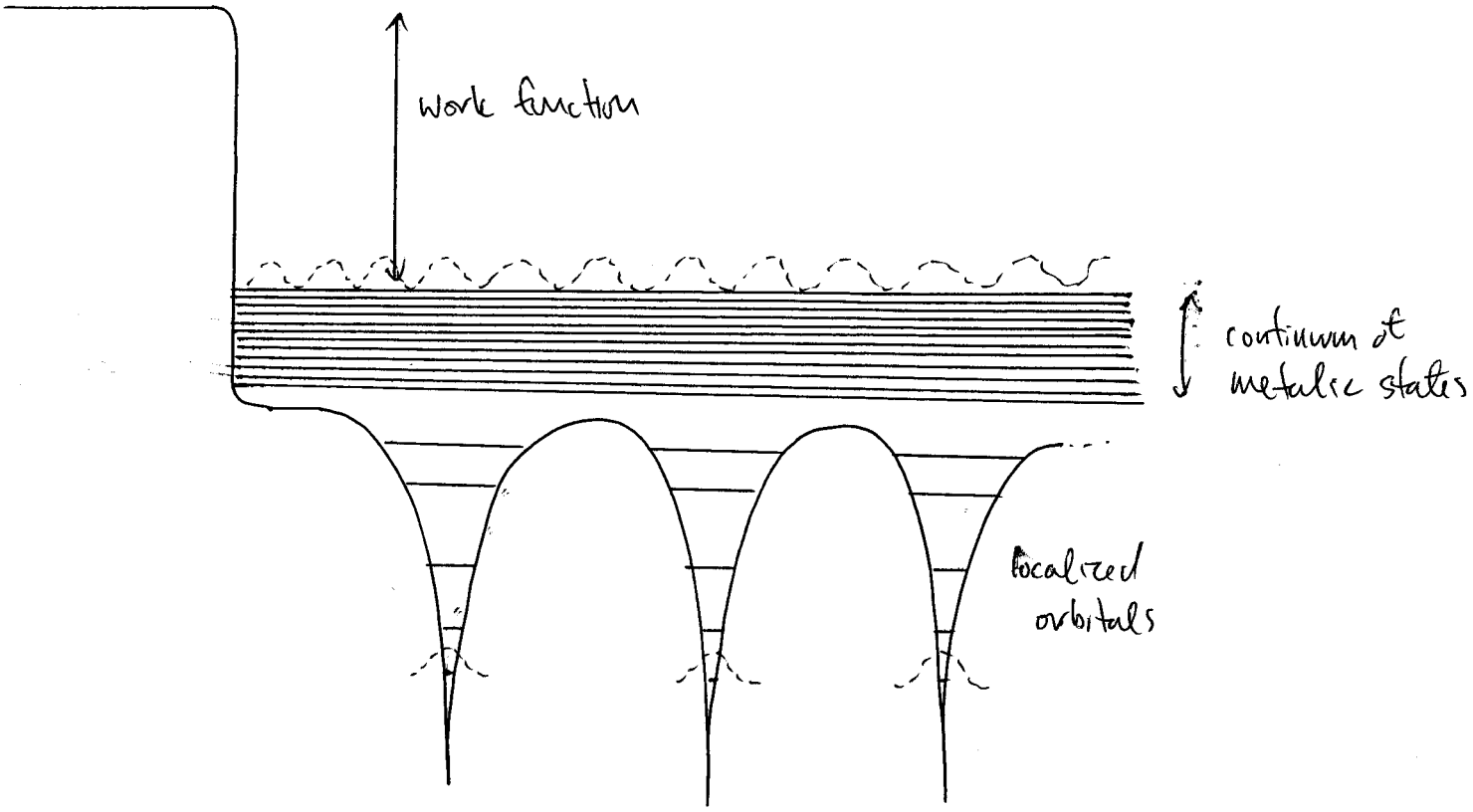
* Let's turn our attention to the electronic degrees of freedom in a solid
  - → electrons that are tightly bound in the inner shells of the constituent atoms are largely chemically inert
  - → even the valence electrons may not be substantially reconfigured, as is the case with the noble gas solids
  - → when there is charge transfer, it often leaves the electrons localized in new positions in the crystal: either at atomic sites (ionic solids) or at interstitial positions along bonding directions (covalent solids)
  - → an important special case is when valence electrons are released into the bulk crystal

* A <u>simple metal</u> is a solid in which some fraction of the electrons are free to move about:
  - → specifically, an odd number of electrons per unit cell (a consequence of band theory)
  - → the electrons are not bound to any atomic site, and we call them delocalized
  - → plane-wave like wavefunctions characteristic of free electrons
  - → flow under heat gradients and applied electric fields
  - → primarily responsible for <u>heat and charge transport</u>

↑ (metal is the opposite of an insulator)



* But how do we get to a free-electron-like model?

