

Nearly Free Electrons [tsc16]

This module builds on the results established in [tsc15]. The fermions are now conduction electrons for the most part. The extent of their freedom depends on the application under consideration.

Thermionic emission (Richardson effect):¹

The conduction band of a metal is approximated by a potential well of semi-infinite width and finite depth as shown.

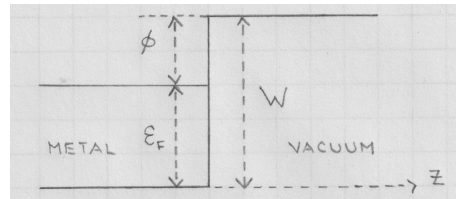
When a cathode is heated up, it emits electrons at a rate R to be calculated. An emission current density J between cathode and anode with a characteristic T -dependence is thus established.

W : depth of well.

ϵ_F : Fermi energy.

ϕ : work function.

A : cathode surface area.



Electron escape conditions (generously sufficient): $p_z > 0$, $\frac{p_z^2}{2m} \geq W$.

For the emission rate we start from an expression derived in [tex62] in the context of kinetic theory [tsc9]:

$$\Rightarrow R \doteq \frac{1}{A} \frac{dN}{dt} = \frac{N}{V} \int_{-\infty}^{+\infty} dv_x \int_{-\infty}^{+\infty} dv_y \int_0^{\infty} dv_z v_z f(\mathbf{v}).$$

Adaptations:

- Transform velocity to momentum: $p_z = mv_z$.
- Replace velocity distribution by fermion occupancy:

$$f(\mathbf{v}) = \frac{1}{N} \langle n_p \rangle_{FD} = [\exp(\beta(p^2/2m - \mu)) + 1]^{-1}.$$

- Uniform density of states in p -space: $D(p) = \frac{gV}{h^3}$ with $g = 2$.
- Split momentum integral: $\int d^3p = 2\pi \int_{\sqrt{2mW}}^{\infty} dp_z \int_0^{\infty} dp_{\perp} p_{\perp}$.

¹This section is adapted from Greiner et al. 1995.

Resulting integral expression:

$$\begin{aligned}
R &= \frac{4\pi}{mh^3} \int_{\sqrt{2mW}}^{\infty} dp_z p_z \int_0^{\infty} dp_{\perp} p_{\perp} \left[\exp\left(\frac{p_{\perp}^2 + p_z^2}{2mk_B T} - \frac{\mu}{k_B T}\right) + 1 \right]^{-1} \\
&= \frac{4\pi k_B T}{h^3} \int_{\sqrt{2mW}}^{\infty} dp_z p_z \ln\left(1 + \exp\left(-\frac{p_z^2}{2mk_B T} + \frac{\mu}{k_B T}\right)\right) \\
&= \frac{4\pi m k_B T}{h^3} \int_W^{\infty} d\epsilon \ln\left(1 + e^{(\mu-\epsilon)/k_B T}\right) \simeq \frac{4\pi m (k_B T)^2}{h^3} e^{-\phi/k_B T}.
\end{aligned}$$

- The integral in the third line follows from the substitution $\epsilon = p_z^2/2m$.
- In the last step, the second term of the logarithm is treated as a perturbation, which is a partial MB limit.
- FD statistics is still contained in the chemical potential, which is approximated as $\mu \simeq \epsilon_F$.

Classically, we use instead [tex112]: $z = e^{\mu/k_B T} = \frac{N}{gV} \lambda_T^3 = \frac{N}{2V} \frac{h^3}{(2\pi m k_B T)^{3/2}}$.

Classical emission rate: $R_{cl} = \frac{N}{V} \sqrt{\frac{k_B T}{2\pi m}} e^{-W/k_B T}$.

Experimental data for the emission current density, $J = eR$, agree with the quantum result: a plot of $\ln(J/T^2)$ versus $1/T$ suggests a straight line.

