

LECTURE NOTES
STATISTICAL MECHANICS
ZCT 207

ACADEMIC YEAR 2009/10

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This set of lecture notes are prepared for the ZCT 207 course offered to mainly second year students in the school of physics, USM. It is basically a set of notes on selected topics from the text book “Statistical physics: An introductory course”, by Daniel J. Amit and Josef Verbin, World Scientific Publishing, 1999. However, the style of explanation and presentation were modified to a certain extent, with additional drawings and graphical representations. Some sections were adopted from other text books, mainly from “Statistical Physics” (2nd Ed.) by F. Mandl, John Wiley 1988 and “Thermal and Statistical Physics”, by Harvey Gould and Jan Tobochnik, free book downloadale from <http://stp.clarku.edu/notes/>.

Course Title: Statistical Mechanics

Course Code: ZCT 207

Credit: 2

Student Learning Time: (28 hour/semester)

Prerequisite: (S) ZCT 212/2 Thermodynamics

Learning Outcome:

At the end of the course, students are able to:

1. Understand the basic statistical physics methodology in describing the behavior of macroscopic physical systems.
2. To explain macroscopic thermodynamical phenomena in proper and clear statistical mechanics terms.
3. To list the procedural knowledge to arrive at a solution for different simple systems.
4. To demonstrate mathematical know-how necessary to solve problems as in (3) above.

Synopsis:

This course introduces the basic concepts of statistical mechanics. It deals with the early form of statistical mechanics and then goes on to modern ideas involving the quantum nature of particles.

Course Content :

The Kinetic Theory of Gases
Essential Background in Thermodynamics
Microscopic States and Average
Microcanonical Ensemble
Subsystems and Temperature
The Canonical Ensemble
Harmonic Oscillator and Einstein Solid
Statistical Mechanics of Classical Systems
Statistical Mechanics of an Ideal Gas
Phonon Gas and the Debye Model
Thermodynamics of Electromagnetic Radiation
Grand Canonical Ensemble
Statistical Mechanics of Identical Quantum Particles

Assessment:

coursework: 30%

final exam: 70%

Final exam format:

- A two-hour paper.

- 5 Questions are prepared. Choose 3 to answer.
- Questions will in the the form of structured type.
- ~ 40% (or slightly less) to test knowledge in theoretical understanding.

Text Book:

Statistical physics: An introductory course, by Daniel J. Amit and Josef Verbin, World Scientific Publishing, 1999.

References:

- 1) Thermal and Statistical Physics, Harvey Gould and Jan Tobochnik (free access e-book downloadable from <http://stp.clarku.edu/notes/>)
- 2) F. Mandl, Statistical Physics (2nd Ed.), John Wiley, 1988.

Topic-by-topic lecture schedule:

| <i>Topic</i> | <i>Lecture</i> |
|--|----------------|
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| Temperature and thermal equilibrium | 1 |
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| | |
|--|----|
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Part I
The kinetic theory of gases

Introduction

- Mechanical system
- Law of dynamics – Newtonian, Quantum, GR
- Interactions
- Initial conditions
- Determination of system's detail evolution
- Time scales: observations vs. interactions
- Time averages
- Classical thermodynamics – details striped-off
- System of many Degree of Freedom (DOF) – statistical treatment (thermo + classical mechanics + statistics)

Chapter 1
Velocity and Position Distributions of
Molecules in a Gas

1.1 Avogadro's law, or the Equation of state of
an ideal gas

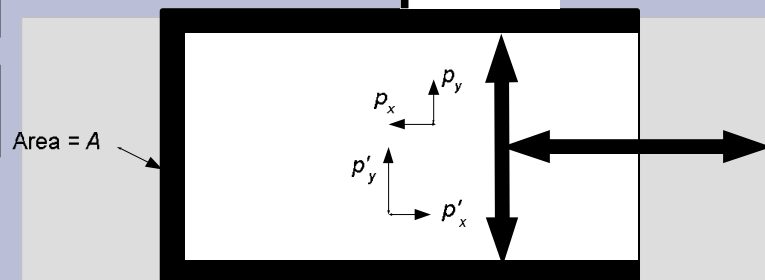
Avogadro's law

- At equal pressure and temperature, equal volumes of gasses contain an equal number of molecules
- N_0 Avogadro's number, 6.023×10^{23} at STP

Derivation of ideal gas pressure with classical Newton's law

- Pressure exerted by ideal gas on wall of container can be derived with Newton's law
- Equation of state for ideal gas can be derived from from such consideration

Gas molecule colliding with the piston



For a fixed v_x

$$\Delta p_x = 2 p_x = 2 m v_x \cdot v_x \Delta t A \cdot n(v_x)$$

$$P(v_x) = 2 m \cdot v_x^2 n(v_x)$$

$$P = \sum_{v_x \geq 0} P(v_x) = 2 m \cdot \sum_{v_x \geq 0} [v_x^2 n(v_x)]$$

Pressure of gas in terms of average KE

$$\langle v_x^2 \rangle = \frac{1}{n} \sum_{all v_x} n(v_x) v_x^2$$

$$n = \sum_{all v_x} n(v_x) = \sum_{v_x \geq 0} n(v_x) + \sum_{v_x < 0} n(v_x)$$

$$P = 2 m \sum_{v_x \geq 0} [v_x^2 n(v_x)] = m n \cdot \langle v_x^2 \rangle$$

$$\langle v^2 \rangle = \langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

$$P = \frac{1}{3} n m \langle v^2 \rangle = \frac{2}{3} \frac{N}{V} \left\langle \frac{1}{2} m v^2 \right\rangle = \frac{2}{3} \frac{E}{V}$$

- Independent of detailed structures of molecules of gas

Average KE and temperature

- Identify average KE with temperature:

$$\left\langle \frac{1}{2} m v^2 \right\rangle = 3 \cdot \frac{1}{2} kT$$

- EOF for ideal gas is obtained: $PV = \frac{2}{3} E = NkT$
- Total energy of system $E = N \cdot (3kT/2)$
- Each degree of freedom DOF of the point-like molecule has an energy $kT/2$

1.2 Temperature and thermal equilibrium

- Ideal gas
- $PV = n R T$
- $n = N/N_0$, number of moles
- $k = R/N_0$
- N_0 Avogadro's number, 6.023×10^{23}
- $k = 1.38 \times 10^{-23} \text{ JK}^{-1}$
- $R = 8.31 \text{ JK}^{-1}$

Two gases at equilibrium

- For a volume containing two ideal gases (masses m_1, m_2) at equilibrium, the number of molecules with velocity \mathbf{v} does not depend on the direction, but only on $|\mathbf{v}|$
 - $\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle = 0$.
 - For two molecules (of different type) with independent $\mathbf{v}_1, \mathbf{v}_2$
- $$\mathbf{v}_{cm} = \frac{1}{m_1 + m_2} (m_1 \mathbf{v}_1 + m_2 \mathbf{v}_2), \mathbf{v}_{rel} = \mathbf{v}_1 - \mathbf{v}_2$$
- $$\langle \mathbf{v}_1 \cdot \mathbf{v}_2 \rangle = 0 \Leftrightarrow \langle \mathbf{v}_{cm} \cdot \mathbf{v}_{rel} \rangle = 0 \Rightarrow \left\langle \frac{1}{2} m_1 v_1^2 \right\rangle = \left\langle \frac{1}{2} m_2 v_2^2 \right\rangle = \frac{3}{2} kT$$
- Two gases at same temperature \Rightarrow same average KE per molecule, irrespective of m

Avogadro's law is consistent with $\left\langle \frac{1}{2} m v^2 \right\rangle = 3 \cdot \frac{1}{2} kT$

- Consider a separate scenario of two gasses with same volumes pressures:

$$P_1 = \frac{2}{3} \frac{N_1}{V_1} \left\langle \frac{1}{2} m_1 v_1^2 \right\rangle; P_2 = \frac{2}{3} \frac{N_2}{V_2} \left\langle \frac{1}{2} m_2 v_2^2 \right\rangle;$$

- If both systems have the same volume and pressure, and are at the same temperature:

$$\left\langle \frac{1}{2} m_1 v_1^2 \right\rangle = \left\langle \frac{1}{2} m_2 v_2^2 \right\rangle = \frac{3}{2} kT$$

- This implies both gases contains same $N_1 = N_2 = N$: Avogadro's law proven
- There is consistency between the known ideal gas law and identification of temperature with kT

NOTE

- We have so far assume the molecule as structureless, point like object

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2}kT$$

is only for point-like particle

- For an ideal gas system made up of point particle (monoatomic gas): $\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2}kT$
- Thermal motion
- Molecule comprised of atoms
- Description of monoatomic gas has to be modified in order to describe thermal motion of molecules

Chap 1.3

Equipartition of energy per molecule and its constituent parts — a fundamental problem

Average KE of CM of molecule

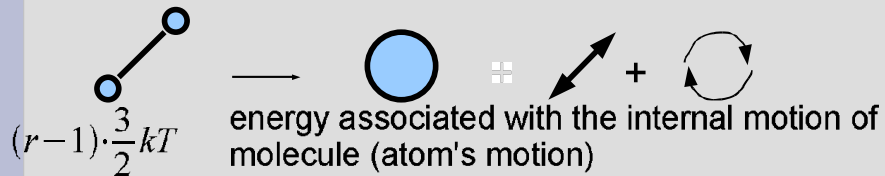
- Want to obtain the average KE of a molecule
- Will derive this for the simple case of diatomic molecule
- First consider the CM of a molecule

$$\langle E_K^{CM} \rangle = \left\langle \frac{1}{2} M_{CM} v_{CM}^2 \right\rangle = \frac{3}{2}kT + \frac{m_1 m_2}{(m_1 + m_2)} \langle \mathbf{v}_1 \cdot \mathbf{v}_2 \rangle = \frac{3}{2}kT$$

Average KE of CM of molecule

- Next, obtain the average KE of a molecule (which includes that contribute by the individual atoms)
- Consider the case of a molecule made up of r atoms
- Each atom's average KE is $\langle E_K^{atom} \rangle = \frac{3}{2} kT$

$$\langle E_K^{mol} \rangle = r \cdot \frac{3}{2} kT = \frac{3}{2} kT + (r-1) \cdot \frac{3}{2} kT$$



Energy associated with internal motion

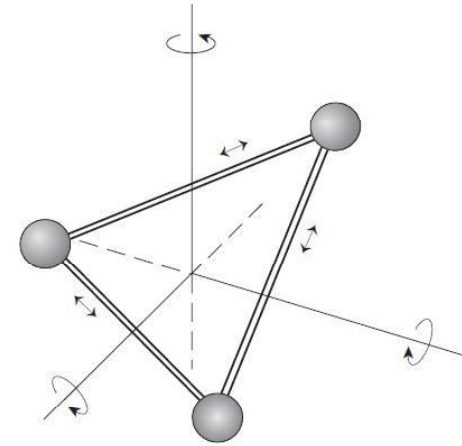


Fig. 1.1.4 Rotations and vibrations of a triatomic molecule.

Molecule with 3 atoms

- $r = 3$

$$\langle E_K^{CM} \rangle = 3 \frac{r}{2} kT = \frac{9}{2} kT$$

$\frac{3}{2} kT$ for translational motion of the CM

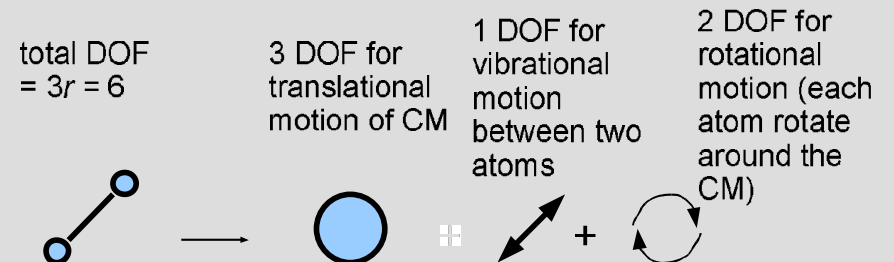
$\frac{3}{2} kT$ for rotational motion of the molecule

$\frac{3}{2} kT$ for vibrational motion of the atoms relative to each other

a total of 9 (=3+3+3) DOF

Each DOF has $\frac{1}{2} kT$ of energy

DOF for diatomic atoms



Modification of EOF for structured molecule

$$PV = \frac{2}{3} E \rightarrow PV = \frac{2}{3r} E$$

E = total kinetic energy of the molecule, potential energy ignored

$$\text{Define } \gamma = 1 + \frac{2}{3r} \quad \text{Definition as according to classical physics}$$

$$PV = (\gamma - 1) E$$

- γ can be measured, providing info on the number of atoms making up the molecule
- $\gamma = 5/3$ for monoatomic molecule
- $\gamma = 4/3$ for diatomic molecule

Heat Capacity problem

- γ measures experimentally does not match that deduced by classical physics
- Diatom:
- DOF (CP) = $3r = 6$;
- $\gamma(\text{CP}) = 1 + 2 / 3r = 4/3 = 1.33$
- But $\gamma(\text{EXP}, T = 100^\circ\text{C}) = 1.4$
- \Rightarrow DOF (EXP, $T = 100^\circ\text{C}$) = $3r = 5 \neq 6$
- "Freezing" of DOF
- CP fails to provide explanation why DOF $\neq 3r$

Effective number of DOF, f

According to strictly classical physics, $\gamma = 1 + \frac{1}{3r}$.

However, this definition does not seem consistent with experiments

Redefinition: $\gamma = 1 + \frac{1}{f}$
 Effective number of DOF, f , number of portion of $kT/2$ that are contained by the average KE of the molecule

ΔE vs. $\sim kT$

- Quantum mechanical excitation energy level of vibrational, rotational motion and internal DOF from internal forces are discrete
- ΔE vs. $\sim kT$
- $\Delta E \sim > eV$; $kT \sim 0.01 eV$ at room temperature
- Experiments only see lower energy excitation states at low T , hence DOF measured $< 3r$



f is temperature dependent

$$E_K^{mol} = \frac{f}{2} kT$$

In general, $f \neq 3r$

For $kT \ll \Delta E$, $f = 3$ (see only $r = 1$)

For $kT \gg \Delta E$, $f \geq 3r$

(see all r (vibration + rotation) + internal excitations from internal forces)

For intermediate kT , $3 \leq f \leq 3r$

Diatomic molecule at high T

$$\gamma(\text{EXP}, T = 2000^\circ\text{C}) = 1.286$$

- \Rightarrow DOF (EXP, $T = 100^\circ\text{C}$) = $f = 7$
- An extra DOF from internal forces is defrozen

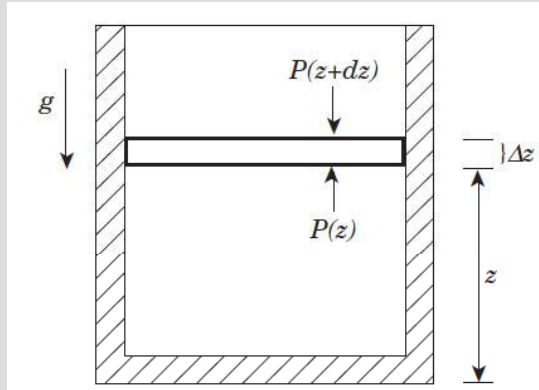
NOTE

AVERAGE KE of atoms in a molecule \neq KE of the atoms in the molecule

Chapter 1.4

The density in an isothermal atmosphere — the Boltzmann factor in the potential energy

Isothermal gas in closed volume under gravitational force



A

Number density of ideal gas at high z

$$\Delta F = (m g) \cdot n(z) \cdot (\Delta z A)$$

At EB,

$$[P(z) - P(z + \Delta z)] \cdot A = \Delta F; \quad P(z) > P(z + \Delta z)$$

Combining both equations above,

$$\frac{dP(z)}{dz} = -m g n(z)$$

Apply $PV = nRT$ to the layer Δz to obtain

$$P(z) = n(z) k T$$

$$n(z) = n(0) \exp\left(-\frac{mgz}{kT}\right)$$

Dependence of density on T

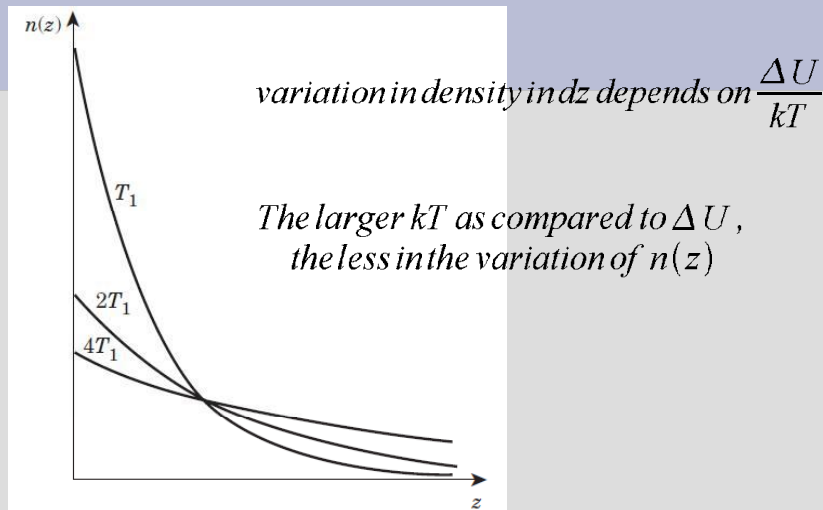


Fig. 1.1.6 The dependence of the density on height in an isothermal atmosphere at three different temperatures. Note: $n(0)$ also depends on T .

Total number of molecules

$$N(h) = A \int_0^h n(z) dz$$

$$N(h)/A = n(0) \frac{kT}{mg} \left(1 - \exp\left(-\frac{mgh}{kT}\right)\right)$$

Assume container of height h has N molecules:

$$n(0) = \frac{Nmg}{AkT} \left[1 - \exp\left(-\frac{mgh}{kT}\right)\right]^{-1}$$

Probability of finding a molecule

$$n(\mathbf{r}) = n(\mathbf{r}_0) \exp\left(\frac{-U(\mathbf{r})}{kT}\right)$$

$\frac{n(\mathbf{r})}{N}$ represents probability to find a molecule in dV at \mathbf{r}

$$P(\mathbf{r}) dV = \frac{n(\mathbf{r})}{N} dV$$

The force field $U(\mathbf{r})$ is associated with the spatial distribution of the particles, $n(\mathbf{r})$

The force field $U(\mathbf{r})$ drives variation in the number density, whereas the thermal motion term kT tends to 'counteract' the variation of n due to the force field by randomising the number distribution

Probability of a given configuration

$$P_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) dV_1 dV_2 \dots dV_N = P_1(\mathbf{r}_1) dV_1 P_2(\mathbf{r}_2) dV_2 \dots P_N(\mathbf{r}_N) dV_N$$

$$= \left[\frac{n(\mathbf{r}_0)}{N}\right]^N \exp\left[\frac{-1}{kT} \sum_{i=1}^N U(\mathbf{r}_i)\right] dV_1 dV_2 \dots dV_N$$

- This is to be read as 'the probability to find particle 1 in the volume of size dV_1 located around \mathbf{r}_1 , particle 2 in the volume of size dV_2 located around \mathbf{r}_2 , ..., particle N in the volume of size dV_N located around \mathbf{r}_N '. Each possible set of $\{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$ is a 'configuration'.
- Hence, there is a tremendously large number of possible configurations. Each configuration has a probability to occur. The probability of the configuration (sometimes called probability distribution) in general depends on E and temperature T .

1.5 The Maxwell-Boltzmann distribution

- How many of the particles in volume dV around \mathbf{r} , i.e. $n(\mathbf{r})dV$ have velocity inside the volume element $d\tau = dv_x dv_y dv_z$ in velocity space?
- $n(\mathbf{r})dV f(\mathbf{v})d\tau = NP(\mathbf{r})f(\mathbf{v})d\tau dV$
- $f(\mathbf{v}) d\tau =$ probability for a particle in $d\tau$
- $f(\mathbf{v})$ is the MB distribution

Derivation of the Maxwell-Boltzmann distribution, $f(\mathbf{v})$

- Assumption 1: In EB, no preferred direction
- $f(\mathbf{v}) = h(v^2)$
- Assumption 2: Orthogonal motions are independent of one another

$$f(\mathbf{v}) = g(v_x^2) g(v_y^2) g(v_z^2)$$

Derivation of the Maxwell-Boltzmann distribution, $f(\mathbf{v})$ (cont.)

$$v^2 = v_x^2 + v_y^2 + v_z^2 \equiv t = x + y + z$$

$$h(v^2) = h(v_x^2 + v_y^2 + v_z^2) = g(v_x^2) g(v_y^2) g(v_z^2)$$

$$\Rightarrow h(t) = g(x) g(y) g(z)$$

Taking total derivative of $h(t)$ with respect to t , and then apply chain rule $d/dt = (dx/dt)d/dx + (dy/dt)d/dy + (dz/dt)d/dz$ to the RHS, we conclude that $(1/h)(dh/dt)$ must be a constant

$$h(v^2) = C e^{\lambda v^2} \Rightarrow f(\mathbf{v}) = C e^{\lambda v^2}$$

$$C > 0, \lambda < 0$$

$$\text{Normalisation gives: } C = \left(\frac{A}{\pi}\right)^{3/2}, A = -\lambda > 0$$

Derivation of A

$$f(v^2) = \left(\frac{A}{\pi}\right)^{3/2} e^{-A v^2}$$

$$\left\langle \frac{mv^2}{2} \right\rangle = \int_{-\infty}^{\infty} \frac{1}{2} m v^2 f(v^2) dv_x dv_y dv_z$$

$$\left\langle \frac{mv^2}{2} \right\rangle = \left(\frac{A}{\pi}\right)^{3/2} \int_{-\infty}^{\infty} \frac{3}{2} m (v_x^2 + v_y^2 + v_z^2) e^{-A(v_x^2 + v_y^2 + v_z^2)} dv_x dv_y dv_z$$

$$= \left(\frac{A}{\pi}\right)^{3/2} \int_{-\infty}^{\infty} v_x^2 e^{-A v_x^2} dv_x \int_{-\infty}^{\infty} v_y^2 e^{-A v_y^2} dv_y \int_{-\infty}^{\infty} v_z^2 e^{-A v_z^2} dv_z$$

Derivation of A (cont.)

$$= \left(\frac{A}{\pi}\right)^{3/2} \int_{-\infty}^{\infty} v_x^2 e^{-A v_x^2} dv_x \int_{-\infty}^{\infty} v_y^2 e^{-A v_y^2} dv_y \int_{-\infty}^{\infty} v_z^2 e^{-A v_z^2} dv_z$$

$$\int_{-\infty}^{\infty} v_x^2 e^{-A v_x^2} dv_x = \frac{1}{2} \left(\frac{\pi}{A^3}\right)^{1/2}$$

The integration above makes use of the Gamma function

$$\Gamma(z) = \int_0^{\infty} t^{z-1} e^{-t} dt$$

$$\Gamma(z) = (z-1)\Gamma(z-1); \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$$

$$\frac{3kT}{2} = \left\langle \frac{mv^2}{2} \right\rangle = \frac{3m}{4A} \Rightarrow A = \frac{m}{2kT}$$

$$f(v^2) d\tau = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{1}{2} \frac{mv^2}{kT}}$$

A system of N particles

- A system of N particles is fully characterised by the set of all spatial position ($3N$) and momentum ($3N$) = $6N$ parameters
- $\{x_1, y_1, z_1, v_{x_1}, v_{y_1}, v_{z_1}, x_2, y_2, z_2, v_{x_2}, v_{y_2}, v_{z_2}, \dots,$
- $x_N, y_N, z_N, v_{x_N}, v_{y_N}, v_{z_N}\} \equiv \{\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, \dots, \mathbf{r}_N, \mathbf{v}_N\}$
- probability of a 'configuration' (or 'state') is

$$P(\mathbf{r}) dV f(\mathbf{v}) d\tau$$

$$= C \exp\left\{-\frac{1}{kT} \sum_{i=1}^N \left[\frac{1}{2} m_i v_i^2 + U(\mathbf{r}_i)\right]\right\} dV_1 dV_2 \dots dV_N d\tau_1 d\tau_2 \dots d\tau_N$$

1.6 Averages and distributions

- Distributions of coordinates $n(\mathbf{r})$ and $f(\mathbf{v})$ allows the calculation of averages of any function of \mathbf{r} or/and \mathbf{v}

$$\langle z \rangle = \frac{\int_0^\infty z P(z) dz}{\int_0^\infty P(z) dz} = \frac{\int_0^\infty z n(z) dz}{\int_0^\infty n(z) dz} = \frac{\int_0^\infty z \exp(-\frac{mgz}{kT}) dz}{\int_0^\infty \exp(-\frac{mgz}{kT}) dz}$$

$$Z(\alpha) = \int_0^\infty \exp(-\alpha z) dz$$

$$\langle z \rangle = \frac{\int_0^\infty z \exp(-\alpha z) dz}{\int_0^\infty \exp(-\alpha z) dz} = -\frac{d}{d\alpha} \ln Z(\alpha);$$

$$\alpha \equiv \frac{mg}{kT}$$

Dimensional argument for $\langle z \rangle$

- $[\alpha] = L^{-1}$, α is the length scale of the problem
- The function $Z(\alpha)$ has dimension of L
- $\Rightarrow Z(\alpha) \propto 1/\alpha$
- $\Rightarrow Z(\alpha) = K/\alpha$

$$\langle z \rangle = -\frac{d}{d\alpha} \ln\left(\frac{K}{\alpha}\right) = \frac{1}{\alpha} = \frac{kT}{mg}$$

Dimensional argument for $\langle |\mathbf{v}^2| \rangle$

$$\langle |\mathbf{v}^2| \rangle = \langle v^2 \rangle = \frac{\int_{-\infty}^{\infty} v^2 f(v^2) dv_x dv_y dv_z}{\int_{-\infty}^{\infty} f(v^2) dv_x dv_y dv_z}$$

$$\langle v^2 \rangle = -\frac{d}{d\alpha} \ln Z(\alpha); Z(\alpha) = \int_0^\infty \exp(-\alpha |v^2|) d\tau$$

$$\alpha = \frac{m}{2kT} \Rightarrow [\alpha] = \left(\frac{T}{L}\right)^2 = [\text{velocity}]^{-2}$$

$$[Z(\alpha)] = [\text{velocity}]^3$$

$$Z(\alpha) = C \alpha^{-3/2}$$

$$\langle v^2 \rangle = -\frac{d}{d\alpha} \ln(C \alpha^{-3/2}) = \frac{3}{2\alpha} = \frac{3kT}{m}$$

Part II Statistical physics with paramagnets

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Describing a system

- System
- Dynamical model:
 - 1 Physical laws governing the system
 - 2 Forces/interactions
- DOF
- Detailed trajectory of all DOF not required
- Only interested in statistical averages
- Time scales: t for observation vs. time for microscopic change
- Examples: microcanonical ensemble (equienergetic); canonical ensemble (equitemperature)

Ensemble

- What is an Ensemble?
- Time averages are replaced by ensemble averages
- "Relative occurrence of allowed states" in an ensemble is given by the probability density
- Knowing the probability density of the ensemble allow us to calculate the averages

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The first law

- For concreteness, think of ideal gas system.
- Conservation of energy: $dE = \delta Q - \delta W$.
- $\delta W = PdV$.
- $dE = \delta Q - PdV$.

State space of a thermodynamical system

- A thermodynamical system at EB is characterised by a set of macroscopic variables.
- A minimal set of these variables defines the state space of the system in question.
- $\{P, V, T\}$ for ideal gas.
- Equation of State (EOF), e.g. $PV = nRT$.
- Given any set of two variables, the third one is determined via EOF.
- Any variable which is determined by the elements in the state space is called a function of state.
- $f = f(a, b, \dots)$, $\{a, b, \dots\} \in$ state space.
- $V = nRT/P$, with $\{P, T\}$ as two independent variables.

Types of thermodynamic variables

- Extensive (proportional to system's size), e.g. volume, number of particles
- Intensive (not proportional to system's size), e.g. pressure, temperature
- Function of state (e.g. internal energy) vs. not function of state (e.g. work, heat).
- δ as in $\delta Q, \delta W$. δ signifies path-dependence of Q, W on the process.
- Operator 'd' as in dE signifies path-independence of E on the process.

The condition for $A_x(x, y)dx + A_y(x, y)dy$ to be an exact differential

- Consider the expression $\delta a = A_x(x, y)dx + A_y(x, y)dy$, where $A_x(x, y)$ and $A_y(x, y)$ are two functions of two variables x, y .
- By definition, δa is an exact differential if it is equal to the difference between some function $z(x, y)$ evaluated at two neighboring points, i.e., if $\delta a = z(x + dx, y + dy) - z(x, y)$.
- The sufficient and necessary conditions for δa to be an exact differential is $\partial A_x(x, y)/\partial y = \partial A_y(x, y)/\partial x$.
- If this condition holds, then $A_x = \frac{\partial z}{\partial x}$, $A_y = \frac{\partial z}{\partial y}$ for some function $z(x, y)$ and δa is the difference of the values of this function.

Checking if a variational expression is an exact differential

- Put simply, given any two functions $M(x, y)$ and $N(x, y)$, obtain their partial derivatives, $\frac{\partial M}{\partial y}$, $\frac{\partial N}{\partial x}$. Then check whether $\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$. If it is, then the expression $M(x, y)dx + N(x, y)dy$ is an exact differential.
- For any exact differential, we can find a function $z(x, y)$ such that $dz = M(x, y)dx + N(x, y)dy$. By integrating both sides, we can obtain the full expression of $z(x, y)$ via $z(x, y) = \int dz = \int M(x, y)dx + \int N(x, y)dy$

What's good of an exact differential

- Often, we encounter variational expression in the form of $f(p, q)dp + g(p, q)dq$ in stat mech. If we can prove that it is an exact differential, then we can integrate them to obtain the function $z(p, q)$ corresponding to the exact differential, of which dz represents the difference between $z(x, y)$ evaluated at two neighboring points.
- If dz is an exact differential, then the integral $z = \int dz$ depends only on the end points of the limit of integration and does not depend on the path over which the integration is performed.

δQ is not an exact differential

- Consider ideal gas: $E = NfkT/2$.
- $\delta Q = PdV + dE = PdV + (Nfk/2)dT$.
- Take $P = P(T, V)$ and use EOF
 $P(T, V) = nRT/V = NkT/V \Rightarrow \delta Q = Nk \left(\frac{f}{2}dT + \frac{T}{V}dV \right)$.
- Compare this to $\delta a = A_x(x, y)dx + A_y(x, y)dy$
- $\partial A_x/\partial y \equiv \partial(f/2)/\partial V = 0$, $\partial A_y/\partial x \equiv \partial(T/V)/\partial T = 1/V$.
- $\partial A_x/\partial y \neq \partial A_y/\partial x$.
- Hence heat transferred Q between two states in a process is not given by the difference in a 'heat function'
 $Q(x + dx, y + dy) - Q(x, y)$.

Types of thermodynamical processes

- Isothermal
- Isochoric
- Isobaric
- Adiabatic

Heat Capacity

- $C_V = (\delta Q / \delta T)_V$ Heat required to change the temperature of a system per δT at constant volume.
- From $\delta Q = Nk \left(\frac{f}{2} dT + \frac{T}{V} dV \right)$, we obtain $C_V = Nkf/2$; Note that at constant volume, $dV = 0$.
- $C_P = (\delta Q / \delta T)_P$ Heat required to change the temperature of a system per δT at constant pressure.
- From $\delta Q = Nk \left(\frac{f}{2} dT + \frac{T}{V} dV \right)$ and $PV = nRT$ we obtain $C_P = Nk(1 + f/2)$ with P a constant.
- $\frac{C_P}{C_V} = \gamma = 1 + \frac{2}{f}$.

Second law of thermodynamics

- It is impossible for any engine working continuously in a cycle to transfer heat from a colder to a hotter body and to produce no other effect.
- Kelvin formulation: It is impossible for an engine working in a cycle to extract heat from a single reservoir, produce an equal amount of work and have no other effect.

Definition of entropy, S

- δQ is not an exact differential, but $\frac{\delta Q}{T}$ is.
- Entropy change $dS = \frac{\delta Q}{T}$ is an exact differential between two states.
- Entropy S is an extensive variable.
- Since dS is an exact differential, S is a state function, which can be expressed as a function of the state variables, e.g. $S = S(T, P)$ or $S = S(T, V)$.
- Furthermore, e.g. the values of S at two different states, e.g. $S(T_1, P_1), S(T_2, P_2)$ do not depend on the path between the two states.

First law in terms of entropy

- First law: $dE = TdS - PdV$.
- Entropy S is an extensive variable.
- For ideal gas, the entropy at $\{P, V, T\}$ is
 $S = \int dS = \int \frac{\delta Q}{T} = Nk \int \left(\frac{f}{2} \frac{dT}{T} + \frac{dV}{V} \right) = Nk \ln(bVT^{f/2})$, b
constant of integration, fixed by initial condition at the
reference system with zero entropy.

