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Notes on
STATISTICAL MECHANICS

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It was certainly not by design that the particles fell into order
They did not work out what they were going to do,
but because many of them by many chances
struck one another in the course of infinite time
and encountered every possible form and movement,
that they found at last the disposition they have,
and that is how the universe was created.

Titus Lucretius Carus (94 BC - 55BC)
de Rerum Natura

Everything existing in the universe is the fruit of chance and necessity.
Democritus (370 BC)

The moving finger writes; and, having writ,
moves on : nor all your piety nor wit
shall lure it back to cancel half a line
nor all your tears wash out a word of it

Omar Khayyam (1048 - 1131)

Whatever happened,
happened for good.
Whatever is happening,
is happening for good.
Whatever will happen,
will happen for good.

Bhagavat Gita

"... Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn ... to study statistical mechanics. Perhaps it will be wise to approach the subject rather cautiously..."

David Goodstein, *States Matter*, Dover (1975) (opening lines)

All models are wrong, some are useful. George E P Box

DRAFT

Contents

Quotes	i
1. Micro-Macro Synthesis	3
1.1 Aim of Statistical Mechanics	3
1.2 Micro - Macro Connections	4
1.2.1 Boltzmann Entropy	4
1.2.2 Boltzmann-Gibbs-Shannon Entropy	4
1.2.3 Heat	5
1.2.4 Work	5
1.2.5 Helmholtz Free Energy	5
1.2.6 Energy Fluctuations and Heat Capacity	6
1.3 Micro World : Determinism and Time-Reversal Invariance	6
1.4 Macro World : Thermodynamics	6
1.5 Books	9
1.6 Extra Reading : Books	13
1.7 Extra Reading : Papers	13
2. Maxwell's Mischief	15
2.1 Experiment and Outcomes	15
2.2 Sample space and events	15
2.3 Probabilities	16
2.4 Rules of probability	16
2.5 Random variable	17
2.6 Maxwell's mischief : Ensemble	18
2.7 Calculation of probabilities from an ensemble	19
2.8 Construction of ensemble from probabilities	19
2.9 Counting of the elements in events of the sample space : Coin tossing	19
2.10 Gibbs ensemble	22
2.11 Why should a Gibbs ensemble be large ?	22
3. Binomial, Poisson, and Gaussian	27
3.1 Binomial Distribution	27
3.2 Moment Generating Function	29

3.3	Binomial \rightarrow Poisson	31
3.4	Poisson Distribution	32
3.4.1	Binomial \rightarrow Poisson à la Feller	33
3.5	Characteristic Function	34
3.6	Cumulant Generating Function	35
3.7	The Central Limit Theorem	35
3.8	Poisson \rightarrow Gaussian	38
3.9	Gaussian	38
4.	Isolated System: Micro canonical Ensemble	41
4.1	Preliminaries	41
4.2	Configurational Entropy	42
4.3	Ideal Gas Law : Derivation	43
4.4	Boltzmann Entropy \rightarrow Clausius' Entropy	44
4.5	Some Issues on Extensivity of Entropy	44
4.6	Boltzmann Counting	44
4.7	Micro canonical Ensemble	45
4.8	Heaviside and his Θ Function	46
4.9	Dirac and his δ Function	46
4.10	Area of a Circle	48
4.11	Volume of an N -Dimensional Sphere	50
4.12	Classical Counting of Micro states	52
4.12.1	Counting of the Volume	52
4.13	Density of States	52
4.13.1	A Sphere Lives on its Outer Shell : Power Law can be Intriguing	53
4.14	Entropy of an Isolated System	53
4.15	Properties of an Ideal Gas	54
4.15.1	Temperature	54
4.15.2	Equipartition Theorem	54
4.15.3	Pressure	54
4.15.4	Ideal Gas Law	55
4.15.5	Chemical Potential	55
4.16	Quantum Counting of Micro states	57
4.16.1	Energy Eigenvalues : Integer Number of Half Wave Lengths in L	58
4.17	Chemical Potential : Toy Model	60
5.	Closed System : Canonical Ensemble	63
5.1	What is a Closed System ?	63
5.2	Toy Model à la H B Callen	63
5.3	Canonical Partition Function	64
5.3.1	Derivation à la Balescu	64
5.4	Helmholtz Free Energy	66
5.5	Energy Fluctuations and Heat Capacity	68

5.6	Canonical Partition Function : Ideal Gas	69
5.7	Method of Most Probable Distribution	70
5.8	Lagrange and his Method.....	73
5.9	Generalisation to N Variables	75
5.10	Derivation of Boltzmann Weight.....	76
5.11	Mechanical and Thermal Properties.....	77
5.12	Entropy of a Closed System.....	78
5.13	Free Energy to Entropy	79
5.14	Microscopic View : Heat and Work	80
	5.14.1 Work in Statistical Mechanics : $W = \sum_i p_i dE_i$	81
	5.14.2 Heat in Statistical Mechanics : $q = \sum_i E_i dp_i$	82
5.15	Adiabatic Process - a Microscopic View	82
5.16	$Q(T, V, N)$ for an Ideal Gas	83
6.	Open System : Grand Canonical Ensemble	87
6.1	What is an Open System ?	87
6.2	Micro-Macro Synthesis : \mathcal{Q} and \mathcal{G}	90
6.3	Statistics of Number of Particles	92
	6.3.1 Euler and his Theorem	92
	6.3.2 \mathcal{Q} : Connection to Thermodynamics.....	92
	6.3.3 Gibbs-Duhem Relation	92
	6.3.4 Average number of particles in an open system, $\langle N \rangle$.	93
	6.3.5 Probability $P(N)$, that there are N particles in an open system	93
	6.3.6 Number Fluctuations	94
	6.3.7 Number Fluctuations and Isothermal Compressibility	95
	6.3.8 Alternate Derivation of the Relation : $\sigma_N^2 / \langle N \rangle^2 =$ $k_B T k_T / V$	97
6.4	Energy Fluctuations	99
7.	Quantum Statistics	105
7.1	Occupation Number Representation.....	105
7.2	Open System and $\mathcal{Q}(T, V, \mu)$	105
7.3	Fermi-Dirac Statistics	108
7.4	Bose-Einstein Statistics	108
7.5	Classical Distinguishable Particles	109
7.6	Maxwell-Boltzmann Statistics	109
	7.6.1 $Q_{MB}(T, V, N) \rightarrow Q_{MB}(T, V, \mu)$	110
	7.6.2 $Q_{MB}(T, V, \mu) \rightarrow Q_{MB}(T, V, N)$	111
7.7	Thermodynamics of an open system	111
7.8	Average number of particles, $\langle N \rangle$	112
	7.8.1 Maxwell-Boltzmann Statistics	112
	7.8.2 Bose-Einstein Statistics	113

7.8.3	Fermi-Dirac Statistics	113
7.8.4	Study of a System with fixed N Employing Grand Canonical Formalism	113
7.9	Fermi-Dirac, Maxwell-Boltzmann and Bose-Einstein Statis- tics are the same at High Temperature and/or Low Densities	114
7.9.1	Easy Method : $\rho\Lambda^3 \rightarrow 0$	114
7.9.2	Easier Method : $\lambda \rightarrow 0$	116
7.9.3	Easiest Method $\hat{\Omega}(n_1, n_2, \dots) = 1$	117
7.10	Mean Occupation Number	117
7.10.1	Ideal Fermions	118
7.10.2	Ideal Bosons	118
7.10.3	Classical Indistinguishable Ideal Particles	118
7.11	Mean Occupation : Some Remarks	119
7.11.1	Fermi-Dirac Statistics	119
7.11.2	Bose-Einstein Statistics	119
7.11.3	Maxwell-Boltzmann Statistics	120
7.11.4	At High T and/or Low ρ all Statistics give the same $\langle n_k \rangle$	120
7.12	Occupation Number : Distribution and Variance	121
7.12.1	Fermi-Dirac Statistics and Binomial Distribution	122
7.12.2	Bose-Einstein Statistics and Geometric Distribution .	122
7.12.3	Maxwell-Boltzmann Statistics and Poisson Distribution	124
8.	Bose-Einstein Condensation	127
8.1	Introduction	127
8.2	$\langle N \rangle = \sum_k \langle n_k \rangle$	127
8.3	Summation to Integration	128
8.4	Graphical Inversion and Fugacity	130
8.5	Treatment of the Singular Behaviour	131
8.6	Bose-Einstein Condensation Temperature	133
8.7	Grand Potential for bosons	134
8.8	Energy of Bosonic System	135
8.8.1	$T > T_{\text{BEC}}$	136
8.8.2	$T \leq T_{\text{BEC}}$	136
8.9	Specific Heat Capacity of bosons	137
8.9.1	$\frac{C_V}{Nk_B}$ for $T > T_{\text{BEC}}$	137
8.9.2	Third Relation : $\frac{1}{\lambda} \frac{d\lambda}{dT} = -\frac{3}{2T} \frac{g_{3/2}(\lambda)}{g_{1/2}(\lambda)}$	138
8.9.3	$\frac{C_V}{Nk_B}$ for $T < T_{\text{BEC}}$	139
8.10	Mechanism of Bose-Einstein Condensation	140
9.	Elements of Phase Transition	147

10. Statistical Mechanics of Harmonic Oscillators 157

 10.1 Classical Harmonic Oscillators 157

 10.1.1 Helmholtz Free Energy 158

 10.1.2 Thermodynamic Properties of the Oscillator System . 159

 10.1.3 Quantum Harmonic Oscillator 159

 10.1.4 Specific Heat of a Crystalline Solid 161

 10.1.5 Einstein Theory of Specific Heat of Crystals 164

 10.1.6 Debye Theory of Specific Heat 165

 10.1.7 Riemann Zeta Function 167

 10.1.8 Bernoulli Numbers 167

Index 169

DRAFT

DRAFT

1. Micro-Macro Synthesis

1.1 Aim of Statistical Mechanics

Statistical mechanics provides a theoretical bridge that takes you from the micro world¹, to the macro world². The chief architects of the bridge were Ludwig Eduard Boltzmann (1844 - 1906), James Clerk Maxwell(1831-1879), Josiah Willard Gibbs(1839-1903) and Albert Einstein(1879-1953).

Statistical Mechanics makes an attempt to derive the macroscopic properties of an object from the properties of its microscopic constituents and the interactions amongst them. It tries to provide a theoretical basis for the empirical thermodynamics - in particular the emergence of the time-asymmetric Second law of thermodynamics from the time-symmetric microscopic laws of classical and quantum mechanics.

- When do we call something, a macroscopic object, and something a microscopic constituent ?

The answer depends crucially on the object under study and the properties under investigation. For example,

- if we are interested in properties like density, pressure, temperature *etc.* of a bottle of water, then the molecules of water are the microscopic constituents; the bottle of water is the macroscopic object.
- in a different context, an atom constitutes a macroscopic object; the electrons, protons and neutrons form its microscopic constituents.
- A polymer is a macroscopic object; the monomers are its microscopic constituents.
- A society is a macroscopic object; men, women, children and perhaps monkeys are its microscopic constituents.

Statistical mechanics asserts that if you know the properties of the microscopic constituents and how they interact with each other, then you can make predictions about its macroscopic behaviour.

¹ of Newton, Schrödinger, Maxwell, and a whole lot of other scientists who developed the subjects of classical mechanics, quantum mechanics, and electromagnetism

² of Carnot, Clausius, Kelvin, Helmholtz and several others responsible for the birth and growth of thermodynamics

1.2 Micro - Macro Connections

1.2.1 Boltzmann Entropy

The first and the most important link, between the micro(scopic) and the macro(scopic) worlds is given by,

$$S = k_B \ln \widehat{\Omega}(E, V, N). \quad (1.1)$$

It was proposed by Boltzmann³. S stands for entropy and belongs to the macro world described by thermodynamics. $\widehat{\Omega}$ is the number of micro states of a macroscopic system⁴. k_B is the Boltzmann constant⁵ that establishes correspondence of the statistical entropy of Boltzmann to the thermodynamic entropy of Clausius⁶.

1.2.2 Boltzmann-Gibbs-Shannon Entropy

More generally we have the Boltzmann-Gibbs-Shannon entropy given by,

$$S = -k_B \sum_i p_i \ln p_i. \quad (1.2)$$

The micro states are labelled by i and the sum is taken over all the micro states of the macroscopic system; The probability is denoted by p_i .

An interesting issue : Normally we resort to the use of probability only when we have inadequate data about the system or incomplete knowledge of the phenomenon under study. Thus, such an enterprise is sort of tied to our ignorance. Keeping track of the positions and momenta of some 10^{30} molecules *via* Newton's equations is undoubtedly an impossible task. It was indeed the genius of Boltzmann which correctly identified that macroscopic phenomena are tailor-made for a statistical description. It is one thing to employ statistics as a convenient tool to study macroscopic phenomena but quite another thing to attribute an element of truth to such a description. But then this is what we are doing precisely in Eq. (1.2) where we express entropy, which is a property of an object, in terms of probabilities. It is definitely a bit awkward to think that a property of an object is determined by what we know or what we do not know about it! But remember in quantum mechanics

³ engraved on the tomb of Ludwig Eduard Boltzmann (1844-1906) in Zentralfriedhof, Vienna.

⁴ For example an ordered set of six numbers, three positions and three momenta specify a single particle. An ordered set of $6N$ numbers specify a macroscopic system of N particles. The string labels a micro state.

⁵ $k_B = 1.381 \times 10^{-23}$ joules (kelvin)⁻¹. We have $k_B = R/A$ where $R = 8.314$ joules (kelvin)⁻¹ is the universal gas constant and $A = 6.022 \times 10^{23}$ (mole)⁻¹ is the Avagadro number.

⁶ Note that the quantity $\ln \widehat{\Omega}$ is a number. Clausius' entropy is measured in units of joules/kelvin. Hence the Boltzmann constant is k_B and has units joules/kelvin. It is a conversion factor and helps you go from one unit of energy (joule) to another unit of energy (kelvin).

the observer, the observed, and the observation are all tied together : the act of measurement places the system, at the time of observation, in one of eigenstates of the observable; we can make only probabilistic statement about the eigenstate the wave function of the system would collapse into. For a discussion on this subtle issue see the beautiful tiny book of Carlo Rovelli⁷ .

Two important entities we come across in thermodynamics are heat and work. They are the two means by which a thermodynamic system transacts energy with its surroundings or with another thermodynamic system. Heat and work are described microscopically as follows.

1.2.3 Heat

$$q = \sum_i E_i dp_i. \quad (1.3)$$

The sum runs over all the micro states. E_i is the energy of the system when it is in micro state i . The probability that the system can be found in micro state i given by p_i . We need to impose an additional constraint that $\sum_i dp_i$ is zero to ensure that the total probability is unity.

1.2.4 Work

The statistical description of work is given by

$$W = \sum_i p_i dE_i. \quad (1.4)$$

E_i is the energy of the system when it is in the micro state labelled by the index i .

1.2.5 Helmholtz Free Energy

An important thermodynamic property of a closed system is Helmholtz free energy given by,

$$F = -k_B T \ln Q(T, V, N). \quad (1.5)$$

Helmholtz free energy $F(T, V, N)$ of thermodynamics⁸ is related to the canonical partition function $Q(T, V, N)$ of statistical mechanics. This is another important micro-macro connection for a closed system. The canonical partition function is the sum of the Boltzmann weights of the micro states of the closed system. $Q(\beta, V, N) = \sum_i \exp(-\beta E_i)$.

⁷ Carlo Rovelli, *Seven Brief Lessons in Physics*, Translated by Simon Carnell and Erica Segre, Allen Lane an imprint of Penguin Books (2015)pp.54-55.

⁸ In thermodynamics Helmholtz free energy, $F(T, V, N)$ is expressed by the Legendre transform of $U(S, V, N)$, where we transform S to T employing the relation

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, N} \quad \text{and } U \text{ to } F : F = U - TS;$$

1.2.6 Energy Fluctuations and Heat Capacity

The next equation that provides a micro-macro synthesis is given by,

$$\sigma_E^2 = k_B T^2 C_V. \quad (1.6)$$

This relation connects the specific heat at constant volume (C_V), which we come across when we study thermodynamics, to the statistical fluctuations (σ_E^2) of energy in a closed system.

We shall see of several such micro-macro connections in the course of study of statistical mechanics. We can say the aim of statistical mechanics is to synthesise the macro world from the micro world. This is not an easy task. Why ? Let us spend a little bit of time on this question.

1.3 Micro World : Determinism and Time-Reversal Invariance

The principal character of the micro world is *determinism* and *time-reversal invariance*. Determinism implies that *the entire past and the entire future is frozen in the present*. The solar system is a good example. If you know the positions and momenta of all the planets now, then the Newtonian machinery is adequate to tell you where the planets shall be a thousand years from now and where they were some ten thousand years ago.

In the micro world of Newton and Schrödinger, we can not tell which direction the time flows. Both directions are equally legitimate and equally unverifiable. Microscopic laws do not distinguish the future from the past. They are time-reversal invariant; *i.e.* the equations are invariant under transformation of $t \rightarrow -t$.

1.4 Macro World : Thermodynamics

On the other hand, the macro world obeys the laws of thermodynamics.

- The **zeroth law** tells us of thermal equilibrium; it provides a basis for the thermodynamic property temperature. It is the starting point for the game of thermodynamics.
- The **first law** is an intelligent articulation of the law of conservation of energy; it provides a basis for the thermodynamic property called the internal energy. You can put in energy into a system or take it out, by heat or by work. Thus the change in the internal energy (dU) of a thermodynamic system equals the energy transacted by it with the surroundings or with another thermodynamic system by heat $\bar{d}q$ and work $\bar{d}W$. Thus $dU = \bar{d}q + \bar{d}W$. The bar on d reminds us that these quantities are small quantities but not exact differentials. Heat and work are not properties of a thermodynamic system; rather they describe thermodynamic processes.

- The **second law** tells us that come what may, an engine can not deliver work equivalent to the energy it has drawn by heat from a heat source. However an engine can draw energy by work and deliver exactly equivalent amount by heat. The second law is a statement of this basic asymmetry between "heat→ work" and "work→ heat" conversions. The Second law provides a basis for the thermodynamic property called entropy. The entropy of a system increases by $dS = \delta q/T$ when it absorbs reversibly δq amount of energy by heat at constant temperature. The second law says that in any process entropy increases or remains constant : $\Delta S \geq 0$.
- The **third law** tells that entropy vanishes at absolute zero temperature. Notice that in thermodynamics only change in entropy is defined : $dS = \delta q/T$. Since dS is an exact differential we can assert S as a thermodynamic variable and it describes a property of the system. The third law demands that this property is zero at absolute zero and hence we can assign a value S at any temperature. We can say the third law provides a basis for absolute zero temperature on entropy scale.

Of these, the second law is tricky. It breaks the time-symmetry present in the microscopic descriptors. Macroscopic behaviour is **not** time-reversal invariant. There is a definite direction of time - the direction of increasing entropy.

How do we comprehend the time asymmetric macroscopic behaviour emerging from the time symmetric microscopic laws ?

Let us make life simpler by attributing two aims to statistical mechanics. The first is to provide a machinery for calculating the thermodynamic properties of a system on the basis of the properties of its microscopic constituents *e.g.* atoms and molecules, and their mutual interactions.

Statistical Mechanics has been eminently successful in this enterprise. This is precisely why we are studying this subject.

The second aim is to derive the Second law of thermodynamics. Statistical Mechanics has not yet had any spectacular success on this count. However, some recent developments in non linear dynamics and chaos, have shown there is indeed an unpredictability in some (non-linear) deterministic system; we now know that *determinism does not necessarily imply predictability*. This statement, perhaps, provides the *raison d'etre* for the 'statistics' in statistical mechanics.

In these lectures I shall not address the second issue - concerning the emergence of time asymmetry observed in macroscopic phenomena. I shall leave this question to the more knowledgeable and better equipped physicists/philosophers. Instead we shall concentrate on how to derive the properties of a macroscopic system from those of its microscopic constituents and their interactions.

I shall tell you of the elementary principles of statistical mechanics. I shall be as pedagogical as possible. Stop me when you do not understand.

I shall cover topics in

- micro canonical ensemble that provides a description of isolated system;
- canonical ensemble, useful in the study of closed system;
- grand canonical ensemble that describes open system.

I shall discuss equilibrium fluctuations of

- energy in canonical ensemble and relate them to heat capacity;
- number of molecules in an open system and relate them to isothermal compressibility.

Within the framework of grand canonical ensemble I shall discuss Bose-Einstein, Fermi-Dirac and Maxwell Boltzmann statistics.

I shall deal with ideal gas, and classical and quantum harmonic oscillators. I shall discuss Bose Einstein condensation in some details with an emphasis on the mechanism.

While on quantum harmonic oscillators, I shall discuss statistical mechanics of phonons emerging due to quantization of displacement field in a crystalline lattice, and photons arising due to quantization of electromagnetic field.

Maxwell's demon is a mischievous entity. The demon has a simple goal. Let me explain briefly.

For every thermodynamic property, we have, in statistical mechanics, a corresponding statistical quantity. We take the average of the statistical quantity over a suitable ensemble⁹ and relate it to its thermodynamic counterpart. Thus entropy is a statistical entity. It is a mere number. It depends on the number of micro states accessible to a macroscopic system, consistent with the constraints. If entropy is statistical then the second law which states that entropy invariably increases in an irreversible process, should be a statistical statement. If so, there is a non-zero probability that the second law would be violated. Maxwell constructed a demon that violates the second law ... a demon that extracts work from an equilibrium system. I shall discuss Maxwell's demon and its later incarnations.

Toward the end, I shall discuss some recent developments in thermodynamics - work fluctuation theorems and second law violations. I shall assume you are all comfortable with calculus. I shall also assume you have a nodding acquaintance with thermodynamics.

Let me end this section by giving a list of some books and articles on statistical mechanics and thermodynamics that have caught my fancy. This list is by no way exhaustive.

⁹ micro canonical, for isolated system, canonical for closed system and grand canonical for open systems

1.5 Books

- **R K Pathria**, *Statistical Mechanics*, Second Edition, Butterworth - Heinemann (1996). A popular book. Starts with a beautiful historical account of the subject. Contains a very large collection of interesting, non-trivial problems, some of which are taxing ! You will learn how to do statistical mechanics from this book.
- **Donald A McQuarrie**, *Statistical Mechanics*, Harper & Row (1976). A beautiful book with emphasis on applications. Contains excellent problems; physical chemists or chemical physicists will feel more at home with this book.
- **R Balescu**,, *Equilibrium and Non-Equilibrium Statistical Mechanics*, Wiley (1975). An insightful book with emphasis on conceptual issues. Irreversibility is explained neatly. I shall tell you how to derive canonical partition function, borrowing from this book.
- **David Goodstein**, *States of Matter*, Dover (2002). A Delightful and entertaining text. You are reminded of Feynman's writing when you read this book. The discussion on dimensional analysis is excellent. This book is a must in your bookshelf.
- **Debashish Chowdhury and Dietrich Stauffer**, *Principles of Equilibrium Statistical Mechanics*, Wiley-VCH (2000). An easy to read and enjoyable book. Discusses applications to several fields. Contains a good collection of interesting problems.
- **F Rief**, *Fundamentals of statistical and thermal physics*, McGraw-Hill (1965). One of the best text books on statistical thermodynamics. Rief develops thermal physics entirely in the vocabulary of statistical mechanics. As a result after reading this book, you will get an uneasy feeling that thermodynamics has been relegated to the status of an uninteresting appendix to statistical mechanics. My recommendation : read this book for learning statistical - thermodynamics; then read Callen and/or Van Ness for learning thermodynamics. Then you will certainly fall in love with both statistical mechanics and thermodynamics separately!
- **Palash B Pal**, *An Introductory Course of Statistical Mechanics*, Narosa (2008). A book with a broad perspective and with emphasis on relativistic systems.
- **D Chandler**, *Introduction to Modern Statistical Mechanics*, Oxford University Press, New York (1987). A book that connects neatly the traditional to modern methods of teaching statistical mechanics; gives an excellent and simple introduction to re-normalization groups. A great book for the teachers also.
- **Claude Garrod**, *Statistical Mechanics and Thermodynamics*, Oxford University Press (1995). A good book at an introductory level; neatly organized; pedagogic; nice problems and exercises. I shall borrow from this book for teaching micro canonical ensemble.

