Conductivity – The Sommerfeld Theory of Metals

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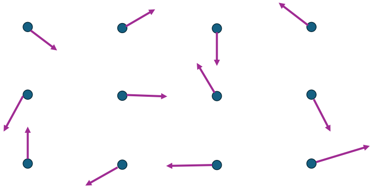
Section 1

Review of the Drude Model

Electron Gas

- Metal has N fixed ions + electron gas (**<u>conduction electrons</u>**).
- The electron gas consists of 1 valence electron per nucleus[1].
- The ions consist of the nucleus plus bound electrons.
- Ionic charge $= Z - e$
- Total charge of electron gas $= Ne$.



Collision outgoing velocities are independent of ingoing velocities

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[1] More generally, n_v valence electrons per nucleus

Collision assumptions

- **Independent electron approximation**

  Neglect $e^- - e^-$ interactions.

  A suprisingly good approximation for many metallic phenomena
- **Free electron approximation**

  Neglect ionic field on e^-.

  A poor approximation for many metallic phenomena
- Electron-ion collisions result in rapid velocity changes
- Between collisions, electrons obey $\mathbf{F} = m\mathbf{a}$ for external $\mathbf{F} = m\mathbf{a}$
- Electron probability of collision in time dt is $\frac{dt}{\tau}$.
  - τ is called the *relaxation time*
  - Electron will on average travel for τ before next collision.
  - Electron on average traveled for τ after last collision.
- τ is independent of electron position or velocity.
- Electrons maintain thermal equilibrium only thru collisions
  - Outgoing velocity is independent of ingoing velocity
  - Outgoing velocity is tied to local temperature
  - E.g. outgoing velocities are higher where local temp is higher

The Force equation and Ohm's Law

- Ohm's Law for constant current: $V = IR$
  - Start with $V = \mathbf{E} \cdot \mathbf{d}$.
  - Relate V to $\mathbf{F}$ with $\mathbf{F} = -e\mathbf{E}$.
  - Between collisions, $\mathbf{F} = m\mathbf{a}$.
  - For constant $\mathbf{F}$ this gives average $\Delta\mathbf{v} = \frac{\mathbf{F}}{m}\tau$
  - Relate I to the average drift velocity of electrons.
  - Then $\rho = \frac{m}{ne^2\tau}$ where $\rho = \frac{L}{A}R$.
- Mean free path is approximately inter-ionic distance
  - τ (inferred from resistance) and $\bar{\mathbf{v}}$ imply MFP.
  - Compute $\bar{\mathbf{v}}$ from Boltzmann distribution (stat mech)
  - Just a coincidence because $\bar{\mathbf{v}}$ is wrong.
    - Otherwise the molar specific heat would be much higher.
    - Per-electron specific heat measured to be ≈ 0
    - Boltzmann dist predicts per-electron specific heat of $\frac{3}{2}kT$
- Other results are derived from the generalized force law

$$\frac{d\bar{\mathbf{p}}(t)}{dt} = -\frac{\bar{\mathbf{p}}(t)}{\tau} + \mathbf{F}(t)$$

  - Just Newton's Law adjusted by probability of collision

The Hall Effect

- Hall effect introduces magnetic field perpendicular to current. Use generalized force law.

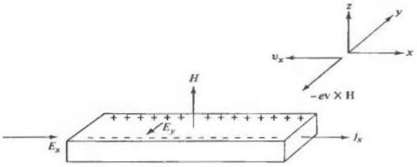


Figure 1.3
Schematic view of Hall's experiment.

  - Magnetic field induces force in $y - direction$
  - But electron-accumulation on edges keeps current in x-direction
- So $E_x = \rho \bar{j}_x$. **Magnetism doesn't effect resistivity!**
  - This was observed experimentally by Hall.
- $E_y = -\omega_c \rho \tau j_x = R_H H j_x$ where the Hall coefficient $R_H = -\frac{1}{nec}$.
- R_H **is independent of** τ **or other properties of the metal.**