In the absence of an anode-driven emission current, the emission rate R must be in thermal equilibrium with the absorption rate R' . The electrons outside the cathode, present at density N/V , can be treated classically.

$$R' = \frac{N}{V} \langle v_z \theta(v_z) \rangle = 2k_B T \frac{2\pi m k_B T}{h^3} e^{-\phi/k_B T} = R.$$

Ingredients:

- Classical ideal gas equation of state: $N/V = p/k_B T$.
- Maxwell distribution [tex56]: $\langle v_z \theta(v_z) \rangle = \sqrt{\frac{k_B T}{2\pi m}}$.
- Grandcanonical pressure [tex94]: $p = \frac{g k_B T}{\lambda_T^3} e^{\mu'/k_B T}$ with $g = 2$.
- Shift of reference energy: $\mu' = \epsilon_F - W$.

Schottky effect:²

Here we are interested in the dependence of the thermionic emission current on the electric field between anode and cathode.

The applied electric field $\mathbf{E} = -E \hat{z}$ lowers the work function. The electronic potential energy outside the metal now has three terms:

$$\Delta V(z) = W - eEz - \frac{ke^2}{4z}.$$

- ▷ W : Potential well depth (reference value).
- ▷ $-eEz$: Effect of uniform field electric field.
- ▷ $-\frac{ke^2}{4z}$: Correction due to positive charge induced on metal surface.³

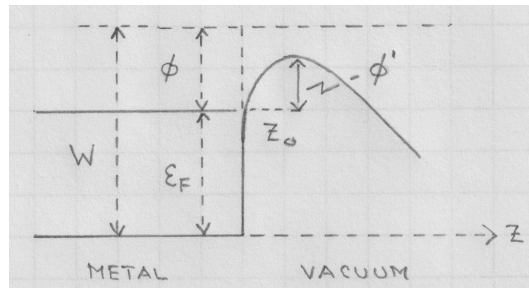
The modified work function ϕ' is determined by the maximum of the effective energy barrier as shown:

$$\frac{d}{dz} \Delta V(z) = 0 \quad \Rightarrow \quad \Delta V(z_0) = W - e^{3/2}(kE)^{1/2} \quad \Rightarrow \quad \phi' = \phi - e^{3/2}(kE)^{1/2}.$$

The characteristic dependence of the emission current density on the applied electric field is known as the Schottky effect:

$$J = J_0 \exp\left(\frac{e^{3/2}\sqrt{kE}}{k_B T}\right).$$

The sketch makes it clear that the result is only valid for weak electric fields. In stronger fields, tunneling (a quantum effect) becomes significant.



²This section is adapted from Greiner et al. 1995.

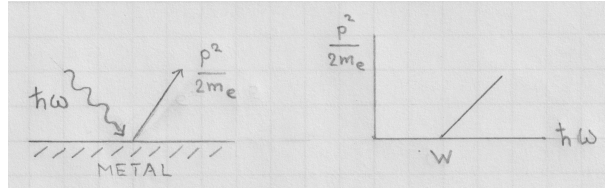
³The structure of this term is inspired by the idea of a mirror charge.

Photoelectric emission (Hallwachs effect):⁴

When a metal surface is illuminated by electromagnetic radiation, electrons are emitted at a rate which depends on the frequency of the radiation.

The energy $\hbar\omega$ of a photon is transferred to a conduction electron in a potential well of depth W .

Condition for photoemission: $\hbar\omega > W$.



Rate of photoemission (expression modified from thermionic emission):

$$R = \frac{4\pi m_e k_B T}{h^3} \int_{W-\hbar\omega}^{\infty} d\epsilon \ln \left(1 + e^{(\mu-\epsilon)/k_B T} \right).$$

The threshold for emission is lowered from W to $W - \hbar\omega$.

- Work function: $\phi \doteq \hbar\omega_0 = W - \mu \simeq W - \epsilon_F$.
- Fugacity (with built-in energy shift): $\eta = e^\delta$, $\delta = \beta\hbar(\omega - \omega_0)$.
- Substitute integration variable: $x \doteq \beta(\epsilon - W + \hbar\omega)$.
- Integrate by parts.
- FD function: $f_2(\eta)$ from [tsl42].

$$\Rightarrow \frac{4\pi m_e}{h^3} (k_B T)^2 \int_0^{\infty} dx \ln(1 + \eta e^{-x}) = \frac{4\pi m_e}{h^3} (k_B T)^2 \underbrace{\int_0^{\infty} \frac{dx x}{\eta^{-1} e^x + 1}}_{f_2(\eta)}.$$

Photoemission current density: $J = eR = \frac{4\pi m_e e}{h^3} (k_B T)^2 f_2(\eta)$.