- **Kerson Huang**, *Statistical Mechanics*, Second Edition, Wiley India (2011). Generations after generations of physicists have learnt statistical mechanics from this book. It is perhaps one of a very few books that take kinetic theory and Boltzmann transport equation as a starting point. Historically, statistical mechanics originated from the work of Ludwig Eduard Boltzmann. After all, it is Boltzmann transport equation - with its collision term obeying stosszahlansatz¹⁰ that establishes irreversible march toward thermal equilibrium - an important point that is either overlooked or not adequately emphasized in most of the text books on statistical mechanics.

The book contains three parts; the first is on thermodynamics; the second on statistical mechanics; and the third on special topics in statistical mechanics.

Do not learn thermodynamics from this book; you will lose interest. The other two parts are excellent - especially the third on special topics.

I would recommend retain your copy of the first edition of this book. Huang has omitted in his second edition, several interesting discussions present in the first edition.

- **Kerson Huang**, *Introduction to Statistical Physics*, Second Edition, CRC Press (2009). I think Huang has made an hurried attempt to 'modernize' his earlier classic : "Statistical Mechanics". I do not recommend this book to students taking their first course in statistical mechanics. However a discerning teacher will find this book very useful. Beware of typos, several of them.
- **J W Gibbs**, *Elementary Principles in Statistical Mechanics*, Schribner, New York (1902). A seminal work on statistical mechanics. It is indeed a thrilling experience to read statistical mechanics in the words of one of its masters. The book looks at canonical formalism in a purely logical fashion. Read this book after becoming a bit familiar with statistical mechanics.
- **Avijit Lahiri**, *Statistical Mechanics : An Elementary Outline*, Revised Edition, Universities Press (2008). A neat and well planned book, though somewhat idiosyncratic. Focuses on bridging the micro world described by quantum mechanics to the macro world of thermodynamics. Concepts like mixed states, reduced states *etc.* provide the basic elements in the development of the subject. The book contains a good collection of worked out examples and problems.
- **Joon Chang Lee**, *Thermal physics - Entropy and Free Energies*, World Scientific (2002). Joon Chang Lee presents statistical thermodynamics in an unorthodox and distinctly original style. The presentation is so simple and so beautiful that you do not notice that the book is written in an awful English and at several places, the language is flawed.

¹⁰ collision number assumption or also known as molecular chaos

- **James P Sethna**, *Entropy, Order Parameters, and Complexity*, Clarendon Press, Oxford (2008). James Sethna covers an astonishingly wide range of modern applications; a book, useful not only to physicists, but also to biologists, engineers, and sociologists. I find exercises and footnotes very interesting; often more interesting than the main text!
- **C Kittel**, and **H Krömer**, *Thermal physics*, W H Freeman (1980). A good book; somewhat terse. I liked the parts dealing with entropy, and Boltzmann weight; contains a good collection of examples.
- **Daniel V Schröder**, *An Introduction to Thermal Physics*, Pearson (2000). Schröder has excellent writing skills. The book reads well. Contains plenty of examples. Somewhat idiosyncratic.
- **M Glazer**, and **J Wark**, *Statistical Mechanics : A Survival Guide*, Oxford University Press (2010). This book gives a neat introduction to statistical mechanics; well organized; contains a good collection of worked-out problems; a thin book and hence does not threaten you !
- **H C Van Ness**, *Understanding Thermodynamics*, Dover (1969). This is an awesome book; easy to read and very insightful. In particular, I enjoyed reading the first chapter on the first law of thermodynamics, the second on reversibility, and the fifth and sixth on the second law. My only complaint is that Van Ness employs British Thermal Units. Another minor point : Van Ness takes the work done by the system as positive and that done on the system as negative. Engineers always do this. Physicists and chemists employ the opposite convention. For them the sign coincides with the sign of change of internal energy caused by the work process. If the transaction leaves the system with higher energy, work done is positive; if it results in lowering of energy, the work done is negative.
- **H B Callen**, *Thermodynamics*, John Wiley (1960). Callen sets the standard for a text book. This book has influenced generations of teachers and students alike, all over the world. Callen is a house hold name in the community of physicists. The book avoids all the pitfalls in the historical development of thermodynamics by introducing a postulational formulation.
- **H B Callen**, *Thermodynamics and an Introduction to thermostatistics*, Second Edition, Wiley, India (2005). Another classic from H B Callen. He has introduced statistical mechanics without undermining the inner strength and beauty of thermodynamics. In fact, the statistical mechanics he presents, enhances the beauty of thermodynamics. The simple toy problem with a red die (the closed system) and two white dice (the heat reservoir), and the restricting sum to a fixed number (conservation of total energy) motivates beautifully the canonical formalism. The pre-gas model introduced for explaining grand canonical ensemble of fermions and bosons is simply superb. I also enjoyed the discussions on

the subtle mechanism underlying Bose condensation. I can go on listing several such gems. The book is full of beautiful insights.

A relatively inexpensive, Wiley student edition of the book is available in the Indian market. Buy your copy now !

- **Gabriel Weinreich**, *Fundamental Thermodynamics*, Addison Wesley (1968). Weinreich is eminently original; has a distinctive style. Perhaps you will feel uneasy when you read this book for the first time. But very soon, you will get used to Weinreich's idiosyncrasy; and you would love this book.
- **N D Hari Dass**, *Principles of Thermodynamics*, CRC Press, Taylor and Francis (2014). A beautiful book on thermodynamics; perhaps the most recent to arrive at the market place. Hari Dass is a great story teller. He has the magic to convert prosaic things into exciting entities. If you are a beginner and plan to learn thermodynamics, I will recommend this book to you. There is pedagogy; titbits of history scattered all through; and no dearth of rigor. You will learn thermodynamics correctly. I will recommend this book to an expert also. I am sure he will find something new and something surprising in every chapter.
The only complaint I have is, the book gives a feeling that the last word on thermodynamics has been said. I don't think so. We are still struggling to know what heat is. Thermodynamics tells us that heat is a process by which energy is transacted amongst macroscopic bodies. This helps because you will not mistake heat for a property of the system. But then this statement does not say anything about what heat is. We know heat is something hidden somewhere in the 10^{24} or so of trajectories; you can not compute these trajectories : not only because the number is obscenely large but also because they are inherently unpredictable due to sensitive dependence on the in initial conditions. It is in this region of the phase space where chaos reigns we have to look for a meaning of heat. I would like to hear of these in the words of Hari Dass, perhaps in the next edition of his book !
- **C B P Finn**, *Thermal Physics*, Nelson Thornes (2001). Beautiful; concise; develops thermodynamics from first principles. Finn brings out the elegance and power of thermodynamics.
- **Max Planck**, *Treatise on Thermodynamics*, Third revised edition, Dover; first published in the year 1897. Translated from the seventh German edition (1922). A carefully scripted master piece; emphasises chemical equilibrium. I do not think any body can explain irreversibility as clearly as Planck does. If you think third law of thermodynamics is irrelevant, then read the last chapter. You may change your opinion.
- **E Fermi**, *Thermodynamics*, Dover (1936). A great book from a great master; concise; the first four chapters (on thermodynamic systems, first law, the Second law, and entropy) are superb. I also enjoyed the parts covering Clapeyron and van der Waal equations.

- **J S Dugdale**, *Entropy and its physical meaning*, Taylor and Francis (1998). An amazing book. Dugdale de-mystifies entropy. This book is not just about entropy alone, as the name would suggest. It teaches you thermodynamics and statistical mechanics. A book that cleverly avoids unnecessary rigour.
- **M W Zamansky**, and **R H Dittman**, *Heat and Thermodynamics, an intermediate textbook*, Sixth edition, McGraw-Hill (1981). A good and dependable book for a first course in thermodynamics.
- **R Shanthini**, *Thermodynamics for the Beginners*, Science Education Unit, University of Peredeniya (2009). Student-friendly. Shanthini has anticipated several questions that would arise in the mind of an oriental student when he or she learns thermodynamics for the first time. The book has a good collection of worked out examples. A bit heavy on heat engines.
- **Dilip Kondepudi** and **Ilya Prigogine**, *Modern Thermodynamics : From heat engines to Dissipative Structures*, John Wiley (1998). Classical, statistical, and non equilibrium thermodynamics are woven into a single fabric. Usually chemists present thermodynamics in a dry fashion. This book is an exception; it tells us learning thermodynamics can be fun. Contains lots of interesting tit-bits on history. Deserves a better cover design; the present cover looks cheap.

1.6 Extra Reading : Books

- **Nicolaus Sadi Carnot**, *Reflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance*, Paris (1824); for English translation see **Sadi Carnot**, *Reflections on the motive power of fire and on machines fitted to develop that power*, in **J Kestin** (Ed.) *The second law of thermodynamics*, Dowden, Hutchinson and Ross, Stroudsburg, PA (1976)p.16
- **J Kestin** (Ed.), *The second law of thermodynamics*, Dowden, Hutchinson and Ross (1976)
- **P Atkin**, *The Second Law*, W H Freeman and Co. (1984)
- **G Venkataraman**, *A hot story*, Universities Press (1992)
- **Michael Guillen**, *An unprofitable experience : Rudolf Clausius and the second law of thermodynamics* p.165, in *Five Equations that Changed the World*, Hyperion (1995)
- **P Atkins**, *Four Laws that drive the Universe*, Oxford university Press (2007).
- **Christopher J T Lewis**, *Heat and Thermodynamics : A Historical Perspective*, First Indian Edition, Pentagon Press (2009)
- **S G Brush**, *Kinetic theory* Vol. 1 : *The nature of gases and of heat*, Pergamon (1965) Vol. 2 : *Irreversible Processes*, Pergamon (1966)

- **S G Brush**, *The kind of motion we call heat*, Book 1 : *Physics and the Atomists* Book 2 : *Statistical Physics and Irreversible Processes*, North Holland Pub. (1976)
- **I Prigogine**, *From Being to Becoming*, Freeman, San Francisco (1980)
- **K P N Murthy**, *Excursions in thermodynamics and statistical mechanics*, Universities Press (2009)

1.7 Extra Reading : Papers

- **K K Darrow**, *The concept of entropy*, American Journal of Physics **12**, 183 (1944).
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- **T Rothman**, *The evolution of entropy*, pp.75-108, in *Science á la mode : physical fashions and fictions* Princeton University Press (1989)
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- **G. Cook**, and **R H Dickerson**, *Understanding the chemical potential*, American Journal of Physics **63**, 738 (1995).
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- T P Suresh, Lisha Damodaran, and K M Udayanandan, *Gibbs' Paradox : Mixing and Non-Mixing Potentials*, Physics Education **32**(3), Article No. 4 (2016).
- **B J Cherayil**, *Entropy and the direction of natural change*, Resonance **6**, 82 (2001)
- **J K Bhattacharya**, *Entropy á la Boltzmann*, Resonance **6**, 19 (2001)
- **J Srinivasan**, *Sadi Carnot and the second law of thermodynamics*, Resonance **6** 42 (2001)
- **D C Shoepf**, *A statistical development of entropy for introductory physics course*, American Journal of Physics **70**, 128 (2002).
- **K P N Murthy**, *Josiah Willard Gibbs and his Ensembles*, Resonance **12**, 12 (2007).

2. Maxwell's Mischief

2.1 Experiment and Outcomes

Toss a coin : You get either "Heads" or "Tails". The experiment has two outcomes. Consider tossing of two coins. Or equivalently toss a coin twice. There are four outcomes : An outcome is an ordered pair. Each entry in the pair is drawn from the set $\{H, T\}$.

We can consider, in general, tossing of N coins. There are 2^N outcomes. Each outcome is an ordered string of size N with entries drawn from the set $\{H, T\}$.

Roll a die : You get one of the six outcomes :

$$\left\{ \cdot, \cdot\cdot, \cdot\cdot\cdot, \cdot\cdot\cdot\cdot, \cdot\cdot\cdot\cdot\cdot, \cdot\cdot\cdot\cdot\cdot\cdot \right\}$$

Consider throwing of N dice. There are then 6^N outcomes. Each outcome is an ordered string of N entries drawn from the basic set of six elements given above.

Select randomly an air molecule in this room and find its position and momentum : Consider the air molecule to be a point particle. In classical mechanics, a point particle is completely specified by its three position (q_1, q_2, q_3) and three momentum (p_1, p_2, p_3) coordinates. An ordered set of six numbers

$$\{q_1, q_2, q_3, p_1, p_2, p_3\}$$

is the outcome of the experiment. A point in the six dimensional phase space represents an outcome of the experiment or the microstate of the system of single molecule. We impose certain constraints *e.g.* the molecule is always confined to this room. Then all possible strings of six numbers, consistent with the constraints, are the outcomes of the experiment.

2.2 Sample space and events

The set of all possible outcomes of an experiment is called the sample space. Let us denote it by the symbol Ω .

- $\Omega = \{H, T\}$ for the toss of a single coin.
- $\Omega = \{HH, HT, TH, TT\}$ for the toss of two coins.

A subset of Ω is called an event. Let $A \subset \Omega$ denote an event. When you perform the experiment if you get an outcome that belongs to A then we say the event A has occurred.

For example consider tossing of two coins. Let event A be described by the statement that *the first toss is H*. Then A consists of the following elements: $\{HH, HT\}$.

The event corresponding to the roll of an even number in a dice, is the subset

$$\left\{ \begin{array}{c} \cdot \\ \cdot \\ \cdot \end{array} \ ; \ \begin{array}{c} \cdot \cdot \\ \cdot \cdot \\ \cdot \cdot \end{array} \ ; \ \begin{array}{c} \cdot \cdot \cdot \\ \cdot \cdot \cdot \\ \cdot \cdot \cdot \end{array} \right\}$$

2.3 Probabilities

Probability is defined for an event. What is the probability of the event $\{H\}$ in the toss of a coin? One-half. This would be your immediate response. The logic is simple. There are two outcomes: "Heads" and "Tails". We have no reason to believe why should the coin prefer "Heads" over "Tails" or *vice versa*. Hence we say both outcomes are equally probable. What is the probability of having at least one "H" in a toss of two coins? The event corresponding this statement is $\{HH, HT, TH\}$ and contains three elements. The sample size contains four elements. The required probability is thus $3/4$. All the four outcomes are equally probable¹. Then the probability of an event is the number of elements in that event divided by the total number of elements in the sample space. For *e.g.*, the event A of rolling an even number in a game of dice, $P(A) = 3/6 = 0.5$. The outcome can be a continuum. For example, the angle of scattering of a neutron is a real number between zero and π . We then define an interval (θ_1, θ_2) , where $0 \leq \theta_1 \leq \theta_2 \leq \pi$, as an event. A *measurable* subset of a sample space is an event.

2.4 Rules of probability

The probability p that you assign to an event, should obey the following rules.

$$\begin{aligned} p &\geq 0 \\ p(A \cup B) &= p(A) + p(B) - p(A \cap B) \\ p(\phi) &= 0 \quad p(\Omega) = 1 \end{aligned} \tag{2.1}$$

¹ Physicists have a name for this. They call it the axiom (or hypothesis or assumption) of *Ergodicity*. Strictly ergodicity is not an assumption; it is absence of an assumption required for assigning probabilities to events.

In the above ϕ denotes a null event and Ω , a sure event.

How does one assign probability to an event ?

Though this question does not bother the mathematicians, the physicists should worry about this². They should find the right way to assign probabilities to get the phenomenon right. We can say that the subject of statistical mechanics mainly deals with finding the right way to characterize a micro state, the sample space, the events and the assigning of probabilities to the events, depending on the system and phenomenon under investigation.

2.5 Random variable

The next important concept in probability theory is random variable, denoted by the symbol $x = X(\omega)$ where ω denotes an outcome and x a real number. Random variable is a way of stamping an outcome with a number: Real number, for a real random variable. Integer, for an integer random variable. Complex number, for a complex random variable³. Thus the random variable $x = X(\omega)$ is a set function.

Consider a continuous random variable $x = X(\omega)$. We define a probability density function $f(x)$ by

$$f(x)dx = P(\omega|x \leq X(\omega) \leq x + dx) \quad (2.2)$$

In other words $f(x)dx$ is the probability of the event (measurable subset) that contains all the outcomes to which we have attached a real number between x and $x + dx$.

Now consider a continuous random variable defined between a to b with $a < b$. We define a quantity called the "average" of the random variable x as

$$\mu = \int_a^b dx x f(x).$$

μ is also called the mean, expectation, first moment *etc.*

Consider a discrete random variable n , taking values from say 0 to N . Let $P(n)$ define the discrete probability. We define the average of the random variable as

² Maxwell and Boltzmann attached probabilities to events in some way; we got Maxwell-Boltzmann statistics.

Fermi and Dirac had their own way of assigning probabilities to Fermions *e.g.* electrons, occupying quantum states. We got Fermi-Dirac statistics.

Bose and Einstein came up with their scheme of assigning probabilities to Bosons, populating quantum states; and we got Bose-Einstein statistics.

³ In fact, we stamped dots on the faces of die; this is equivalent to implementing the idea of an integer random variable: attach an integer between one and six to each outcome.

For a coin, we stamped "Heads" on one side and "Tails" on the other. This is in the spirit of defining a random variable; we have stamped figures instead of numbers.

$$\mu = \sum_{n=0}^N n P(n).$$

But then, we are accustomed to calculating the average in a different way. For example I am interested in knowing the average marks obtained by the students in a class, in the last mid-semester examination. How do I calculate it ? I take the marks obtained by each of you, sum them up and divide by the total number of students. That is it. I do not need notions like probabilities, probability density, sum over the product of the random variable and the corresponding probability, integration of the product of the continuous random variable and its probability density function *etc.*

Historically, before Boltzmann and Maxwell, physicists had no use for probability theory in their work. Newton's equations are deterministic. There is nothing chancy about a Newtonian trajectory. We do not need probabilistic description in the study of electrodynamics described by Maxwell equations; nor do we need probability to comprehend and work with Einstein's relativity - special or general.

However mathematicians had developed the theory of probability as an important and sophisticated branch of mathematics.

It was Ludwig Eduard Boltzmann who brought, for the first time, the idea of probability into physical sciences; he was championing the cause of kinetic theory of heat and atomic theory of matter. Boltzmann transport equation is the first ever equation written for describing the time evolution of a probability distribution.

2.6 Maxwell's mischief : Ensemble

However, Maxwell, had a poor opinion about a physicist's ability to comprehend mathematicians' writings on probability theory, in general, and the meaning of average as an integral over a probability density, in particular.

After all, if you ask a physicist to calculate the average age of a student in the class, he'll simply add the ages of all the students and divide by the number of students.

To be consistent with this practice, Maxwell proposed the notion of an **ensemble** of outcomes of an experiment (or an ensemble of realisations of a random variable). Let us call it Maxwell ensemble ⁴.

Consider a collection of a certain number of independent realisations of the toss of a single coin. We call this collection a Maxwell ensemble if it obeys certain conditions, see below.

Let N denote the number of elements in the ensemble. Let n_1 denote the number "Heads" and n_2 number of "Tails". We have $n_1 + n_2 = N$. If $n_1 = Np$,

⁴ Later we shall generalise the notion of Maxwell ensemble and talk of ensemble as a collection identical copies of a macroscopic system. We shall call it a Gibbs ensemble

and hence $n_2 = Nq$, then we say the collection of outcomes constitutes a Maxwell ensemble.

Thus an ensemble holds information about the outcomes of the experiment constituting the sample space; it also holds information about the probability of each outcome. The elements of an ensemble are drawn from the sample space; however each element occurs in an ensemble as often as to reflect correctly its probability.

For example consider an experiment of tossing a p -coin⁵ with $p = 0,75$; then a set of four elements given by $\{H, H, H, T\}$ is a candidate for an ensemble underlying experiment. . A set of eight elements $\{H, H, H, H, H, H, T, T\}$ is also an equally valid ensemble for this experiment. Thus the size of an ensemble is somewhat arbitrary. If the number of times each outcome occurs in the ensemble is consistent with its probability it would suffice.

2.7 Calculation of probabilities from an ensemble

Suppose we are given the following ensemble : $\{H, T, H, H, T\}$. By looking at the ensemble, we can conclude that the sample space contains two outcomes $\{H, T\}$.

We also find that the outcome H occurs thrice and T occurs twice. Hence We also conclude that the probability of H is $3/5$ and that of T is $2/5$.

2.8 Construction of ensemble from probabilities

We can also do the reverse. Given the outcomes and their probabilities, we can construct an ensemble. Let n_i denote the number of times an outcome i occurs in an ensemble. Let N denote the total number of elements of the ensemble. Choose n_i such that n_i/N equals p_i ; note that we have assumed that p_i is already known.

2.9 Counting of the elements in events of the sample space : Coin tossing

Consider tossing of N identical coins or tossing of a single coin N times. Let us say the coin is fair. In other words $P(H) = P(T) = 1/2$.

Let $\Omega(N)$ denote the set of all possible outcomes of the experiment. An outcome is thus a string N entries, each entry being "H" or "T". The number of elements of this set $\Omega(N)$ is denoted by the symbol, $\hat{\Omega}(N)$. We have

⁵ a p -coin is one for which the probability of 'Heads' is p and that of the 'Tails' is $q = 1 - p$.

$$\widehat{\Omega}(N) = 2^N.$$

Let $\Omega(n_1, n_2; N)$ denote a subset of $\Omega(N)$, containing only those outcomes with n_1 'Heads' and n_2 'Tails'. Note $n_1 + n_2 = N$. How many outcomes are there in the set $\Omega(n_1, n_2; N)$?

Let $\widehat{\Omega}(n_1, n_2; N)$ denote the number of elements in the event $\Omega(n_1, n_2; N)$. In what follows I shall tell you how to derive an expression⁶ for $\widehat{\Omega}(n_1, n_2; N)$.

Take one outcome belonging to the event $\Omega(n_1, n_2; N)$. There will be n_1 'Heads' and n_2 'Tails' in that outcome. Imagine for a moment that all these 'Heads' are distinguishable. If you like, you can label them as H_1, H_2, \dots, H_{n_1} . Carry out permutation of all the 'Heads' and produce $n_1!$ new configurations. From each of these new configurations, produce $n_2!$ configurations by carrying out the permutations of the n_2 'Tails'. Thus from one outcome belonging to $\Omega(n_1, n_2; N)$, we have produced $n_1! \times n_2!$ new configurations. Repeat the above for each element of the set $\Omega(n_1, n_2; N)$, and produce $\widehat{\Omega}(n_1, n_2; N)n_1!n_2!$ configurations. A moment of thought will tell you that this number should be the same as $N!$. Therefore

$$\widehat{\Omega}(n_1, n_2; N) \times n_1! \times n_2! = N!$$

Let us work out an example explicitly to illustrate the above. Consider tossing of five coins. There are $2^5 = 32$ outcomes/microstates listed below. The number in the brackets against each outcome denotes the number of "Heads" in that outcome.

Table 2.1. List of 32 outcomes of tossing five coins. Given in brackets is the number of "Heads" in each outcome

1.	H	H	H	H	H	(5)	17.	T	H	H	H	H	(4)
2.	H	H	H	H	T	(4)	18.	T	H	H	H	T	(3)
3.	H	H	H	T	H	(4)	19.	T	H	H	T	H	(3)
4.	H	H	H	T	T	(3)	20.	T	H	H	T	T	(2)
5.	H	H	T	H	H	(4)	21.	T	H	T	H	H	(3)
6.	H	H	T	H	T	(3)	22.	T	H	T	H	T	(2)
7.	H	H	T	T	H	(3)	23.	T	H	T	T	T	(1)
8.	H	H	T	T	T	(2)	24.	T	T	H	H	H	(3)
9.	H	T	H	H	H	(4)	25.	T	T	H	H	T	(2)
10.	H	T	H	H	T	(3)	26.	T	T	H	T	H	(2)
11.	H	T	H	T	H	(3)	27.	T	T	H	T	T	(1)
12.	H	T	H	T	T	(2)	28.	T	T	T	H	T	(1)
13.	H	T	T	H	H	(3)	29.	T	T	T	H	H	(2)
14.	H	T	T	H	T	(2)	30.	T	T	T	H	T	(1)
15.	H	T	T	T	H	(2)	31.	T	T	T	T	H	(1)
16.	H	T	T	T	T	(1)	32.	T	T	T	T	T	(0)

The outcomes numbered 4, 6, 7, 10, 11, 13, 18, 19, 20, 25 are the ones with three "Heads" and two "tails". These are the elements of the event $\Omega(n_1 = 3; n_2 = 2; N = 5)$.

