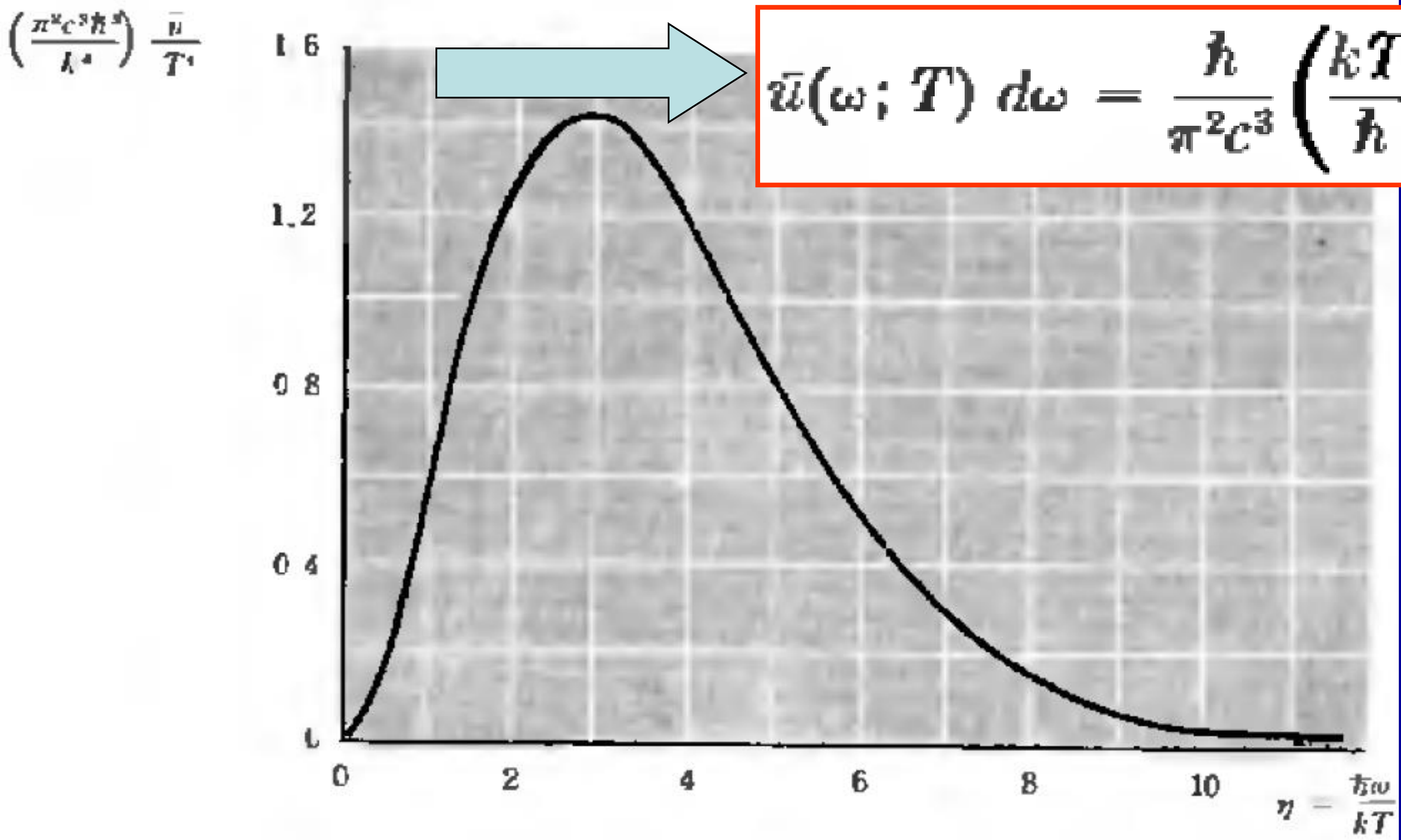
$$\bar{u}(\omega; T)\, d\omega = [2f(\kappa)(4\pi\kappa^2\, d\kappa)](\hbar\omega) = \frac{8\pi\hbar}{c^3} f(\kappa)\omega^3\, d\omega$$

$$\bar{u}(\omega; T)\, d\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3\, d\omega}{e^{\beta\hbar\omega} - 1}$$

Ideal gas in the classical limit
9.13 Electromagnetic radiation in thermal equilibrium inside enclosure

Use dimensionless parameter $\eta \equiv \beta\hbar\omega = \dfrac{\hbar\omega}{kT}$

$$\bar{u}(\omega; T)\, d\omega = \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^4 \frac{\eta^3\, d\eta}{e^\eta - 1}$$



Ideal gas in the classical limit
9.13 Electromagnetic radiation in thermal equilibrium inside enclosure

Note a simple scaling property

$$\frac{\hbar\bar{\omega}_1}{kT_1} = \frac{\hbar\bar{\omega}_2}{kT_2} = \bar{\eta}$$

$$\frac{\bar{\omega}_1}{T_1} = \frac{\bar{\omega}_2}{T_2}$$

Wien's displacement law

The mean total energy density in all frequencies

$$\bar{u}_0(T) = \int_0^\infty \bar{u}(T;\omega)\,d\omega$$

$$\bar{u}_0(T) = \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^4 \int_0^\infty \frac{\eta^3\,d\eta}{e^\eta - 1}$$

