$\boxed{\text{Kovová väzba}}$

"atóm" = škatuľa $a \times a \times a$ → vln. funkcia zákl. stavu

$$\boxed{H = \frac{\vec{P}^2}{2m}}$$

$$\psi \sim \sin\frac{\pi x}{a}\sin\frac{\pi y}{a}\sin\frac{\pi z}{a}$$

energia zákl. stavu $\varepsilon_0 = \frac{3\pi^2}{2}\frac{\hbar^2}{ma^2}$

N "atómov": energia $N\varepsilon_0$ (1 el/atóm)

Ukážeme, že energia sa zníži pri delokalizovaní elektrónov v celom kryštáli: uvažujme kryštál $\Omega = L^3$ (kocka), pričom $\Omega = Na^3$. Nech $N \gg 1$. Potom $L \gg a$ a energie elektrónov závisia slabo od okraj. podmienok.

Zvolíme (Born - von Kármán):

$$\psi(x,y,z+L) = \psi(x,y,z)$$
$$\psi(x,y+L,z) = \psi(x,y,z)$$
$$\psi(x+L,y,z) = \psi(x,y,z)$$

"periodické okr. podmienky"

↓

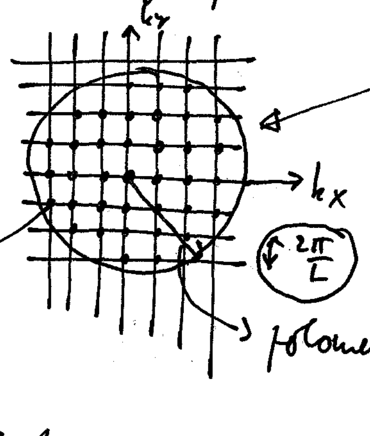
vln. funkcie $\psi_k(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{k}\cdot\vec{r}}$ $\quad \vec{k} = \frac{2\pi}{L}\underbrace{(m,n,l)}_{\text{celé čísla}}$

Máme: $\int_\Omega d^3r\, |\psi_k(\vec{r})|^2 = 1$

$$\vec{P}\psi_k(\vec{r}) = \hbar\vec{k}\,\psi_k(\vec{r})$$

$$H\psi_k(\vec{r}) = \varepsilon_k\psi_k(\vec{r}) \longrightarrow \varepsilon_k = \frac{\hbar^2\vec{k}^2}{2m}$$

Elektrónový plyn pri $T = 0$



Fermiho plocha (oddeľuje obsadené a neobsadené stavy)

polomer = k_F

obsadené stavy v $\vec{k}$-priestore

objem v $\vec{k}$-priestore pripadajúci na 1 dovolený $\vec{k}$-bod: $\left(\frac{2\pi}{L}\right)^3$

Počet častíc

$$N = \underset{\text{spin}}{2}\sum_{k<k_F} 1 = 2\left(\frac{L}{2\pi}\right)^3 \int_{k<k_F} d^3k = \frac{2\Omega}{8\pi^3}\cdot\frac{4\pi k_F^3}{3}$$

$$n = \frac{N}{\Omega} = \frac{k_F^3}{3\pi^2} \to \boxed{k_F = (3\pi^2 n)^{1/3}}$$

Fermiho vlnový vektor

Energia:

$$E = 2\sum_{k<k_F}\varepsilon_k = 2\left(\frac{L}{2\pi}\right)^3\int d^3k\,\frac{\hbar^2k^2}{2m} = \frac{\Omega}{5\pi^2}\,\frac{\hbar^2 k_F^5}{2m}$$

$$\to \boxed{\frac{E}{N} = \frac{3}{5}\varepsilon_F} \qquad \boxed{\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}}$$

Fermiho energia

Porovnanie energie lokaliz. a delokaliz. elektrónov:

lokaliz.: $E_{lok} = N\varepsilon_0 = \underline{N\cdot\frac{3\pi^2}{2}\frac{\hbar^2}{ma^2}}$ (*)

delokaliz.: $E_{delok} = N\cdot\frac{3}{5}\varepsilon_F = N\cdot\frac{3}{5}\frac{\hbar^2k_F^2}{2m} = N\cdot\frac{3}{5}\frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$

1 el/atóm: $n = \frac{1}{a^3} \to E_{delok} = \underline{\underline{N\cdot\frac{3(3\pi^2)^{2/3}}{10}\frac{\hbar^2}{ma^2}}}$ (**)

$$\frac{E_{lok}}{N\cdot\frac{\hbar^2}{ma^2}} = 14{,}8 \quad , \quad \frac{E_{delok}}{N\cdot\frac{\hbar^2}{ma^2}} = 2{,}9$$