Take outcome No. 4. Label the three heads as H_1, H_2 and H_3 . Carry out permutations of the three "Heads" and produce $3! = 6$ elements. These are Take an element from the above set. Label the 'Tails' as T_1 and T_2 . Carry

⁶ I remember I have seen this method described in a book on Quantum Mechanics by Gasiorowicz. Check it out

Table 2.2. In outcome no. 4, see Table (2.1), the Heads are permuted

(4)	H	H	H	T	T		H ₂	H ₃	H ₁	T	T
	H ₁	H ₂	H ₃	T	T		H ₃	H ₁	H ₂	T	T
	H ₁	H ₃	H ₂	T	T		H ₃	H ₂	H ₁	T	T
	H ₂	H ₁	H ₃	T	T						

out permutation of the 'Tails' and produce $2! = 2$ elements. Do this for each of the above six elements.

Thus from the outcome No, 4, we have produced $3! \times 2! = 12$ outcomes, listed below. Repeat the above exercise on the outcomes numbered

Table 2.3. The twelve outcomes produced from outcome No. 5

(4)	H	H	H	T	T		H ₂	H ₃	H ₁	T ₁	T ₂
	H ₁	H ₂	H ₃	T ₁	T ₂		H ₂	H ₃	H ₁	T ₂	T ₁
	H ₁	H ₂	H ₃	T ₂	T ₁		H ₃	H ₁	H ₂	T ₁	T ₂
	H ₁	H ₃	H ₂	T ₁	T ₂		H ₃	H ₁	H ₂	T ₂	T ₁
	H ₁	H ₃	H ₂	T ₂	T ₁		H ₃	H ₂	H ₁	T ₁	T ₂
	H ₂	H ₁	H ₃	T ₁	T ₂		H ₃	H ₂	H ₁	T ₂	T ₁
	H ₂	H ₁	H ₃	T ₂	T ₁						

6, 7, 10, 11, 13, 18, 19, 20, 25. Table below depicts the results for outcome no. 6.

Table 2.4. The twelve outcomes produced from outcome No. 6

(6)	H	H	T	H	T		H ₂	H ₃	T ₁	H ₁	T ₂
	H ₁	H ₂	T ₁	H ₃	T ₂		H ₂	H ₃	T ₂	H ₁	T ₁
	H ₁	H ₂	T ₂	H ₃	T ₁		H ₃	H ₁	T ₁	H ₂	T ₂
	H ₁	H ₃	T ₁	H ₂	T ₂		H ₃	H ₁	T ₂	H ₂	T ₁
	H ₁	H ₃	T ₂	H ₂	T ₁		H ₃	H ₂	T ₁	H ₁	T ₂
	H ₂	H ₁	T ₁	H ₃	T ₂		H ₃	H ₂	T ₂	H ₁	T ₁
	H ₂	H ₁	T ₂	H ₃	T ₁						

Thus we produce $\widehat{\Omega}(n_1 = 3, n_2 = 2; N = 5) \times n_1! \times n_2!$ outcomes. This number is just the number of permutations of $N = 5$ objects labelled H_1, H_2, H_3, T_1, T_2 and it equals $N!$. Therefore,

$$\widehat{\Omega}(n_1 = 3, n_2 = 2; N = 5) = \frac{5!}{3!2!} = 10$$

$\widehat{\Omega}(n_1, n_2; N)$ is called the binomial coefficient⁷

⁷ We have the binomial expansion given by

$$(a + b)^N = \sum_{\{n_1, n_2\}}^* \frac{N!}{n_1!n_2!} a^{n_1} b^{n_2}$$

2.10 Gibbs ensemble

Following Gibbs, we can think of an ensemble as consisting of large number of identical mental copies of a macroscopic system⁸. All the members of an ensemble are in the same macro state⁹. However they can be in different micro states. Let the micro states of the system under consideration, be indexed by $\{i = 1, 2, \dots\}$. The number of elements of the ensemble in micro state j divided by the size of the ensemble equals the probability of the system to be in micro state j . It is intuitively clear that the size of the ensemble should be large ($\rightarrow \infty$) so that it can capture exactly the

probabilities of different micro states of the system¹⁰. Let me elaborate on this issue, see below.

2.11 Why should a Gibbs ensemble be large ?

What are the values of n_1 and n_2 for which $\widehat{\Omega}(n_1, n_2; N)$ is maximum¹¹ ?

It is readily shown that for $n_1 = n_2 = N/2$ the value of $\widehat{\Omega}(n_1, n_2; N)$ is maximum. Let us denote this number by the symbol $\widehat{\Omega}^m(N)$. We have, $\widehat{\Omega}^m(N) = \widehat{\Omega}(n_1 = N/2, n_2 = n/2; N)$.

Thus we have

The sum runs over all possible values of $\{n_1, n_2\}$. The superscript \star on the summation sign should remind us that only those values of n_1 and n_2 consistent with the constraint $n_1 + n_2 = N$ are permitted.

⁸ For example the given coin is a system. Let p denote the probability of "Heads" and $q = 1 - p$ the probability of "tails". The coin can be in a micro state "Heads" or in a micro state "Tails".

⁹ This means the values of p and q are the same for all the coins belonging to the ensemble.

¹⁰ If you want to estimate the probability of Heads in the toss of a single coin experimentally then you have to toss a large number of identical coins. Larger the size of the ensemble more (statistically) accurate is your estimate .

¹¹ you can find this in several ways. Just guess it. I am sure you would have guessed the answer as $n_1 = n_2 = N/2$. We know that the binomial coefficient is largest when $n_1 = n_2 = N/2$ if N is even, or when n_1 and n_2 equal the two integers closest to $N/2$ for N odd. That is it.

If you are more sophisticated, take the derivative of $\widehat{\Omega}(n_1, n_2; N)$ with respect to n_1 and n_2 with the constraint $n_1 + n_2 = N$, set it zero; solve the resulting equation to get the value of N for which the function is an extremum. Take the second derivative and show that the extremum is a maximum.

You may find it useful to take the derivative of logarithm of $\widehat{\Omega}(n_1, n_2; N)$; employ Stirling approximation for the factorials : $\ln(m!) = m \ln(m) - m$ for large m . Stirling approximation to large factorials is described in the next section.

You can also employ any other pet method of yours to show that, for $n = N/2$, the function $\widehat{\Omega}(n; N)$ is maximum.

$$\widehat{\Omega}(N) = \sum_{\{n_1, n_2\}}^* \frac{N!}{n_1! n_2!} = 2^N; \quad (* \Rightarrow n_1 + n_2 = N) \quad (2.3)$$

$$\widehat{\Omega}^m(N) = \widehat{\Omega}(n_1 = n_2 = N/2; N) = \frac{N!}{(N/2)! (N/2)!} \quad (2.4)$$

Let us evaluate $\widehat{\Omega}^m(N)$ for large values of N . We employ Stirling's first approximation¹² : $N! = N^N \exp(-N)$ and get

$$\widehat{\Omega}^m(N) = \frac{N^N \exp(-N)}{[(N/2)^{(N/2)} \exp(-N/2)]^2} = 2^N \quad (2.5)$$

The above implies that almost all the outcomes of the experiment belong to the event with equal number of 'Heads' and 'Tails'. The outcomes with unequal number of 'Heads' and 'Tails' are so overwhelmingly small that the difference falls within the small error arising due to the first Stirling approximation.

For estimating the tiny difference between $\widehat{\Omega}(N)$ and $\widehat{\Omega}^m(N)$, let us employ the second Stirling approximation¹³ :

¹² First Stirling Approximation : $N! \approx N^N \exp(-N)$.

We have, $N! = N \times (N-1) \times \dots \times 3 \times 2 \times 1$. Therefore,

$$\begin{aligned} \ln N! &= \ln 1 + \ln 2 + \ln 3 + \dots + \ln N \\ &= \sum_{k=1}^N \ln(k) \approx \int_1^N \ln x \, dx = (x \ln x - x) \Big|_1^N = N \ln N - N - 1 \\ &\approx N \ln N - N \\ N! &\approx N^N \exp(-N) \end{aligned}$$

¹³ A better approximation to large factorials is given by Stirling's second formula : $N! \approx N^N \exp(-N) \sqrt{2\pi N}$. We have

$$\begin{aligned} \Gamma(N+1) = N! &= \int_0^\infty dx \, x^N e^{-x} = \int_0^\infty dx \, e^{F(x)} \\ F(x) &= N \ln x - x; \quad F'(x) = \frac{N}{x} - 1; \quad F''(x) = -\frac{N}{x^2} \end{aligned}$$

Set $F'(x) = 0$; this gives $x^* = N$. At $x = x^*$ the function $F(x)$ is maximum. (Note : $F''(x = x^*)$ is negative). Carrying out Taylor expansion and retaining only upto quadratic terms, we get,

$$F(x) = F(x^*) + \frac{(x - x^*)^2}{2} F''(x = x^*) = N \ln N - N - \frac{(x - N)^2}{2N}$$

We have,

$$\begin{aligned} N! = \int_0^\infty dx \, e^{F(x)} &= N^N e^{-N} \int_0^\infty dx \exp \left[-\frac{(x - N)^2}{2N} \right] \\ &= N^N e^{-N} \sqrt{N} \int_{-\sqrt{N}}^\infty dx \exp(-x^2/2) \underset{N \rightarrow \infty}{\sim} N^N e^{-N} \sqrt{2\pi N} \end{aligned}$$

$$N! = N^N \exp(-N) \sqrt{2\pi N}$$

and get

$$\begin{aligned} \widehat{\Omega}^m(N) &= \widehat{\Omega}(n_1 = n_2 = N/2; N) \\ &= 2^N \times \sqrt{\frac{2}{\pi N}} \\ &= \widehat{\Omega}(N) \times \sqrt{\frac{2}{\pi N}} \end{aligned} \quad (2.6)$$

Let us define $S(\Omega(n_1, n_2; N)) = \ln \widehat{\Omega}(n_1, n_2; N)$ as entropy of the event $\Omega(n_1, n_2; N)$. For $n_1 = n_2 = N/2$ we get an event with largest entropy. Let us denote it by the symbol $S_B(N)$.

Let $S_G = S(\Omega(N)) = N \ln 2$ denote the entropy of the sure event. It is the logarithm of the number of outcomes of the experiment of tossing N independent and fair coins.

Taking logarithm of the terms on both sides of Eq. (2.6) we get,

$$S_B = S_G - \frac{1}{2} \ln N - \frac{1}{2} \ln(2/\pi) \quad (2.7)$$

$$N \xrightarrow{\sim} \infty S_G - \frac{1}{2} \ln N \quad (2.8)$$

The entropy of the sure event is of the order of N ; the entropy of the event with $N/2$ "Heads" and $N/2$ "Tails" is less by an extremely small quantity of the order of $\ln(N)$. Hence when you toss a very large number of coins independently you will get almost always $N/2$ "Heads" and $N/2$ "Tails".

For example take a typical value for $N = 10^{23}$. We have $S_G = 0.69 \times 10^{23}$ and $S_B = 0.69 \times 10^{23} - 24.48$.

Note that only when N is large, we have S_B equals S_G . It is precisely because of this, we want the number of elements to be large, while constructing a Gibbs ensemble. We should ensure that all the micro states of the system are present in the ensemble in proportions, consistent with their probabilities.

For example I can simply toss N independent fair coins just once and if N is large then I am assured that there shall be $(N/2) \pm \epsilon$ "Heads" and $(N/2) \mp \epsilon$ "Tails", where ϵ is negligibly small : of the order of \sqrt{N} . Consider the probability for random variable n to take values outside the interval

$$\left(\frac{N}{2} - \epsilon \frac{N}{2}, \frac{N}{2} + \epsilon \frac{N}{2} \right)$$

where ϵ is an arbitrarily small number. Let us denote this probability as $P_{\text{out}}(N)$. One can show that in the limit $N \rightarrow \infty$, the probability $P_{\text{out}}(N)$ goes to zero.

Take $\epsilon = 1/100$ and calculate $P_{\text{out}}(N)$ for $N = 10^3, 10^4, 10^5, 10^6$, and 10^8 . The table below depicts the results, and we see that P_{out} nearly zero for large N .

Table 2.5. Probability that in a toss of N coins, the number of Heads deviates by more than one percent from $N/2$

N	$\epsilon = 1/100; P_{\text{out}} =$ $1 - P\left(\frac{N}{2} - \epsilon \frac{N}{2} \leq n \leq \frac{N}{2} + \epsilon \frac{N}{2}\right)$
10^3	0.752
10^4	0.317
10^5	0.002
10^6	1.5×10^{-23}
10^7	2.7×10^{-2174}

In statistical mechanics we consider a macroscopic system which can be in any of its numerous microscopic states. These micro states are analogous to the outcomes of an experiment. In fact the system switches spontaneously from one micro state to another when in equilibrium. We can say the set of all micro states constitute a micro state space which is the analogue of the sample space. We attach a real number representing the numerical value of a property *e.g.* energy, to each micro state. This is analogous to random variable. We can define several random variables on the same micro state space to describe different macroscopic properties of the system.

DRAFT

3. Binomial, Poisson, and Gaussian

3.1 Binomial Distribution

Consider a system consisting of one coin. It has two micro states : H and T. The probability for the system to be in micro state H is p and that in micro state T is $q = 1 - p$.

Consider the case with $p = 0.6$ and hence $q = 1 - p = 0.4$. A possible Maxwell ensemble of micro states is A popular book. Starts with a b

$$\{T, H, H, H, T, H, H, T, H, T\}.$$

Notice that the ensemble contains ten elements. Six elements are H and four are T. This is consistent with the given probabilities: $\mathcal{P}(H) = 6/10$; and $\mathcal{P}(T) = 4/10$.

However a Gibbs ensemble is constructed by actually tossing N identical and independent coins. In the limit $N \rightarrow \infty$, sixty percent of the coins shall be in micro state H and forty, T. To ensure this we need to take the size of the ensemble N , to be very large. How large ? You will get an answer to this question in what follows.

Let us say, we attempt to construct the ensemble by actually carrying out the experiment of tossing identical coins or by tossing the same coin several times independently. What is the probability that in the experiment there shall be n_1 'Heads' and hence $n_2 = (N - n_1)$ 'Tails' ? Let us denote this by the symbol $B(n_1, n_2; N)$, where N is the number of independent identical coins tossed or number of times a coin is tossed independently. It is readily seen,

$$B(n_1, n_2; N) = \frac{N!}{n_1! n_2!} p^{n_1} q^{n_2} ; \quad n_1 + n_2 = N. \quad (3.1)$$

$B(n_1, n_2; N)$ is called the Binomial distribution. Let $n_1 = n$, $n_2 = N - n$, we can write the Binomial distribution for the single random variable n as,

$$B(n; N) = \frac{N!}{n!(N - n)!} p^n q^{N-n}$$

Figure (3.1) depicts Binomial distribution for $N = 10$, $p = 0.5$ (Left) and 0.35 (Right). **First moment of n** : What is average value of n ? The average, also called the mean, the first moment, the expectation value *etc.* is denoted by the symbol $\langle n \rangle$ and is given by,

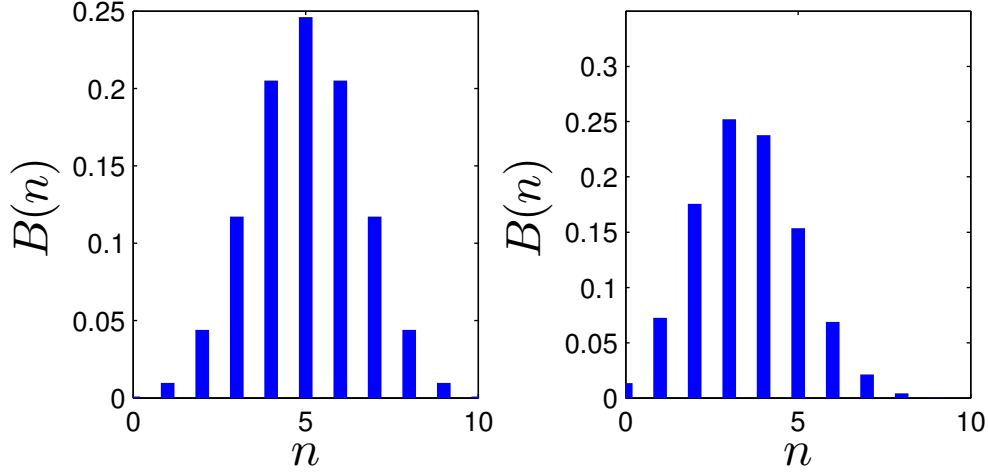


Fig. 3.1. Binomial distribution : $B(n; N) = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n}$ with $N = 10$; $B(n; N)$ versus n ; depicted as sticks; (Left) $p = 0.5$; (Right) $p = .35$.

$$\begin{aligned}
 \langle n \rangle &= \sum_{n=0}^N n B(n; N) = \sum_{n=1}^N n \frac{N!}{n!(N-n)!} p^n q^{N-n}, \\
 &= Np \sum_{n=1}^N \frac{(N-1)!}{(n-1)! [N-1-(n-1)]!} p^{n-1} q^{N-1-(n-1)}, \\
 &= Np \sum_{n=0}^{N-1} \frac{(N-1)!}{n!(N-1-n)!} p^n q^{N-1-n}, \\
 &= Np(p+q)^{N-1} = Np.
 \end{aligned}$$

Second factorial moment of n : The second factorial moment of n is defined as $\langle n(n-1) \rangle$. It is calculated as follows.

$$\begin{aligned}
 \langle n(n-1) \rangle &= \sum_{n=0}^N n(n-1) B(n; N), \\
 &= \sum_{n=2}^N n(n-1) \frac{N!}{n!(N-n)!} p^n q^{N-n}, \\
 &= N(N-1)p^2 \sum_{n=2}^N \frac{(N-2)!}{(n-2)! [(N-2)-(n-2)]!} p^{n-2} q^{(N-2)-(n-2)}, \\
 &= N(N-1)p^2 \sum_{n=0}^{N-2} \frac{(N-2)!}{n! [(N-2)-n]!} p^n q^{(N-2)-n}.
 \end{aligned}$$

$$= N(N-1)p^2(q+p)^{N-2} = N(N-1)p^2. \quad (3.2)$$

Moments of n : We can define higher moments. The k -th moment is defined as

$$M_k = \langle n^k \rangle = \sum_{n=0}^N n^k B(n). \quad (3.3)$$

Variance of n : An important property of the random variable is variance. It is defined as,

$$\sigma_n^2 = \sum_{n=0}^N (n - M_1)^2 B(n), = \sum_{n=0}^N n^2 B(n) - M_1^2, = M_2 - M_1^2. \quad (3.4)$$

We have,

$$\begin{aligned} \langle n(n-1) \rangle &= N(N-1)p^2, \\ \langle n^2 \rangle - \langle n \rangle &= N^2 p^2 - Np^2, \\ \langle n^2 \rangle &= N^2 p^2 - Np^2 + Np, \\ \sigma_n^2 = \langle n^2 \rangle - \langle n \rangle^2 &= Npq. \end{aligned} \quad (3.5)$$

The square-root of variance is called the standard deviation. A relevant quantity is the relative standard deviation. It is given by the ratio of the standard deviation to the mean. For the Binomial random variable, we have,

$$\frac{\sigma_n}{\langle n \rangle} = \frac{1}{\sqrt{N}} \sqrt{\frac{q}{p}}. \quad (3.6)$$

The relative standard deviation is inversely proportional to \sqrt{N} . It is small for large N . It is clear that the number of elements N , in a Gibbs ensemble should be large enough to ensure that the relative standard deviation is as small as desired. Let me now describe a smart way of generating the moments of a random variable.

3.2 Moment Generating Function

Let $B(n)$ denote the probability that n coins are in micro state "Heads" in an ensemble of N coins. We have shown that,

$$B(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}. \quad (3.7)$$

The moment generating function is defined as

$$\tilde{B}(z) = \sum_{n=0}^N z^n B(n). \quad (3.8)$$

The first thing we notice is that $\tilde{B}(z = 1) = 1$. This guarantees that the probability distribution $B(n)$ is normalised. The moment generating function is like a discrete transform of the probability distribution function. We transform the variable n to z .

Let us now take the first derivative of the moment generating function with respect to z . We have,

$$\begin{aligned}\frac{d\tilde{B}}{dz} &= \tilde{B}'(z) = \sum_{n=0}^N n z^{n-1} B(n), \\ z\tilde{B}'(z) &= \sum_{n=0}^N n z^n B(n).\end{aligned}\quad (3.9)$$

. Substitute in the above $z = 1$. We get,

$$\tilde{B}'(z = 1) = \langle n \rangle. \quad (3.10)$$

Thus the first derivative of \tilde{B} evaluated at $z = 1$ generates the first moment.

Now take the second derivative of $\tilde{B}(z)$ to get

$$\begin{aligned}\frac{d^2\tilde{B}}{dz^2} &= \sum_{n=0}^N n(n-1)z^{n-2}B(n), \\ z^2\frac{d^2\tilde{B}}{dz^2} &= \sum_{n=0}^N z^n n(n-1) B(n).\end{aligned}\quad (3.11)$$

Substitute in the above $z = 1$ and get,

$$\left.\frac{d^2\tilde{B}}{dz^2}\right|_{z=1} = \langle n(n-1) \rangle, \quad (3.12)$$

For the Binomial random variable, we can derive the moment generating function :

$$\tilde{B}(z) = \sum_{n=0}^N z^n B(n) = \sum_{n=0}^N \frac{N!}{n!(N-n)!} (zp)^n q^{N-n}, = (q + zp)^N. \quad (3.13)$$

The moments are generated as follows.

$$\frac{d\tilde{B}}{dz} = N(q + zp)^{N-1}p, \quad (3.14)$$

$$\langle n \rangle = \left.\frac{d\tilde{B}}{dz}\right|_{z=1} = Np, \quad (3.15)$$

$$\frac{d^2\tilde{B}}{dz^2} = N(N-1)(q + zp)^{N-2}p^2, \quad (3.16)$$

$$\langle n(n-1) \rangle = \left.\frac{d^2\tilde{B}}{dz^2}\right|_{z=1} = N(N-1)p^2. \quad (3.17)$$

3.3 Binomial → Poisson

When N is large, it is clumsy to calculate quantities employing Binomial distribution. Consider the following situation.

I have N molecules of air in this room of volume V . The molecules are distributed uniformly in the room. In other words the number density, denoted by ρ is same at all points in the room. Consider now an imaginary small volume $v < V$ completely contained in the room. Consider an experiment of choosing randomly an air molecule from this room. The probability that the molecule shall be in the small volume is $p = v/V$; the probability that it shall be out side the small volume is $q = 1 - (v/V)$. There are only two possibilities. We can use Binomial distribution to calculate the probability for n molecules to be present in v .

Consider first the problem with $V = 10M^3$, $v = 6M^3$ and $N = 10$. The value of p for the Binomial distribution is 0.6. The probability of finding n molecules in v is then,

$$B(n; N = 10) = \frac{10!}{n!(10-n)!} (0.1)^n (0.9)^{10-n}. \quad (3.18)$$

The table below gives the probabilities calculated from the Binomial distribution.

Table 3.1. Probabilities calculated from Binomial distribution : $B(n; N = 10, p = .1)$

n	$B(n; 10)$	n	$B(n; 10)$
0	0.0001	6	0.2508
1	0.0016	7	0.2150
2	0.0106	8	0.1209
3	0.0425	9	0.0403
4	0.1115	10	0.0060
5	0.2007	—	—

Consider the same problem with $v = 10^{-3} M^3$ and $N = 10^5$. We have $p = 10^{-4}$ and $Np = 10$. Immediately we recognise that Binomial distribution is not appropriate for this problem. Calculation of the probability of finding n molecules in v involves evaluation of factorial of 100000.

