Low Temperature Properties of the Bose-Einstein and Fermi-Dirac Equations

W. C. Troy
Contents

1. The Models.

2. Einstein Model For Cooling A solid.

3. Fermi-Dirac Two State Paramagnetism Model

1. The Models

\[ N = \frac{D}{e^{\frac{(\epsilon - \mu)}{kT}} - 1}, \quad \epsilon > \mu \quad \text{(BE)} \]

\[ N = \frac{D}{e^{\frac{(\epsilon - \mu)}{kT}} + 1} \quad \text{(FD)} \]

\( N \) = most probable number of particles with energy \( \epsilon \).

\( \mu \) = chemical potential, \( \epsilon = h\nu \) = quantum of energy,

\( \nu \) = frequency, \( h \) = Planck’s constant,

\( T \) = temperature (K), \( k \) = Boltzmann’s constant.
Homework Problems

\[ N = \frac{D}{e^{\frac{(\epsilon - \mu)}{kT}} - 1}, \quad \epsilon > \mu \quad (\text{BE}) \]

Prove: \[ \lim_{T \to 0^+} N = 0. \] \hspace{4cm} (1)

\[ N = \frac{D}{e^{\frac{(\epsilon - \mu)}{kT}} + 1} \quad (\text{FD}) \]

Prove: \[ \lim_{T \to 0^+} N = \begin{cases} 
0, & \epsilon > \mu \\
1, & \epsilon < \mu 
\end{cases} \] \hspace{4cm} (2)
**Textbooks**

1.) D. Halliday and R. Resnick, Fundamentals of Physics
2.) P. Tipler and R. LLewellyn, Modern Physics
3.) D. Schroeder, Thermal Physics
4.) D. Griffiths, Quantum Mechanics
2. Einstein Model For A Solid

- R. Feynman - 1982 - proposed that development of a quantum computer is theoretically possible.

**The Question.** Can a solid be cooled to a temperature $T_0 > 0$ where all quanta of thermal energy are drained off, leaving the object in the ground state? If ‘yes,’ quantum effects are expected (superposition of states). This result may lead to quantum computing devices.

Laser cooling - techniques based on radiation pressure remove energy and reduce vibrations:

2006 - vibrations in glass ’doughnuts’ were reduced by cooling to T=11 mK

2006 - wobbles in mirrors were reduced by cooling to T=10 mK
2006-2009

• Further refinements of laser techniques were developed to cool sticks, sails, drums and other multi-atom objects to low temperatures where vibrations are quelled.

• Papers ‘flowed in’ as researchers competed to remove every quantum of energy from an object, leaving it in the ground state where quantum effects are expected.

2009-2010

- 63 quanta left - Park and Wang, Nature Physics 2009
- 37 quanta left - Schliesser et al, Nature Physics 2009
- 30 quanta left - Groblacher et al, Nature Physics 2009
- 4 quanta left - Rocheleau et al, Nature 2010
2010 - 2011

• O’Connell et al (Nature, 2010) reduced a quantum drum (one trillion atoms) to its ground state at

\[ T_0 \approx 20\text{mK} \]

- Science magazine 2010 breakthrough of the year.

• Teufel et al (Nature, 2011) reduced a drum (\(10^{-13} \text{ kg}\)) to its ground state where it stayed for 100 microseconds, much longer than the 6 nano second result of O’Connell et al.
Theory

Our Goal. Answer the question theoretically: can all quanta of thermal energy be drained from a solid?

\[ T_0 \equiv \text{Lowest Possible Temperature} \]

Models.

- Einstein 1907 Model For A Solid.
- Stat. Mech. Microcanonical Mds.: \[ T_0 > 0. \]

Goal: show that \[ T_0 > 0. \]
Einstein (1907) developed a formula for specific heat

\[ C_v = 1 \frac{\partial U}{n \partial T} \]

in terms of \( T \) and the quantum \( \epsilon = \hbar \nu \).