Ultraviolet (UV) radiation:

- ▷ $\omega > \omega_0$ and $\hbar(\omega - \omega_0) \gg k_B T$
- ▷ $\eta \gg 1 \Rightarrow f_2(\eta) \simeq \frac{1}{2}(\ln \eta)^2 = \frac{1}{2}\delta^2$.
- ▷ $J = \frac{m_e e}{2\pi h} (\omega - \omega_0)^2$ (independent of temperature).

⁴This section is adapted from Greiner et al. 1995.

Infrared (IR) radiation:

- ▷ $\omega < \omega_0$ and $\hbar|\omega - \omega_0| \gg k_B T$
- ▷ $\eta \ll 1 \Rightarrow f_2(\eta) \simeq \eta = e^\delta = e^{\beta\hbar(\omega - \omega_0)}$.
- ▷ $J = \frac{4\pi m_e e}{h^3} (k_B T)^2 e^{(\hbar\omega - \phi)/k_B T}$ (thermionic emission with shift in ϕ).

Threshold radiation:

- ▷ $\omega = \omega_0 \Rightarrow \eta = 1 \Rightarrow f_2(1) = \frac{1}{2}\zeta(2) = \frac{\pi^2}{12}$.
- ▷ $J = \frac{\pi^3 m_e e}{3h^3} (k_B T)^2$.

Pauli paramagnetism (PPM):

Langevin-Brillouin paramagnetism (see [tsc12]) originates in the spin alignment of (unpaired) localized electrons with an external magnetic field.

Pauli paramagnetism originates in the spin alignment of (highly degenerate) conduction electrons. These electrons are spin-paired with high probability. Spin alignment requires most electrons to move to higher energy levels.

Conduction electrons have charge and spin degrees of freedom. Here we assume that the (negative) electron charges are fully screened by the (positive) charge of localized ions. Electrons can move freely.

It is useful to compare the electron gas with spin-polarized FD gases, specifically their thermodynamic potentials.

- ▷ *Spin-polarized FD gases*: + (−) means all spins up (down).

Internal energies:

$$U_\pm \doteq U_0(S_\pm, V_\pm, N_\pm) = T_\pm S_\pm - p_\pm V_\pm + \mu_\pm N_\pm.$$

Helmholtz potentials and grand potentials via Legendre transform:

$$A_\pm \doteq A_0(T_\pm, V_\pm, N_\pm) = U_\pm - T_\pm S_\pm = -p_\pm V_\pm + \mu_\pm N_\pm,$$

$$\Omega_\pm \doteq \Omega_0(T_\pm, V_\pm, \mu_\pm) = A_\pm - \mu_\pm N_\pm = -p_\pm V_\pm.$$

Each free energy has three control variables.

The thermodynamics of spin-polarized FD gases has been analyzed in [tsc15] if we set $g = 1$. Spin is not a degree of freedom.

▷ *Electron gas*

Internal energy:

$$U(S, V, M, N) = TS - pV + HM + \mu N.$$

Helmholtz potential, Gibbs potential, and grand potential via different Legendre transforms:

$$A(T, V, M, N) = U - TS = -pV + HM + \mu N,$$

$$G(T, V, H, N) = A - HM = -pV + \mu N,$$

$$\Omega(T, V, H, \mu) = G - \mu N = -pV.$$

Each free energy has four control variables.

The electron spin is a degree of freedom. There is no coupling between electrons. They only interact statistically via the exclusion principle.

PPM analyzed in canonical ensemble:⁵

System of N electrons with momenta $\mathbf{p} = \hbar\mathbf{k}$ and a (scaled) magnetic moments $m_z = \pm\frac{1}{2}$. In a box of volume V , the \mathbf{k} are a discrete set.

Nonrelativistic one-particle energy in a uniform magnetic field H :

$$\epsilon_{\mathbf{k}}^{\pm} = \epsilon_{\mathbf{k}} \mp \frac{H}{2}, \quad \epsilon_{\mathbf{k}} = \frac{\hbar^2|\mathbf{k}|^2}{2m}.$$

Occupation numbers of single-electron states: $n_{\mathbf{k}}^{\pm} = 0, 1$.