What is the right distribution for this problem and problems of this kind? To answer this question, consider what happens to the Binomial distribution in the limit of $N \rightarrow \infty$, $p \rightarrow 0$, and $Np = \mu$, a constant¹. Note that

$$Np = Nv/V = \rho v = \text{constant}.$$

We shall show below that in this limit, Binomial goes over to Poisson distribution.

3.4 Poisson Distribution

We start with

$$\tilde{B}(z) = (q + zp)^N. \quad (3.19)$$

We can write the above as

$$\begin{aligned} \tilde{B}(z) &= q^N \left(1 + \frac{zp}{q}\right)^N, \\ &= (1-p)^N \left(1 + \frac{zp}{q}\right)^N, \end{aligned} \quad (3.20)$$

$$= \left(1 - Np \frac{1}{N}\right)^N \left(1 + \frac{zNp \frac{1}{N}}{q}\right)^N. \quad (3.21)$$

In the above replace Np by μ and q by 1 to get,

$$\tilde{B}(z) = \left(1 - \frac{\mu}{N}\right)^N \left(1 + \frac{z\mu}{N}\right)^N.$$

In the limit of $N \rightarrow \infty$ we have by definition²,

$$\begin{aligned} \tilde{B}(z) &\sim \exp(-\mu) \exp(z\mu), \\ &= \tilde{P}(z). \end{aligned} \quad (3.22)$$

Thus in the limit $N \rightarrow \infty$, $p \rightarrow 0$ and $Np = \mu$, we find $\tilde{B}(z) \rightarrow \tilde{P}(z)$, given by

$$\tilde{P}(z) = \exp[-\mu(1-z)]. \quad (3.23)$$

¹ Note that for a physicist, large is infinity and small is zero.

² exponential function is defined as

$$\exp(x) = \lim_{N \rightarrow \infty} \left(1 + \frac{x}{N}\right)^N$$

The coefficient of z^n in the power series expansion of $\tilde{P}(z)$ gives $P(n)$,

$$P(n) = \frac{\mu^n}{n!} \exp(-\mu). \quad (3.24)$$

The above is called the Poisson distribution³. Thus in the limit of $N \rightarrow \infty$, $p \rightarrow 0$, $Np = \mu$, the Binomial distribution goes over to Poisson distribution. Figure (3.2) depicts Poisson distribution for $\mu = 1.5$ and 9.5.

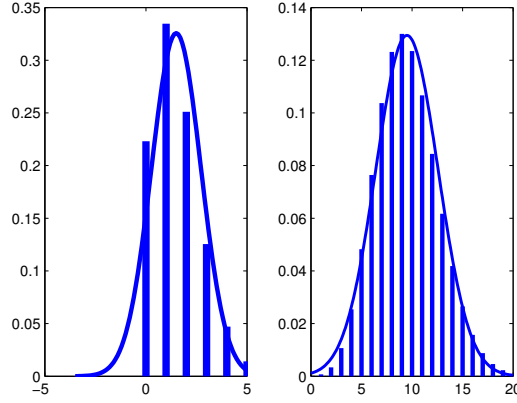


Fig. 3.2. Poisson distribution with mean μ , depicted as sticks. Gaussian distribution with mean μ and variance $\sigma^2 = \mu$ depicted by continuous line. (Left) $\mu = 1.5$; (Right) $\mu = 9.5$. For large μ Poisson and Gaussian coincide

3.4.1 Binomial \rightarrow Poisson à la Feller

Following Feller⁴, we have

³ We shall come across Poisson distribution in the context of Maxwell-Boltzmann statistics. Let n_k denote the number of 'indistinguishable classical' particles in a single-particle state k . The random variable n_k is Poisson-distributed.

⁴ William Feller, *An Introduction to PROBABILITY : Theory and its Applications*, Third Edition Volume 1, Wiley Student Edition (1968)p.153

$$\begin{aligned}
\frac{B(n; N)}{B(n-1; N)} &= \frac{N! p^n q^{N-n}}{n! (N-n)!} \frac{(n-1)! (N-n+1)!}{N! p^{n-1} q^{N-n+1}}, \\
&= \frac{p (N-n+1)}{n q}, \\
&= \frac{N p - p (n-1)}{n q}, \\
\left(\begin{matrix} N \rightarrow \infty \\ p \rightarrow 0 \\ Np = \mu \end{matrix} \right) &\sim \frac{\mu}{n}. \tag{3.25}
\end{aligned}$$

Thus we get for large N , $B(n; N) = B(n-1; N)\mu/n$.

Start with $B(n=0; N) = q^N$. We have

$$q^N = (1-p)^N \tag{3.26}$$

$$= \left(1 - \frac{Np}{N}\right)^N \tag{3.27}$$

$$= \left(1 - \frac{\mu}{N}\right)^N \tag{3.28}$$

$$\stackrel{N \rightarrow \infty}{\sim} \exp(-\mu). \tag{3.29}$$

Thus for $N \rightarrow \infty$, we get $B(n=0; N) = P(n=0; \mu) = \exp(-\mu)$. We get,

$$P(n=1; N) = \mu \exp(-\mu), \tag{3.30}$$

$$P(n=2; N) = \frac{\mu^2}{2!} \exp(-\mu), \tag{3.31}$$

$$P(n=3; N) = \frac{\mu^3}{3!} \exp(-\mu). \tag{3.32}$$

Finally prove by induction

$$P(n; N) = \frac{\mu^n}{n!} \exp(-\mu).$$

The next item in the agenda is on Gaussian distribution. It is a continuous distribution defined for $-\infty \leq x \leq +\infty$. Before we take up the task of obtaining Gaussian from Poisson (in the limit $\mu \rightarrow \infty$), let us learn a few relevant and important things about continuous distribution.

3.5 Characteristic Function

Let $x = X(\omega)$ be a continuous random variable, and $f(x)$ its probability density function. The Fourier transform of $f(x)$ is called the characteristic function of the random variable $x = X(\omega)$:

$$\phi_X(k) = \int_{-\infty}^{+\infty} dx \exp(-ikx) f(x).$$

Taylor expanding the exponential in the above, we get

$$\phi_X(k) = \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} \int_{-\infty}^{\infty} dx x^n f(x) = \sum_{n=0}^{\infty} \frac{(-ik)^n}{n!} M_n. \quad (3.33)$$

Thus the characteristic function generates the moments.

3.6 Cumulant Generating Function

The logarithm of the characteristic function is called the cumulant generating function. $\psi_X(k) = \ln \phi_X(k)$. Let us write the above as,

$$\begin{aligned} \psi_X(k) &= \ln \left(1 + \sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} M_n \right), \\ &= \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{n} \left(\sum_{m=1}^{\infty} \frac{(-ik)^m}{m!} M_m \right)^n. \end{aligned} \quad (3.34)$$

We now express $\psi_X(k)$ as a power series in k as follows

$$\psi_X(k) = \sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \zeta_n. \quad (3.35)$$

where ζ_n is called the n -th cumulant.

From the above equations we can find the relation between moments and cumulants.

3.7 The Central Limit Theorem

Let $\{X_i : i = 1, 2, \dots, N\}$ denote N random variables and let

$$Y = \sum_{i=1}^N X_i \quad (3.36)$$

be their sum. Note Y is a random variable and its probability density function is formally given by,

$$\begin{aligned} f_Y(y) &= \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \cdots \\ &\quad \cdots \int_{-\infty}^{+\infty} dx_N f(x_1, x_2, \dots, x_N) \delta \left(y - \sum_{i=1}^N x_i \right) \end{aligned} \quad (3.37)$$

If the random variables are mutually independent then their joint density can be written as the product of their individual probability densities, see below.

$$f(x_1, x_2, \dots, x_N) = f_1(x_1)f_2(x_2) \cdots f_N(x_N) \quad (3.38)$$

where the symbol $f_i(x_i)$ denotes the probability density function of the random variable X_i . Therefore we have,

$$\begin{aligned} f_Y(y) &= \int_{-\infty}^{+\infty} dx_1 f_1(x_1) \int_{-\infty}^{+\infty} dx_2 f_2(x_2) \cdots \\ &\quad \cdots \int_{-\infty}^{+\infty} dx_N f_N(x_N) \delta\left(y - \sum_{i=1}^N x_i\right) \end{aligned} \quad (3.39)$$

Now, multiply both sides of the equation above by $\exp(-iky)$ and integrate over y from $-\infty$ to $+\infty$. The Left Hand Side gives the characteristic function of the random variable Y .

$$\int_{-\infty}^{+\infty} dy \exp(-iky) f_Y(y) = \phi_Y(k) \quad (3.40)$$

Thus we get,

$$\begin{aligned} \phi_Y(k) &= \int_{-\infty}^{+\infty} dy \exp(-iky) \int_{-\infty}^{+\infty} dx_1 f_1(x_1) \int_{-\infty}^{+\infty} dx_2 f_2(x_2) \cdots \\ &\quad \cdots \int_{-\infty}^{+\infty} dx_N f_N(x_N) \delta\left(y - \sum_{i=1}^N x_i\right) \end{aligned} \quad (3.41)$$

In the right hand side of the above, the integral over y can be carried out making use of a property of Dirac-delta function⁵, and we get,

⁵

$$\int_{-\infty}^{+\infty} dx f(x) \delta(x - x_0) = f(x_0)$$

$$\begin{aligned}
\phi_Y(k) &= \int_{-\infty}^{+\infty} dx_1 f_1(x_1) \int_{-\infty}^{+\infty} dx_2 f_2(x_2) \cdots \\
&\quad \cdots \int_{-\infty}^{+\infty} dx_N f_N(x_N) \exp[-ik(x_1 + x_2 + \cdots + x_N)] \\
&= \int_{-\infty}^{+\infty} dx_1 \exp(-ikx_1) f_1(x_1) \int_{-\infty}^{+\infty} dx_2 \exp(-ikx_2) f_2(x_2) \cdots \\
&\quad \cdots \int_{-\infty}^{+\infty} dx_N \exp(-ikx_N) f_N(x_N) \\
&= \phi_1(k) \times \phi_2(k) \times \cdots \times \phi_N(k)
\end{aligned} \tag{3.42}$$

where $\phi_i(k)$ is the characteristic function of X_i and it is given by,

$$\phi_i(k) = \int_{-\infty}^{+\infty} dx \exp(-ikx) f_i(x) \tag{3.43}$$

If the random variables are also identically distributed, then we have

$$\phi_Y(k) = [\phi_X(k)]^N \tag{3.44}$$

where $\phi_X(k)$ is the characteristic function of the common distribution.

Now consider the scaled random variable,

$$Y = \frac{X_1 + X_2 + \cdots + X_N}{N} \tag{3.45}$$

The characteristic function of Y can be obtained following the procedure described above except that we have the scaled variable k/N . Thus,

$$\begin{aligned}
\phi_Y(k) &= [\phi_X(k \rightarrow k/N)]^N \\
&= \exp[N \ln \phi_X(k \rightarrow k/N)], \\
&= \exp \left[N \sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \frac{\zeta_n}{N^n} \right] \\
&= \exp \left[\sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \frac{\zeta_n}{N^{n-1}} \right], \\
&= \exp \left[-ik\mu - \frac{k^2}{2!} \frac{\sigma^2}{N} + \mathcal{O}(1/N^2) \right] \\
&\underset{N \rightarrow \infty}{\sim} \exp \left[-ik\mu - \frac{k^2}{2!} \frac{\sigma^2}{N} \right].
\end{aligned} \tag{3.46}$$

Thus the characteristic function of Y , in the limit $N \rightarrow \infty$ is given by $\phi_Y(k) = \exp(-ik\mu - (k^2/2!)\sigma^2/N)$. This is indeed the characteristic function of the Gaussian random variable with mean μ and variance σ^2/N , see below.

Thus the sum of N independent and identically distributed random variables (with finite variance) tends to have a Gaussian distribution for large N . This is called the central limit theorem.

3.8 Poisson \rightarrow Gaussian

Let us show now that for large values of the mean the Poisson distribution tends to a Gaussian. Start with the moment generating function of the Poisson random variable:

$$\tilde{P}(z; \mu) = \exp[-\mu(1 - z)].$$

Substitute $z = \exp(-ik)$ and get,

$$\tilde{P}(k; \mu) = \exp[-\mu \{1 - \exp(-ik)\}].$$

Carry out the power series expansion of the exponential function and get,

$$\tilde{P}(k; \mu) = \exp \left[\sum_{n=1}^{\infty} \frac{(-ik)^n}{n!} \mu \right]. \quad (3.47)$$

We recognize the above as the cumulant expansion of a distribution for which all the cumulants are the same μ . For large value of μ , it is adequate to consider only small values of k . Hence we retain only terms upto quadratic in k . Thus for k small, we have,

$$\tilde{P}(k) = \exp \left[-ik\mu - \frac{k^2}{2!}\mu \right]. \quad (3.48)$$

The above is the Fourier transform or the characteristic function of a Gaussian random variable with mean as μ and variance also as μ .

Thus in the limit $\mu \rightarrow \infty$, Gaussian distribution with mean and variance both equal to μ is a good approximation to Poisson distribution with mean μ , see Fig. 2.

3.9 Gaussian

A Gaussian of mean μ and variance σ^2 is given by

$$G(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp \left[-\frac{(x - \mu)^2}{2\sigma^2} \right]. \quad (3.49)$$

The characteristic function is given by the Fourier transform formally expressed as $\tilde{G}(k) = \int_{-\infty}^{+\infty} dx \exp(-ikx)G(x)$. The integral can be worked out, and I leave it as an exercise. We get, $\tilde{G}(k) = \exp[-ik\mu - k^2\sigma^2/2]$. Consider a Gaussian of mean zero and variance σ^2 . It is given by

$$g(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\frac{x^2}{\sigma^2}\right]. \quad (3.50)$$

The width of the Gaussian distribution is 2σ . The Fourier transform of $g(x)$ is denoted $\tilde{g}(k)$ and is given by

$$\tilde{g}(k) = \exp\left[-\frac{1}{2}k^2\sigma^2\right]. \quad (3.51)$$

The Fourier transform is also a Gaussian with zero mean and standard deviation $1/\sigma$. The width of $\tilde{g}(k)$ is $2/\sigma$. The product of the width of $g(x)$ and the width of its Fourier transform $\tilde{g}(k)$ is 4.

If $g(x)$ is sharply peaked then its Fourier transform $\tilde{g}(k)$ will be broad and *vice versa*.

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4. Isolated System: Micro canonical Ensemble

4.1 Preliminaries

Our aim is to study an isolated system of N number of point particles with an energy E and confined to a volume V . The particles do not interact with each other. We shall see how to count the number of micro states, denoted by the symbol $\widehat{\Omega}$, of the system. $\widehat{\Omega}$ will be, in general, a function of energy E , volume V and the number of particles N . We shall carry out both classical as well as quantum counting of the micro states and find that both lead to the same expressions for entropy.

Before we address the full problem, we shall consider a simpler problem of counting the micro states taking into account only the spatial coordinates neglecting completely the momentum coordinates. Despite this gross simplification, we shall discover that the machinery of statistical mechanics helps us derive the ideal gas law¹.

¹ I must tell you of a beautiful derivation of the ideal gas law by Daniel Bernoulli (1700-1782). It goes as follows. Bernoulli imagined air to be made of billiard balls all the time in motion, colliding with each other and with the walls of the container. When a billiard ball bounces off the wall, it transmits a certain momentum to the wall and Bernoulli imagined it as pressure. It makes sense. First consider air contained in a cube of side one meter. There is a certain amount of pressure felt by the wall. Now imagine the cube length to be doubled without changing the speeds of the molecules. In modern language this assumption is the same as keeping the temperature constant. The momentum transferred per collision remains the same. However since each billiard ball molecule has to travel twice the distance between two successive collisions with the wall, the force on the wall should be smaller by a factor of two. Also pressure is force per unit area. The area of the side of the cube is four times more now. Hence the pressure should be less by a further factor of four. Taking into account both these factors, we find the pressure should be eight times less. We also find the volume of cube is eight times more. From these considerations, Bernoulli concluded that the product of pressure and volume must be a constant when there is no change in the molecular speeds - a brilliant argument based on simple scaling ideas.

4.2 Configurational Entropy

Consider placing a single particle in a volume V divided into two equal halves. Let $\epsilon = V/2$. There are two ways, see Fig. (4.1). We have,



Fig. 4.1. Two ways of keeping a particle in a box divided into two equal parts. $\epsilon = V/2$

$$\widehat{\Omega}(V, N = 1, \epsilon = V/2) = \frac{V}{\epsilon} = 2 \quad \text{and} \quad S = k_B \ln \widehat{\Omega} = k_B \ln(2). \quad (4.1)$$

Now consider distributing two distinguishable particles in these two cells each of volume $\epsilon = V/2$, see Fig. (4.2). We then have

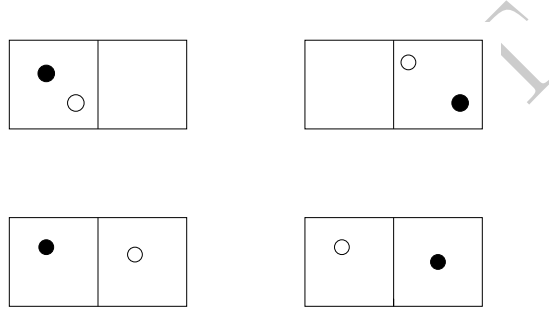


Fig. 4.2. Four ways of keeping two distinguishable particles in a box divided into two equal halves. $\epsilon = V/2$.

$$\widehat{\Omega}(V, N = 2, \epsilon = V/2) = \left(\frac{V}{\epsilon}\right)^2 = 4 \quad \text{and} \quad S = k_B \ln \widehat{\Omega} = 2k_B \ln(2). \quad (4.2)$$

For N particles we have,

$$\widehat{\Omega}(V, N, \epsilon = V/2) = \left(\frac{V}{\epsilon}\right)^N = 2^N, \quad \text{and} \quad S = k_B \ln \widehat{\Omega} = Nk_B \ln(2). \quad (4.3)$$

Let us now divide the volume equally into V/ϵ parts and count the number of ways or organizing N (distinguishable) particles. We find $\widehat{\Omega}(V, N) = \left(\frac{V}{\epsilon}\right)^N$, and

$$\begin{aligned}
S &= k_B \ln \widehat{\Omega} = Nk_B \ln(V/\epsilon) \\
&= Nk_B \ln V - Nk_B \ln \epsilon.
\end{aligned} \tag{4.4}$$

4.3 Ideal Gas Law : Derivation

Differentiate S given by Eq. (4.4), with respect V . We get,

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{Nk_B}{V}. \tag{4.5}$$

From thermodynamics² we have

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}. \tag{4.6}$$

Thus we see from Eq. (4.5) and Eq. (4.6)

$$PV = Nk_B T. \tag{4.7}$$

² In thermodynamics we start with $U \equiv U(S, V)$ for a given quantity of say an ideal gas. We have formally,

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV.$$

We identify the physical meaning of the partial derivatives as follows.

Thus internal energy can change in a (quasi static) reversible process either by heat ($= TdS$), or by work ($= -PdV$). Hence we have the first law of thermodynamics

$$dU = TdS - PdV.$$

We have then,

$$T = \left(\frac{\partial U}{\partial S}\right)_V ; \quad P = -\left(\frac{\partial U}{\partial V}\right)_S.$$

Let us now consider $S \equiv S(U, V)$, a natural starting point for statistical mechanics. We have,

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

To express the partial derivatives in the above in terms of T and P , we rearrange the terms in the first law equation (4.6) as,

$$dS = \frac{1}{T}dU + \frac{P}{T}dV.$$

Equating the pre-factors of dU and dV in the above two equation, we get,

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}; \quad \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}.$$

4.4 Boltzmann Entropy \longrightarrow Clausius' Entropy

From Eq. (4.4), we have,

$$dS = \frac{Nk_B}{V}dV. \quad (4.8)$$

Employing the equation of state : $PV = Nk_B T$, which we have derived, we can rewrite the above as

$$dS = \frac{PdV}{T}. \quad (4.9)$$

Consider an isothermal process in an ideal gas. We have $dU = 0$. This implies $TdS = PdV$. When the system absorbs a certain quantity of heat q isothermally and reversibly, we have $q = TdS = PdV$. Equating PdV to q in Eq. (4.9), we get

$$dS = \frac{q}{T}, \quad (4.10)$$

which shows that Boltzmann entropy is consistent with the thermodynamic entropy.

4.5 Some Issues on Extensivity of Entropy

The expression for entropy given below,

$$S(V, N) = Nk_B \ln V - Nk_B \ln \epsilon, \quad (4.11)$$

is not extensive. If I double the value of V and of N , I expect S to be doubled. It does not. Mathematically S is extensive if it is a first order homogeneous function V and N . In other words we should have $S(\lambda V, \lambda N) = \lambda S(V, N)$. The above expression for entropy does not satisfy this rule. This is called Gibbs' paradox. More precisely Gibbs formulated the paradox in terms of entropy of mixing of like and unlike gases. We shall see these in details later when we consider closed system described by canonical ensembles. .

4.6 Boltzmann Counting

To restore the extensive property of entropy, Boltzmann introduced an ad-hoc notion of indistinguishable particles. $N!$ permutations of the particles, should all be counted as one micro state since they are *indistinguishable*. Hence,

$$\widehat{\Omega}(V, N) = \frac{1}{N!} \left(\frac{V}{\epsilon} \right)^N. \quad (4.12)$$

$$\begin{aligned}
S(V, N) &= k_B \ln \widehat{\Omega}(V, N), \\
&= k_B [N \ln V - N \ln N + N - N \ln \epsilon], \\
&= Nk_B \ln \left(\frac{V}{N} \right) + Nk_B - Nk_B \ln \epsilon.
\end{aligned} \tag{4.13}$$

In the above, I have expressed $\ln N! = N \ln N - N$, employing Stirling's first formula for a large factorial. We find that this prescription of Boltzmann restores the extensivity of entropy; *i.e.* we find

$$S(\lambda V, \lambda N) = \lambda S(V, N). \tag{4.14}$$

Boltzmann counting, at best, can be considered as a patch work. You don't pull down a well-built wall because there is a small crack in it. Instead you cover the crack by pasting a paper over it. A good formalism is not dismissed because of a flaw³. You look for a quick fix. Boltzmann counting provides one. In fact non extensivity of entropy is a pointer to a deeper malady. The fault is not with statistical mechanics but with classical formalism employed to describe ideal gas. For the correct resolution of the Gibbs' paradox we have to wait for the arrival of quantum mechanics.

4.7 Micro canonical Ensemble

Time has come for us to count the micro states of an isolated system of N non interacting point particles confined to a volume V , taking into considerations the positions as well as the momenta of all the particles.

Each particle for its specification requires six numbers : three positions and three momenta. The entire system can be specified by a string of $6N$ numbers. In a $6N$ dimensional phase space the system is specified by a point. The phase space point is all the time moving. We would be interested determining the region of the phase space accessible to the system when it is in equilibrium. If we are able to count the phase space volume, then we can employ the first micro-macro connection proposed by Boltzmann and get an expression for entropy as a function of energy, volume and the number of particles.

The system is isolated. It does not transact energy with the surroundings; not does it transact matter. Hence its energy remains a constant. The

³ Desperate and often elaborate patch work are not new to physicists. They have always indulged 'papering' when cracks appear in their understanding of science. A spectacular example is the entity aether proposed to justify the wave nature of light; Maxwell's work showed light is a wave. Waves require medium for propagation. Hence the medium aether, with exotic properties, was proposed to carry light.

potential energy is zero since the particles do not interact with each other. The kinetic energy is given by

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m}. \quad (4.15)$$

The system is thus confined to the surface of a $3N$ dimensional sphere. We need a formula for the volume of a hyper-sphere in $3N$ dimensions. To this end we need to know of Heaviside⁴ theta function and Dirac⁵ delta function.

4.8 Heaviside and his Θ Function

Define a function

$$f(x; \epsilon) = \begin{cases} 0 & \text{for } -\infty \leq x \leq -\frac{\epsilon}{2}; \\ \left(\frac{1}{\epsilon}\right) x + \frac{1}{2} & \text{for } -\frac{\epsilon}{2} \leq x \leq +\frac{\epsilon}{2}; \\ 1 & \text{for } +\frac{\epsilon}{2} \leq x \leq +\infty. \end{cases} \quad (4.16)$$

where $\epsilon > 0$.