**A1.** Each atom is a 3D quantum oscillator, which is attached to a preferred position by a spring.

**A2.** \( q > 0 \) quanta of energy have been added to the solid.

**A3.** Each quantum has energy \( \epsilon = \nu \hbar \).
Petit-Dulong Law of Specific Heat

- P. L. Dulong (1785 - 1838) - French physicist and chemist.
- A. T. Petit (1791-1820) - French physicist.
- 1819 - Petit-Dulong Law of specific heat:

\[ C_v = \frac{1}{n} \frac{\partial U}{\partial T} = 5.94 \left( \frac{\text{cal}}{\text{gm K}} \right) . \]

- A. T. Petit and P. L. Dulong, "Recherches sur quelques points importants de la Théorie de la Chaleur," Annales de Chimie et de Physique 10 (1819)
Specific Heat: \( C_v = \frac{1}{n} \frac{\partial U}{\partial T} \)

- Dulong and Petit (1819): for all solids,
  \[
  C_v = 5.94 \left( \frac{\text{cal}}{\text{gm K}} \right).
  \]

- Weber (1875), Kopp (1904), Dewar (1904):
  \[
  0 < C_v << 5.94
  \]
  for many solids at low \( T \).
Einstein Formula (1907):

\[ C_v = 5.94 \left( \frac{\epsilon}{kT} \right)^2 \frac{\exp\left(\frac{\epsilon}{kT}\right)}{(\exp\left(\frac{\epsilon}{kT}\right) - 1)^2}, \quad 0 < T < \infty. \]

Figure 1. \( C_v \) vs. scaled temperature for diamond.
\[ \theta = \text{temperature where } C_v = \frac{1}{2} (5.94) \approx 2.97 \]

Lewis and Randall: ‘Thermodynamics And The Free Energy Of Chemical Substances‘ (1923)
Behavior of $C_v$ as $T \to 0^+$

$$C_v = 5.94 \left( \frac{\epsilon}{kT} \right)^2 \frac{\exp(\frac{\epsilon}{kT})}{(\exp(\frac{\epsilon}{kT}) - 1)^2}, \quad 0 < T < \infty.$$  

It is easily verified that

$$\lim_{T \to 0^+} C_v = 0.$$  \hspace{1cm} (3)

Can $T \to 0$ as the number of quanta decreases to zero?

To answer this, study the derivation of $C_v$. 

---

Low Temperature Properties of the Bose-Einstein and Fermi-Dirac Equations – p.17/46
$N =$ no. of atoms, $N' = 3N =$ no. of degrees of freedom.

$W =$ no. of ways to distribute $q$ quanta of energy over $N'$ degrees of freedom:

$$W = \frac{(q + N' - 1)!}{q!(N' - 1)!}.$$ 

Entropy:

$$S = k \ln(W) = k \ln \left( \frac{(q + N' - 1)!}{q!(N' - 1)!} \right).$$

Simplification: de Moivre - Stirling approximation to $n!$
James Stirling 1692-1770

- Scottish mathematician.
- 1715 - Oxford - expelled from Baliol college for correspondence supporting the 1708 Scottish "Gathering of the Brig o’ Turk" uprising against the Stuarts.
Stirling’s Formula

• 1733 - de Moivre, "Miscellanes Analytica,"

\[ N! \sim \text{[constant]} \sqrt{N} \left( \frac{N}{e} \right)^N \quad \text{as} \quad N \to \infty. \]

• 1733 - Stirling, "Methodus Differentials,"

\[ N! \sim \sqrt{2\pi N} \left( \frac{N}{e} \right)^N \quad \text{as} \quad N \to \infty. \]

• Statistical Mechanics and Physics textbooks:

\[ \ln(N!) = N \ln(N) - N, \quad N \gg 1. \]
Derivation of $C_v$

Apply \( \ln(M!) = M \ln(M) - M \) when \( M \gg 1 \).

\[
S = k \left( \ln((q + N' - 1)!) - \ln(q!) - \ln((N' - 1)!) \right)
\]

becomes

\[
S = k \left( (q + N' - 1) \ln(q + N' - 1) - q \ln(q) - (N' - 1) \ln(N' - 1) \right)
\]

Therefore,

\[
\frac{dS}{dq} = k \ln \left( 1 + \frac{N' - 1}{q} \right).
\]
Internal Energy:

\[ U = q\epsilon + \frac{N'}{2} \epsilon \quad \text{and} \quad \frac{dU}{dq} = \epsilon. \]

Temperature:

\[ \frac{1}{T} = \frac{\partial S}{\partial U} = \frac{dS}{dq} = \frac{k}{\epsilon} \ln \left( 1 + \frac{N' - 1}{q} \right). \]

Conclusion I:

\[ T_0 = \lim_{q \to 0^+} T = 0. \]
Invert Temperature Equation:

\[ q = \frac{N' - 1}{e^{\frac{\epsilon}{kT}} - 1}, \quad N' = 3nN_A. \]

\[ U = q\epsilon + N'\frac{\epsilon}{2} = \frac{(N' - 1)\epsilon}{e^{\frac{\epsilon}{kT}} - 1} + N'\frac{\epsilon}{2}. \]