Energy of N -electron state:

$$E_N = \sum_{\sigma=\pm} \sum_{\mathbf{k}} \epsilon_{\mathbf{k}}^{\sigma} n_{\mathbf{k}}^{\sigma} = \sum_{\mathbf{k}} \left[\epsilon_{\mathbf{k}} (n_{\mathbf{k}}^+ + n_{\mathbf{k}}^-) - \frac{H}{2} (n_{\mathbf{k}}^+ - n_{\mathbf{k}}^-) \right].$$

Canonical partition function of electron gas (formally):

$$\begin{aligned} Z_N &= \sum_{\{n_{\mathbf{k}}^{\sigma}\}} \exp \left(-\beta \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} (n_{\mathbf{k}}^+ + n_{\mathbf{k}}^-) + \frac{\beta H}{2} (N_+ - N_-) \right), \\ &= \sum_{N_+=0}^N e^{(\beta H/2)(2N_+ - N)} \underbrace{\left[\sum_{\{n_{\mathbf{k}}^+\}} e^{-\beta \epsilon_{\mathbf{k}} n_{\mathbf{k}}^+} \right]}_{Z_{N_+}^0} \underbrace{\left[\sum_{\{n_{\mathbf{k}}^-\}} e^{-\beta \epsilon_{\mathbf{k}} n_{\mathbf{k}}^-} \right]}_{Z_{N_-}^0}. \end{aligned} \quad (1)$$

⁵This section is adapted from Huang 1987. An alternative analysis, which treats the electron gas as a system of statistically interacting particles, is carried out in the grand-canonical ensemble and will be presented in a later module.

- Number of electrons with spin up/down: $N_{\pm} = \sum_{\mathbf{k}} n_{\mathbf{k}}^{\pm}$.
- The sum \sum' is subject to the constraint $N_+ + N_- = N$.
- The sum \sum'' is constrained to fixed N_+ .
- The sum \sum''' is constrained to fixed $N_- = N - N_+$.
- The canonical partition functions $Z_{N_{\pm}}^0$ pertain to spin-polarized FD particles and are related to identical Helmholtz free-energy functions:

$$Z_{N_{\pm}}^0 = e^{-\beta A_0(T, V, N_{\pm})}.$$

Gibbs free energy of electron gas, formally from (1):

$$\begin{aligned} G(T, V, H, N) &\doteq -k_B T \ln Z_N & (2) \\ &= \frac{1}{2} H N - k_B T \ln \left(\sum_{N_+=0}^N e^{\beta [H N_+ - A_0(T, V, N_+) - A_0(T, V, N - N_+)]} \right). \end{aligned}$$

For $N \gg 1$ the sum in (2) is dominated by the largest term. All other terms contribute logarithmic corrections to extensivity.

Dominant term in Gibbs free energy:

$$\begin{aligned} G(T, V, H, N) &= \frac{1}{2} H N - H N_+ + A_0(T, V, N_+) + A_0(T, V, N - N_+) \\ &= A_0(T, V, N_+) + A_0(T, V, N_-) - \frac{1}{2} H (N_+ - N_-). \end{aligned}$$

Natural independent variables of Helmholtz potential $A(T, V, M, N)$:

- temperature: T ,
- volume: V ,
- magnetization: $M = \frac{1}{2}(N_+ - N_-)$,
- number of electrons: $N = N_+ + N_-$.

Helmholtz potential from Gibbs potential via Legendre transform:

$$\begin{aligned} A(T, V, M, N) &= G(T, V, H, N) + H M \\ &= A_0(T, V, N/2 + M) + A_0(T, V, N/2 - M). \end{aligned}$$

The functions $A_0(T, V, N_{\pm})$ for spin-polarized fermions can be inferred by Legendre transform from results derived in [tsc15] by setting $g = 1$:

$$\Omega_0(T, V, k_B T \ln z_{\pm}) = -\frac{k_B T V}{\lambda_T^{\mathcal{D}}} f_{\mathcal{D}/2+1}(z_{\pm}), \quad N_{\pm} = \frac{V}{\lambda_T^{\mathcal{D}}} f_{\mathcal{D}/2}(z_{\pm}).$$

$$\Rightarrow A_0(T, V, N_{\pm}) = \Omega_0(T, V, k_B T \ln z_{\pm}) + N_{\pm} k_B T \ln z_{\pm}.$$

PPM thermodynamic potentials and functions:

By substitution we arrive at a parametric expression for the Helmholtz potential $A(T, V, M, N)$ of the electron gas in the form,

$$\begin{aligned} A &= \frac{k_B T V}{\lambda_T^{\mathcal{D}}} \sum_{\sigma} [f_{\mathcal{D}/2}(z_{\sigma}) \ln z_{\sigma} - f_{\mathcal{D}/2+1}(z_{\sigma})], \\ N &= \sum_{\sigma} N_{\sigma} = \frac{V}{\lambda_T^{\mathcal{D}}} \sum_{\sigma} f_{\mathcal{D}/2}(z_{\sigma}), \\ M &= \frac{1}{2} \sum_{\sigma} \sigma N_{\sigma} = \frac{V}{2\lambda_T^{\mathcal{D}}} \sum_{\sigma} \sigma f_{\mathcal{D}/2}(z_{\sigma}), \end{aligned}$$

where the two parameters z_+, z_- control the two variables M and N .

The thermodynamic variables conjugate to N and M are derived from

$$A = A_0(T, V, N_+) + A_0(T, V, N_-), \quad N_+ = \frac{N}{2} + M, \quad N_- = \frac{N}{2} - M.$$

– Chemical potential:

$$\begin{aligned} \mu &\doteq \left(\frac{\partial A}{\partial N} \right)_{TVM} = \frac{\partial A_0}{\partial N_+} \frac{\partial N_+}{\partial N} + \frac{\partial A_0}{\partial N_-} \frac{\partial N_-}{\partial N} = (\mu_+) \left(\frac{1}{2} \right) + (\mu_-) \left(\frac{1}{2} \right) \\ &= \frac{1}{2} (\mu_+ + \mu_-) = \frac{1}{2} k_B T \ln(z_+ z_-) = \frac{1}{2} k_B T \sum_{\sigma} \ln z_{\sigma}. \end{aligned}$$

– Magnetic field:

$$\begin{aligned} H &\doteq \left(\frac{\partial A}{\partial M} \right)_{TVN} = \frac{\partial A_0}{\partial N_+} \frac{\partial N_+}{\partial M} + \frac{\partial A_0}{\partial N_-} \frac{\partial N_-}{\partial M} = (\mu_+) (1) + (\mu_-) (-1) \\ &= \mu_+ - \mu_- = k_B T \ln \frac{z_+}{z_-} = k_B T \sum_{\sigma} \sigma \ln z_{\sigma}. \end{aligned}$$

Thermodynamic functions are first derivatives of thermodynamic potentials. They come in conjugate pairs, of which one is a natural independent variable of any given thermodynamic potential. Here we have four such pairs:

- ▷ T, S : temperature and entropy,
- ▷ H, M : magnetic field and magnetization,
- ▷ p, V : pressure and volume,
- ▷ μ, N : chemical potential and number of particles.

We have already established parametric expression for H, M, μ, N . The volume V always appears explicitly. The temperature T appears explicitly and is contained in the fugacities z_σ . That leaves pressure p and entropy S .

The grand potential is derived from the Helmholtz potential by a twofold Legendre transform:

$$\Omega(T, V, H, \mu) = A(T, V, M, N) - HM - \mu N = -pV.$$

Its parametric representation reads as follows:

$$\begin{aligned}\Omega &= -\frac{k_B T V}{\lambda_T^{\mathcal{D}}} \sum_{\sigma} f_{\mathcal{D}/2+1}(z_{\sigma}), \\ H &= k_B T \sum_{\sigma} \sigma \ln z_{\sigma}, \\ \mu &= \frac{1}{2} k_B T \sum_{\sigma} \ln z_{\sigma},\end{aligned}$$

where the two parameters z_+, z_- control the two variables H and μ .