→ general hamiltonian for N_{el} electrons and N_{ions} atomic cores:

$$H = \sum_{i=1}^{N_{el}} \frac{\vec{p}_i^{\,2}}{2M_{el}} + \sum_{I=1}^{N_{ions}} \frac{\vec{P}_I^{\,2}}{2M_{ions,I}} + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}$$

$$- \sum_i \sum_I \frac{Z_I e^2}{|\vec{r}_i - \vec{R}_I|} + \sum_{I<J} \frac{Z_I Z_J e^2}{|\vec{R}_I - \vec{R}_J|}$$

→ in the Born-Oppenheimer approx ($M_I \gg m_e$), we can treat the ions as slow, semiclassical degrees of freedom

→ in the extreme, their motion is <u>quenched</u>: $\vec{R} = \vec{R}^{(0)}$ positions are optimized energetically and are fixed ($\vec{P} = 0$), hence defining a rigid lattice

→ we now have a hamiltonian for the electrons only:

$$H = \sum_i \left[\frac{p_i^2}{2m_e} + U(\vec{r}_i) \right] + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}$$

where $U(\vec{r}) = \sum_I \frac{Z_I e^2}{|\vec{r} - \vec{R}_I|}$ is a static, periodic potential

→ the first term ($H_{1\text{-body}}$) alone has a solution that is a single Slater determinant based on products of the single-particle eigenstates

→ the second term ($H_{2\text{-body}}$) introduces non-trivial many-body correlations

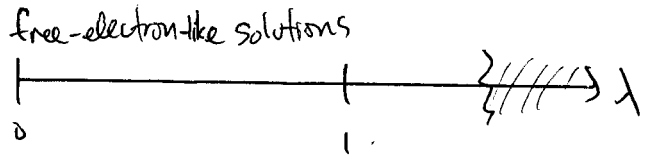
→ think about the combined hamiltonian as

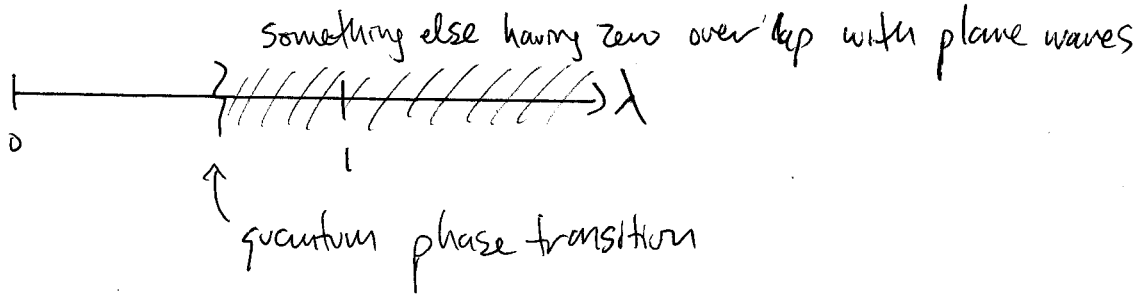
$$H = H_{1\text{-body}} + \lambda H_{2\text{-body}}$$

in the limit $\lambda \to 1$

→ if λ is sufficiently small, then the Coulomb contribution is a weak perturbation

→ two possibilities: $\lambda=1$ either is or is not adiabatically connected to the solution at $\lambda=0$





* How do we know when it is correct to assume $\lambda=1$ is small?