Transparency

- When is a metal transparent to light?
- Method: Maxwell's equations in presence of collisions
  - A radiative solution has the form $\mathbf{E}(t) = \mathbf{E}(\omega)e^{-i\omega t}$
  - Apply generalized force law to $\mathbf{F} = e\mathbf{E}$.
  - Current is proportional to momentum.
  - Maxwell's equations involve current.
  - So
    $$-\nabla^2\mathbf{E} = \frac{\omega^2}{c^2}\epsilon(\omega)\mathbf{E}$$
    where $\epsilon(\omega) = 1 + \frac{4\pi i\tau ne^2}{m(1-i\omega\tau)}$
- Take $\omega\tau >> 1$.
  - Then $\epsilon(\omega) \approx 1 - \frac{\omega_P^2}{\omega^2}$ where $\omega_P = \frac{4\pi ne^2}{m}$.
    - ω_P is the "plasma frequency"
    - By relationship of τ to resistivity, $\omega_P\tau >> 1$ for most metals
  - When $\omega < \omega_P$ then $\epsilon(\omega) < 0$ and $\mathbf{E}$ dies exponentially
  - When $\omega > \omega_P$, $\mathbf{E}$ oscillates $\mathbf{E}(x) \propto e^{-i\frac{\omega}{c}x}$
    - This is radiation through the wire – i.e. **transparency**

Section 2

Review of statistical mechanics

Postulate of Equal A Priori Probabilities – Example 1

An isolated system in equilibrium is equally likely to be in any of its accessible states.

No restrictions on single-particle states

Table: Total of three dice adding up to 7.
No restrictions.

Die 1	**Die 2**	**Die 3**
1	1	5
1	5	1
1	2	4
1	4	2
1	3	3
2	1	4
2	4	1
2	2	3
2	3	2
...	...	...
...	...	...

3 dice add up to a total of 7.
15 possible configurations.

- 5 configs where the *red system* is 1, so $P_7(1) = 5/15 = 33\%$.
- Similarly, $P_7(2) = 4/15 = 27\%$.
- Etc. until $P_7(5) = 1/15 = 7\%$.

Postulate of Equal A Priori Probabilities – Example 2

An isolated system in equilibrium is equally likely to be in any of its accessible states.

Restrictions: 2 particles can't be in same single-particle state

Table: Total of three dice adding up to 7. With restrictions.

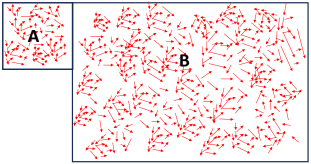
Die 1	**Die 2**	**Die 3**
1	2	4
1	4	2
2	1	4
2	4	1
...	...	...
...	...	...

3 dice add up to a total of 7.
6 possible configurations.

- 2 configs where the *red system* is 1, so $P(1) = 2/6 = 33\%$.
- Similarly, $P_7(2) = 2/6 = 33\%$.
- $P_7(4) = 2/6 = 33\%$.
- $P_7(1) = P_7(3) = P_7(5) = 0$

Distributions

Figure: Total energy is E_{tot}. Total particles $= N_{\text{tot}}$.



- System B has many more states than system A.
- A and B are free to exchange energy (but not particles)
- For electron gas, assume independent and free e^- approximation
  - Then the single-electron energy is $E = \frac{p^2}{2m} = \frac{1}{2}mv^2$
- Thermal equilibrium $\implies$ Law of Equal a Priori Probability
- Thermal distributions: e^--density distribution about $\mathbf{v}$ is $f(\mathbf{v})d\mathbf{v}$

Section 3

Maxwell-Boltzmann and Fermi-Dirac Distributions

Comparison of MB and FD distributions

- Classical mechanics $\Longrightarrow$ Maxwell-Boltzmann distribution.
- Quantum mechanics for fermions $\Longrightarrow$ Fermi-Dirac distribution.
    - Actually, QM predicts $\mathbf{p}$ distribution.
    - We cheat by claiming $\mathbf{p} = m\mathbf{v}$
- MB: Maxwell-Boltzmann (distinguishable particles)
    - $f_{MB}(\mathbf{v}) = n\left(\frac{m\beta}{2\pi}\right)^{\frac{3}{2}} e^{-\beta E}$ $(\beta = \frac{1}{k_B T})$
- FD: Fermi-Dirac (indisting. particles & Pauli exclusion)
    - $f_{FD}(\mathbf{v}) = \frac{\left(\frac{m}{\hbar}\right)^3}{4\pi^3} \frac{1}{1+e^{\beta(E-k_B T_0)}}$ $(\beta =$ inverse temperature$)$
    - Set T_0, the **Fermi temperature**, by $\int d^3v f_{FD}(\mathbf{v}) = n$

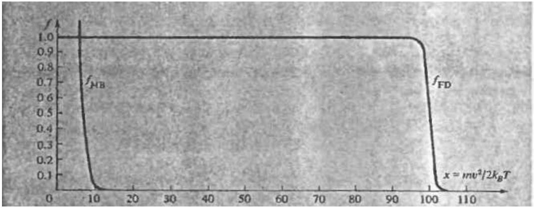


Figure: Distributions for typical metallic densities at room temperature. $T/T_0 = .01$j. f is rescaled.