Heat capacities in terms of entropy

- Let $S = S(T, V)$, $\Rightarrow \frac{\delta Q}{T} = dS = \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial V} dV$.
- Taking $\frac{\delta Q}{T}$ at constant volume ($\Rightarrow dV = 0$),
 $C_V = \left(\frac{\delta Q}{\delta T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$.
- Let $S = S(T, P)$, $\Rightarrow \frac{\delta Q}{T} = dS = \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial P} dP$.
- Taking $\frac{\delta Q}{T}$ at constant pressure ($\Rightarrow dP = 0$),
 $C_P = \left(\frac{\delta Q}{\delta T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P$.

Heat capacities from other state function E

- Previously we have seen that heat capacities can be derived if
from entropy, which is one example of state functions in
thermodynamics.
- The total energy of the system E is also a state function from
which heat capacities can be derived.
- Let $E = E(T, V)$, $\Rightarrow \delta E = \frac{\partial E}{\partial T} dT + \frac{\partial E}{\partial V} dV$.
- $\delta Q = dE$ at constant volume
- $C_V = \left(\frac{\delta Q}{\delta T} \right)_V = \left(\frac{\partial E}{\partial T} \right)_V$.

Entalpy and heat capacity at constant pressure

- Define Entalpy as $H = E + PV$.
- $\delta Q = dE + PdV$.
- $\delta Q = dH - VdP$.
- Let $H = H(P, T)$
- $\delta Q = \left(\frac{\partial H}{\partial T} \right) dT + \left(\frac{\partial H}{\partial P} - V \right) dP$
- $\Rightarrow \left(\frac{\delta Q}{\delta T} \right)_P = C_P = \left(\frac{\partial H}{\partial T} \right)_P$.

Energy as thermodynamic potential

- The energy is a thermodynamic potential when expressed in terms of S and V : $E = E(S, V)$
- $dE = TdS - PdV$, $\{S, V\}$ as variables, $\{T, P\}$ as the coefficients to the exact differential dS, dV .
- Given the thermodynamic potential $E(S, V)$, $\{T, P\}$ can be derived from it.
- $dE = \left(\frac{\partial E}{\partial S}\right) dS + \left(\frac{\partial E}{\partial V}\right) dV$.
- $T = \left(\frac{\partial E}{\partial S}\right)_V$.
- $P = -\left(\frac{\partial E}{\partial V}\right)_S$.

Entropy as thermodynamic potential

- $dS = \frac{dE}{T} + \frac{PdV}{T}$.
- Given the thermodynamic potential $S(E, V)$, $\{T, P\}$ can be derived from it.
- $S = S(E, V) \rightarrow dS = \left(\frac{\partial S}{\partial E}\right) dE + \left(\frac{\partial S}{\partial V}\right) dV$.
- $\Rightarrow \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V, P = T \left(\frac{\partial S}{\partial V}\right)_E$.

Thermodynamic potential, Function of states

- S, E, H are examples of thermodynamic potential (a.k.a function of states) from which the thermodynamical information of the system can be derived.
- Once a thermodynamic potential is given, all the thermodynamic properties can be derived from it.

Chemical potential, μ

- When N changes in a thermodynamical process, chemical work is done, via $dE = TdS - PdV + \mu dN$, with $E = E(V, S, N)$

More 'convenient thermodynamical potential (for experiment)'

- S, E are difficult potential to control experimentally.
- Legendre transformation to obtain more convenient potential
- Example: $H = E + PV$, where the T.P E is transformed to H by shifting it by the product of two thermodynamic variables P, V .
- Helmholtz free energy, $F = E - TS$.
- $\Rightarrow dF = dE - TdS - SdT \Rightarrow dF = \mu dN - PdV - SdT$.
- $\Rightarrow F = F(N, V, T)$.
- $\{T, S\}$ or $\{\mu, P, S\}$ can be derived from F
- $\left(\frac{\partial F}{\partial E}\right)_{S,T} = 1, \left(\frac{\partial F}{\partial S}\right)_{E,T} = -T, \left(\frac{\partial F}{\partial T}\right)_{E,T} = -S$.
- $\left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu, \left(\frac{\partial F}{\partial V}\right)_{N,T} = -P, \left(\frac{\partial F}{\partial T}\right)_{N,V} = -S$.

Maxwell relations

- $\left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu \Rightarrow \left(\frac{\partial \mu}{\partial T}\right)_{V,N} = \left(\frac{\partial^2 F}{\partial T \partial N}\right)_{T,V,N}$
 $\left(\frac{\partial \mu}{\partial V}\right)_{T,N} = \left(\frac{\partial^2 F}{\partial V \partial N}\right)_{T,V,N}$
- $\left(\frac{\partial F}{\partial V}\right)_{N,T} = -P \Rightarrow -\left(\frac{\partial P}{\partial T}\right)_{V,N} = \left(\frac{\partial^2 F}{\partial T \partial V}\right)_{T,V,N}$
 $-\left(\frac{\partial P}{\partial N}\right)_{V,T} = \left(\frac{\partial^2 F}{\partial N \partial V}\right)_{T,V,N}$
- $\left(\frac{\partial F}{\partial T}\right)_{N,V} = -S \Rightarrow \left(\frac{\partial \mu}{\partial T}\right)_{V,N} = \left(\frac{\partial^2 F}{\partial T \partial N}\right)_{T,V,N}$
 $\left(\frac{\partial \mu}{\partial V}\right)_{T,N} = \left(\frac{\partial^2 F}{\partial V \partial N}\right)_{T,V,N}$

Maxwell relations (cont.)

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_{T,N} &= \left(\frac{\partial P}{\partial T}\right)_{V,N}, \\ -\left(\frac{\partial P}{\partial N}\right)_{V,T} &= \left(\frac{\partial \mu}{\partial V}\right)_{T,N}, \\ -\left(\frac{\partial S}{\partial N}\right)_{T,N} &= \left(\frac{\partial \mu}{\partial T}\right)_{V,N}. \end{aligned} \quad (1)$$

Grand potential ('thermodynamic potential'), Ω

- $\Omega = F - \mu N = E - TS - \mu N$.
- Take $\Omega = \Omega(T, V, \mu)$, and use $dE = TdS - PdV + \mu dN$
- $d\Omega = -PdV - SdT - Nd\mu$.

$$\begin{aligned} S &= -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} \\ P &= -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} \\ N &= -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} \end{aligned}$$

$C_{V,N}$ in terms of F

- Show that $C_{V,N}$ can be derived from F :
- $C_{V,N} = \left(\frac{\partial E}{\partial T}\right)_{N,V} = T \left(\frac{\partial S}{\partial T}\right)_{N,V} = -T \left(\frac{\partial^2 F}{\partial T^2}\right)_{N,V}$.

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Magnetic moment system

- Magnetic dipole moment, μ .
- $U_{\text{mag}} = -\mu \cdot \mathbf{B} = -\mu B \cos \theta$. This is a potential energy (orientationally dependent)
- For a collection of atoms in an external magnetic field \mathbf{H} , \mathcal{M} , magnetization density or magnetization per unit volume will be induced as a response to external magnetic field.
- \mathcal{M} in turn will give rise to an induced magnetic field via $\mathbf{B}_{\text{ind}} = 4\pi\mathcal{M}$.
- An individual magnetic dipole moment in the material will interact with an effective field, called magnetic induction $\mathbf{B} = \mathbf{H} + \mathbf{B}_{\text{ind}} = \mathbf{H} + 4\pi\mathcal{M}$.

\mathbf{M}, \mathbf{P} as thermodynamic variables

- Magnetisation, $\mathbf{M} = V\mathcal{M} = N\langle\mu\rangle$.
- $\{\mathbf{H}, \mathbf{M}\}$ is a pair of variables characterising the magnetic moment system (c.f. the set of variables $\{P, V\}$ characterizing an ideal gas system).
- We wish to formulate the first law $\delta Q = dE + \delta W$ in magnetic variables $\{\mathbf{H}, \mathbf{M}, T\}$
- Work done by system when \mathbf{H} change by $d\mathbf{H}$, $\delta W = ?$
- $\Delta U_{\text{mag}} = [-\mu \cdot (\mathbf{H} + d\mathbf{H})] - [-\mu \cdot \mathbf{H}] = -\mu \cdot d\mathbf{H}$. Work done by the system (comprised of only one moment) is obtained via conservation of mechanical energy, $\delta W = -\Delta U = \mu \cdot d\mathbf{H}$.
- $dE = \delta Q - \mu \cdot d\mathbf{H} \Rightarrow TdS = dE + \mu \cdot d\mathbf{H}$

Derivatives of S

- $dE = TdS - \mathbf{M} \cdot d\mathbf{H} \Rightarrow S = S(E, H)$.
- $\left(\frac{\partial S}{\partial E}\right)_H = \frac{1}{T}$; $\left(\frac{\partial S}{\partial H}\right)_E = \frac{M}{T}$.

$E^* = E + \mathbf{M} \cdot \mathbf{H}$

- By Legendre transformation, define the potential function
 $E^* = E + \mathbf{M} \cdot \mathbf{H}$
- $dE = TdS - \mathbf{M} \cdot d\mathbf{H}$.
- $dE^* = TdS + \mathbf{M} \cdot d\mathbf{H}$.
- $\left(\frac{\partial S}{\partial E^*}\right)_H = \frac{1}{T}$; $\left(\frac{\partial S}{\partial M}\right)_{E^*} = -\frac{H}{T}$.

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Types of magnetic system

- Type of magnetic systems depend on how the system responds to the external magnetic field.
- Paramagnetic
- Diamagnetic
- Ferromagnetic

spin-half magnetic moment

- Electron's orbital motion in an atom \mathbf{L} and the intrinsic spin \mathbf{S} of the electron give rise to magnetic moment of the atom.
- Magnetic dipole moment of an atom is usually measured in unit of Bohr magneton, $\mu_B = \frac{e\hbar}{2m}$, m mass of electron.
- In simplest case, angular momentum does not contribute to the magnetic moment of an atom: $\boldsymbol{\mu} = -2\mu_B\mathbf{S}$, with $\mathbf{S} = \pm\frac{1}{2}\hat{z}$.
- 'spin-half' magnetic ion.
- A single spin-half magnetic moment in external magnetic field, $E = -\boldsymbol{\mu} \cdot \mathbf{H} = \sigma H\mu_B$, with $\sigma = +1(-1)$ if \mathbf{H} parallel (antiparallel) with $\boldsymbol{\mu}$.
- σ is called the 'projection' of the spin. A spin could have two possible projections, either $\sigma = +1$ or $\sigma = -1$.

Configurations of spin-1/2 system

- The microscopic state (configuration) of a spin-1/2 magnetic system comprised of N spin-1/2 magnetic moment in an external magnetic field is characterised by the set of $\{\sigma_1, \sigma_2, \dots, \sigma_N\}$.
- $E(\sigma_1, \sigma_2, \dots, \sigma_N) = -\mu_B H \sum_{i=1}^N \sigma_i$.
- The system has 2^N microscopic states.

PDF

- In statistical mechanics, we wish to know the probability for a certain microscopic state to appear along the systems trajectory in configuration space, so that we can calculate the averages of a system's macroscopic properties.
- The probability of a system in a configuration $\{\sigma_1, \sigma_2, \dots, \sigma_N\}$ is denoted by $P(\sigma_1, \sigma_2, \dots, \sigma_N)$, \rightarrow probability distribution function (PDF).
- Each microscopic state $\{\sigma_1, \sigma_2, \dots, \sigma_N\}$ has a probability of occurrence, denoted by $P(\sigma_1, \sigma_2, \dots, \sigma_N)$
- In most cases in stat mech, PDF is the single most important piece of information we are after. Once we know what $P(\sigma_1, \sigma_2, \dots, \sigma_N)$ is, calculation of the averages is simply a technical problem.

Average of an observable

- Examples of observable:
 $E(\sigma_1, \sigma_2, \dots, \sigma_N) = -H\mu_B \sum_{i=1}^N \sigma_i$,
 $M(\sigma_1, \sigma_2, \dots, \sigma_N) = \mu_B \sum_{i=1}^N \sigma_i$.
- Note that an observable's state depends on the configuration $\{\sigma_1, \sigma_2, \dots, \sigma_N\}$.
- The average of an observable is
 $\langle A \rangle = \sum_{\{\sigma\}} P(\sigma_1, \sigma_2, \dots, \sigma_N) A(\sigma_1, \sigma_2, \dots, \sigma_N)$.
- In the present case, $\sum_{\{\sigma\}}$ is the sum over 2^N states.

$$P(\sigma) = \sum'_{\{\sigma\}} P(\sigma_1, \dots, \sigma_N)$$

- Consider the summation $P(\sigma_I) = \sum'_{\{\sigma\}} P(\sigma_1, \dots, \sigma_N)$.
- $\sum'_{\{\sigma\}}$ sums all the σ_i 's except one (σ_I).
- σ_I is the projection of spin with index $I \in \{1, 2, \dots, N\}$; σ_I can have only two values, 1 or -1.
- $P(\sigma_I)$ is the probability of the spin with index I to have a projection σ_I .
- Specifically, $P(\sigma_I = +1)$ is the probability that spin with index I has a projection +1; $P(\sigma_I = -1)$ the probability that spin with index I has a projection -1.

$$\langle \sigma \rangle$$

- $\sum_{\sigma_I=\pm 1} \sigma_I P(\sigma_I)$ then represents the average projection of spin with index I , i.e. $\sum_{\sigma_I=\pm 1} \sigma_I P(\sigma_I) = \langle \sigma_I \rangle$
- Since $I \in \{1, 2, \dots, N\}$, $\langle \sigma_1 \rangle = \langle \sigma_2 \rangle = \dots = \langle \sigma_N \rangle$.
- Convince yourself that the average projection of the spin-1/2 paramagnetic system is

$$\langle \sigma \rangle = \frac{\sum_{I=1}^N \sigma_I P(\sigma_I)}{N} = \frac{\sum_{\sigma_I=\pm 1} N \sigma_I P(\sigma_I)}{N} = \sum_{\sigma_I=\pm 1} \sigma_I P(\sigma_I)$$

$$\langle M \rangle \text{ and } \langle E \rangle$$

$$\begin{aligned} \langle M \rangle &= N \mu_B \langle \sigma \rangle \\ &= \mu_B N \cdot \sum_{\sigma_I=\pm 1} \sigma_I P(\sigma_I) \\ &= \mu_B N \cdot [\sigma_+ P(\sigma_+) + \sigma_- P(\sigma_-)] \\ &= \mu_B N \cdot [+1 \cdot P(\sigma = +1) + (-1) \cdot P(\sigma = -1)]. \end{aligned}$$

$$\langle E \rangle = -H \langle M \rangle = -NH \mu_B \cdot [+1 \cdot P(\sigma = +1) + (-1) \cdot P(\sigma = -1)]$$

Note that the relation $\langle E \rangle = -H \langle M \rangle$ is obtained from considering the potential energy of a single spin μ coupled to magnetic field H , $\epsilon = -\mu \cdot H \Rightarrow N\epsilon = -N\mu \cdot H \Rightarrow E = -M \cdot H$.

Covariance between two spins

- $P(\sigma_i, \sigma_j) = \sum''_{\sigma} P(\sigma_i, \dots, \sigma_j)$, \sum'' sums all spins but that of indices i, j (i.e. the sum involves only $N - 2$ terms).
- Covariance between any two spins, $C(i, j) = \langle \sigma_i, \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle$.
- $C(i, j) = 0$ if spins i and j are independent of each other.
- $C(i, j) > 0 (< 0)$ if one spin encourages the other to have the same (opposite) value.

How does $P(\sigma_1, \dots, \sigma_N)$ look like?

- Wait until the next chapter
- Once the explicit form of $P(\sigma_1, \dots, \sigma_N)$ is known we can proceed to calculate $\langle M \rangle$, $\langle E \rangle$.

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Macrostate, microstate, representative point and phase space

- Representative point is a point in phase space that represents the instantaneous microstate of the system.
- 'Trajectory' of a system refers to the 'movement' or time evolution of the representation point in the phase space of the system.
- The representative point will visit all accessible microstates (subjected to physical constraints) at certain probability for each microstate in the phase space. (Imagine the rep. point 'moves around' the phase space at an amazingly fast rate, visiting the microstates so fast that it effectively samples all the accessible microstates in a macroscopic time scale).

Macrostate, microstate, representative point and phase space (cont.)

- A given macrostate is an effective 'state' resulted from the averaging of all accessible microstates of the system.
- Each microstate has a certain probability to be 'visited' as compared to others, and their probability distribution are subjected to different boundary conditions or physical constraints.
- The collection of all the accessible microstates is called an ensemble.
- The averaging of all the accessible microstates can be calculated if we know probability distribution of the ensemble.

Macrostate, microstate, representative point and phase space (cont.)

- Knowing the probability distribution of an ensemble is crucial as it allows us to abstract many desired physical information (e.g. heat capacity, mechanical properties, magnetic/electric susceptibility, pressure, etc.) related to the system.

Thermal equilibrium

- Thermal equilibrium: A state to which the system has evolved after a long enough time, so that by now all the microscopic states appear at the same occurrence rate during its time evolution.

Microcanonical ensemble

- System subjected to different physical constraints are described by different types of ensembles.
- The description of an ensemble with constant energy (microcanonical ensemble) is different from that which is not (e.g. that with constant temperature and in thermal contact with a heat reservoir - a canonical ensemble.)
- In a microcanonical ensemble, all accessible microstates has the same energy, and each of the microstate are equally probable (this is generally not the case for other types of ensemble) - *equal a priori postulate*
- $P(\sigma_1, \dots, \sigma_N) = \frac{1}{\Gamma(E)}$, $\Gamma(E)$ the number of microstates with energy E .

Derivation of $\Gamma(E)$

- $N = N_+ + N_-$, $q = N_+ - N_-$, $E(\sigma_1, \dots, \sigma_N) = -\mu_B H q$ (individually N_- , N_+ can vary but their difference and their sum must not).
- Since for a microcanonical ensemble, E is a constant, so is q .
- The number of ways of dividing N objects into two groups, $\Gamma(E) = \frac{N!}{N_+!N_-!}$
- $P(\sigma_1, \dots, \sigma_N) = 1/\Gamma(E) = \frac{\left(\frac{N}{2} - \frac{E}{2\mu_B H}\right)! \left(\frac{N}{2} + \frac{E}{2\mu_B H}\right)!}{N!}$

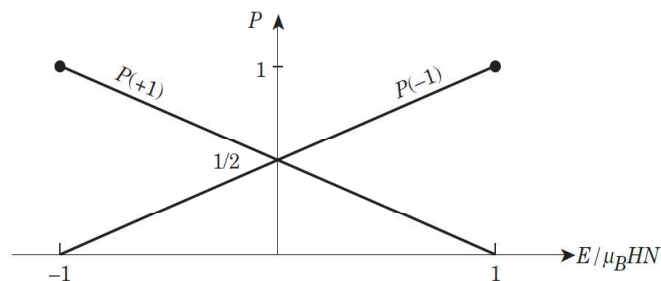
Calculating $\langle M \rangle$

- In a microcanonical ensemble, E is a constant, leading to $q = N_+ - N_-$ also a constant.
- For any microscopic state r , $M_r = q\mu_B$
 $\Rightarrow \langle M \rangle = \mu_B q = -E/H$ simply because all microstates are identical.

Calculating $P(\sigma)$

- $P(\sigma = +1) = \frac{N_+}{N}$
- Express $P(\sigma = +1)$ in terms of E, H, N (by making use of $\mu_B q = -E/H$) gives
- $P(\sigma = +1) = \frac{1}{2} \left(1 - \frac{E/N}{2\mu_B H} \right)$
- $P(\sigma = -1) = \frac{N_-}{N} = 1 - P(\sigma = +1) = \frac{1}{2} \left(1 + \frac{E/N}{2\mu_B H} \right)$
- What is the preferred orientation of the spins with respect to the field H when (i) $E < 0$? (ii) $E > 0$?

Graphical representation of $P(\sigma)$



Limiting cases of the spin system

- Max of the energy is $E = \mu_B H N$. When this happens, $P(-1) = 1, P(+1) = 0$, \Rightarrow all spins are anti-parallel to the field H .
- Min of the energy is $E = -\mu_B H N$. When this happens, $P(-1) = 0, P(+1) = 1$, \Rightarrow all spins are parallel to the field H .
- When $E = 0$, $P(-1) = 1/2, P(+1) = 1/2$, \Rightarrow a 50-50 mixture of spins parallel and antiparallel to H .
- Note that we can control the energy of the system E by controlling H .
- $\langle \sigma \rangle = \sum_{\sigma=\pm} P(\sigma)\sigma = P(+1) - P(-1) = -\frac{E}{N\mu_B H} = \frac{q}{N}$.

Combinatoric correlation effect

- $C(i, j) = \frac{1}{N-1} \left(\frac{q^2}{N^2} - 1 \right) < 0 \Rightarrow$ correlation exist between any two spins. (Since there is no interactions among the spins, we intuitively expect no such correlation in the first place.)
- Such correlation effect is independent of the distance between spin i and j . It is an effect arised not from interactions among the spins but from the combinatorics: the combinatorics of $N - 1$ and $N - 2$ are different.
- Taking thermodynamic limit $N \rightarrow \infty$ eliminate such spurious effect as this correlation scales as $1/N$.

Comparing $\Gamma(E)$ at different energy

- Note that $\Gamma(E)$ varies sharply with $\frac{E}{\mu_B H}$, esp when N is large. The denser the number of states (a.k.a larger Γ) for a given E the more probable are these states (as compared to states at other energy for which Γ is less as dense). Table below shows for the case $N = 10$.

| | | | | | | | | | | | |
|-------------|-----|----|----|-----|-----|-----|-----|-----|----|----|----|
| $E/\mu_B H$ | -10 | -8 | -6 | -4 | -2 | 0 | 2 | 4 | 6 | 8 | 10 |
| Γ | 1 | 10 | 45 | 120 | 210 | 252 | 210 | 120 | 45 | 10 | 1 |

- Largest Γ occurs at $E = 0$.

States with high probabilities vs. states with lowest energy

- If the system were allow to exchange energy with surrounding (no more a microcanonical ensemble), the system can also visit microstates with different energy E . In such scenario the system will tend to prefer states with lowest energy (which is generally not $E = 0$).
- Hence, for system in a non-microcanonical ensemble a 'tag-of-war' between the more probably microstates (states with large Γ) and states with lower energy (but with lower Γ) will be fought.
- We would like to know what happen to the system in the tag-of-war when $N \rightarrow \infty$.
- To do so we will have to deal with large number, $N \sim 10^{22}$.

Stirling formula and Boltzmann's formula

- $n! \approx n^n e^{-n} \sqrt{2\pi n} \Rightarrow \ln n! \approx (n + \frac{1}{2}) \ln n - n$ (the approx. become more accurate as $n \gg 1$)
- Boltzmann formula: $\ln \Gamma \equiv \frac{1}{k} S \approx - \left(\frac{N}{2} - \frac{E}{2\mu_B H} \right) \ln \left(\frac{1}{2} - \frac{E/N}{2\mu_B H} \right) - \left(\frac{N}{2} + \frac{E}{2\mu_B H} \right) \ln \left(\frac{1}{2} + \frac{E/N}{2\mu_B H} \right)$.
- S is an extensive quantity, indentified as the entropy in thermodynamics.
- S is obtained by applying Stirling's formula to $\ln \Gamma$ as appeared in the definition of S , $S = k \ln \Gamma$, where $\Gamma = \frac{N!}{N_+! N_-!}$
- $\ln \Gamma = \ln N! - \ln N_+! - \ln N_-! = \dots$

S per spin in unit of k vs. energy per spin in unit of $\mu_B H$

- Note that despite being a poor approximation at the limit $N \rightarrow 0$, S/Nk as given by the Boltzmann formula reproduces expected behavior at $E/\mu_B H N = \pm 1$ where S/Nk vanishes.
- Since $\Gamma = e^{kS}$, a vanishing S means only $\Gamma = 1$ state is possible.

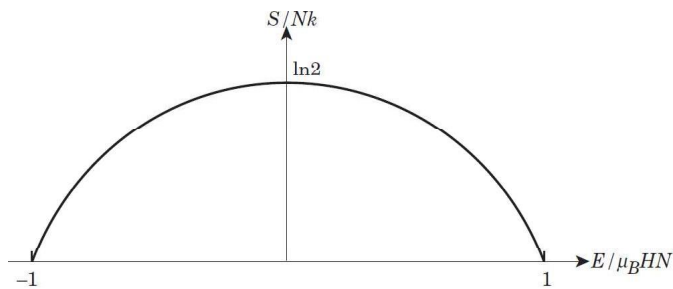


Fig. 2.3.2 The “entropy” per spin for the paramagnet.

Γ at the limit $N \rightarrow \infty$

- When $N \gg 1$, $\Gamma(E) = C(N) \exp\left(-\frac{E^2}{2N\mu_B^2 H^2}\right)$, a Gaussian curve sharply peaked at $\frac{E/N}{\mu_B H} = 0$
- $C(N)$ is a E -independent constant that is determined by the normalisation condition $\int \Gamma(E) dE = 2^N$.

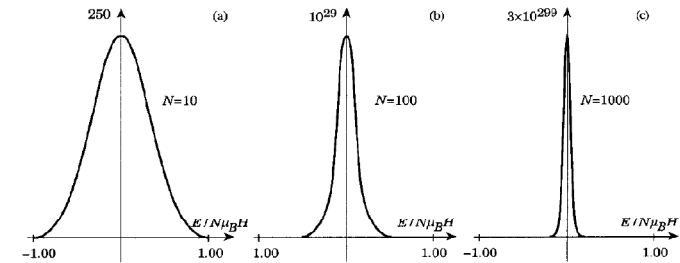


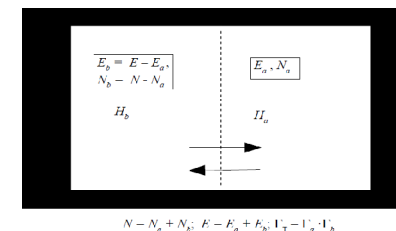
Fig. 2.3.3 Graphs of the number of states as a function of the dimensionless variable $E/(N\mu_B H)$, for (a) $N = 10$, (b) $N = 100$, (c) $N = 1000$. The vertical scale is different in each of the graphs.

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Two systems at thermal contact

- Consider two systems a, b (with number of spins N_a, N_b and external magnetic fields $H_a = H_b = H$) at thermal contact.
- The combined systems can be considered as a microcanonical ensemble (with energy E and number of particle $N \gg 1$) artificially ‘separated’ into two sections.
- $E = E_a + E_b$, $N = N_a + N_b$ are constants, and $E_a = -\mu_B H_a \sum_{i=1}^{N_a} \sigma_i$
- Take the system’s independent variable as E_a



$$N = N_a + N_b; E = E_a + E_b; 1 \uparrow = 1 \downarrow$$

Condition for thermal equilibrium

- $\Gamma_T(E_a) = \Gamma_a \cdot \Gamma_b = \Gamma(E_a) \cdot \Gamma(E - E_b) = \exp\left(\frac{S_a + S_b}{k}\right)$.
- At thermal equilibrium, $\Gamma_T(E_a)$ will be sharply peaked at some value $E_a = \bar{E}_a$, for which $\Gamma(E_a)$ is a maxima
 $\Rightarrow \frac{\partial \Gamma(E_a)}{\partial E_a} \Big|_{E=\bar{E}_a} = 0$
- $\frac{1}{k} \frac{\partial S_a}{\partial E_a} \Big|_{E_a=\bar{E}_a} = -\frac{1}{k} \frac{\partial S_b}{\partial E_b} \Big|_{E_b=\bar{E}_b} = \frac{1}{k} \frac{\partial S_b}{\partial E_b} \Big|_{E_b=\bar{E}_b} = \frac{1}{k} \frac{\partial S_b}{\partial E_b} \Big|_{E_b=\bar{E}_b} = \frac{1}{k} \frac{\partial S_b}{\partial E_b} \Big|_{E_b=\bar{E}_b}$
- Note the constraint $E = \bar{E}_a + \bar{E}_b$.
- Hence we identify the quantity $\beta = \frac{1}{k} \frac{\partial S_a}{\partial E_a} \Big|_{E_a=\bar{E}_a} = \frac{1}{k} \frac{\partial S_b}{\partial E_b} \Big|_{E_b=\bar{E}_b}$ on both systems must be equal at thermal equilibrium.

The parameter β

- One can define the parameter $\beta = \frac{1}{k} \frac{\partial S}{\partial E}$ for any system with entropy $S(E)$.
- The parameter β for an isolated paramagnet system is

$$\beta = \frac{1}{2\mu_B H} \ln \left[\frac{\left(\frac{1}{2} - \frac{E/N}{\mu_B H}\right)}{\left(\frac{1}{2} + \frac{E/N}{\mu_B H}\right)} \right]$$
- The log term can be identified as $\ln \left[\frac{P(\sigma=+1)}{P(\sigma=-1)} \right]$, so that
- $\frac{P(\sigma=+1)}{P(\sigma=-1)} = \exp(2\mu_B H \beta)$.

$P(\sigma) \sim e^{-\beta \epsilon(\sigma)}$

- Since

$$\frac{P(\sigma = +1)}{P(\sigma = -1)} = \exp(2\mu_B H \beta), \quad (2)$$
- If we write $P(\sigma = +1) = C \exp(+\beta \mu_B H \cdot 1)$,
 $P(\sigma = -1) = C \exp(\beta \mu_B H \cdot (-1))$, Eq. (2) is reproduced.
- Define $\epsilon(\sigma) = -\mu_B H \sigma$, where σ represents the projection of the spin along the field H ($\sigma = +1$ if the spin is parallel to, and $\sigma = -1$ if the spin is antiparallel to, the external field H).
- Then $P(\sigma) = C \exp(-\beta \epsilon(\sigma))$
- This is the probability of the spin to have a projection σ . The probability depends exponentially on the product of the β parameter and the energy of the spin $\epsilon(\sigma)$ on that projection.

The normalisation constant in $P(\sigma) = C e^{-\beta \epsilon(\sigma)}$

- $P(\sigma) = C \exp[-\beta \epsilon(\sigma)]$
- $\sum_{\{\sigma=1,-1\}} P(\sigma) = 1 \Rightarrow$
 $C [\exp(-\beta \epsilon(\sigma = +1)) + \exp(-\beta \epsilon(\sigma = -1))] =$
 $C [\exp(-\beta \mu_B H) + \exp(\beta \mu_B H)] = 1$
- $C^{-1} = e^{-\beta \mu_B H} + e^{\beta \mu_B H}$
- In a more convenient form (to be used later)
 $C^{-1} = \sum_{\{\sigma=\pm\}} e^{-\beta \epsilon(\sigma)}$

$\Gamma_T, \frac{1}{k} S_T$ as a function of E_a

- $\Gamma_T(E_a) = \Gamma_a \cdot \Gamma_b = C_a \exp\left(-\frac{E_a^2}{2N_a\mu_B^2 H^2}\right) \cdot C_b \exp\left(-\frac{(E-E_a)^2}{2N_b\mu_B^2 H^2}\right)$.
- $S_T(E_a)/k = \ln \Gamma_T = \ln(C_a C_b) - \frac{1}{2\mu_B^2 H^2} \left[\frac{E_a^2}{N_a} + \frac{(E-E_a)^2}{(N-N_a)} \right]$.
- By completing the square, max of S_T/k as a function of E_a can be easily obtained:

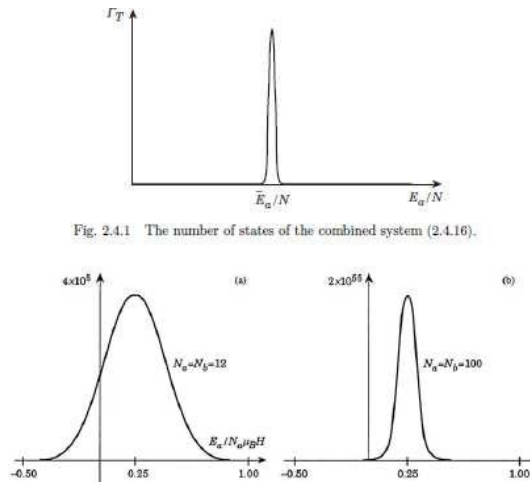
$$\frac{1}{k} S_T|_{max} = \frac{1}{k} S_T(E_a = \bar{E}_a = \frac{N_a E}{N}).$$

- In terms of \bar{E}_a ,
- $$\frac{1}{k} S_T(E_a) = \ln(C_a C_b) - \frac{1}{2\mu_B^2 H^2} \left[\frac{N}{N_a N_b} (E_a - \bar{E}_a)^2 + \frac{E^2}{N} \right].$$

Width of Γ_T in the thermodynamic limit

- $\Gamma_T(E_a) = C_T \exp\left[-\frac{N}{2\mu_B^2 H^2 N_a N_b (E_a - \bar{E}_a)^2}\right]$.
- A gaussian distribution with width $\Delta E_a = \mu_B H \sqrt{\frac{N_a N_b}{N}}$
- Note: The general form of a gaussian is $\sim \exp\left(-\frac{(x-\mu)^2}{2s^2}\right)$.
- The ratio $\frac{\Delta E_a}{E_a} \sim N^{-1/2} \xrightarrow{N \rightarrow \infty} 0 \Rightarrow$ 'extremely sharp peak' in the thermodynamic limit.