**Specific Heat:** \( C_v = \frac{1}{n} \frac{\partial U}{\partial T} \).

\[ C_v = 5.94 \left( \frac{\epsilon}{kT} \right)^2 \frac{\exp\left(\frac{\epsilon}{kT}\right)}{(\exp\left(\frac{\epsilon}{kT}\right) - 1)^2}, \quad 0 < T < \infty. \]

**Conclusion II:**

\( C_v \) exists for all \( T > 0 \) and \( \lim_{T \to 0^+} C_v = 0. \)
Widely quoted:

$$\lim_{T \to 0^+} C_v = 0.$$ \hspace{1cm} (4)

Property (4) is mathematically questionable because its derivation is based on

$$\ln(q!) = q \ln(q) - q,$$

which loses accuracy as \( q \to 0^+ \).
The Error In Stirling’s Approximation At Low $q$:

$$\ln(q!) = q \ln(q) - q$$

When $q=10$ Relative Error = 13 Percent.
When $q=2$ Relative Error = 188 Percent.

When $q=2$ Stirling’s Approximation Gives

$$0.69 = -0.61$$

When $q=1$ Stirling’s Approximation Gives

$$0 = -1$$
New Derivation

Replace Stirling ’s approximation

\[ \ln(M!) = M \ln(M) - M \]

with the exact formula

\[ \ln(M!) = \ln(\Gamma(M + 1)), \]

where the Gamma function \( \Gamma(z) \) is defined by

\[ \Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt, \quad Re(z) > 0. \]

Basic Property: \( M! = \Gamma(M + 1) \) when \( M \) is a positive integer.
Entropy $S = k \ln \left( \frac{(q+N'-1)!}{q!(N'-1)!} \right)$ becomes

$$S = k \left( \ln(\Gamma(q + N')) - \ln(\Gamma(q + 1)) - \ln(\Gamma(N')) \right).$$

$$U = q\epsilon + N'\frac{\epsilon}{2}.$$  

$$\frac{1}{T} = \frac{dS}{dq} \quad \frac{dU}{dq}$$

$$\frac{1}{T} = \frac{k}{\epsilon} \left( \frac{\Gamma'(q + N')}{\Gamma(q + N')} - \frac{\Gamma'(q + 1)}{\Gamma(q + 1)} \right) \quad \forall q \geq 0.$$
Temperature:

\[ T = \frac{\epsilon}{k} \left( \frac{\Gamma'(q + N')}{\Gamma(q + N')} - \frac{\Gamma'(q + 1)}{\Gamma(q + 1)} \right)^{-1} > 0 \quad \forall q \geq 0. \]

Specific heat:

\[ C_V = \frac{1}{n} \frac{dU}{dT} = \frac{1}{n} \frac{dU}{dq} \frac{d}{dq} = \]

\[ -\frac{k}{n} \left( \frac{\Gamma'(q + N')}{\Gamma(q + N')} - \frac{\Gamma'(q + 1)}{\Gamma(q + 1)} \right) \left[ \frac{d}{dq} \left( \frac{\Gamma'(q + N')}{\Gamma(q + N')} - \frac{\Gamma'(q + 1)}{\Gamma(q + 1)} \right) \right]^{-1} > 0 \quad \forall q \geq 0. \]
Lowest Temperature:

\[ T_0 = \lim_{q \to 0^+} T = \frac{\nu \hbar}{k} \left( \frac{\Gamma'(N')}{\Gamma(N')} + \gamma \right)^{-1} > 0. \]

\( \gamma = \text{Euler's constant. } T_0 \text{ is large when } \nu \text{ is large!} \)

Lowest Specific heat:

\[ \lim_{q \to 0^+} C_v = \]

\[ -\frac{k}{n} \left( \frac{\Gamma'(N')}{\Gamma(N')} - \frac{\Gamma'(1)}{\Gamma(1)} \right)^2 \left[ \frac{d}{dq} \left( \frac{\Gamma'(q + N')}{\Gamma(q + N')} - \frac{\Gamma'(q + 1)}{\Gamma(q + 1)} \bigg|_{q=0} \right) \right]^{-1} \]