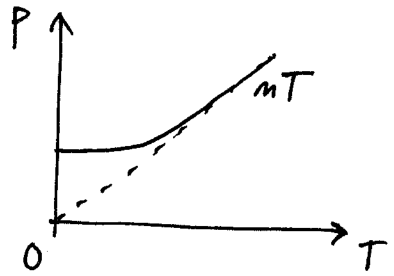
$\Longrightarrow$ delokalizované elektróny majú nižšiu energiu

$\Longrightarrow$ **KOVOVÁ VÄZBA**

Stavová rovnica el. plynu ($T=0$)

$$p = -\frac{\partial E(N,\Omega)}{\partial\Omega} \qquad E(N,\Omega) = \frac{3}{5}(3\pi^2)^{2/3}\frac{\hbar^2}{2m}\frac{N^{5/3}}{\Omega^{2/3}} \to p = \frac{2}{3}\frac{E}{\Omega}$$

$$\boxed{p = \frac{2}{5}n\varepsilon_F} \longleftarrow = \frac{2}{3}\cdot\frac{3}{5}n\varepsilon_F$$



Klas. plyn: $p = nT$

fermióny: pri $T\to 0$ ostáva tlak >0

(Pauliho princíp $\to$ QM tlak)

Hustota stavov (= počet stavov v jednotkovom objeme so spinom σ na jednotku energie)

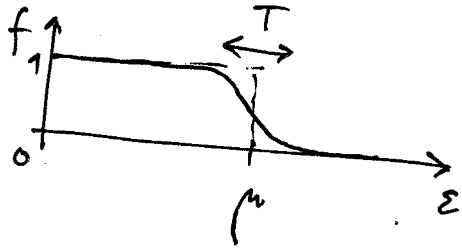
$$G(\varepsilon) \equiv \frac{\text{počet stavov s energiou} < \varepsilon}{\text{objem}} = \frac{1}{\Omega}\left(\frac{L}{2\pi}\right)^3 \int d^3k = \frac{1}{8\pi^3}\,\frac{4\pi k^3}{3}$$

$$G(\varepsilon) = \frac{1}{6\pi^2}\left(\frac{2m\varepsilon}{\hbar^2}\right)^{3/2} \longleftarrow \qquad \varepsilon = \frac{\hbar^2 k^2}{2m}$$

hustota stavov $N(\varepsilon) = \frac{dG}{d\varepsilon} \longrightarrow \boxed{N(\varepsilon) = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon}}$

Elektrónový plyn pri $T > 0$:

$$\begin{cases} N = 2\sum_k f_k \\ E = 2\sum_k \varepsilon_k f_k \end{cases} \qquad \boxed{f_k = \frac{1}{e^{\frac{\varepsilon_k - \mu}{T}} + 1}} \quad \text{Fermi-Dirac}$$



možno písať:

$$\frac{N}{\Omega} = 2\int_0^\infty d\varepsilon\, N(\varepsilon) f(\varepsilon), \qquad \frac{E(T)}{\Omega} = 2\int_0^\infty d\varepsilon\, N(\varepsilon) f(\varepsilon)\,\varepsilon$$

Sommerfeldov rozvoj:

$$\boxed{\int_0^\infty d\varepsilon\, H(\varepsilon) f(\varepsilon) = \int^\mu d\varepsilon\, H(\varepsilon) + \frac{\pi^2}{6} T^2 H'(\mu) + \frac{7\pi^4}{360} T^4 H'''(\mu) + \dots}$$

Dôkaz:

definujme $K(\varepsilon) = \int_0^\varepsilon d\varepsilon'\, H(\varepsilon') \longrightarrow H(\varepsilon) = \frac{dK}{d\varepsilon}$

per partes: $$\int_0^\infty d\varepsilon\, H(\varepsilon) f(\varepsilon) = K(\varepsilon) f(\varepsilon)\Big]_0^\infty + \int_0^\infty d\varepsilon\, K(\varepsilon) \underbrace{\left(-\frac{\partial f}{\partial \varepsilon}\right)}_{\text{lokalizovaná okolo } \mu}$$

zaniká na $-\infty$

Taylorov rozvoj okolo $\varepsilon=\mu$:

$$K(\varepsilon) = K(\mu) + \sum_{n=1}^{\infty} \left.\frac{d^nK}{d\varepsilon^n}\right|_{\varepsilon=\mu} \frac{(\varepsilon-\mu)^n}{n!}$$

$$\to \int_0^\infty d\varepsilon\, H(\varepsilon) f(\varepsilon) = K(\mu) \underbrace{\int_{-\infty}^{\infty} d\varepsilon \left(-\frac{\partial f}{\partial \varepsilon}\right)}_{=1} + \sum_{n=1}^{\infty} \frac{d^nK}{d\varepsilon^n} \frac{1}{n!} \underbrace{\int_{-\infty}^{\infty} d\varepsilon (\varepsilon-\mu)^n \left(-\frac{\partial f}{\partial \varepsilon}\right)}_{\underbrace{\frac{1}{4T}\int_{-\infty}^{\infty} \frac{d\varepsilon\,(\varepsilon-\mu)^n}{ch^2\left(\frac{\varepsilon-\mu}{2T}\right)}}_{= \frac{1}{2}(2T)^n \int_{-\infty}^{\infty} \frac{dx\, x^n}{ch^2 x}}}$$