Figure showing Γ_T as function of $\frac{E_a}{N}$



Entropy of paramagnet in terms of M

- The paramagnetic system as a whole has induced magnetisation M due to its response to the external magnetic field H . The interaction between the magnetisation ($= N\mu_B \sum_i^N \sigma_i$) and the external magnetic field H gives rise to the potential energy $E = -MH$.
- The entropy S for the paramagnetic system can be expressed in terms of magnetisation $M = -E/H$:

$$S = S(M) = -\frac{1}{2} k \left[(N + M/\mu_B) \ln(1 + M/N\mu_B) + (N - M/\mu_B) \ln(1 - M/N\mu_B) - 2N \ln 2 \right].$$

dS in terms of dM

$$dS = \frac{\partial S}{\partial M} dM = -\frac{k}{2\mu_B} \ln \left(\frac{1 + M/N\mu_B}{1 - M/N\mu_B} \right) dM = -k\beta H dM \quad (3)$$

- Compare this to the thermodynamical equation for the paramagnetic system $TdS = dE^* - HdM$, where $E^* = E + MH$.
- But for paramagnetic system we know $E = -MH \Rightarrow E^* = 0 \Rightarrow dE^* = 0 \Rightarrow$ the first law for paramagnetic system is reduced to

$$dS = -(H/T)dM \quad (4)$$

Finally, we found what β is: the inverse temperature

- Comparing Eqs.(3),(4), $\Rightarrow \beta = \frac{1}{kT}$
- β is called the inverse temperature.

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Canonical ensemble

- A microcanonical ensemble is isolated, characterised by constant E, N
- Subdivide the isolated system into one small section (system a characterised by E_a, n) from the rest (the heat bath, characterised by $E_b(\gg E_a), N_b(\gg n)$).
- $E_a + E_b = E, n + N_b = N$
- System a is a microcanonical ensemble. It constantly exchanges energy with the heat bath with $\Delta E \ll E$ so that both a and b are maintained at constant common temperature $T \Rightarrow$ Both systems are in thermal equilibrium.

Comparison with microcanonical ensemble

- Microcanonical ensemble = canonical ensemble + heat bath.
- As a comparison, since E is constant in the microcanonical ensemble, each state has the same probability of occurrence (this is called the *equal a priori postulate*).
- A microcanonical ensemble is characterised by a constant energy, while a canonical ensemble is characterised by a constant temperature, exchanging small energy with a heat bath.
- Microcanonical ensemble: $\{E, N, H\}$ vs. canonical ensemble: $\{T, N, H\}$

Probability distribution of a canonical ensemble

- The probability distribution of the canonical ensemble,

$$\begin{aligned}
 P(\sigma_1, \dots, \sigma_n) &= P(\sigma_1) \cdots P(\sigma_n) \\
 &= C_1 \exp(-\beta \epsilon_1) \cdots C_n \exp(-\beta \epsilon_n) \\
 &= (\prod_i^n C_i) \exp(-\beta \sum_i^n \epsilon_i) \\
 &= C \exp(-\beta \sum_i^n \epsilon_i) = C \exp(-\beta E)
 \end{aligned}$$

- $C_i^{-1} = \sum_{\{\sigma_i=\pm\}} e^{-\beta \epsilon_i(\sigma_i)}$
- $E = \sum_i^n \epsilon_i$
- $\epsilon_i = -\mu_B H \sigma_i$

The normalisation constant, C

- $C^{-1} = \prod_i^n C_i^{-1} =$
 $(\sum_{\{\sigma_1=\pm\}} e^{-\beta \epsilon_1(\sigma_1)}) (\sum_{\{\sigma_2=\pm\}} e^{-\beta \epsilon_2(\sigma_2)}) \cdots (\sum_{\{\sigma_n=\pm\}} e^{-\beta \epsilon_n(\sigma_n)}) =$
 $\sum_{\{\sigma_1=\pm\}} \sum_{\{\sigma_2=\pm\}} \cdots \sum_{\{\sigma_n=\pm\}} e^{-\beta \sum_i^n \epsilon_i(\sigma_i)}$
- $C^{-1} = \sum_{\{\sigma=\pm 1\}} \sum_{\{\sigma_i=\sigma_1\}}^{\{\sigma_i=\sigma_n\}} e^{-\beta \sum_i^n \epsilon_i(\sigma_i)}$

The Boltzmann distribution $C \exp(-\beta E)$

- Boltzmann distribution also occurs in ideal gas system in terms of $P \sim \exp\left(-\frac{mv^2}{2kT}\right)$
- Unlike the microcanonical ensemble, the total energy of the microstates of a canonical ensemble E is not constant as the system a exchanges energy with the heat bath.
- Each state of the canonical ensemble $(\sigma_1, \sigma_2, \dots, \sigma_n)$ of total energy $E = -\mu_B H \sum_i^n \sigma_i$ has a probability to be visited with a weight $\exp(-\beta E)$, so that those states with larger energy will be relatively less visited by the system as compared to those at lower energy.

Derivation of Γ_T based on canonical ensemble approach

- We will derive Γ_T for the isolated system (heat bath + canonical ensemble) by assuming $N_a \ll n, E_a \ll E_b, E, E = E_a + E_b$ fixed.
- $\Gamma_T = \Gamma_a \Gamma_b = \Gamma(E_a) \Gamma(E_b) = \Gamma(E_a) \Gamma(E - E_a) = \frac{1}{k} \exp(S_a + S_b) = \frac{1}{k} \exp(S(E_a) + S(E - E_a))$
- Use Taylor expansion to expand the $S(E - E_a)$ term to first order in E_a , i.e.,
- $S(E - E_a) \approx S(E) - E_a \frac{\partial S(E)}{\partial E} = S(E) - E_a k\beta = S(E) - \frac{E_a}{T}$
- $\Gamma_T \approx \exp\left[\frac{1}{k}(S(E_a) + S(E) - \frac{E_a}{T})\right] \approx \exp\left[\frac{1}{k}(S(E) - \frac{E_a}{T})\right] = \text{const} \cdot \exp(-E_a/kT)$
- In the above expansion, we have used $\frac{\partial S(E)}{\partial E} = k\beta$ and the approximation $S(E) + S(E_a) \approx S(E)$.

Comparison between the canonical and microcanonical descriptions

- Both approaches are valid and equivalent, but the canonical approach is easier to handle mathematically.
- $\Gamma_T = \exp(\frac{1}{k}S(E) - E_a\beta) = \text{const} \cdot \exp(-E_a/kT)$ looks more natural and easier than that obtained from microcanonical approach.
- Canonical ensemble is more natural than microcanonical one.
- In real life, it's easier to fix temperature in experiments than fixing the energy of a subsystem, hence canonical ensemble is preferred.
- Next, we would like to analyse the paramagnetic system using the canonical approach.

Partition function, Z

- The inverse of the normalisation constant as appeared in the probability distribution of the canonical ensemble $P = Ce^{-\beta E_a}$ is defined as the partition function:
- $Z \equiv C^{-1} = \sum_{\sigma=\pm} \sum_{\{\sigma_i=\sigma_n\}} e^{-\beta \sum_i^n \epsilon_i(\sigma_i)} = \sum_{\text{all microstates}} e^{-\beta E(\text{all microstates})}$
- $P(\sigma_1 \cdots \sigma_n) = \frac{1}{Z} e^{-\beta E_a}$
- From now on we will drop the subscript a in E_a as it is understood from the context E refers to the energy of the canonical ensemble.
- The partition function is very useful as we can calculate the averages of many useful quantities of the ensemble by taking partial derivative of it with respect to some controlled variables.

The importance of partition function

- In statistical mechanics we wish to calculate the averages of useful physical observables of an ensemble.
- This can be done if we know the probability distribution function of the ensemble P via $\langle Q \rangle = \sum_{\text{all microstates}} Q(\sigma_1, \cdots, \sigma_n) P(\sigma_1, \cdots, \sigma_n)$
- However, instead of working with P , we can work with Z to derive $\langle Q \rangle$ much more conveniently
- To know a system is to know its partition function

Deriving $\langle E \rangle$ from partition function

- $\langle E \rangle = \sum_{\text{all microstates}} E(\sigma_1, \dots, \sigma_n) P(\sigma_1, \dots, \sigma_n) = \frac{1}{Z} \sum_{\{\sigma\}} E(\sigma_1, \dots, \sigma_n) e^{-\beta E(\sigma_1, \dots, \sigma_n)}$
- $\frac{\partial Z}{\partial \beta} = \frac{\partial}{\partial \beta} \left[\sum_{\{\sigma_1, \dots, \sigma_n\}} e^{-\beta E(\sigma_1, \dots, \sigma_n)} \right] = - \sum_{\{\sigma_1, \dots, \sigma_n\}} E(\sigma_1, \dots, \sigma_n) e^{-\beta E(\sigma_1, \dots, \sigma_n)}$
- $\langle E \rangle = - \frac{\frac{\partial}{\partial \beta} \left[\sum_{\{\sigma_1, \dots, \sigma_n\}} e^{-\beta E(\sigma_1, \dots, \sigma_n)} \right]}{\sum_{\{\sigma_1, \dots, \sigma_n\}} e^{-\beta E(\sigma_1, \dots, \sigma_n)}} = - \frac{\frac{\partial Z}{\partial \beta}}{Z} = - \frac{\partial \ln Z}{\partial \beta}$
- Similarly, $\langle M \rangle = \frac{\partial \ln Z}{\partial H}$ (derive this)

Partition function of a single spin

- Note that $Z = \prod_{i=1}^n \left(\sum_{\sigma_i = \pm} e^{-\beta \epsilon_i(\sigma_i)} \right) = z_1 z_2 \dots z_n$
- Each z_i are identical
 $z_i = z = (e^{-\beta \mu_B H} + e^{\beta \mu_B H}) = 2 \cosh(\beta \mu_B H)$
- Hence $Z = z^n = 2^n \cosh^n(\beta \mu_B H)$

$\langle E \rangle$ and $\langle M \rangle$ as functions of $\beta \mu_B H$

- $\langle E \rangle = - \frac{\partial \ln Z}{\partial \beta} = - \frac{n \partial \ln z}{\partial \beta} = \dots = -n \mu_B H \tanh(\mu_B H \beta)$
- Using $\langle M \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial H}$, $\langle M \rangle = n \mu_B \tanh(\mu_B H \beta)$. This can alternatively be obtained using the simple fact that $\langle M \rangle$ and $\langle E \rangle$ are simply related by $\langle E \rangle = -H \langle M \rangle$

$\langle \sigma \rangle$ as function of $x = \beta \mu_B H$

- The average magnetisation $\langle M \rangle$ can be expressed in terms of the average projection of a single spin $\langle \sigma \rangle$ via $\langle M \rangle = n \langle \sigma \rangle$. Note $-1 \leq \langle \sigma \rangle / \mu_B \leq +1$.
- $\langle \sigma \rangle / \mu_B = \tanh x$

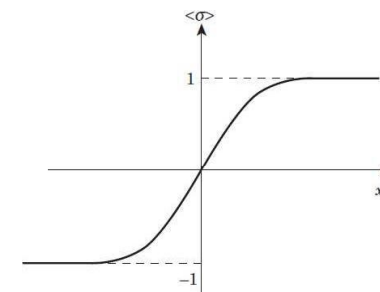


Fig. 2.5.1 $\langle \sigma \rangle$ as a function of $x = \beta \mu_B H$.

'Tug-of-war' between kT and $-\mathbf{H} \cdot \boldsymbol{\sigma}$

- $x = \beta\mu_B H = \frac{\mu_B H}{T}$ (Note: $x < 0$ means we are taking H to point in the opposite direction; T must always be positive)
- The spin system are under the 'tug-of-war' between the thermal energy kT (that tends to randomize the spin configuration) and the external field H 's potential energy $-\mathbf{H} \cdot \boldsymbol{\sigma}$ (that tends to align the spins along the field's direction)

Physical interpretation of $\langle \sigma \rangle$ vs $x = \beta\mu_B H$

Holding H fixed, and vary x

- $x \rightarrow 0^- \equiv T \rightarrow \infty^+$ with $H < 0 \Rightarrow \sigma \rightarrow 0^-$
- $x \rightarrow 0^+ \equiv T \rightarrow \infty^+$ with $H > 0 \Rightarrow \sigma \rightarrow 0^+$
- As $kT \gg |-\mathbf{H} \cdot \boldsymbol{\sigma}|$ the thermal energy in the system dominates over the H field's, causing the spins to fluctuate violently (thermal fluctuation) and result in zero average spin.
- $x \rightarrow \infty^- \equiv T \rightarrow 0^+$ with $H < 0 \Rightarrow \sigma \rightarrow 1^-$
- $x \rightarrow \infty^+ \equiv T \rightarrow 0^+$ with $H > 0 \Rightarrow \sigma \rightarrow 1^+$
- As $kT \ll |-\mathbf{H} \cdot \boldsymbol{\sigma}|$ the H field's energy dominates over the thermal energy in the system, causing the spins to align along the H field's direction.

Physical interpretation of $\langle \sigma \rangle$ vs $x = \beta\mu_B H$ (cont.)

Holding T fixed ($T > 0$), and vary x

- $x \rightarrow 0^- \equiv H \rightarrow 0^- \Rightarrow \sigma \rightarrow 0^-$
- $x \rightarrow 0^+ \equiv H \rightarrow 0^+ \Rightarrow \sigma \rightarrow 0^+$
- As $|-\mathbf{H} \cdot \boldsymbol{\sigma}| \ll kT$ the system was dominated by the thermal energy, causing the spins to fluctuate violently (thermal fluctuation) and result in zero average spin.
- $x \rightarrow \infty^- \equiv H \rightarrow \infty^- \Rightarrow \sigma \rightarrow 1^-$
- $x \rightarrow \infty^+ \equiv H \rightarrow \infty^+ \Rightarrow \sigma \rightarrow 1^+$
- As $|-\mathbf{H} \cdot \boldsymbol{\sigma}| \gg kT$ the system was dominated by H field's energy, causing the spins to align along the H field's direction.

The temperature scale of the spin-1/2 paramagnetic system Θ

- Define the characteristic temperature scale as $\Theta = \mu_B H / k$
- If $T \gg \Theta$, thermal fluctuation dominates, and we have $\langle \sigma \rangle \rightarrow 0$
- If $T \ll \Theta$, magnetic field's energy dominates, and we have alignment $\langle \sigma \rangle \rightarrow \pm 1$.

χ , magnetic susceptibility per spin

- $\langle M \rangle$ is the respond of the paramagnetic system when subjected to the external influence, H
- Hence we define the response function χ , the magnetic susceptibility per spin, as a measure of how good a paramagnetic system response the the H field.
- $\langle M \rangle = n\chi H$
- Our previous statistical treatment predicts χ to behave theoretically as

$$\chi = \langle M \rangle / H = \frac{\mu_B^2}{kT}$$

Curie law

- The inverse dependence of χ on T was indeed observed experimentally in the region $T \ll \Theta = \mu_B H / k$.
- The experimental observation that establishes $\chi \propto \frac{1}{T}$ is called the Curie law.
- However, experimental behavior of χ deviates from Curie law in the region $T \ll \Theta$ (Reason: ...)

Heat capacity at constant H per spin

- By definition, heat capacity per spin (specific heat capacity) of the paramagnetic system at constant field H is given by $c_H = \frac{1}{n} \left(\frac{\delta Q}{\delta T} \right)_H$
- First law on paramagnetic system at constant field, $\delta Q = \delta E - M dH = \delta E$
- $\delta E = \delta (n\mu_B H \tanh(\mu_B H \beta)) = -n\mu_B H \operatorname{sech}^2(\mu_B H \beta) \delta(\beta \mu_B H)$
- $\frac{1}{n} \left(\frac{\delta E}{\delta T} \right)_H = -(\mu_B H)^2 \operatorname{sech}^2(\mu_B H \beta) \frac{\delta \beta}{\delta T}$
- $\delta \beta = \delta \left(\frac{1}{kT} \right) = -\frac{\delta T}{kT^2} \Rightarrow \frac{\delta \beta}{\delta T} = -\frac{1}{kT^2}$
- $c_H = \left(\frac{\delta E}{\delta T} \right)_H = \frac{(\mu_B H)^2 \operatorname{sech}^2(\mu_B H \beta)}{kT^2}$

c_H vs. $\frac{kT}{\mu_B H}$

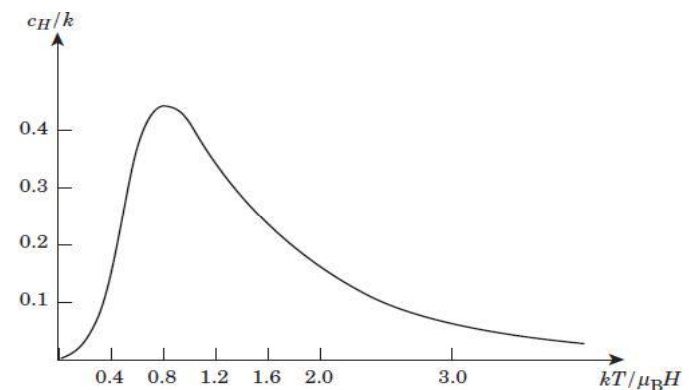


Fig. 2.5.2 The specific heat (2.5.18).

Entropy per spin as function of $\frac{kT}{\mu_B H}$

- Earlier on we have mentioned

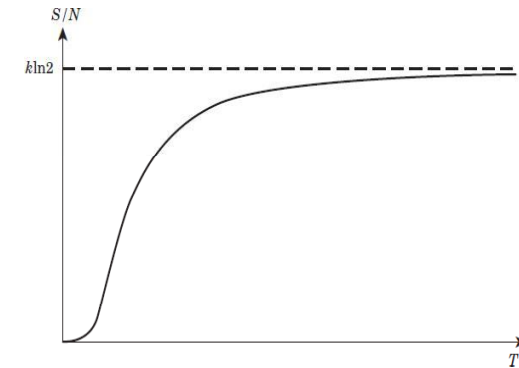
$$S(M) = -\frac{1}{2}k[(N + M/\mu_B) \ln(1 + M/N\mu_B) + (N - M/\mu_B) \ln(1 + M/N\mu_B) - 2N \ln 2].$$

- Now we know $M = N\mu_B \tanh(\beta\mu_B H)$. Substitute this into S above, we obtain $S = S(T, H)$ (after some algebraic manipulation of the hyperbolic function,

$$S(T, H) = Nk \left\{ \ln \left[2 \cosh \left(\frac{\mu_B H}{kT} \right) \right] - \frac{\mu_B H}{kT} \tanh \left(\frac{\mu_B H}{kT} \right) \right\}$$

- Note that here N refers to the number of spin in the system (same definition as the symbol n used in earlier slide).

$S(T, H)$ vs. T at constant H

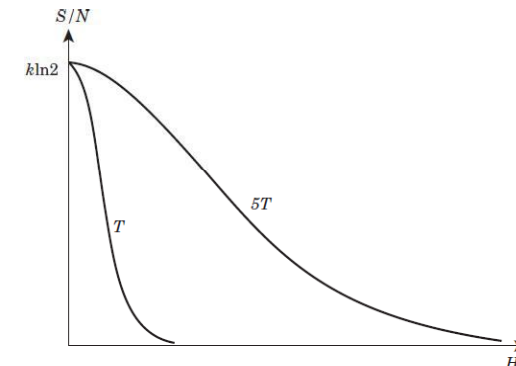


$S(T, H)$ vs. T at constant H

- As temperature increases to infinity, entropy per spin saturates to the limiting value $k \ln 2$.
- As entropy saturates, system becomes maximally disordered (system's states becomes totally randomized)
- In the opposite limit, $T \rightarrow 0$, entropy per spin $\rightarrow 0$
- As entropy is approaching zero, system tends to be totally ordered
- System tends to be totally ordered, as only the unique state in which all spin aligned with H is allowed in this limit

$S(T, H)$ vs. H at constant T

- As H increases to infinity, entropy per spin $\rightarrow 0$
- In the opposite limit, $H \rightarrow 0$, entropy per spin saturates to the limiting value $k \ln 2$.



- Note that entropy per spin shrinks to its minimum $k \ln 2$ faster at lower temperature than at a higher temperature, illustrating the effect that thermal effect presents resistance to the system to reduce in entropy.

Part III Statistical physics and thermodynamics

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General remarks

- All the conclusion obtained based on statistical mechanics treatment on a system must pass the test of confirmity with the laws of thermodynamics.
- In principle the microcanonical ensemble and canonical ensemble descriptions of a system are equivalent. The difference is that one description may be more convinient than the other.
- We will use canonical ensemble for the upcoming analysis.
- The stat mech method applied on paramagnetic system to obtain properties of interesting observeables as averages of the microscopic states is also valid to other thermodynamical systems other than paramagnetic system, e.g. ideal gas, photon gas and fermi gas (in near free electron gas model for metal)

Deriving thermodynamical laws from statistical mechanics

- The relative probability for a state i to appear in the ensemble is $e^{-\beta E_i}$ to that $\frac{P_i}{P_j} = e^{-\beta(E_i - E_j)}$
- The partition function $Z(T, V, N) = \sum_i e^{-\beta E_i}$ allows us to derive averages e.g. $\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$
- Thermodynamical quantities (work, entropy, Helmholtz free energy) can be derived using $Z(T, N, V)$
- We can also find a correspondence between the first law and statistical mechanics based on $Z(T, N, V)$
- Our mission: To establish the statistical origin of the thermodynamical laws.

Macroscopic work done by a system

- Work done by a system in a quasi-static process, δW , due to variation in X , is a macroscopic quantity.
- δW is an average of all the work done in all microstates:

$$\delta W = \sum_{\text{all } i} \delta W_i P(E_i) = Z^{-1} \sum_{\text{all } i} \delta W_i e^{-\beta E_i}$$

- We will show that, after some algebra of plugging $\delta W_i = -\frac{\partial E_i}{\partial X} dX$ into δW above,

$$\delta W = \frac{1}{\beta} \frac{\partial \ln Z}{\partial X} dX$$

where the 'thermodynamic force' is now expressed in terms of partition function $\frac{1}{\beta} \frac{\partial}{\partial X} \ln Z$

Work done by a system in microstate i

- In ideal gas system, $\delta W = PdV$; In paramagnetic system, $\delta W = -MdH$.
- Variation in the external thermodynamic parameter X ($X = V$ in gas and $X = H$ in spin system) causes work done by the system δW
- Hence, in general, $Z = Z(T, X, N)$
- Energy of a microscopic state i , E_i , hence must be dependent on X : $E_i = E_i(X)$
- 'Force' resulted from variation in X can be derived from $F_i = -\frac{\partial E_i}{\partial X}$
- Work done by the system in state i due to variation in X is then $\delta W_i = F_i dX = -\frac{\partial E_i}{\partial X} dX$

Application of $\delta W = \frac{1}{\beta} \frac{\partial \ln Z}{\partial X} dX$ on paramagnetic system

- The parameter X in this case is identified as $X \equiv H$
- The 'thermodynamic force' in state i as appeared in $\delta W_i = -\frac{\partial E_i}{\partial X} dX$ is actually the magnetisation M_i in state i

$$F_i = -\frac{\partial E_i}{\partial X} \equiv -\frac{\partial E_i}{\partial H} = M_i$$

- Explicitly,

$$\begin{aligned} M_i &= -\frac{\partial E_i}{\partial H} \\ &= \frac{\partial}{\partial H} [\mu_B H \cdot (\sigma_1 + \sigma_2 + \dots + \sigma_n)] \\ &= \mu_B \cdot (\sigma_1 + \sigma_2 + \dots + \sigma_n) \end{aligned}$$

- $$\delta W = -Z^{-1} \sum_i \frac{\partial E_i}{\partial H} e^{-\beta E_i} dH = \frac{1}{\beta} \frac{\partial \ln Z}{\partial H} dH$$

Application of $\delta W = \frac{1}{\beta} \frac{\partial \ln Z}{\partial X} dX$ on paramagnetic system (cont.)

- The coefficient to dH can be easily identified as

$$\frac{1}{\beta} \frac{\partial \ln Z}{\partial H} \equiv \langle M \rangle, \quad (1)$$

a result we have encountered earlier.

- Note that the average of M can also be obtained in terms of the probability $P(\sigma_1, \sigma_2, \dots, \sigma_n)$, $\langle M \rangle = \sum_i M_i P_i = \mu_B \cdot \sum_{\{\sigma\}} (\sigma_1 + \sigma_2 + \dots + \sigma_n) \cdot P(\sigma_1, \sigma_2, \dots, \sigma_n)$.
- Mathematically it is obviously more cumbersome to obtain $\langle M \rangle$ by summing over all configuration $\sum_{\{\sigma\}}$ than deriving it via Z as done in Eq. (1).

Application of $\delta W = \frac{1}{\beta} \frac{\partial \ln Z}{\partial X} dX$ on ideal gas system

- The parameter X in this case is identified as $X \equiv V$
- The 'thermodynamic force' in state i as appeared in $\delta W_i = -\frac{\partial E_i}{\partial X} dX$ is actually the pressure P_i in state i

$$F_i = -\frac{\partial E_i}{\partial X} \equiv -\frac{\partial E_i}{\partial V} = P_i$$

- $$\delta W = -Z^{-1} \sum_i \frac{\partial E_i}{\partial V} e^{-\beta E_i} dV = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} dV$$

Application of $\delta W = \frac{1}{\beta} \frac{\partial \ln Z}{\partial X} dX$ on ideal gas system (cont.)

- The coefficient to dV can be easily identified as

$$\frac{1}{\beta} \frac{\partial \ln Z}{\partial V} \equiv P,$$

a result we have encountered earlier.

- In terms of the probability, the pressure is

$$P = Z^{-1} \sum_i P_i e^{-\beta E_i}$$

Recap

- We introduce the generalisation of the definition of 'work done' on a system due to variation of an external parameter X . In this generalisation, the 'thermodynamical force' causes the system's energy to vary when X varies. In a sense the 'thermodynamical force' can be considered as a response of the system due to variation in X . The response of the system (the force) can be identified as the 'conjugate' variable to X (e.g., if X is V , the 'force' is P).
- By applying the generalised definitions of thermodynamical force and work done on each microscopic state, we obtain the macroscopic work done on a system by calculating the statistical averaging of the microscopic work. And we recover the known results

$$\frac{1}{\beta} \frac{\partial \ln Z}{\partial V} \equiv P, \quad \frac{1}{\beta} \frac{\partial \ln Z}{\partial H} \equiv M$$

- This shows consistency between statistical mechanics and thermodynamics.

ΔE_i for an ideal gas

- So far we still have not worked out the expression of E_i , the microscopic energy state i of the ideal gas system. We need this expression since the 'thermodynamic force' is $-\frac{\partial E_i}{\partial V}$
- The dependence of E_i on the volume V is somewhat subtle, as on first appearance the energy of the system suppose to depend only on the sum of the individual particle's velocity, $E = \sum_i \epsilon_i = \frac{1}{2} m v_i^2$.
- The change of E_i due to variation of the volume is effected by the fact that the gas is confined in the volume, and the number of particle is conserved.
- We would like to explain in the next few slide how the effect of the variation in volume leads to the change of the energy of the system via the effect caused to the molecule's velocity distribution near to the piston.

Momentum of a particle after being bounced off the wall moving with velocity $u \ll v$

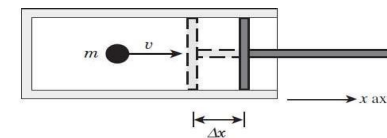
- For a particle bounced against the quasi-statically moving wall, the momentum before and after bouncing off the wall is respectively $p_I = mv$ and $p_F = m(2u - v)$, causing the kinetic energy of the particle to change by $p_F^2/(2m) - p_I^2/(2m) \approx -2muv$
- $p_I = m(2u - v)$ can be derived by, e.g. analysing the bouncing in the moving frame of the wall. In this frame, the velocity before and after bouncing is respectively $v_I' = v - u$ and $v_F' = -(v - u)$. Translate v_F' back to the lab frame (via the Galilean transformation $v' = v - u$), $v_F = v_F' + u = 2u - v \Rightarrow p_I = mv_F = m(2u - v)$.

ΔE_i for an ideal gas (cont.)

- A quasi-static variation in V causes slight variation in the velocity of the gas near the piston, causing the energy E_i to vary at the order of u/v , where v velocity of the gas near the piston, $u (\ll v)$, the quasi-static speed of pushing/expanding the piston.
- In fact we will only need to workout how E_i is varied as V varies; or in other words we would work out the quantity ΔE_i due to ΔV .

ΔE_i due to the bounced particle

- Within an time interval of Δt , the volume swept by the particle from the left is $v\Delta tA$
- $(\Delta E)_v \approx -2muv \cdot n(v) \cdot v\Delta tA = -2mv^2 \cdot n(v) \cdot (u\Delta xA) = -2mv^2 \cdot n(v) \cdot \Delta V$.
- $(\Delta E)_i = \sum_v (\Delta E)_v \approx -2m \sum_v v^2 n_i(v) \Delta V$.
- In the limit $\Delta V \rightarrow 0$, $\frac{\Delta E_i}{\Delta V} \rightarrow \frac{\partial E_i}{\partial V} \approx -2m \sum_v v^2 n_i(v)$
- $-2m \sum_v v^2 n_i(v)$ is the pressure P_i in mircorstate i .



3.1.1 A gas molecule transferring momentum to a piston.

Recap

Hence we have illustrated in the previous few slides the subtle mechanism through which the variation in volume ΔV leads to variation in the energy of the ideal gas system with constant N .

Deriving ΔQ by making use of the partition function

- First law: $\delta Q = d\langle E \rangle + \delta W$
- $\delta W = \frac{1}{\beta} \frac{\partial \ln Z}{\partial X} dX$
- $\langle E \rangle \equiv E = -\frac{\partial \ln Z}{\partial \beta}$
- Note also $dE = dE(\beta, X)$. It means the internal energy change is due to variation in temperature and the external parameter X (e.g. volume)
- $dE = \frac{\partial E}{\partial X} dX + \frac{\partial E}{\partial \beta} d\beta$
- $\frac{\partial E}{\partial X} dX = -\frac{\partial^2 \ln Z}{\partial X \partial \beta} dX$
- $\frac{\partial E}{\partial \beta} d\beta = -\frac{\partial^2 \ln Z}{\partial \beta^2} d\beta$
- $\delta Q = \left(\frac{1}{\beta} \frac{\partial \ln Z}{\partial X} - \frac{\partial^2 \ln Z}{\partial X \partial \beta} \right) dX - \frac{\partial^2 \ln Z}{\partial \beta^2} d\beta$

δQ is not an exact differential but $\beta \delta Q$ is

- $\delta Q = \left(\frac{1}{\beta} \frac{\partial \ln Z}{\partial X} - \frac{\partial^2 \ln Z}{\partial X \partial \beta} \right) dX - \frac{\partial^2 \ln Z}{\partial \beta^2} d\beta \equiv M(X, \beta) dX + N(X, \beta) d\beta$.
- $\frac{\partial M}{\partial \beta} - \frac{\partial N}{\partial X} \neq 0 \Rightarrow \delta Q$ is not an exact differential.