\( > 0. \)
Derivative Free Method

**Goal:** Derive temperature formula without differentaition.

\[
S = k \ln \left( \frac{(q + N' - 1)!}{q!(N' - 1)!} \right).
\]

\[
U = q \nu h + N' \frac{\nu h}{2}.
\]

\[
\frac{1}{T} = \frac{\Delta S}{\Delta U} = \frac{S(q + 1) - S(q)}{U(q + 1) - U(q)} = \frac{k}{\nu h} \ln \left( \frac{q + N'}{q + 1} \right).
\]

\[
T^0 = \lim_{q \to 0} T = \frac{\nu h}{k \ln(N')} > T_0 = \frac{\nu h}{k} \left( \frac{\Gamma'(N')}{\Gamma(N')} + \gamma \right)^{-1} > 0.
\]
Comparison With Experiment

O’Connell et al (Nature, 2010): \( \nu = 6 \times 10^9 \text{Hz} \), one trillion atoms.

Ground state at \( T_0 = 20 \text{mK} \)

New Temperature Formula:

Ground state at \( q = 0, \; T_0 = 9.8 \text{mK} \)
$T_0 = \lim_{q \to 0^+} T = 23.205 \, (K) \text{ and } \lim_{q \to 0^+} C_v = 0.63 \times 10^{-20}$
$T_0 = \lim_{q \to 0^+} T = 23.205 \; (K)$ and $\lim_{q \to 0^+} C_v = .63 \times 10^{-20}$
When \( N! = \Gamma(N + 1) \), the new derivation gives

\[
\lim_{q \to 0^+} T = T_0 > 0 \quad \text{and} \quad \lim_{q \to 0^+} U = \frac{N' \epsilon}{2} = \text{Ground State}.
\]

Does this happen experimentally?

Le et al, Science (2011), show how two diamonds can exhibit quantum entanglement at room temperature.
3. Fermi-Dirac Model

\[ N = \frac{D}{e^{\frac{(\epsilon - \mu)}{kT}} + 1} \quad \text{(FD)} \]

\[ \lim_{T \to 0^+} N = \begin{cases} 
0, & \epsilon > \mu \\
1, & \epsilon < \mu
\end{cases} \quad \text{(5)} \]

Two-state paramagnetism model (Schroeder, Thermal Physics, p. 98):

Paramagnetic materials (e.g. magnesium, molybdenum), are attracted to a magnetic field, \( \bar{B} \). The material does not retain magnetic properties when \( \bar{B} \) is removed.
Two State Model

Assumptions: a paramagnetic system has \( N \gg 1 \) electrons attracted to external field \( \vec{B} = B_0 \hat{k}, B_0 > 0 \).
\( N_1 \gg 1 \) electrons are in the up-state,
\( N_2 \gg 1 \) electrons are in the down-state

\[
N = N_1 + N_2
\]

Energies: \( U_1 = -\mu_B B_0, \quad U_2 = \mu_B B_0 \)

\[
\mu_B = \frac{e h}{4 \pi m} = 9.27 \times 10^{-24} \text{ Joules/Tesla}
\]

Total Energy: \( U = \mu_B B_0 (N_2 - N_1) = \mu_B B_0 (N - 2N_1) \)
Entropy: \( S = k \ln \left( \frac{N!}{N_1!N_2!} \right) = k \ln \left( \frac{N!}{N_1!(N-N_1)!} \right) \)

\( N >> 1, N_1 >> 1, N - N_1 >> 1 \)

\( S \approx k \left( N \ln(N) - N_1 \ln(N_1) - (N - N_1) \ln(N - N_1) \right) \)

**Total Energy:** \( U = \mu_B B_0 (N - 2N_1) \)

\( \frac{1}{T} = \frac{\partial S}{\partial U} = \frac{dS/dN_1}{dU/dN_1} \)

Solve for \( N_1 : \quad N_1 = \frac{N}{\exp \left( -\frac{2\mu_B B_0}{kT} \right) + 1} \)
\[ N_1 = \frac{N}{\exp\left(-\frac{2\mu_B B_0}{kT}\right) + 1} \]

\[ \lim_{T \to 0^+} N_1 = N \]

Solve for \( T \):
\[ T = -\frac{2\mu_B B_0}{k \ln\left(\frac{N}{N_1} - 1\right)} \]

\[ \lim_{N_1 \to N^-} T = 0 \]