FD distribution at $T = 0$

- Take $T \to 0$.

$$\lim_{\beta\to\infty} f_{FD}(\mathbf{v}) = \lim_{\beta\to\infty} \frac{\left(\frac{m}{\hbar}\right)^3}{4\pi^3}\frac{1}{1+e^{\beta(E-k_B T_0)}} = \begin{cases} \frac{1}{4}\left(\frac{m}{\pi\hbar}\right)^3 & \text{if } v \le \frac{\left(3\pi^2 n\right)^{\frac{1}{3}}}{m}\hbar, \\ 0 & \text{if } v > \frac{\left(3\pi^2 n\right)^{\frac{1}{3}}}{m}\hbar. \end{cases}$$

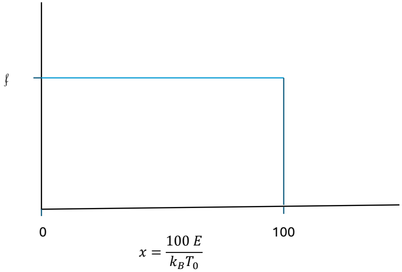
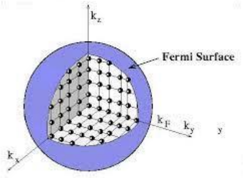


Figure: Fermi-Dirac distribution as $T \to 0$

- This distribution should be derivable from the QM ground state

QM ground state for electrons

- Electrons are fermions: Pauli exclusion principle
  - Two electrons per momentum eigenstate – spin up,down



- Assume finite volume with periodic boundary conditions.
  - Momentum eigenstates are plane waves
  - $\sum_{p<p_F} \to \mathcal{V} \int_{p=0}^{p_F} \frac{d^3p}{(2\pi\hbar)^3}$
  - Then take $N \to \infty, \mathcal{V} \to \infty$ with fixed electron density $n = \frac{N}{\mathcal{V}}$.
- Compute the number of momentum-states with $|\mathbf{p}| \leq |\mathbf{p}_f|$.

$$\mathcal{V} \int_{p=0}^{p_F} \frac{d^3p}{(2\pi\hbar)^3} = \frac{4\pi}{(2\pi\hbar)^3} \mathcal{V} \int_{p=0}^{p_F} p^2 dp = \frac{4\pi\hbar}{3(2\pi\hbar)^3} \mathcal{V}(p_F)^3 = \frac{\mathcal{V}p_F^3}{6\pi^2\hbar^3}$$

- Multiply by 2 for the two spin states:
  $N = \frac{\mathcal{V}p_F^3}{3\pi^2\hbar^3} \implies p_F = \left(3\pi^2 n\right)^{\frac{1}{3}} \hbar$ like the FD distribution at $T = 0$.

Section 4

0-temperature consequences

Average speed and kinetic energy

- MB distribution:
  - $\bar{v^2} = \frac{1}{n}\int d^3v f_{MB}(\mathbf{v}) v^2 = \frac{4\pi}{n}\int_0^\infty dv f_{MB}(v) v^4 = \frac{3k_BT}{m}$
    - **Room temperature** $T = 300^\circ K$. Then[2] $\mathbf{\bar{v} = 1.2x10^5 m/s}$
    - **Average kinetic energy is** $\mathbf{\bar{E} = \frac{1}{2}m\bar{v}^2 = 0.04}\mathrm{eV}$
- FD distribution: See the figure. (would be similar for $T = 0$)
  - Define $v_F = \sqrt{2k_BT_0/m}$. Then $\frac{1}{2}mv_F^2 = k_BT_0$.
  - $f_{FD} \approx \frac{\left(\frac{m}{\hbar}\right)^3}{4\pi^3}$ if $v > v_F$ otherwise $f_{FD} \approx 0$, for T of room temp.
  - Then $n = 4\pi\frac{\left(\frac{m}{\hbar}\right)^3}{4\pi^3}\int_0^{v_F} dv v^2 = 4\pi\frac{\left(\frac{m}{\hbar}\right)^3}{4\pi^3}\frac{v_F^3}{3} \implies v_F = (3n\pi^2)^{\frac{1}{3}}\frac{\hbar}{m}$
    - **Copper:** $n \approx 2.8x10^{22}/cm^3$. Then $\mathbf{T_0 = 8.1x10^{4\circ}K}$.
  - $\bar{v}^2 = \frac{1}{n}\int d^3v f_{FD}(\mathbf{v}) v^2 = 4\pi\frac{\left(\frac{m}{\hbar}\right)^3}{4n\pi^3}\int_0^{v_F} dv v^4 = \frac{3\hbar^2\pi}{5m^2}\left(9n^2\pi\right)^{\frac{1}{3}}$
    - **Copper:** $\mathbf{\bar{v} = 1.2x10^6 m/s}$.
    - **Average kinetic energy is** $\mathbf{\bar{E} = \frac{1}{2}m\bar{v}^2 = 7.0}\mathrm{eV}$