Define

$$\Theta(x) = \lim_{\epsilon \rightarrow 0} f(x; \epsilon).$$

$\Theta(x)$ is called the step function, Heaviside step function, unit step function or theta function. It is given by,

$$\Theta(x) = \begin{cases} 0 & \text{for } -\infty \leq x < 0; \\ 1 & \text{for } 0 < x \leq +\infty. \end{cases} \quad (4.17)$$

Figure (4.3) depicts $f(x; \epsilon)$ for $\epsilon = 2, 1, 1/2$ and the theta function obtained in the limit of $\epsilon \rightarrow 0$.

4.9 Dirac and his δ Function

Start with the function $f(x; \epsilon)$ defined by Eq. (4.16). Take the derivative of the function. We find that the derivative is $1/\epsilon$, when $-\epsilon/2 < x < \epsilon/2$ and zero otherwise, Define,

⁴ Oliver Heaviside(1850-1925)

⁵ Paul Adrien Maurice Dirac(1902-1984)

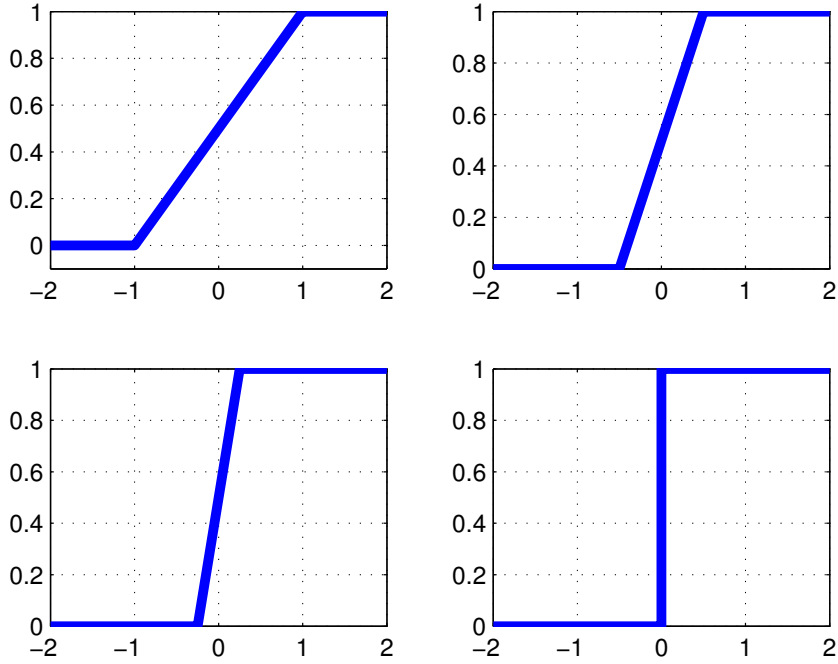


Fig. 4.3. $f(x; \epsilon)$ versus x . (Top Left) $\epsilon = 2$; (Top Right) $\epsilon = 1$; (Bottom Left) $\epsilon = 1/2$; (Bottom Right) $\Theta(x)$

$$g(x; \epsilon) = \frac{df}{dx} = \begin{cases} 0 & \text{for } -\infty \leq x < -\epsilon/2; \\ \frac{1}{\epsilon} & \text{for } -\epsilon/2 < x < +\epsilon/2; \\ 0 & \text{for } +\epsilon/2 < x \leq +\infty. \end{cases} \quad (4.18)$$

Figure(4.4) depicts $g(x; \epsilon)$ for $\epsilon = 2, 1, 1/2, 1/4$.

The Dirac-delta function is defined as,

$$\delta(x) = \lim_{\epsilon \rightarrow 0} g(x; \epsilon). \quad (4.19)$$

Consider the following integral.

$$I = \int_{-\infty}^{+\infty} dx g(x; \epsilon). \quad (4.20)$$

We find that the integral is the same for all values of ϵ . This gives us an important property of the Dirac-delta function:

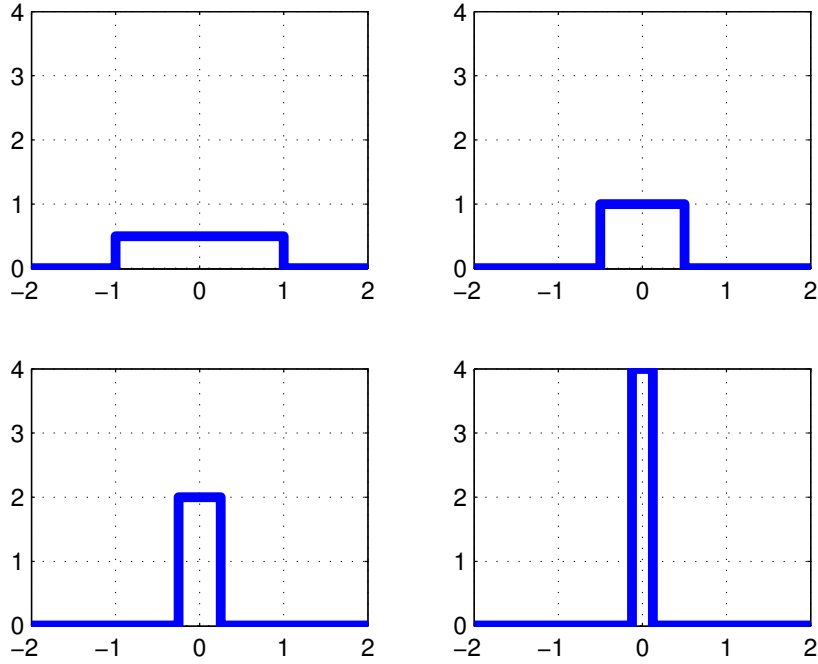


Fig. 4.4. $g(x; \epsilon) = \frac{df}{dx}$ versus x . (Top Left) $\epsilon = 2$; (Top Right) $\epsilon = 1$; (Bottom Left) $\epsilon = 1/2$; (Bottom Right) $\epsilon = 1/4$

$$\int_{-\infty}^{+\infty} dx \delta(x) = 1. \quad (4.21)$$

4.10 Area of a Circle

Let us demonstrate how to use the theta function and delta function to derive an expression for a circle of radius R . Let us denote the area of a circle by the symbol $V_2(R)$ - the 'volume' of a two dimensional 'sphere' of radius R . A little thought will tell you,

$$V_2(R) = \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \Theta \left(R^2 - \sum_{i=1}^2 x_i^2 \right). \quad (4.22)$$

Let

$$y_i = x_i/R \text{ for } i = 1, 2.$$

Then,

$$V_2(R) = R^2 \int_{-\infty}^{+\infty} dy_1 \int_{-\infty}^{+\infty} dy_2 \Theta \left(R^2 \left(1 - \sum_{i=1}^2 y_i^2 \right) \right). \quad (4.23)$$

We have

$$\Theta(\lambda x) = \theta(x) \quad \forall \lambda > 0.$$

Therefore,

$$V_2(R) = R^2 \int_{-\infty}^{+\infty} dy_1 \int_{-\infty}^{+\infty} dy_2 \Theta \left(1 - \sum_{i=1}^2 y_i^2 \right) \quad (4.24)$$

$$= R^2 V_2(R = 1). \quad (4.25)$$

We can now write Eq. (4.22) as

$$V_2(R = 1)R^2 = \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \Theta \left(R^2 - \sum_{i=1}^2 x_i^2 \right). \quad (4.26)$$

Now differentiate both sides of the above equation with respect to the variable R . We have already seen that the derivative of a Theta function is the Dirac-delta function. Therefore

$$V_2(R = 1)2R = 2R \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \delta \left(R^2 - \sum_{i=1}^2 x_i^2 \right). \quad (4.27)$$

Now multiply both sides of the above equation by $\exp(-R^2)dR$ and integrate over the variable R from 0 to ∞ . We get,

$$V_2(R = 1) \int_0^{\infty} \exp(-R^2)2RdR = \int_0^{\infty} \exp(-R^2) 2RdR \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \delta \left(R^2 - \sum_{i=1}^2 x_i^2 \right). \quad (4.28)$$

$$V_2(R = 1) \int_0^{\infty} dt \exp(-t) = \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \exp(-x_1^2 - x_2^2). \quad (4.29)$$

$$V_2(R = 1) \times 1 = \left[\int_{-\infty}^{+\infty} dx \exp(-x^2) \right]^2. \quad (4.30)$$

$$V_2(R = 1) = \left[2 \int_0^{\infty} dx \exp(-x^2) \right]^2 = \left[\int_0^{\infty} dx x^{-1/2} \exp(-x) \right]^2. \quad (4.31)$$

$$V_2(R = 1) = \left[\int_0^{\infty} x^{(1/2)-1} \exp(-x) dx \right]^2 = [\Gamma(1/2)]^2 = \pi. \quad (4.32)$$

Thus $V_2(R) = V_2(R = 1) \times R^2 = \pi R^2$, a result we are all familiar with.

4.11 Volume of an N -Dimensional Sphere

The volume of an N - dimensional sphere of radius R is formally given by the integral,

$$V_N(R) = \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \cdots \int_{-\infty}^{+\infty} dx_N \Theta \left(R^2 - \sum_{i=1}^N x_i^2 \right), \quad (4.33)$$

Change the coordinate system from

$$\{x_i : i = 1, N\} \text{ to } \{y_i = x_i/R : i = 1, N\}.$$

$$dx_i = R dy_i \forall i = 1, N;$$

$$\Theta \left(R^2 \left[1 - \sum_{i=1}^N y_i^2 \right] \right) = \Theta \left(1 - \sum_{i=1}^N y_i^2 \right).$$

We have,

$$V_N(R) = R^N \int_{-\infty}^{+\infty} dy_1 \int_{-\infty}^{+\infty} dy_2 \cdots \int_{-\infty}^{+\infty} dy_N \Theta \left(1 - \sum_{i=1}^N y_i^2 \right); \quad (4.34)$$

$$= V_N(R = 1)R^N. \quad (4.35)$$

where $V_N(R = 1)$ is the volume of an N - dimensional sphere of radius unity.

To find the volume of N -dimensional sphere of radius R , we proceed as follows.

$$V_N(R = 1)R^N = \int_{-\infty}^{+\infty} dx_1 \cdots \int_{-\infty}^{+\infty} dx_N \Theta \left(R^2 - \sum_{i=1}^N x_i^2 \right). \quad (4.36)$$

Differentiate both sides of the above expression with respect to R and get,

$$\begin{aligned} NV_N(R = 1)R^{N-1} &= \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \cdots \\ &\quad \cdots \int_{-\infty}^{+\infty} dx_N \delta \left(R^2 - \sum_{i=1}^N x_i^2 \right) 2R. \end{aligned} \quad (4.37)$$

Now, multiply both sides by $\exp(-R^2)dR$ and integrate over R from 0 to ∞ .
The Left Hand Side:

$$LHS = NV_N(R = 1) \int_0^{\infty} dR \exp(-R^2)R^{N-1}. \quad (4.38)$$

Let $x = R^2$; then $dx = 2RdR$. This give

$$dR = \frac{1}{2} \frac{dx}{x^{1/2}}.$$

We get,

$$\begin{aligned} LHS &= V_N(R=1) \frac{N}{2} \int_0^\infty x^{\frac{N}{2}-1} \exp(-x) dx, \\ &= V_N(R=1) \frac{N}{2} \Gamma\left(\frac{N}{2}\right), \\ &= \Gamma\left(\frac{N}{2} + 1\right) V_N(R=1). \end{aligned} \quad (4.39)$$

The Right Hand Side :

$$\begin{aligned} RHS &= \int_0^\infty dR \exp(-R^2) \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \cdots \\ &\quad \cdots \int_{-\infty}^{+\infty} dx_N \delta\left(R^2 - \sum_{i=1}^N x_i^2\right) 2R; \end{aligned} \quad (4.40)$$

$$t = R^2 ; dt = 2RdR,$$

$$\begin{aligned} RHS &= \int_0^\infty dt \exp(-t) \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \cdots \\ &\quad \int_{-\infty}^{+\infty} dx_N \delta\left(t - \sum_{i=1}^N x_i^2\right), \\ &= \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 \cdots \int_{-\infty}^{+\infty} dx_N \exp[-(x_1^2 + x_2^2 + \cdots + x_N^2)], \\ &= \left[\int_{-\infty}^{+\infty} dx \exp(-x^2) \right]^N \\ &= \pi^{N/2}. \end{aligned} \quad (4.41)$$

Thus we get

$$V_N(R=1) = \frac{\pi^{N/2}}{\Gamma\left(\frac{N}{2} + 1\right)}. \quad (4.42)$$

$$V_N(R) = \frac{\pi^{N/2}}{\Gamma\left(\frac{N}{2} + 1\right)} R^N. \quad (4.43)$$

4.12 Classical Counting of Micro states

Consider an isolated system of N non-interacting point particles. Each particle requires 3 position coordinates and 3 momentum coordinates for its specification. A string of $6N$ numbers denotes a micro state of the system. Let us first find the volume of the phase space accessible to the system. The integral over $3N$ spatial coordinates gives V^N . We have, $E = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$. The volume of the phase space of the system with energy $\leq E$ is the volume of a $3N$ dimensional sphere of radius $\sqrt{2mE}$.

4.12.1 Counting of the Volume

Let us measure the volume of the phase space in units of h^{3N} , where h is Planck constant. We have

$$\Delta x \Delta p_x \geq h.$$

Thus h^{3N} is the volume of a "minimum uncertainty" cube. Thus we have

$$\widehat{\Omega}(E, V, N) = \frac{V^N (2\pi m E)^{3N/2}}{h^{3N} \Gamma(\frac{3N}{2} + 1)}. \quad (4.44)$$

4.13 Density of States

Let $g(E)$ denote the density of (energy) states. $g(E)dE$ gives the number of micro states with energy between E and $E + dE$. In other words,

$$\widehat{\Omega}(E) = \int_0^E g(E') dE'. \quad (4.45)$$

From the above, we find

$$g(E, V, N) = \left(\frac{\partial \widehat{\Omega}(E, V, N)}{\partial E} \right)_{V, N}. \quad (4.46)$$

Let us take the partial derivative of $\widehat{\Omega}(E, V, N)$ with respect to E and get,

$$g(E, V, N) = \frac{V^N (2\pi m)^{3N/2}}{h^{3N} \Gamma(\frac{3N}{2} + 1)} \frac{3N}{2} E^{(3N/2)-1}. \quad (4.47)$$

Let us substitute $N = 1$ in the above and get the single particle density of states, $g(E, V)$ as,

$$g(E, V) = \frac{V}{h^3} \frac{\pi}{4} (8m)^{3/2} E^{1/2}. \quad (4.48)$$

4.13.1 A Sphere Lives on its Outer Shell : Power Law can be Intriguing

In the limit of $N \rightarrow \infty$, the volume of a thin outer shell tends to the volume of the whole sphere. This intriguing behaviour is a consequence of the power law behaviour.

$$\begin{aligned} \frac{V_N(R) - V_N(R - \Delta R)}{V_N(R)} &= \frac{R^N - (R - \Delta R)^N}{R^N}, \\ &= 1 - \left(1 - \frac{\Delta R}{R}\right)^N = 1 \text{ for } N \rightarrow \infty. \end{aligned} \quad (4.49)$$

Consider the case with $R = 1$ and $\Delta R = 0.1$. The percentage of the total volume contained in the outermost shell of an N dimensional sphere for $N = 1, 2, \dots, 10$ is given in the table below. . Hence in the limit of $N \rightarrow \infty$

Table 4.1. Percentage of volume of an N dimensional sphere contained in a thin outer shell between $R = 0.90$ and 1

N	$\frac{V_N(R = 1) - V_N(R = 0.9)}{V_N(R = 1)} \times 100$	N	$\frac{V_N(R = 1) - V_N(R = 0.9)}{V_N(R = 1)} \times 100$
1	10.000%	8	57.000%
2	19.000%	9	61.000%
3	27.000%	10	65.000%
4	34.000%	20	88.000%
5	41.000%	40	99.000%
6	47.000%	60	99.000%
7	52.000%	80	99.980%
		100	99.997%

the number of micro states with energy less than or equal to E is nearly the same as the number of micro states with energy between $E - \Delta E$ and E .

4.14 Entropy of an Isolated System

From Eq. (4.44) we see that

$$S(E, V, N) = Nk_B \left[\ln V + \frac{3}{2} \ln \left(\frac{E}{N}\right) + \frac{3}{2} \ln \left(\frac{4\pi m}{3h^2}\right) + \frac{3}{2} \right]. \quad (4.50)$$

We find that the above expression for entropy is not extensive :

$$S(\lambda E, \lambda V, \lambda N) \neq \lambda S(E, V, N).$$

To restore extensivity of entropy we shall follow Boltzmann's prescription and divide $\Omega(E, V, N)$, see Eq. (4.44), by $N!$.

$$\widehat{\Omega}(E, V, N) = \frac{V^N}{h^{3N}} \frac{1}{N!} \frac{(2\pi m E)^{3N/2}}{\Gamma(\frac{3N}{2} + 1)}. \quad (4.51)$$

The corresponding entropy is then,

$$S(E, V, N) = Nk_B \left[\ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln\left(\frac{E}{N}\right) + \frac{3}{2} \ln\left(\frac{4\pi m}{3h^2}\right) + \frac{5}{2} \right]. \quad (4.52)$$

It is clear that the expression for entropy given above is extensive.

4.15 Properties of an Ideal Gas

4.15.1 Temperature

The temperature of an ideal gas, as a function of E , V , and N , is given by

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} = \frac{3Nk_B}{2E} \Rightarrow T = \frac{2E}{3Nk_B}. \quad (4.53)$$

4.15.2 Equipartition Theorem

The energy of the system is thus given by,

$$E = 3N \left(\frac{1}{2}k_B T\right). \quad (4.54)$$

The above is called equi-partition theorem. Each quadratic term⁶ in the Hamiltonian carries an energy of $k_B T/2$.

4.15.3 Pressure

The pressure of an isolated system of ideal gas as a function of E , V , and N , is given by,

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T} = \frac{Nk_B}{V}, \quad (4.55)$$

$$P = \frac{Nk_B T}{V}. \quad (4.56)$$

Substituting in the above T as a function of E , V , and N , see Eq. (4.53), we get,

$$P = \frac{2E}{3V}. \quad (4.57)$$

⁶ For an ideal gas $H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$. There are $3N$ quadratic terms in the Hamiltonian.

4.15.4 Ideal Gas Law

See the expression for P given in Eq.(4.56). We have the ideal gas law, $PV = Nk_B T$.

4.15.5 Chemical Potential

An expression for the chemical potential as a function of E , V , and N is derived as follows.

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}. \quad (4.58)$$

Therefore,

$$\mu = -k_B T \ln\left(\frac{V}{N}\right) - \frac{3}{2}k_B T \ln\left(\frac{4\pi m E}{3N h^2}\right). \quad (4.59)$$

Substituting in the above, the expression for T in terms of E and N , from Eq. (4.53), we get micro canonical chemical potential⁷,

$$\mu = -\frac{2E}{3N} \ln\left(\frac{V}{N}\right) - \frac{E}{N} \ln\left(\frac{4\pi m E}{3N h^2}\right). \quad (4.60)$$

In the above expression for the micro canonical chemical potential, let us substitute

$$E = 3Nk_B T/2$$

and get canonical chemical potential⁸,

$$\begin{aligned} \mu &= -k_B T \ln\left(\frac{V}{N}\right) - \frac{3}{2}k_B T \ln\left(\frac{2\pi m k_B T}{h^2}\right), \\ &= -k_B T \ln\left(\frac{V}{N}\right) + 3k_B T \ln(\Lambda). \end{aligned} \quad (4.61)$$

where Λ is the thermal or quantum wavelength⁹ given by,

⁷ Chemical potential for an isolated system; it is expressed as a function of E , V , and N

⁸ chemical potential of a closed system : it is expressed as a function of T , V , and N .

⁹ Consider a particle with energy $k_B T$. We have

$$E = k_B T = \frac{p^2}{2m}; \quad p^2 = 2mk_B T; \quad p = \sqrt{2mk_B T}.$$

The de Broglie wavelength associated a particle having momentum p is

$$\Lambda = \frac{h}{p} = \frac{h}{\sqrt{2mk_B T}}.$$

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}. \quad (4.62)$$

Let the number density be denoted by ρ . We have thus $\rho = N/V$. We can write the chemical potential in a compact form, as follows.

$$\begin{aligned} \mu &= -k_B T \ln\left(\frac{V}{N}\right) + 3k_B T \ln(\Lambda), \\ &= k_B T \ln \rho + k_B T \ln \Lambda^3, \\ &= k_B T \ln(\rho \Lambda^3). \end{aligned} \quad (4.63)$$

- When the density of particles is small, and temperatures are high, then $\rho \Lambda^3 \ll 1$. Note that the thermal wavelength Λ is inversely proportional to (square root of) temperature. Hence it is small at high temperatures. Hence at high temperatures and/or low densities, the chemical potential is negative and large.
- At $\rho \Lambda^3 = 1$, the chemical potential is zero.
- At low temperatures and high densities, $\rho \Lambda^3 \gg 1$. The chemical potential is positive.

Figure (4.5) shows typical classical behaviour of chemical potential with change of temperature.

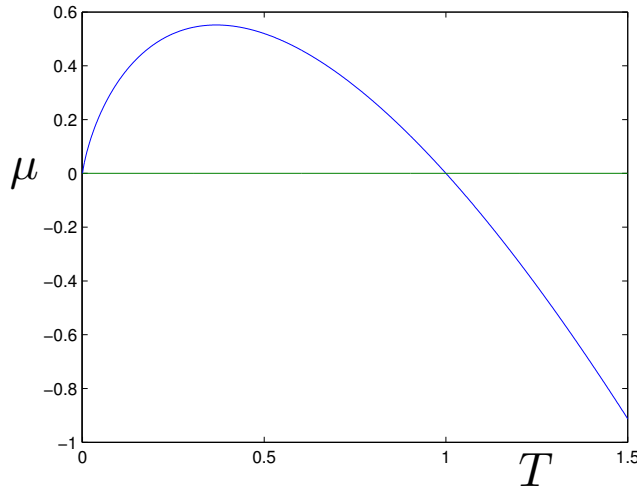


Fig. 4.5. μ versus T for a classical ideal gas. $\mu = -(3T/2) \ln(T)$. We have set $k_B = h = \rho/(2\pi m)^{3/2} = 1$

I have set $k_B = h = \frac{\rho}{(2\pi m)^{3/2}} = 1$ for producing the above graph. From the figure we observe that at high temperatures μ is negative; at low temperatures it is positive; as T decreases μ increases, reaches a maximum and then decreases to zero at zero temperature.

4.16 Quantum Counting of Micro states

We have done *classical counting* of micro states and showed that for an isolated system of a single particle confined to a volume V , the number of micro states with energy less than ϵ , is given by

$$\widehat{\Omega}(\epsilon, V) = \frac{V}{h^3} \frac{(2\pi m\epsilon)^{3/2}}{\Gamma((3/2) + 1)}, \quad (4.64)$$

We have obtained the above by substituting $N = 1$ in the equation,

$$\widehat{\Omega}(E, V, N) = \frac{1}{h^{3N}} \frac{V^N}{N!} \frac{(2\pi mE)^{3N/2}}{\Gamma\left(\frac{3N}{2} + 1\right)}.$$

Now let us do *quantum counting* of micro states ¹⁰.

¹⁰ A fundamental entity in quantum mechanics is the wave function $\psi(\mathbf{q}, t)$, where \mathbf{q} is the position vector. The wave function is given a physical interpretation that

$$\psi^*(\mathbf{q}, t)\psi(\mathbf{q}, t)d\mathbf{q}$$

gives the probability of finding the system in an elemental volume $d\mathbf{q}$ around the point \mathbf{q} at time t . Since the system has to be somewhere, for, otherwise we would not be interested in it, we have the normalization,

$$\int \psi^*(\mathbf{q}, t)\psi(\mathbf{q}, t)d\mathbf{q} = 1,$$

where the integral is taken over the entire coordinate space - each of the x , y and z coordinates extending from $-\infty$ to $+\infty$.

