Modell freier Elektronen, Sommerfeld & Bethe 1933

Annahmen zur Beschreibung betrifft nur Leitungselektronen

- adiabatische oder Born-Oppenheimer Näherung

  Trennung von Kernbewegung & elektronischen Freiheitsgraden

- Ein-Elektronen-Näherung

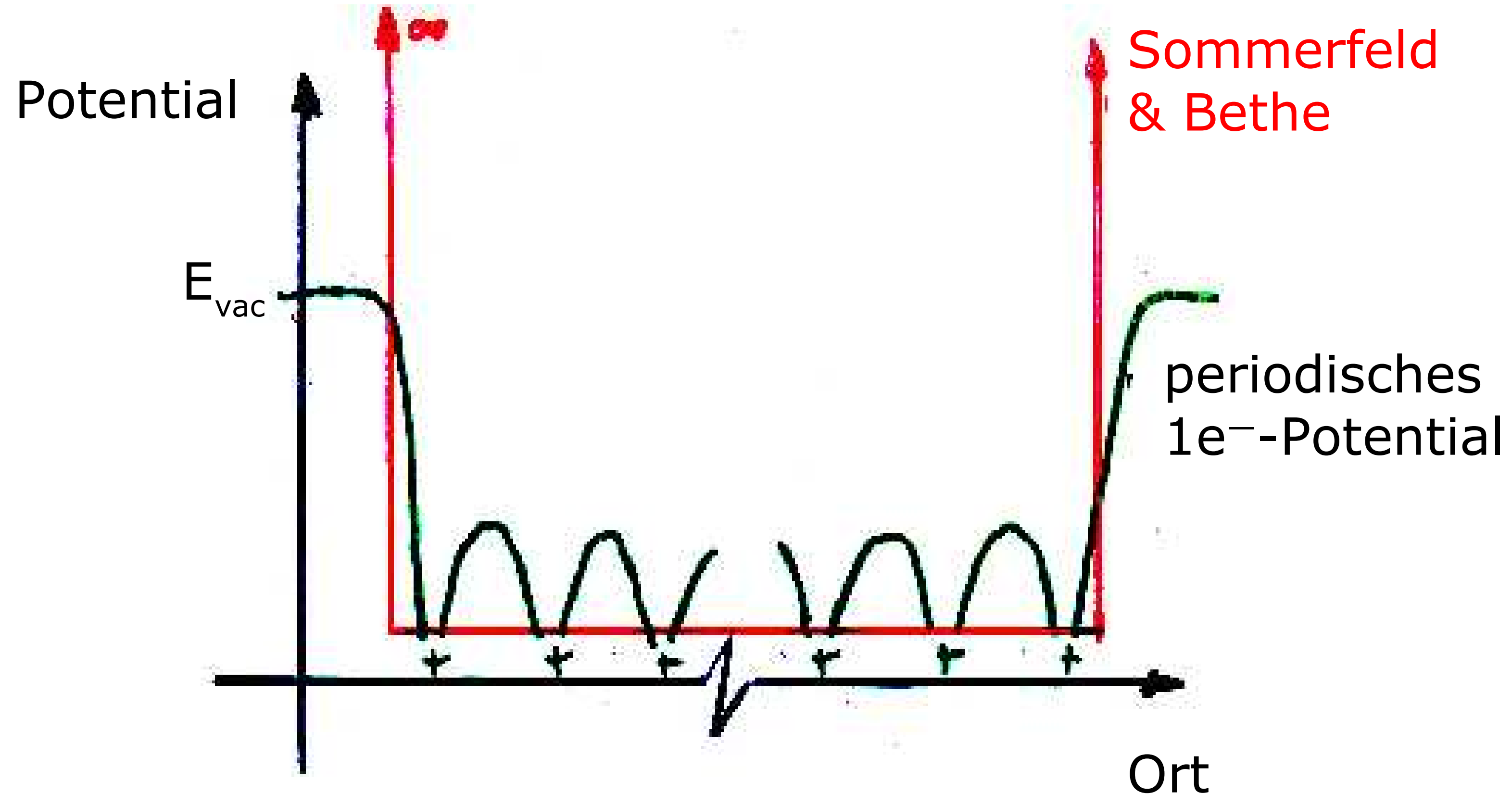
  Festkörper (Ionen & Elektronen) beschrieben durch

  Potential, dessen Eigenzustände aufgefüllt werden

  (# Supraleitung, Magnetismus)

- Freies Elektronengas (Potential $V = 0$)

Zusammengefasst: Metall = 3D-Potentialtopf



Warum sind Elektronen nahezu frei?

- Elektron-Ion-WW am stärksten bei kleinen r
  dort verhindert Pauliprinzip Elektronenanhäufung
- Mobilität der Leitungselektronen führt zu Abschirmung

1. Density of states $D(\varepsilon)$ for a $d=3$ metal

Schrödinger equation in $d=3$: $\vec{r}=(x,y,z)$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi(\vec{r})=\varepsilon\,\Psi(\vec{r})$$

Solution with periodic boundary conditions:

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

$\Rightarrow$ Plane wave: $\underline{\Psi(\vec{r})=e^{i\vec{k}\vec{r}}}$

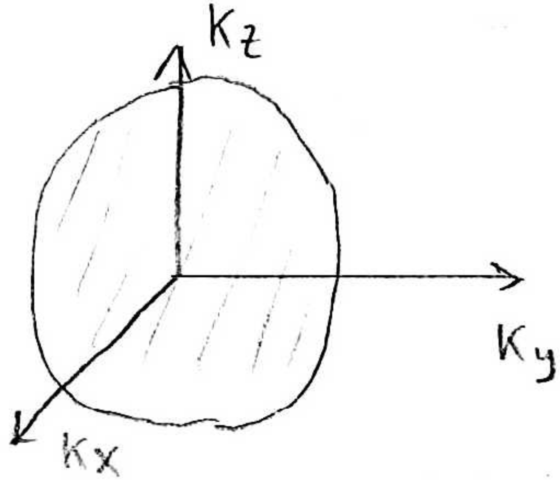
with $k_x=\ldots,-\frac{2\pi}{L},0,+\frac{2\pi}{L},\frac{4\pi}{L}$

$k_y=$ ______

$k_z=$ ______

Substituting $\Psi(\vec{r})$ in Schröd. eq.:

$$\underline{\varepsilon=\frac{\hbar^2k^2}{2m}=\frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right)} \qquad (1)$$



The set of k_x, k_y, k_z of (1) belong to a sphere of energy ε.

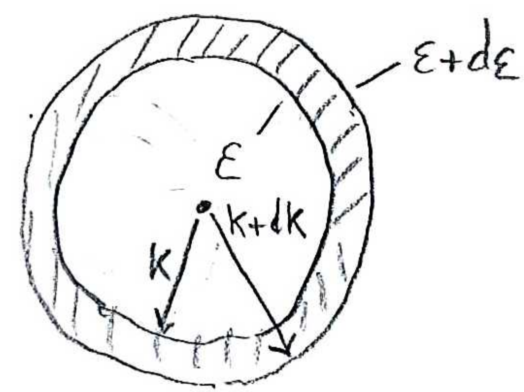
In a volume $\left(\frac{2\pi}{L}\right)^3$, there 2 states:

