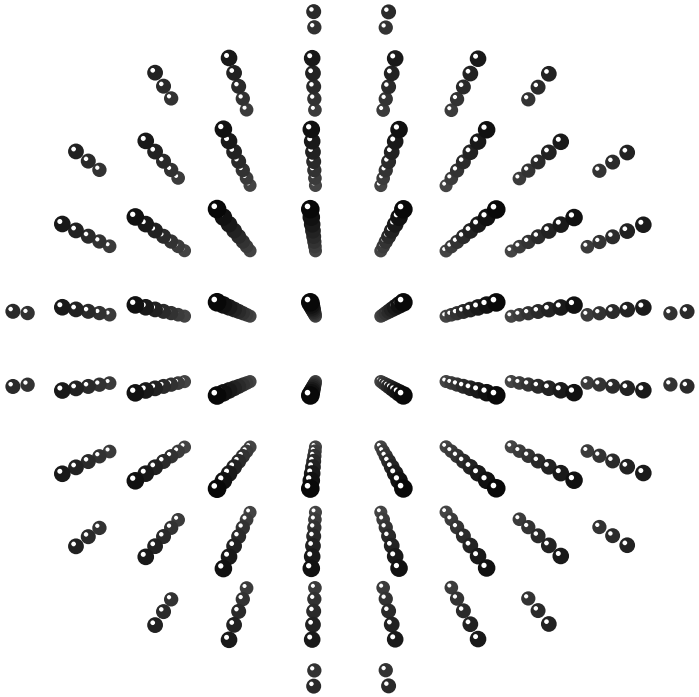
The Single-Electron Model



$$\hat{\mathcal{H}} = \sum_l \frac{\hat{P}_l^2}{2M_l} + \frac{1}{2}\sum_{l\neq l'} \frac{q_l q_{l'}}{|\hat{R}_l - \hat{R}_{l'}|}. \qquad \text{(L1)}$$

Approximations

$$\hat{\mathcal{H}} = \sum_l \frac{\hat{P}_l^2}{2M_l} + \frac{1}{2}\sum_{l\neq l'} \frac{q_l q_{l'}}{|\hat{R}_l - \hat{R}_{l'}|}$$

Nuclei treated as classical potentials. Many electrons combined with nuclei in closed shells to form ions.

All electronic degrees of freedom eliminated, turned to effective potential for ions. Phonon dynamics.

Ions treated classically. Studies of cohesive energy, molecular dynamics.

Ions treated as static potential. **Born-Oppenheimer approximation**.

Coulomb interaction incorporated self-consistently into lattice potential. **Single electron approximation**, partially justified by Fermi liquid theory

Ionic potential eliminated, interacting electrons move in uniform positive potential. **Jellium,** starting point for field theoretic work.

Ions arranged in a lattice, forming periodic potential for single electrons. Starting point for first-principles' calculations. Weak ionic potentials justified by **pseudopotentials.**

Ionic potential eliminated. **Free Fermi gas**, surprisingly effective with alkali metals.

Approximations

Main physical idea is the Pauli principle, which has two consequences:

1. It populates solids with electrons whose energies would classically signify temperatures on the order of 10,000 K.
2. It prevents all electrons but those whose energy differs slightly from the highest occupied state from participating in transport processes

Important terms:

- Occupation number
- Fermi energy
- Fermi surface
- Density of states
- Sommerfeld expansion
- Effective mass

The Basic Hamiltonian

$$\hat{\mathcal{H}}\Psi = \sum_{l=1}^{N}\left(\frac{-\hbar^2\nabla_l^2}{2m} + U(\vec{r}_l)\right)\Psi(\vec{r}_1 \ldots \vec{r}_N) = \mathcal{E}\Psi(\vec{r}_r \ldots \vec{r}_N). \tag{L2}$$

Single electron problem:

$$\left(\frac{-\hbar^2\nabla^2}{2m} + U(\vec{r})\right)\psi_l(\vec{r}) = \mathcal{E}_l\psi_l(\vec{r}), \tag{L3}$$

Free electron gas

$$\frac{-\hbar^2}{2m}\sum_{l=1}^{N}\nabla_l^2\Psi(\vec{r}_1 \ldots \vec{r}_N) = \mathcal{E}\Psi(\vec{r}_1 \ldots \vec{r}_N), \tag{L4}$$