Ideal gas in the classical limit
9.13 Electromagnetic radiation in thermal equilibrium inside enclosure

$$\bar{u}_0(T) = \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^4 \int_0^\infty \frac{\eta^3\, d\eta}{e^\eta - 1}$$

$$\Rightarrow \quad \boxed{\bar{u}_0(T) \propto T^4}$$

Stefan-Boltzmann law

$$\boxed{\bar{u}_0(T) = \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^4 \int_0^\infty \frac{\eta^3\, d\eta}{e^\eta - 1}}$$

Can be integrated numerically

$$\int_0^\infty \frac{\eta^3\, d\eta}{e^\eta - 1} = \frac{\pi^4}{15}$$

$$\Rightarrow \quad \boxed{\bar{u}_0(T) = \frac{\pi^2}{15}\frac{(kT)^4}{(c\hbar)^3}}$$

Ideal gas in the classical limit
9.13 Electromagnetic radiation in thermal equilibrium inside enclosure

Calculation of radiation pressure

The pressure contribution from a photon in state s

$$-\partial\epsilon_s/\partial V$$

Mean pressure due to all photons

$$\bar{p} = \sum_s \bar{n}_s \left(-\frac{\partial \epsilon_s}{\partial V} \right)$$

$$\begin{aligned}\epsilon_s = \hbar\omega = \hbar c\kappa &= \hbar c(\kappa_x{}^2 + \kappa_y{}^2 + \kappa_z{}^2)^{\frac{1}{2}} \\ &= \hbar c \left(\frac{2\pi}{L}\right) (n_x{}^2 + n_y{}^2 + n_z{}^2)^{\frac{1}{2}}\end{aligned}$$

Ideal gas in the classical limit
9.13 Electromagnetic radiation in thermal equilibrium inside enclosure

Calculation of radiation pressure

$$\epsilon_s = CL^{-1} = CV^{-\frac{1}{3}},$$

$$\frac{\partial \epsilon_s}{\partial V} = -\frac{1}{3} C V^{-\frac{4}{3}} = -\frac{1}{3}\frac{\epsilon_s}{V}$$

$$\bar{p} = \sum_s \bar{n}_s \left(\frac{1}{3}\frac{\epsilon_s}{V}\right) = \frac{1}{3V}\sum_s \bar{n}_s \epsilon_s = \frac{1}{3V}\bar{E}$$

$$\bar{p} = \tfrac{1}{3}\bar{u}_0$$

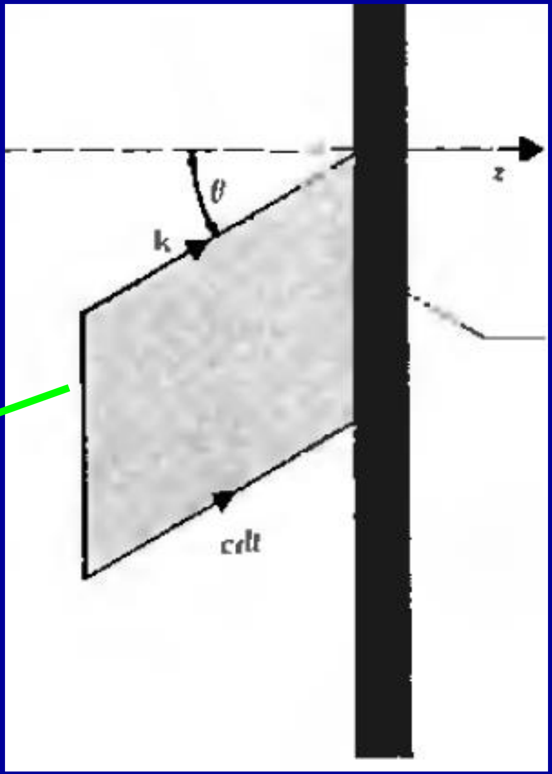
Ideal gas in the classical limit
9.13 Electromagnetic radiation in thermal equilibrium inside enclosure

Calculating radiation pressure by detailed kinetic argument

G+ is the momentum along z to wall;

G- is the momentum along z leaving wall

$$\boxed{\bar{p} = \frac{1}{dA}\left[G_z^{(+)} - \left(-G_z^{(+)}\right)\right] = \frac{2G_z^{(+)}}{dA}}$$



$$G_z^{(+)} = \frac{1}{dt}\int_{\kappa_z>0}[2f(\boldsymbol{\kappa})\,d^3\boldsymbol{\kappa}](c\,dt\,dA\cos\theta)(\hbar\kappa_z)$$

$$\boxed{\bar{p} = 2c\hbar\int_{\kappa_z>0}[2f(\boldsymbol{\kappa})\,d^3\boldsymbol{\kappa}]\frac{\kappa_z^{\,2}}{\kappa}}$$

Ideal gas in the classical limit
9.13 Electromagnetic radiation in thermal equilibrium inside enclosure

Calculating radiation pressure by detailed kinetic argument

$$\bar{p} = 2c\hbar \int_{\kappa_z>0} [2f(\boldsymbol{\kappa})\ d^3\boldsymbol{\kappa}] \frac{\kappa_z^2}{\kappa}$$

by symmetry

$$\bar{p} = c\hbar \int [2f(\kappa)\ d^3\boldsymbol{\kappa}] \frac{\kappa_z^2}{\kappa} = \frac{1}{3} c\hbar \int [2f(\kappa)\ d^3\boldsymbol{\kappa}] \frac{(\kappa_x^2 + \kappa_y^2 + \kappa_z^2)}{\kappa}$$

$$\bar{p} = \frac{1}{3} \int [2f(\boldsymbol{\kappa})\ d^3\boldsymbol{\kappa}](c\hbar\kappa) = \frac{1}{3}\bar{u}_0$$