- spin-up state $\uparrow$
- spin-down state $\downarrow$

$\underset{\sim\sim}{D(\varepsilon)}$

- Density of states: number of e^- states in the range ε, $\varepsilon + d\varepsilon$

number of states $\quad dN = D(\varepsilon)\, d\varepsilon$



Expression of $D(\varepsilon)$ $(d=3)$:

$$dN = \underbrace{2}_{\text{spin}\uparrow \text{ and spin}\downarrow} \times \frac{4\pi k^2 dk}{\left(\frac{2\pi}{L}\right)^3}$$

volume in k-space

We have then:

$$D(\varepsilon)\,d\varepsilon = \frac{L^3 k^2 dk}{\pi^2}$$

$V = L^3$

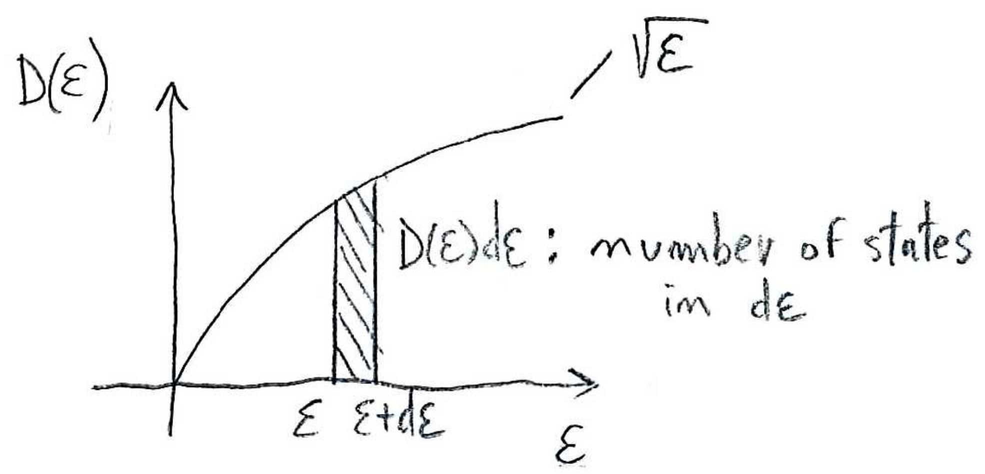
$$\Rightarrow \quad D(\varepsilon) = \frac{V \cdot k^2}{\pi^2 \left(\frac{d\varepsilon}{dk}\right)}$$

since $\varepsilon = \frac{\hbar^2 k^2}{2m}$: $\begin{cases} k = \frac{\sqrt{2m\varepsilon}}{\hbar} \\ \frac{d\varepsilon}{dk} = \frac{\hbar^2}{m} k = \hbar \sqrt{\frac{2}{m}} \sqrt{\varepsilon} \end{cases}$

And finally:

$$\boxed{D(\varepsilon) = \frac{V(2m)^{3/2}}{2\hbar^3 \pi^2} \sqrt{\varepsilon}}$$

$[D(\varepsilon)] = \frac{1}{eV}$



Fermi energy ε_F energy of the topmost filled level in the ground state ($T=0$) of the N electron system.

$$N = \int_0^{\varepsilon_F} D(\varepsilon)\, d\varepsilon$$

number of e^-

$$= \frac{V (2m)^{3/2}}{2\hbar^3 \pi^2} (\varepsilon_F)^{3/2} \frac{2}{3}$$

$$\Rightarrow \quad \underline{\varepsilon_F = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3}}$$

$$\varepsilon = \frac{\hbar^2}{2m} k^2$$

The Fermi wavevector:

$$\underline{k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3}}$$

Fermi velocity:

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

Fermi temperature:

$$\underline{T_F = \frac{\varepsilon_F}{k_B}}$$

⚠ NOT THE TEMPERATURE OF THE ELECTRON GAS

logisch, denn gleich verteilt ergäbe sich $\frac{N}{\varepsilon_F}$

$$\underline{D(\varepsilon) = \frac{3}{2} \frac{N}{\varepsilon_F} \sqrt{\frac{\varepsilon}{\varepsilon_F}}} \quad \& \quad \underline{D(\varepsilon_F) = \frac{3}{2} \frac{N}{\varepsilon_F}}$$

Beispiel **Cu**

n	$8{,}5 \times 10^{22}$ cm^{-3}
k_F (10^{10} m^{-1})	1,35 (≈ 2 π/a)
v_F (10^5 m/s)	15,6 (≈ 0.05 c)
E_F (eV)	7,0
T_F (K)	82000 (≈ 13 T_{Sonne})

T_F ist nicht die Temperatur des Elektronengases

Gas? Fermigas!

Nicht jedes e- kann E=0 haben

Dichte der inneren Energie – Gas vs. Fermigas $(T \to 0)$

$$\frac{U}{V} = \int_0^\infty E\, D(E)\, f(E)\, \frac{1}{V}\, dE$$

bei $T = 0 \Rightarrow$

$$\frac{U}{V} \to \int_0^{E_F} E\, \frac{3}{2}\frac{n}{E_F}\sqrt{E/E_F}\, dE = \frac{3}{5} E_F n = \frac{3}{5} k_B T_F n$$

- (mittl.) Energie pro Elektron:

$$\frac{U}{V} \Big/ n = \frac{3}{5} k_B T_F \quad (= \text{konst})$$

- klass. Gas: $\frac{3}{2} kT \quad \to 0$ bei $T \to 0$

Quantengas von Fermionen vs. klass. Gas

- Da $T_F \gg 300K$:

  Therm. Energie ist „unwichtig"

  ~ „$T = 0$" ist oft gute Näherung

3D Zustandsdichte, allgm. Fall

$$dN = 2 \cdot \frac{V}{(2\pi)^3} \int_{E}^{E+dE} d\vec{k}$$

Zerlege $d\vec{k}$ in $d\vec{S}_E$ und $dk_\perp$

Nutze $dE = |\vec{\nabla}_k E|\, dk_\perp$

$$\Rightarrow \frac{dN}{V} = D(E)\,dE = 2 \cdot \frac{1}{(2\pi)^3} \int_{E=\text{const}} \frac{d\vec{S}_E}{|\vec{\nabla}_k E|}\, dE$$

$\Rightarrow$ schwache Dispersion $\hat{=}$ hohe DOS

v. Hove Singularitaten

2. The Fermi-Dirac distribution

Link to macroscopic quantities. $U(T)$, C_V, ...

Phonons:

$$U(T) = \int_0^{+\infty} \hbar\omega \; D(\omega) \; f_{BE}(\omega,T) \, d\omega$$

$$f_{BE}(\omega,T) = \frac{1}{e^{\hbar\omega/k_BT} - 1}$$

Electrons:

$$U(T) = \int_0^{+\infty} \varepsilon \; D(\varepsilon) \; f_{FD}(\varepsilon,T) \, d\varepsilon$$