Periodic Boundary Conditions

$$\begin{aligned}
\Psi(x_1+L,y_1,z_1\ldots,z_N) &= \Psi(x_1,y_1,z_1\ldots z_N) \\
\Psi(x_1,y_1+L,z_1\ldots,z_N) &= \Psi(x_1,y_1,z_1\ldots z_N). \\
&\vdots
\end{aligned} \tag{L5}$$

$$\psi_{\vec{k}} = \frac{1}{\sqrt{\mathcal{V}}} e^{i\vec{k}\cdot\vec{r}} \tag{L6}$$

with $\vec{k}$ of the form

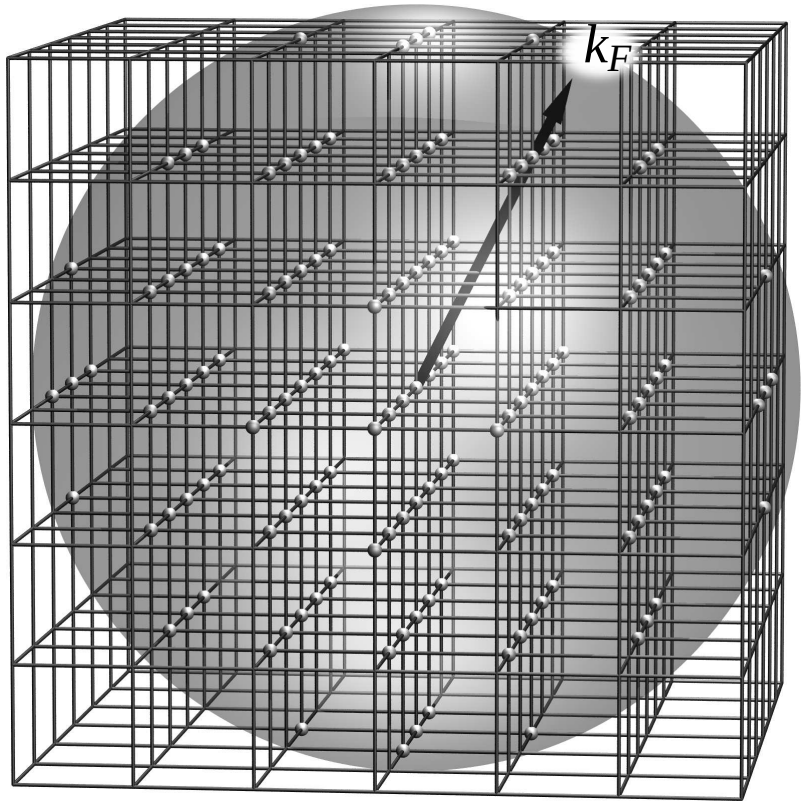
$$\vec{k} = \frac{2\pi}{L}(l_x, l_y, l_z)\,. \tag{L7}$$

The eigenvalue corresponding to the eigenfunction (6) is

$$\mathcal{E}^0_{\vec{k}} = \frac{\hbar^2 k^2}{2m} \tag{L8}$$

Occupation number $f_{\vec{k}}$ of a state indexed by $\vec{k}$ is 1 if this one-electron state is part of the ground state, and 0 otherwise.

Densities of States



$\vec{k}$ states described by Eq. (L7) occupy a cubic lattice in $\vec{k}$ or reciprocal space, with neighboring points separated by distances of $2\pi/L$,

k space volume per state is $(2\pi/L)^3$.

Densities of States

$$\sum_{\vec{k}} F_{\vec{k}}, \tag{L9}$$

$$\int d\vec{k} F_{\vec{k}} = \sum_{\vec{k}} \left(\frac{2\pi}{L}\right)^3 F_{\vec{k}} \tag{L10}$$

$$\Rightarrow \sum_{\vec{k}} F_{\vec{k}} = \frac{\mathcal{V}}{(2\pi)^3} \int d\vec{k} F_{\vec{k}}. \tag{L11}$$

corresponds to

$$\delta_{\vec{k}\vec{q}} \rightarrow \frac{(2\pi)^3}{\mathcal{V}} \delta(\vec{k} - \vec{q}). \tag{L12}$$

Definition of Density of States D

Density of electronic states or density of levels

$$D_{\vec{k}} = 2\frac{1}{(2\pi)^3}, \tag{L13}$$

defined so that

$$\sum_{\vec{k}\sigma} F_{\vec{k}} = \mathcal{V}\int d\vec{k} D_{\vec{k}} F_{\vec{k}}. \tag{L14}$$