  → (slightly circular) when we find that a material behaves like a simple metal

  → (more formally) when justified by <u>Fermi Liquid</u> theory; in that case, $\lambda=1$ looks like $\lambda=0$ but with some renormalized parameters (e.g. an ~~effective~~ mass)

* Almost all the basic features of a simple metal can be understood in terms of a non-interacting gas of fermions living in a periodic potential

Ideal quantum gases

* non-interacting collections of fermions and bosons
* Statistical-mechanical treatment requires a choice of ensemble:
  → fundamental thermodynamic identity

$$dE = TdS - PdV + \mu dN,$$

arises since the internal energy $E = E(S, V, N)$ is a function of the three extensive quantities, entropy, volume, and particle number

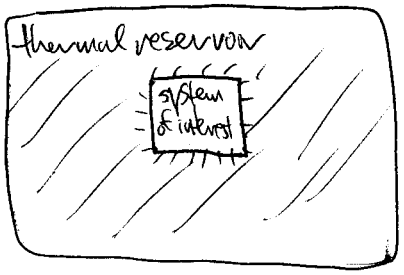
  → temperature, pressure, and chemical potential are derived quantities

$$T = \left(\frac{\partial E}{\partial S}\right)_{VN}, \quad -P = \left(\frac{\partial E}{\partial V}\right)_{SN}, \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{SV}$$

  → quantum systems (almost always) have a unique ground state, so then entropy vanishes:

$$S = 0, \quad \mu = \left(\frac{\partial E_{GS}}{\partial N}\right)_{V}$$

  → but real-world systems aren't isolated; experiments are usually performed in thermal equilibrium at temperature T



heat exchange between subsystems

→ convenient to make a Legendre transform to variables (T,V,N) or (T,P,N):

Helmholtz free energy $F = E - TS$

Gibbs free energy $G = E - TS + PV$

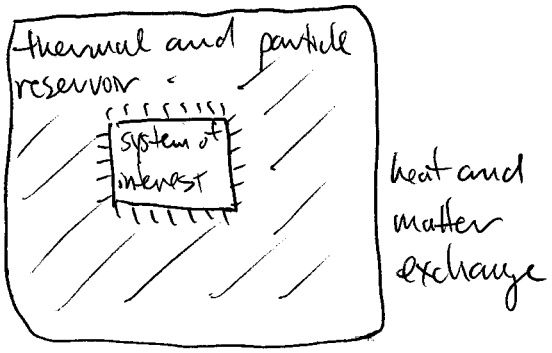
with small changes

$$dF = -SdT - PdV + \mu dN$$

$$dG = -SdT + VdP + \mu dN$$

→ particle number may not be fixed either; e.g. a metal in electric contact with a ground

→ work in (T, V, μ) coordinates by defining the thermodynamic potential



$$\Omega = F - \mu N = E - TS - \mu N$$

with $d\Omega = -SdT - PdV - Nd\mu$

and $S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V\mu}$, $P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T\mu}$,

$$N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{TV}$$

* micro- and macroscopic descriptions connected by the grand partition function

$$\mathcal{Z} \equiv \sum_N \sum_\alpha e^{-\beta(E_\alpha^{(N)} - \mu N)}$$

$$= \sum_N \sum_\alpha \langle N,\alpha | e^{-\beta(\hat{H} - \mu \hat{N})} | N,\alpha \rangle$$

$$= \mathrm{Tr}\, e^{-\beta(\hat{H} - \mu \hat{N})}$$

→ here, α labels all quantum states for a fixed number of particles N ; $\beta = \frac{1}{k_B T}$

→ $\hat{H}$ and $\hat{N}$ are hamiltonian and number operators acting on the space of kets $|N,\alpha\rangle$

→ we assert (assuming ergodicity, etc.) that

$$\Omega(T, V, \mu) = -k_B T \log \mathcal{Z}$$

→ all quantities are expressed as averages

$$\langle \hat{O} \rangle = \frac{\mathrm{Tr}\, \hat{O} e^{-\beta(\hat{H} - \mu \hat{N})}}{\mathrm{Tr}\, e^{-\beta(\hat{H} - \mu \hat{N})}} = \mathrm{Tr}\, \hat{\rho} \hat{O}$$

$$\xrightarrow{T \to 0} \frac{\langle gs | \hat{O} | gs \rangle}{\langle gs | gs \rangle}$$

density matrix

$$\hat{\rho} = \frac{1}{\mathcal{Z}} e^{-\beta(\hat{H} - \mu \hat{N})}$$

* Consider a one-body Hamiltonian $\hat{H}_0$

→ expressed in the abstract occupation number Hilbert space

$$\hat{H}_0 = \sum_\alpha \varepsilon_\alpha \hat{n}_\alpha$$

$$\hat{N} = \sum_\alpha \hat{n}_\alpha$$

and $$\hat{H}_0 - \mu \hat{N} = \sum_\alpha (\varepsilon_\alpha - \mu)\hat{n}_\alpha$$