A central problem in quantum mechanics is the calculation of $\psi(\mathbf{q}, t)$ for the system of interest. We shall be interested in the time independent wave function $\psi(\mathbf{q})$ describing a stationary states of the system.

How do we get $\psi(\mathbf{q})$?

Schrödinger gave a prescription : Solve the equation $\mathcal{H}\psi(\mathbf{q}) = E\psi(\mathbf{q})$, with appropriate boundary conditions.

We call this the time independent Schrödinger equation.

\mathcal{H} is the Hamiltonian operator

$$\mathcal{H} = -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{q}). \quad (4.65)$$

The first operator on the right is kinetic energy and the second the potential energy.

4.16.1 Energy Eigenvalues : Integer Number of Half Wave Lengths in L

Let me tell you how to obtain the energy eigenvalues without invoking Schrödinger equation. Consider a particle confined to a one dimensional box of length L . We recognise the segment L must contain integral number of half wave lengths - so that the wave function vanishes at the boundaries of the one dimensional box. In other words,

$$L = n \times \frac{\lambda}{2} \quad : \quad n = 1, 2, \dots \quad (4.68)$$

$$\lambda = \frac{2L}{n} \quad : \quad n = 1, 2, \dots \quad (4.69)$$

Substitute the above in the de Broglie relation

$$p = \frac{h}{\lambda} = \frac{h}{2L}n \quad : \quad n = 1, 2, \dots$$

This yields

$$\epsilon_n = \frac{p^2}{2m} = \frac{h^2}{8mL^2} n^2 \quad : \quad n = 1, 2, \dots$$

Consider a particle in an $L \times L \times L$ cube - a three dimensional infinite well. The energy of the system is given by

$$\epsilon_{n_x, n_y, n_z} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2),$$

where $n_x = 1, 2, \dots$, $n_y = 1, 2, \dots$, and $n_z = 1, 2, \dots$.

E in the Schrödinger equation is a scalar ... a real number... called energy. It is an eigenvalue of the Hamiltonian operator : we call it energy eigenvalue.

The Schrödinger equation is a partial differential equation. Once we impose boundary condition on the solution, then only certain discrete energies are permitted. We call these energy eigenvalues.

Energy Eigenvalue by Solving Schrödinger Equation Once we specify boundary conditions, then a knowledge of the Hamiltonian is sufficient to determine its eigenvalues and the corresponding eigenfunctions. There will be usually several eigenvalues and corresponding eigenfunctions for a given system.

For a single particle in a one dimensional infinite well

$$\mathcal{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}. \quad (4.66)$$

Solve the one dimensional Schrödinger equation with the boundary condition : the wave function vanishes at the boundaries. Show that the energy eigenvalues are given by

$$\epsilon_n = \frac{h^2}{8mL^2} n^2; \quad n = 1, 2, \dots \quad (4.67)$$

The ground state is $(n_x, n_y, n_z) = (1, 1, 1)$; it is non degenerate; the energy eigenvalue is

$$\epsilon_{1,1,1} = \frac{3h^2}{8mL^2}. \quad (4.70)$$

The first excited state is three-fold degenerate. The corresponding energy eigenvalue is

$$\epsilon_{2,1,1} = \epsilon_{1,2,1} = \epsilon_{1,1,2} = \frac{3h^2}{4mL^2}. \quad (4.71)$$

We start with,

$$\epsilon = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2).$$

We can write the above as,

$$n_x^2 + n_y^2 + n_z^2 = \frac{8mL^2\epsilon}{h^2} = R^2. \quad (4.72)$$

(n_x, n_y, n_z) represents a lattice point in the three dimensional space. The equation $n_x^2 + n_y^2 + n_z^2 = R^2$ says we need to count the number of lattice points that are at a distance R from the origin. It is the same as the number of lattice points that are present on the surface of a sphere of radius R in the positive quadrant; note that the x , y , and z coordinates of the lattice points are all positive. It is difficult to count the number of lattice points lying on the surface of a sphere. Instead we count the number of points contained in a thin spherical shell. To calculate this quantity we first count the number of points inside a sphere of radius

$$R = \left(\frac{8mL^2\epsilon}{h^2} \right)^{1/2}$$

and take one-eighth of it. Let us denote this number by $\widehat{\Omega}(\epsilon)$. We have,

$$\widehat{\Omega}(\epsilon) = \frac{1}{8} \frac{4}{3} \pi R^3 = \frac{\pi}{6} \left(\frac{8mL^2\epsilon}{h^2} \right)^{3/2}. \quad (4.73)$$

We recognize $V = L^3$ and write the above equation as

$$\begin{aligned} \widehat{\Omega}(\epsilon, V) &= \frac{V}{h^3} \frac{\pi}{6} (8m\epsilon)^{3/2} = \frac{V}{h^3} \frac{4\pi}{3} (2m\epsilon)^{3/2}, \\ &= \frac{V}{h^3} \frac{4\pi}{3} \frac{(2\pi m\epsilon)^{3/2}}{\pi^{3/2}} = \frac{V}{h^3} \frac{(2\pi m\epsilon)^{3/2}}{(3/2)(1/2)\sqrt{\pi}}, \\ &= \frac{V}{h^3} \frac{(2\pi m\epsilon)^{3/2}}{(3/2)(1/2)\Gamma(1/2)} = \frac{V}{h^3} \frac{(2\pi m\epsilon)^{3/2}}{\Gamma((3/2) + 1)}. \end{aligned} \quad (4.74)$$

The above is exactly the one we obtained by classical counting, see Eq. (4.64) Notice that in quantum counting of micro states, the term h^3 comes naturally, while in classical counting it is hand-put¹¹.

The density of (energy) states is obtained by differentiating $\widehat{\Omega}(\epsilon, V)$ with respect to the variable ϵ . We get

$$g(\epsilon, V) = \frac{V}{h^3} \frac{\pi}{4} (8m)^{3/2} \epsilon^{1/2}. \quad (4.75)$$

The important point is that the density of energy states is proportional to $\epsilon^{1/2}$.

4.17 Chemical Potential : Toy Model

Following Cook and Dickerson¹² consider an isolated system of two identical, distinguishable and non-interacting particles occupying non-degenerate energy levels $\{0, \epsilon, 2\epsilon, 3\epsilon, \dots\}$, such that the total energy of the system is 2ϵ . Let $\widehat{\Omega}(E = 2\epsilon, N = 2)$ denote the number of micro states of the two-particle system with total energy $E = 2\epsilon$. Aim is to calculate $\widehat{\Omega}(E = 2\epsilon, N = 2)$

We label the two particles as A and B . The micro states with total energy 2ϵ are given in Table (4.2 : LEFT). We find that $\widehat{\Omega}(E = 2\epsilon, N = 2) = 3$. The entropy of the two-particle system with energy $E = 2\epsilon$ is given by

$$S(E = 2\epsilon, N = 2) = k_B \ln \widehat{\Omega}(E = 2\epsilon, N = 2) = k_B \ln(3).$$

Now add a particle, labelled C , such that the energy of the system does

Table 4.2. LEFT : Three micro states of a two-particles system with total energy 2ϵ . RIGHT : Six micro states of a three-particles system with total energy 2ϵ

0	ϵ	2ϵ
A	-	B
B	-	A
-	A,B	-

0	ϵ	2ϵ
A,B	-	C
B,C	-	A
C,A	-	B
A	B,C	-
B	C,A	-
C	A,B	-

not change. Let $\widehat{\Omega}(E = 2\epsilon, N = 3)$ denote the number of micro states of the

¹¹ We wanted to count the phase space volume. We took h^3 as the volume of a six-dimensional cube. We considered the six-dimensional phase space (of a single particle) as filled with non-overlapping exhaustive set of such tiny cubes. We have to do all these because of Boltzmann ! He told us that entropy is logarithm of number of micro states. We need to count the number of micro states.

¹² See G Cook and R H Dickerson, *Understanding the chemical potential*, American Journal of Physics **63**(8), 737 (1995)

three-particle system with a total energy of $E = 2\epsilon$. Table (4.2 : RIGHT) lists the micro states.

We find $\widehat{\Omega}(E = 2\epsilon, N = 3) = 6$. The entropy is given by

$$S(E = 2\epsilon, N = 3) = k_B \ln \widehat{\Omega}(E = 2\epsilon, N = 3) = k_B \ln(6).$$

We find $S(E = 2\epsilon, N = 3) > S(E = 2\epsilon, N = 2)$. Note that

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V}.$$

In other words, μ is the change in energy of the system when one particle is added in such a way that the entropy and volume of the system remain unchanged.

Let us now remove ϵ amount of energy from the three-particles system and count the number of micro states. Table(4.3) shows that the number of micro states of the three particles system with energy $2\epsilon - \epsilon = \epsilon$ is three.

Table 4.3. Three micro states of a three-particles system with total energy ϵ

0	ϵ
A,B	C
B,C	A
C,A	B

Thus to a two-particle system with energy 2ϵ , if we add a particle, we should remove ϵ of energy to keep entropy the same. Therefore $\mu = -\epsilon$.

DRAFT

5. Closed System : Canonical Ensemble

5.1 What is a Closed System ?

A closed system is one which does not exchange material with the surroundings. However, it does exchange energy. It is in thermal contact with the surroundings. We idealize the surroundings as a "heat bath"¹.

Thus, a closed system in thermal equilibrium, is characterized by T , V and N . The system is not isolated. Hence its micro states are not all equiprobable.

5.2 Toy Model à la H B Callen

Consider² a fair red die representing the system and two fair white dice representing the surroundings. A string of three numbers, each lying between 1 and 6 constitutes a micro state of the three dice system. There are $6^3 = 216$ micro states and they are all equally probable³. In particular the system-dice (the red one) shall be in one of its six micro states with equal probability.

Let us now impose the condition that the three dice add to 6. Under this condition, let us enquire if the six micro states of the dice are equally probable.

Let $P(k)$ denote the probability that the red die shows up k given the three dice add to 6. Because of the condition imposed, the red die can be in any one of the four states, $\{1, 2, 3, 4\}$ only; and these four micro states are not equally probable. The probabilities can be calculated as follows.

We find that for the three-dice system, there are 10 micro states with the property that the three dice add to 6. These are listed in Table(1).

¹ A "heat bath" transacts energy with the system, but its temperature does not change.

² Herbert B Callen, *Thermodynamics and an Introduction to Thermostatistics*, Second Edition, Wiley (2006)

³ All micro states are equally probable : Ergodicity.

Table 5.1. The ten micro states of Callen's three-dice system with the constraint that they add to ten

No.	W	R	W
1	1	1	4
2	2	1	3
3	3	1	2
4	4	1	1
5	1	2	3

No.	W	R	W
6	2	2	2
7	3	2	1
8	1	3	2
9	2	3	1
10	1	4	1

The ten micro states are equally probable. These are the micro states of the universe - which consists of the system and its surroundings. The universe constitutes an isolated system.

Of these ten micro states of the universe, there are four micro states for which the system die shows up in its microstate 1; therefore $P(1) = 0.4$. Similarly we can calculate the other probabilities :

$$P(2) = 0.3; P(3) = 0.2; P(4) = 0.1; P(5) = P(6) = 0.0$$

The important point is that the system is not found in all its microstates with equal probability.

From the above toy model, we can say that if we consider the system and its surroundings together to constitute the universe and demand that the universe has a fixed energy, then the system will not be in its micro states with equal probability.

What is the probability of a micro state of a closed system ? We shall calculate the probability in the next section employing two different methods. The first involves Taylor expansion of $S(E)$. I learnt of this, from the book of Balescu⁴. The second is based on the method of most probable distribution, described in several books⁵.

5.3 Canonical Partition Function

5.3.1 Derivation à la Balescu

A closed system, its boundary and the bath - constitute the universe; the universe is an isolated system. We know for an isolated system, all micro states are equally probable. Let \mathcal{E} denote the energy of the universe. It remains a constant.

Now consider a particular micro state of the closed system. Let us label it as C . Let its energy be $E(C)$. Note that $E(C) \ll \mathcal{E}$. When the closed system is in

⁴ R Balescu, *Equilibrium and non-equilibrium statistical mechanics*, Wiley (1975).

⁵ see e.g. R. K. Pathria, *Statistical Mechanics*, Second Edition Butterworth Heine-
mann (2001)p.45

its micro state C , the surroundings can be in any one of $\widehat{\Omega}(\mathcal{E} - E(C))$ micro states of the universe⁶.

For the universe, which is an isolated system, all the micro states are equally probable. Thus we can say that the probability of finding the closed system in its micro state C is given by,

$$P(C) = \frac{\widehat{\Omega}(\mathcal{E} - E(C))}{\widehat{\Omega}_t}, \quad (5.1)$$

where we have denoted the total number of micro states of the universe as $\widehat{\Omega}_t$.

We have $S(\mathcal{E} - E(C)) = k_B \ln \widehat{\Omega}(\mathcal{E} - E(C))$. Therefore

$$\widehat{\Omega}(\mathcal{E} - E(C)) = \exp \left[\frac{1}{k_B} S(\mathcal{E} - E(C)) \right]. \quad (5.2)$$

Also since $E(C) \ll \mathcal{E}$, we can Taylor expand $S(\mathcal{E} - E(C))$ around \mathcal{E} retaining only the first two terms. We get,

$$\begin{aligned} S(\mathcal{E} - E(C)) &= S(\mathcal{E}) - E(C) \left(\frac{\partial S}{\partial E} \right)_{E=\mathcal{E}}, \\ &= S(\mathcal{E}) - \frac{1}{T} E(C). \end{aligned} \quad (5.3)$$

Substituting the above in the expression for $P(C)$, we get,

$$\begin{aligned} P(C) &= \frac{\exp[S(\mathcal{E})/k_B]}{\widehat{\Omega}_t} \exp \left[-\frac{E(C)}{k_B T} \right], \\ &= \alpha \exp[-\beta E(C)], \end{aligned} \quad (5.4)$$

where α is a constant and $\beta = 1/(k_B T)$. We can evaluate α completely in terms of the properties of the closed system by the normalization condition for the probabilities, see below.

$$\sum_C P(C) = 1, \quad (5.5)$$

$$\alpha \sum_C \exp[-\beta E(C)] = 1, \quad (5.6)$$

$$Q(T, V, N) = \frac{1}{\alpha} = \sum_C \exp[-\beta E(C)]. \quad (5.7)$$

where $Q(T, V, N)$ is called the **canonical partition function**.

Canonical Partition Function : Transform of Density of States

We start with

⁶ I am considering that a micro state of the universe can be thought of as a simple juxtaposition of the micro state of closed system and the micro state of the surroundings. The system and the surroundings interact at the boundaries and hence there shall exist micro states of the isolated system which can not be neatly viewed as the system micro state juxtaposed with the surroundings micro state. Such micro states are so few in number we shall ignore them.

$$Q(\beta, V, N) = \sum_i \exp[-\beta E_i(V, N)] , \quad (5.8)$$

where, $\beta = 1/[k_B T]$, and the sum runs over all the micro states of a closed system at temperature T , volume V and number of particles N . Let $\widehat{\Omega}(E, V, N)$ denote the density of (energy) states. In other words $\widehat{\Omega}(E, V, N)dE$ is the number of micro states having energy between E and $E + dE$. The canonical partition function, see Eq. (5.8), can be written as an integral over energy,

$$Q(\beta, V, N) = \int_0^\infty dE \widehat{\Omega}(E, V, N) \exp[-\beta E(V, N)] . \quad (5.9)$$

We see that the canonical partition function is a 'transform' of the density of states . The "variable" energy is transformed to the "variable" temperature. The transform helps us go from a micro canonical (ensemble) description (of an isolated system) with independent variables E , (V and N) to a canonical (ensemble) description (of a closed system) with independent variables T , (V , and N). The density of states is a steeply increasing function of E . The exponential function $\exp(-\beta E)$ decays with E for any finite value of β . The decay is steeper at higher value of β or equivalently at lower temperatures. The product shall be, in general, sharply peaked at a value of E determined by β .

When β is small (or temperature is large) the integrand would peak at a large value of E . When β is high (at low temperatures) it would peak at a low value of E .

5.4 Helmholtz Free Energy

The internal energy U of thermodynamics is obtained by averaging the statistical energy E over a canonical ensemble. A closed system will invariably be found with an energy $U = \langle E \rangle$ but for extremely small (relative) fluctuations around U ; these fluctuations are proportional to the inverse of the square root of the number of molecules. Consider,

$$Q(\beta, V, N) = \int_0^\infty dE \widehat{\Omega}(E, V, N) \exp[-\beta E(V, N)] . \quad (5.10)$$

In the above replace the integral over E by the value of the integrand, evaluated at $E = \langle E \rangle = U$. We get,

$$Q = \widehat{\Omega}(E = U, V, N) \exp(-\beta U) ; \ln Q = \ln \widehat{\Omega}(U, V, N) - \beta U ,$$

$$\begin{aligned} -k_B T \ln Q &= U - T k_B \ln \widehat{\Omega}(U, V, N) \\ &= U - TS(U, V, N). \end{aligned} \quad (5.11)$$

We identify the right hand side of the above as (Helmholtz) free energy ⁷ :

$$F(T, V, N) = U - TS(U, V, N) ; \frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V, N} . \quad (5.12)$$

⁷ Legendre Transform : Start with $U(S, V, N)$. Concentrate on the dependence of U on S . Can this dependence be described in an equivalent but alternate way ? Take the slope of the curve $U(S)$ at S . We have

$$T(S, V, N) = \left(\frac{\partial U}{\partial S} \right)_{V, N}.$$

We can plot T against S ; but then it will not uniquely correspond to the given curve $U(S)$. All parallel curves in the U - S plane shall lead to the same $T(S)$. It is the intercept that will tell one curve from the other, in the family. Let us denote the intercept by the symbol F . We have

$$\frac{U(S, V, N) - F}{S} = T; \quad F(T, V, N) = U(S, V, N) - TS; \quad T = \left(\frac{\partial U}{\partial S} \right)_{V, N}.$$

The equation for micro canonical temperature, is inverted and entropy is expressed as a function of T , V , and N . Employing the function $S(T, V, N)$ we get $U(T, V, N)$ and $F(T, V, N)$. The above is called Legendre transform. S transforms to 'slope' T and $U(S)$ transforms to the intercept $F(T)$. We call $F(T, V, N)$ as Helmholtz free energy.

Example: Consider U expressed as a function of S , V , and N :

$$U(S, V, N) = \alpha \frac{S^3}{NV}.$$

We get

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, N} = \alpha \frac{3S^2}{NV}.$$

Inverting, we get,

$$S = \sqrt{\frac{NVT}{3\alpha}}.$$

We then get internal energy as a function of temperature,

$$U = \sqrt{\frac{NV}{3\alpha}} \left(\frac{T}{3} \right)^{3/2}.$$

The Helmholtz free energy is then expressed as

$$F = U - TS = -2 \left(\frac{NV}{\alpha} \right)^{1/2} \left(\frac{T}{3} \right)^{3/2}.$$

ENTHALPY : $H(S, P, N)$. Start with $U(S, V, N)$. Carry out the Legendre transform of $V \rightarrow -P$ and $U(S, V, N) \rightarrow H(S, P, N)$.

$$H(S, P, N) = U + PV; \quad P = \left(\frac{\partial U}{\partial V} \right)_{S, N}.$$

GIBBS FREE ENERGY : $G(T, P, N)$. Start with $U(S, V, N)$. Transform $S \rightarrow T$, $V \rightarrow -P$, and $U \rightarrow G(T, P, N)$.

$$G(S, P, N) = U - TS + PV; \quad T = \left(\frac{\partial U}{\partial S} \right)_{V, N}; \quad P = \left(\frac{\partial U}{\partial V} \right)_{S, N}.$$

GRAND POTENTIAL : $\mathcal{G}(T, V, \mu)$. Start with $U(S, V, N)$. Transform $S \rightarrow T$, $N \rightarrow \mu$, and $U \rightarrow \mathcal{G}(T, P, N)$.

$$\mathcal{G}(T, V, \mu) = U - TS - \mu N, \quad T = \left(\frac{\partial U}{\partial S} \right)_{V, N}, \quad \mu = \left(\frac{\partial U}{\partial N} \right)_{S, N}.$$

Thus we get a relation between (the microscopic description enshrined in) the canonical partition function (of statistical mechanics) and (the macroscopic description given in terms of) (Helmholtz) free energy (of thermodynamics) : $F(T, V, N) = -k_B T \ln Q(T, V, N)$. Statistical mechanics aims to connect the micro world (of say atoms and molecules) to the macro world (of solids and liquids). In other words it helps you calculate the macroscopic properties of a system say a solid, in terms of the properties of its microscopic constituents (atoms and molecules) and their interactions.

Boltzmann started the game of statistical mechanics by first proposing a micro - macro connection for an isolated system, in the famous formula engraved on his tomb: $S = k_B \ln \hat{\Omega}$. You will come across several micro-macro connections in this course on statistical mechanics. The formula, $F(T, V, N) = -k_B T \ln Q(T, V, N)$, provides another important micro - macro connection.

5.5 Energy Fluctuations and Heat Capacity

The average energy of a system is formally given by, $\langle E \rangle = \sum_i E_i p_i$, where p_i is the probability of the micro state i and E_i is the energy of the system when in micro state i . For a closed system, $p_i = Q^{-1} \exp(-\beta E_i)$, where $Q(T, V, N)$ is the (canonical) partition function given by

$$Q = \sum_i \exp(-\beta E_i).$$

We have,

$$\begin{aligned} \langle E \rangle &= \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)}, \\ &= \frac{1}{Q} \sum_i E_i \exp(-\beta E_i), \\ &= -\frac{1}{Q} \frac{\partial Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial \beta}. \end{aligned} \quad (5.13)$$

We identify $\langle E \rangle$ with the internal energy, usually denoted by the symbol U in thermodynamics.

We have,

$$U = -\frac{1}{Q} \frac{\partial Q}{\partial \beta}, \quad (5.14)$$

$$\left(\frac{\partial U}{\partial \beta} \right)_V = -\frac{1}{Q} \frac{\partial^2 Q}{\partial \beta^2} + \left(\frac{1}{Q} \frac{\partial Q}{\partial \beta} \right)^2 = -[\langle E^2 \rangle - \langle E \rangle^2] = -\sigma_E^2. \quad (5.15)$$

Now write,

$$\frac{\partial U}{\partial \beta} = \frac{\partial U}{\partial T} \times \frac{\partial T}{\partial \beta} = C_V (-k_B T^2). \quad (5.16)$$

We get the relation between the fluctuations of energy of an equilibrium system and the reversible heat required to raise the temperature of the system by one degree Kelvin :

$$\sigma_E^2 = k_B T^2 C_V. \quad (5.17)$$

The left hand side of the above equation represents the fluctuations of energy when the system is in equilibrium. The right hand side is about how the system would respond when you heat it⁸. Note C_V is the amount of reversible heat you have to supply to the system at constant volume to raise its temperature by one degree Kelvin. The equilibrium fluctuations in energy are related to the linear response; *i.e.* the response of the system to small perturbation⁹.

5.6 Canonical Partition Function : Ideal Gas

I shall derive an expression for the canonical partition function of an ideal gas of N molecules confined to a volume V and at temperature T . I shall do the derivation by a method that involves the density of states

We first derive an expression for the density of (energy) states, denoted by $g(E)$ from micro canonical ensemble. $g(E)dE$ is the number of micro states of an isolated system with energy between E and $E + dE$. Formally, we have

$$g(E) = \frac{\partial \widehat{\Omega}}{\partial E} \quad (5.18)$$

$$\widehat{\Omega} = \frac{V^N}{N!} \frac{1}{h^{3N}} \frac{(2\pi m E)^{3N/2}}{\Gamma(\frac{3N}{2} + 1)}. \quad (5.19)$$

Therefore the density of (energy) states is given by,

$$\begin{aligned} g(E) &= \frac{\partial \widehat{\Omega}}{\partial E} = \frac{V^N}{N!} \frac{1}{h^{3N}} \frac{(2\pi m)^{3N/2}}{\Gamma(\frac{3N}{2} + 1)} \frac{3N}{2} E^{\frac{3N}{2}-1}, \\ &= \frac{V^N}{N!} \frac{1}{h^{3N}} \frac{(2\pi m)^{3N/2}}{\Gamma(\frac{3N}{2})} E^{\frac{3N}{2}-1} \end{aligned} \quad (5.20)$$

where we have made use of the relation

$$\Gamma\left(\frac{3N}{2} + 1\right) = \left(\frac{3N}{2}\right) \Gamma\left(\frac{3N}{2}\right). \quad (5.21)$$

The partition function is obtained as a "transform" of the density of states where the variable E transformed to the variable β .

$$Q(\beta, V, N) = \frac{V^N}{N!} \frac{1}{h^{3N}} \frac{(2\pi m)^{3N/2}}{\Gamma(\frac{3N}{2})} \int_0^\infty dE \exp(-\beta E) E^{\frac{3N}{2}-1}. \quad (5.22)$$

Consider the integral,

$$I = \int_0^\infty dE \exp(-\beta E) E^{\frac{3N}{2}-1}. \quad (5.23)$$

Let,

⁸ Notice that σ^2 is expressed in units of Joule². The quantity $k_B T^2$ is expressed in units of Joule-Kelvin. C_V is in Joule/Kelvin. Thus $k_B T^2 C_V$ has units of Joule².