For a given T, probability to find 1 e^- at an energy ε

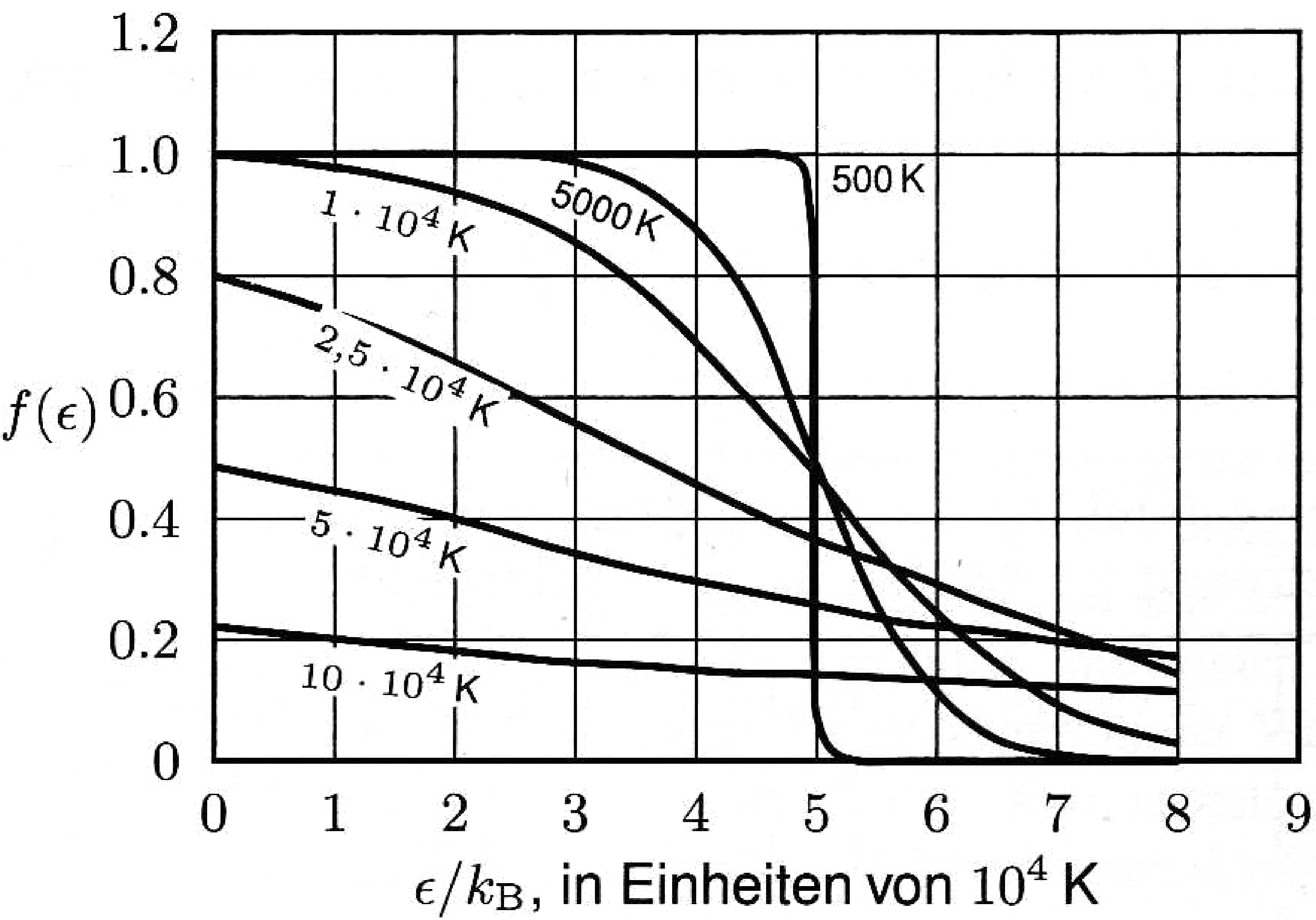
$$f_{FD}(\varepsilon,T) = \frac{1}{e^{(\varepsilon-\mu)/k_BT} + 1}$$

Fermi-Dirac distribution

$\parallel \mu \simeq \varepsilon_F$

$\hookrightarrow$ Chemical potential

Fermiverteilung

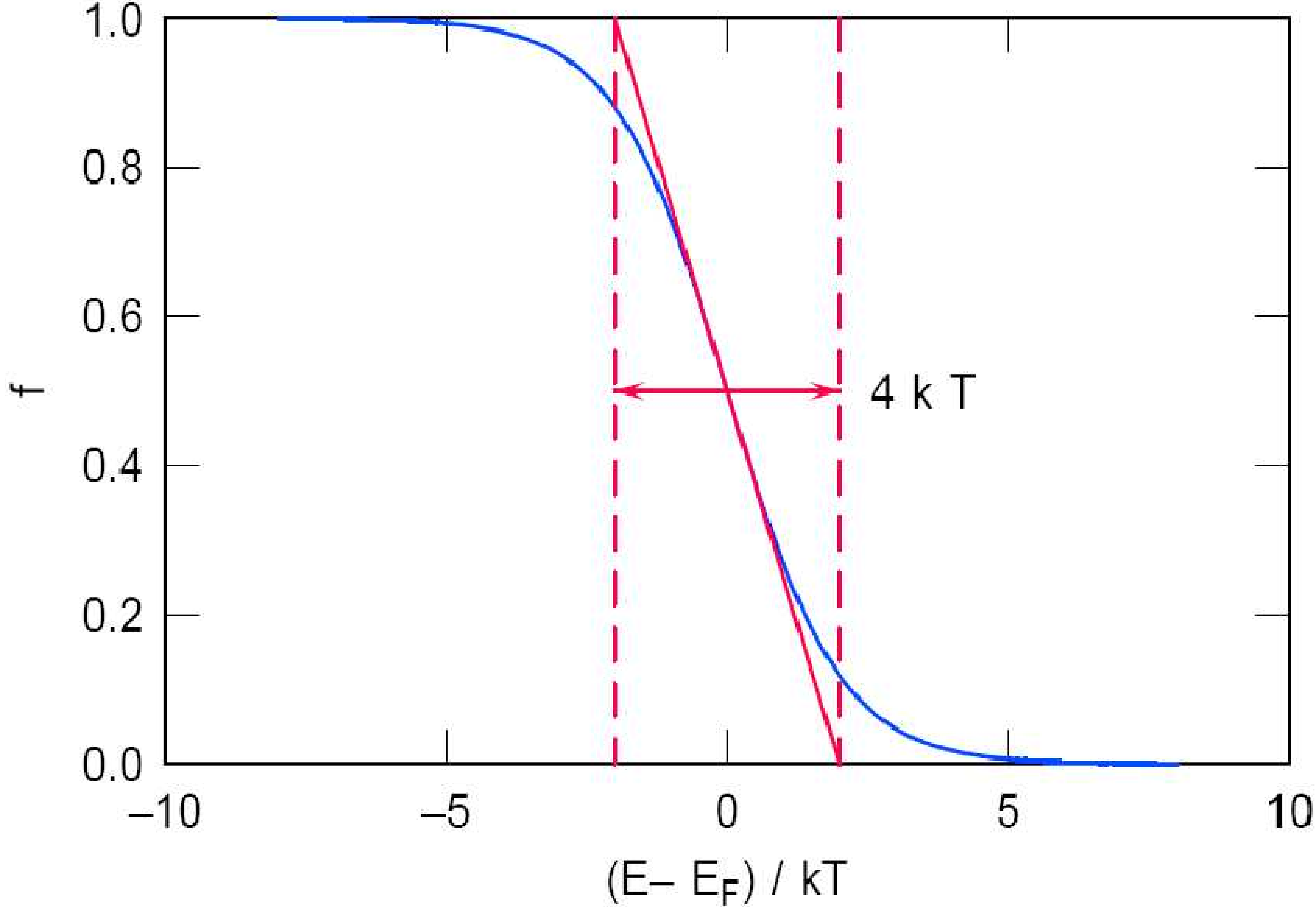


Fermi-Dirac-Verteilung für $T_F = E_F / k_B = 50000$ K

$f(\varepsilon) = 0{,}5$ bei $\varepsilon = \mu$ (chemisches Potential)