Ideal gas in the classical limit
9.14 Nature of radiation in an enclosure

Define f(k,r) is the mean number of photons per unit volume at r with k in [k,k+dk] with polarization by α

1. The number f is independent of $\mathbf{r}$; i.e., the radiation field is homogeneous.

suppose f(k,r) are different at two positions;
Two identical small bodies are at these positions;
Different amounts of radiations are on these two bodies;
They will absorb different energy per unit time;
Their T will become different

$$f_\alpha(\boldsymbol{\kappa},\mathbf{r}) = f_\alpha(\boldsymbol{\kappa}) \qquad \text{independent of } \mathbf{r}$$

Ideal gas in the classical limit
9.14 Nature of radiation in an enclosure

Define f(k,r) is the mean number of photons per unit volume at r with k in [k,k+dk] with polarization by α

2. The number f is independent of the direction of $\boldsymbol{\kappa}$, but depends only on $|\boldsymbol{\kappa}|$; i.e., the rediation field is isotropic.

suppose f(k) depends on direction of k , i.e., f is greater if k points north than if points east;
Considering two identical bodies. The body on the north would have more radiation than that on east. Then they would the different temperature;

$$f_\alpha(\boldsymbol{\kappa}) = f_\alpha(\kappa), \qquad \text{where } \kappa \equiv |\boldsymbol{\kappa}|$$

Ideal gas in the classical limit
9.14 Nature of radiation in an enclosure

Define f(k,r) is the mean number of photons per unit volume at r with k in [k,k+dk] with polarization by α

3. The number f is independent of the direction of polarization of the radiation, i.e., the radiation field in the enclosure is unpolarized.

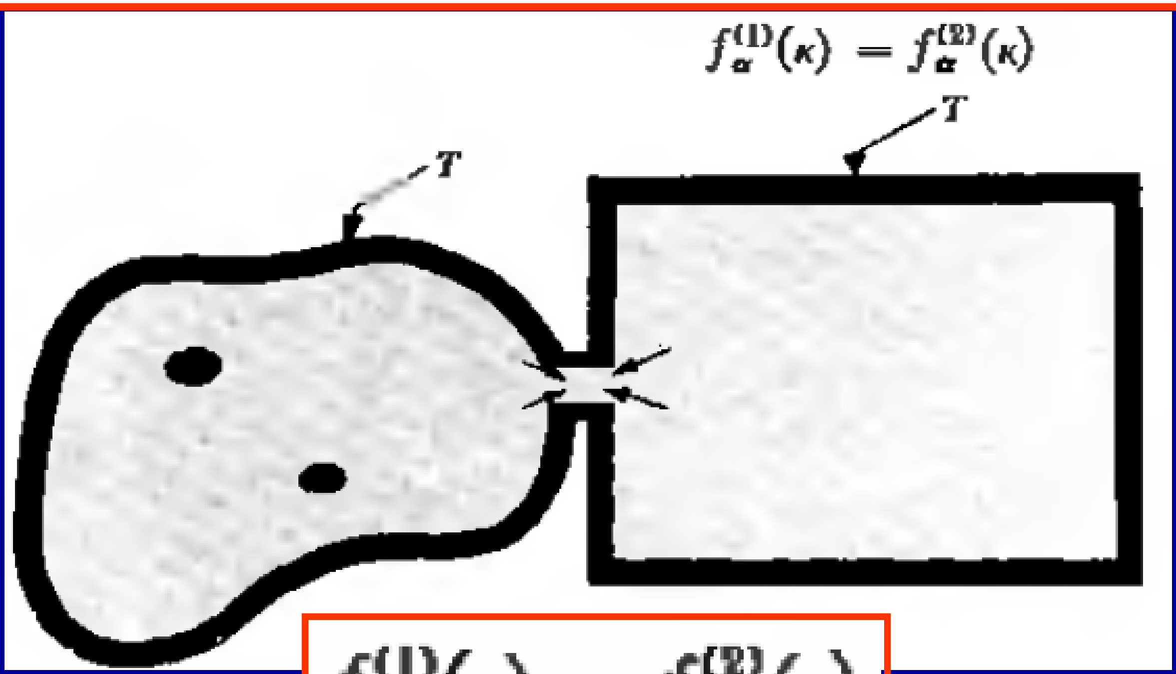
suppose f(k) depends on direction of polarization;
Considering two small bodies surrounded by filters which transmit different directions of polarizations;
Then they have different radiations and different T.

$$f_1(\kappa) = f_2(\kappa)$$

Ideal gas in the classical limit
9.14 Nature of radiation in an enclosure

Define f(k,r) is the mean number of photons per unit volume at r with k in [k,k+dk] with polarization by α

4. The function f does not depend on the shape nor volume of the enclosure, nor on the material of which it is made, nor on the bodies it may contain.