The pressure follows directly from $\Omega = -pV$:

$$p = \frac{k_B T}{\lambda_T^{\mathcal{D}}} \sum_{\sigma} f_{\mathcal{D}/2+1}(z_{\sigma}).$$

The entropy can be derived in two ways from what we already have [tex161]:

$$\begin{aligned}S &= -\left(\frac{\partial A}{\partial T}\right)_{V, M, N} = -\left(\frac{\partial \Omega}{\partial T}\right)_{V, H, \mu} \\ &= k_B \sum_{\sigma=\pm} N_{\sigma} \left[\left(\frac{\mathcal{D}}{2} + 1\right) \frac{f_{\mathcal{D}/2+1}(z_{\sigma})}{f_{\mathcal{D}/2}(z_{\sigma})} - \ln z_{\sigma} \right].\end{aligned}$$

The internal energy is obtained via another Legendre transform [tex162]:

$$U = A + TS = \frac{\mathcal{D}}{2} k_B T \sum_{\sigma=\pm} N_{\sigma} \frac{f_{\mathcal{D}/2+1}(z_{\sigma})}{f_{\mathcal{D}/2}(z_{\sigma})}.$$

It is a thermodynamic potential if (parametrically) expressed as $U(S, V, M, N)$.

PPM response functions:

Pauli paramagnetism is characterized by thermal, magnetic, and mechanical response functions including the following:

- Heat capacity [tex163]: $C_{VM} = \left(\frac{\partial U}{\partial T} \right)_{VMN}$.
- Heat capacity [tex164]: $C_{VH} = \left(\frac{\partial U}{\partial T} \right)_{VHN}$.
- Isothermal susceptibility [tex165]: $\chi_{TV} = \left(\frac{\partial M}{\partial H} \right)_{TVN}$.
- Isothermal susceptibility [tex165]: $\chi_{Tp} = \left(\frac{\partial M}{\partial H} \right)_{TpN}$.
- Isothermal compressibility [tx166]: $\kappa_{TM} = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{TMN}$.
- Isothermal compressibility [tx166]: $\kappa_{TH} = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{THN}$.
- Isobaric expansivity [tex167]: $\alpha_{pM} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{pMN}$.
- Isobaric expansivity [tex167]: $\alpha_{pH} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{pHN}$.

PPM magnetization curves (numerical analysis):

Graphical representations of M versus H at fixed (and discretely varied) T reveal signature attributes of magnetic models or materials.

We choose convenient scales, in part introduced earlier for FD gases [tsc15]:

$$\begin{aligned} \triangleright \lambda_{T_v}^{\mathcal{D}} &= \frac{V}{N} \quad \Rightarrow \quad k_B T_v = \frac{\Lambda}{(V/N)^{2/\mathcal{D}}}, \quad \Lambda \doteq \frac{h^2}{2\pi m}, \\ \triangleright \epsilon_F &= k_B T_F = k_B T_v [\Gamma(\mathcal{D}/2 + 1)]^{2/\mathcal{D}}. \end{aligned}$$

Scaled variables in use for magnetization curves (two alternatives):

$$\bar{M} \doteq \frac{M}{N}, \quad \bar{H} \doteq \frac{H}{k_B T_v}, \quad \bar{T} \doteq \frac{T}{T_v}, \quad \hat{H} \doteq \frac{H}{k_B T_F}, \quad \hat{T} \doteq \frac{T}{T_F}.$$

Next we construct from the two-parameter representations of thermodynamic functions a one-parameter representations for $\bar{M}(\bar{T}, \bar{H})$ or $\bar{M}(\hat{T}, \hat{H})$.