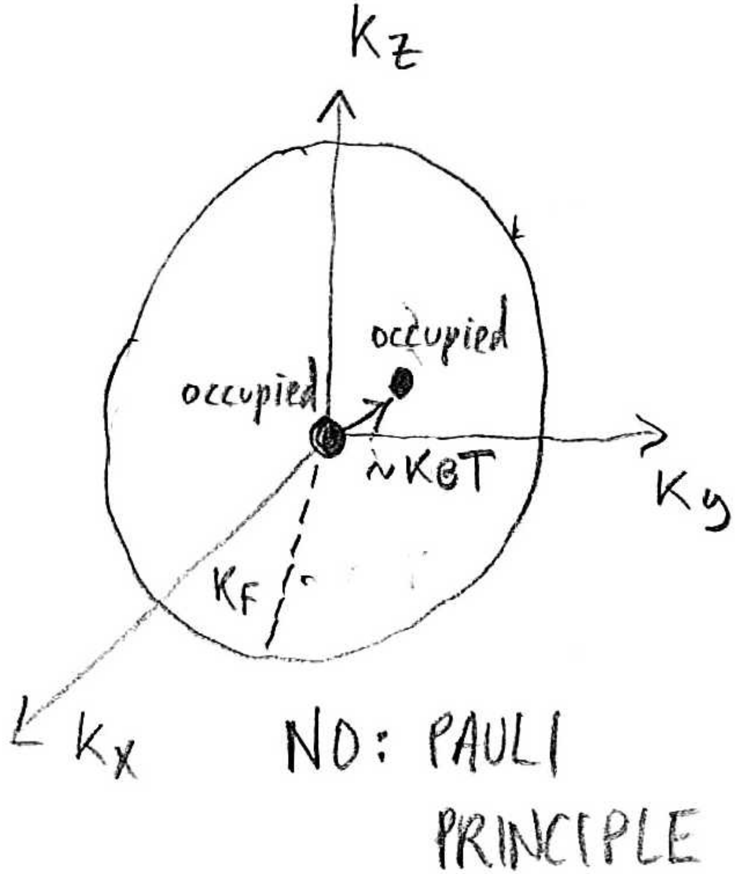
$\mu \approx E_F$ für $T \ll T_F$

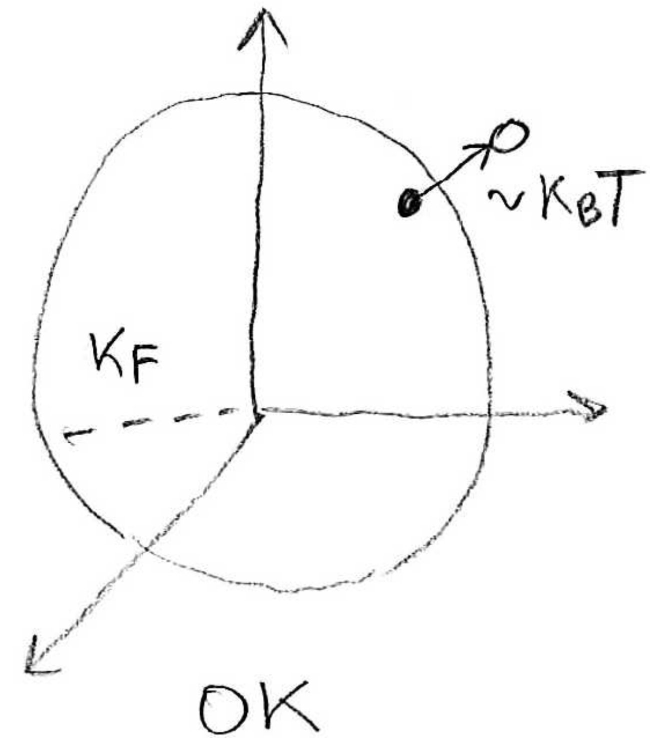
- $T = 0$: step function
- $T \neq 0$: step is smoothed out around ε_F
  Typical width: $4 k_B T$
- At usual temperatures (~ 300K), smoothing is small since $T \ll T_F$



Fermi–Verteilung

f_{FD} accounts for the Pauli principle:





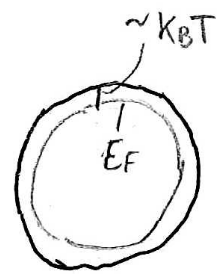
3. Specific heat C_V $(d=3)$

- Experimentally for a metal: $C_V = \gamma_{exp} T + \cdots$
- Drude model: $C_V = \frac{3}{2} N K_B$
  ([illegible])
- Free e^- model (Sommer Feld): $C_V = \gamma T$

① Correct T-dependence

② $\gamma \sim \gamma_{exp}$

Qualitative evaluation of C_V

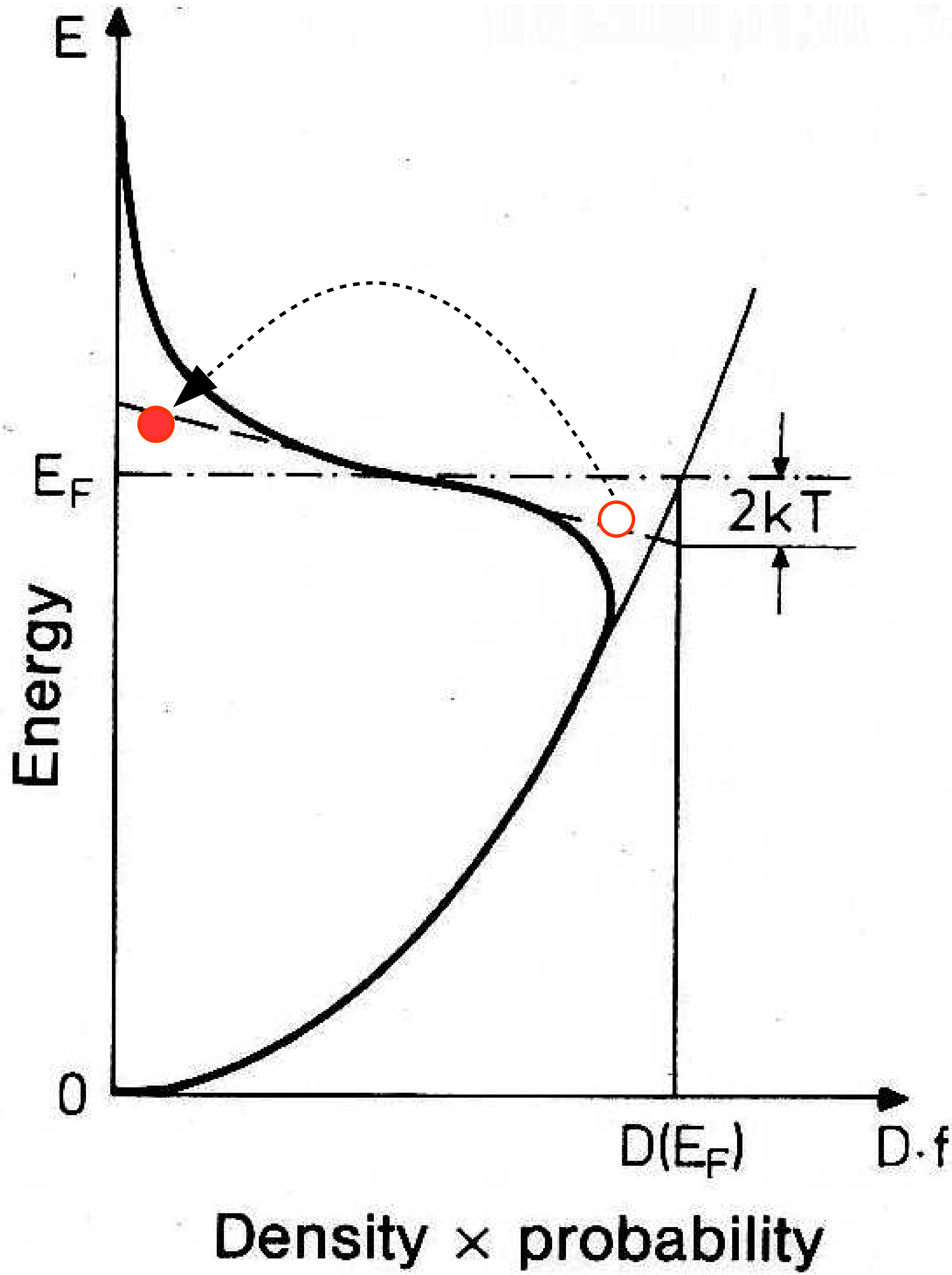


Energy excitation : $\sim K_B T$

Number of excited e^- : $\sim N \frac{T}{T_F}$

The kinetic energy U is : $U \sim \left(\frac{NT}{T_F}\right) \cdot K_B T$

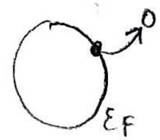
and $C_V = \frac{dU}{dT} \sim N K_B \frac{T}{T_F}$