To avoid perpetually writing $D_{\vec{k}}$, adopt the notation

$$\int [d\vec{k}] \equiv \frac{2}{\mathcal{V}}\sum_{\vec{k}} = \int d\vec{k} D_{\vec{k}} = \frac{2}{(2\pi)^3}\int d\vec{k} \tag{L15}$$

Energy Density of States

From here onwards, red question marks bracket areas deliberately left blank so that students can fill them in!

$$\sum_{\vec{k}\sigma} F(\mathcal{E}_{\vec{k}}) = \mathcal{V} \int d\mathcal{E}\, D(\mathcal{E}) F(\mathcal{E}) \qquad . \tag{L16}$$

To find $D(\mathcal{E})$, note that

$$\sum_{\vec{k}\sigma} F(\mathcal{E}_{\vec{k}}) \quad = \quad ?$$

$$? \Rightarrow D(\mathcal{E}) = \int [d\vec{k}]\, \delta(\mathcal{E} - \mathcal{E}_{\vec{k}}) \qquad . \tag{L19}$$

Results for Free Electrons

$$D(\mathcal{E}) = \int [d\vec{k}]\, \delta(\mathcal{E} - \mathcal{E}^0_{\vec{k}}) \tag{L20}$$

$$= ?$$

$$? = \frac{m}{\hbar^3 \pi^2} \sqrt{2m\mathcal{E}} \tag{L23}$$

$$= 6.812 \cdot 10^{21} \sqrt{\mathcal{E}/\mathrm{eV}}\, \mathrm{eV}^{-1}\, \mathrm{cm}^{-3}. \tag{L24}$$

Results for Free Electrons

Electrons in sphere of radius k_F is

$$N = \sum_{\vec{k}\sigma} f_{\vec{k}} \tag{L25}$$

$$= ?$$

$$? \frac{\mathcal{V} k_F^3}{3\pi^2}, \tag{L28}$$

$$k_F = (3\pi^2 n)^{1/3} = 3.09\ [n \cdot \text{Å}^3]^{1/3}\,\text{Å}^{-1}. \tag{L29}$$

Results for Free Electrons

radius parameter r_s

$$\frac{4\pi}{3} r_s^3 \equiv \frac{\mathcal{V}}{N} \Rightarrow r_s = \left[\frac{3}{4\pi} \frac{\mathcal{V}}{N} \right]^{1/3}. \tag{L30}$$

Fermi energy, $\mathcal{E}_F$, or Fermi level

$$\mathcal{E}_F = \frac{\hbar^2 k_F^2}{2m} = 36.46 \, [n \cdot \text{Å}^3]^{2/3} \text{eV}. \tag{L31}$$

Fermi surface, electrons with energy $\mathcal{E}_F$.

$$v_F = \hbar k_F / m = 3.58 \, [n \cdot \text{Å}^3]^{1/3} \cdot 10^8 \, \text{cm s}^{-1}. \tag{L32}$$

$$D(\mathcal{E}_F) = \frac{3}{2} \frac{n}{\mathcal{E}_F} = 4.11 \cdot 10^{-2} \, [n \cdot \text{Å}^3] \, \text{eV}^{-1} \, \text{Å}^{-3}. \tag{L33}$$

One- and Two-Dimensional Formulae

One dimension:

$$D_{\vec{k}} = 2\left(\frac{1}{2\pi}\right)^d. \tag{L34}$$

$$D(\mathcal{E}) = ? \qquad ? \tag{L35}$$

Two dimensions:

$$D(\mathcal{E}) = ? \qquad ? \tag{L36}$$

Statistical mechanics of noninteracting electrons

$$Z_{\rm gr} = \sum_{\rm states} e^{\beta(\mu N - \mathcal{E})} \tag{L37}$$

$$= \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \sum_{n_3=0}^{1} \ldots ? \qquad ? \tag{L38}$$