S in terms of the partition function

- $\beta \delta Q$ is an exact differential

$$\frac{\partial(\beta M)}{\partial \beta} - \frac{\partial(\beta N)}{\partial X} = 0 \Rightarrow \beta \delta Q \equiv k^{-1} dS$$

- Wish to find $S = S(\beta, X)$
- $\beta \delta Q = k^{-1} dS = k^{-1} \int dS = k^{-1} \left(\int \frac{\partial S}{\partial X} dX + \int \frac{\partial S}{\partial \beta} d\beta \right) = k^{-1} \left(\int \left(\frac{\partial \ln Z}{\partial X} - \beta \frac{\partial^2 \ln Z}{\partial X \partial \beta} \right) dX - \int \frac{\beta \partial^2 \ln Z}{\partial \beta^2} d\beta \right) = k^{-1} \left(\int \frac{\partial}{\partial X} \left[\ln Z - \beta \frac{\partial \ln Z}{\partial \beta} \right] dX + \int \frac{\partial}{\partial \beta} \left[\ln Z - \beta \frac{\partial \ln Z}{\partial \beta} \right] d\beta \right)$
- $S(\beta, X) = k \ln Z - k\beta \frac{\partial \ln Z}{\partial \beta} = k \ln Z + \frac{E}{T}$

Helmholtz free energy $F = E - TS$ in terms of the partition function

- By definition, Helmholtz free energy as defined in thermodynamic is $F = E - TS$
- Compare this with $S = k \ln Z + E/T \Rightarrow -kT \ln Z = E - TS$
- $F \equiv -kT \ln Z$, which is consistent with the thermodynamic relation $S = -\left(\frac{\partial F}{\partial T}\right)_{X,N}$ (check this)

Thermodynamics and statistical mechanics

- The thermodynamical quantities $\delta Q, \delta W, S, E$ and F are all derivable from the canonical partition function Z
- In other words, knowing Z knows the thermodynamical properties of the system

Deriving paramagnetic system's thermodynamics from its canonical partition function

- $Z(T, H, N) = \left[2 \cosh\left(\frac{\mu_B H}{kT}\right)\right]^N$
- $F = -kT \ln Z = -NkT \ln\left(2 \cosh\frac{\mu_B H}{kT}\right)$
- $S = -\left(\frac{\partial F}{\partial T}\right)_{X,N} = Nk \left[\ln\left(2 \cosh\frac{\mu_B H}{kT}\right) - \frac{\mu_B H}{kT} \tanh\frac{\mu_B H}{kT}\right]$
- E can be obtained from $F = E - TS \Rightarrow E = F + TS = \dots = -N\mu_B \tanh\frac{\mu_B H}{kT}$
- c_H can be obtained from S via the following: $c_H = \left(\frac{\delta Q}{\delta T}\right)_{H,N} = \left(\frac{T dS}{\delta T}\right)_{H,N} = \left(\frac{T \frac{\partial S}{\partial T} dT}{\delta T}\right)_{H,N} = \left(T \frac{\partial S}{\partial T}\right)_{H,N} = \dots = \frac{\mu_B^2 H^2}{kT^2 \cosh^2(\mu_B H/kT)}$

S is maximal for isolated system with constant energy

- For two system a, b in thermal contact, but with $E_a + E_b = E$ a constant, thermal equilibrium between them is characterised by $\frac{\partial S(E_a)}{\partial E_a}|_{E_a=\bar{E}_a} = \frac{\partial S(E-E_a)}{\partial E_b}|_{E_b=E-\bar{E}_a} = T$. This also means the total entropy is a maximum, $\frac{\partial}{\partial E_a} [S(E_a) + S(E - E_a)]_{E_a=\bar{E}_a} = 0$. A maximal entropy of the combined system corresponds to the most probable macrostate, where $\Gamma_T(E_a = \bar{E}_a)$ is the highest. This is the case for the microcanonical ensemble.
- On the other hand, consider a canonical ensemble at constant temperature and is in thermal contact with a heat bath. The ensemble can exchange energy with the heat bath, so that the microscopic states can have different energies E_i . What quantity at thermal equilibrium is maximum?

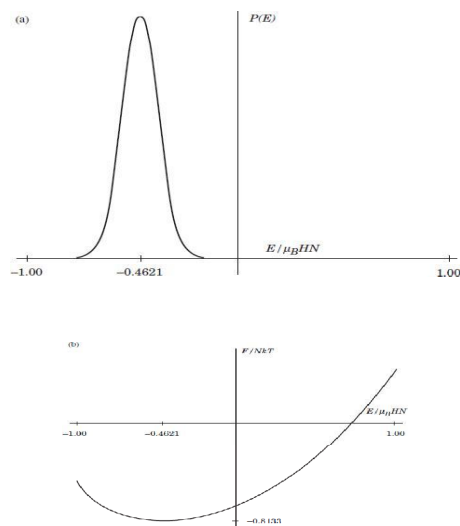
$e^{S/k}$ vs. $e^{-\beta E}$ in canonical ensemble

- The probability for a canonical ensemble in a macroscopic energy E is $P(E) = Z^{-1} e^{-\beta E} \Gamma(E) = Z^{-1} e^{-\beta E} e^{S/k}$.
- $e^{-\beta E}$ favours lower energy (note that T is kept constant) whereas $e^{S/k}$ favours large entropy (tug-of-war).
- Writing $P(E) = Z^{-1} e^{\frac{1}{k}(S - \frac{E}{T})} = Z^{-1} e^{-F/kT}$, the most probable state will be achieved for maximal $-\frac{F}{kT}$ (equivalent to minimum in F/kT)
- Condition for maximum in $-F/kT$ is $-\frac{1}{T} \frac{\partial F}{\partial E} = \frac{\partial}{\partial E} (S - \frac{E}{T}) = 0 \Rightarrow \frac{\partial S}{\partial E} = \frac{1}{T}$

F as function of E for paramagnetic system

- $F(E) = E - TS = E + kT \left[\left(\frac{N}{2} - \frac{E}{2\mu_B H} \right) \ln \left(\frac{N}{2} - \frac{E}{2\mu_B H} \right) + \left(\frac{N}{2} + \frac{E}{2\mu_B H} \right) \ln \left(\frac{N}{2} + \frac{E}{2\mu_B H} \right) \right]$
- $P(E) = Z^{-1} e^{-\beta F(E)}$
- From the graph for $N = 200$ we see that $F(E)$ has a minimum and $P(E)$ has a maximum, both are attained at the same energy $E = \bar{E}$.

F and P as function of E for paramagnetic system



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Quantum harmonic oscillator

- A single spin's projection is represented by $\sigma = \pm 1$, where there is only two states per spin.
- The energy of the spin is simply given by $E(\sigma) = -\sigma H$
- Now consider another similar 'spin-like' object, where there are more than two possible states per 'spin'. We call this a QHO. In fact the number of state per QHO, n , is not 2 but unlimited, $n = 0, 1, 2, \dots$
- The energy of a QHO is given by $\epsilon(n) = (n + \frac{1}{2})\hbar\omega$.
- A QHO is a good representation of atoms oscillating with fixed angular frequency ω , and is pegged at the equilibrium position at lattice site.
- The energy of a QHO is quantised

Quantum harmonic oscillator (cont.)

- $n = 0$ correspond to the ground state of the QHO. $n \leq 1$, the QHO is said to be excited. n is also referred as 'degree of excitation'.
- A QHO excited to state n corresponds to n phonons, each with energy $\frac{1}{2}\hbar\omega$.

Energy levels of a QHO

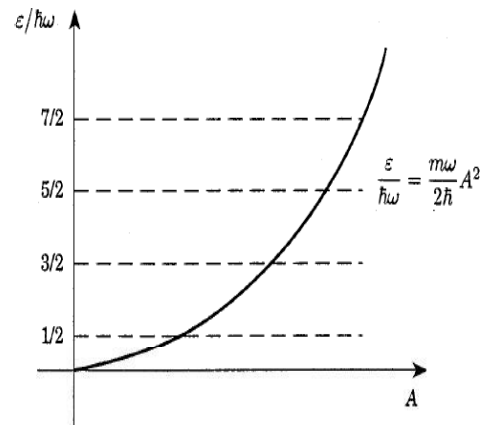


Fig. 3.2.1 The energy levels of a harmonic oscillator: Dashed lines — the quantized levels; full line — energy of classical oscillator vs amplitude A .

Quantum harmonic oscillator vs. spin

- In comparison to a 2-state spin, such a QHO is not subjected to any external field, hence its energy does not depend on the external parameter such as in the case of $E(\sigma) = -\sigma H$
- Instead of $\sigma = \pm 1$, the QHO has $n = 0, 1, 2, \dots$
- The natural unit of energy of a spin is $\mu_B H$; for a QHO it is $\hbar\omega$.

What we want to know of the QHO ensemble

- Consider a canonical ensemble with N non-coupling (in other words, non-interacting) QHO in a heat bath.
- The microrstate of the system is characterised by the set $\{n_1, n_2, \dots, n_N\}$, where each oscillator i takes on values $n_i = 0, 1, 2, \dots$.
- The energy of the system in one particular microstate is

$$E(n_1, n_2, \dots, n_N) = \epsilon_1(n_1) + \epsilon_2(n_2) + \dots + \epsilon_N(n_N) = \sum_{i=1}^{i=N} \epsilon(n_i),$$

where $\epsilon_i(n_i) = \epsilon(n_i) = (n_i + \frac{1}{2})\hbar\omega$.

- We would like to calculate the averages of the macroscopic observables e.g. $\langle n \rangle$, $\langle E \rangle$, free energy, etc., using stat mech method.

Example of a particular microstate of QHO ensemble with 6 oscillator

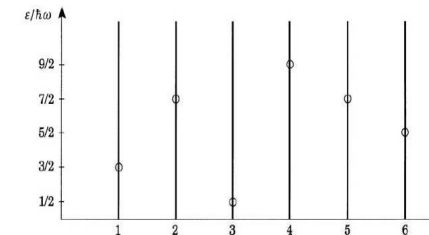


Fig. 3.2.2 A state of a system of six oscillators: $n_1 = 1, n_2 = 3, n_3 = 0, n_4 = 4, n_5 = 3, n_6 = 2$.

What we want to know of the QHO ensemble

- Consider a canonical ensemble with N non-coupling (in other words, non-interacting) QHO in a heat bath.
- The microrstate of the system is characterised by the set $\{n_1, n_2, \dots, n_N\}$, where each oscillator i takes on values $n_i = 0, 1, 2, \dots$.
- We would like to calculate the averages of the macroscopic observables e.g. $\langle n \rangle$, $\langle E \rangle$, free energy, etc., using stat mech method.

Partition function for system of uncoupled oscillators

$$\begin{aligned} Z &= \sum_{\{n_1, n_2, \dots, n_N\}} e^{-\beta E(n_1, n_2, \dots, n_N)} \\ &= \sum_{\{n_1, n_2, \dots, n_N\}} e^{-\beta \epsilon(n_1)} e^{-\beta \epsilon(n_2)} \dots e^{-\beta \epsilon(n_N)} \\ &= \prod_{i=1}^{i=N} z_i = z_1 z_2 \dots z_N = z^N, \end{aligned} \quad (2)$$

where $z_i = \sum_{n_i=0}^{n_i=\infty} e^{-\beta \epsilon(n_i)} = \sum_{n_i=0}^{n_i=\infty} e^{-\beta(\frac{1}{2} + n_i)\hbar\omega} = z_1 = z_2 = \dots = z_N \equiv z$.

Calculating average energy of a single QHO

- $z = \sum_{n=0}^{\infty} e^{-\beta(\frac{1}{2}+n)\hbar\omega} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$.
- Note that $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$, $x < 1$ (geometric series)
- $\langle \epsilon \rangle = -\frac{\partial \ln z}{\partial \beta}$
- Let $x = \beta\hbar\omega \Rightarrow \frac{dx}{d\beta} = \hbar\omega$
- $\langle \epsilon \rangle = -\frac{\partial \ln z}{\partial \beta} = -\frac{dx}{d\beta} \frac{\partial \ln z}{\partial x} = -\frac{dx}{d\beta} \frac{\partial}{\partial x} \left[-\frac{x}{2} - \ln(1 - e^{-x}) \right] = \hbar\omega \left(\frac{1}{2} + \frac{1}{e^x - 1} \right)$

Calculating average degree of excitation $\langle n \rangle$ for a single QHO

- $x = \frac{\hbar\omega}{kT} = \hbar\omega\beta$
- $\langle n \rangle = \frac{\sum_n n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = \frac{\sum_n n e^{-\beta(n+\frac{1}{2})\hbar\omega}}{\sum_n e^{-\beta(n+\frac{1}{2})\hbar\omega}} = \frac{\sum_n n e^{-nx}}{\sum_n e^{-nx}} = \frac{-\frac{\partial}{\partial x} \sum_n e^{-nx}}{\sum_n e^{-nx}} = -\frac{\partial}{\partial x} \ln(\sum_n e^{-nx}) = -\frac{\partial}{\partial x} \ln\left(\frac{1}{1-e^{-x}}\right) = \frac{1}{e^x - 1} = \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}$
- Note that $\sum_n e^{-nx} = \frac{1}{1-e^{-x}}$ is a result from series expansion.
- $\langle n \rangle$ is the average value of the degree of excitation of the oscillator. It is also known as Bose-Einstein distribution. Note that in this distribution, the number of phonon excited, n , in a single oscillator is not limited, $n = 0, 1, 2, 3, \dots$

Behaviour of $\langle n \rangle$ at low and high temperature limits

Bose-Einstein distribution:

$$\langle n \rangle = \frac{1}{e^{\frac{\hbar\omega}{kT}} - 1}$$

$$\lim_{kT \ll \hbar\omega} \langle n \rangle = \lim_{x \rightarrow \infty} \frac{1}{e^x - 1} \approx e^{-x} = e^{-\frac{\hbar\omega}{kT}}$$

$$\lim_{kT \gg \hbar\omega} \langle n \rangle = \lim_{x \rightarrow 0} \frac{1}{e^x - 1} \approx \frac{1}{\left(1 + \frac{x}{1!} + \frac{x^2}{2!} + \dots\right) - 1} \approx \frac{x}{2} = \frac{\hbar\omega}{kT}$$

Graph showing average excitation number vs. $\frac{\hbar\omega}{kT}$

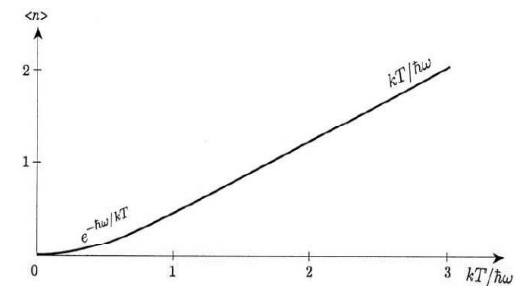


Fig. 3.2.3 The temperature dependence of the average degree of excitation of a harmonic oscillator.

$\langle n \rangle$ changes more readily wrp to $kT/\hbar\omega$ in the limit $kT \gg \hbar\omega$; In the limit $kT \ll \hbar\omega$, variation in $kT/\hbar\omega$ does not change $\langle n \rangle$ much because kT is too small to excite the oscillator from ground state $n = 0$ to the next excited state, a process which requires at least an energy of the amount $\hbar\omega$.

Free energy of a QHO, f

- $z = \frac{e^{\frac{x}{2}}}{1 - e^{-x}}; x = \frac{\hbar\omega}{kT}$
- $f = -kT \ln z = -\frac{1}{\beta} \ln z = \frac{x}{2} + \frac{1}{\beta} \ln(1 - e^{-x}) = \frac{\hbar\omega}{2} + kT \ln(1 - e^{-\frac{\hbar\omega}{kT}})$
- $f = \epsilon - Ts \Rightarrow s = \frac{\epsilon - f}{T}$
- Entropy per QHO, s can be obtained either via $f = \epsilon - Ts$ or $s = \left(\frac{\partial f}{\partial T}\right)$
- $s = \dots = -k [\ln(1 - e^{-x}) - x(e^x - 1)^{-1}]$

Transitional temperature

- kT vs. $\hbar\omega$
- The temperature at which both energies are 'half-fight' is $T_{hf} \approx \hbar\omega/k$
- In the region $T \ll T_{hf}$ ($T \gg T_{hf}$), we are in the region of 'low temperature limit' ('low temperature limit').

QHO system as Einstein solid

- Einstein model of a simple solid:
- A solid made up of N atoms vibrating in 3D can be modelled as a simple system comprised of $3N$ QHO, where each QHO describes vibration of an atom about its EB position in one direction.
- Each QHO representing the atom does not interact with each other but vibrate independently.
- Each atom is executing a SHM (simple harmonic motion) in x -, y - and z - direction in space.
- Each of this vibration mode can be modelled as a QHO in that direction.

Helmholtz free energy and average energy of the Einstein solid

- $\langle E \rangle$ of a Einstein solid can be computed using expression of the previous calculation for ϵ : $\langle E \rangle = 3N\langle \epsilon \rangle$, since an Einstein solid comprised of N atoms are to be represented by $3N$ independent QHOs.
- $Z = z^{3N}; z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$
- $\ln Z = 3N \ln z = 3N \left[-\frac{\beta\hbar\omega}{2} - \ln(1 - e^{-\beta\hbar\omega}) \right]$
- $F = -kT \ln Z = -3NkT \ln z = 3N \left[\frac{\hbar\omega}{2} + \frac{1}{\beta} \ln(1 - e^{-\beta\hbar\omega}) \right]$
- $E = -\frac{\partial \ln Z}{\partial \beta} = 3N \frac{\partial}{\partial \beta} \left[\frac{\beta\hbar\omega}{2} + \ln(1 - e^{-\beta\hbar\omega}) \right] = 3N\hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right]$

Average energy of the Einstein solid at $kT \gg \hbar\omega$ limit

$$\lim_{kT \gg \hbar\omega} \langle E \rangle \approx 3NkT$$

- High temperature (large kT), and/or soft solid (tiny $\hbar\omega$)
- Equipartition law of classical physics is in operation here. According to the law, each DOF has an average energy of $kT/2$. In the case here, for each QHO, there are 3 + 3 DOF: 3 for KE, and 3 for PE. Each DOF of the kinetic energy has average KE of $kT/2$, whereas each of the potential energy DOF has average PE of $kT/2$. $3N$ QHOs then make up the total energy of $3NkT$.

Equipartition theorem

- Equipartition theorem: Every variable of phase space on which the energy depends quadratically, contributes $\frac{1}{2}kT$ to the average energy.
- Since the kinetic energy is $E_K \sim p^2$ for all three components (i.e. all x, y and z components) the average kinetic energy of each of these DOF is $\frac{1}{2}kT$.
- In the special case of a harmonic oscillator as it is here, the potential energy $U \sim r^2$, hence the average energy of $\langle U \rangle = \frac{1}{2}kT$ for all three DOF.
- However, in general, if $U \not\sim r^2$, $\langle U \rangle \neq \frac{1}{2}kT$

Average energy of the Einstein solid at $kT \ll \hbar\omega$ limit

$$\lim_{kT \ll \hbar\omega} \langle E \rangle \approx 3NkT \left(e^{-\frac{\hbar\omega}{kT}} + \frac{1}{2} \right)$$

- Low temperature (tiny kT), and/or stiff solid (large $\hbar\omega$)
- The classical law of equipartition fails in this limit as the effectively DOF $3N \left(e^{-\frac{\hbar\omega}{kT}} + \frac{1}{2} \right)$ is less than $3N$ (some DOF is 'frozen')
- The freezing of DOF is due to the onset of quantum mechanical effect at low x limit.

Molar specific heat capacity of Einstein solid

- $E = 3N\hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right]$
- $C = \frac{\partial E}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial E}{\partial \beta} = -k\beta^2 \frac{\partial E}{\partial \beta} = \dots = 3R(\beta\hbar\omega)^2 \frac{e^{\hbar\omega\beta}}{(e^{\beta\hbar\omega} - 1)^2}$
(Let $N = N_0, R = kN_0$)
- $\lim_{kT \gg \hbar\omega} C = 3R$ (Dulong-Petit law)
- $\lim_{kT \ll \hbar\omega} C = 3R(\beta\hbar\omega)^2 e^{-\hbar\omega\beta}$

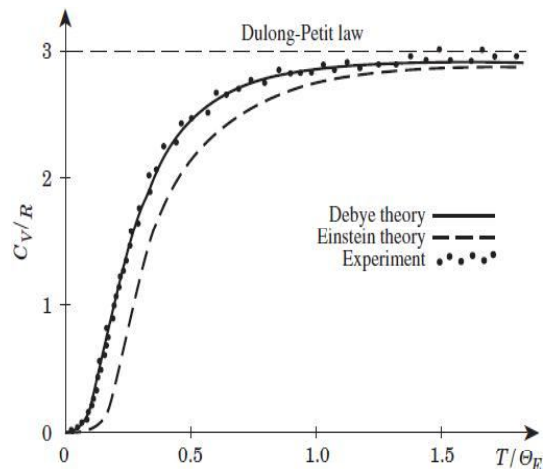
Heat capacity problem in classical physics and its solution

- According to classical physics, solid's molar specific heat capacity is expected to be $3R$ irrespective of temperature, as each DOF in the solid should contribute equally $kT/2$ to the average energy per atom, $\langle \epsilon \rangle$.
- However, experimental measurement of molar specific heat of solid shows that the DOF inferred from the measured heat capacities in these solid are much smaller than was expected by equipartition law.
- Classical physics cannot provide satisfactory explanation to these 'missing' (or 'frozen') DOF as inferred by the experimental results.
- This poses a big problem to the validity of classical physics in explaining the heat capacity of solid.
- The Einstein model of solid solves the heat capacity problem by quantising the energy of the vibration in terms of phonon modes.

Einstein temperature

- $\Theta_E = \hbar\omega/k$ (the 'half-fight' temperature, with ω constant) characterises a given solid, which is in turn characterised by the stiffness of that solid.
- Soft solid: Lead, $\Theta_E \approx 90$ K
- Hard solid: Diamond, $\Theta_E \approx 2000$ K
- In terms of Einstein temperature the specific heat capacity is
$$C = 3R \left(\frac{\Theta_E}{T} \right)^2 \frac{\exp(\frac{\Theta_E}{T})}{[\exp(\frac{\Theta_E}{T}) - 1]^2}$$
- Plotting C vs. $\frac{T}{\Theta_E}$ for different solid should yield a common curve.
- For lead, room temperature is 'hot' as $\Theta_E(\text{lead}) \approx 90$ K c.f $T_{\text{room}} = 300$ K; For diamond, room temperature is 'cold' as $\Theta_E(\text{diamond}) \approx 2000$ K c.f $T_{\text{room}} = 300$ K
- Hence at room temperature, their molar specific heats are generally different.

Curve of C_V/R as function of $\frac{T}{\Theta_E}$



Incompleteness of the Einstein model

- Behaviour of C vs. T as predicted by Einstein model confirms well with experiment only in the limits $x \ll 1$ and $x \gg 1$, but not perfect in the intermediate range of $x \approx 1$.
- Reason: Interactions between the oscillators are not taken into account - Debye model corrects for this effect.

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Classical system comprise of a particle moving in 1D space

- Consider a classical mechanical system comprised of a particle with mass m that can move along the x -axis, and is subjected to a potential field, $U(x)$.
- The potential $U(x)$, or called the force field, will exert a force on the particle, and this force tells the particle how it should move according the Newtonian law, $F = md^2x/dt^2$. Usually the force on the particle depends only on the location x but not on the momentum (equivalent to its velocity).
- $\{p_x, x\}$ are the two variables that completely characterise the 1-particle system.

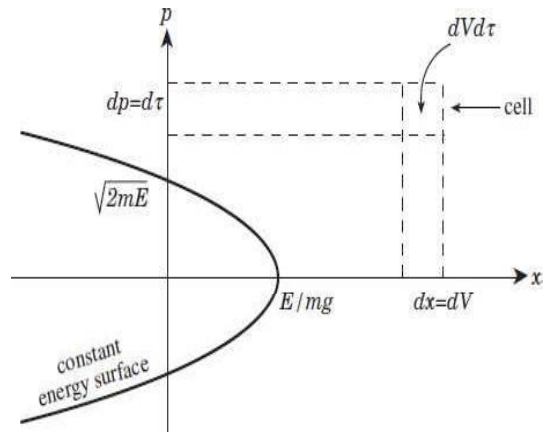
Classical system comprise of a particle moving in 1D space (cont.)

- In other words, we need 1+1 variables to specify the state of the system, $\{x; p_x\}$.
- The state of the one-particle system hence is specified by a point in a 2-D **phase space**.
- The point representing the system's state shall trace out a path in the phase space, which is a curve $p_x - x$ which mathematical relation is determined by the dynamical equation that relates p_x to x .

Example of a 2-D phase space

- As an example, consider a particle that is subjected to a gravitational field (where $U = -mgx$), and is moving only along the vertical direction x .
- The dynamical equation that relates p_x to x is obtained via conservation of energy, $E = K(p_x) + U(x) = p_x^2/2m - mgx$, where E is a constant. The curve traced out by the particle in the 2D phase space is thus $p_x = \pm\sqrt{2m(E - mgx)}$

2D phase space curve of a classical particle in gravitational field



Partition function of one-particle system

- The total energy of the particle is $E = K + U$
- The probability of finding a particle in a state $\{x, p\}$ is

$$P(x, p) = \frac{1}{z_c} e^{-\beta E(x, p)} dx dp_x = \frac{1}{z_c} e^{-\beta \left(\frac{p_x^2}{2m} + U(x) \right)} dx dp_x$$
 where z_c is the single particle partition function.
- $dx dp$ is the 'volume element' in the (1+1)-D phase space.
- Generically, for a particle moving in 3-D real space, its 'volume element' in the phase space is given by

$$dx \cdot dy \cdot dz \cdot dp_x \cdot dp_y \cdot dp_z \equiv d^3 \mathbf{r} d^3 \mathbf{p} \equiv dV d\tau$$
 We can think that such a 6-dimensional quantity is the 'volume' of a point in the 6-D phase space.
- $z_c = \int e^{-\beta \left[\frac{p_x^2}{2m} + U(x) \right]} dx dp_x$
- Knowing z_c allows us to calculate averages of desired observables of the system, e.g. $\langle x \rangle$, $\langle K \rangle$, $\langle U \rangle$, etc.
- $\langle A \rangle = \int A(x, p_x) P(x, p_x) dx dp_x = \frac{1}{z_c} \int A(x, p_x) e^{-\beta \left(\frac{p_x^2}{2m} + U(x) \right)} dx dp_x$

Average KE of 1D classical particle

- $\langle K \rangle = \frac{\int e^{-\beta U(x)} dx \cdot \int \frac{p_x^2}{2m} e^{-\beta \left(\frac{p_x^2}{2m} \right)} dp_x}{\int e^{-\beta U(x)} dx \cdot \int e^{-\beta \left(\frac{p_x^2}{2m} \right)} dp_x} = \frac{\int \frac{p_x^2}{2m} e^{-\beta \left(\frac{p_x^2}{2m} \right)} dp_x}{\int e^{-\beta \left(\frac{p_x^2}{2m} \right)} dp_x} = -\frac{\partial}{\partial \beta} \ln \left(\int e^{-\beta \left(\frac{p_x^2}{2m} \right)} dp_x \right) = -\frac{\partial}{\partial \beta} \ln z_K$
- The integration similar to $z_K = \int e^{-\beta \left(\frac{p_x^2}{2m} \right)} dp_x$ has been encountered in Part I. The explicit expression of z_K can be obtained (without carrying out the integration explicitly) by using dimensional argument to yield $z_K = C\alpha^{-1/2}$, where $\alpha = \frac{\beta}{2m}$.
- Hence, $\langle K \rangle = -\frac{\partial}{\partial \beta} \ln z_K = -\frac{\partial}{\partial \beta} \ln \left(C \left(\frac{\beta}{2m} \right)^{-1/2} \right) = \frac{1}{2} kT$.

Average potential energy of 1D classical particle

- $\langle U \rangle = \frac{\int e^{-\beta \left(\frac{p_x^2}{2m} \right)} dp_x \cdot \int U(x) e^{-\beta U(x)} dx}{\int e^{-\beta U(x)} dx \cdot \int e^{-\beta \left(\frac{p_x^2}{2m} \right)} dp_x} = \frac{\int U(x) e^{-\beta U(x)} dx}{\int e^{-\beta U(x)} dx} = -\frac{\partial}{\partial \beta} \ln z_U$; $z_U = \int e^{-\beta U(x)} dx$
- For illustration purpose take $U(x) = \frac{1}{2} \kappa x^2$ (Hooke's law)
- Use dimensional argument: $[z_U] = L$;
 $[\kappa] = [\text{energy}] / L^2 = \frac{ML^2 T^{-2}}{L^2} = MT^{-2}$;
 $[\beta] = \frac{1}{[E]} = m^{-1} L^{-2} T^2 \Rightarrow ([\kappa][\beta])^{-1/2} = L^1$.
- To match the dimension between $[z_U]$ and $[\beta \kappa]$, z_U is expected to be related via $z_U = c(\kappa \beta)^{-1/2}$, giving $\ln z_U = \ln c - \frac{1}{2} \ln \kappa - \frac{1}{2} \ln \beta \Rightarrow$
- $\langle U \rangle = -\frac{\partial}{\partial \beta} \ln z_U = \frac{1}{2\beta} = \frac{1}{2} kT$.

Generalisation to 3D case

- In previous 1-D example, we see that for the 1D particle subjected to a force field $\sim r^2$ and in contact to a heat bath, the particle has two DOF (one associate with kinetic energy and the other potential energy), for which the particle's total energy is being shared. Each DOF carries $kT/2$ of energy, making up the total energy of $kT/2 + kT/2 = kT$.
- The 1D scenario can be easily generalised to a particle moving in 3D
- In the case of a classical particle moving in 3D, there are 3 DOF associated with the thermal motion ($p_x^2/2m, p_y^2/2m, p_z^2/2m$). Each of these kinetic energy DOF carries average energy $kT/2$.

Generalisation to 3D case (cont.)

- In general a classical particle moving in 3D is subjected to an potential $U(x, y, z)$. The potential energy shall also contribute to the total number of DOF to the particle. The number of potential DOF depends on the forms of the potential (e.g. $U(x, y, z) = -mgz$ or $U(x, y, z) = \frac{1}{2}(\kappa_x x^2 + \kappa_y y^2 + \kappa_z z^2)$).
- Each of the potential energy DOF may or may not contribute $\frac{1}{2}kT$ of energy to the average energy.
- If the potential is quadratically depending on the spatial coordinate, it is; else, it is not.
- Counting the potential energy DOF could be not as straight forward as is for the kinetic energy DOF.
- Note that in the 3-D ideal gas system, the average energy is $3 \cdot \frac{kT}{2}$ as it has no DOF associated with the potential energy.

Partition function for a system with N particles moving in 3D

- The phase space of such a system is $6N$ dimensional, where each point in the phase space is specified by $6N$ coordinates, $\{(\mathbf{r}_1, \mathbf{p}_1), (\mathbf{r}_2, \mathbf{p}_2), \dots, (\mathbf{r}_N, \mathbf{p}_N)\}$. Each of the allowed microstates of the system is represented by a point in the phase space.
- The probability to find the system in a particular configuration:

$$p[(\mathbf{r}_1, \mathbf{p}_1), (\mathbf{r}_2, \mathbf{p}_2), \dots, (\mathbf{r}_N, \mathbf{p}_N)] = \frac{1}{Z_c} \exp\{-\beta[E((\mathbf{r}_1, \mathbf{p}_1), (\mathbf{r}_2, \mathbf{p}_2), \dots, (\mathbf{r}_N, \mathbf{p}_N))]\}$$
$$dV_1 dV_2 \dots dV_N d\tau_1 d\tau_2 \dots d\tau_N$$

$d\tau = dp_x dp_y dp_z$ is the volume element in the momentum subspace.

Partition function for a system with N particle moving in 3D (cont.)

The N -body partition function is written as

$$Z_c = \int (dV d\tau)^N \exp\{-\beta E[(\mathbf{r}_1, \mathbf{p}_1), (\mathbf{r}_2, \mathbf{p}_2), \dots, (\mathbf{r}_N, \mathbf{p}_N)]\}$$

Total energy of a microscopic state

- The total energy of a microstate, $E[(\mathbf{r}_1, \mathbf{p}_1), (\mathbf{r}_2, \mathbf{p}_2), \dots, (\mathbf{r}_N, \mathbf{p}_N)]$, is made up of the kinetic energy part and the potential energy part. In most cases, the kinetic energy terms depends only on the momenta, whereas the potential energy on positions of the particles of the system:

$$E[(\mathbf{r}_1, \mathbf{p}_1), (\mathbf{r}_2, \mathbf{p}_2), \dots, (\mathbf{r}_N, \mathbf{p}_N)] = E_K(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

- $$E_K(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i}$$
- $$U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_{i=1}^N U_{1p}(\mathbf{r}_i) + \sum_{i,j=1}^{i,j=N} U_{2p}(\mathbf{r}_i, \mathbf{r}_j) + \dots$$

Averages of observable in a system of N classical particle

- Given the form of $U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ and $E_K(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$, we can derive the partition function of a classical microcanonical ensemble,

$$Z_c = \int (d\tau dV)^N e^{-\beta E[(\mathbf{r}_1, \mathbf{p}_1), (\mathbf{r}_2, \mathbf{p}_2), \dots, (\mathbf{r}_N, \mathbf{p}_N)]}$$

- And then we can calculate the average of any observable,

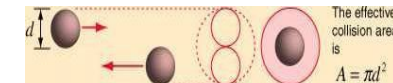
$$\langle A[(\mathbf{r}_1, \mathbf{p}_1), (\mathbf{r}_2, \mathbf{p}_2), \dots, (\mathbf{r}_N, \mathbf{p}_N)] \rangle = \frac{1}{Z_c} \int (d\tau dV)^N A[(\mathbf{r}_1, \mathbf{p}_1), (\mathbf{r}_2, \mathbf{p}_2), \dots, (\mathbf{r}_N, \mathbf{p}_N)] \times e^{-\beta E[(\mathbf{r}_1, \mathbf{p}_1), (\mathbf{r}_2, \mathbf{p}_2), \dots, (\mathbf{r}_N, \mathbf{p}_N)]}$$

Outline

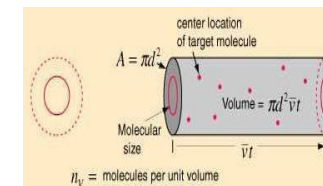
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Mean Free Path

- The mean free path or average distance between collisions for a gas molecule may be estimated from kinetic theory



- In time t , the circle would sweep out the volume shown and the number of collisions can be estimated from the number of gas molecules that were in that volume.



Mean Free Path (cont.)