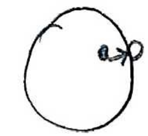
1b

Fig. 6.7. Explanation of the specific heat capacity of quasi-free metal electrons. The effect of raising the temperature from 0 K to T is to allow electrons from $\leq 2kT$ below the Fermi energy to be promoted to $\leq 2kT$ above E_F. The tangent (– – –) intersects the energy axis at $E_F + 2kT$

energy needed to take e^- from ε_F to energies $\varepsilon > \varepsilon_F$



energy needed to bring e^- from energies below ε_F to ε_F



$$\Delta U(T) = \int_{\varepsilon_F}^{+\infty} (\varepsilon - \varepsilon_F)\, D(\varepsilon)\, f(\varepsilon,T)\, d\varepsilon + \int_0^{\varepsilon_F} (\varepsilon_F - \varepsilon)\, D(\varepsilon)\big(1 - f(\varepsilon,T)\big)\, d\varepsilon$$

$$C_V = \frac{d\Delta U}{dT}$$

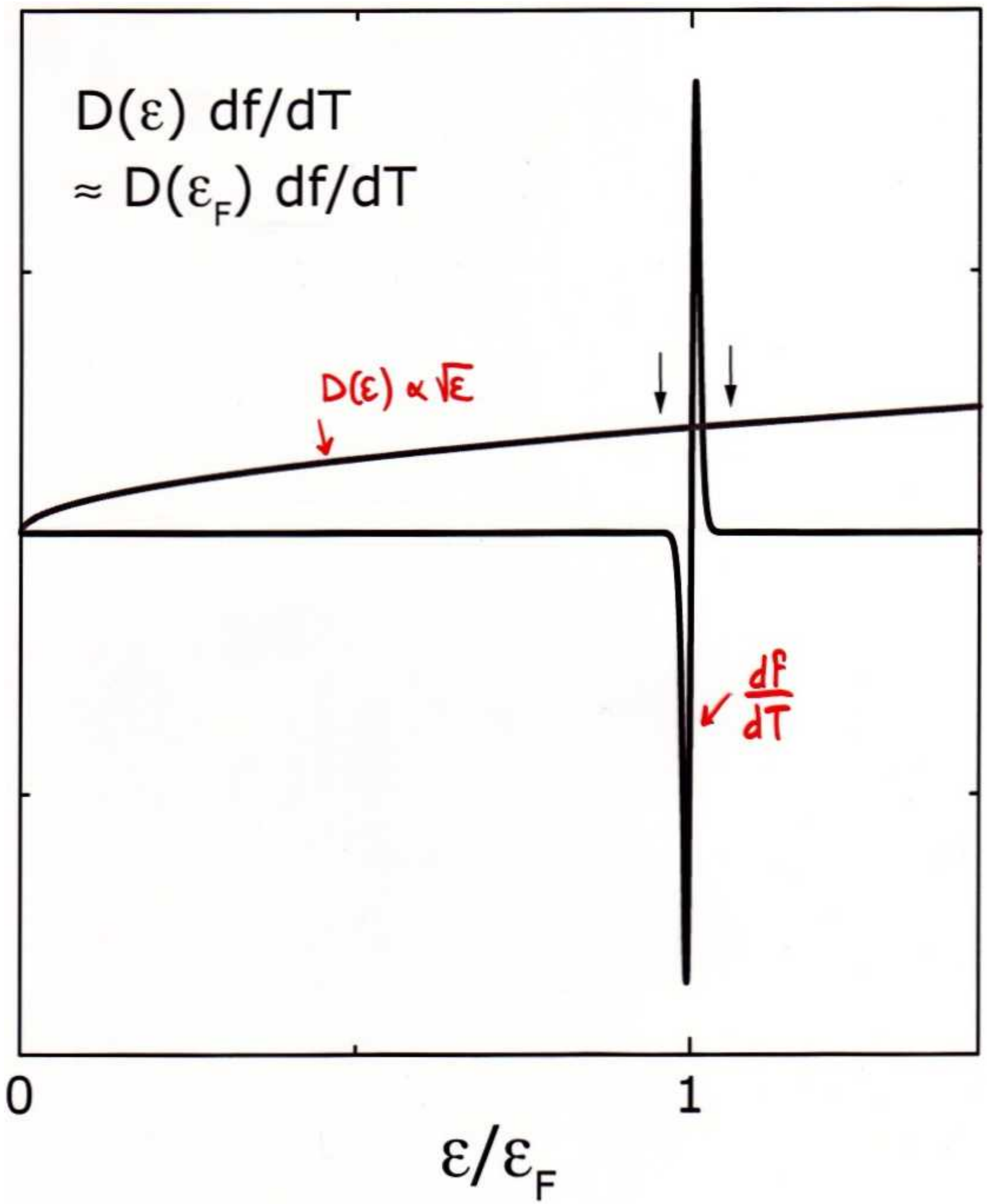
$$C_V = \int_{\varepsilon_F}^{+\infty} (\varepsilon - \varepsilon_F)\, D(\varepsilon)\, \frac{df}{dT}\, d\varepsilon - \int_0^{\varepsilon_F} (\varepsilon_F - \varepsilon)\, D(\varepsilon)\, \frac{df}{dT}\, d\varepsilon$$

$$= \int_0^{+\infty} (\varepsilon - \varepsilon_F)\, D(\varepsilon)\, \frac{df}{dT}\, d\varepsilon \simeq D(\varepsilon_F) \int_0^{+\infty} (\varepsilon - \varepsilon_F)\, \frac{df}{dT}\, d\varepsilon$$

$$\frac{df}{dT} = \frac{d}{dT}\left(\frac{1}{e^{(\varepsilon - \varepsilon_F)/k_B T} + 1}\right) = \frac{\varepsilon - \varepsilon_F}{k_B T^2}\, \frac{e^{(\varepsilon - \varepsilon_F)/k_B T}}{\left(e^{(\varepsilon - \varepsilon_F)/k_B T} + 1\right)^2}$$

eigentlich μ, aber $\varepsilon_F \approx \mu$.

Introduce $x = \dfrac{\varepsilon - \varepsilon_F}{k_B T}$



T_F = 80000 K

T = 300 K

$$C_V = K_B^2 T \quad D(\varepsilon_F) \int_{-\frac{\varepsilon_F}{K_B T}}^{+\infty} \frac{x^2 e^x}{(e^x+1)^2}\, dx$$

$$T \ll T_F : \quad -\frac{\varepsilon_F}{K_B T} \longrightarrow -\infty$$

$$C_V = K_B^2 T \, D(\varepsilon_F) \underbrace{\int_{-\infty}^{+\infty} \frac{x^2 e^x}{(e^x+1)^2}\, dx}_{= \frac{\pi^2}{3}}$$