$$\boxed{f_\alpha^{(1)}(\kappa) = f_\alpha^{(2)}(\kappa)}$$

Conduction electrons in metal
9.16 consequence of Fermi Dirac distribution

Electron obeys FD statistics

$$\bar{n}_s = \frac{1}{e^{\alpha+\beta\epsilon_s}+1} = \frac{1}{e^{\beta(\epsilon_s-\mu)}+1}$$

$$\mu \equiv -\frac{\alpha}{\beta} = -kT\alpha$$

Fermi energy

$$\sum_s \bar{n}_s = \sum_s \frac{1}{e^{\beta(\epsilon_s-\mu)}+1} = N$$

Fermi function $$F(\epsilon) \equiv \frac{1}{e^{\beta(\epsilon-\mu)}+1}$$

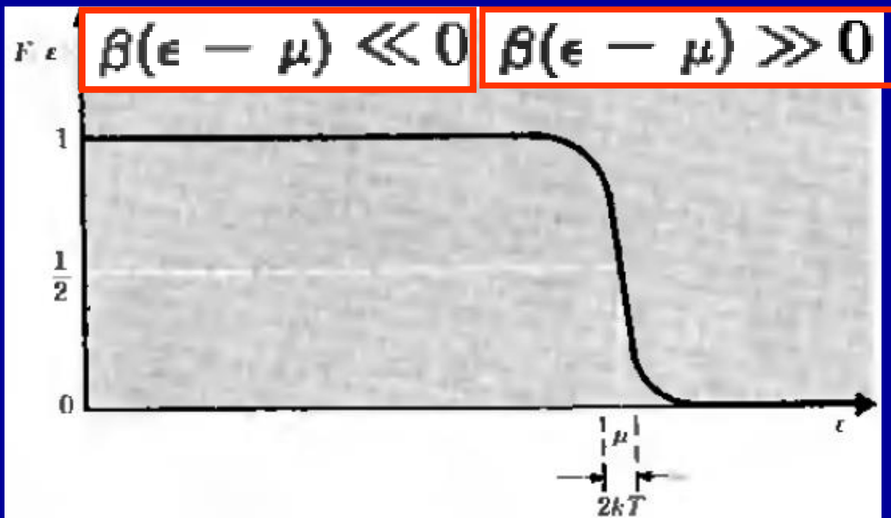
$e^{\beta(\epsilon-\mu)} \gg 1$ → **Maxwell-Boltzmann distribution**

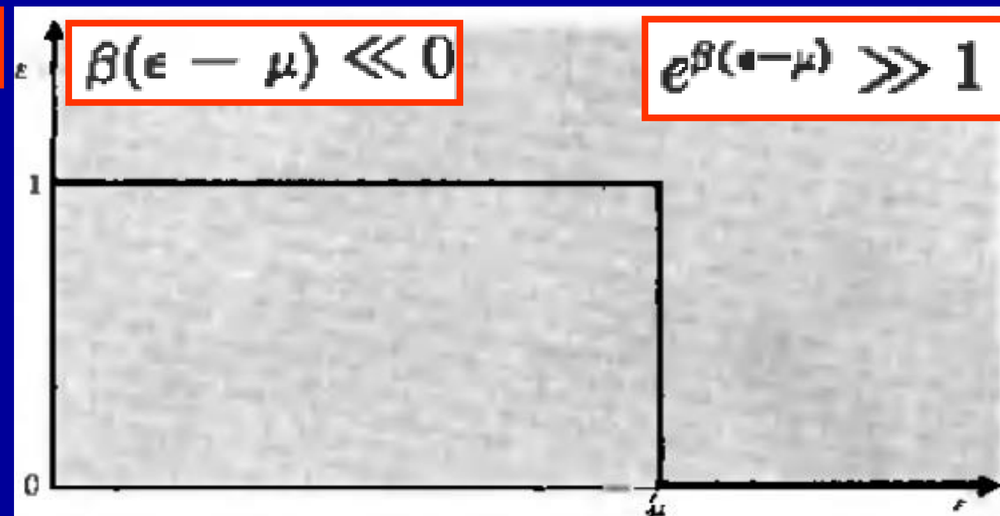
$\beta(\epsilon-\mu) \ll 0$ → $F(\epsilon) = 1.$

Conduction electrons in metal

9.16 consequence of Fermi Dirac distribution

Electron obeys FD statistics





$$F(\epsilon) \equiv \frac{1}{e^{\beta(\epsilon-\mu)}+1}$$

Calculate Fermi energy of a gas at T=0;