⁹ first order perturbation.

$$x = \beta E \text{ then } dx = \beta dE, \quad (5.24)$$

$$I = \frac{1}{\beta^{3N/2}} \int_0^\infty dx x^{\frac{3N}{2}-1} \exp(-x), \quad (5.25)$$

$$= \frac{\Gamma(\frac{3N}{2})}{\beta^{3N/2}}. \quad (5.26)$$

Substituting the above in the expression for the partition function we get,

$$Q(T, V, N) = \frac{V^N}{N!} \frac{1}{h^{3N}} (2\pi m k_B T)^{3N/2} = \frac{V^N}{N!} \frac{1}{\Lambda^{3N}}, \quad (5.27)$$

where

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}. \quad (5.28)$$

First check that Λ has the dimension of length. Λ is called thermal wavelength or quantum wavelength. It is approximately the de Broglie wavelength of a particle with energy $p^2/2m = k_B T$. We have $p = \sqrt{2m k_B T}$. Therefore

$$\Lambda = \frac{h}{p} = \frac{h}{\sqrt{2m k_B T}} \approx \frac{h}{\sqrt{2\pi m k_B T}}.$$

A wave packet can be constructed by superimposing plane waves of wavelengths in the neighbourhood of Λ . Thus a wave is spatially localized in a volume of the order of Λ^3 . Consider a gas with number density ρ . The inter particle distance is of the order of $\rho^{1/3}$. Consider the situation $\rho \Lambda^3 \ll 1$. The particles are far apart. The wave packets do not overlap. Classical description will suffice. Quantum effects manifest when $\rho \Lambda^3 \gg 1$: when density is large and temperature is low.

5.7 Method of Most Probable Distribution

Let us now derive an expression for the canonical partition function employing the **method of most probable distribution**. Consider an isolated system representing the universe. For convenience we imagine it to be a big cube. It contains molecules moving around here and there, hitting against each other and hitting against the wall. The universe is in equilibrium¹⁰. Let the temperature be T . The universe attains that temperature for which its entropy is maximum, under the constraints of energy, volume and number of particles, imposed on it.

Let us imagine that the universe, represented by a big cube, is divided into a set of small cubes of equal volumes by means of imaginary walls. Each cube represents a macroscopic part of the universe.

Each small cube is, in its own right, a macroscopic object with a volume V . Since the the walls of a small cube permits molecules and energy to move across, the number of molecules in a cube, is not a constant. It shall fluctuate around a

¹⁰ Remember that an isolated system left to itself will eventually reach a state of equilibrium whence all its macroscopic properties are y unchanging with time; also a macroscopic (intensive) property property shall be the same at all regions in the system.

mean value; the fluctuations, however, are extremely small. What remains constant is the chemical potential, μ .

The above observations hold good for energy also. Energy is not a constant. It fluctuates around a mean value; the fluctuations are small; what remains fixed is the temperature, T .

Let \mathcal{A} denote the number of cubes contained in the big cube.

The universe - the big cube, has a certain amount energy say \mathcal{E} and certain number of molecules \mathcal{N} and a certain volume \mathcal{V} and these quantities are constants.

You can immediately see that what we have is Gibbs' grand canonical ensemble of open systems : each small cube represents an open system. and is a member of a grand canonical ensemble. All the members are identical as far as their macroscopic properties are concerned. This is to say the volume V , the temperature T and chemical potential μ are all the same for all the members.

Now, let us imagine that the walls are made impermeable to movement of molecules across. A cube **can not** exchange matter with its neighbouring cubes. Let us also assume that each cube contains exactly N molecules. However energy in a cube is not fixed. Energy can flow from one cube to its neighbouring cubes. This constitutes a canonical ensemble¹¹.

Aim :

To find the probability for the closed system to be in **its** micro state i .

First, we list down all the micro states of the system. Let us denote the micro states as $\{1, 2, \dots\}$. Note that the macroscopic properties T , V , and N are the same for all the micro states. In fact the system switches from one micro state to another, incessantly. Let E_i denote the energy of the system when it is in micro state i . The energy can vary from one micro state to another.

To each cube, we can attach an index i . The index i denotes the micro state of the closed system with fixed T , V and N . An ordered set of \mathcal{A} indices uniquely specifies a micro state of the universe.

Let us take an example. Let the micro states of the closed system be denoted by the indices $\{1, 2, 3\}$. There are only three micro states. Let us represent the isolated system by a big square and construct nine small squares, each of which represents a member of the ensemble. Each square is attached with an index which can be 1, 2 or 3. Thus we have a micro state of the universe represented by the following

Table 5.2. A micro state with occupation number representation (2, 3, 4)

3	1	2
2	3	3
2	3	1

¹¹ Usually, canonical ensemble is constructed by taking a system with a fixed value of V and N and assembling a large number of them in such a way that each is in thermal contact with its neighbours. Usually these are called mental copies of the system. The system and its mental copies are then isolated. The isolated system constitutes the universe. All the mental copies are identical macroscopically in the sense they all have the same value of T , V and N . Also other macroscopic properties defined as averages of a stochastic variable *e.g.* energy are also the same for all the mental copies. But these mental copies will often differ, one from the other, in their microscopic properties.

In the above micro state, there are two squares with index 1, three with index 2 and four with index 3. Let $\{a_1 = 2, a_2 = 3, a_3 = 4\}$ be the occupation number string of the micro state. There are several micro states having the same occupation number string. I have given below a few of them.

133	233	121	112	123
212	312	232	223	123
323	321	232	333	233

Table 5.3. A few micro states with the same occupation number representation of $(2, 3, 4)$. There are 1260 micro states with the same occupation number representation

Notice that all the micro states given above have the same occupation number string $\{2, 3, 4\}$. How many micro states are there with this occupation number string? We have

$$\widehat{\Omega}(2, 3, 4) = \frac{9!}{2!3!4!} = 1260 \quad (5.29)$$

I am not going to list all the 1260 of the microstates belonging to the occupation number string $\{2, 3, 4\}$

Let me generalize and say that a string of occupation numbers is denoted by the symbol $\tilde{a} = \{a_1, a_2, \dots\}$, where $a_1 + a_2 + \dots = \mathcal{A}$. We also have an additional constraint namely $a_1 E_1 + a_2 E_2 + \dots = \mathcal{E}$.

Let $\widehat{\Omega}(\tilde{a}) = \widehat{\Omega}(a_1, a_2, \dots)$ denote the number of micro states of the universe belonging to the string \tilde{a} . For a given string, we can define the probability for the closed system to be in its micro state indexed by i as

$$p_i(\tilde{a}) = \frac{a_i(\tilde{a})}{\mathcal{A}} \quad (5.30)$$

Note, the string $\tilde{a} = \{a_1, a_2, \dots\}$ obeys the following constraints.

$$\sum_{i=1}^{\mathcal{A}} a_i(\tilde{a}) = \mathcal{A} \quad \forall \text{ strings } \tilde{a} \quad (5.31)$$

$$\sum_{i=1}^{\mathcal{A}} a_i(\tilde{a}) E_i = \mathcal{E} \quad \forall \text{ strings } \tilde{a} \quad (5.32)$$

Note that the value of p_i varies from one string to another. It is reasonable to obtain the average value of p_i over all possible strings \tilde{a} . We have

$$P_i = \sum_{\tilde{a}} \left(\frac{a_i(\tilde{a})}{\mathcal{A}} \right) \mathcal{P}(\tilde{a}) \quad (5.33)$$

where

$$\mathcal{P}(\tilde{a}) = \frac{\widehat{\Omega}(\tilde{a})}{\sum_{\tilde{a}} \widehat{\Omega}(\tilde{a})}. \quad (5.34)$$

We are able to write the above because all the elements of an ensemble have the same probability given by inverse of the size of the ensemble. In the above,

$$\widehat{\Omega}(\tilde{a}) = \frac{\mathcal{A}!}{a_1! a_2! \dots}, \quad (5.35)$$

where we have used a simple notation $a_i = a_i(\tilde{a}) \forall i = 1, 2, \dots$.

Let us take a look at $\widehat{\Omega}(\tilde{a})$ for various strings \tilde{a} . For large \mathcal{A} the number $\widehat{\Omega}(\tilde{a})$ will be overwhelmingly large for a particular string, which we shall denote as \tilde{a}^* . We can ensure this by taking $\mathcal{A} \rightarrow \infty$. Note that \mathcal{A} should be large enough so that even a micro state of smallest probability is present in the ensemble atleast once.

Thus we can write

$$\begin{aligned} P_i &= \frac{a_i(\tilde{a}^*)}{\mathcal{A}} \frac{\widehat{\Omega}(\tilde{a}^*)}{\widehat{\Omega}(\tilde{a}^*)}, \\ &= \frac{a_i(\tilde{a}^*)}{\mathcal{A}}, \\ &= \frac{a_i^*}{\mathcal{A}} \end{aligned} \quad (5.36)$$

Thus the problem reduces to finding that string \tilde{a}^* for which $\widehat{\Omega}(\tilde{a})$ is a maximum. Of course there are two constraints on the string. They are

$$\sum_j a_j(\tilde{a}) = \mathcal{A} \forall \tilde{a}; \quad (5.37)$$

$$\sum_j a_j(\tilde{a}) E_j = \mathcal{E} \forall \tilde{a}. \quad (5.38)$$

We need to find the maximum (or minimum) of a function of a many variable under one or several constraints on the variables. In the above example there are two constraints. We shall tackle this problem employing the Lagrange method of undetermined multipliers and to this we turn our attention below.

5.8 Lagrange and his Method

Let me pose the problem through a simple example.

A mountain be described by $h(x, y)$ where h is a function of the variable x and y . h is the elevation of the mountain at a point (x, y) on the plane.

I want to find out (x^*, y^*) at which h is maximum.

We write

$$dh = \frac{\partial h}{\partial x} dx + \frac{\partial h}{\partial y} dy = 0 \quad (5.39)$$

If dx and dy are independent then $dh = 0$ if and only if

$$\frac{\partial h}{\partial x} = 0 \quad (5.40)$$

$$\frac{\partial h}{\partial y} = 0 \quad (5.41)$$

We have two equations and two unknowns. In principle we can solve the above two equations and obtain (x^*, y^*) at which h is maximum.

Now imagine there is a road on the mountain which does not necessarily pass through the peak of the mountain. If you are travelling on the road, then what is the highest point you will pass through ? In the equation

$$dh = \frac{\partial h}{\partial x} dx + \frac{\partial h}{\partial y} dy = 0 \quad (5.42)$$

the infinitesimals dx and dy are not independent. You can choose only one of them independently. The other is determined by the constraint which says that you have to be on the road.

Let the projection of the mountain-road on the plane be described by the curve

$$g(x, y) = 0.$$

This gives us a constraint

$$\frac{\partial g}{\partial x} dx + \frac{\partial g}{\partial y} dy = 0 \quad (5.43)$$

From the above we get,

$$dy = -\frac{\left(\frac{\partial g}{\partial x}\right)}{\left(\frac{\partial g}{\partial y}\right)} dx \quad (5.44)$$

We then have,

$$dh = \frac{\partial h}{\partial x} dx + \frac{\partial h}{\partial y} dy = 0 \quad (5.45)$$

$$= \frac{\partial h}{\partial x} dx + \frac{\partial h}{\partial y} \left[-\frac{\left(\frac{\partial g}{\partial x}\right)}{\left(\frac{\partial g}{\partial y}\right)} \right] dx = 0, \quad (5.46)$$

$$= \left[\frac{\partial h}{\partial x} - \left\{ \frac{\left(\frac{\partial h}{\partial y}\right)}{\left(\frac{\partial g}{\partial y}\right)} \right\} \frac{\partial g}{\partial x} \right] dx = 0. \quad (5.47)$$

In the above dx is an arbitrary non-zero infinitesimal. Hence the above equality holds good if and only if the terms inside the square bracket is zero. We have,

$$\frac{\partial h}{\partial x} - \lambda \frac{\partial g}{\partial x} = 0, \quad (5.48)$$

where we have set,

$$\lambda = \frac{\left(\frac{\partial h}{\partial y}\right)}{\left(\frac{\partial g}{\partial y}\right)}. \quad (5.49)$$

We have an equation similar to Eq. (5.48) involving partial derivative with respect to the variable y , which follows from the definition, see Eq. (5.49), of the Lagrange undetermined multiplier, λ .

Thus we have two independent equations,

$$\frac{\partial h}{\partial x} - \lambda \frac{\partial g}{\partial x} = 0, \quad (5.50)$$

$$\frac{\partial h}{\partial y} - \lambda \frac{\partial g}{\partial y} = 0. \quad (5.51)$$

We can solve and get $x^* \equiv x^*(\lambda)$ and $y^* = y^*(\lambda)$. The value of x and y at which $h(x, y)$ is maximum under constraint $g(x, y) = 0$ can be found in terms of the unknown Lagrange multiplier λ .

Of course we can determine the value of λ by substituting the solution $(x^*(\lambda), y^*(\lambda))$ in the constraint equation : $g(x^*(\lambda), y^*(\lambda)) = 0$.

5.9 Generalisation to N Variables

Let $f(x_1, x_2, \dots, x_N)$ be a function of N variables. The aim is to maximize f under one constraint $g(x_1, x_2, \dots, x_N) = 0$.

We start with

$$df = \sum_{i=1}^N \frac{\partial f}{\partial x_i} dx_i = 0 \quad (5.52)$$

for maximum. In the set $\{dx_1, dx_2, \dots, dx_\mu, \dots, dx_N\}$, not all are independent. They are related by the constraint

$$\sum_{i=1}^N \frac{\partial g}{\partial x_i} dx_i = 0 \quad (5.53)$$

We pick up one of the variable, say x_μ and write

$$dx_\mu = - \sum_{i=1, i \neq \mu}^N \frac{\left(\frac{\partial g}{\partial x_i}\right)}{\left(\frac{\partial g}{\partial x_\mu}\right)} dx_i \quad (5.54)$$

Substitute the above in the expression for df . We get,

$$\sum_{i=1, i \neq \mu}^N \left[\frac{\partial f}{\partial x_i} - \lambda \frac{\partial g}{\partial x_i} \right] dx_i = 0 \quad (5.55)$$

where

$$\lambda = \frac{\left(\frac{\partial f}{\partial x_\mu}\right)}{\left(\frac{\partial g}{\partial x_\mu}\right)} \quad (5.56)$$

There are only $N - 1$ values of dx_i . We have eliminated dx_μ . Instead we have the undetermined multiplier λ . Since $dx_i : i = 1, N$ and $i \neq \mu$ are all independent of each other we can set each term in the sum to zero. Therefore

$$\frac{\partial f}{\partial x_i} - \lambda \frac{\partial g}{\partial x_i} = 0 \quad \forall i \neq \mu \quad (5.57)$$

From the definition of λ we get

$$\frac{\partial f}{\partial x_\mu} - \lambda \frac{\partial g}{\partial x_\mu} = 0 \quad (5.58)$$

Thus we have a set of N equations

$$\frac{\partial f}{\partial x_i} - \lambda \frac{\partial g}{\partial x_i} = 0 \quad \forall i = 1, N \quad (5.59)$$

There are N equations and N unknowns. In principle we can solve the equation and get

$$x_i^* \equiv x_i^*(\lambda) \quad \forall i = 1, N,$$

where the function h is maximum under constraint

$$g(x_1, x_2, \dots, x_N) = 0.$$

The value of the undetermined multiplier λ can be obtained by substituting the solution in the constraint equation.

If we have more than one constraints we introduce separate Lagrange multipliers for each constraint. Let there be $m \leq N$ constraints. Let these constraints be given by

$$g_i(x_1, x_2, \dots, x_N) = 0 \quad \forall i = 1, m.$$

We introduce m number of Lagrange multipliers, $\lambda_i : i = 1, m$ and write

$$\frac{\partial f}{\partial x_i} - \lambda_1 \frac{\partial g_1}{\partial x_i} - \lambda_2 \frac{\partial g_2}{\partial x_i} \dots - \lambda_m \frac{\partial g_m}{\partial x_i} = 0 \quad \forall i = 1, N \quad (5.60)$$

where the $m \leq N$.

5.10 Derivation of Boltzmann Weight

Let us return to our problem of finding P_i - the probability that a closed equilibrium system (with macroscopic properties T, V, N) will be found in its micro state i with energy E_i . Employing the method of most probable distribution, we have found that,

$$P_i = \frac{a_i^*}{\mathcal{A}} \quad (5.61)$$

where \mathcal{A} is the number of elements of the canonical ensemble and $a_j^* = a_j(\tilde{a}^*)$.

\tilde{a}^* is that string for which $\hat{\Omega}(\tilde{a})$ is maximum, under two constraints.

$$\hat{\Omega}(\tilde{a}) = \frac{\mathcal{A}!}{a_1! a_2! \dots} \quad (5.62)$$

The two constraints are

$$\sum_j a_j(\tilde{a}) = \mathcal{A} \quad (5.63)$$

$$\sum_j a_j(\tilde{a}) E_j = \mathcal{E} \quad (5.64)$$

We extremize entropy given by $\ln \widehat{\Omega}(\vec{a})$.

$$\ln \widehat{\Omega}(a_1, a_2, \dots) = \ln \mathcal{A}! - \sum_j a_j \ln a_j + \sum_j a_j \quad (5.65)$$

We introduce two Lagrange multipliers α and β and write

$$\begin{aligned} \frac{\partial \ln \widehat{\Omega}(a_1, a_2, \dots)}{\partial a_i} - \alpha \frac{\partial (a_1 + a_2 + \dots - \mathcal{A})}{\partial a_i} \\ - \beta \frac{\partial (a_1 E_1 + a_2 E_2 + \dots - \mathcal{E})}{\partial a_i} = 0 \end{aligned} \quad (5.66)$$

Let a_j^* denote the solution of the above equation. We get,

$$-\ln a_j^* - \alpha - 1 - \beta E_j = 0 \quad \forall j = 1, 2, \dots \quad (5.67)$$

The above can be written in a convenient form

$$a_j^* = \gamma \exp(-\beta E_j) \quad (5.68)$$

where $\gamma = \exp(-\alpha - 1)$. We thus have,

$$P_j = \eta \exp(-\beta E_j)$$

where $\eta = \gamma/\mathcal{A}$.

Thus we get the probability that a closed system shall be found in its micro state j in terms of the constants η (which can be expressed as a function of the Lagrange multiplier α) and β (which is the Lagrange multiplier for the constraint on the total energy of the isolated system).

The task now is to evaluate the constants η and β . The constant η can be evaluated by imposing the normalization condition : $\sum_j P_j = 1$. The closed system has to be in one of its micro state with unit probability. Thus we have,

$$P_j = \frac{1}{Q} \exp(-\beta E_j) \quad (5.69)$$

$$Q(\beta, V, N) = \sum_j \exp(-\beta E_j) \quad (5.70)$$

We call Q the canonical partition function.

What is the nature of the Lagrange multiplier β ? On physical ground we identify

$$\beta = \frac{1}{k_B T}.$$

This we do by making a correspondence to thermodynamics. I shall refer you to

- Donald A McQuairrie, *Statistical Mechanics*, Harper and Row (1976)pp.35-44, for this.

5.11 Mechanical and Thermal Properties

In statistical mechanics, we have a random variable corresponding to a property *e.g.* energy, E . We take an average of this random variable over a canonical ensemble and denote it by $\langle E \rangle$. This quantity corresponds to the internal energy, usually denoted by the symbol U , of thermodynamics : $U = \langle E \rangle$. This establishes a micro-macro connection.

Energy of a closed system varies, in general, from one micro state to another. An equilibrium system visits a sequence of micro states dictated by Newtonian dynamics. Averaging over the visited microstates during the observation time gives us the time average. Instead, invoking 'ergodicity', we average over a Gibbs' ensemble and equate it to the thermodynamics property. Thus, energy averaged over a canonical ensemble, gives internal energy of thermodynamics, see below.

$$p_i = \frac{\exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} \quad (5.71)$$

$$\langle E \rangle = \sum_i E_i p_i = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} \quad (5.72)$$

We are able to establish a connection between statistical mechanics and thermodynamics for a mechanical property like energy; notice energy is a 'private' property of a micro state; in other words I can attach a numerical value for the property called energy to each microstate. Hence we are able to average this property over a canonical ensemble and get the internal energy.

How do we calculate a thermal property like entropy ? First we notice, entropy is not a 'private' property of a micro state. We can not attach a numerical value for entropy to a microstate. Entropy is a "social" property or a 'collective' property. Hence entropy can not be easily calculated the way we calculated energy. For an isolated system, we could write an expression for entropy as $S = k_B \ln \hat{\Omega}(E, V, N)$ since all the micro states are equally probable¹²

What is the expression for entropy of a closed system ? To this issue we turn our attention below.

5.12 Entropy of a Closed System

Consider the expression $-\sum_i p_i \ln p_i$ in the context of canonical ensemble. In an earlier lecture we talked of the number of micro states of an isolated system. The isolated system is constructed as follows : Assemble a large number of closed systems. Each closed system is in thermal contact with its neighbouring closed systems. Let $\eta = \{i : i = 1, 2, \dots\}$ label the micro states of a closed system. Let \mathcal{A} denote the number of closed systems in the ensemble. The ensemble is isolated. We have thus an isolated system. We call it the universe. We describe a micro state of the universe by specifying the index i for each of its members. The index comes from the set η defined earlier. The micro states of the universe system are all equally probable; we group them and denote a group by specifying the string $\{a_1, a_2, \dots\}$ where a_i is the number of elements of the ensemble, having the index i . We have

$$\hat{\Omega}(a_1, a_2, \dots) = \frac{\mathcal{A}!}{a_1! a_2! \dots} \quad (5.73)$$

The aim is to find $\{a_i^* : i = 1, 2, \dots\}$ that maximizes $\hat{\Omega}$. For convenience we maximize $\ln \hat{\Omega}$. Let us consider the limit $a_i \rightarrow \infty \forall i$. Also consider the variables $p_i = a_i / \mathcal{A}$. Then

¹² The probability of a microstate in a micro canonical ensemble is $p_i = 1 / \hat{\Omega}(E, V, N) \forall i$. Hence $k_B \ln \hat{\Omega} = -k_B \sum_i p_i \ln p_i$

$$\ln \widehat{\Omega} = \mathcal{A} \ln \mathcal{A} - \mathcal{A} - \sum_i a_i \ln a_i + \sum_i a_i \quad (5.74)$$

$$= \sum_i a_i \ln \mathcal{A} - \sum_i a_i \ln a_i \quad (5.75)$$

$$= - \sum_i a_i \ln \left(\frac{a_i}{\mathcal{A}} \right) \quad (5.76)$$

$$= -\mathcal{A} \sum_i p_i \ln p_i \quad (5.77)$$

$$\frac{\ln \widehat{\Omega}}{\mathcal{A}} = - \sum_i p_i \ln p_i \quad (5.78)$$

The above is the entropy of one of the \mathcal{A} number of closed systems constituting the the universe. Thus, $-\sum_i p_i \ln p_i$ provides a natural formula for the entropy of a system whose micro states are not equi-probable.