Tielo integrálu nepárne!

Iba pre párne n; možno ich vypočítať a dostaneme tak Sommerfeldov rozvoj

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Závislosť $\mu = \mu(T)$

$$\frac{N}{\Omega} = 2\int_0^\infty d\varepsilon N(\varepsilon) f(\varepsilon) = 2\int^{\mu} d\varepsilon N(\varepsilon) + \frac{\pi^2}{3} T^2 N'(\mu)$$

pri $T=0$: $\frac{N}{\Omega} = 2\int^{\varepsilon_F} d\varepsilon N(\varepsilon)$ → Porovnaním

$$\int^{\varepsilon_F} d\varepsilon N(\varepsilon) = \int^{\mu} d\varepsilon N(\varepsilon) + \frac{\pi^2}{6} T^2 N'(\mu) \quad (*)$$

Nech $\mu = \varepsilon_F + \delta\mu$; ukážeme, že $\delta\mu = O(T^2)$

$$(*) \to \quad \delta\mu N(\varepsilon_F) + \frac{\pi^2}{6} T^2 N'(\varepsilon_F) = 0 \to \boxed{\delta\mu = -\frac{\pi^2}{6} T^2 \frac{N'(\varepsilon_F)}{N(\varepsilon_F)}}$$

korekcia rádu $\frac{T^2}{\varepsilon_F} \ll \varepsilon_F$!

(Typické hodnoty $\varepsilon_F \sim 1\,eV$!)

Merné teplo

$$C_V = \frac{1}{\Omega}\left(\frac{\partial E}{\partial T}\right)_\Omega \qquad \frac{E(T)}{\Omega} = 2\int^{\mu} d\varepsilon\, N(\varepsilon)\varepsilon + \frac{\pi^2}{3} T^2 \left[N(\varepsilon)\varepsilon\right]'_{\varepsilon=\mu}$$

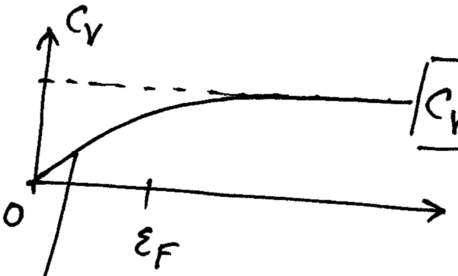
s presnosťou do rádu T^2:

$$\frac{E(T)}{\Omega} = 2\int^{\varepsilon_F} d\varepsilon\, N(\varepsilon)\varepsilon + 2\,\delta\mu\, N(\varepsilon_F)\varepsilon_F + \frac{\pi^2}{3}T^2\left[N'(\varepsilon_F)\varepsilon_F + N(\varepsilon_F)\right]$$

súčet $= 0$

$$\boxed{E(T) = E(0) + \frac{\pi^2}{3}T^2 N(\varepsilon_F)\Omega} \rightarrow \boxed{C_V = \frac{2\pi^2}{3}N(\varepsilon_F)\,T}$$

$$\boxed{N(\varepsilon_F) = \frac{3}{4}\frac{n}{\varepsilon_F}}$$

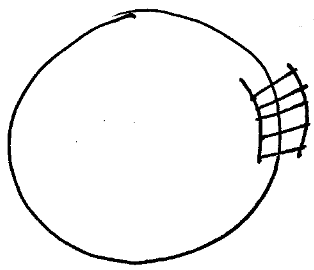


$\boxed{C_V = \frac{3}{2}n}$ klasická štatistika $T \gg \varepsilon_F$

$\boxed{C_V = \frac{\pi^2}{2}\frac{T}{\varepsilon_F}n}$ kvantová štatistika, $T \ll \varepsilon_F$

$C_V \to 0$ pri $T \to 0$ (3. veta termodynamická)

<u>fyz. zmysel</u>: vo fermiónovom systéme sú excitované iba stavy okolo ε_F!



počet stavov: $\sim N(\varepsilon_F)\,T\,\Omega$

každý z nich zvýši energiu o T