$$\boxed{\epsilon = \frac{p^2}{2m} = \frac{\hbar^2\kappa^2}{2m}}$$

Conduction electrons in metal
9.16 consequence of Fermi Dirac distribution

Electron obeys FD statistics

At T=0, all states of lowest energy are filled up to Fermi E

$$\mu_0 = \frac{p_F{}^2}{2m} = \frac{\hbar^2 \kappa_F{}^2}{2m}$$

All states with k<k_F are filled; while those with k<k_F are empty

Volume of sphere with k_F $\left(\frac{4}{3}\pi \kappa_F{}^3\right)$

In k space, there are $(2\pi)^{-3}V$ **translational states**

For each translational state, a electron has two spin states

Conduction electrons in metal

9.16 consequence of Fermi Dirac distribution

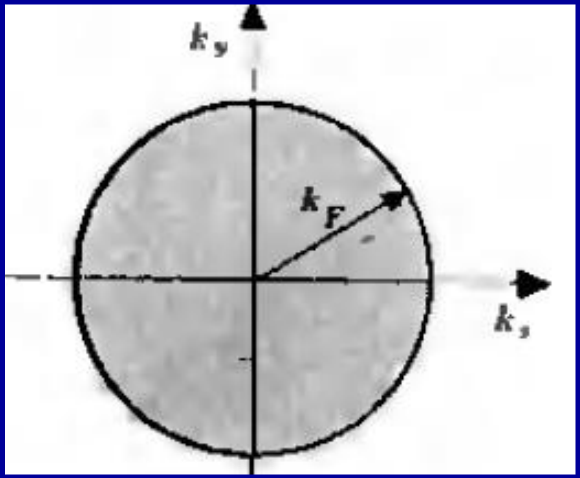
Electron obeys FD statistics

At T=0, all states of lowest energy are filled up to Fermi E

$$\boxed{2\frac{V}{(2\pi)^3}\left(\frac{4}{3}\pi\kappa_F^3\right) = N}$$

$$\Rightarrow \quad \kappa_F = \left(3\pi^2\frac{N}{V}\right)^{\frac{1}{3}}$$

$$\Rightarrow \quad \lambda_F \equiv \frac{2\pi}{\kappa_F} = \frac{2\pi}{(3\pi^2)^{\frac{1}{3}}}\left(\frac{V}{N}\right)^{\frac{1}{3}}$$



All states with $\lambda<\lambda_F$ are occupied, while other are empty

$$\mu_0 = \frac{\hbar^2}{2m}\kappa_F^2 = \frac{\hbar^2}{2m}\left(3\pi^2\frac{N}{V}\right)^{\frac{2}{3}}$$

Conduction electrons in metal
9.16 consequence of Fermi Dirac distribution

Electron obeys FD statistics

At T=0, all states of lowest energy are filled up to Fermi E

$$\mu_0 = \frac{\hbar^2}{2m}\kappa_F^2 = \frac{\hbar^2}{2m}\left(3\pi^2\frac{N}{V}\right)^{\frac{2}{3}}$$

Estimate T_F for copper

$$\boxed{T_F \equiv \frac{\mu_0}{k} \approx 80{,}000°\mathrm{K}}$$

At room T $\quad kT \ll \mu_0$

$$\mu \approx \mu_0$$

Conduction electrons in metal
9.16 consequence of Fermi Dirac distribution

Electron obeys FD statistics

At T=0, Cv=?

$$\boxed{C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V}$$

If electrons obeyed MB statistics; equipartition theorem gives

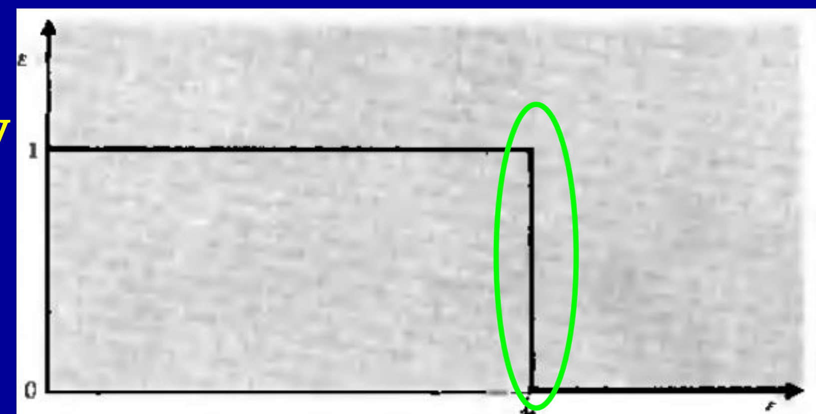
$$\boxed{\bar{E} = \tfrac{3}{2}NkT \qquad \text{and} \qquad C_V = \tfrac{3}{2}Nk}$$

Conduction electrons in metal
9.16 consequence of Fermi Dirac distribution

Electron obeys FD statistics

In fact, electrons obey FD statistics

$\epsilon \ll \mu,$ **All states are completely filled and remain so when T is changed**



The small energy range kT near μ; in this region, $F \propto e^{-\beta\epsilon}$ ⇒ $\frac{3}{2}k$

$$\boxed{N_{\text{eff}} \approx \rho(\mu)kT}$$

⇒ $$\boxed{C_V \approx N_{\text{eff}}\left(\tfrac{3}{2}k\right) \approx \tfrac{3}{2}k^2\rho(\mu)T}$$

Conduction electrons in metal

9.16 consequence of Fermi Dirac distribution

Electron obeys FD statistics

Roughly only a fraction of kT/μ electrons are in the tail

$$N_{eff} \approx \left(\frac{kT}{\mu}\right) N$$

$$C_V \approx \frac{3}{2} Nk \left(\frac{kT}{\mu}\right) = \nu \frac{3}{2} R \left(\frac{T}{T_F}\right)$$