- The mean free path could then be taken as the length of the path divided by the number of collisions.

$$\text{Mean free path estimate} = \frac{\text{Distance traveled } \bar{v}t}{\underbrace{\pi d^2 \bar{v} t n_V}_{\text{Volume of interaction}}} = \frac{\text{Mean distance per collision } 1}{\underbrace{\pi d^2 n_V}_{\text{Number of molecules per unit volume}}}$$

Mean Free Path (cont.)

- The expression of mean free path for idea gas is obtained (i) by replacing $\bar{v} \rightarrow \sqrt{2}\bar{v}$ to correct for the effect of relative motion among the colliding particles, and (ii) $n_V = \frac{N_0 P}{RT}$ to give

$$\lambda = \frac{RT}{\sqrt{2}d^2 N_0 P}$$

- At STP ($N = N_0 \sim 10^{23}$, $P \sim 10^5 \text{ Pa}$, $kT \sim 10^{-21} \text{ J}$), the mean free path is much larger than average size of the molecule ($d \sim 10^{-9} \text{ m}$) and also the distance between the molecules $\sim (\frac{N_0}{V})^{1/3}$
- Hence we can ignore the effect arise from collision among the particles in our consideration of ideal gas system.

1-particle approximation

- Ideal gas system with N particles subjected to vanishing external potential field will be treated with partition function method to derive all the known results obtained from thermodynamics and kinetic theory.
- Assume '1 particle approximation': the energy of the system can be written as a sum of energies, each depending only on the state of one particle, so that the probability of a given state of the system can be written as the product of the probabilities of the separate particles.
- This means that knowing one particle's partition function z_c allows us to derive the properties of the system easily via $Z_c = z_c^N$

Probability density for the ideal gas system

$$P[(\mathbf{r}_1, \mathbf{p}_1), \dots, (\mathbf{r}_N, \mathbf{p}_N)]$$

- Total energy $E[(\mathbf{r}_1, \mathbf{p}_1), \dots, (\mathbf{r}_N, \mathbf{p}_N)] = \sum_{i=1}^N \epsilon_i(\mathbf{r}_i, \mathbf{p}_i)$, where

$$\epsilon_i(\mathbf{r}_i, \mathbf{p}_i) = \frac{\mathbf{p}_i^2}{2m_i} + U(x_i)$$

The probability for a configuration is

$$\begin{aligned} & p[(\mathbf{r}_1, \mathbf{p}_1), \dots, (\mathbf{r}_N, \mathbf{p}_N)] \\ &= P[(\mathbf{r}_1, \mathbf{p}_1), \dots, (\mathbf{r}_N, \mathbf{p}_N)] dV_1 d\tau_1 \dots dV_N d\tau_N \\ &= \frac{1}{Z_c} \exp\{-\beta E[(\mathbf{r}_1, \mathbf{p}_1), \dots, (\mathbf{r}_N, \mathbf{p}_N)]\} dV_1 d\tau_1 \dots dV_N d\tau_N \\ &= \frac{1}{z_c} (e^{-\beta \epsilon_1} dV_1 d\tau_1) \dots \frac{1}{z_c} (e^{-\beta \epsilon_N} dV_N d\tau_N) \end{aligned}$$

The partition function for one particle z_c

Assuming all masses in the ideal gas system are identical,
 $m_i = m, \forall i \in \{1, 2, \dots, N\}$,

$$z_c = \int dV_i d\tau_i e^{-\beta \epsilon_i(\mathbf{r}_i, \mathbf{p}_i)} = \int dV_i e^{-\beta U(\mathbf{r}_i)} \int d\tau_i e^{-\beta \frac{\mathbf{p}_i^2}{2m}} = V_i (2\pi mkT)^{3/2}$$

- The potential $U(\mathbf{r}_i)$ vanishes for all particles in the ideal gas system, $\Rightarrow \int dV_i e^{-\beta U(\mathbf{r}_i)} = V_i = V$

Integration of $\int e^{-\frac{\beta \mathbf{p}^2}{2m}} d\tau$

- Dimensional argument only solve z_c up to a constant, so need to integrate explicitly.
- Let $\alpha = \beta/2m = \frac{1}{2mkT}$, $t = \alpha p_x^2$ so that $dt = 2\alpha^{1/2} t^{1/2} dp_x$.
- $\int_{p_x \rightarrow -\infty}^{p_x \rightarrow \infty} e^{-\frac{\beta p_x^2}{2m}} dp_x = \frac{2}{\alpha^{1/2}} \int_0^{\infty} e^{-t} t^{-1/2} dt$.
- Gamma function: $\Gamma(n) = \int_0^{\infty} t^{n-1} e^{-t} dt$; $\Gamma(1/2) = \sqrt{\pi}$
- $\int_{p_x \rightarrow -\infty}^{p_x \rightarrow \infty} e^{-\frac{\beta p_x^2}{2m}} dp_x = (2mkT\pi)^{1/2}$.

$$\begin{aligned} \int e^{-\frac{\beta \mathbf{p}^2}{2m}} d\tau &= \int_{p_x \rightarrow -\infty}^{p_x \rightarrow \infty} \int_{p_y \rightarrow -\infty}^{p_y \rightarrow \infty} \int_{p_z \rightarrow -\infty}^{p_z \rightarrow \infty} e^{-\frac{\beta(p_x^2 + p_y^2 + p_z^2)}{2m}} dp_x dp_y dp_z \\ &= (2mkT\pi)^{3/2} \end{aligned}$$

Deriving all the familiar quantities for ideal gas from z_c

- $z_c \rightarrow Z = z_c^N \rightarrow F \rightarrow S \rightarrow C_V \rightarrow C_P \rightarrow$ Maxwell-Boltzmann distribution.
- $\ln Z = \ln z_c^N = N \ln \left[V (2\pi mkT)^{3/2} \right] = N \ln V + \frac{3}{2} N \ln(2\pi mkT)$
- $F = -kT \ln Z = \dots = -NkT \left[\ln V + \frac{3}{2} \ln(2\pi mkT) \right]$
- $P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = NkT/V$ (volume 'pops' up from this approach)
- $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk \left[\ln V + \frac{3}{2} \ln(2\pi mkT) + \frac{3}{2} \right]$
- $C_V = T \left(\frac{\partial S}{\partial T}\right)_{V,N} = \dots 3Nk$.
- $C_P = T \left(\frac{\partial S}{\partial T}\right)_{P,N} = \dots \frac{5}{2} Nk$.
- $\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \dots \frac{3}{2} NkT$

Maxwell-Boltzmann distribution

The N particle system probability distribution is composed of the product of all individual 1-particle probability densities:

$$\begin{aligned} &P[(\mathbf{r}_1, \mathbf{p}_1), \dots, (\mathbf{r}_N, \mathbf{p}_N)] dV_1 d\tau_1 \dots dV_N, d\tau_N \\ &= P(\mathbf{r}_1, \mathbf{p}_1) dV_1 d\tau_1 \dots P(\mathbf{r}_N, \mathbf{p}_N) dV_N d\tau_N \end{aligned}$$

Maxwell-Boltzmann distribution (cont.)

- For any particle i , $P_i(\mathbf{r}_i, \mathbf{p}_i)dV_i d\tau_i = \frac{1}{z_c} e^{-\beta \left[\frac{p_i^2}{2m_i} + U(\mathbf{r}_i) \right]} dV_i d\tau_i$, which is just the Maxwell-Boltzmann distribution we encountered in Part I when investigating the ideal gas system with kinetic theory (there the MB distribution is in velocity representation, $P(\mathbf{r})dV \cdot f(\mathbf{v})d\tau$).
- $P_i(\mathbf{r}_i, \mathbf{p}_i)$ is obtained by integrating out all N particles DOF except one from $P[(\mathbf{r}_1, \mathbf{p}_1), \dots, (\mathbf{r}_N, \mathbf{p}_N)]$, i.e.,

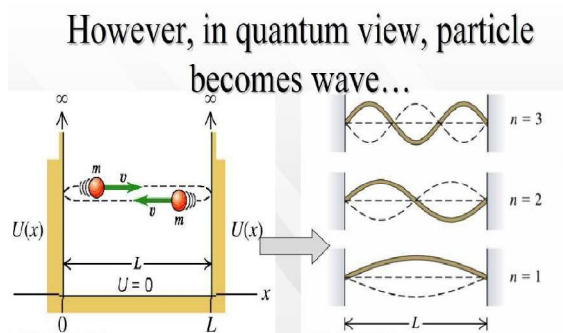
$$P_i(\mathbf{r}_i, \mathbf{p}_i) = \int P[(\mathbf{r}_1, \mathbf{p}_1), \dots, (\mathbf{r}_N, \mathbf{p}_N)] dV_1 d\tau_1 \cdots dV_{i-1} d\tau_{i-1} dV_{i+1} d\tau_{i+1} \cdots dV_N$$

A quantum particle in an infinite quantum well

- Consider a quantum 'particle' confined in a quantum well which is finite in width (a) but infinite in height.
- In the quantum picture, the 'particle' loses its particle character; it is instead be pictured as a *matter wave* that is mathematically represented by a wave function.
- The 'well' is actually a potential trap that confines the 'particle'. If the 'particle' hits the wall, it feels an infinite bouncing force that keeps the particle from being found outside the well.
- The wavefunction of the quantum particle forms a standing wave in the well, where each standing wave mode is characterised by $n = 1, 2, \dots$:

$$\lambda_n = \frac{2a}{n}$$

Pictorial description of quantisation of de Broglie wavelength in a 1-D infinite quantum well



- The 'particle' is no more pictured as a particle bouncing between the walls but a de Broglie wave that is trapped inside the infinite quantum well, in which they form standing waves

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Energy levels of the infinite quantum well

- The momentum of the quantum particle is related to its wavelength via $p_n = \frac{h}{\lambda_n}$, so that its energy is $\epsilon_n = \frac{p_n^2}{2m} = \frac{n^2 h^2}{8ma^2}$. We refer each ϵ_n as 'energy level n '.
- For a quantum particle confined in a 3D quantum well (which is effectively a 'cube' with sides $a \times b \times c$), the energy levels are characterised by three positive integers, n, p, q :

$$\epsilon_{n,p,q} = \left(\frac{n^2}{a^2} + \frac{p^2}{b^2} + \frac{q^2}{c^2} \right) \frac{h^2}{8m}$$

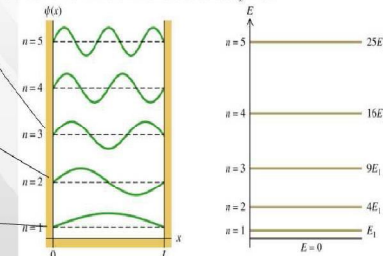
Pictorial description of the quantised energy levels in a 1-D infinite quantum well

- Some terminology
- $n = 1$ corresponds to the ground state
- $n = 2$ corresponds to the first excited state, etc

$n = 3$ is the second excited state, 4 nodes, 3 antinodes

$n = 2$ is the first excited state, 3 nodes, 2 antinodes

$n = 1$ is the ground state (fundamental mode): 2 nodes, 1 antinode



• Note that lowest possible energy for a particle in the box is not zero but $E_0 (= E_1)$, the zero-point energy.

• This a result consistent with the Heisenberg uncertainty principle

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Quantum particles vs. classical particles

- In the present case, the particle obeys a different set of physical laws than a classical particle. Specifically, the quantum particle is pictured as a wave and has a 'wavelength' (de Broglie wavelength) which is related to the momentum of the particle.
- The momentum in turns is related to the particle's energy via $\epsilon_{n,p,q} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$. Hence, the energy levels of the quantum particle trapped in the infinite well is specified by a set of 3 positive integer quantum numbers n, p, q via $\epsilon_{n,p,q} = \left(\frac{n^2}{a^2} + \frac{p^2}{b^2} + \frac{q^2}{c^2}\right) \frac{h^2}{8m}$.
- Apart from this the calculation for the partition function is the same as for a classical case.
- There are other more subtle differences between a quantum particle and a classical particle, which effects are not considered here (e.g. identical particle effects that arise when considering the quantum nature of the particles). Anyway such subtle quantum effects will NOT change the way we calculate the partition function using the method discussed so

Partition function of the quantum particle in a 3D quantum box

- We will now derive the partition function of a quantum particle in a 3D quantum box, in which the particle is immersed in a heat bath at a constant temperature.

$$\begin{aligned}
 z &= \sum_{n,p,q} \exp(-\beta \epsilon_{n,p,q}) \\
 &= \sum_{n,p,q} \exp\left(-\frac{\beta h^2 n^2}{8ma^2} - \frac{\beta h^2 p^2}{8mb^2} - \frac{\beta h^2 q^2}{8mc^2}\right) \\
 &= \sum_{n=1}^{\infty} e^{-\frac{\beta h^2 n^2}{8ma^2}} \cdot \sum_{p=1}^{\infty} e^{-\frac{\beta h^2 p^2}{8mb^2}} \cdot \sum_{q=1}^{\infty} e^{-\frac{\beta h^2 q^2}{8mc^2}} \\
 &= z_x \cdot z_y \cdot z_z
 \end{aligned}$$

The length scale characteristic to the quantum well in a heat bath, λ_T

- The length scale of the problem is the size of the de Broglie wavelength when the particle is in thermal equilibrium with the heat bath, namely, when $\frac{p^2}{2m} = \frac{h^2}{\lambda^2 2m} = \frac{1}{2} kT \Rightarrow \lambda_T = \frac{h}{\sqrt{mkT}}$.
- This length scale is to be compared to the length scale of the quantum well, $\sim a$.
- We would need the ratio of the length scale $\frac{\lambda_T}{2a}$ in the summation for the partition function.

Converting the Riemannian sum of z_x into an integral

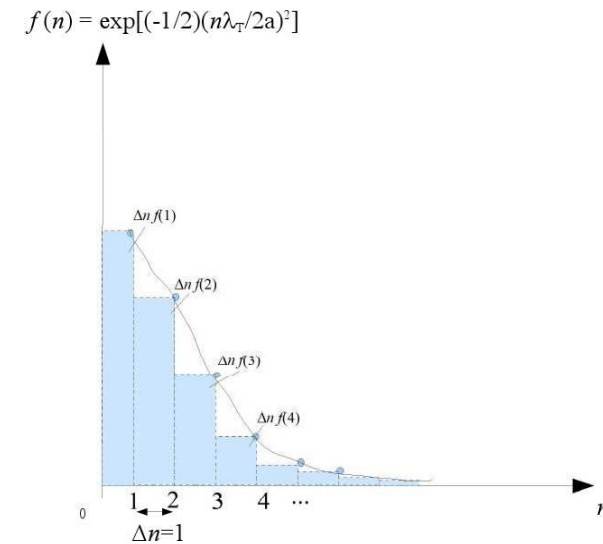
Write the partition function for the x -component of the quantum particle z_x in terms of λ_T :

$$\begin{aligned} z_x &= \sum_{n=1}^{\infty} e^{\frac{-\beta \hbar^2 n^2}{8ma^2}} = \sum_{n=1}^{\infty} e^{-\frac{1}{2} \left(\frac{n\lambda_T}{2a} \right)^2} = \\ &= e^{-\frac{1}{2} \left(\frac{1\lambda_T}{2a} \right)^2} (\Delta n) + e^{-\frac{1}{2} \left(\frac{2\lambda_T}{2a} \right)^2} (\Delta n) + \dots \\ &= \sum_{n=1}^{\infty} \Delta n \cdot f(n). \end{aligned}$$

This is a Riemannian sum of a function $f(n) = e^{-\frac{1}{2}s_n^2}$ with interval $\Delta n = 1$, where $s_n = \frac{n\lambda_T}{2a}$.

- $\Delta s = \left(\frac{\lambda_T}{2a} \right) \cdot \Delta n$

Riemannian sum of $f(n)$



Converting the Riemannian sum of z_x into an integral (cont.)

- The Riemannian sum written in terms of $s \equiv s_n$ is

$$\sum_{n=1}^{\infty} e^{\frac{-\beta \hbar^2 n^2}{8ma^2}} = \sum_{s=\frac{\lambda_T}{2a}}^{\infty} e^{-\frac{1}{2}s^2} \left(\frac{2a}{\lambda_T} \right) \Delta s,$$

where we have replaced Δn by $\Delta s \left(\frac{2a}{\lambda_T} \right)$. The summation over the discrete variable n is now transformed into the summation over s , which is approximately a continuous variable in the limit $\frac{\lambda_T}{2a} \rightarrow 0$. Hence,

$$\sum_{n=1}^{\infty} e^{\frac{-\beta \hbar^2 n^2}{8ma^2}} = \sum_{s=\frac{\lambda_T}{2a}}^{\infty} e^{-\frac{1}{2}s^2} \left(\frac{2a}{\lambda_T} \right) \Delta s \xrightarrow{\frac{\lambda_T}{2a} \rightarrow 0} \left(\frac{2a}{\lambda_T} \right) \int e^{-\frac{1}{2}s^2} ds$$

$$\lim_{\frac{\lambda_T}{2a} \rightarrow 0} z_x = \left(\frac{2a}{\lambda_T} \right) \int_0^{\infty} e^{-\frac{1}{2}s^2} ds$$

The variable s is related to the momentum

- The particle's wave function forms a standing wave in the well. The x -component of the standing wave obeys $\frac{\lambda_n}{2} = a$, and the standing wave is related to the momentum $p_x = \frac{h}{\lambda_n}$
- Hence $s = \frac{\lambda_T p_x}{h}$.
- We can then convert the integration over s into an integration over p_x (with $ds = \frac{\lambda_T}{h} dp_x$):

$$\left(\frac{2a}{\lambda_T} \right) \int_0^{\infty} e^{-\frac{1}{2}s^2} ds = \left(\frac{2a}{h} \right) \int_0^{\infty} e^{-\frac{\lambda_T^2 p_x^2}{2h^2}} dp_x = \left(\frac{a}{h} \right) \int_{-\infty}^{\infty} e^{-\frac{\beta p_x^2}{2m}} dp_x$$

The partition function for the 3-D infinite quantum well, $z = z_x \cdot z_y \cdot z_z$ in the limit $\lambda_T \ll 2a$

- In the limit $\lambda_T \ll 2a$,

$$\begin{aligned} z &= z_x \cdot z_y \cdot z_z \\ &= \frac{a}{h} \int_{-\infty}^{\infty} e^{-\frac{\beta p_x^2}{2m}} dp_x \cdot \frac{b}{h} \int_{-\infty}^{\infty} e^{-\frac{\beta p_y^2}{2m}} dp_y \cdot \frac{c}{h} \int_{-\infty}^{\infty} e^{-\frac{\beta p_z^2}{2m}} dp_z \\ &= \frac{abc}{h^3} \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} \mathbf{p}^2} d^3 \mathbf{p} \\ &= \frac{V}{h^3} \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} \mathbf{p}^2} d^3 \mathbf{p}. \end{aligned}$$

- Here we use the notation $d^3 \mathbf{p} = dp_x dp_y dp_z$ in place of $d\tau$.

Comparing z in the $\lambda_T \ll 2a$ limit with z_c

- Compare z (in the $\lambda_T \ll 2a$ limit) to the 1-particle partition function of a classical ideal gas system (where $U = 0$):

$$\begin{aligned} \lim_{\lambda_T \ll 2a} z &= \frac{V}{h^3} \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} \mathbf{p}^2} d^3 \mathbf{p} \quad \text{vs.} \\ z_c &= \int dV e^{-\beta U(\mathbf{r})} \cdot \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} \mathbf{p}^2} d^3 \mathbf{p} = V \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} \mathbf{p}^2} d^3 \mathbf{p}. \end{aligned}$$

- $[z_c] = [L]^3 [\text{momentum}]^3$ whereas in the case of a particle in a 3D quantum well, $[z] = 1$ due to the presence of h^3 .
- It is reckoned that a dimensionless canonical partition function (z as above) is a more 'natural' than that with a dimension (z_c as above) (more on this later).

z in the classical limit reduces to z_c , except for a factor of $\frac{1}{h^3}$.

- Note that $\lambda_T \ll 2a$ corresponds to the classical limit where the de Broglie wavelength is too tiny to cause quantum effect. This is also the limit of high temperature.
- The result for z for the particle trapped in a 3D box in the limit $\lambda_T \ll 2a$ should reduce to that of the classical one, z_c , except for the fact that z is dimensionless due to the presence of h^3 (more on this in a few more slides later).

z in the quantum limit

- In the opposite limit, where the $\lambda_T \gg 2a$ (e.g. at extremely low temperature, during which the de Broglie wavelength becomes very large as compared to the characteristic length scale of the system), the partition function z_c is no more given by $\int dV e^{-\beta U(\mathbf{r})} \cdot \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} \mathbf{p}^2} d^3 \mathbf{p}$.
- In this limit very interesting quantum phenomena will arise (such as Bose-Einstein condensation) ...
- In this limit the approximation $\lambda_T \ll 2a$ is no more valid. The summation over n as appeared in the 1-particle partition function e.g. $z_x = \sum_{n=1}^{\infty} e^{-\beta \frac{n^2 h^2}{8ma^2}}$ has to be carried out in a way different than that was done previously. We will not derive z in the quantum limit here.

A quantum state in the phase space has a volume $\frac{d\tau dV}{h^3}$

- From the derivation of z in the classical limit, we reckon that this partition function, z , is in principle a discrete sum (not an integration over a continuous variables $\{\mathbf{p}, \mathbf{r}\}$).

$$z = \sum_k \exp\left(-\frac{\beta \mathbf{p}_k^2}{2m}\right) \frac{\Delta V_k \Delta \tau_k}{h^3}$$

- In the discrete sum of the 1-particle partition function z , the 'point' in the phase space has a 'volume' of $\frac{\Delta \tau_k \Delta V_k}{h^3}$, but not $\Delta \tau_k \Delta V_k$ as was thought earlier (see the relevant part in Chap 3, Part III).

Z the canonical partition function of N particle in the classical limit

- 1-particle quantum partition function,

$$z = \frac{1}{h^3} \int dV d\tau \exp\left\{-\beta \left[\frac{\mathbf{p}^2}{2m} + U(\mathbf{r})\right]\right\}$$
- For a system of N particles in a 3-D infinite quantum well,

$$Z = z^N = \int \left(\frac{dV d\tau}{h^3}\right)^N e^{-\beta E(\{\mathbf{r}_i, \mathbf{p}_i\})}$$
- $\langle A \rangle = \frac{1}{Z} \int \left(\frac{dV d\tau}{h^3}\right)^N A(\{\mathbf{r}_i, \mathbf{p}_i\}) e^{-\beta E(\{\mathbf{r}_i, \mathbf{p}_i\})}$

'Correction' to the classical partition function, z_c (to make it dimensionless)

- In the view that a partition function should be dimensionless (like in the case of z , which is more natural), the classical partition function obtained in earlier attempts can be made dimensionless by 'correcting' it via the replacement $z_c \rightarrow \frac{z_c}{h^3}$.
- With this correction, the free energy F in the classical system will admit an extra constant $\sim \ln h^3$, and so is the entropy.
- Despite this additional term most of the derived thermodynamical quantities would remain unchanged because they are mostly derivatives of the free energy or the entropy.
- The effect of the correction term $\ln h^3$ in F and S will be mostly cancel out and disappear.
- From now on, all classical partition function should be replaced by $z_c \rightarrow z_c = \frac{1}{h^3} \int dV e^{-\beta U(\mathbf{r})} \cdot \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m} \mathbf{p}^2} d^3 \mathbf{p}$.

Part IV From Ideal Gas to Photon Gas

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 - 3.1 The Debye model (Notes based on (i) Mandl (ii) Amit et. al.)

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 - 4.2 Radiatoin density
 - 4.3 Black body radiation

Outline

- 1 Chapter 3 Phonon Gas and the Debye Model
 - 3.1 The Debye model (Notes based on (i) Mandl (ii) Amit et. al.)

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Energy of uncoupled oscillators in Einstein solid

- Einstein solid is a system comprised of N uncoupled atoms which vibrations are modelled as oscillations of $3N$ independent harmonic oscillators. The partition function of each DOF is

$$z = \sum_{n=0}^{n=\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} = \frac{e^{-\beta\frac{\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} = \frac{e^{-\frac{x}{2}}}{1 - e^{-x}}; \quad x \equiv \frac{\hbar\omega}{kT}.$$

- The average energy of a single oscillator in the Einstein solid is easily derived via

$$\epsilon = -\frac{\partial \ln z}{\partial \beta} = \hbar\omega \left[\frac{1}{2} + \frac{1}{e^x - 1} \right]. \quad (1)$$

Total energy of a coupled homonic oscillator system

- We will consider a solid crystal of size $L \times L \times L = V$ comprised of N coupled vibrating atoms.
- In general, in the presence of an interaction between the atoms, ω_α will not be the same (as it was in the case of Einstein solid, see Eq. (1)).
- Hence, in the presence of a harmonic potential between any pairs of atoms, each ω_α are different in the sum in the total energy E given by

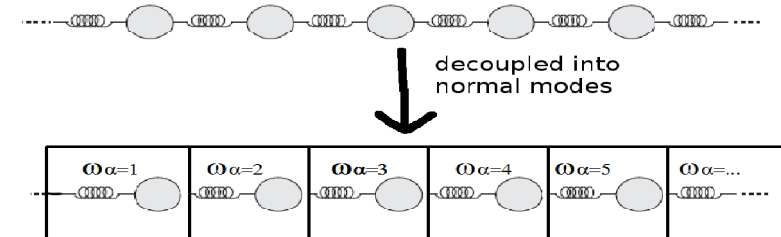
$$E = \sum_{\alpha=1}^{3N} \epsilon_\alpha = \sum_{\alpha=1}^{3N} \left\{ \frac{1}{2} \hbar\omega_\alpha + \frac{\hbar\omega_\alpha}{\exp(\beta\hbar\omega_\alpha) - 1} \right\} \quad (2)$$

- We need to know what are the characteristic frequencies of the normal modes ω_α in order to obtain E .

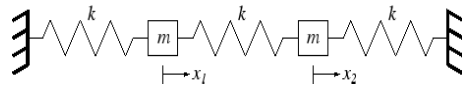
“Collective vibration” - the normal modes

- In the presence of inter-atomic “spring” (a.k.a the force arise from harmonic potential) the vibration has to be pictured not as the vibration associated to a single atom but as a collective vibration of the whole crystal about their equilibrium positions. These collective vibrations are called ‘normal modes’.
- We can think of the vibrations of the N coupled HO to be effectively described by N independent normal modes.
- In a system of N vibrating atoms, where each atoms is to be represented by a 3-D harmonic oscillator, the system is effectively represented by $3N$ independent normal modes, $\alpha = 1, 2, 3 \dots, 3N$.
- ‘Decoupling’ N 3D coupled harmonic oscillator into $3N$ independent (decoupled) normal modes.

Picturing the decoupling of coupled oscillators into normal (independent) modes



Example of 2 normal modes comprised from two coupled HO



$$m\ddot{x}_1 = -kx_1 - kx_1 + kx_2; m\ddot{x}_2 = -kx_2 - kx_2 + kx_1$$

$$m\ddot{x}_1 = -kx_1 - k(x_1 - x_2); m\ddot{x}_2 = -kx_2 - k(x_1 - x_2)$$

Linear combination of the solution to the coupled equation

$$x_{v1} = x_1 + x_2 = a_+ \cos(\omega_+ t + \alpha_+); x_{v2} = x_1 - x_2 = a_- \cos(\omega_- t + \alpha_-)$$

x_{v1}, x_{v2} are the normal modes. Each of them describes an independent HO with angular frequencies ω_-, ω_+ respectively ($\omega_- \neq \omega_+$). This analysis illustrates the trick to ‘decouple’ two coupled oscillators into two independent HO, hence making the mathematical description of the motion of the whole system much easier.

Polarisation modes of a wave

We will compare three different types of waves categorised according to the relative orientations of the oscillations with respect to the direction of the propagation of the wave.

- Electromagnetic wave is a transverse wave. It has two independent polarisations, each in a direction perpendicular to the wave’s direction of travel. There are two polarisation modes here, both are transverse modes.
- Acoustic waves in fluids are longitudinal waves. The direction of oscillation of the elastic medium is along the direction of travel. In this case, there is only one mode of polarisation, i.e. the longitudinal polarisation mode.
- For sound waves in an solid medium, there are three polarizations: one longitudinal mode, and two transverse modes.

Polarisation modes of a wave (cont.)

- We can think of a polarisation mode as a DOF in which the energy of the wave is being carried. For example, if there are three polarisations in the sound wave in solid, that means the wave's energy in the solid is being carried by three independent 'channels'.

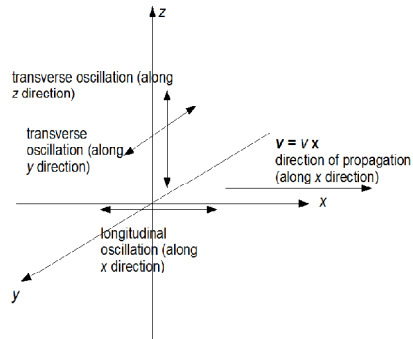


Figure: Relative orientations of the oscillations with respect to the direction of the propagation of the wave.

Debye's assumptions

- The systems of coupled harmonic oscillators in an elastic medium. The normal modes are sound waves. These normal modes form standing waves within the boundary of the solid.
- To find the normal modes under the Debye assumptions, we need only to find the different modes of standing waves which are possible in the medium.
- To do this, Debye assumes that:
 - The wavelength of these sound waves $\lambda_\alpha \gg a$, a the interatomic distance for all frequencies ω_α .
 - The medium is isotropic.
 - The medium is non-dispersive.

Debye's assumptions (cont.)

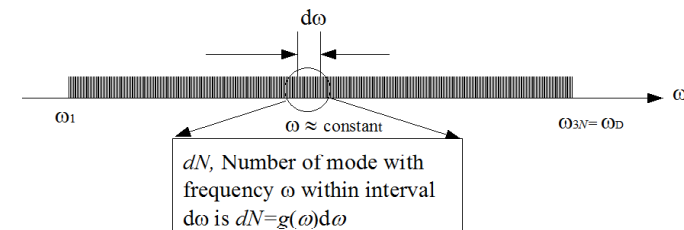
- Assumption (1) means one can ignore the discrete atomic structure of the solid and describe it as a homogeneous elastic medium.
- Assumption (2) means that the velocity of propagation of elastic waves is independent of their directions.
- Assumption (3) means that dispersion relation that relates the angular frequency ω with the wave number $q = \frac{2\pi}{\lambda}$ is simply $\omega = vq$, v the phase velocity of the sound wave.
- The group velocity v_g is given by $\frac{d\omega}{dq} = v_g$. For non-dispersive medium, $v_g = v = \frac{\omega}{q}$. In other words, the phase velocity and group velocity of the sound wave are the same.

Counting the number of stationary wave modes in an angular frequency interval $d\omega$

- For sound waves in the Debye solid of volume V , the number of stationary wave modes with angular frequency between ω and $\omega + d\omega$ is given by the product of density of state $g(\omega)$ with $d\omega$:

$$dN = g(\omega)d\omega = \frac{V\omega^2 d\omega}{2\pi^2} \left[\frac{2}{v_L^3} + \frac{1}{v_T^3} \right]$$

- Density of state, $g(\omega)$ = number of microstates per unit frequency of a single photon. Its derivation shall be presented shortly.



Derivation of density of state DOS function $g(\omega)$

- Consider a box of dimension $V = L \times L \times L$, containing a 3-D stationary wave in it (see figure).

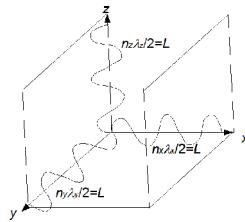


Figure: Stationary waves in a box.

- In each Cartesian direction, the equations of the standing waves are

$$n_x \frac{\lambda_x}{2} = L, n_y \frac{\lambda_y}{2} = L, n_z \frac{\lambda_z}{2} = L$$

- Equivalently, in terms of the wave vector $q = \frac{2\pi}{\lambda}$,

$$q_x = \frac{n_x \pi}{L}, q_y = \frac{n_y \pi}{L}, q_z = \frac{n_z \pi}{L}$$

Derivation of density of state DOS function $g(\omega)$ (cont.)

- Each stationary wave is characterised by $\mathbf{q} = \{q_x, q_y, q_z\} = \left\{ \frac{n_x \pi}{L}, \frac{n_y \pi}{L}, \frac{n_z \pi}{L} \right\}$
- $q = |\mathbf{q}|$
- A stationary wave mode can be represented by a volume element in the 3-D q -space, $dq_x dq_y dq_z = \left(\frac{\pi}{L}\right)^3$.

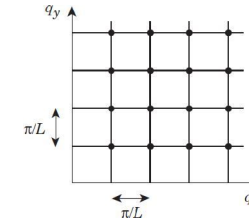


Figure: 2-D representation of the q -space.

- Number density of the modes, defined as the number of modes per unit volume in q -space, is then given by $\left(\frac{L}{\pi}\right)^3$.

Derivation of density of state DOS function $g(\omega)$ (cont.)

- Now, we ask the question: What is dN , the number of standing wave modes with a wave vector whose magnitude lying in the interval $[q, q + dq]$?
- dN is given by $dV \times$ (number density of modes), where dV is the volume of a shell with thickness dq in the first quadrant in the q -space (see figure).

