Two-dimensional metal


Area of the circle

$$
2 \frac{\pi k^{2}}{\left(\frac{2 \pi}{L}\right)^{2}}=N \longmapsto N=\frac{L^{2}}{2 \pi} k^{2}=(\quad) \quad D(E)=\frac{d N}{d E}=(\quad)
$$

The realized distribution of $N_{\mathrm{i}}$ minimizes the Gibbs free energy

$$
F=E-T S-\mu N \text { where } E=\sum N_{\mathrm{i}} E_{\mathrm{i}}, \quad N=\sum N_{\mathrm{i}} \text {. }
$$

$f(E)$

50000 K for metals $\longrightarrow \underset{\mathrm{F}}{\longrightarrow}$

Fermi-Dirac distribution When $T=0$ :

$$
\begin{array}{ll}
E<\mu & f(E)=\frac{1}{e^{-\infty}+1}=[\quad \\
E>\mu & f(E)=\frac{1}{e^{+\infty}+1}=(\quad)
\end{array}
$$

$$
E_{\mathrm{F}}=\mu: \text { chemical potential }
$$

$$
\begin{aligned}
& \text { So differentiation of } F \text { as for } N_{\mathrm{i}} \text { is zero to give, } \\
& \left.\begin{array}{l}
\text { So differentiation of } F \text { as for } N_{\mathrm{i}} \text { is zero to give, } \\
\left.\begin{array}{cc}
\frac{\partial F}{\partial N_{i}}=E_{i}+k_{\mathrm{B}} T\left(\ln N_{i}-\ln \left(C_{i}-N_{i}\right)\right)-\mu=0 \\
\frac{C_{i}-N_{i}}{N_{i}}=\left(e^{\frac{E_{i}-\mu}{k_{\mathrm{B}} T}}\right)
\end{array}\right)
\end{array} \begin{array}{c}
\text { Occupation } \\
f\left(E_{i}\right)=\frac{N_{i}}{C_{i}}=
\end{array}\right]
\end{aligned}
$$

Fermi statistics: only one electron can occupy a state.


## 0000000

## Occupied by $N_{\mathrm{i}}$ electrons

$N_{\mathrm{i}}$ electrons are in the $C_{\mathrm{i}}$ states with energy $E$.
We cannot distinguish $N_{\mathrm{i}}$ electrons, so that the statistical weight is the number to choose $N_{\mathrm{i}}$ from $C_{\mathrm{i}}$ :

The definition of entropy in statistical mechanics is

$$
W_{i}=\frac{C_{i}!}{N_{i}!\left(C_{i}-N_{i}\right)!}
$$

$$
\begin{aligned}
S & =k_{\mathrm{B}} \ln W=k_{\mathrm{B}} \ln \prod_{i} W_{i}=k_{\mathrm{B}} \sum_{i} \ln W_{i}=k_{\mathrm{B}} \sum_{i} \ln \frac{C_{i}!}{N_{i}!\left(C_{i}-N_{i}\right)!} \\
= & k_{\mathrm{B}} \sum_{\mathrm{i}}\left(C_{i} \ln C_{i}-N_{i} \ln N_{i}-\left(C_{i}-N_{i}\right) \ln \left(C_{i}-N_{i}\right)\right) \\
& \text { Stirling' equation } \ln N!=N \ln N-N
\end{aligned}
$$