$$c_V^{(e)} = \gamma T$$

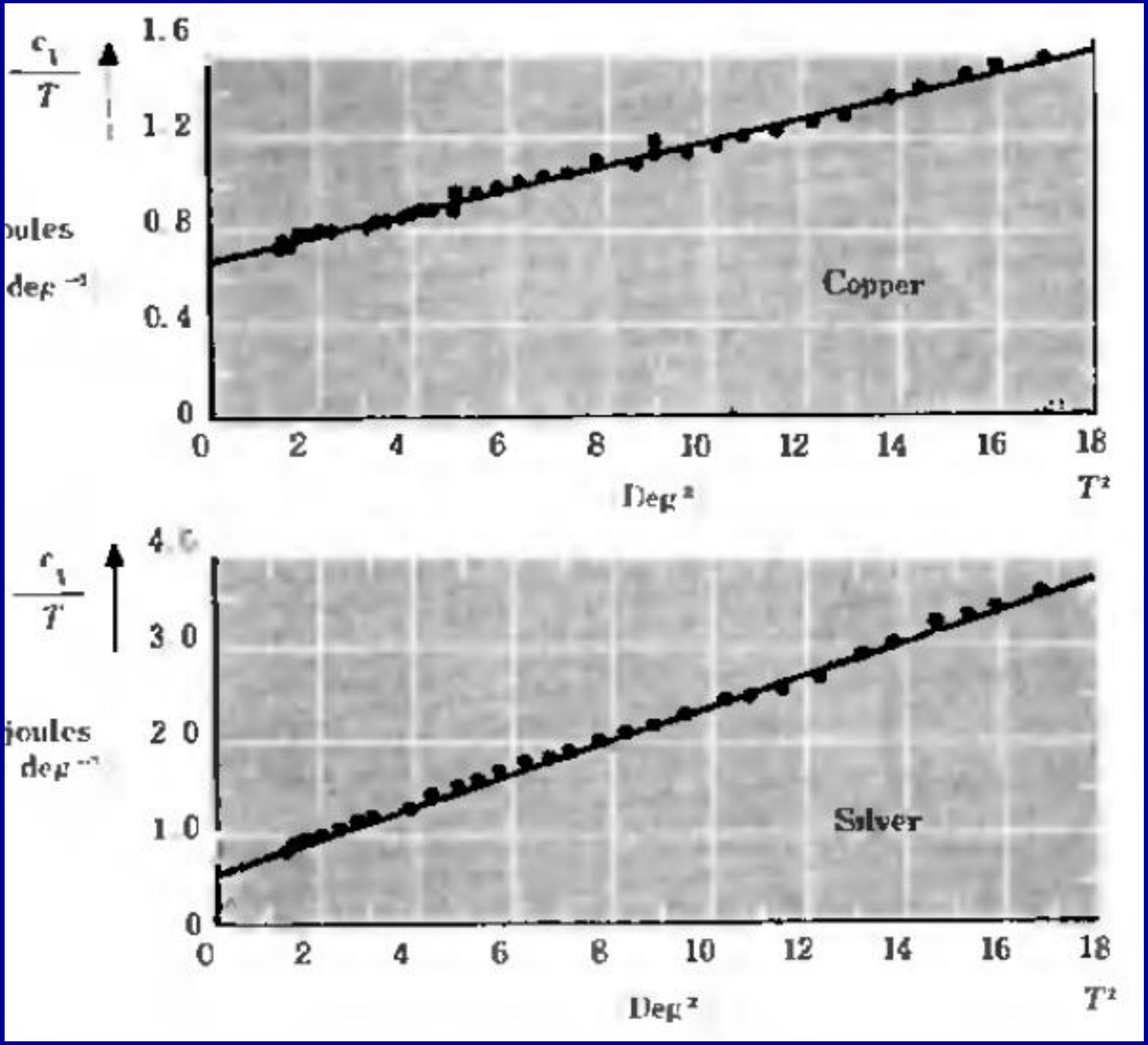
$$c_V = c_V^{(e)} + c_V^{(L)} = \gamma T + A T^3$$

Conduction electrons in metal

9.16 consequence of Fermi Dirac distribution

Electron obeys FD statistics

$$\frac{c_V}{T} = \gamma + AT^2$$

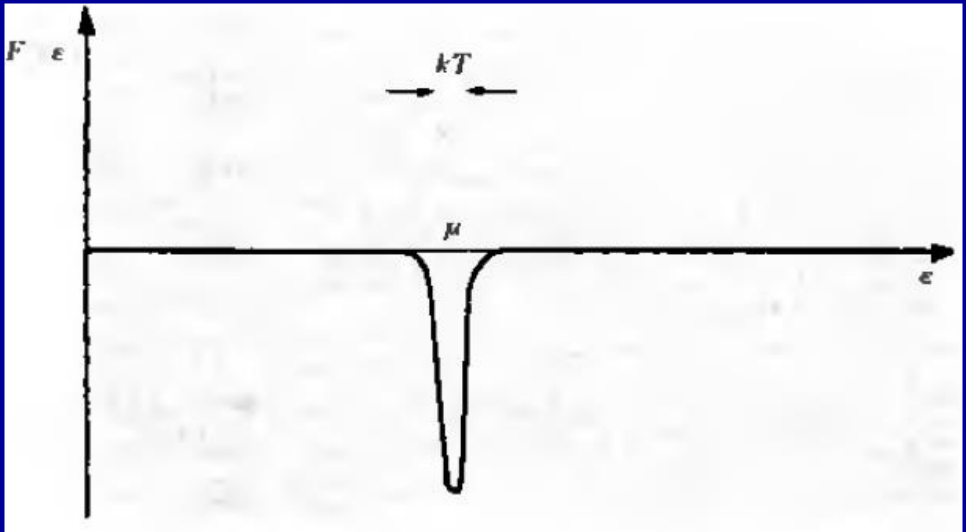


Conduction electrons in metal
9.17 Quantitative calculation of electronic specific heat

$$\bar{E} = \sum_r \frac{\epsilon_r}{e^{\beta(\epsilon_r - \mu)} + 1}$$

$$\bar{E} = 2\int F(\epsilon)\epsilon\, \rho(\epsilon)\, d\epsilon = 2\int_0^\infty \frac{\epsilon}{e^{\beta(\epsilon-\mu)} + 1}\rho(\epsilon)\, d\epsilon$$

$$2\int F(\epsilon)\rho(\epsilon)\, d\epsilon = 2\int_0^\infty \frac{1}{e^{\beta(\epsilon-\mu)} + 1}\rho(\epsilon)\, d\epsilon = N$$