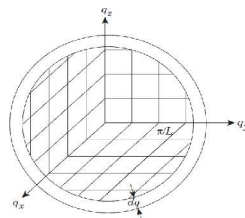


Figure: A shell of thickness dq , radius q , in the 3-D q -space. We wish to count the number of modes contained in the first quadrant of the sphere.

- $dV = \frac{1}{8} \cdot d\left(\frac{4}{3}\pi q^3\right) = \frac{1}{8} \cdot 4\pi q^2 dq$, $dN = \frac{1}{8} \cdot 4\pi q^2 dq \times \left(\frac{L}{\pi}\right)^3$

Derivation of density of state DOS function $g(\omega)$ (cont.)

- We can express dN in terms of $d\omega$ by replacing dq by $dq = \frac{dq}{d\omega} d\omega$ so that now we have

$$dN = \frac{1}{8} \cdot 4\pi q^2 \frac{1}{\left(\frac{d\omega}{dq}\right)} d\omega \times \left(\frac{L}{\pi}\right)^3$$

- The magnitude of the wave vector q is related to the angular frequency ω via
 - $v_p = \omega/q$, v_p phase velocity of the normal mode.
 - $v_g = \frac{d\omega}{dq}$, v_g group velocity of the normal mode.
- In the special case of a non dispersive medium (Debye solid is assumed to be such a medium), $v_g = v_p = v$.

$$dN = \frac{1}{8} \cdot 4\pi \left(\frac{\omega}{v_p}\right)^2 \frac{1}{v_g} d\omega \left(\frac{L}{\pi}\right)^3 = \frac{V\omega^2}{2\pi^2 v^3} d\omega \equiv g(\omega) d\omega.$$

- $g(\omega)$ is the density of state, DOF, in frequency representation.
- $\frac{V\omega^2}{2\pi^2 v^3} d\omega \equiv g(\omega) d\omega$ is the number of normal modes in the frequency interval $[\omega, \omega + d\omega]$ for a given polarisation.

Derivation of density of state DOS function $g(\omega)$ (cont.)

- In an solid, there are three independent polarisations, and each of them contributes independently to the number of normal modes of the sound waves in the solid.
- For the longitudinal polarisation, the number of normal modes in the frequency interval $[\omega, \omega + d\omega]$ is

$$dN_L(\omega) = \frac{V\omega^2}{2\pi^2 v_L^3} d\omega,$$

and for the two transverse polarisations, their contributions are

$$dN_{T1}(\omega) + dN_{T2}(\omega) = \frac{V\omega^2}{2\pi^2 v_T^3} d\omega + \frac{2V\omega^2}{2\pi^2 v_T^3} d\omega.$$

- Totalling up,

$$\begin{aligned} dN(\omega) &= dN_L(\omega) + dN_{T1}(\omega) + dN_{T2}(\omega) \\ &= \frac{V\omega^2}{2\pi^2} \left[\frac{1}{v_L^3} + \frac{2}{v_T^3} \right] d\omega. \end{aligned} \quad (3)$$

Debye frequency ω_D

- The total number of stationary modes is known to be $3N$. This sets a 'cut-off' angular frequency to ω , known as Debye frequency ω_D .
- The total number of modes in the solid, obtained by integrating $dN = g(\omega)d\omega$ from $\omega = 0$ to ω_D must be approximately equal to $3N$ (see figure), i.e.,

$$\int_{\omega=0}^{\omega=\omega_D} g(\omega) d\omega = 3N.$$

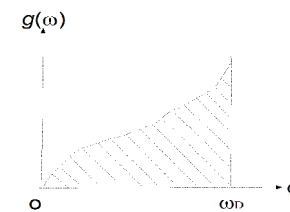


Figure: The area under the curve $g(\omega)d\omega$ vs. ω represents the number of modes, $\int_0^{\omega} g(\omega)d\omega$.

Debye frequency ω_D (cont.)

- Upon substituting $g(\omega)d\omega = \frac{V\omega^2 d\omega}{2\pi^2} \left[\frac{2}{v_L^3} + \frac{1}{v_T^3} \right]$ into the above equation, we obtain the explicit form of the Debye frequency,

$$\omega_D = \left(6\pi^2 \frac{N}{V} \right)^{1/3} \bar{v},$$

where \bar{v} is the mean velocity of the sound waves defined as

$$\frac{3}{\bar{v}^3} = \frac{1}{v_L^3} + \frac{2}{v_T^3}.$$

- Debye frequency of a solid depends on the average speed of sound wave \bar{v} in that solid, which is a characteristic of that solid.

Average energy E of the Debye solid

- Now, we are ready to calculate the total energy $E = \sum_{\alpha=1}^{3N} \left\{ \frac{1}{2} \hbar \omega_{\alpha} + \frac{\hbar \omega_{\alpha}}{\exp(\beta \hbar \omega_{\alpha}) - 1} \right\}$ in Eq. (2).
- First, the average energy in the frequency interval $\omega, \omega + d\omega$ is given as $dE = (\text{no. of modes in the interval } \omega, \omega + d\omega) \times (\text{average energy of each mode with frequency } \omega)$

$$dE = dN \times \left\{ \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{\exp(\beta \hbar \omega) - 1} \right\},$$

where

$$dN = g(\omega) d\omega = V \frac{3\omega^2 d\omega}{2\pi^2 \bar{v}^3}.$$

Average energy E of the Debye solid in terms of DOS and BE distribution

- Integrating over ω from $\omega = 0$ to $\omega = \omega_D$, we obtain the total average energy in terms of Debye temperature defined as $\Theta_D = \hbar\omega_D/k$ and $x_D = \frac{\Theta_D}{T}$.
- The average energy can be written in the following form:

$$\begin{aligned}
 E &= \int dE = \int dN \times \left\{ \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \right\} \\
 &= \int_{\omega=0}^{\omega=\omega_D} V \frac{3\omega^2 d\omega}{2\pi^2 \bar{v}^3} \times \left\{ \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \right\} \\
 &= \frac{9}{8} Nk\Theta_D + \int_0^{\omega_D} \hbar\omega \cdot \frac{1}{e^{\beta\hbar\omega} - 1} \cdot \frac{3V\omega^2}{2\pi^2 \bar{v}^3} d\omega \\
 &= \frac{9}{8} Nk\Theta_D + \int_0^{\omega_D} \hbar\omega \langle n \rangle g(\omega) d\omega \quad (4)
 \end{aligned}$$

Ignoring the zero-point energy

- Note that the constant term $\frac{9}{8}Nk\Theta_D$ originates from $\frac{1}{2}\hbar\omega$ as appeared in $\epsilon_n = (\frac{1}{2} + n)\hbar\omega$. It is associated with the zero point energy of the QHC, which will not contribute to the heat capacities of the solid. (Recall that heat capacities involves taking the derivative of E with respect to the temperature variable T .)
- In the following we will ignore the zero-point energy term as it will (almost) not contribute to any physical observations. Most physical observables (quantities that can be measured experimentally) do not involve the absolute energy. Only the differences between energy states matter.

Summing over α

Roughly speaking, in arriving at the expression for E , we simply do the following (such calculation will be encountered again in summing over the photon's contribution when dealing with black body radiation):

$$\begin{aligned}
 \sum_{\alpha} (\dots) &\rightarrow \int_{q=0}^{q=q_D} (\dots) \times 3 \times \frac{1}{8} \cdot 4\pi q^2 dq \cdot \frac{V}{\pi^3} \\
 &= \int_{\omega=0}^{\omega=q_D} (\dots) 3 \times \frac{1}{8} \cdot 4\pi \left(\frac{\omega}{v_p} \right)^2 \frac{1}{\frac{d\omega}{dq}} d\omega \cdot \frac{V}{\pi^3},
 \end{aligned}$$

where we have used $dq = \frac{dq}{d\omega} d\omega$, $v_p = \bar{v}$, $v_g = \frac{d\omega}{dq} = \bar{v}$ for the sound wave in an elastic medium (dispersionless).

$$\Rightarrow E = \int_0^{\omega_D} \hbar\omega (e^{\beta\hbar\omega} - 1)^{-1} \left(\frac{3\omega^2 V}{2\pi^2 \bar{v}^3} \right) d\omega$$

Interpretation of $\int_0^{\omega_D} \hbar\omega \langle n \rangle g(\omega) d\omega$

- $\langle n \rangle = \frac{1}{e^{\beta\hbar\omega} - 1}$ is the average number of phonon. We have seen this expectation value while discussing the Einstein solid.
- Interpretation of Eq. (4):
The average energy contributed by the normal mode with angular frequency in the interval $\omega, \omega + d\omega$ is
(the energy of a phonon, $\hbar\omega$) \times (average number of phonon excitation, $\langle n \rangle$) \times (number of available states in the frequency interval $\omega, \omega + d\omega$, $g(\omega)d\omega$)
- The total energy is then obtained by integrating over the angular frequency from $\omega = 0$ till $\omega = \omega_D$.

Energy per unit frequency per unit volume, $\rho(\omega)$

- It is also useful to define the energy per unit frequency per unit volume, $\rho(\omega)$, via

$$E/V = \int_{\omega=0}^{\omega=\omega_D} \rho(\omega) d\omega,$$

with

$$\rho(\omega) = \frac{\hbar\omega \cdot \langle n \rangle \cdot g(\omega)}{V} = \frac{3}{2\pi^2 v^3} \frac{\hbar\omega^3}{e^{\beta\hbar\omega} - 1}, \quad \omega < \omega_D.$$

Heat capacity from E

- From first law, $dE = \delta Q + pdV \Rightarrow C_V = \left(\frac{\delta E}{\delta T}\right)_V = \frac{\partial E}{\partial T}|_V = \frac{\partial \beta}{\partial T} \frac{\partial E}{\partial \beta}|_V = -k\beta^2 \cdot \frac{\partial}{\partial \beta} \left[\frac{3V}{2\pi^2 v^3} \int_{\omega=0}^{\omega=\omega_D} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \omega^2 d\omega \right] \Rightarrow$

$$\begin{aligned} C &= \frac{3kV}{2\pi^2 v^3} \int_0^{\omega_D} \frac{(\hbar\omega/kT)^2 e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2} \omega^2 d\omega \\ &= 3Nk \left\{ \frac{3}{x_D^3} \int_0^{x_D} \frac{x^4 e^x dx}{(e^x - 1)^2} \right\} \\ &\equiv \frac{9Nk}{x_D^3} \int_0^{x_D} F(x) dx \end{aligned}$$

- C does not have a closed-form solution for finite ω_D (or equivalently, x_D); it has to be integrated numerically for exact result.

Heat capacity at high temperature limit

- In the high temperature limit, $T \gg \Theta_D \equiv x_D \ll 1$, i.e. the variable $0 \leq x \leq x_D \ll 1$.

$$\begin{aligned} \frac{x^4 e^x}{(e^x - 1)^2} &= \frac{x^4}{(e^x - 1)(1 - e^{-x})} = \frac{x^4}{2(\cosh x - 1)} \\ &= \frac{x^4}{2\left(\frac{x^2}{2!} + \frac{x^4}{4!} + \dots\right)} \approx x^2 \end{aligned}$$

The heat capacity in the $T \gg \Theta_D$ limit then becomes

$$C = 3Nk \left\{ \frac{3}{x_D^3} \int_0^{x_D} \frac{x^4 e^x dx}{(e^x - 1)^2} \right\} \approx \frac{9Nk}{x_D^3} \int_0^{x_D} x^2 dx = 3Nk.$$

This is just the Dulong-Petit's law.

Heat capacity at the low temperature limit, $T \ll \Theta_D$

- In the low temperature limit, $kT \ll k\Theta_D$, $x_D \gg 1$, and the variable $0 \leq x \leq \infty$.
- In the limit $x \rightarrow \infty$, the integrand in C behaves like $\sim x^4 e^{-x} \rightarrow 0$.
- Hence we can replace $\int_0^{x_D} F(x) dx$ by $\int_0^{\infty} F(x) dx$.

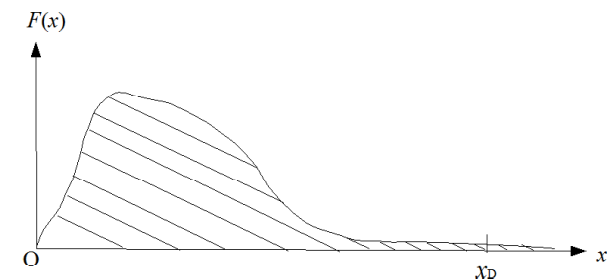


Figure: Area under the curve $F(x)$ vs. x . In the limit $T \ll \Theta_D$, $\int_0^{x_D} F(x) dx \approx \int_0^{\infty} F(x) dx$.

Integration of $\int_{x=0}^{x=\infty} \frac{x^3 dx}{e^x - 1}$ and $\int_{x=0}^{x=\infty} \frac{x^2 dx}{e^x - 1}$

$$\int_0^{\infty} \frac{x^{n-1}}{e^x - 1} dx = \left(\frac{1}{1^n} + \frac{1}{2^n} + \frac{1}{3^n} \cdots \right) \Gamma(n)$$

$$\Gamma(n+1) = n! \text{ if } n = 0, 1, 2, \dots$$

The Riemann zeta function $\zeta(n)$ is

$$\left(\frac{1}{1^n} + \frac{1}{2^n} + \frac{1}{3^n} \cdots \right) = \frac{\pi^4}{90} \text{ for } n = 4,$$

$$\left(\frac{1}{1^n} + \frac{1}{2^n} + \frac{1}{3^n} \cdots \right) \approx 1.202 \text{ for } n = 3 \text{ (Apéry's constant)}$$

$$\int_{x=0}^{x=\infty} \frac{x^3}{e^x - 1} dx = \Gamma(4) \left(\frac{1}{1^4} + \frac{1}{2^4} + \frac{1}{3^4} \cdots \right) = \frac{\pi^4}{90} \cdot 3! = \frac{\pi^4}{15}$$

$$\int_{x=0}^{x=\infty} \frac{x^2}{e^x - 1} dx = \Gamma(3) \left(\frac{1}{1^3} + \frac{1}{2^3} + \frac{1}{3^3} \cdots \right) \approx 1.202 \times 2! \approx 2.404$$

Heat capacity C in the low temperature limit $T \ll \Theta_D$

$$\begin{aligned} \lim_{T \ll \Theta_D} C &= 9Nk \left(\frac{T}{\Theta_D} \right)^3 \left[\int_0^{\infty} \frac{x^4 e^x dx}{(e^x - 1)^2} \right] \\ &= 9Nk \left(\frac{T}{\Theta_D} \right)^3 \left[\frac{4\pi^4}{15} \right] = \frac{12}{5} \pi^4 Nk \left(\frac{T}{\Theta_D} \right)^3 \quad (5) \end{aligned}$$

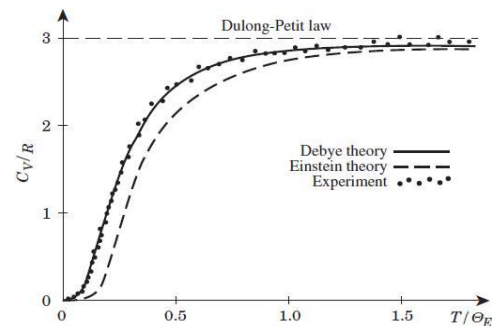
- Compare this with Einstein's model at low temperature,

$$C = 3R \left(\frac{\Theta_E}{T} \right)^2 \frac{\exp(\Theta_E/T)}{[\exp(\Theta_E/T) - 1]^2}$$

Comparison between Debye and Einstein model with experimental data

Debye model fits experimental curve well in all low, high and intermediate temperatures.

Both models approaches Dulong-Petit law at high temperature, $T \gg \Theta_D, \Theta_E$ (why?)



...

- ...

Outline

- 1 Chapter 3 Phonon Gas and the Debye Model
 - 3.1 The Debye model (Notes based on (i) Mandl (ii) Amit et. al.)

- 2 Chapter 4 Thermodynamics of Electromagnetic Radiation
 - 4.1 General considerations of radiation at thermal equilibrium
 - 4.2 Radiation density
 - 4.3 Black body radiation

Radiation inside a cavity in matter at thermal equilibrium

The system of wall + radiation reaches thermal equilibrium at a characteristic temperature. When this is achieved, the temperature at each point in space remains constant (with minor fluctuation).

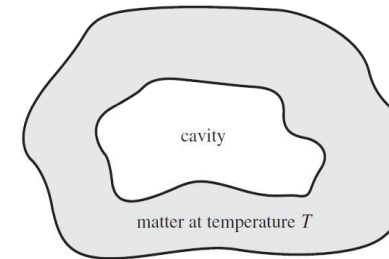


Figure: Radiation inside a cavity in matter - the average energy does not depend on either the shape of the cavity or the type of matter surrounding it, but depends only on the temperature.

Energy density of the EM radiation in a cavity at thermal equilibrium

- At thermal EB, the amount of energy at each wavelength of the EM radiation in the cavity is characterised by the energy density around this frequency, $\rho(\omega)$. $\rho(\omega)d\omega$ denotes the amount of energy (of the EM radiation) per unit volume for wavelength between $\omega, \omega + d\omega$ at temperature T .
- Second law of thermodynamics assures that at EB, the energy density $\rho(\omega)$ is independent of the structure of the cavity or of the surrounding material.
- Furthermore, $\rho(\omega)$ is independent of the position in the cavity, i.e., at all points in the cavity, $\rho(\omega)$ is identical.
- We wish to know what $\rho(\omega)$ is using stat mech treatment.

EM radiation in the cavity are harmonic oscillators

- In solid, sound waves are treated as phonons, which are excitation of independent harmonic oscillation modes, characterised by n_α and 3-component polarisation vector \mathbf{q} .
- In similarly manner, the EM radiation (instead of sound wave) in the cavity is modelled as photons (instead of phonons). These photons, like phonons, are independent harmonic oscillation modes representing (just like the sound wave in solid) standing EM waves that are established within the cavity at EB.

Phonons in solid vs. photons in vacuum cavity

- In the solid, oscillations of the atoms give rise to the phonons (sound wave); whereas in the case of EM radiation in a closed cavity, it's the oscillations of the atoms of the cavity wall that give rise to the photon (EM radiation).
- In the solid, we resort to the (model-dependent) Debye assumption for the dispersive relation $\omega = v|\mathbf{q}|$; whereas for the EM radiation in the cavity (assumed to be vacuum), the dispersion relation is well known (model independent):
 $\omega = c|\mathbf{q}|$.
- In both cases, the energy of the harmonic oscillators (photon, phonon) are given by $\epsilon_n = (n + \frac{1}{2})\hbar\omega$

Number of phonon mode is finite

- For phonon in solids, there exists an upper bound for the phonon's frequency ω_D , which is the result of the fact that the number of normal mode is finite ($3N$). The existence of ω_D can also be understood as a result of the fact that the sound's wavelength must not be smaller than the distance between two atoms (Reminder: the higher the frequency the shorter the wavelength).
- This boundary condition applies to sound wave in the solid because of the nature of sound wave as mechanical wave. (Reminder: mechanical wave requires a medium - the atoms + their 'springs' - to propagate).
- Hence the contribution of, e.g. average energy and energy density, from the phonon mode truncates when $\omega > \omega_D$.

Phonon has 3 polarisations

- In addition, due to the fact that sound waves are mechanical wave, it has three polarisations, which is reflected in the fact that \mathbf{q} has three components (q_x, q_y, q_z).

Photon's mode is infinite, and has only 2 polarisations

- For photon in the vacuum cavity, there is no upper bound for the photon's mode because photon is electromagnetic wave, not mechanical wave.
- Hence, for the case of EM radiation in a cavity, there is no upper bound for the normal mode as in the case of phonon in solid.
- The derivation procedure to obtain energy density of radiation in a cavity is exactly the same as for phonon in solid except:
 - 1 There is no upper bound for the normal mode
 - 2 Photon has only two polarisation component

Partition function of a single oscillator

- For a single harmonic oscillator (with index α), $z_\alpha = \sum_{n_\alpha=0}^{n_\alpha=\infty} e^{-\beta n_\alpha \hbar \omega_\alpha}$; $\alpha = 1, 2, 3, \dots$. Note that there is no upper bound to α which reflects the fact that number of photon mode is infinite. Also we have ignored the $\frac{1}{2}\hbar\omega$ term in the energy $\epsilon_n = (\frac{1}{2} + n)\hbar\omega$ since its contribution to most calculation (e.g. that to the free energy, probability density, etc.) will be cancelled out.
- From the study of series, $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$ for $|x| < 1$
- By identifying $x \equiv (e^{-\beta\hbar\omega_\alpha})^{-1}$, $z_\alpha = (1 - e^{-\beta\hbar\omega_\alpha})^{-1}$.

Partition function and free energy of the EM radiation in the cavity as a sum over α

$$\begin{aligned} Z &= z_{\alpha=1} z_{\alpha=2} z_{\alpha=3} \dots \\ &= \left(1 - e^{-\beta\hbar\omega_1}\right)^{-1} \left(1 - e^{-\beta\hbar\omega_2}\right)^{-1} \left(1 - e^{-\beta\hbar\omega_3}\right)^{-1} \dots \end{aligned}$$

$$\begin{aligned} F &= -kT \ln Z = \\ &kT \left[\ln \left(1 - e^{-\beta\hbar\omega_1}\right) + \ln \left(1 - e^{-\beta\hbar\omega_2}\right) + \ln \left(1 - e^{-\beta\hbar\omega_3}\right) + \dots \right] \\ &= kT \sum_{\alpha=1,2,3,\dots} \ln \left(1 - e^{-\beta\hbar\omega_\alpha}\right) \end{aligned}$$

Sum over α

- Summing over α means summing over all normal modes of the EM radiation (or equivalently, all possible photons states)
- The summation over α proceeds exactly as the previous case for phonon modes in the Debye solid, except that now, instead of 3 polarisations, the phonon has only two polarisations:

$$\begin{aligned} F &= kT \sum_{\alpha=1,2,3,\dots} \ln \left(1 - e^{-\beta\hbar\omega_\alpha}\right) \\ &= \frac{kTV}{c^3\pi^2} \int_0^\infty \omega^2 \ln \left[1 - e^{-\beta\hbar\omega}\right] d\omega \quad (6) \end{aligned}$$

Sum over α (cont.)

In arriving at the expression for F , we simply do the following (such calculation was encountered before when we were summing over the phonon's contribution in the Debye model):

$$\begin{aligned} \sum_{\alpha} (\dots) &\rightarrow \int_{q=0}^{q=\infty} (\dots) \times 2 \times \frac{1}{8} \cdot 4\pi q^2 dq \cdot \frac{V}{\pi^3} \\ &= \int_{\omega=0}^{\omega=\infty} (\dots) \times 2 \times \frac{1}{8} \cdot 4\pi \left(\frac{\omega}{v_p}\right)^2 \frac{1}{\frac{d\omega}{dq}} d\omega \cdot \frac{V}{\pi^3}, \end{aligned}$$

where we have used $dq = \frac{dq}{d\omega} d\omega$, $v_p = c$, $v_g = \frac{d\omega}{dq} = c$ for EM wave in vacuum (dispersionless).

$$\Rightarrow E = \int_0^\infty \hbar\omega (e^{\beta\hbar\omega} - 1)^{-1} \left(\frac{\omega^2 V}{c^3\pi^2}\right) d\omega$$

DOS, energy density and number density

- $E = \int_0^\infty \langle n \rangle \hbar \omega g(\omega) d\omega$
- $\langle n \rangle = (e^{\beta \hbar \omega} - 1)^{-1}$
- Density of state (number of microstate per unit frequency) of a single photon

$$g(\omega) = \frac{\omega^2 V}{c^3 \pi^2} \quad (\text{c.f. } \frac{3\omega^2 V}{2\bar{V}^3 \pi^2} \text{ for phonons}).$$

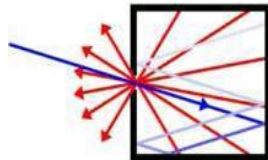
- Energy density of the EM field in the cavity = energy per unit volume per unit frequency,
 $\rho(\omega) = \langle n \rangle \cdot g(\omega) \cdot \hbar \omega / V = \frac{\hbar \omega^3}{c^3 \pi^2} (e^{\beta \hbar \omega} - 1)^{-1}$
- $\rho(\omega) / (\hbar \omega) =$ photon number density = average number of photon per unit volume per unit frequency:

$$n(\omega) = \frac{\omega^2}{c^3 \pi^2} (e^{\beta \hbar \omega} - 1)^{-1}.$$

What is a black body

- Now consider the cavity has a small aperture (tiny hole) with area $\Delta A \ll A$, $A =$ the area to the cavity.
- EM radiation that 'falls' through the aperture and get trapped into the cavity has negligible chance to re-escape from the aperture via multiple internal reflection within the cavity.
- Hence we can picture the aperture as a perfect absorber of any external EM radiation that fall on it. The aperture is called the *black body*, so named because it is a perfect EM absorber.
- The wall is made up of vibrating atoms that has thermal energy that is directly related to the non-zero temperature of the wall. Effectively all EM radiation falls through the aperture will be 'absorbed' by vibrating atoms, but later re-emitted by the atoms as EM radiation at various frequency.

What is a black body (cont.)



- At the same time EM radiation that is being built up within the cavity due to re-emission of the wall atoms will escape through the aperture at a certain rate. The emission of EM radiation from within the cavity through the aperture is very much similar to the scenario of a gas in a container escaping through a small hole on the wall of the container. Here we have a 'photon gas' instead of a gas molecule made of classical particle.

What is a black body (cont.)

- As time passes, the temperature of the cavity wall will gradually enter a phase where it becomes effectively constant. The rate at which EM energy is absorbed via the aperture is balanced by the rate EM energy is emitted via the aperture. In this phase, thermodynamic equilibrium is achieved: every single atom on the cavity wall has the same constant temperature.
- We can model the thermal EB between the EM radiation in the cavity with the vibrating atoms at a constant temperature T as a canonical ensemble: EM radiation in the cavity are represented as the photon modes, whereas thermal vibration of the atoms at constant T , with which the photons interact, act as the background 'heat bath'.

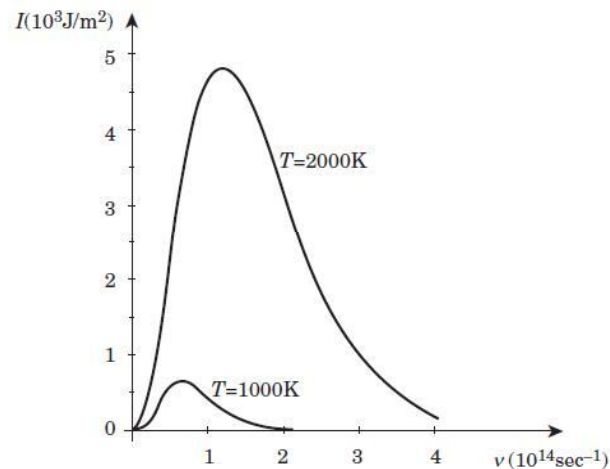
Emissivity

- The rate of EM energy emitted through the aperture is measured in terms of energy going through the hole per unit time per unit area per unit frequency, $I(\omega)$, the emissivity.
- When considering the energy rate emitted through the aperture, we must specify at which frequency the rate is being considered. $I(\omega)d\omega$ hence represents the amount of energy per unit time per unit area emitted through the aperture around the frequency $\omega \pm d\omega$

Emissivity is the quantity measured in experiment

- $I(\omega)$ can be experimentally measured e.g., photodiode can be used to measure $dW(\omega) = I(\omega)d\omega$, the power of radiation emitted from a black body aperture at a given narrow frequency range, say $\omega \pm d\omega$. The width of the photodiode determines the frequency width $d\omega$.
- To measure $dW(\omega)$ at a different ω , a prism is used to diffract the EM radiation so that their wavelength is 'spread out' at different angles upon exiting the other sides of the prism. Then $dW(\omega)/d\omega$ as a function of ω is plotted:

Experimental graph of emissivity vs. frequency

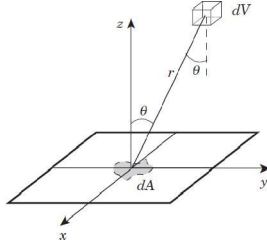


Emissivity in terms of energy density

- Emissivity of the black body (a.k.a. the aperture) is clearly related to the energy density of the EM radiation within the cavity. The larger the energy density is in the cavity, so is the emissivity.
- It turns out that if the energy density in the cavity is $\rho(\omega)$, the emissivity $\times d\omega$ through the aperture is

$$I(\omega)d\omega = \frac{c}{4}\rho(\omega)d\omega.$$

Deriving energy density from emissivity



- This relation is derived by summing all the contribution of the EM radiation's energy (at a particular frequency interval, $\omega \pm d\omega$) in all volume elements $dV = r^2 dr \sin \theta d\theta d\phi$ in the cavity flowing through the aperture (of area ΔA) within an time interval dt . The amount of energy flowing through ΔA perpendicularly in dt is

$$\Delta E = \int_0^{cdt} dr \int_0^{\frac{\pi}{2}} d\theta \int_0^{2\pi} d\phi \rho(\omega) d\omega \frac{\Delta A \cos \theta}{4\pi r^2}$$

Deriving energy density from emissivity (cont.)

- Integrating over $d^3\mathbf{r}$, $\Delta E = \int_0^{cdt} dr \int_0^{\frac{\pi}{2}} d\theta \int_0^{2\pi} d\phi dV \rho(\omega) d\omega \frac{\Delta A \cos \theta}{4\pi r^2} = \frac{c}{4} \rho(\omega) d\omega dt \Delta A$
- By definition,

$$I(\omega) = \frac{\Delta E}{\Delta A d\omega dt} = \frac{c}{4} \rho(\omega)$$

Planck's equation for emissivity

- Putting everything together, we now can predict theoretically how the emissivity as a function angular frequency:

$$I(\omega) = \frac{c}{4} \rho(\omega) = \frac{c}{4} \frac{\hbar \omega^3}{c^3 \pi^2} (e^{\beta \hbar \omega} - 1)^{-1} = \frac{1}{4\pi^2 c^2} \frac{\hbar \omega^3}{e^{\beta \hbar \omega} - 1}$$

- Emissivity can also be expressed as a function of frequency ν instead of angular frequency ω via $\nu = 2\pi\omega$.

Planck's emissivity in classical limits

- In the classical limit, $x = \beta \hbar \omega \ll 1$, the energy density reduces to $\rho(\omega) = \frac{kT\omega^2}{\pi^2 c^3}$. Note that the constant \hbar has disappeared in the classical limit, signifying that quantum effect has effectively dropped out from the picture.
- $\rho(\omega) = \frac{kT\omega^2}{\pi^2 c^3}$ is a well-know classical law called 'Rayleigh-Jeans law' derived by classical physicists trying to describe blackbody radiation spectrum using purely classical statistical physics arguments.
- RJ laws only fits the experimental curve of a blackbody radiation (at a give temperature) at low frequency but fails at high frequencies.

Stefan-Boltzmann law

- $W = \int_{\omega=0}^{\omega=\infty} I(\omega) d\omega$ represents the total energy emitted per unit time per unit area through the aperture contributed by all frequencies.
- $W = W(T) = \frac{1}{4\pi^2 c^2} \int_0^\infty \frac{\hbar \omega^3}{e^{\beta \hbar \omega} - 1} d\omega = \sigma T^4$, where $\sigma = \frac{2\pi^5 K^4}{15 h^3 c^2} = 5.67 \times 10^{-8} \text{ J s}^{-1} \text{ m}^{-2} \text{ K}^{-4}$

Wien's displacement law

- Wien's displacement law:

$$\frac{\hbar \omega_{\max}}{kT} = \frac{\hbar c}{kT \lambda_{\max}} = 2.822.$$

Note: recall that $\omega \lambda = 2\pi c$.

- Often Wien's displacement law is also stated as $\lambda_{\max} T = 2.898 \times 10^{-3} \text{ m} \cdot \text{K}$.

Wien's displacement law (cont.)