Using the mathematical fact that

$$\sum_{n_1=0}^{N} \sum_{n_2=0}^{N} \ldots \sum_{n_M=0}^{N} \prod_{l=1}^{M} A_{n_l} = ? \qquad ? \tag{L39}$$

one has that

$$Z_{\rm gr} = ?$$

$$? \tag{L41}$$

Statistical mechanics of noninteracting electrons

Therefore the grand potential is given by

$$\Pi \equiv -k_B T \ln Z_{\rm gr} \tag{L42}$$

$$= -k_B T \sum_l \ln\left[1 + e^{\beta[\mu - \mathcal{E}_l]}\right]. \tag{L43}$$

$$= -k_B T \mathcal{V} \int d\mathcal{E}\,? \qquad ? \tag{L44}$$

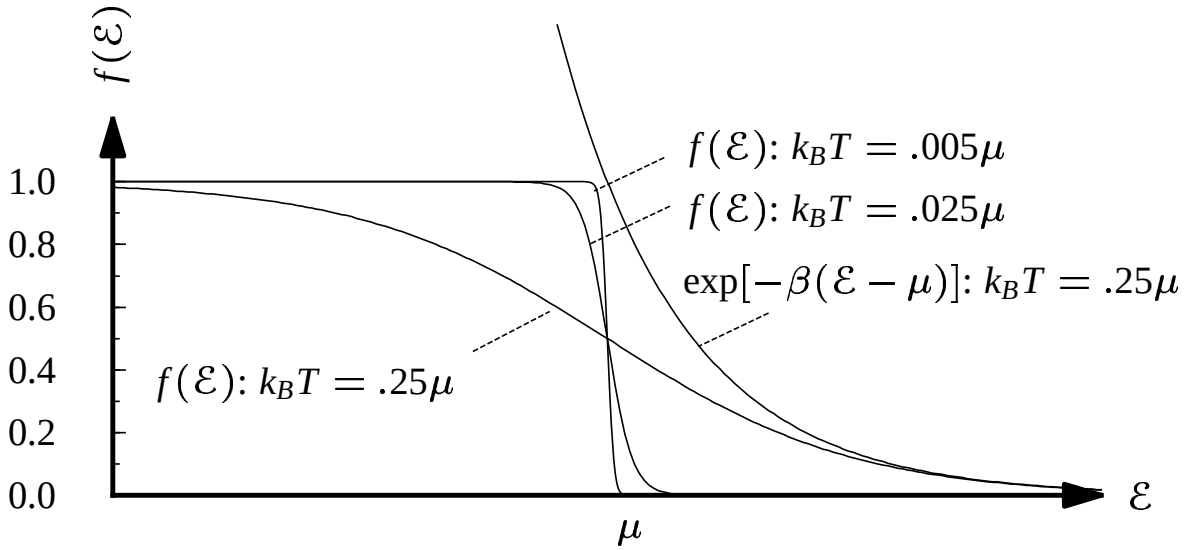
Fermi Function

$$N = ?$$

$$? \Rightarrow n = ? \qquad ? \qquad \text{(L47)}$$

where...

Fermi Function



$$f(\mathcal{E}) = ? \qquad ? \tag{L48}$$

$$f_{\vec{k}} = ? \qquad ? \tag{L49}$$

$$\frac{\partial \beta \Pi}{\partial \beta}\Big|_{\mu} = \mathcal{E} - \mu N = \mathcal{V} \int d\mathcal{E}'\, D(\mathcal{E}')\,(\mathcal{E}' - \mu)\, f(\mathcal{E}') \tag{L50}$$

$$\Rightarrow \frac{\mathcal{E}}{\mathcal{V}} = \int d\mathcal{E}'\, D(\mathcal{E}')\, \mathcal{E}'\, f(\mathcal{E}'). \tag{L51}$$

Classical Limit

Boltzmann statistics

$$f(\mathcal{E}) = Ce^{-\beta\mathcal{E}}. \tag{L52}$$

when

$$f(\mathcal{E}) \ll 1 \Rightarrow e^{\beta(\mathcal{E}-\mu)} \gg 1. \tag{L53}$$

At low temperatures

$$f(\mathcal{E}) \rightarrow ? \qquad ? \tag{L54}$$

Fermi temperature:

$$T_F = \mathcal{E}_F / k_B, \tag{L55}$$

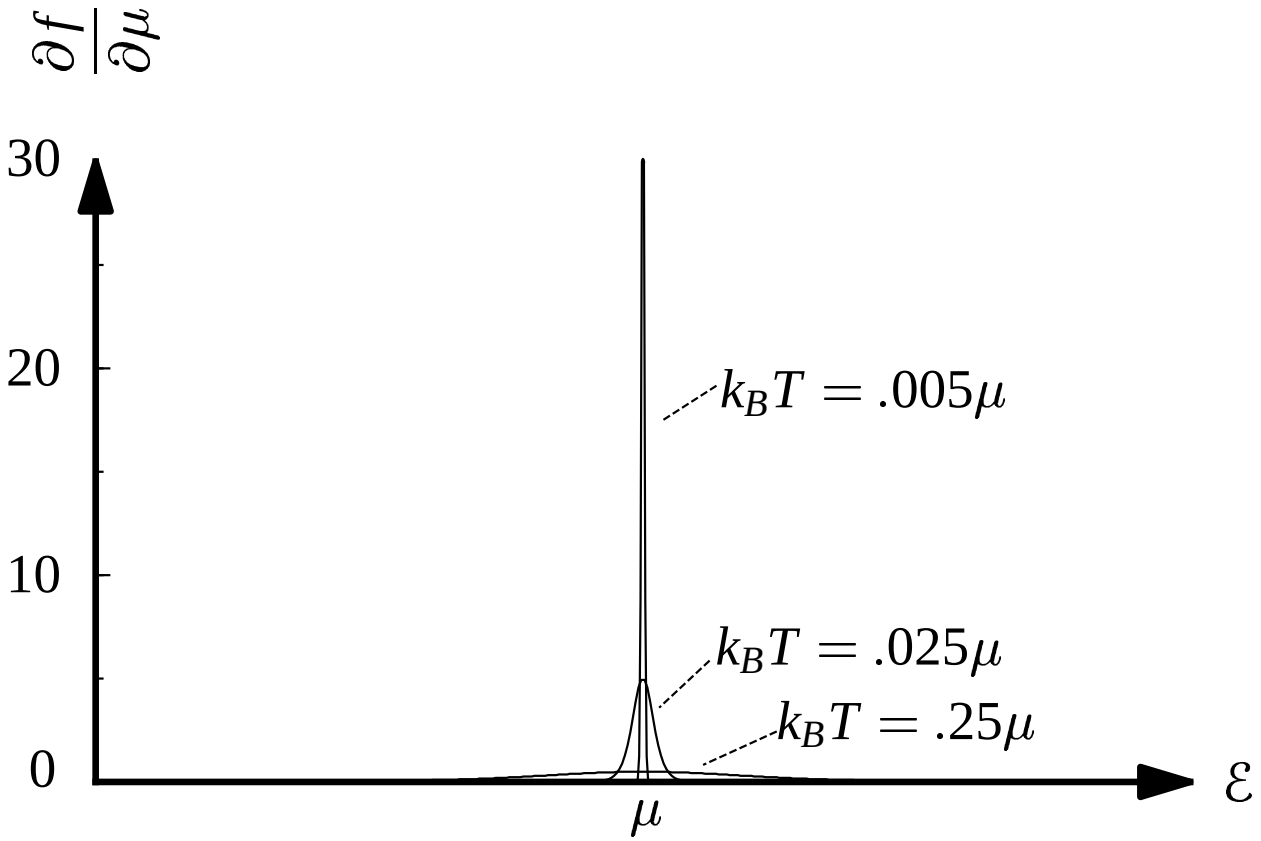
Elements as free electron gases

Element	Z	n ($10^{22}\,\mathrm{cm}^{-3}$)	k_F ($10^{8}\,\mathrm{cm}^{-1}$)	$\mathcal{E}_F$ (eV)	T_F ($10^{4}\,\mathrm{K}$)	v_F ($10^{8}\,\mathrm{cm\,s}^{-1}$)	r_s/a_0
Li	1	4.60	1.11	4.68	5.43	1.28	3.27
Ag	1	5.86	1.20	5.50	6.38	1.39	3.02
Be	2	24.72	1.94	14.36	16.67	2.25	1.87
Al	3	18.07	1.75	11.66	13.53	2.02	2.07
Sn	4	14.83	1.64	10.22	11.86	1.89	2.22
Sb	5	16.54	1.70	10.99	12.75	1.97	2.14
Mn	4	32.61	2.13	17.28	20.05	2.46	1.70
Fe	2	16.90	1.71	11.15	12.94	1.98	2.12
Co	2	18.18	1.75	11.70	13.58	2.03	2.07
Ni	2	18.26	1.76	11.74	13.62	2.03	2.07