$$\underline{C_V = \frac{\pi^2}{3} D(\varepsilon_F) K_B^2 T}$$

$$D(\varepsilon_F) = \frac{3}{2}\frac{N}{\varepsilon_F}$$

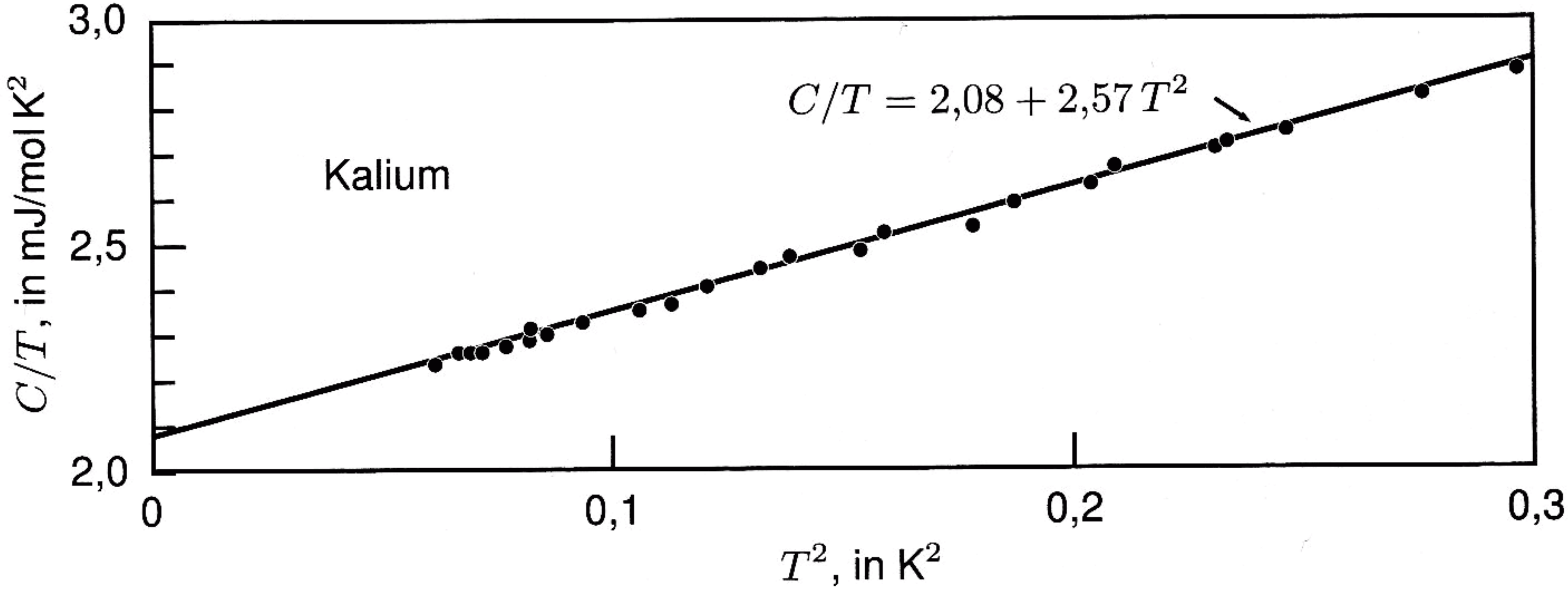
$$\underline{= \frac{\pi^2}{2} N K_B \frac{T}{T_F}}$$

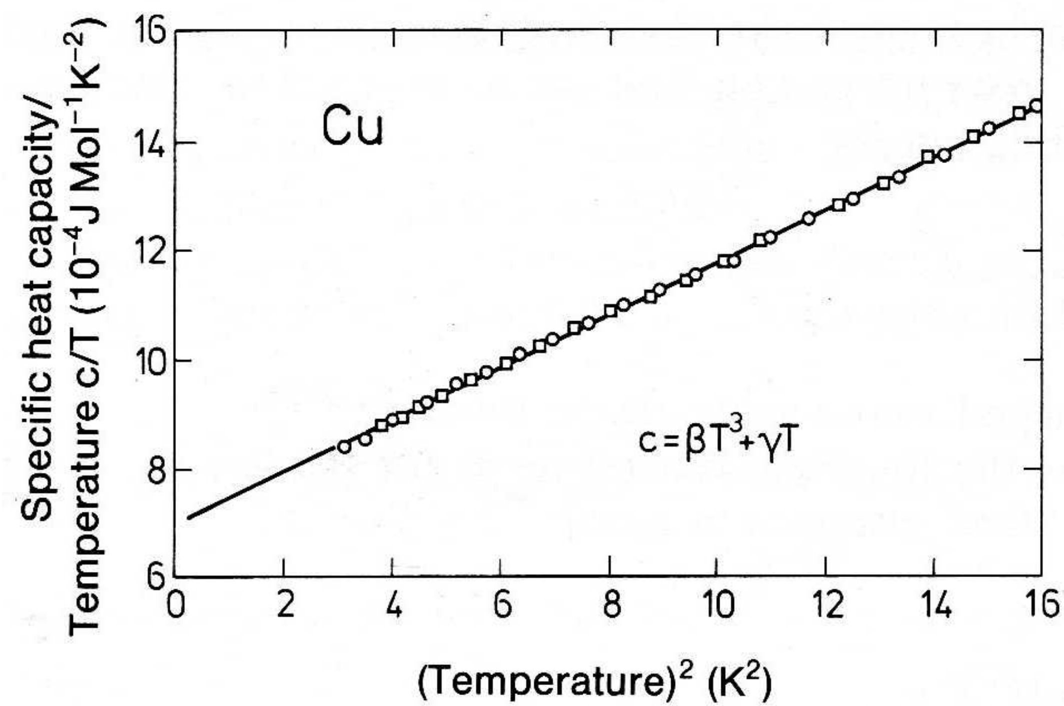
$$\frac{C_V}{C_V(\text{Drude})} = \frac{\frac{\pi^2}{2} N K_B \frac{T}{T_F}}{\frac{3}{2} N K_B} \sim 10^{-2}$$

$$\underline{C_V = \underbrace{\gamma T}_{e^-} + \underbrace{A T^3}_{\text{phonons}}}$$

$$\Leftrightarrow \quad \frac{C_V}{T} = \gamma + A T^2$$

Wärmekapazität von Metallen





3

Electronic specific heat: Experiment vs free-electron-model

$C_V = \gamma\, T + \beta\, T^3$

Metal	$\boldsymbol{\gamma_{exp}}$ (10^{-3} J/Mol K^2)	$\boldsymbol{\gamma_{exp}/\gamma_{theo}}$
K	2.0	1.1
Ag	0.66	1.02
Cu	0.69	1.37
Na	1.7	1.5
Al	1.35	1.6
Li	1.7	2.3
Fe	4.98	10.0
Co	4.98	10.3
Ni	7.02	15.3

$C_V = \frac{\pi^2}{3} D(\varepsilon_F) k_B^2 T$

Nur elektronischer Anteil:

$C_V \sim D(E_F)$ $D(E_F) = 3/2\ N/E_F$ $E_F = \hbar^2/2\ (3\ \pi^2\ N/V)\ 1/m$

- $C_V \sim m$
- definiere m^* 'specific heat effective mass'
- $\gamma_{exp}/\gamma_{theo} = m^*/m$

Metall	$\boldsymbol{\gamma_{exp}/\gamma_{theo} = m^*/m}$		
K	1.1		
Ag	1.02		
Cu	1.37		
Na	1.5		
Al	1.6		
Li	2.3		
Fe	10.0	*d-Metall*	
Co	10.3	*d-Metall*	
Ni	15.3	*d-Metall*	
$CeAl_3$	~ 1000	''*Heavy Fermions*''	*f-Elektronen*

Elevated D at E_F: Free-electron-model fails

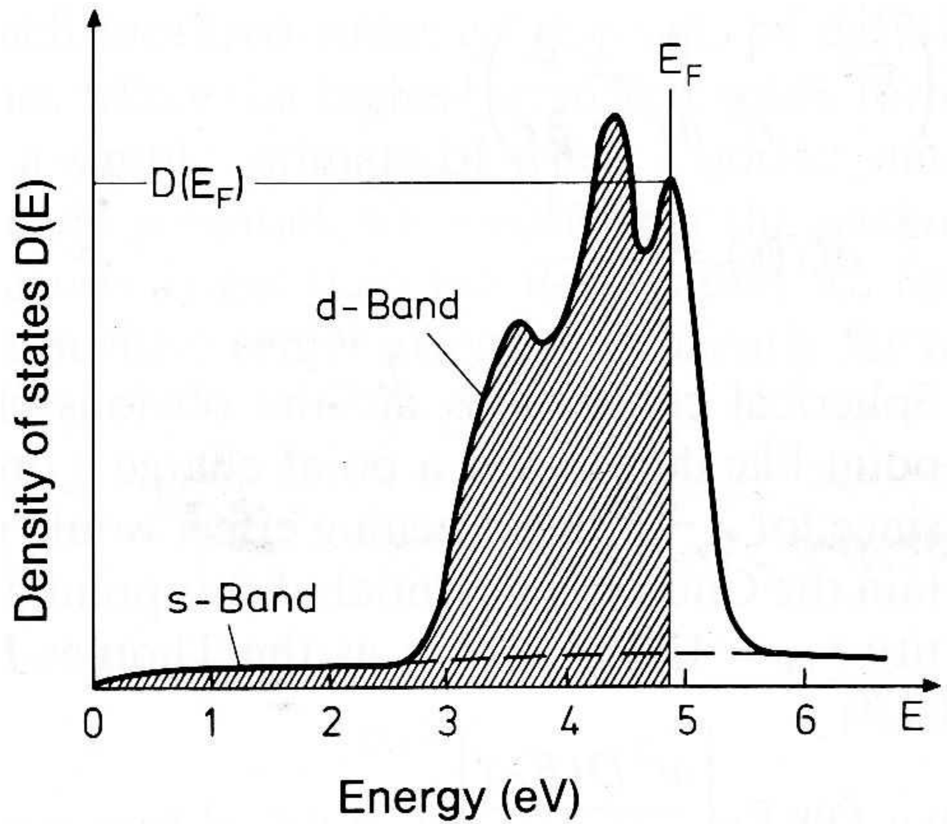
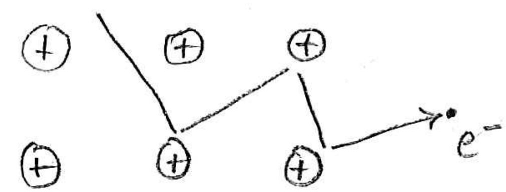