- One can deduce Wien's displacement law and the value of the constant from the emissivity $I(\omega) \sim \frac{x^3}{e^x - 1}$, $x = \beta \hbar \omega$.
- To obtain the Wien's displacement law, one extremises the emissivity curve, i.e. finds the value x_{\max} at which the emissivity is an extremum:

$$\left. \frac{\partial I(x)}{\partial x} \right|_{x_{\max}} = 0$$

to obtain $3x_{\max}^2 (e^{x_{\max}} - 1) - e^{x_{\max}} x_{\max}^3 = 0$. Use numerical method to find the root of this algebraic equation:

$$x_{\max} = \frac{\hbar \omega_{\max}}{kT} = 2.82144.$$

Free energy of the EM radiation in the cavity

$$\begin{aligned} F &= \frac{kTV}{c^3 \pi^2} \int_0^\infty \omega^2 \ln [1 - e^{-\beta \hbar \omega}] \omega d\omega \\ &\quad \downarrow x = \beta \hbar \omega \\ &= \frac{(kT)^4 V}{c^3 \hbar^3 \pi^2} \int_0^\infty x^2 \ln [1 - e^{-x}] dx \\ &\quad \downarrow \text{integration by parts} \\ &= -\frac{(kT)^4 V}{c^3 \hbar^3 \pi^2} \cdot \frac{1}{3} \int_0^\infty x^3 (1 - e^{-x}) dx \\ &= -\frac{(kT)^4 V \pi^2}{45 (\hbar c)^3} = -\frac{4\sigma}{3c} VT^4 \end{aligned}$$

Entropy, heat capacity and average number of photon of the EM radiation in the cavity

$$\begin{aligned}
 S &= -\left(\frac{\partial F}{\partial T}\right)_V = \frac{16\sigma}{3c} VT^3 \\
 C_V &= T\left(\frac{\partial S}{\partial T}\right) = \frac{16\sigma}{c} VT^3 \\
 \langle N \rangle &= V \int_0^\infty n(\omega) d\omega = V \cdot \int_0^\infty \frac{1}{\pi^2 c^3} \frac{\omega^2}{e^{\beta\hbar\omega} - 1} d\omega \\
 &\quad \downarrow x = \beta\hbar\omega \\
 &= \left(\frac{kT}{\hbar c}\right)^3 \int_0^\infty \frac{x^2}{e^x - 1} dx
 \end{aligned}$$

Chemical potential of the photon gas

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,N} = 0$$

- The free energy is independent of μ , hence the result $\left(\frac{\partial F}{\partial N}\right)_{T,N} = 0$
- μ is zero for photon is closely related to the fact that photon's number is not conserved in the cavity (due to absorption and re-emission by the wall).
- Photons are created and annihilated freely as a result of absorption and emission by the walls of the container.

Pressure of the photon gas

This can be calculated from the free energy via $P = \left(\frac{\partial F}{\partial V}\right)_T$:

$$P = \left(\frac{\partial \left[\frac{4\sigma}{3c} VT^4\right]}{\partial V}\right)_T = \frac{4\sigma}{3c} T^4 \quad (7)$$

Average energy E and energy density $u(T)$

The average energy of the EM radiation in the cavity (with volume V) is

$$\begin{aligned}
 E &= \int_0^\infty \hbar\omega (e^{\beta\hbar\omega} - 1)^{-1} \left(\frac{\omega^2 V}{c^3 \pi^2}\right) d\omega \\
 &\quad \downarrow x = \beta\hbar\omega \\
 E &= \frac{V\hbar}{\pi^2 c^3} \frac{k^4 T^4}{\hbar^4} \int_0^\infty \frac{x^3}{(\beta\hbar)^4} \cdot \frac{dx}{e^x - 1} \\
 &= \frac{V\hbar}{\pi^2 c^3} \frac{k^4 T^4}{\hbar^4} \left(\frac{\pi^4}{15}\right) = \frac{Vk^4 T^4 \pi^2}{15\hbar^3 c^3}
 \end{aligned}$$

- Energy density = energy per unit volume,

$$u(T) = E/V = \frac{Vk^4 T^4 \pi^2}{15\hbar^3 c^3} = \frac{4\sigma T^4}{c} \quad (8)$$

Pressure of the photo gas in terms of energy density $u(T)$

- For photon gas, we can obtain the relation between photon's pressure P and the energy density $u(T)$ by combining the expression for P , Eq. (7), and $u(T)$, Eq. (8), for the photon gas to obtain

$$P = \frac{1}{3}u(T)$$

- Recall for the case of ideal gas as we learned that $P = \frac{1}{3}nm\langle v^2 \rangle = \frac{2}{3}\frac{N}{V}m\langle \frac{v^2}{2} \rangle = \frac{2}{3}E/V = \frac{2}{3}u(T)$. This describe an ideal gas system in which each particle is moving with average energy $\langle \frac{mv^2}{2} \rangle = \langle \frac{p^2}{2m} \rangle$.
- The comparison above make it obvious that the photons in the cavity indeed do behave very much like a system of classical gas which is corpuscular in nature. We hence think of the quantum of light, photon, behaves like a particle.

Part V Of fermions and bosons

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Grand partition function as generalisation of canonical ensemble

- In canonical ensemble comprised of N number of particles, the partition function of the ensemble is $Z(T, V, N) = \sum_i e^{-\beta E_i}$, where E_i is the total energy of all the N particles in a microstate i , $E_i = \sum_{j=1}^N \epsilon_j$.
- Note that the summation in $Z(T, V, N)$ implicitly assumes that the system's total number of particle, N is fixed.
- Grand canonical ensemble (GCE) is the generalisation of the canonical ensemble. In GCE the constraint that N being a fixed number is relaxed, i.e., N is made a variable, and the effect of the variation due to N is to be taken care of by using chemical potential.

Grand partition function

- A microstate in GCE, labelled by α , is specified by
 - 1 N , the number of particle in state α , and
 - 2 the microscopic state i of these N particles.
- The PDF (probability distribution function) of a GCE takes the form of

$$P_\alpha \sim e^{-\beta(E_i - \mu N)}$$

- The partition function of a GCE, called the *grand partition function*, is

$$\mathcal{Z}(T, V, \mu) = \sum_\alpha e^{-\beta(E_i - \mu N)}$$

- Adding or taking away particle from the system (\Rightarrow variation in partial number N) involve energy cost. Such energy cost is taken care of by the term μN in the exponent.

Summation over α in the grand partition function

- The summation in \mathcal{Z} is divided into two parts: First, sum over the states i at a constant N , and then in the second step, sum over all N :

$$\mathcal{Z}(T, V, \mu) = \sum_N \overbrace{\left(e^{\beta\mu N} \sum_i e^{-\beta E_i} \right)}^{\text{a function in terms of } N} = \sum_N e^{\beta\mu N} Z(T, V, N)$$

- Since in GCE the number of particle (N) in the summation $e^{-\beta\mu N} \sum_{i=0}^N (\dots)$ is treated as a variable, $e^{-\beta\mu N} \sum_{i=0}^N (\dots)$ is a function of N . Hence we would also need to sum over all possible value of N , i.e. $\sum_{N=0}^{\infty} e^{-\beta\mu N} \left[\sum_{i=0}^N (\dots) \right]$.

Summation over α in the grand partition function (cont.)

- This is to be compared with the canonical ensemble, where the total number N is a constant, not a variable, hence no summing over the variable N is to be done in evaluating the canonical partition function.

Free energy and averages in GCE

- Since $F(T, V, N) = -kT \ln Z(T, V, N) \Rightarrow Z(T, V, N) = e^{-\beta F(T, V, N)}$

$$Z(T, V, \mu) = \sum_N e^{\beta \mu N} e^{-\beta F(T, V, N)} = \sum_N e^{\beta[\mu N - F(T, V, N)]}$$

- As for the case of canonical ensemble, the average of an observable A is then simply given by

$$\begin{aligned} \langle A \rangle &= \sum_{\alpha} A_{\alpha} P_{\alpha} = Z^{-1} \sum_{\alpha} A(N, i) e^{-\beta(E_i - \mu N)} \\ &= Z^{-1} \sum_N \left(\sum_i A(N, i) e^{-\beta(E_i - \mu N)} \right) \end{aligned}$$

Average pressure from \mathcal{Z}

- In the GCE, average work done by the system as a result of variation in an external variable X is given by

$$\delta W = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial X} dX$$

- In the case of $X \equiv V$, work done by the system when V varies by dV is $\delta W = PdV \Rightarrow$

$$\delta W = PdV \equiv \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial V} dV$$

- Comparing the coefficients to dV , we can then easily identify

$$P = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial V}$$

Average number of particle N from \mathcal{Z}

- In the GCE, average number of particles N is given by

$$N \equiv \langle N \rangle = Z^{-1} \sum_N \left(\sum_i N e^{\beta(\mu N - E_i)} \right) = \frac{\sum_N (\sum_i N e^{\beta(\mu N - E_i)})}{\sum_N (\sum_i e^{\beta(\mu N - E_i)})}$$

- Note the denominator in N is $\frac{1}{\beta} \frac{\partial \mathcal{Z}}{\partial \mu} = \sum_N (\sum_i \mu e^{\beta(\mu N - E_i)})$

$$N = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu}$$

Identifying the stat mech origin of the grand potential Ω

- Recall that in thermodynamics we mentioned the grand potential Ω , defined as

$$\Omega(T, V, \mu) = F - \mu N = E - TS - \mu N,$$

from which we derived pressure and number of particle in the system via (i) $P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T, \mu}$, (ii) $N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V}$.

- Comparing these with what were just derived from the grand canonical ensemble using \mathcal{Z} , i.e.

$$P = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial V}, N = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu}$$

we then can easily identify that the grand potential Ω is related to \mathcal{Z} via

$$\Omega = -kT \ln \mathcal{Z}$$

which is a generalisation of $F = -kT \ln Z$.

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Systems of classical particles are continuous

- For systems made up of classical particles, the states of the system are specified by the simultaneous momentum and coordinates of the particles $\{\mathbf{p}_i, \mathbf{r}_i\}$. Their states are continuous in the sense the momentum and spatial position of the particles are continuous variables. The energy of the states of the system is also continuous. e.g. $\epsilon_i = \frac{p_i^2}{2m_i}$ because momentum is continuous.

Systems of quantum particles are discrete

- On the other hand, systems made up of quantum particles (e.g. photons, phonons) are different from that made up of classical particles:
 - 1 The states of the quantum system is discrete in the sense that it requires a set of discrete number to specify the state (instead of specifying the set of continuous variables $\{\mathbf{p}_i, \mathbf{r}_i\}$)
 - 2 The energy of a state of the quantum system is quantized, in the sense that the energy can only assume values that are specified by discrete numbers, e.g. energy of a phonon mode in the Debye model is quantised $\epsilon_{n,p,q} = \frac{\hbar^2}{8m} \left(\frac{n^2}{a^2} + \frac{m^2}{b^2} + \frac{q^2}{c^2} \right)$, $\{n, p, q\}$ a set of positive interger, zero included.

A quantum particle is represented by a wavefunction, ψ_k

- A quantum particle is not to be treated as 'particle-like' but rather as a wave, which is represented by a wave function ψ_k .
- The index k , a short-hand notation representing the set of discrete number $k \equiv \{n, p, q\}$ specifies the state of the quantum 'particle'.

Boundary condition on ψ_k quantises the momenta

- The wavefunction ψ_k must obey boundary condition arisen from the finiteness of size of the system in each spatial direction, e.g. $\frac{\lambda_x}{2} = na$.
- The wavelengths of the wavefunction in turn are related to the momenta.
- Since the wavelengths are constrained by condition of the form $\frac{\lambda_x}{2} = na$, the momenta of the quantum particle in each spatial directions become quantized.
- As a result, $p_x = \frac{h}{\lambda_x} = \frac{nh}{2a}$ (similar condition also applies to momentum in the y- and z- directions)

Single particle state (SPS)

- Specifying the state of a single quantum particle is to specify the set of three discrete numbers $k \equiv \{n, p, q\}$ for that particle.
- For a given set of three numbers $\{n, p, q\}$ a positive integer is assigned to k , e.g. $k = 1 \equiv \{0, 0, 0\}$, $k = 2 \equiv \{0, 0, 1\}$, $k = 3 \equiv \{0, 1, 1\}$, etc.
- ϵ_k represents the energy of a quantum particle in the state k . k is the label of a **single particle state (SPS)**.
- In principle, the SPS index k runs from 1 to infinity.
- Usually, higher k indexes higher excited states (energy higher, momentum higher).

n_k occupancy number

- Consider a system comprised of N non interacting particles (recall that the phonons in the Debye model or the photons in the blackbody cavity are such particles).
- There are many SPS states available to be occupied by these particle.
- We can liken the SPS available to be occupied by the particles in the system as 'addresses' of houses. In the system, there are in principle infinite 'addresses' (SPS) ($k = 1, 2, 3, \dots, \infty$), and each house can be occupied by any number of particles.
- We will use n_k to denote the *occupancy number* of SPS k .
- n_k can be any integer between 0 to infinity.

Example of specifying a state of 6 quantum particles

- For the sake of concreteness, consider an example where there are $N = 6$ particles in the system. A particular microstate α may look like the following:
- Particles with indices $j = 1, 2, 3$ are in the SPS $k = 1 \equiv \{0, 0, 0\}$, particles with indices $j = 4, 5$ are in the SPS $k = 2 \equiv \{0, 0, 1\}$, and the last particle, with index $j = 6$ is in the $k = 3 \equiv \{0, 1, 1\}$ SPS.

Specifying the state of system is to list down the set of all occupancy numbers $\{n_{k=1}, n_{k=2}, n_{k=3}, \dots\}$

- We can specify the state α by the set $\{k_{j=1} = k_{j=2} = k_{j=3} = 1; k_{j=4} = k_{j=5} = 2; k_{j=6} = 3\}$.
- Or, equivalently, $\{n_{k=1} = 3, n_{k=2} = 2, n_{k=3} = 1\}$. This turns out to be the more convenient way to specify a state rather than listing $\{k_j\}$.
- Listing all the occupation numbers $\{n_k\}$ for all SPS $k = \{1, 2, \dots\}$ amount to a statement of the microstate of the system.
- If we count the number of particle in each SPS address, and sum up the number of all the particle counted, we must have $n_{k=1} + n_{k=2} + \dots + n_{k=\infty} = \sum_k n_k = N$.

Two types of quantum particles: Fermion and Bosons

- It turns out all the quantum particles in our Universe can be categorised into two types based on the way they occupy a single particle state in a quantum many-particle system:
 - 1 Fermion: $n_k = \{0, 1\}$. These particles has spin $\frac{\hbar}{2}, \frac{3\hbar}{2}, \frac{5\hbar}{2}, \dots$, and their wavefunctions are antisymmetric, e.g. $\psi(1)\psi(2) = -\psi(2)\psi(1)$. They are said to obey *Pauli exclusive principle* because no more than one quantum particle can occupy a same quantum state.
 - 2 Boson: $n_k = \{0, 1, 2, \dots\}$. These particles has integer spins $0\hbar, 1\hbar, 2\hbar, \dots$. There is no limit on how many boson can occupy a single particle state.

Quantum particles are identical

- One of the intrinsic differences between Quantum particles and classical particles is that quantum particles of the same type are *indistinguishable*.
- For example two electron or two photons are indistinguishable in the sense that the intrinsic properties ('quantum numbers') that characterise any electron (e.g. e, m_e, spin) are universal.
- All electrons are exactly identical. As a consequence, if you exchange two electrons located at $\{x_1, x_2\}$ respectively you can't experimentally distinguish between the configuration $\{e_1 \text{ at } x_1, e_2 \text{ at } x_2\}$ from $\{e_2 \text{ at } x_1, e_1 \text{ at } x_2\}$.
- The indistinguishability of quantum particles gives rise to many subtle effects that render the physical behavior of quantum systems very much different from the classical ones.

Bosonic and fermionic systems requires grand canonical ensemble

- We have to employ grand canonical ensemble (GCE) to describe these quantum many-particle system.
- We need GCE because the occupancy number n_k for a fixed k is to become a variable. We will need to deal with the summation of the form $\prod_{k=1}^{k=\infty} \left\{ \sum_{n_k=0}^{n_k=\infty} (\dots) \right\}$ while summing up all microscopic states to obtain the grand partition function \mathcal{Z} .
- Be reminded that in GCE, there are two independent variables, namely $k \in \{1, 2, \dots\}$ and n_k . For boson, $n_k \in \{0, 1, 2, \dots\}$; for fermion, $n_k \in \{0, 1\}$. In order to obtain the grand partition function \mathcal{Z} , we must sum over both k and n_k .

Energy of a SPS in GCE, ϵ_k , includes a chemical potential,

μ

- There are infinite one-particle state (SPS) in the GCE, each is labelled by $k = 1, k = 2, \dots, k = \infty$.
- Each of these SPS is occupied by n_k particles, and each of these particle has energy ϵ_k .
- Hence the energy of a SPS k is given by $\epsilon_k = n_k (\epsilon_k - \mu)$.
- μ enters the expression of the energy in the SPS because we are working in a GCE, which necessitates the introduction of the extra variable to take care of the variation in particle number n_k .

Constructing the grand partition function \mathcal{Z} from the SPS grand partition function \mathcal{Z}_k (cont.)

- In other words, knowing the SPS grand partition function \mathcal{Z}_k , \mathcal{Z} can be constructed according to Eq. (1) (and hence all thermodynamical properties).

Constructing the grand partition function \mathcal{Z} from the SPS grand partition function \mathcal{Z}_k

- Consider that we fix a particular SPS k . The grand partition function for that SPS is obtained by summing over all possible values of n_k , the occupation number in the SPS k , i.e.

$$\mathcal{Z}_k = \sum_{n_k} e^{-\beta n_k (\epsilon_k - \mu)}.$$

- The grand partition function \mathcal{Z} is constructed by taking the product of all the SPS grand partition function from $k = 1$ to $k = \infty$, i.e.

$$\mathcal{Z} = \mathcal{Z}_{k=1} \cdot \mathcal{Z}_{k=2} \cdot \mathcal{Z}_{k=3} \cdots = \prod_{k=1}^{\infty} \mathcal{Z}_k \quad (1)$$

SPS grand partition function for fermions $\mathcal{Z}_k^{(F)}$

- For fermions only $n_k \in 0, 1$ are allowed.
- The SPS grand partition function is

$$\mathcal{Z}_k^{(F)} = \sum_{n_k=0,1} e^{-\beta n_k (\epsilon_k - \mu)} = e^{-\beta \cdot 0 \cdot (\epsilon_k - \mu)} + e^{-\beta \cdot 1 \cdot (\epsilon_k - \mu)} = 1 + e^{\beta(\mu - \epsilon_k)}$$

SPS grand partition function for bosons $\mathcal{Z}_k^{(B)}$

- For bosons $n_k \in \{0, 1, 2, \dots\}$
- The SPS grand partition function is

$$\mathcal{Z}_k^{(B)} = \sum_{n_k=0}^{n_k=\infty} e^{\beta n_k (\mu - \epsilon_k)}$$

- To obtain $\mathcal{Z}_k^{(B)}$, we substitute $x = e^{\beta(\mu - \epsilon)}$ so that

$$\mathcal{Z}_k^{(B)} = \sum_{n_k=0}^{n_k=\infty} x^{n_k}$$

SPS grand partition function for bosons $\mathcal{Z}_k^{(B)}$ (cont.)

- The sum $\sum_{n_k=0}^{n_k=\infty} x^{n_k}$ converges to $\frac{1}{1-x}$ only if

$$x = e^{\beta(\mu - \epsilon)} < 1 \equiv \mu < \epsilon_k.$$

- $\mathcal{Z}_k^{(B)} = (1 - e^{\beta(\mu - \epsilon)})^{-1}, \mu < \epsilon_k \forall k$

Grand thermodynamic potential for fermions $\Omega^{(F)}(T, V, \mu)$

- Grand thermodynamic potential for fermions

$$\begin{aligned} \Omega^{(F)}(T, V, \mu) &= -kT \ln(\mathcal{Z}_1 \cdot \mathcal{Z}_2 \cdot \mathcal{Z}_3 \cdot \dots) \\ &= -kT [\ln \mathcal{Z}_1 + \ln \mathcal{Z}_2 + \ln \mathcal{Z}_3] = -kT \sum_{k=1}^{k=\infty} \ln \mathcal{Z}_k \\ &= -kT \sum_{k=1}^{k=\infty} \ln(1 + e^{\beta(\mu - \epsilon_k)}) \end{aligned}$$

Grand thermodynamic potential for bosons $\Omega^{(B)}(T, V, \mu)$

- Grand thermodynamic potential for bosons is

$$\Omega^{(B)}(T, V, \mu) = -kT \sum_{k=1}^{k=\infty} \ln(1 - e^{\beta(\mu - \epsilon_k)})$$

The average particle number of a GCE

- First we would like to use the grand potential function to evaluate the average particle number of a GCE at fixed volume and temperature, which can be obtained from the relations

$$\langle N \rangle = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{V, T}$$

Fermi-Dirac (FD) distribution

$$\langle N^F \rangle = - \left(\frac{\partial \Omega^{(F)}}{\partial \mu} \right)_{V, T} = \sum_k \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1} = \sum_k \langle n_k^{(F)} \rangle$$

where

$$\langle n_k^{(B)} \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1}, \quad (2)$$

is the expectation (or the average) occupation number in SPS state k in a fermionic system. Eq. (2) is the celebrated Fermi-Dirac distribution.

Bose-Einstein (BE) distribution

$$\langle N^B \rangle = - \left(\frac{\partial \Omega^{(B)}}{\partial \mu} \right)_{V, T} = \sum_k \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1} = \sum_k \langle n_k^{(B)} \rangle; \quad \mu < \epsilon_k \forall k$$

where

$$\langle n_k^{(B)} \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1}, \quad (3)$$

is the expectation (or the average) occupation number in SPS state k in a bosonic system. Eq. (3) is the celebrated Bose-Einstein distribution.

Phonon or phonon modes are bosonic particles with energy

$$\epsilon_k = \hbar\omega$$

- Note that $\langle N^B \rangle$ reduces to $\langle n \rangle = (e^{\beta\epsilon_k} - 1)^{-1}$ when $\mu = 0$ and $\epsilon_k = \hbar\omega$. This is the expectation occupation number for the Debye model and blackbody cavities. In both of these systems, the phonon and photon are boson, and have chemical potential zero. We can interpret the phonon or photon modes as bosonic particles with energy $\epsilon_k = \hbar\omega$ for all SPS k .

The average occupation numbers of a single particle state as a function of $\beta(\epsilon - \mu)$

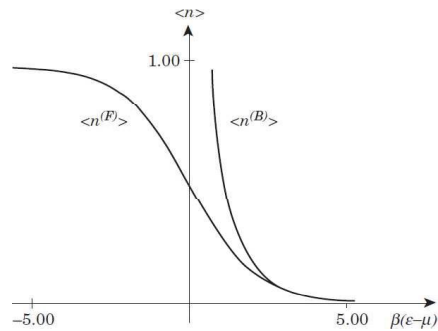


Figure: The average occupation numbers of a single particle state as a function of $\beta(\epsilon - \mu)$. The index k has been omitted

Features of Fermi-Dirac distribution

- In the limit $\beta(\epsilon_k - \mu) \rightarrow \infty$, the Fermi-Dirac distribution reduces to the Maxwell-Boltzmann distribution, $\sim e^{-\beta\epsilon_k}$. This corresponds to the classical limit (high temperature or large ϵ_k)
- In the limit $\beta(\epsilon_k - \mu) \rightarrow -\infty$, $\langle n^{(F)} \rangle \rightarrow 1$. This corresponds to the quantum limit. It happens when $\epsilon_k < \mu$ and $kT \ll \epsilon_k - \mu$.
- $0 \leq \langle n^{(F)} \rangle \leq 1$.
- Unlike the BE case, μ can be larger or smaller than ϵ_k in the FD case. The constraint $\mu < \epsilon_k$ does not apply to fermion.
- As such, $\beta(\epsilon_k - \mu)$ for the FD case can lie in both the positive and negative domain $\forall k$.

Features of Bose-Einstein distribution

- ϵ_k is always larger than μ for bosonic system.
- In the limit $\beta(\epsilon_k - \mu) \rightarrow \infty$, the Bose-Einstein distribution reduces to the Maxwell-Boltzmann distribution, $\sim e^{-\beta\epsilon_k}$. This corresponds to the classical limit (high temperature or large ϵ_k)
- In the limit $\beta(\epsilon_k - \mu) \rightarrow 0$, $\langle n^{(B)} \rangle \rightarrow \infty$. This corresponds to the quantum limit. It happens when $kT \ll \epsilon - \mu$.
- Also note that the divergence originates from the $e^{\beta(\epsilon_k - \mu)} - 1$ term in the denominator of $\langle n^{(B)} \rangle$. Since the corresponding sign for the FD case is a '+', no such divergence occurs for Fermion.
- $0 \leq \langle n^{(F)} \rangle \leq \infty$.
- $\beta(\epsilon_k - \mu)$ is limited to lie in the positive domain $\forall k$.

Outline

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 - 1.2 Connection to thermodynamics
- 2 Chapter 2 Statistical Mechanics of Identical Quantum Particles
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- 3 Chapter 3 Electrical Conductivity in Metals
 - 3.1 The Drude model
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 - 3.5 Metals at room temperature
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Wiednamm-Frank law

- Classically, people believe that the electrons in the metal contribute significantly to both the electrical conductivity and thermal conductivity.
- The ratio of electrical conductivity to thermal conductivity for metal, $\frac{\bar{K}}{\sigma}$, as measured by Wiedmann-Frank (middle 19th century) is roughly a constant $\times T$, where the constant is

$$\sim 2 \times 10^{-8} \text{W}\Omega/\text{K}^2.$$

This constant is also relatively independent of the materials.

Electrical conductivity

- Electrical conductivity of metals is closely related to the *drift velocity* of the free electrons in the metal under an electric field E .
- The drift velocity is the effective velocity of the electrons that have to undergo frequent collision in the metal while drifting along the direction $-E$ under the electric force $-eE$.
- The drift velocity is also called the thermal velocity)
- Between successive collisions, the electrons move as free particles under 'free-fall' due to the force $-eE$. The acceleration due to the force $-eE$ on an electron is $a = -eE/m$, hence $v = v_0 - \frac{eE}{m}t$.
- The free-fall motion only lasted on average τ , defined as the mean free time. It is the average free-fall time between two successive collision among the electrons.

Assumptions in Drude's model

- Drude in 1900 treated electron in metal as though they behave essentially like freely moving idea gas obeying kinetic theory of gases with Boltzmann distribution.
- Drude assumed that
 - The electron gas is assumed to be in a state of thermodynamic equilibrium.
 - the free-electron in metals contributes significantly to both electrical conductivity and thermal conductivity of metals. ¹
 - Although electrons are charged, the interaction between them are negligible and they do not effect one another's motion.
- Both \bar{K} and σ can be derived by considering the transport phenomena of a freely moving particle system.

¹Actually, one of Drude's assumption is wrong: It turns out that the electrons do not contribute significantly to the heat capacity except at extremely low temperature.

Electrical conductivity (cont.)

- Hence the average velocity, i.e. the drift velocity, is $\bar{v} = \langle v_0 - \frac{eE}{m}t \rangle = -\tau \frac{eE}{m}$.
- The flowing of electrons moving with an average velocity of \bar{v} gives rise to a current density.
- By definition, the current density is given by $J = -e\bar{v}n = -en(-\tau \frac{eE}{m}) = \frac{ne^2\tau}{m}E$, where n electron number density of the metal.
- The conductivity of a metal is defined as the current flowing as a respond to an external electric field E via $J = \sigma E$.
- Combining both $J = -e\bar{v}n$ and E via $J = \sigma E$, we arrive at the expression of the electrical conductivity in terms of the mean free time τ ,

$$\sigma = \frac{ne^2\tau}{m}. \quad (4)$$

Thermal conductivity

- The thermal conductivity is given by

$$\bar{K} = \frac{1}{3} n \bar{v} \ell c = \frac{1}{3} n \bar{v}^2 c \tau, \quad (5)$$

where c the specific heat capacity per electron, ℓ the mean free path. We have used the relation $\ell = \bar{v} \tau$.

- This result is obtained by analysing the transport phenomena using kinetic theory of gases. Detailed derivation of this equation can be found in page 67 of Amit.

\bar{K}/σ in the Drude model

- Up to now, the expressions for σ and \bar{K} are completely generic, as we have not specified what the average kinetic energy $\epsilon = \frac{1}{2} m \bar{v}^2$ and the heat capacity c of the electron gas are.
- In Drude's model, the ideal electron gas assumes Maxwell-Boltzmann velocity distribution, $m \bar{v}^2 = 3kT$.
- Drude's model also assumes the electron gas obeys classical thermodynamics, and the electrons obey equipartition law, where the electronic contribution to heat capacities of the metal is $c = 3k/2$ per electron.²
- Hence, the Drude model predicts

$$\frac{\bar{K}}{\sigma} = \frac{m \bar{v}^2 c}{3e^2} = \frac{3k^2 T}{2e^2} = 1.11 \times 10^{-8} \text{W}\Omega/\text{K}^2 \times T.$$

²As mentioned earlier, this turns out to be not true, as there is no experimental evidence that electron gas obeys equipartition law.

A critique of the Drude model

- Drude's model is partially successful: the order of magnitude estimate of the ratio $\frac{\bar{K}}{\sigma T} \approx \times 10^{-8} \text{W}\Omega/\text{K}^2$ is right, but is still about 2 times too small when compared to the experimental values.
- Purely classical treatment leads to quantitatively incorrect prediction for the ratio $\frac{\bar{K}}{\sigma T}$. The prediction of $\frac{\bar{K}}{\sigma T}$ in the Drude's model turns out to be of the same order of magnitude as that of the experimental data is somewhat a coincidence.
- A correct treatment for \bar{K} and σ should take into account of the quantum statistical behavior of electrons in metal, which was so done in the Sommerfeld model.

A critique of the Drude model (cont.)

- It turns out that actually the free electrons do not obey equipartition law in metals, and their contribution to the heat capacity in metals is negligible at room temperature as compared to that contributed by phonons.
- In the Sommerfeld model (which treats the free electrons in metal as quantum particles), we shall see that in fact the heat capacity of metals contributed by free electrons is indeed much smaller than $3k/2$.
- We will also see that in the Sommerfeld model the wrong assumption of equipartition law of electron as applied to the heat capacity c was actually compensated by a larger (and numerically correct) contribution from the velocity term in \bar{K} .

Grand partition function of a Fermi gas

- In Sommerfeld's model the free electrons in metal (as a 3D container of a volume V) are treated as free quantum particles obeying fermi statistics.
- We will call the quantum version of free electron gas the *Fermi gas*.
- Each of the electron in the free electron gas has kinetic energy of a free particle given by $\epsilon = \frac{p^2}{2m}$.
- From the previous chapter, the grand partition function such a fermion system is known,

$$\mathcal{Z} = \prod_k \mathcal{Z}_k^{(F)},$$

$$\text{where } \mathcal{Z}_k^{(F)} = 1 + e^{\beta(\mu - \epsilon_k)}.$$

The average number of electron in the Fermi gas

- $\Omega^{(F)} = -kT \ln \mathcal{Z} = -kT \sum_k \ln (1 + e^{\beta(\mu - \epsilon_k)})$, from which we can derive the average number of electron in the grand ensemble,

$$\begin{aligned} N &= -\frac{\partial \Omega}{\partial \mu} \\ &= kT \sum_k \frac{\partial}{\partial \mu} \ln (1 + e^{\beta(\mu - \epsilon_k)}) \\ &= \sum_k \frac{1}{1 + e^{\beta(\epsilon_k - \mu)}} = \sum_k \frac{1}{1 + e^{\beta(\epsilon_k - \mu)}} \\ &= \sum_k \frac{1}{1 + e^{\beta(\frac{p^2}{2m} - \mu)}}. \end{aligned}$$

The summation over SPS k for N

- The summation over the SPS index k is to be replaced by the summation over all momentum states in the metal's volume V : i.e.,

$$\sum_k \rightarrow 2 \times V \int \frac{d^3 \mathbf{p}}{h^3},$$

so that

$$\sum_k \frac{1}{1 + e^{\beta(\frac{p^2}{2m} - \mu)}} = 2V \int \frac{d^3 \mathbf{p}}{h^3} \left[1 + e^{\beta(\frac{p^2}{2m} - \mu)} \right]^{-1}.$$

- The factor 2 is to take care of the fact that each electron has two spin states.
- Hence, the average number of electron in the metal is given by

$$N = 2V \int \frac{d^3 \mathbf{p}}{h^3} \frac{1}{1 + e^{\beta(\frac{p^2}{2m} - \mu)}}, \quad (6)$$

PDF of the Fermi gas in momentum space

- From Eq. (6) we can derive dN , given by

$$dN = \frac{2V}{h^3} \frac{d^3 \mathbf{p}}{1 + e^{\beta(\frac{p^2}{2m} - \mu)}}.$$

- $\frac{dN}{N}$ is the probability to find an electron with momentum \mathbf{p} around the velocity volume element $d^3 \mathbf{p}$.
- By definition, this is just the PDF in momentum space for the free electrons in the metal, i.e.

$$\frac{dN}{N} = \frac{2V}{Nh^3} \frac{d^3 \mathbf{p}}{1 + e^{\beta(\frac{p^2}{2m} - \mu)}} = \frac{2}{nh^3} \frac{d^3 \mathbf{p}}{1 + e^{\beta(\frac{p^2}{2m} - \mu)}} \equiv f(\mathbf{p}) d^3 \mathbf{p},$$

where $n = N/V$ is the number density of free electron in the metal.

- This is the Fermi-Dirac analogue of the Maxwell-Boltzmann momentum distribution function for the case of classical free particles.

PDF is all you need

- The PDF in momentum space is the most important ingredient we need for the purpose to predict the physical behavior of the free electron in metal (e.g., mean energy, electrical conductivity, electronic contribution to heat capacity, etc.)