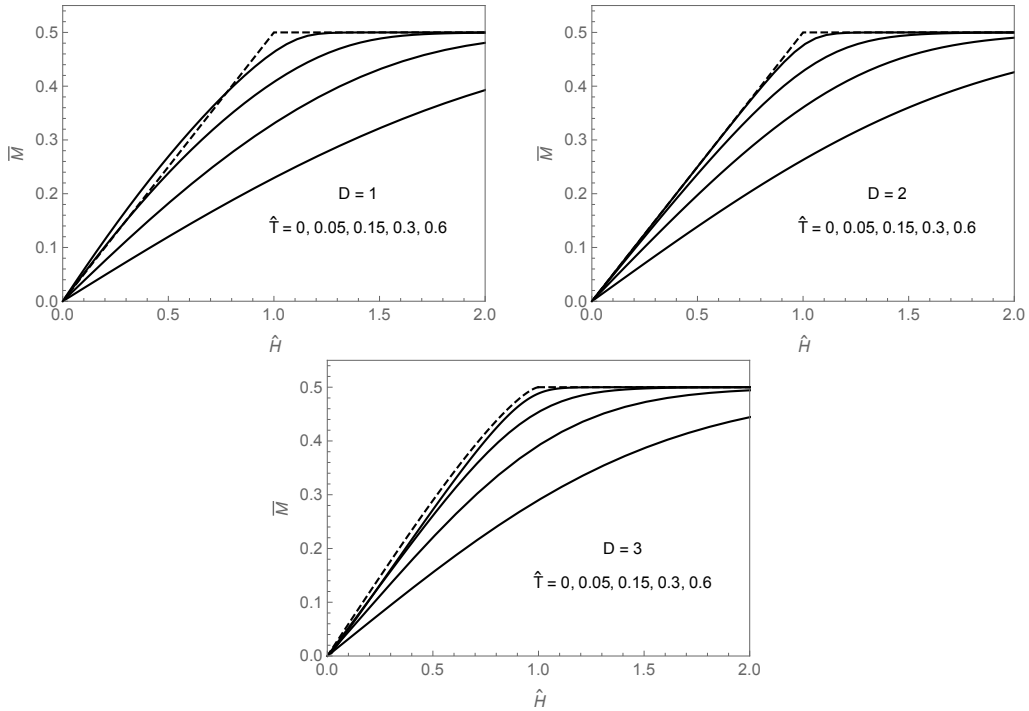
$$\begin{aligned}\bar{H} &= \bar{T} \ln \frac{z_+}{z_-}, \quad z = \sqrt{z_+ z_-} \quad \Rightarrow \quad z_{\pm} = z e^{\pm \bar{H}/2\bar{T}}. \\ \Rightarrow \bar{M} &= \frac{1}{2} \frac{f_{\mathcal{D}/2}(z e^{\bar{H}/2\bar{T}}) - f_{\mathcal{D}/2}(z e^{-\bar{H}/2\bar{T}})}{f_{\mathcal{D}/2}(z e^{\bar{H}/2\bar{T}}) + f_{\mathcal{D}/2}(z e^{-\bar{H}/2\bar{T}})}, \\ \lambda_T^{\mathcal{D}} \frac{N}{V} &= \left(\frac{k_B T_v}{k_B T} \right)^{\mathcal{D}/\epsilon} = \bar{T}^{-\mathcal{D}/2} = f_{\mathcal{D}/2}(z e^{\bar{H}/2\bar{T}}) + f_{\mathcal{D}/2}(z e^{-\bar{H}/2\bar{T}}).\end{aligned}$$

with z in the role of the parameter. Alternatively, for $\bar{M}(\hat{T}, \hat{H})$ we have

$$\bar{M} = \frac{1}{2} \frac{f_{\mathcal{D}/2}(z e^{\hat{H}/2\hat{T}}) - f_{\mathcal{D}/2}(z e^{-\hat{H}/2\hat{T}})}{f_{\mathcal{D}/2}(z e^{\hat{H}/2\hat{T}}) + f_{\mathcal{D}/2}(z e^{-\hat{H}/2\hat{T}})}, \quad (3)$$

$$\hat{T}^{-\mathcal{D}/2} = \Gamma(\mathcal{D}/2 + 1) \left[f_{\mathcal{D}/2}(z e^{\hat{H}/2\hat{T}}) + f_{\mathcal{D}/2}(z e^{-\hat{H}/2\hat{T}}) \right]. \quad (4)$$

The numerical analysis of Eqs. (3) and (4) as carried out in [tex180] produces the magnetization curves represented by the solid curves.



- At high \hat{T} , the curves are similar to those of Langevin-Brillouin paramagnetism with similar saturation effects.
- At low \hat{T} , the slope remains finite and saturation occurs at $\hat{H} = 1$ in the limit $\hat{T} \rightarrow 0$ unlike in Langevin-Brillouin paramagnetism.