Sommerfeld Expansion

Paradox that density of states too small solved by

$$c_V \propto TD(\mathcal{E}_F), \tag{L56}$$



Sommerfeld Expansion

$$\langle H \rangle = \int_{-\infty}^{\infty} d\mathcal{E}\, H(\mathcal{E}) f(\mathcal{E}). \tag{L57}$$

$$\langle H \rangle = \int_{-\infty}^{\mu} d\mathcal{E}\, H(\mathcal{E}) + \sum_{n=1}^{\infty} ?$$

$$? \Rightarrow \langle H \rangle = \int_{-\infty}^{\mu} d\mathcal{E}\, H(\mathcal{E}) + \frac{\pi^2}{6} [k_B T]^2 H'(\mu) + \frac{7\pi^4}{360} [k_B T]^4 H'''(\mu) + \ldots. \tag{L62}$$

Specific Heat

$$c_{\mathcal{V}} = \frac{1}{\mathcal{V}} \frac{\partial \mathcal{E}}{\partial T} \Big|_{N\mathcal{V}} . \tag{L63}$$

$$\frac{\mathcal{E}}{\mathcal{V}} \quad = \quad ?$$

? (L65)

$$\frac{\partial \mu}{\partial T} \Big|_{N\mathcal{V}} = - \frac{\frac{\partial N}{\partial T} \Big|_{\mu\mathcal{V}}}{\frac{\partial N}{\partial \mu} \Big|_{T\mathcal{V}}} . \tag{L66}$$

$N = \mathcal{V} \int d\mathcal{E}'$? ? (L67)

$$\frac{\partial \mu}{\partial T} \Big|_{N\mathcal{V}} = ? \qquad ? \tag{L68}$$

Specialize to Free Fermi Gas

$$\mu = ? \qquad ? \tag{L69}$$

To order T^2

$$\begin{aligned} \frac{\mathcal{E}}{\mathcal{V}} &= \int_0^{\mathcal{E}_F} d\mathcal{E}'\, \mathcal{E}' D(\mathcal{E}') + \frac{\pi^2}{6}(k_B T)^2 D(\mathcal{E}_F) \\ &\quad + \mathcal{E}_F \left\{ (\mu - \mathcal{E}_F) D(\mathcal{E}_F) + \frac{\pi^2}{6}(k_B T)^2 D'(\mathcal{E}_F) \right\} \end{aligned} \tag{L70}$$

$$\Rightarrow \frac{\mathcal{E}}{\mathcal{V}} = \int_0^{\mathcal{E}_F} d\mathcal{E}\, \mathcal{E} D(\mathcal{E}) + \frac{\pi^2}{6}(k_B T)^2 D(\mathcal{E}_F) \tag{L71}$$

$$\Rightarrow c_{\mathcal{V}} = \frac{\pi^2}{3} k_B^2 T D(\mathcal{E}_F). \tag{L72}$$

As predicted, $c_{\mathcal{V}} \propto D(\mathcal{E}_F) T$.

Linear coeffi cient, Sommerfeld parameter

$\gamma \equiv c_{\mathcal{V}} / T$

Specialize to Free Fermi Gas

$$\gamma \equiv \frac{c_V}{T} = ? \qquad ? \tag{L73}$$

Specifi c heat effective mass of the electron.

Specialize to Free Fermi Gas

Metal	Z	γ (mJ mole^{-1} K^{-2})		Metal	Z	γ (mJ mole^{-1} K^{-2})	
		Expt.	Eq. (L73)			Expt.	Eq. (L73
Li	1	1.65	0.74	Al	3	1.35	0.91
Na	1	1.38	1.09	Ga	3	0.60	1.02
K	1	2.08	1.67	In	3	1.66	1.23
Rb	1	2.63	1.90	Sn	4	1.78	1.41
Cs	1	3.97	2.22	Pb	4	2.99	1.50
Cu	1	0.69	0.50	Sb	5	0.12	1.61
Ag	1	0.64	0.64	Bi	5	0.008	1.79
Au	1	0.69	0.64	Mn	2	12.8	1.10
Be	2	0.17	0.5	Fe	2	4.90	1.06
Mg	2	1.6	0.99	UPt_3		450	
Ca	2	2.73	1.51	UBe_{13}		1100	
Sr	2	3.64	1.79				
Ba	2	2.7	1.92				
Zn	2	0.64	0.75				
Cd	2	0.69	0.95				

Stewart (1983), and Stewart (1984).

Specialize to Free Fermi Gas

Heavy Fermions