The real electron number is $D(E) \times f(E)$


Internal energy of metal electrons

$$
U(T)=\int_{0}^{\infty}\left(E-E_{\mathrm{F}}\right) D(E) f(E) d E
$$

$$
\text { Specific heat Measured from } E_{\mathrm{F}}=0 \text {. }
$$

$$
C_{V}=\frac{\partial U}{\partial T}=\int_{0}^{\infty}\left(E-E_{\mathrm{F}}\right) D(E) \frac{\partial f(E)}{\partial T} d E
$$

$$
\text { where } f\left(E_{i}\right)=\frac{1}{e^{\frac{E_{i}-\mu}{k_{\mathrm{B}} T}}+1}=\frac{1}{e^{x}+1} \quad x=\frac{E-\mu}{k_{\mathrm{B}} T} \text { gives }
$$

$$
\frac{\not \partial}{\partial \Gamma}=(\quad)^{+1} d x=\frac{d E}{k_{\mathrm{B}} T}
$$

$$
\frac{\partial f(E)}{\partial T} \text { is nonzero only near } E_{\mathrm{F}} \text {. }
$$


so that approximated to be
$D(E) \sim D\left(E_{\mathrm{F}}\right)$.


If free electron is an ideal gas, according to the Dulong-Petit theorem, the specific heat is $C_{\mathrm{v}}=3 R$. However, it is less than
$-\frac{T}{T_{\mathrm{F}}} \approx \frac{300 \mathrm{~K}}{50000 \mathrm{~K}} \approx 10^{-2}$Owing to the Fermi distribution, only $k_{\mathrm{B}} T$ electrons near $E_{\mathrm{F}}$ are excited, and contribute to the specific heat.Metal electrons are "Fermi" particles!
Only phonons
Fermi gas
cf. Classical gas
At low temperatures ( $<50 \mathrm{~K}$ ), the lattice vibration (photon) decays as $C_{\mathrm{v}} \propto T^{3}$ so that


$$
\underset{\mathrm{v}}{C_{\mathrm{v}}=\gamma T+\beta T^{3}} \text { free electron phonon } \quad \frac{C_{v}}{T}=\gamma+\beta T^{2}
$$

Experimental estimation of $\gamma \rightarrow D\left(E_{\mathrm{F}}\right)$ from the low-temperature ( $<4 \mathrm{~K}$ ) specific heat.


$$
\begin{aligned}
C_{V} & =D\left(E_{\mathrm{F}}\right) \int_{0}^{\infty}\left(E-E_{\mathrm{F}}\right) \frac{\partial f(E)}{\partial T} d E \\
& =D\left(E_{\mathrm{F}}\right) \int_{0}^{\infty}\left(k_{\mathrm{B}} T x\right) \frac{x}{T} \frac{e^{x}}{\left(e^{x}+1\right)^{2}} k_{\mathrm{B}} T d x \\
& =k_{\mathrm{B}}^{2} T D\left(E_{\mathrm{F}}\right) \underbrace{\left(x^{2} \frac{e^{x}}{\left(e^{x}+1\right)^{2}} d x\right.} \pi^{2 / 3} \text { from table of integrals } \\
& =\left(\begin{array}{ll}
C_{\mathrm{V}}=\gamma T \\
\text { Specific heat of metal electrons }
\end{array}\right.
\end{aligned}
$$

or using $\quad D\left(E_{\mathrm{F}}\right)=\frac{3}{2} \frac{N}{E_{\mathrm{F}}}=\frac{3}{2} \frac{N}{k_{\mathrm{B}} T_{\mathrm{F}}} T_{\mathrm{F}}$ : Fermi temperature
$C_{v}=\frac{\pi^{2}}{3} \frac{3}{2} \frac{N}{k_{\mathrm{B}} T_{\mathrm{F}}} k_{\mathrm{B}}^{2} T=\frac{\pi^{2}}{2} N k_{\mathrm{B}} \frac{T}{T_{\mathrm{F}}}=\frac{\pi^{2}}{2} n R \frac{T}{T_{\mathrm{F}}}$
Gas constant

Bose-Einstein statistics
Insert $N_{\mathrm{i}}$ particles in $C_{\mathrm{i}}$ levels, allowing any particles in the same level.