Fig. 6.9. Qualitative behavior of the density of states $D(E)$ for the conduction band of a transition metal. The strong contribution of the d-electrons in the vicinity of the Fermi level lies on top of that of the s-band (*partially dashed*)

4. Conductivity

Drude's model: conductivity determined by scattering between e^- and ions of the lattice



Free mean-path between two scattering events:

$$L_\phi \sim \mathring{A}$$

Experiment: $L_\phi \sim 1\,cm = 10^8\,\mathring{A}$!!

(zB. Ausbreitung von Wärmepulsen) PRL 18, 855 (1967)

Free electron model:

Eq. of motion of e^- in an electric Field:

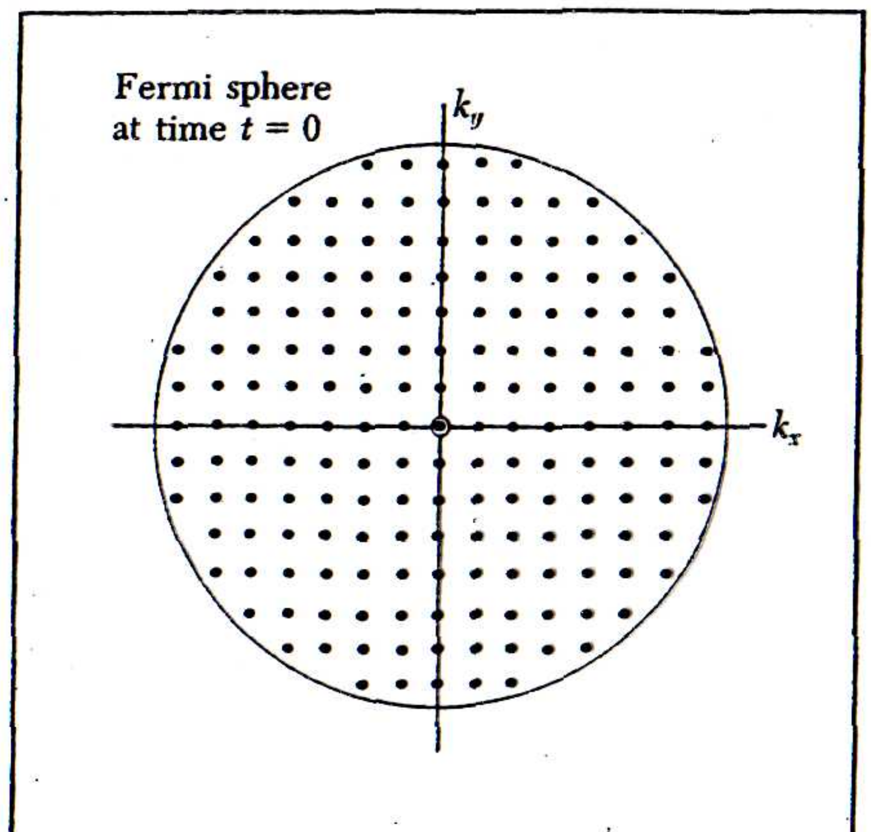
$$\dot{\vec{p}} = m\frac{d\vec{v}}{dt} = \hbar\frac{d\vec{K}}{dt} = -e\vec{E}$$

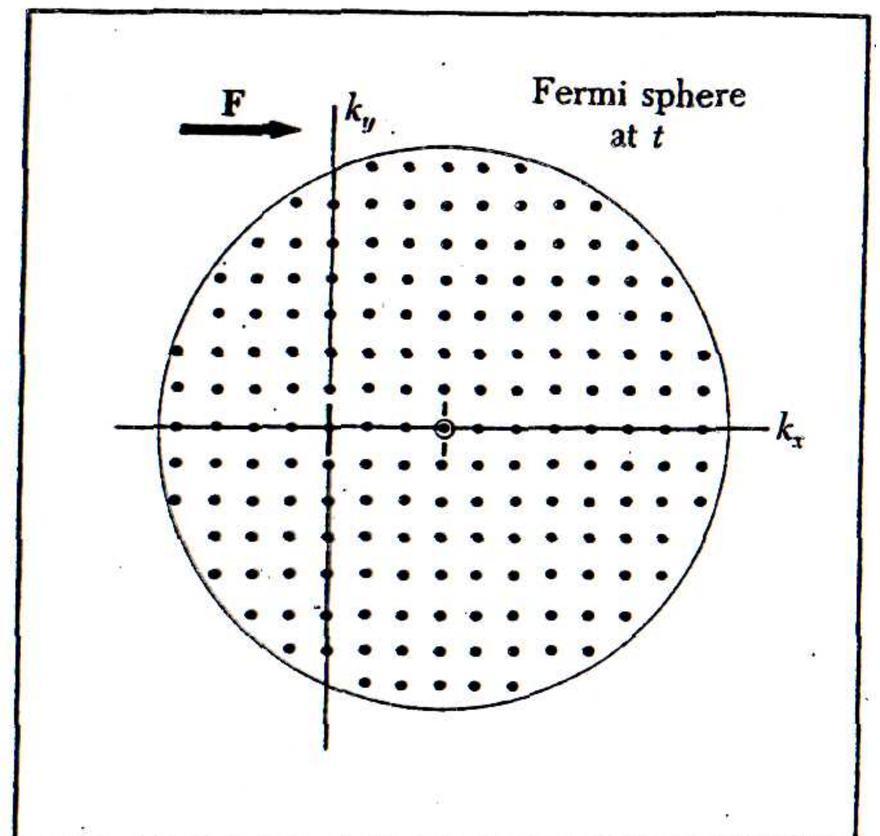
Integral $\int$

$$\vec{K}(t) - \vec{K}(0) = -e\vec{E}t/\hbar$$

4a

Displacement of Fermi sphere





- Something missing in the eq. motion: FRICTION

If no friction, displacement of the Fermi sphere $= +\infty$

$$\underline{m \frac{d\vec{v}}{dt} = -e\vec{E} - \frac{m\vec{v}}{\tau}}$$

- Steady state regime: $\frac{d\vec{v}}{dt} = \vec{0} \quad \Rightarrow \quad \underline{\vec{v} = -\frac{e\vec{E}\tau}{m}}$

Introduce: $\begin{cases} \vec{J} = -ne\vec{v} \\ \vec{J} = \sigma\vec{E} \end{cases}$ (like Drude model)