Average energy $\langle \epsilon \rangle$ from momentum PDF

- But first we would like to use it to calculate the most obvious macroscopical physical quantity that is momentum-related, i.e., the average energy (purely kinetic) $\langle \epsilon \rangle$ of the electrons in the metal

$$\langle \epsilon \rangle = \int \frac{p^2}{2m} f(\mathbf{p}) d^3 \mathbf{p}$$

- $\langle \epsilon \rangle$ can be evaluated in terms of $\epsilon = \frac{p^2}{2m} \Rightarrow dp = \left(\frac{m}{2\epsilon}\right)^{1/2} d\epsilon$.

$$\begin{aligned} \langle \epsilon \rangle &= \int \frac{p^2}{2m} f(\mathbf{p}) d^3 \mathbf{p} \\ &= \int \frac{p^2}{2m} \cdot \frac{2}{nh^3} \frac{1}{1 + e^{\beta(\frac{p^2}{2m} - \mu)}} \cdot 4\pi p^2 dp \\ &= \int \epsilon \cdot \frac{8\pi}{nh^3} \frac{1}{1 + e^{\beta(\epsilon - \mu)}} \cdot 2m\epsilon \left(\frac{m}{2\epsilon}\right)^{1/2} d\epsilon \end{aligned}$$

$f_\epsilon(\epsilon)$ the energy distribution function

- $\langle \epsilon \rangle$ can be further cast into the convenient form

$$\langle \epsilon \rangle = \int_0^\infty \epsilon f_\epsilon(\epsilon) d\epsilon,$$

$f_\epsilon(\epsilon)$ the energy distribution function given by

$$f_\epsilon(\epsilon) = \underbrace{\frac{4\pi(2m)^{3/2}\epsilon^{1/2}}{h^3}}_{\text{degeneracy factor}} \cdot \underbrace{\frac{1}{1 + e^{\beta(\epsilon - \mu)}}}_{\text{average number at energy } \epsilon} \cdot \frac{V}{N}.$$

- $f_\epsilon(\epsilon)$ tells us how the quantum states of the Fermi gas system is occupied as a function of energy and temperature (c.f. this with PDF in momentum space).

Density of state (DOS), $g(\epsilon)$

- The degeneracy factor $g(\epsilon) = \frac{4\pi(2m)^{3/2}\epsilon^{1/2}}{h^3}$ is also known as density of state.
- Most commonly $g(\epsilon)$ is just called 'density of state' (DOS).
- It is the number of quantum states that are *available* to be occupied between ϵ and $\epsilon + d\epsilon$.
- $g(\epsilon)$ is quite general and is independent of the statistical nature of the particle.
- It describes the number of states at each energy level that are available to be occupied.
- A high DOS at a specific energy level means that there are many states available for occupation.
- A DOS of zero means that no states can be occupied at that energy level.

$n_\epsilon(\epsilon)$ as a probability

- We should also familiar with the term $n_\epsilon(\epsilon) = \frac{1}{1+e^{\beta(\epsilon-\mu)}}$. It is just the Fermi-Dirac occupation function.
- It is the average number of fermion (in this case, electron) at energy state ϵ . Note that the form of $n_\epsilon(\epsilon)$ suggests that the average number of electron at an energy state ϵ depends strongly on temperature.
- One may interpret $n_\epsilon(\epsilon)$ as the *probability* of how the electrons shall be distributed at different energy states (i.e. ϵ) as a function of temperature
- Multiplying this probability with the DOS tell us how are the quantum states *actually* being occupied as a function of energy.

Chemical potential μ is temperature and number density dependent

- In general, the chemical potential μ is also dependent on temperature and number density n , which could be worked out from the expression of the average number of electron in the metal N in Eq. (6).
- In terms of ϵ , this is

$$\begin{aligned} N &= \int \frac{2V}{h^3} \frac{1}{1+e^{\beta(\frac{p^2}{2m}-\mu)}} \cdot 4\pi p^2 dp \\ &= \int \frac{8\pi V}{h^3} \frac{1}{1+e^{\beta(\epsilon-\mu)}} \cdot 2m\epsilon \left(\frac{m}{2\epsilon}\right)^{1/2} d\epsilon \\ \Rightarrow n &= \frac{N}{V} = (2m)^{3/2} \frac{4\pi}{h^3} \int_0^\infty \frac{\epsilon^{1/2}}{1+e^{\beta(\epsilon-\mu)}} d\epsilon \quad (7) \end{aligned}$$

DOS and the statistical nature of the particles determine the behavior of an ensemble.

- The behavior of the electron in the metal, as according to the Sommerfeld model, is determined by the statistical nature (as inferred in $n_\epsilon(\epsilon)$) and also the DOS of the system.
- In general, the overall behavior of an ensemble is determined by the DOS of the system, and whether the particles are fermions or bosons.

Implicitly dependence of μ on β and n

- Eq (7) renders μ to implicitly depend on β and n , as the RHS of the equation,

$$\int_0^\infty \frac{\epsilon^{1/2}}{1+e^{\beta(\epsilon-\mu)}} d\epsilon$$

is an implicit function of β and μ .

- Note that the integrand ϵ is to be integrated out from the picture, hence the it is not a function of the variable ϵ .

What's next

- In what follows, we would like to investigate the behavior of the free electron in the Sommerfeld model at both limits of high and low temperatures.

To establish the temperature dependence of $n_\epsilon(\epsilon)$, first establish the temperature dependence of μ

$$n_\epsilon(\epsilon) = n_\epsilon(\epsilon, \mu) = \left[1 + e^{\beta(\mu - \epsilon_k)}\right]^{-1}.$$

- We wish to know what will happen to the Fermi-Dirac occupation number $n_\epsilon(\epsilon)$ in the limits when $T \rightarrow 0$ (equivalent to $\beta \rightarrow \infty$) and when $T \rightarrow \infty$ (equivalent to $\beta \rightarrow 0$).
- To do so, we must first establish the temperature dependence of μ at low and high temperature limits.

First, how does μ behave in the high temperature limit, $\beta \rightarrow 0$?

- To answer this, take a look at

$$n \sim \int_0^\infty \frac{\epsilon^{1/2}}{1 + e^{\beta\epsilon} e^{-\beta\mu}} d\epsilon$$

- n , as a physical quantity, must never become infinite under all conditions.
- Note that in the $\epsilon \rightarrow \infty, \beta \rightarrow 0$ limit, $e^{\beta\epsilon} \rightarrow \text{constant}$.
- As a consequence, the integral $\frac{\epsilon^{1/2}}{1 + e^{\beta\epsilon} e^{-\beta\mu}} \sim \frac{\epsilon^{1/2}}{1 + \text{constant} \cdot e^{-\beta\mu}}$ in the $\epsilon \rightarrow \infty, \beta \rightarrow 0$ limits.
- If $-\beta\mu \rightarrow \text{constant}$ in the $\epsilon \rightarrow \infty$ limit, then the integral will behave like $\sim \frac{\epsilon^{1/2}}{\text{constant}}$, rendering the integration and hence n to diverge.
- Hence μ should behave according to $e^{-\beta\mu} \rightarrow \infty$ as $\beta \rightarrow 0$ so that the integration does not 'explode' in the $\epsilon \rightarrow \infty$ limit.

The FD distribution reduces to MB distribution in high temperature limit

- We conclude the high temperature limit behavior:

$$\lim_{\beta \rightarrow 0} \mu/\beta = -\infty,$$

- Or in other words, μ becomes more and more negative as T increases.
- This limiting behavior, when applied to the Fermi-Dirac occupation function $n_\epsilon(\epsilon)$, allows us to conclude that in the high T limit,

$$n_\epsilon(\epsilon) \sim C \exp(-\beta\epsilon),$$

- where $C = \exp(\beta\mu)$.
- This is just the classical Boltzmann distribution.

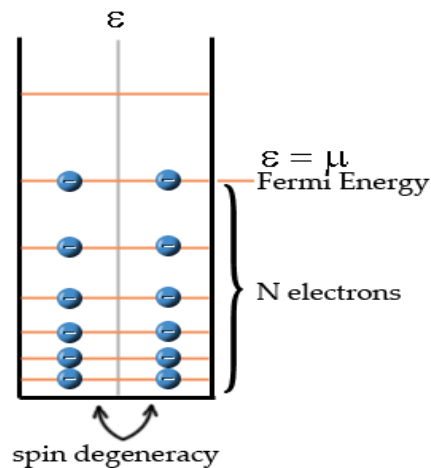
How μ behaves in the low temperature limit, $\beta \rightarrow \infty$?

- Look at $n_\epsilon(\epsilon) = \frac{1}{1+e^{\beta(\epsilon-\mu)}}$ for the answer.
- If $\epsilon > \mu$, $\lim_{\beta \rightarrow \infty} \frac{1}{1+e^{\beta(\epsilon-\mu)}} = 0$
- If $\epsilon < \mu$, $\lim_{\beta \rightarrow \infty} \frac{1}{1+e^{\beta(\epsilon-\mu)}} = 1$.
- The occupation number of a particular energy states ϵ by the electron of a given spin is either 0 or 1, depending on whether the energy level ϵ is above or below the chemical potential μ at that temperature.

Degenerate Fermi gas

- The previous result applies to electrons with a fixed spin. An electron may have two spin states, e.g. spin up or spin down.
- Taking spin degeneracy into account, all the energy levels below μ is occupied by one spin up state electron, and one spin down state electron, resulting in each state below $\epsilon = \mu$ to be occupied by effectively two electrons.
- No electron is to be found at energy above the threshold energy $\epsilon = \mu$.
- That means, in the $T \rightarrow 0$ limit, if there are N electrons in the metal, they will fill up each energy level right from bottom of the energy states at $\epsilon = 0$ until the highest energy level defined as $\epsilon_F = \mu$.
- Such state of an electron gas is called a *degenerate Fermi gas*.

Figurative representation of degenerate Fermi gas



Fermi energy

- This way of stacking up all particles in their energy level from bottom up in the ensemble is to be contrasted with the classical Boltzmann distribution for ideal gas according to $n_\epsilon \sim e^{-\beta\epsilon}$, where all particles in the MB distribution will concentrate at the ground level $\epsilon = 0$ in the $\beta \rightarrow \infty$ limit.
- In contrast, the particles in the degenerate Fermi gas stack against each other obeying the rules that only two electrons of opposite spins are allowed in each energy level. This is a quantum feature of fermions consistent with Pauli's exclusive principle.
- The so-called *Fermi energy*, given by $\epsilon_F = \frac{h^2}{2m} \left(\frac{3n}{8\pi}\right)^{2/3}$, is a particular important energy scale that characterises the Sommerfeld model.
- It is defined as the highest occupied energy level in a degenerate Fermi gas at $T = 0$.

Chemical potential at $T = 0$ is ϵ_F

- Fermi energy is the maximal (kinetic) energy state occupied by electrons at $T = 0$. It also play the as chemical potential at $T = 0$.
- Chemical potential in general is temperature dependent.
- At $T = 0$, the value of μ , $\mu_0 = \mu(T = 0)$ is then simply equals to the Fermi energy ϵ_F .

Derivation of $\epsilon_F = \mu_0$

- Split the integration of n of Eq. (7) into

$$n = (2m)^{3/2} \frac{4\pi}{h^3} \left[\underbrace{\int_0^{\mu_0} \epsilon^{1/2} n_\epsilon(\epsilon) d\epsilon}_{n_\epsilon(\epsilon)=1} + \underbrace{\int_{\mu_0}^{\infty} \epsilon^{1/2} n_\epsilon(\epsilon) d\epsilon}_{\text{vanishes because } n_\epsilon(\epsilon)=0} \right]$$
$$= (2m)^{3/2} \frac{4\pi}{h^3} \cdot \frac{2}{3} \mu_0^{3/2}.$$

This will give $\mu_0 = \frac{h^2}{2m} \left(\frac{3n}{8\pi}\right)^{2/3} \equiv \epsilon_F$.

3D momentum space

- The N free electrons in the metal will fill the energy levels from the bottom in energy space up to the Fermi energy level.
- Each electron in the energy level i has a corresponding momentum \mathbf{p}_i where $\epsilon_i = \mathbf{p}_i^2/2m$.
- We can imagine each of this state be represented by a point in a 3D momentum space. A vector in the 3D momentum space, $\mathbf{p}_i = \{p_{xi}, p_{yi}, p_{zi}\}$, then represents a quantum state which energy is ϵ_i .
- The electron's start to fill up the energy states from $\epsilon = 0$ up to $\epsilon = \epsilon_F$. Similarly, in the 3D momentum space, these electron will first fill up the lowest momentum states.
- The radius square $|\mathbf{p}_i|^2$ is proportional to the energy of ϵ_i .

Volume element in momentum space, $d^3\mathbf{p}$

- Recall that a 'point' in phase space represents a state which occupies a volume element of $d^3\mathbf{p}d^3\mathbf{r} = h^3$ in the phase space.
- Now, we are considering a point in momentum space (not a phase space). What is the volume element in momentum space representing a momentum state?
- A point in momentum space can be considered as the special case where the spatial contribution being integrated out from the original phase space volume, symbolically,

$$d^3\mathbf{r}d^3\mathbf{p} = h^3 \text{ (phase space volume element)}$$
$$\downarrow \int d^3\mathbf{r} = V$$
$$d^3\mathbf{p} = h^3/V,$$

where V is the 3D volume of the metal containing the free electrons.

Volume element in momentum space, $d^3\mathbf{p}$ (cont.)

- Hence, each 'point' in momentum space occupies a volume of h^3/V , and each of this 'point' represents a quantum state. Each quantum state accommodates two electrons (one for spin up and one for spin down), as allowed by Pauli Exclusion Principle.
- The sphere in the momentum space containing all the states occupied by the Fermi gas is called the Fermi sphere. It has a radius of p_F (definition will be given later).

Counting number of states in the momentum space of radius p_F

- Since there are N free electrons in the metal, we can calculate the radius of the sphere in the momentum space in which these N electrons reside.
- Let the radius of the sphere be p_F , then the volume is $V_F = \frac{4}{3}\pi p_F^3$.
- The number of 'points' in V_F is $V_F/(h^3/V)$ since each 'point' has a volume element of h^3/V .
- Each of these points has a degeneracy of 2 (i.e. each momentum state in the 3D momentum space represents two electrons, one for spin up and one for spin down), hence we have $2 \times V_F V/h^3 = N$, which gives p_F in terms of $n = N/V$:

$$p_F = \left(\frac{3n}{8\pi}\right)^{1/3} h.$$

Fermi sphere in momentum space

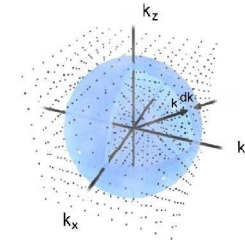


Figure: Representation of a 3D Fermi sphere in momentum space. Each point in the sphere represents a momentum state, and each of these states (a 'point' in the sphere) occupies a 'volume' element of h^3/V . In the figure, the symbol k is used instead of p for momentum.

Fermi momentum, Fermi velocity

- p_F is called the Fermi momentum. It defines the radius of the Fermi sphere. Fermi momentum is the largest momentum of the free electron in the metal in $T = 0$.
- Comparing it with the Fermi energy $\epsilon_F = \left(\frac{3n}{8\pi}\right)^{2/3} \frac{h^2}{2m}$, we can write

$$\epsilon_F = \frac{p_F^2}{2m}.$$

- Fermi velocity is defined as $v_F = p_F/m$.
- We also define Fermi temperature via $kT_F = \epsilon_F$. T_F corresponds to the temperature for which a classical particle must attain in order to have an energy of ϵ_F .

Table showing Fermi energy, temperature, velocity

Table 5.3.3. Values of the Fermi energy, Fermi velocity and Fermi temperature for several metals. For the last row, the Fermi wavelength, see Exercise 3.18.

| | Li | Be | Na | Mg | Al | K | Cu | Ag | Sb | Au |
|------------------------------|-----|------|-----|-----|------|------|-----|-----|------|-----|
| ϵ_F (eV) | 4.7 | 14.3 | 3.2 | 7.1 | 11.7 | 2.1 | 7.0 | 5.5 | 10.9 | 5.5 |
| v_F (10^6 m s $^{-1}$) | 1.3 | 2.25 | 1.1 | 1.6 | 2.0 | 0.85 | 1.6 | 1.4 | 2.0 | 1.4 |
| T_F (10^4 K) | 5.5 | 16.6 | 3.8 | 8.2 | 13.6 | 2.5 | 8.2 | 6.4 | 12.7 | 6.4 |
| λ_F (Å) | | | | | | | | | | |

Fermi gas of most metals is degenerate at room temperature

- For $T \gg T_F$, the free electron gas behaves classically; for $T \ll T_F$, the free electrons in metal behave like a degenerate Fermi gas.
- Since T_F for most metals are of the order $\sim 10^4$ K, this leads to the fact that at room temperature electrons in most metal behave as degenerate Fermi gas rather than as classical particle.
- This explains the unsatisfactory prediction of the Drude model (which assumes the electron as classical gas at room temperature).

Chemical potential in the low and high temperature limits

- At this point, we conclude that
 - 1 the low temperature limit behavior of chemical potential is such that $\lim_{\beta \rightarrow \infty} \mu = \epsilon_F$, a positive constant.
 - 2 In the high temperature limit, $\lim_{\beta \rightarrow 0} \mu = -\infty$.
 - 3 Somewhere between $T = 0$ to $T = \infty$, μ decreases monotonically from ϵ_F at $T = 0$ to become more negative as T increases. At $T = 0.989 T_F$, $\mu_0 = 0$.
- Be noted that for different types of particles have different μ . For example, photon and phonon have $\mu = 0$.
- But for other elementary particles (such as electron, proton, etc) in a GCE, μ is generally a function of temperature, and is particle-type specific.

Graph of chemical potential as function of T/T_F

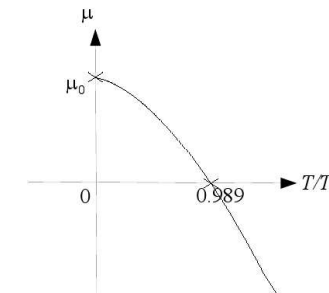


Figure: Chemical potential as function of T/T_F . μ is a monotonically decreasing function of temperature.

If $\mu(T) \approx \epsilon_F$, it's approximately a degenerate Fermi gas at T

- $\mu = \epsilon_F$ is the condition that characterises a degenerate Fermi gas. However, $\mu(T)$ at any arbitrary temperature T is not exactly equal ϵ_F . We would like to know up to what temperature $\mu = \epsilon_F$ holds.
- Knowing this allows us to justify whether electrons in a metal do behave as degenerate Fermi gas or otherwise at an temperature T .

Is $\mu(T) \approx \epsilon_F$ a good approximation at room temperature? (cont.)

- We note that in the low temperature limit,
 $T \ll T_F \Leftrightarrow kT \ll \epsilon_F$,

$$\exp\left[\frac{\epsilon_F}{kT}\left(x - \frac{\mu}{\epsilon_F}\right)\right] \rightarrow 0$$

if

$$x - \frac{\mu}{\epsilon_F} < 0.$$

- In such case, the RHS of Eq. (9) becomes

$$\approx \int_0^{\mu/\epsilon_F} x^{1/2} dx = \frac{2}{3} \left(\frac{\mu}{\epsilon_F}\right)^{3/2}.$$

Equate this to the LHS of Eq. (9) = $\frac{2}{3}$, we arrive at $\mu = \epsilon_F$.

Is $\mu(T) \approx \epsilon_F$ a good approximation at room temperature?

- To do so, we define the dimensionless variable $x = \epsilon/\epsilon_F$ and cast n of Eq. (7) in terms of ϵ_F

$$n = \frac{8\pi}{3} \left(\frac{2m\epsilon_F}{h^2}\right)^{3/2} = (2m)^{3/2} \frac{4\pi}{h^3} \int_0^\infty \frac{\epsilon^{1/2}}{1 + e^{\beta(\epsilon-\mu)}} d\epsilon$$

$$\Rightarrow \frac{2}{3} \epsilon_F^{3/2} = \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{1 + e^{\beta(\epsilon-\mu)}} \quad (8)$$

$$\Rightarrow \frac{2}{3} = \int_0^{\mu/\epsilon_F} \frac{x^{1/2}}{1 + \exp\left[\frac{\epsilon_F}{kT}\left(x - \frac{\mu}{\epsilon_F}\right)\right]} dx + \int_{\mu/\epsilon_F}^\infty \{ \cdot \} dx. \quad (9)$$

Yes, it is.

- In other words, as long as $T \ll T_F$, making $\mu(T) = \epsilon_F$ does not violate Eq. (9).
- What this means is that in the limit $T \ll T_F$, which is fulfilled for most metals at room temperature, the chemical potential at a non-zero temperature $\mu(T)$, with $T \ll T_F$, is well approximated by the Fermi energy ϵ_F , justifying the treatment that the free electrons in metal at room temperature behave like a degenerate Fermi gas.

FD distribution is a step function at $T = 0$

- For the Fermi gas at degenerate state at $T = 0$, $n_\epsilon(\epsilon)$ is a step function in ϵ .
- The Fermi gas begins to deviate from a step function at temperature $T > 0$. The deviation becomes prominent when $T \rightarrow T_F$ or larger.

FD distribution at different temperatures

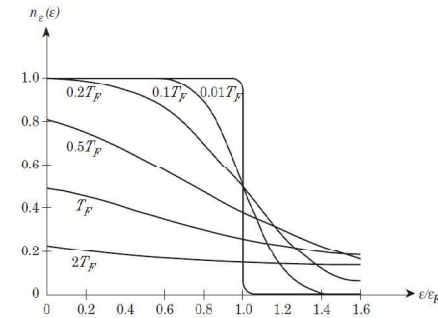


Figure: The FermiDirac occupation function at different temperatures as a function of the dimensionless variable $x = \epsilon/\epsilon_F$. Note that the function deviates from a step function as temperature increases. The tail at which $\epsilon > \epsilon_F$ for $T > 0$ K contains excited electrons into energy states above the Fermi energy level, which are otherwise unoccupied at $T = 0$.

We wish to work out what is the electronic heat capacity in the Sommerfeld model

- From the previous discussion on Debye model, we already knew that phonon vibrations explain fairly well the heat capacity of crystalline lattice at all temperature. Electronic contribution to the heat capacities hence should be tiny. We wish to verify that this is indeed the case.
- To this end we would like to use the free electron's number density distribution (as predicted in the Sommerfeld model) to work out what would be the contribution of the free electron to the heat capacity of metal at a temperature $0 < T \ll T_F$.

The FD distribution has a 'tail' beyond $\epsilon > \epsilon_F$

- First, we would need to know what the average energy of the electrons in a metal $\langle \epsilon \rangle$ is at temperature $0 < T \ll T_F$.
- In terms of ϵ_F , $f_\epsilon(\epsilon) = \frac{3}{2} \epsilon_F^{-3/2} \epsilon^{1/2} [1 + e^{\beta(\epsilon - \mu)}]^{-1}$.
- Note that $n_\epsilon(\epsilon) = [1 + e^{\beta(\epsilon - \mu)}]^{-1}$ is not a strict step function for $T \neq 0$ as is $n_\epsilon(\epsilon)$ at $T = 0$.
- However, as long as $0 < T \ll T_F$, the tail of $n_\epsilon(\epsilon)$ for $0 < T \ll T_F$ extends slightly beyond $\frac{\epsilon}{\epsilon_F} = 1$.
- The slight distortion of $n_\epsilon(\epsilon)$ for $0 < T \ll T_F$ as compared to $n_\epsilon(\epsilon)$ at $T = 0$ can be considered as a perturbation effect due to the non-zero temperature $0 < \frac{T}{T_F} \ll 1$. See the fig. of $n_\epsilon(\epsilon)$ at various T as a function of $\frac{\epsilon}{\epsilon_F}$.

Taylor expands $\langle \epsilon \rangle$ at $\epsilon = \mu$

- Also at $0 < T \ll T_F$, $\mu(T)$ is slightly shifted to the right of μ_0 (which is the chemical potential at $T = 0$), e.g. $\mu(T) \gtrsim \mu_0 \equiv \epsilon_F$.
- Hence for $0 < T \ll T_F$, we can Taylor expand $\langle \epsilon \rangle$ at $\epsilon = \mu(T)$ to the second order in $\frac{T}{T_F}$.

Taylor expands $\langle \epsilon \rangle$ at $\epsilon = \mu$ (cont.)

- i.e, for $0 < T \ll T_F$,

$$\begin{aligned}
 \langle \epsilon \rangle &= \int_0^\infty f_\epsilon(\epsilon) \epsilon d\epsilon \\
 &= \frac{3}{2} \epsilon_F^{-3/2} \int_0^\infty \epsilon^{3/2} [1 + e^{\beta(\epsilon-\mu)}]^{-1} d\epsilon \\
 &= \frac{3}{2} \epsilon_F^{-3/2} \int_0^\mu \epsilon^{3/2} [1 + e^{\beta(\epsilon-\mu)}]^{-1} d\epsilon \\
 &\quad + \frac{3}{2} \epsilon_F^{-3/2} \int_\mu^\infty \epsilon^{3/2} [1 + e^{\beta(\epsilon-\mu)}]^{-1} d\epsilon \\
 &= \frac{3}{2} \epsilon_F^{-3/2} \int_0^\mu \epsilon^{3/2} d\epsilon + \text{perturbative terms in } \frac{T}{T_F}
 \end{aligned} \tag{10}$$

The temperature independent term

- This first term in the RHS of Eq (10) is the non-perturbative term (temperature independent) where $[e^{\beta(\epsilon-\mu)} + 1]^{-1} = 1$ for $\epsilon < \mu$.
- Hence, it can be easily integrated as

$$\frac{3}{2} \epsilon_F^{-3/2} \int_0^\mu \epsilon^{3/2} d\epsilon = \frac{3}{2} \epsilon_F^{-3/2} \cdot \frac{2}{5} \mu^{5/2} = \frac{3}{5} \frac{\mu^{5/2}}{\epsilon_F^{3/2}}.$$

- This unperturbed term is temperature independent.

The perturbative term due to T/T_F

- The temperature dependent perturbation arises from the integration from the tail of $n_\epsilon(\epsilon)$ for the energy range of $\epsilon = \mu$ and beyond, i.e. $\frac{3}{2} \epsilon_F^{-3/2} \int_\mu^\infty \epsilon^{3/2} [1 + e^{\beta(\epsilon-\mu)}]^{-1} d\epsilon$.
- It turns out that (after some lengthy algebra), the second order temperature-perturbed term is

$$\frac{3}{2} \cdot \frac{\pi^2}{4} \mu^{1/2} \frac{(kT)^2}{\epsilon_F^{3/2}} = \frac{3\mu^{1/2} \epsilon_F^{1/2} \pi^2}{8} \left(\frac{T}{T_F} \right)^2.$$

- The first order term in the Taylor expansion vanishes coincidentally.

$\langle \epsilon \rangle$ as a function of temperature

Putting everything together, we now have

$$\langle \epsilon \rangle \simeq \frac{3}{5} \frac{\mu^{5/2}}{\epsilon_F^{3/2}} + \frac{3\mu^{1/2}\epsilon_F^{1/2}\pi^2}{8} \left(\frac{T}{T_F} \right)^2. \quad (11)$$

Note that in Eq (11), $\langle \epsilon(T) \rangle$ is explicitly a function of $T, \mu(T)$.

Obtaining C_V from $\langle \epsilon(T) \rangle$ requires $\mu(T)$ be expressed in terms of N, T

- Next, we would like to obtain the heat capacity of the metal due to the free electron, which is to be derived by taking the partial derivative of $\langle \epsilon \rangle$ with respect to temperature at constant V and N , i.e.

$$C_V = N \left(\frac{\partial \langle \epsilon \rangle}{\partial T} \right)_{N,V}.$$

- To this end, we must express $\mu(T)$ in terms of N, T so that $\langle \epsilon(T) \rangle$ is expressed as function of T without the μ -dependence.

μ as implicit function of T by Taylor expanding Eq. (8)

- In order to express μ in terms of T and N , use the integral relation for ϵ_F in Eq. (8),

$$\frac{2}{3}\epsilon_F^{3/2} = \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{1 + e^{\beta(\epsilon - \mu)}}.$$

- Again, the RHS of (8) is made up of the unperturbed term (comes from the integration for the range $\epsilon = 0$ to $\epsilon = \mu$) and the temperature perturbed term (comes from the integration for the range $\epsilon = \mu$ and beyond).
- Lengthy algebra like that leading to Eq. (11) leads to

$$1 = \frac{3}{2} \frac{\epsilon_F^{-3/2}}{\epsilon_F^{3/2}} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{1 + e^{\beta(\epsilon - \mu)}} \simeq \frac{\mu^{3/2}}{\epsilon_F^{3/2}} + \frac{\pi^2}{8} \left(\frac{\epsilon_F}{\mu} \right)^{1/2} \left(\frac{T}{T_F} \right)^2. \quad (12)$$

Binomial expansion of Eq. (12) using approximation

$$\mu \approx \epsilon_F$$

- Eq. (12) is an algebraic equation expressing how μ is implicitly dependent on T .
- To obtain μ as a function of T explicitly, we approximate $\mu \approx \epsilon_F$ for the μ in the $\frac{T}{T_F}$ term in the RHS, so that Eq. (12) is approximately

$$1 \simeq \frac{\mu^{3/2}}{\epsilon_F^{3/2}} + \frac{\pi}{8} \left(\frac{T}{T_F} \right)^2,$$

leading to

$$\mu \simeq \epsilon_F \left[1 - \frac{\pi^2}{8} \left(\frac{T}{T_F} \right)^2 \right]^{2/3} = \epsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 + \dots \right]$$

- Inserting $\mu = \mu(T)$ in to Eq. (11), we have

$$\langle \epsilon \rangle \simeq \frac{3}{5} \epsilon_F \left[1 + \frac{5\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right]$$

where higher order terms in $\left(\frac{T}{T_F} \right)^4$ is ignored.

- Note that in the limit $T \rightarrow 0$, the average energy $\langle \epsilon \rangle$ is $\frac{3}{5} \epsilon_F$.

Deriving C_V from $\langle \epsilon \rangle$

- Hence, the heat capacity of the metal due to the degenerate Fermi electron gas is

$$\begin{aligned} C_V &= N \left(\frac{\partial \langle \epsilon \rangle}{\partial T} \right)_{N,V} \\ &= \frac{3N\epsilon_F}{5} \frac{\partial}{\partial T} \left[1 + \frac{5\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right] \\ &= \frac{\pi^2 N k}{2} \left(\frac{T}{T_F} \right). \end{aligned}$$

C_V from Sommerfeld model is just what we would wish for

- The result is just what we would wish to obtain in the beginning, that indeed the electronic contribution to the heat capacity to metal is much suppressed than what was predicted by the classical equipartition theorem.
- In classical theory, the equipartition law (incorrectly) predicts that each electron contributes $\frac{3}{2}k$ to the heat capacity, which is not observed in experiment.
- The Sommerfeld model predicts that the electron contribution to the specific heat capacity of metal is $\frac{\pi^2}{2} \frac{T}{T_F} k \ll \frac{3}{2}k$, a result that is consistent with the Debye model on the heat capacity of metal.

Phonon vs electronic contribution to C_V in high and low temperatures

- In most ranges of temperature the heat capacity is dominated by phonon's contribution over electron's.
- At low temperature, i.e. $T \ll \Theta_D$, phonon's contribution is $\propto T^3$ whereas electron's is $\propto T$.
- Hence, below certain temperature threshold, electron's contribution will dominate over phonon's, and the heat capacity's temperature dependence displays a $\propto T$ behavior rather than $\propto T^3$, which is observed experimentally.

Recaping Drude's model

In the Drude model,

- Thermal conductivity is given by Eq (5), $\bar{K} = \frac{1}{3}n\bar{v}^2c\tau$.
- Electrical conductivity is given by Eq (4), $\sigma = \frac{ne^2\tau}{m}$.
- Heat capacity per electron, $c = \frac{3k}{2}$,
- Average kinetic energy, $\frac{m\bar{v}^2}{2} = \frac{3kT}{2}$
- The ratio, $\frac{\bar{K}}{\sigma} = \frac{m\bar{v}^2c}{3e^2} = \frac{3k^2}{2e^2}T$.
- Next, we would like to see how Sommerfeld model calculates these quantities.

Bingo! Sommerfeld model's prediction for the ratio $\frac{K}{\sigma}$

- In Sommerfeld model, $c = \frac{\pi^2}{2} \frac{kT}{T_F}$, $\bar{v} = v_F$.
- Hence

$$\frac{\bar{K}}{\sigma} = \frac{m\bar{v}^2c}{3e^2} = \frac{\pi^2k^2}{3e^2}T = 2.44 \times 10^{-8} \text{W}\Omega/\text{K}^2T.$$

- The coefficient to the temperature in the ratio is

$$\frac{\pi^2k^2}{3e^2} / \frac{3k^2}{2e^2} T = \frac{2\pi^2}{9} \sim 2$$

times larger than that in Drude's model.

- As such, the Sommerfeld model provides a much satisfying quantitative explanation to the Wiedemann-Franz law.