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[2] It's common, but wrong, to say that $\bar{v} = \sqrt{\bar{v^2}}$, but for highly-peaked dists., the approximation is valid.

Mean free path

- Recall the mean free path is $\mathcal{L} = \bar{v}\tau$.
- Also recall that τ is related to the resistivity ρ by $\tau = \frac{m}{ne^2\rho}$.
  - For Cu, $\rho = 1.7$ micro-ohm centimeters so $\tau = 2.5^{-14}$ secs.
- **MB: MFP $= \bar{\mathbf{v}}\tau = 2.5\text{x}10^{-14}\text{s} \quad \text{x} \quad 1.2\text{x}10^{5}\text{m}/\text{s} = 30\text{Å}$**
- **FD: MFP $= \bar{\mathbf{v}}\tau = 2.5\text{x}10^{-14}\text{s} \quad \text{x} \quad 1.2\text{x}10^{6}\text{m}/\text{s} = 300\text{Å}$**
- The classical theory predicts a MFP about 10 times the copper inter-ionic distance, which is larger than we'd expect. But the quantum theory predicts a MFP 100 times the copper inter-ionic distance.
- QM cannot predict **x** and **v** simultaneously, so it's generally not possible to compute (or even talk about) a MFP obtained using electron speeds. Sommerfeld's theory blends QM and classical arguments. Ashcroft and Mermin discuss the justification.

Specific Heat – the lowest order approximation

- The constant-volume specific heat of the electron gas $c_V = \frac{\partial \bar{E}}{\partial T}$.
- Comparing the FD distribution figures above at $T = 300^\circ K$ and below at $T = 0^\circ K$ we see that $\bar{E}$ is $\approx$ T-independent.
  - **So, for the FD distribution (quantum), $\mathbf{c_V \approx 0}$**
  - **In good agreement with experiment**
- For the MB distribution we obtained $\bar{E} \approx \frac{3}{2} k_B T$.
  - **So, for the MB distribution (classical), $\mathbf{c_V \approx \frac{3}{2} k_B}$**
  - **Disagrees completely with experiment**
- For higher order approximations, perform a temperature-expansion.

Section 5

Specific Heat at non-zero temperature

Mean values at non-zero temperature

- Write energy E as $E(v)$ and define[3] $f_{FD}(E)dE \equiv f_{FD}(\mathbf{v})d^3v$.
- Then
$$f_{FD}(E) = g(E)f(E)$$
where $g(E) = \frac{\sqrt{2Em^3}}{\pi^2\hbar^3}$ and $f(E) = \frac{1}{1+e^{\frac{E-k_BT_0}{k_BT}}}$.
- The average of $\mathcal{P}(E)$ is then $\bar{\mathcal{P}} = \int_0^\infty \left[\mathcal{P}(E)g(E)\right] f(E)dE$.

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[3] This is an abuse of notation. Should use a different function name.

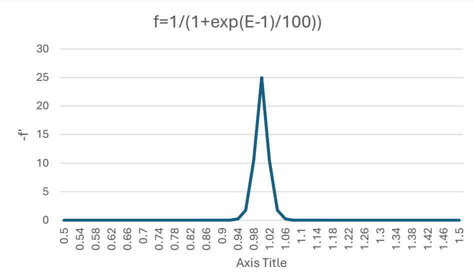
The Sommerfeld expansion part I

- Integrate by parts

$$\bar{\mathcal{P}} = -\int_0^\infty K(E) f'(E) dE$$

where $K(E) = \int_0^E \left[\mathcal{P}(E')g(E')\right] dE'$ (antiderivative)

- f' spikes around $k_B T_0$ so Taylor-expand K around $E = k_B T_0$.