→ partition function is

$$\mathcal{Z}_0 = e^{-\beta \Omega_0(T,V,\mu)} = \mathrm{tr}\, e^{-\beta(\hat{H}_0 - \mu\hat{N})}$$

$$= \sum_{\{n_1, n_2 \cdots n_\alpha\}} \langle n_1 n_2 \cdots n_\alpha | e^{\beta(\mu\hat{N} - \hat{H}_0)} | n_1 n_2 \cdots n_\infty \rangle$$

↑ complete set of states having n_i particles in the i^{th} orbital / level

$$= \sum_{\{n_1 \cdots n_\alpha\}} \exp\left[\beta\left(\mu \sum_i n_i - \sum_i \varepsilon_i n_i\right)\right]$$

$$= \sum_{n_1} e^{\beta(\mu - \varepsilon_1)} \cdot \sum_{n_2} e^{\beta(\mu-\varepsilon_2)} \cdot \cdots \sum_{n_\infty} e^{\beta(\mu - \varepsilon_\infty)}$$

factorizes into traces over each orbital

$$\boxed{= \prod_i \mathrm{Tr}_i\, e^{-\beta(\varepsilon_i - \mu)\hat{n}_i}} = \prod_i \sum_{n_i}^{(?)} e^{\beta(\mu - \varepsilon_i)}$$

* Particle statistics enters here:

$\sum_{n_i=0}^{\infty}$ bosons

$\sum_{n_i=0}^{1}$ fermions

→ for bosons,

$$\mathcal{Z} = \prod_i \sum_{n=0}^{\infty} \left(e^{\beta(\mu-\varepsilon_i)}\right)^n = \prod_i \left(1 - e^{\beta(\mu-\varepsilon_i)}\right)^{-1}$$

(geometric series)

$$\Omega_0 = -k_B T \log \prod_i \left(1 - e^{\beta(\mu-\varepsilon_i)}\right)^{-1}$$

$$= +k_B T \sum_i \log\left(1 - e^{\beta(\mu-\varepsilon_i)}\right)$$

→ for fermions,

$$\mathcal{Z} = \prod_i \sum_{n=0}^{1} \left(e^{\beta(\mu-\varepsilon_i)}\right)^n = \prod_i \left(1 + e^{\beta(\mu-\varepsilon_i)}\right)$$

$$\Omega_0 = -k_B T \sum_i \log\left(1 + e^{\beta(\mu-\varepsilon_i)}\right)$$

→ differ only by a sign:

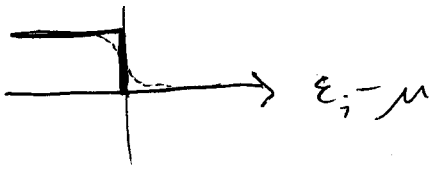
$$\Omega_0 = \pm k_B T \sum_i \log\left(1 \mp e^{\beta(\mu-\varepsilon_i)}\right)$$

* total particle number $\langle \hat{N} \rangle = -\frac{\partial \Omega_0}{\partial \mu} = \sum_i n_i^0$

where $n_i^0 = \frac{1}{e^{\beta(\varepsilon_i - \mu)} \mp 1}$ is the occupation number of level i

→ for fermions, $0 \leq n_i^0 \leq 1$ in accordance with the Pauli principle

→ approaches a step function in the zero temperature limit



Free electrons

* Simple one-body hamiltonian: $\hat{H} = \sum_{k,\sigma} \varepsilon_k \hat{n}_{k,\sigma}$

→ k labels the wavevectors of the $e^{i\vec{k}\cdot\vec{r}}$ modes in a $V = L \times L \times L$ box, and $\sigma = \uparrow, \downarrow$ (spin)

→ $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$ is the free electron dispersion arising from the kinetic energy $\left(\frac{1}{2m}\left(\frac{\hbar \vec{\nabla}}{i}\right)^2 e^{i\vec{k}\cdot\vec{r}}\right) e^{-i\vec{k}\cdot\vec{r}}$