σ → conductivity

$$\Rightarrow \underline{\sigma = \frac{ne^2\tau}{m}}$$

For Copper: $\sigma(4K) = 6 \cdot 10^{12}\ \Omega^{-1} m^{-1}$, $T = 4K$

$\Rightarrow \tau = 2.5\ 10^{-9}\ s\ (4K)$

Mean-free path: $L_\phi = v_F\, \tau$

$v_F = 15.6\ 10^5\ m.s^{-1}$ $\Rightarrow$ $\underline{L_\phi \sim 0.4\ cm}$

Copper

Friction in Free e^--model:

e^- collisions with: 1) Impurities, lattice imperfections

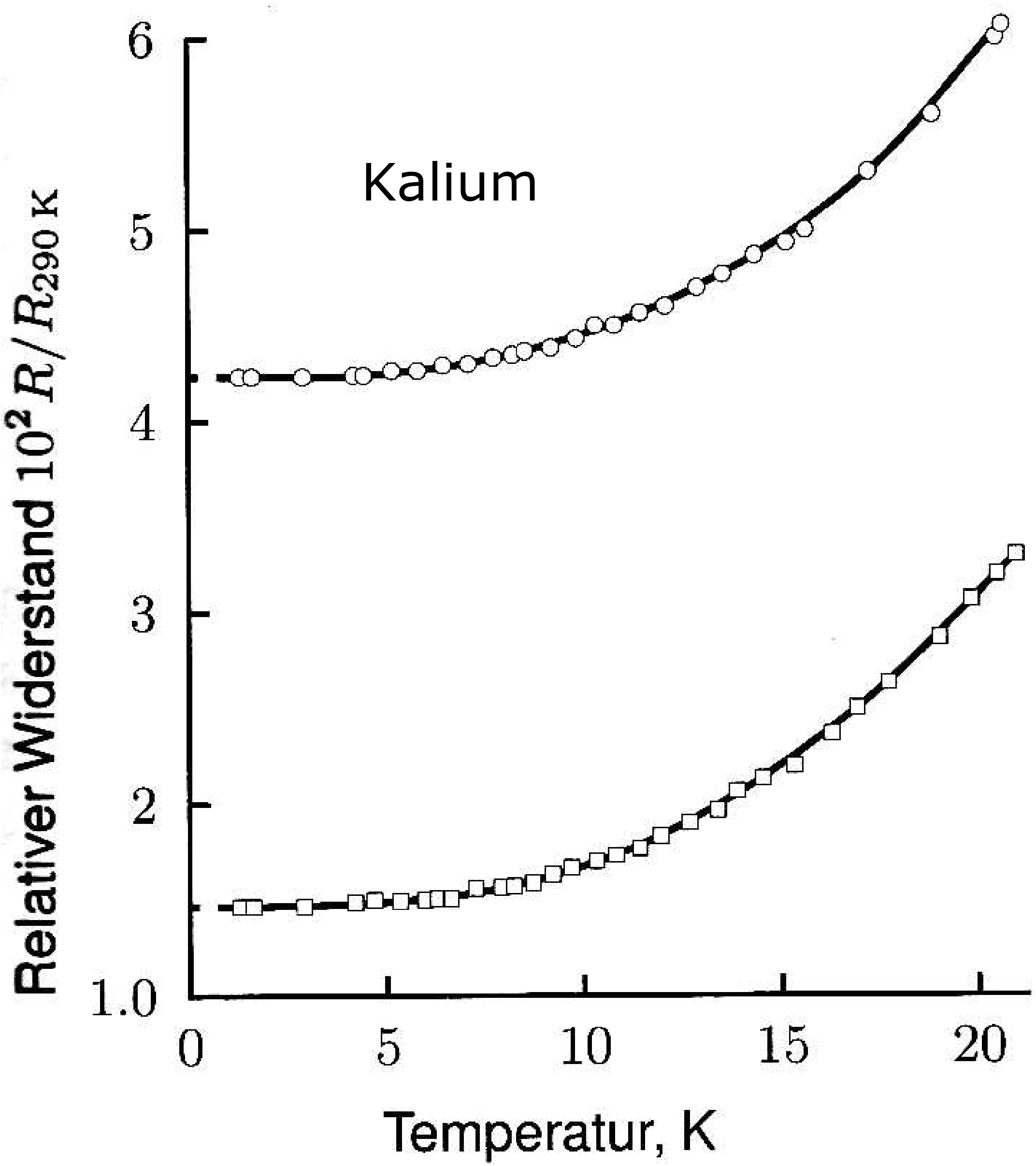
2) phonons

Temperaturabhängigkeit des Widerstands

4b

'Reibung' im Sommerfeldmodell?

Defekte & Phononen



Bei tiefen T:

$$\rho = \frac{1}{\sigma} = A + B\,T^5$$

Defekte   Phononen

Widerstand zweier Kalium Proben.

(D.K.C. MacDonald und K. Mendelsohn)

Restwiderstände bei T $\rightarrow$ 0K zeigen unterschiedliche Defektkonzentrationen an.

Thermische Leitfähigkeit κ des freien Elektronengases

$$\text{Erinnerung an Phononen:} \quad \kappa = \frac{1}{3} c_V v \lambda$$

$$\text{verwende} \quad c_{el} = \frac{1}{2}\pi^2 n k_B \frac{T}{T_F} = \frac{1}{2}\pi^2 n k_B \frac{k_B T}{E_F}$$

$$\text{und} \quad E_F = \frac{1}{2} m v_F^2$$

$$\text{gibt:} \quad \kappa_{el} = \frac{\pi^2}{3} \frac{n k_B^2 T}{m v_F^2} v_F \lambda = \frac{\pi^2}{3m} k_B^2 T \tau \qquad \tau = \frac{\lambda}{v_F}$$

$$\text{Werte einsetzten, Resultat:} \quad \kappa_{el} \gg \kappa_{ph}$$

Wiedemann-Franz-Gesetz

$$\frac{\kappa_{el}}{\sigma} = \frac{\pi^2 n k_B^2 T \tau / 3m}{n e^2 \tau / m} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T = LT$$

Lorenzzahl $L = \frac{\kappa}{\sigma T} = 2{,}45 \cdot 10^{-8} \frac{W\Omega}{K^2}$

$L \cdot 10^8$ WΩ/K^2

	0°C	100°C
Ag	2,31	2,37
Au	2,35	2,40
Cd	2,42	2,43
Cu	2,23	2,33
Mo	2,61	2,79
Pb	2,47	2,56
Pt	2,51	2,60
Sn	2,52	2,49
W	3,04	3,20
Zn	2,31	2,33

Zusammenfassung: Transportgrößen κ, σ

Drude: Klassisches Gas, Maxwell-Boltzmann-Verteilung

$$f_{MB}(v) = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

Sommerfeld: Fermigas, Fermiverteilung

$$f_F(v) = 2\left(\frac{m}{h}\right)^3 \left(\exp\left(\frac{\frac{1}{2}mv^2 - \mu}{k_B T}\right) + 1\right)^{-1}$$

AC, DC Leitfähigkeit: *f* irrelevant!

$$\kappa = \frac{1}{3} v^2 \tau c_V$$

Bei Übergang von Drude zu Sommerfeld ...

c_V verändert um ~ $k_B T/E_F$

v^2 nicht mehr $k_B T/m$ sondern 2 E_F/m, gibt Faktor $E_F/k_B T$

folglich: κ unverändert.

Also: c_V-Problem gelöst, κ & σ immer noch OK

Sommerfeld: Offene Fragen

- $R_H = -1/ne$

  aber: T, B-abhängig, Vorzeichenwechsel
- Magnetwiderstand nicht Null
- σ_{DC}: T-abhängig
- linearer c_V Term: Potenz OK,

  aber Zahlenwerte falsch für Edel- & Ü.metalle

- Was bestimmt Zahl der Leitungselektronen?
- Warum gibt es Isolatoren?

  B isoliert, Al leitet - gleiche Gruppe des PSE

Grundannahmen des Sommerfeldmodells

(1) Freie Elektronen

Ionen bewirken lediglich Ladungsneutralität

keine WW mit Elektronen

(2) Unabhängige Elektronen

keine e-e WW

(3) Relaxationszeitnäherung

Stoßresultat unabhängig von Impulsen vor Stoß

Hauptproblem (für's Erste): (1)