These limits are both invalid because the Stirling approximation requires \( N - N_1 >>> 1 \)
Entropy: \( S = k \ln \left( \frac{N!}{N_1!(N-N_1)!} \right) = k \ln \left( \frac{\Gamma(N+1)}{\Gamma(N_1+1)\Gamma(N-N_1+1)} \right) \)

Total Energy: \( U = \mu_B B_0 (N - 2N_1) = \frac{heB_0}{4\pi m} (N - 2N_1) \)

\[ \frac{1}{T} = \frac{\partial S}{\partial U} = \frac{dS/dN_1}{dU/dN_1} \]

\[ T = \frac{heB_0}{2\pi mk} \left( \frac{\Gamma'(N_1+1)}{\Gamma(N_1+1)} - \frac{\Gamma'(N-N_1+1)}{\Gamma(N-N_1+1)} \right) \]

\[ \lim_{N_1 \to N-} T = \frac{heB_0}{2\pi mk} \left( \frac{\Gamma'(N+1)}{\Gamma(N+1)} - \frac{\Gamma'(1)}{\Gamma(1)} \right) > 0 \]
Application

BPPH (2,2-diphenyl-1-picrylhydrazyl) - paramagnetic powder

(2) Schroeder, Thermal Physics, pp.106-108

\[ N = 2.3 \times 10^{23}, B_0 = 2.06, k = 1.38 \times 10^{-23}, \mu_B = 9.27 \times 10^{-24} \]

\[ \lim_{N_1 \to N^-} T = T_1 = \frac{h e B_0}{2 \pi m k \left( \frac{\Gamma'(N+1)}{\Gamma(N+1)} - \Gamma'(1) \right)} = 0.05K > 0 \]

Experiment: > 99 percent magnetization at \( T \approx 2K \)
Acknowledgement

- Stefanos Folias
- S. J. Anderson
- Richard Field
- Toby Chapman
- Stuart Hastings
Debye Formula

Einstein Specific Heat (1907):

\[ C_v = 5.94 \left( \frac{\epsilon}{kT} \right)^2 \frac{\exp(\frac{\epsilon}{kT})}{\left(\exp(\frac{\epsilon}{kT}) - 1\right)^2}, \ 0 < T < \infty. \]

Debye Specific Heat (1913):

\[ C_v = 9Nk \left( \frac{T}{T_D} \right)^3 \int_0^{T_D \frac{T}{T}} \frac{x^4e^x}{(e^x - 1)^2}dx, \ 0 < T < \infty. \]

\[
< N > = \frac{1}{\exp\left(\frac{\epsilon}{kT}\right) - 1}, \quad 0 < T < \infty.
\]

**P₁:** Thermal energy is present at every positive \( T > 0 \).

**P₂:** \( T \to 0 \) as \( < N > \to 0 \). i.e. \( T_0 = 0 \).

**P₂:** Quantum effects become important when \( < N > < 1 \).

\[
< N > < 1 \quad \text{when} \quad T < \frac{\epsilon}{k \ln(2)}.
\]
Current theory (e.g. Teufel et al, Nature, 2011) - the Bose-Einstein equation

\[
< N > = \frac{1}{\exp(\frac{\epsilon}{kT}) - 1}, \quad 0 < T < \infty,
\]

for a single atom represents the entire solid:

\[
< N > = \text{ave. no. of quanta in 1 particle state with energy } \epsilon.
\]

\[
\epsilon = h\nu = \text{quantum of energy},
\]

\[
\nu = \text{frequency}, \quad h = \text{Planck’s constant},
\]

\[
T = \text{temperature (K)}, \quad k = \text{Boltzman’s constant}.
\]

\[ < N > = \frac{1}{\exp\left(\frac{\epsilon}{kT}\right) - 1}, \quad 0 < T < \infty. \]

**P₁:** Thermal energy is present at every positive \( T > 0 \).

**P₂:** \( T \to 0 \text{ as } < N > \to 0 \). i.e. \( T₀ = 0 \).

**P₂:** Quantum effects become important when \( < N > < 1 \).

\[ < N > < 1 \text{ when } T < \frac{\epsilon}{k \ln(2)}. \]
Comparison With Experiment

O’Connell et al experiment: ground state achieved when

\[ \langle N \rangle = 0.07, \quad \nu = 6\text{GHz} \quad \text{and} \quad T = 20\text{mK} \]

The one atom model

\[ \langle N \rangle = \langle N/D \rangle = \frac{1}{\exp\left(\frac{\epsilon}{kT}\right) - 1} \]

predicts

Ground State At \( T = 106\text{mK} \)