- $f'(E - k_B T_0)$ is even, so only keep even terms of K's expansion

$$\bar{\mathcal{P}} = -\int_0^\infty \sum_{j=0}^\infty \frac{(E - k_B T_0)^{2j}}{(2j)!} \left.\frac{d^{2j} K(E)}{dE^{2j}}\right|_{E = k_B T_0} f'(E) dE \qquad (1)$$

The Sommerfeld expansion part II

- This expansion can be manipulated[4] to

$$\bar{\mathcal{P}} = \int_0^{k_B T_0} \left[\mathcal{P}(E) g(E)\right] dE + \sum_{j=1}^{\infty} a_j (k_B T)^{2j} \left. \frac{d^{2j-1}\left[\mathcal{P}(E) g(E)\right]}{dE^{2j-1}} \right|_{E = k_B T_0}$$

  where $a_j = \left(2 - \frac{1}{2^{2(j-1)}}\right) \zeta(2j)$

- That is the **Sommerfeld Expansion**.

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[4] For details, see Appendix C (*The Sommerfeld Expansion*) of Ashcroft and Mermin

T_0

- Find T_0 by setting $\mathcal{P}(E) = 1$ so $\bar{\mathcal{P}} = n$. Recall $g(E) = \frac{\sqrt{2Em^3}}{\pi^2\hbar^3}$.

  $$n = \int_0^{k_B T_0} g(E)dE + a_1(k_B T)^2 g'(E)\Big|_{E=k_B T_0} + \ldots$$

  $$= \frac{\sqrt{8m^3}}{3\pi^2\hbar^3}(k_B T_0)^{\frac{3}{2}}\left(1 + a_1\frac{3}{4}\left(\frac{T}{T_0}\right)^2 + \ldots\right)$$

- Solve for T_0 with ansatz $T_0 = k_B a\left(1 + b\left(\frac{T}{a}\right)^2 + \ldots\right)$
  - Rewrite, and eventually substitute $a_1 = \frac{\pi^2}{6}$

    $$n = \frac{\sqrt{8m^3}}{3\pi^2\hbar^3}\left(k_B a\left(1 + b\left(\frac{T}{a}\right)^2 + \ldots\right)\right)^{\frac{3}{2}}\left(1 + a_1\frac{3}{4}\left(\frac{T}{a}\right)^2 + \ldots\right)$$

    $$= \frac{\sqrt{8m^3}}{3\pi^2\hbar^3}(k_B a)^{\frac{3}{2}}\left(1 + \left(\frac{T}{a}\right)^2\left(\frac{3b}{2} + a_1\frac{3}{4} + \ldots\right)\right)$$

  - $k_B a = \left(3\pi^2 n\right)^{\frac{2}{3}}\frac{\hbar^2}{2m}$.
  - Coefficient of T^2 must be 0. So $b = -\frac{1}{2}a_1 = -\frac{\pi^2}{12}$

$\bar{E}$ and c_V

- From the Sommerfeld expansion, and again using $g(E) = \frac{\sqrt{2Em^3}}{\pi^2\hbar^3}$

$$\begin{aligned}
\bar{E} &= \int_0^{k_B T_0} E g(E) dE + a_1 (k_B T)^2 (Eg)'(E)\Big|_{E=k_B T_0} + \ldots \\
&= \frac{\sqrt{8m^3}}{5\pi^2\hbar^3} (k_B T_0)^{\frac{5}{2}} \left(1 + a_1 \frac{15}{4}\left(\frac{T}{T_0}\right)^2 + \ldots\right) \\
&= \frac{\sqrt{8m^3}}{5\pi^2\hbar^3} \left(k_B a(1 + b\left(\frac{T}{a}\right)^2 + \ldots)\right)^{\frac{5}{2}} \left(1 + a_1 \frac{15}{4}\left(\frac{T}{a}\right)^2 + \ldots\right) \\
&= \frac{\sqrt{8m^3}}{5\pi^2\hbar^3} (k_B a)^{\frac{5}{2}} \left(1 + \frac{5\pi^2}{12}\left(\frac{T}{a}\right)^2 + \ldots\right)
\end{aligned} \tag{2}$$

- Then the specific heat is

$$c_V = \frac{d\bar{E}}{dT} = \frac{\pi^2}{2}\frac{T}{T_0} n k_B + \ldots \tag{3}$$

- At very low temps, the conduction-electron contribution to c_V is dominant. Alkali metals agree with experiment.