The number to arrange $N_{\mathrm{i}}$ particles and $C_{i}-1$ partitions.

$$
W_{i}=\frac{\left(C_{i}+N_{i}-1\right)!}{N_{i}!\left(C_{i}-1\right)!}
$$


$C_{\mathrm{i}}-1 \rightarrow C_{\mathrm{i}}$ gives

$$
\ln W_{i}=\left(C_{i}+N_{i}\right) \ln \left(C_{i}+N_{i}\right)-N_{i} \ln N_{i}-C_{i} \ln C_{i}
$$

Put this in $F=E-T S-\mu N$, and differentiation as for $N_{\mathrm{i}}$ is put zero to
$f\left(E_{i}\right)=\frac{N_{i}}{C_{i}}=[\quad$ Bose-Einstein statistics

$$
\begin{array}{lll}
T \rightarrow 0 \\
E_{\mathrm{i}}-\mu>0 & e^{+\infty \rightarrow+\infty} & f(E) \rightarrow 0 \\
E_{\mathrm{i}}-\mu=0 & e^{0 \rightarrow 1} & f(E) \rightarrow+\infty
\end{array}
$$

$\mu \stackrel{+}{E_{-}}$

$$
E_{\mathrm{i}}-\mu \rightarrow \hbar \omega \text { gives } \quad f\left(E_{i}\right)=\frac{1}{e^{\frac{h \omega}{k_{\mathrm{B}} T}}-1}
$$

Planck distribution

Phonon (lattice vibration) is Bose-Einstein particle.
Photon (light) is the same $\rightarrow$ black body

$$
f\left(E_{i}\right)=\frac{1}{e^{\frac{E_{i}-\mu}{k_{\mathrm{B}} T}} \pm 1}\left\{\begin{array}{l}
+ \\
-(
\end{array}\right.
$$

Quantum statistics
$E-\mu \gg k_{\mathrm{B}} T$ leads to $e^{\text {large }} \gg 1 \quad f\left(E_{i}\right)=e^{-\frac{E_{i}-\mu}{k_{\mathrm{B}} T}}$
Boltzmann (classical) distribution

## Classical distribution

Each $i$-th state has $n_{i}$ particles, with the
total $N=\sum n_{i}$ particles.
The statistical weight is

```
\mp@subsup{n}{4}{4}
n
```



SO

$$
\begin{aligned}
& W=\frac{N!}{n_{1}!n_{2}!n_{3}!\cdot \cdots} \quad \ln N!=N \ln N \\
& \ln W=\ln \frac{N!}{n_{1}!n_{2}!n_{3}!\cdot \cdots}=N \ln N-\sum_{i} n_{i} \ln n_{i}
\end{aligned}
$$

Put this in $F=E-T S-\mu N \quad\left(S=k_{B} \ln W\right)$

$$
F=\sum_{i} E_{i} n_{i}-k_{\mathrm{B}} T\left(N \ln N-\sum_{i} n_{i} \ln n_{i}\right)-\mu \sum_{i} n_{i}
$$

Differentiation as for $n_{\mathrm{i}}$ is zero to give,

$$
f\left(E_{i}\right)=\frac{1}{e^{\frac{E_{i}-\mu}{k_{\mathrm{B}} T}}-1}
$$

Light (photon), Lattice vibration (phonon), ${ }^{4} \mathrm{He}$
Boltzmann distribution : classical particles
$\mu$
$f(E)$
$f\left(E_{i}\right)=e^{-\frac{E_{i}-\mu}{k_{\mathrm{B}} T}}$

$$
f\left(E_{i}\right)=\frac{1}{e^{\frac{E_{i}-\mu}{k_{\mathrm{B}} T}}+1}
$$

Fermi distribution : Particles with half-integer spin
quantum number : electron, proton, neutron, ${ }^{3} \mathrm{He}$

Everything approaches to Boltzmann at $E_{\mathrm{i}}-\mu \gg k_{\mathrm{B}} T$.

One-dimensional metal

$$
E=\frac{\hbar^{2} k_{x}^{2}}{2 m}=\text { const. leads to } k_{x}=k_{\mathrm{F}}=\text { const. }
$$

 $=$ does not move)