Conduction electrons in metal
9.17 Quantitative calculation of electronic specific heat

Evaluation of integral $\int_0^\infty F(\epsilon)\varphi(\epsilon)\,d\epsilon$

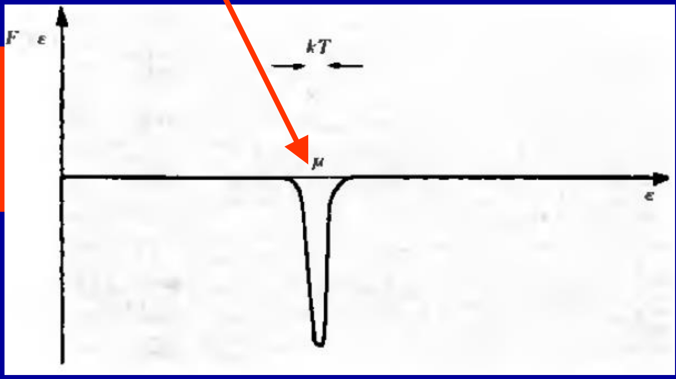
$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\,d\epsilon = [F(\epsilon)\psi(\epsilon)]_0^\infty - \int_0^\infty F'(\epsilon)\psi(\epsilon)\,d\epsilon$$

$F(\infty) = 0,$

$\psi(0) = 0$

$\psi(\epsilon) \equiv \int_0^\epsilon \varphi(\epsilon')\,d\epsilon'$

$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\,d\epsilon = -\int_0^\infty F'(\epsilon)\psi(\epsilon)\,d\epsilon$$



Conduction electrons in metal

9.17 Quantitative calculation of electronic specific heat

Evaluation of integral

$$\psi(\epsilon) = \psi(\mu) + \left[\frac{d\psi}{d\epsilon}\right]_\mu (\epsilon - \mu) + \frac{1}{2}\left[\frac{d^2\psi}{d\epsilon^2}\right]_\mu (\epsilon - \mu)^2 + \cdots$$

$$= \sum_{m=0}^{\infty} \frac{1}{m!}\left[\frac{d^m\psi}{d\epsilon^m}\right]_\mu (\epsilon - \mu)^m$$

$$\boxed{\int_0^\infty F\varphi\, d\epsilon = -\sum_{m=0}^{\infty} \frac{1}{m!}\left[\frac{d^m\psi}{d\epsilon^m}\right]_\mu \int_0^\infty F'(\epsilon)(\epsilon - \mu)^m\, d\epsilon}$$

Conduction electrons in metal
9.17 Quantitative calculation of electronic specific heat

Evaluation of integral

$$\int_0^\infty F'(\epsilon)(\epsilon-\mu)^m\,d\epsilon = -\int_0^\infty \frac{\beta e^{\beta(\epsilon-\mu)}}{(e^{\beta(\epsilon-\mu)}+1)^2}(\epsilon-\mu)^m\,d\epsilon$$

$$= -\beta^{-m}\int_{-\beta\mu}^{\infty}\frac{e^x}{(e^x+1)^2}x^m\,dx$$

$$\boxed{\int_0^\infty F'(\epsilon)(\epsilon-\mu)^m\,d\epsilon = -(kT)^m I_m}$$

$$I_m \equiv \int_{-\infty}^{\infty}\frac{e^x}{(e^x+1)^2}x^m\,dx$$

$$\boxed{\frac{e^x}{(e^x+1)^2} = \frac{1}{(e^x+1)(e^{-x}+1)}}$$ even function for x

Conduction electrons in metal
9.17 Quantitative calculation of electronic specific heat

Evaluation of integral

$$I_m \equiv \int_{-\infty}^{\infty} \frac{e^x}{(e^x+1)^2} x^m \, dx$$

$$I_m = 0 \qquad \text{if } m \text{ is odd}$$

$$I_0 = \int_{-\infty}^{\infty} \frac{e^x}{(e^x+1)^2} dx = -\left[\frac{1}{e^x+1}\right]_{-\infty}^{\infty} = 1$$

$$\int_0^\infty F\varphi \, d\epsilon = \sum_{m=0}^{\infty} I_m \frac{(kT)^m}{m!} \left[\frac{d^m\psi}{d\epsilon^m}\right]_\mu = \psi(\mu) + I_2 \frac{(kT)^2}{2} \left[\frac{d^2\psi}{d\epsilon^2}\right]_\mu + \cdot$$

$$I_2 = \frac{\pi^2}{3}$$

$$\int_0^\infty F(\epsilon)\varphi(\epsilon) \, d\epsilon = \int_0^\mu \varphi(\epsilon) \, d\epsilon + \frac{\pi^2}{6} (kT)^2 \left[\frac{d\varphi}{d\epsilon}\right]_\mu + \cdots$$