Section 6

Appendix on the derivation of a_n in the Sommerfeld Expansion

Derivation I

- By changing variables in Eq. (1) Ashcroft and Mermin derive

$$a_n = -\int_{-k_B T_0}^{\infty} \frac{x^{2n}}{(2n)!} \left(\frac{1}{1+e^x} \right)' dx$$

- They say that "by elementary manipulations" $a_n = \left(2 - \frac{1}{2^{2n-1}}\right) \zeta(2n)$
- Here are the elementary manipulations.
    - First, integrate by parts for $x > 0$.

$$\begin{aligned} a_n^{>} &= \int_0^{\infty} \left(\frac{x^{2n}}{(2n)!} \right)' \left(\frac{1}{1+e^x} \right) dx \\ &= \int_0^{\infty} \left(\frac{x^{2n-1}}{(2n-1)!} \right) \left(\frac{1}{1+e^x} \right) dx \end{aligned}$$

    - Note[5]

$$\frac{1}{1+e^x} = e^{-x} \frac{1}{1+e^{-x}} = e^{-x} \sum_{m=0}^{\infty} \left(-e^{-x}\right)^m = \sum_{m=0}^{\infty} (-1)^m e^{-(m+1)x}$$

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[5] $\frac{1}{1+y} = \sum (-y)^n$ when $y < 1$

Derivation II

- Change variables to $y = (m+1)x$ so $x^{(2n-1)}dx = \frac{1}{(m+1)^{2n}} y^{(2n-1)} dy$.
- Then
$$a_n^> = \sum_{m=0}^{\infty} (-1)^m \frac{1}{(m+1)^{2n}} \int_0^\infty \frac{y^{(2n-1)}}{(2n-1)!} e^{-y} dy$$
- In general,
$$\begin{aligned} \int_0^\infty z^k e^{-z} dz = (-1)^k \frac{d^k}{d\alpha^k} \int_0^\infty e^{-\alpha z} dz \Big|_{\alpha=1} &= (-1)^k \left(\frac{d^k}{d\alpha^k} \left(\frac{-1}{\alpha} \right) \right) \Big|_{\alpha=1} \\ &= (-1)^k (-1)^k k! \end{aligned}$$
- So
$$a_n^> = \sum_{m=0}^{\infty} (-1)^m \frac{1}{(m+1)^{2n}}$$
- This sum is known as the Dirichlet η function $\eta(2n)$.

Derivation III

- Next integrate by parts $a_n^< = -\int_{-k_B T_0}^{0} \frac{x^{2n}}{(2n)!} \left(\frac{1}{1+e^x} \right)' dx$
- Note[6] $a_n^< = -\int_{-k_B T_0}^{0} \frac{x^{2n}}{(2n)!} \left(\frac{1}{1+e^x} - 1 \right)' dx$

$$a_n^< = \int_{-k_B T_0}^{0} \frac{x^{2n-1}}{(2n-1)!} \left(\frac{1}{1+e^x} - 1 \right) dx - \left(\frac{x^{2n}}{(2n)!} \left(\frac{1}{1+e^x} - 1 \right) \right) \Bigg|_{-k_B T_0}^{0}$$

- The last term can be dropped if $k_0 T_0$ is large enough.[7]
- Change variables $x = -z$, expand[7] $\frac{1}{1+e^{-z}} - 1$

$$\begin{aligned} a_n^< &= -\int_{0}^{k_B T_0} \frac{z^{2n-1}}{(2n-1)!} \sum_{m=0}^{\infty} (-1)^{m+1} e^{-(m+1)z} dz \\ &\approx \int_{0}^{\infty} \frac{z^{2n-1}}{(2n-1)!} \sum_{m=0}^{\infty} (-1)^{m} e^{-(m+1)z} dz \qquad (4) \\ &= a_n^> \end{aligned}$$

- Therefore $a_n = a_n^< + a_n^> = 2\eta(2n) = \left(2 - 2^{2-2n}\right) \zeta(2n)$

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[6] The derivative of a constant is 0

[7] The expansion depends on an approximation that the integrand is essentially 0 when $x <= -k_B T_0$