→ in the thermodynamic limit, the sum crosses over to an integral over a continuum of states

$$\sum_k \overset{L\to\infty}{\rightsquigarrow} V \int \frac{d^3k}{(2\pi)^3}$$

* Since $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$ is isotropic in k-space, we can switch to a DOS formulation

$$\varepsilon = \frac{\hbar^2 k^2}{2m}, \quad d\varepsilon = \frac{\hbar^2}{2m} 2k dk$$

→ change of integration measure

$$\frac{1}{(2\pi)^3} 4\pi k^2 dk = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{\varepsilon d\varepsilon}{2\varepsilon^{\frac{1}{2}}} = \frac{1}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \varepsilon^{1/2} d\varepsilon$$

→ $\langle \hat{N} \rangle = \sum_{k,\sigma} \langle \hat{n}_{k,\sigma} \rangle = 2 \sum_k \langle \hat{n}_k \rangle$ (assume symmetric in spin)

$$= 2 \int \frac{d^3k}{(2\pi)^3} \frac{1}{e^{\beta(\varepsilon_k - \mu)} + 1}$$

$$= \frac{2V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty d\varepsilon \frac{\varepsilon^{1/2}}{e^{\beta(\varepsilon - \mu)} + 1}$$

→ $-\Omega_0 = 2k_B T \sum_k \log\left(1 + e^{\beta(\mu - \varepsilon_k)}\right)$

$$= 2k_B T \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty d\varepsilon\, \varepsilon^{1/2} \log\left(1 + e^{\beta(\mu - \varepsilon)}\right)$$

$$= \frac{2}{3} \cdot \frac{2V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty d\varepsilon \, \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)}+1} \qquad \text{(integration by parts)}$$

$$\rightarrow E = 2 \sum_k \varepsilon_k \langle \hat{n}_k \rangle$$

$$= 2V \int \frac{d^3k}{(2\pi)^3} \, \frac{\varepsilon_k}{e^{\beta(\varepsilon_k-\mu)}+1}$$

$$= \frac{2V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot \int_0^\infty d\varepsilon \, \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)}+1} = \frac{3}{2}(-\Omega_0)$$

* At fixed electron filling we have to invert $N(\mu)/V = \text{const}$ and solve for the chemical potential

→ trivial in the $T=0$ limit where

Heaviside function

$$\frac{1}{e^{(\varepsilon-\mu)/k_B T}+1} \xrightarrow{T\to 0} \begin{cases} 0 & \varepsilon > \mu \\ 1 & \varepsilon < \mu \end{cases} = \theta(\mu-\varepsilon)$$

→ low-energy configuration obtained by filling all states up to the Fermi energy

$$\mu = E_F$$

→ density is now

$$\frac{N}{V} = \frac{2}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{E_F} d\varepsilon\, \varepsilon^{1/2}$$

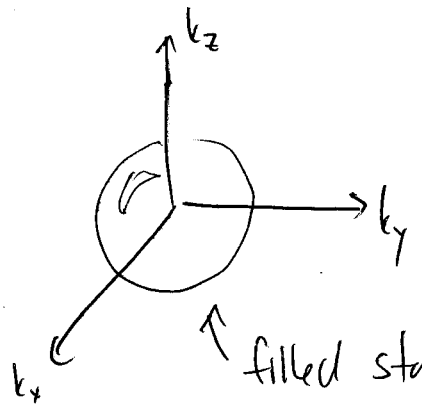
$$= \frac{2}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{2}{3}E_F^{3/2}$$

→ well-define Fermi energy

$$E_F = \left(\frac{6\pi^2}{2}\right)^{2/3}\frac{\hbar^2}{2m}\left(\frac{N}{V}\right)^{2/3} \equiv \frac{\hbar^2 k_F^2}{2m}$$

and Fermi wavevector

$$k_F = \left(\frac{6\pi^2 N}{2V}\right)^{1/3}$$



↑ filled states fill a sphere in k-space called the Fermi sea

→ the Fermi surface $|\vec{k}| = k_F$ separates the filled and unfilled states

→ total energy is

$$\frac{E}{V} = \frac{2}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{E_F} d\varepsilon\, \varepsilon^{3/2} = \frac{2}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{2}{5}E_F^{5/2}$$

→ equation of state: $-\Omega_0 = \frac{2}{3}E = \frac{2}{5}NE_F$

* Consider nonzero but still small temperatures ($k_BT \ll E_F$)