Conduction electrons in metal
9.17 Quantitative calculation of electronic specific heat

$$\int_0^\infty F(\epsilon)\varphi(\epsilon)\,d\epsilon = \int_0^\mu \varphi(\epsilon)\,d\epsilon + \frac{\pi^2}{6}(kT)^2\left[\frac{d\varphi}{d\epsilon}\right]_\mu + \cdots$$

Calculation of specific heat

$$\bar{E} = 2\int_0^\mu \epsilon\rho(\epsilon)\,d\epsilon + \frac{\pi^2}{3}(kT)^2\left[\frac{d}{d\epsilon}(\epsilon\rho)\right]_\mu$$

$$2\int_0^\mu \epsilon\rho(\epsilon)\,d\epsilon = 2\int_0^{\mu_0} \epsilon\rho(\epsilon)\,d\epsilon + 2\int_{\mu_0}^\mu \epsilon\rho(\epsilon)\,d\epsilon =$$

$$= \bar{E}_0 + 2\mu_0\rho(\mu_0)(\mu - \mu_0)$$

$$\bar{E} = \bar{E}_0 + 2\mu_0\rho(\mu_0)(\mu - \mu_0) + \frac{\pi^2}{3}(kT)^2[\rho(\mu_0) + \mu_0\rho'(\mu_0)]$$

Normalization:

$$2\int_0^\mu \rho(\epsilon)\,d\epsilon + \frac{\pi^2}{3}(kT)^2\rho'(\mu) = N$$

Conduction electrons in metal

9.17 Quantitative calculation of electronic specific heat

Calculation of specific heat

Normalization:

$$2\int_0^{\mu}\rho(\epsilon)\,d\epsilon+\frac{\pi^2}{3}(kT)^2\rho'(\mu)=N$$

$$2\int_0^{\mu}\rho(\epsilon)\,d\epsilon=2\int_0^{\mu_0}\rho(\epsilon)\,d\epsilon+2\int_{\mu_0}^{\mu}\rho(\epsilon)\,d\epsilon=N+2\rho(\mu_0)(\mu-\mu_0)$$

$$\boxed{2\rho(\mu_0)(\mu-\mu_0)+\frac{\pi^2}{3}(kT)^2\rho'(\mu_0)=0}$$

$$\boxed{(\mu-\mu_0)=-\frac{\pi^2}{6}(kT)^2\frac{\rho'(\mu_0)}{\rho(\mu_0)}}$$

Conduction electrons in metal
9.17 Quantitative calculation of electronic specific heat

Calculation of specific heat

$$\boxed{(\mu - \mu_0) = -\frac{\pi^2}{6}(kT)^2\frac{\rho'(\mu_0)}{\rho(\mu_0)}}$$

$$\bar{E} = \bar{E}_0 - \frac{\pi^2}{3}(kT)^2\mu_0\rho'(\mu_0) + \frac{\pi^2}{3}(kT)^2[\rho(\mu_0) + \mu_0\rho'(\mu_0)]$$

$$\boxed{\bar{E} = \bar{E}_0 + \frac{\pi^2}{3}(kT)^2\rho(\mu_0)}$$

$$\boxed{C_V = \frac{\partial \bar{E}}{\partial T} = \frac{2\pi^2}{3}k^2\rho(\mu_0)T}$$

?

Conduction electrons in metal

9.17 Quantitative calculation of electronic specific heat

Calculation of specific heat

$$C_V = \frac{\partial \bar{E}}{\partial T} = \frac{2\pi^2}{3} k^2 \rho(\mu_0) T$$

$$\rho(\epsilon)\, d\epsilon = \frac{V}{(2\pi)^3}\left(4\pi\kappa^2 \frac{d\kappa}{d\epsilon}\, d\epsilon\right) = \frac{V}{4\pi^2}\frac{(2m)^{3/2}}{\hbar^3}\epsilon^{1/2}\, d\epsilon$$

$$\mu_0 = \frac{\hbar^2}{2m}\left(3\pi^2 \frac{N}{V}\right)^{2/3}$$

$$\rho(\mu_0) = V\frac{m}{2\pi^2\hbar^2}\left(3\pi^2\frac{N}{V}\right)^{1/3}$$

$$\rho(\mu_0) = \left[\frac{m}{2\pi^2\hbar^2}(3\pi^2 N)^{1/3}\right]\left[\frac{1}{\mu_0}\frac{\hbar^2}{2m}(3\pi^2 N)^{2/3}\right] = \frac{3}{4}\frac{N}{\mu_0}$$

Conduction electrons in metal

9.17 Quantitative calculation of electronic specific heat

Calculation of specific heat

$$\boxed{C_V = \frac{\partial \bar{E}}{\partial T} = \frac{2\pi^2}{3} k^2 \rho(\mu_0) T}$$

$$C_V = \frac{\pi^2}{2} k^2 \frac{N}{\mu_0} T = \frac{\pi^2}{2} kN \frac{kT}{\mu_0}$$

$$\boxed{c_V = \frac{3}{2} R \left(\frac{\pi^2}{3} \frac{kT}{\mu_0}\right)}$$

$$\boxed{C_V \approx \frac{3}{2} Nk \left(\frac{kT}{\mu}\right) = \nu \frac{3}{2} R \left(\frac{T}{T_F}\right)}$$

Crude estimate

Class-work

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Homework

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