PPM magnetization curves at $T = 0$ (exact analysis):

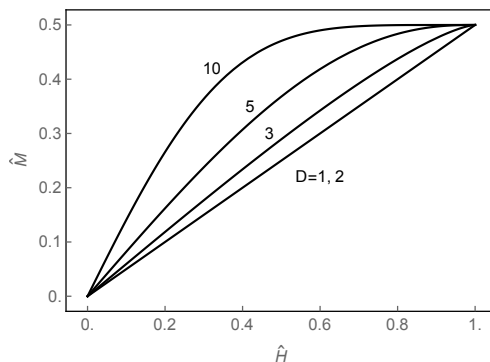
An explicit expression for the inverse of $\bar{M}(0, \hat{H})$ can be extracted from (3) and (4) via asymptotic expansion [tex181]:

$$\hat{H} = \left(\frac{1}{2} + \bar{M}\right)^{2/\mathcal{D}} - \left(\frac{1}{2} - \bar{M}\right)^{2/\mathcal{D}}.$$

This relation can be inverted analytically for $\mathcal{D} = 1, 2, 4, 6, 8$ at least:

$$\bar{M}_1(0, \hat{H}) = \bar{M}_2(0, \hat{H}) = \frac{1}{2} \hat{H}, \quad \bar{M}_4(0, \hat{H}) = \frac{1}{2} \hat{H} \sqrt{2 - \hat{H}^2}, \quad \dots$$

Initial slope ($\hat{T} = 0$ susceptibility): $\lim_{\hat{H} \rightarrow 0} \frac{d}{d\hat{H}} \bar{M}(0, \hat{H}) = \mathcal{D} 2^{2/\mathcal{D}-3}$.



PPM magnetization curves in $\mathcal{D} = 2$ (exact analysis):

The simplicity of $f_1(z) = \ln(1+z)$ makes it possible to process the parametric result (3)-(4) into the explicit result for $\mathcal{D} = 2$ [tex182]:

$$\bar{M}(\hat{T}, \hat{H}) = \frac{\hat{H}}{2} - \hat{T} \text{Arctanh} \left(\frac{\sinh(\hat{H}/2\hat{T})}{\sqrt{\sinh^2(\hat{H}/2\hat{T}) + e^{1/\hat{T}}}} \right).$$

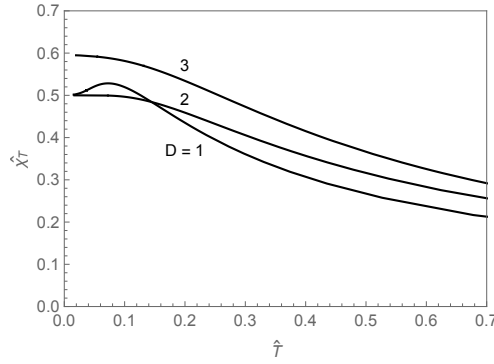
The low-temperature limit of this expression is subtle. The second term disappears if $\hat{H} < 1$, leaving the strictly linear first term, $\bar{M} = \hat{H}/2$. If $\hat{H} > 1$, the second term becomes $(1 - \hat{H})/2$, producing a constant, saturated magnetization, $\bar{M} = 1/2$ [tex182].

PPM isothermal susceptibility at $\hat{H} = 0$:

We have noted that the initial slope of the magnetization $\bar{M}(\hat{T}, \hat{H})$ varies with \mathcal{D} and \hat{T} in non-systematic ways.

The zero-field isothermal susceptibility, investigated in [tex183], illuminates the non-systematic \hat{T} -dependence:

$$\hat{\chi}_T \doteq \left(\frac{\partial \bar{M}}{\partial \hat{H}} \right)_{\hat{T}} = \frac{1}{4\hat{T}} \frac{f_{\mathcal{D}/2-1}(z)}{f_{\mathcal{D}/2}(z)} \underset{\hat{T} \rightarrow 0}{\rightsquigarrow} \mathcal{D} 2^{2/\mathcal{D}-3}, \quad \hat{T}^{-\mathcal{D}/2} = 2\Gamma(\mathcal{D}/2+1)f_{\mathcal{D}/2}(z).$$



PPM correction to Langevin-Brillouin result at high temperature:

The high- \bar{T} expansion of the magnetization curve yields the following expression [tex184]:

$$\bar{M} = \frac{1}{2} \tanh \left(\frac{\bar{H}}{2\bar{T}} \right) \left[1 - \frac{1}{2} (2\bar{T})^{-\mathcal{D}/2} \text{sech}^2 \left(\frac{\bar{H}}{2\bar{T}} \right) + \dots \right].$$

The leading term represents the equation of state of an ideal Langevin-Brillouin two-level paramagnet [tex85].

The leading correction has a negative sign. Double occupancy, which is rare at high \bar{T} , is only open to electrons with opposite spin direction.