→ more work to invert density to extract μ

→ define $\alpha = \beta\mu = \frac{\mu}{k_BT}$ ← finite

↖ small, tending to zero

→ expand in power series around large α

* Thermodynamic potential under change of variables $x = (\varepsilon - \mu)/k_BT$

$$-\Omega_0 = \frac{2}{3} \cdot \frac{2V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} (k_BT)^{5/2} \underbrace{\int_{-\mu/k_BT}^{\infty} dx \; \frac{(x+\mu/k_BT)^{3/2}}{e^x+1}}$$

$$\equiv I(\alpha) = \int_{-\alpha}^{\infty} dx \; \frac{(x+\alpha)^{3/2}}{e^x+1}$$

→ break $I(\alpha)$ into $x<0$ and $x>0$ pieces

$$I(\alpha) = \int_{-\alpha}^{0} dx \; \frac{(x+\alpha)^{3/2}}{e^x+1} + \int_0^{\infty} dx \; \frac{(\alpha+x)^{3/2}}{e^x+1}$$

↖ apply $x \to -x$ and $(e^{-x}+1)^{-1} = 1 - (e^x+1)^{-1}$

$$= \int_0^{\alpha} dx \; (\alpha-x)^{3/2} + \int_0^{\infty} dx \; \frac{(\alpha+x)^{3/2} - (\alpha-x)^{3/2}}{e^x+1} + \underbrace{\int_{\alpha}^{\infty} dx \; \frac{(\alpha-x)^{3/2}}{e^x+1}}$$

numerator

$$(\alpha+x)^{3/2} - (\alpha-x)^{3/2} = 3x\alpha^{\frac{1}{2}} + \mathcal{O}(\alpha^{-\frac{3}{2}})$$

$\sim e^{-\alpha}$

exponentially small

$$= \frac{2}{5}\alpha^{5/2} + \frac{\pi^2}{4}\alpha^{\frac{1}{2}} + \cdots$$

$$= \left(\frac{1}{k_B T}\right)^{\frac{5}{2}} \left(\frac{2}{5}\mu^{5/2} + (k_B T)^2 \frac{\pi^2}{4}\mu^{1/2} + \cdots \right)$$

→ hence,

$$-\Omega_0 = \frac{2V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{2}{3}\left[\frac{2}{5}\mu^{5/2} + (k_B T)^2\frac{\pi^2}{4}\mu^{\frac{1}{2}} + \cdots\right]$$

↑ neglecting terms higher order in T

and

$$N = -\frac{\partial \Omega_0}{\partial \mu} = \frac{2V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\frac{2}{3}\left[\mu^{3/2} + (k_B T)^2\frac{\pi^2}{8\mu^{1/2}} + \cdots\right]$$

→ recall that the Fermi level is

$$\mu(T=0) = E_F = \left(\frac{6\pi^2}{2}\right)^{2/3}\frac{\hbar^2}{2m}\left(\frac{N}{V}\right)^{2/3}$$

so that

$$\mu = \varepsilon_F\left[1 + \frac{\pi^2}{0}\left(\frac{k_B T}{\mu}\right)^2 + \cdots\right]^{-\frac{2}{3}}$$

$$\simeq \varepsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{\varepsilon_F}\right)^2 + \cdots\right]$$

* The energy is

$$E = \frac{3}{2}(-\Omega_0) = \frac{2V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[\frac{2}{5}\mu^{5/2} + (k_BT)^2\frac{\pi^2}{4}\mu^{1/2} + \cdots\right]$$

$$= \frac{2V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[\frac{2}{5}\varepsilon_F^{5/2}\left(1-\frac{\pi^2}{12}\left(\frac{k_BT}{\varepsilon_F}\right)^2\right)^{5/2}\right.$$

$$\left. + (k_BT)^2\frac{\pi^2}{4}\varepsilon_F^{1/2}\left(1-\frac{\pi^2}{12}\left(\frac{k_BT}{\varepsilon_F}\right)^2\right)\right]^{\frac{1}{2}}$$

$$= E\Big|_{T=0} + \frac{\pi^2}{2}N\frac{(k_BT)^2}{\varepsilon_F}$$

→ we can immediately identify the specific heat

$$C_V = \frac{\partial E}{\partial T} = \frac{\pi^2}{2}Nk_B\left(\frac{k_BT}{\varepsilon_F}\right)$$