Physicists would prefer to measure entropy in units of Joules per Kelvin. For, that is what they have learnt from Clausius, who defined

$$dS = \frac{q}{T},$$

where dS is the entropy gained by a system when it receives an energy of q Joules by heat in a reversible process at a constant temperature of T Kelvin. Hence we define,

$$S = -k_B \sum_i p_i \ln p_i. \quad (5.79)$$

This expression for entropy is natural for a closed system described by a canonical ensemble. We call it Boltzmann-Gibbs-Shannon entropy.

5.13 Free Energy to Entropy

We start with the thermodynamic relation

$$F(T, V, N) = U - TS \quad (5.80)$$

We recognize that $F(T, V, N)$ is the Legendre transform of the fundamental equation $U(S, V, N)$ where we transform the variable S in favour of T defined as

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, N} \quad (5.81)$$

We re-write the expression for F as,

$$-\frac{S}{k_B} = \beta(F - U) \quad (5.82)$$

We make use of the following,

$$Q = \sum_i \exp(-\beta E_i)$$

$$p_i = \frac{1}{Q} \exp(-\beta E_i);$$

$$F = -k_B T \ln Q$$

$$U = \langle E \rangle = \frac{1}{Q} \sum_i E_i \exp(-\beta E_i)$$

and write,

$$\begin{aligned} -\frac{S}{k_B} &= \beta \left[-k_B T \ln Q - \frac{1}{Q} \sum_i E_i \exp(-\beta E_i) \right] \\ &= -\ln Q \left[\frac{1}{Q} \sum_i \exp(-\beta E_i) \right] - \beta \frac{1}{Q} \sum_i E_i \exp(-\beta E_i) \\ &= \sum_i \left[\left\{ \frac{1}{Q} \exp(-\beta E_i) \right\} \left\{ -\ln Q - E_i \beta \right\} \right] \\ &= \sum_i \left[\left\{ \frac{1}{Q} \exp(-\beta E_i) \right\} \ln \left\{ \frac{\exp(-\beta E_i)}{Q} \right\} \right] \\ &= \sum_i p_i \ln p_i \end{aligned} \quad (5.83)$$

from which we get the Boltzmann-Gibbs-Shannon entropy,

$$S = -k_B \sum_i p_i \ln p_i.$$

5.14 Microscopic View : Heat and Work

The thermodynamic energy U is identified with statistical energy E averaged over a suitable Gibbs ensemble. We use micro canonical ensemble for isolated system, canonical ensemble for closed system, and grand canonical ensemble for open system. Let $p_i : i = 1, 2, \dots$ denote formally an ensemble. p_i is the probability of a micro state of the system under consideration.

For example if the system is isolated, then all micro states are equally probable. We simply count the number of micro states of the system; let us say there are $\widehat{\Omega}$ micro states. Inverse of this shall be the probability of a micro state.

For an isolated system $p_i = 1/\widehat{\Omega}$.

For a closed system, $p_i = \frac{1}{Q} \exp(-\beta E_i)$.

For an open system $p_i = \frac{1}{Q} \exp(-\beta E_i + \beta \mu N_i)$

We can write, in general, $U = \sum_i p_i E_i$. This equation suggests that the internal energy of a closed system can be changed by two ways.

1. change $\{E_i : i = 1, 2, \dots\}$ keeping $\{p_i : i = 1, 2, \dots\}$ the same. This we call as work. Note that the energy eigenvalue change when we change the boundary condition, *i.e.* when we move the boundary thereby changing the volume.
2. change $\{p_i : i = 1, 2, \dots\}$ keeping $\{E_i : i = 1, 2, \dots\}$ the same. The changes in p_i should be done in such way that $\sum_i p_i = 1$. This we call as heat.

Thus we have,

$$dU = \sum_i p_i dE_i + \sum_i^* E_i dp_i \quad (5.84)$$

where the superscript $*$ in the second sum should remind us that all dp_i s are not independent and that they should add to zero.

In the first sum we change E_i by $dE_i \forall i$ keeping $p_i \forall i$ unchanged.

In the second sum we change p_i by $dp_i \forall i$ keeping E_i unchanged for all i and ensuring $\sum_i dp_i = 0$.

5.14.1 Work in Statistical Mechanics : $W = \sum_i p_i dE_i$

We have

$$\begin{aligned} \sum_i p_i dE_i &= \sum_i p_i \frac{\partial E_i}{\partial V} dV \\ &= \frac{\partial (\sum_i p_i E_i)}{\partial V} dV \\ &= \frac{\partial \langle E \rangle}{\partial V} dV \\ &= \frac{\partial U}{\partial V} dV \\ &= -PdV = W \end{aligned} \quad (5.85)$$

5.14.2 Heat in Statistical Mechanics : $q = \sum_i E_i dp_i$

Method-1

We start with the first term on the right hand side of Eq. (5.84).

$$S = -k_B \sum_i p_i \ln p_i, \quad (5.86)$$

$$dS = -k_B \sum_i^* [1 + \ln p_i] dp_i, \quad (5.87)$$

$$TdS = dq = -k_B T \sum_i^* \ln p_i dp_i, \quad (5.88)$$

$$= -k_B T \sum_i^* [-\beta E_i - \ln Q] dp_i \text{ since } p_i = \frac{e^{-\beta E_i}}{Q} \quad (5.89)$$

$$= \sum_i^* E_i dp_i \quad (5.90)$$

Method-2

Alternately, we recognize that change of entropy is brought about by change of probabilities of microstates and *vice versa*, keeping their respective energies the same. Thus,

$$\sum_i E_i dp_i = \sum_i E_i \frac{\partial p_i}{\partial S} dS \quad (5.91)$$

$$= \frac{\partial (\sum_i E_i p_i)}{\partial S} dS = \frac{\partial \langle E \rangle}{\partial S} dS = \frac{\partial U}{\partial S} dS = TdS = q \quad (5.92)$$

5.15 Adiabatic Process - a Microscopic View

In an adiabatic process, the system does not transact energy by heat. Hence the probabilities $\{p_i\}$ of the micro states do not change during an adiabatic process. The only way the internal energy can change is through change of $\{\epsilon_i\}$. For a particle confined to a box, quantum mechanics tells us that the energy eigenvalue is inversely proportional to the square of the length of the box.

$$\epsilon_i \sim \frac{1}{L^2} \quad (5.93)$$

$$\sim V^{-2/3} \quad (5.94)$$

$$\frac{\partial \epsilon_i}{\partial V} \sim V^{-5/3} \quad (5.95)$$

First law of thermodynamics tells us $dU = dQ + dW$; For an adiabatic process $dQ = 0$; if the process is reversible then $dW = -PdV$. Therefore,

$$dU = \sum_i p_i \frac{\partial \epsilon_i}{\partial V} dV \quad (5.96)$$

$$-PdV \sim V^{-5/3} dV \quad (5.97)$$

$$PV^{5/3} = \Theta, \text{ a constant.} \quad (5.98)$$

5.16 $Q(T, V, N)$ for an Ideal Gas

I shall derive an expression for the canonical partition function of an ideal gas of N molecules confined to a volume V and at temperature T .

Formally the partition function is given by,

$$Q(T, V, N) = \frac{V^N}{N!} \frac{1}{h^{3N}} \int_{-\infty}^{+\infty} dp_1 \int_{-\infty}^{+\infty} dp_2 \cdots \cdots \int_{-\infty}^{+\infty} dp_{3N} \exp \left[-\frac{\beta}{2m} (p_1^2 + p_2^2 \cdots + p_{3N}^2) \right] \quad (5.99)$$

$$= \frac{V^N}{N!} \frac{1}{h^{3N}} \left[\int_{-\infty}^{+\infty} dp \exp \left(-\frac{\beta}{2m} p^2 \right) \right]^{3N} \quad (5.100)$$

$$= \frac{V^N}{N!} \frac{1}{h^{3N}} \left[\int_{-\infty}^{+\infty} dp \exp \left(-\frac{1}{2} \frac{p^2}{mk_B T} \right) \right]^{3N} \quad (5.101)$$

Consider the integral

$$I = \int_{-\infty}^{+\infty} dp \exp \left(-\frac{1}{2} \frac{p^2}{mk_B T} \right) \quad (5.102)$$

since the integrand is an even function, we can write the above as

$$I = 2 \int_0^{+\infty} dp \exp \left(-\frac{1}{2} \frac{p^2}{mk_B T} \right) \quad (5.103)$$

Let

$$x = \frac{p^2}{2mk_B T} \quad (5.104)$$

Therefore,

$$dx = \frac{p}{mk_B T} dp \quad (5.105)$$

$$dp = \sqrt{\frac{mk_B T}{2}} \frac{1}{x^{1/2}} dx \quad (5.106)$$

The integral can now expressed as

$$\begin{aligned}
 I &= \sqrt{2mk_B T} \int_0^\infty dx x^{-1/2} \exp(-x) \\
 &= \sqrt{2mk_B T} \int_0^\infty dx x^{(1/2)-1} \exp(-x) \\
 &= \sqrt{2mk_B T} \Gamma\left(\frac{1}{2}\right) \\
 &= \sqrt{2\pi mk_B T} \quad \text{since } \Gamma(1/2) = \sqrt{\pi}
 \end{aligned} \tag{5.107}$$

The canonical partition function is thus given by,

$$Q(\beta, V, N) = \frac{V^N}{N!} \frac{1}{h^{3N}} (2\pi mk_B T)^{3N/2} \tag{5.108}$$

We write the above as

$$Q(T, V, N) = \frac{V^N}{N!} \frac{1}{\Lambda^{3N}} \tag{5.109}$$

$$\Lambda(T) = \frac{h}{\sqrt{2\pi mk_B T}}. \tag{5.110}$$

Energy

$$\ln Q = N \ln\left(\frac{V}{N}\right) + N - 3N \ln(\Lambda) \tag{5.111}$$

$$-\langle E \rangle = \frac{\partial \ln Q}{\partial \beta} = -3N \frac{\partial \ln \Lambda}{\partial \beta} \tag{5.112}$$

$$\ln \Lambda = \ln(h/\sqrt{2\pi m}) + (1/2) \ln \beta \tag{5.113}$$

$$U = \langle E \rangle = \frac{3Nk_B T}{2} \tag{5.114}$$

The above shows that energy is equi-partitioned amongst the $3N$ degrees of freedom; each degree of freedom carries $k_B T/2$ of energy.

Heat capacity

The heat capacity is given by

$$C_V = \frac{\partial U}{\partial T} = \frac{3Nk_B}{2}$$

We have $nR = Nk_B$, where n is the number of moles and R the universal gas constant. Thus heat capacity per mole of the substance - the so-called molar specific heat is given by,

$$\frac{C_V}{n} = \frac{3R}{2} \tag{5.115}$$

$$R = 8.315 \text{ J } (mol)^{-1} K^{-1} = 1.9873 \text{ Cal. } (mol)^{-1} K^{-1}; 3R/2 = 2.9809 \approx \text{cal. } (mol)^{-1} K^{-1}$$

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6. Open System : Grand Canonical Ensemble

Grand Canonical Ensemble is useful in the study of open systems.

6.1 What is an Open System ?

An open system is one which exchanges energy and matter with its surroundings. The surroundings act as a heat bath as well as a particle (or material) bath.

- A heat bath transacts energy with the system. The temperature of the heat bath does not change because of the transaction.
- A material (or particle) bath transacts matter (or particles) with the system. The chemical potential of the material bath does not change because of the transaction.

The system is in thermal equilibrium with the surroundings¹. The system is also in diffusional equilibrium with the surroundings². The system can be described by its temperature, T , volume, V and chemical potential, μ . Notice that T , μ , and V are independent properties of an open system. Since the system is *not isolated*, its micro states are *not equi-probable*. Our aim is to calculate the probability of a micro state of the open system.

Let us take the open system, its boundary and surroundings and construct a universe, which constitutes an isolated system. *We are interested in constructing an isolated system because, we want to start with the only assumption we make in statistical mechanics : all the micro states of an isolated system are equally probable.* We have called this the *ergodic* hypothesis.

Let \mathcal{E} denote the total energy of the universe. $\mathcal{E} \gg E$, where E is the (average or typical) energy of the open system under study.

Let \mathcal{N} denote the total number of particles in the universe. $\mathcal{N} \gg N$, where N is the (average or typical) number of particles in the open system. \mathcal{V} is the total volume of the universe. The universe is characterized by \mathcal{E} , \mathcal{N} , and \mathcal{V} and these are held at constant values.

We want to describe the open system in terms of its own micro states. Let C be a micro state of the open system. Let

- $E(C)$ be the energy of the open system when it is in its micro state C and
- let $N(C)$ be the number of particles in the open system when it is in its micro state C .

¹ equality of temperature signals thermal equilibrium.

² equality of chemical potential ensures diffusional or material equilibrium. Of course, equality of pressure shows mechanical equilibrium.

When the open system is in micro state C the universe can be in any one of its innumerable micro states³ such that the energy of the surroundings is $\mathcal{E} - E(C)$ and the number of particles in the surroundings is $\mathcal{N} - N(C)$.

Let $\Omega_C = \Omega(\mathcal{E} - E(C), \mathcal{N} - N(C))$, denote the subset of micro states of the universe having a common property given by the following. When the universe is in a micro state belonging to Ω_C , then the system is in the chosen micro state C and the surroundings can be in any of its microstates having energy $\mathcal{E} - E(C)$ and number of particles $\mathcal{N} - N(C)$. Let $\widehat{\Omega}_C$ denote the number of elements in the subset (event) Ω_C . Following Boltzmann we define a statistical entropy associated with the event Ω_C as

$$\begin{aligned} S_C &= k_B \ln \widehat{\Omega}_C \\ &= k_B \ln \widehat{\Omega}(\mathcal{E} - E(C), \mathcal{N} - N(C)) \\ &= S(\mathcal{E} - E(C), \mathcal{N} - N(C)). \end{aligned} \quad (6.1)$$

Since $E(C) \ll \mathcal{E}$, and $N(C) \ll \mathcal{N}$, we can Taylor-expand S retaining only the first two terms. We have

$$\begin{aligned} S(\mathcal{E} - E(C), \mathcal{N} - N(C)) &= S(\mathcal{E}, \mathcal{N}) \\ &\quad - E(C) \left(\frac{\partial S}{\partial E} \right)_{\mathcal{N}} \Big|_{\mathcal{E}, \mathcal{N}} \\ &\quad - N(C) \left(\frac{\partial S}{\partial N} \right)_{\mathcal{E}} \Big|_{\mathcal{E}, \mathcal{N}} \end{aligned} \quad (6.2)$$

From the first law of thermodynamics we have, for a reversible process,

$$dE = TdS - PdV + \mu dN \quad (6.3)$$

from which it follows,

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \quad (6.4)$$

We have

$$S \equiv S(E, V, N) \quad (6.5)$$

$$dS = \left(\frac{\partial S}{\partial E} \right)_{V, N} dE + \left(\frac{\partial S}{\partial V} \right)_{E, N} dV + \left(\frac{\partial S}{\partial N} \right)_{E, V} dN \quad (6.6)$$

³ The picture I have is the following. I am visualizing a micro state of the isolated system as consisting of two parts. One part holds the signature of the open system; the other holds the signature of the surroundings. For example a string of positions and momenta of all the particles in the isolated system defines a micro state. This string consists of two parts. The first part s contains the string of positions and momenta of all the particle in the open system and the second part contains the positions and momenta of all the particles in the surroundings. Since the system is open the length system-string is a fluctuating quantity and so is the length of bath-string. However the string of the isolated system is of fixed length. I am neglecting those micro states of the isolated system which hold the signature of the interaction between the system and the surroundings at the boundaries.

Comparing the coefficients of dE , dV and dN , in equations (6.4) and (6.6), we get,

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}; \quad \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}; \quad \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T} \quad (6.7)$$

Therefore,

$$S(\mathcal{E} - E(C), \mathcal{N} - N(C)) = S(\mathcal{E}, \mathcal{N}) - \frac{1}{T}E(C) + \frac{\mu}{T}N(C) \quad (6.8)$$

The probability of the micro state C is given by

$$P(C) = \frac{\widehat{\Omega}(\mathcal{E} - E(C), \mathcal{N} - N(C))}{\widehat{\Omega}_{\text{Total}}} \quad (6.9)$$

We are able to write the above because of the postulate of ergodicity : *All micro states of the universe - an isolated system, are equally probable.* We have,

$$\begin{aligned} P(C) &= \frac{1}{\widehat{\Omega}_{\text{Total}}} \exp \left[\frac{1}{k_B} S(\mathcal{E} - E(C), \mathcal{N} - N(C)) \right] \\ &= \frac{1}{\widehat{\Omega}_{\text{Total}}} \exp \left[\frac{S(\mathcal{E}, \mathcal{N})}{k_B} - \frac{E(C)}{k_B T} + \frac{\mu N(C)}{k_B T} \right] \\ &= \alpha \exp[-\beta \{E(C) - \mu N(C)\}]. \end{aligned} \quad (6.10)$$

In the above, the constant α can be determined by the normalization condition, $\sum_c P(C) = 1$, where the sum runs over all the micro states of the open system. We have,

$$P(C) = \frac{1}{\mathcal{Q}} \exp[-\beta \{E(C) - \mu N(C)\}] \quad (6.11)$$

where the grand canonical partition function is given by

$$\mathcal{Q}(T, V, \mu) = \sum_C \exp[-\beta \{E(C) - \mu N(C)\}] \quad (6.12)$$

The fugacity is given by $\lambda = \exp(\beta\mu)$; then we can write the grand canonical partition function as,

$$\mathcal{Q}(T, V, \lambda) = \sum_C \lambda^{N(C)} \exp[-\beta E(C)] \quad (6.13)$$

- Collect those micro states of a grand canonical ensemble with a fixed value of N . Then these micro states constitute a canonical ensemble described the canonical partition function, $Q(T, V, N)$.
- Collect all the micro states of a grand canonical ensemble with a fixed energy and fixed number of particles. Then these micro states constitute a microcanonical ensemble.

Thus we can write the grand canonical partition function as,

$$\mathcal{Q}(T, V, \lambda) = \sum_{N=0}^{\infty} \lambda^N Q(T, V, N) \quad (6.14)$$

Let $Q_1(T, V)$ denote single-particle canonical partition function. We have

$$Q(T, V, N) = Q_N(T, V) = \frac{Q_1^N}{N!}. \quad (6.15)$$

Therefore,

$$\mathcal{Q}(T, V, \mu) = \sum_{N=0}^{\infty} \frac{\lambda^N Q_1^N}{N!} = \exp(\lambda Q_1) \quad (6.16)$$

Grand canonical ensemble is an extremely useful ensemble. The reason is that the constraint of constant N required for calculating the canonical ensemble is often mathematically awkward⁴.

6.2 Micro-Macro Synthesis : \mathcal{Q} and \mathcal{G}

- Entropy is the thermodynamic counter part of the statistical mechanical micro canonical partition function - the density of states. We have $S(E, V, N) = k_B \ln \widehat{\Omega}(E, V, N)$.
- Helmholtz free energy is the thermodynamic counter part of the statistical mechanical canonical partition function, $Q(T, V, N)$. We have $F(T, V, N) = -k_B T \ln Q(T, V, N)$.

What is the thermodynamic counter part of the grand canonical ensemble ? Let us call it, the "grand" potential and denote it by the symbol \mathcal{G} . \mathcal{G} is a function of T , V , and μ . $\mathcal{G}(T, V, \mu)$, is obtained from $U(S, V, N)$ by Legendre transform of $S \rightarrow T$ and $N \rightarrow \mu$. We have,

$$\mathcal{G}(T, V, \mu) = U(S, V, N) - TS - \mu N \quad (6.17)$$

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, N} : \quad \mu = \left(\frac{\partial U}{\partial N} \right)_{S, V} \quad (6.18)$$

Some authors *e.g.* Donald A McQuairrie, *Statistical Mechanics*, Harper and Row (1976) would like to identify PV as the thermodynamic counter part of the grand canonical ensemble. The correspondence is

$$\mathcal{G} = -PV = -k_B T \ln \mathcal{Q}.$$

⁴ We shall experience this while trying to evaluate the canonical partition function for fermions and bosons. We will not be able to carry out the sum over occupation numbers because of the constraint that they add up to a constant N . Hence we shall multiply the restricted sum by λ^N and sum over all possible values of N . This would remove the restriction and we shall express the partition function as sum over (micro states) of product (over occupation numbers). We shall interpret λ as fugacity. The chemical potential and fugacity are related : $\lambda = \exp(\beta\mu)$. All these can be viewed as mathematical tricks. The language of grand canonical ensemble gives a physical meaning to these mathematical tricks.

Let us establish such a relation between \mathcal{G} and \mathcal{Q} .

$\mathcal{G} = -k_B T \ln \mathcal{Q}$: We follow the same method we employed for establishing the connection between Helmholtz free energy and canonical partition function. We have,

$$\mathcal{Q}(T, V, \lambda) = \sum_i \exp[-\beta(E_i - \mu N_i)] \quad (6.19)$$

where the sum runs over all the micro states i of the open system. E_i is the energy of the system when in micro state i , and N_i is the number of particles in the system when in its micro state i .

We replace the sum over micro states by sum over energy and number of particles. Let $g(E, N)$ denote the density of states. We have then,

$$\mathcal{Q}(T, V, \mu) = \int dE \int dN g(E, N) \exp[-\beta(E - \mu N)] \quad (6.20)$$

The contribution to the integrals come overwhelmingly from a single term at We then get,

$$\mathcal{Q}(T, V, \mu) = g(\langle E \rangle, \langle N \rangle) \exp[-\beta(\langle E \rangle - \mu \langle N \rangle)] \quad (6.21)$$

Let us denote $\langle E \rangle$ by E and $\langle N \rangle$ by N . Taking logarithm on both sides,

$$\ln \mathcal{Q} = \ln g(E, N) - \beta(E - \mu N) \quad (6.22)$$

We then have,

$$-k_B T \ln \mathcal{Q} = -T[k_B \ln g(E, N)] + E - \mu N = E - TS - \mu N = \mathcal{G} \quad (6.23)$$

Alternately, we start with $\mathcal{Q} = \sum_{N'} \lambda^{N'} Q(T, V, N')$ In principle, the number of particles in an equilibrium open system is not a fixed number. It fluctuates from one micro state to another. However the fluctuations are very small; it can be shown that the relative fluctuations are inversely proportional to the size of the system. In the above expression for \mathcal{Q} , only one term contributes overwhelmingly to the sum over N' . Let the value of N' for which the $\lambda^{N'} Q(T, V, N')$ is maximum be N . Hence the sum over N' can be replaced by a single entry with $N' = N$.

$$\mathcal{Q}(T, V, \mu) = \lambda^N Q(T, V, N) \quad (6.24)$$

$$\ln \mathcal{Q}(T, V, \mu) = \beta \mu N + \ln Q(T, V, N) = \frac{\mu N}{k_B T} + \ln Q(T, V, N) \quad (6.25)$$

$$k_B T \ln \mathcal{Q} = \mu N + k_B T \ln Q(T, V, N) \quad (6.26)$$

While studying Canonical ensembles we have shown that

$$F(T, V, N) = -k_B T \ln Q(T, V, N).$$

Therefore we can write the above equation as,

$$k_B T \ln \mathcal{Q} = \mu N - F(T, V, N) \quad (6.27)$$

$$-k_B T \ln \mathcal{Q} = F - \mu N = U - TS - \mu N = \mathcal{G} \quad (6.28)$$

Recall the discussions on Legendre Transform : We start with $U \equiv U(S, V, N)$. Transform S in favour of the "slope" T (partial derivative of U with respect to S). We get the "intercept" $F(T, V, N)$ as $U - TS$. Let us carry out one more transform : $N \rightarrow \mu$. *i.e.* transform N in favour of the slope μ (partial derivative of U with respect to N); μ is the chemical potential. We get the "intercept" $\mathcal{G}(T, V, \mu)$ - the grand potential. We have $\mathcal{G}(T, V, \mu) = U - TS - \mu N$. Thus we have, $\mathcal{G}(T, V, \mu) = -k_B T \ln \mathcal{Q}(T, V, \mu)$

6.3 Statistics of Number of Particles

The grand canonical partition function \mathcal{Q} of statistical mechanics (micro world) corresponds to the grand potential (\mathcal{G}) of thermodynamics (macro world). We have $\mathcal{G}(T, V, \mu) = -k_B T \ln \mathcal{Q}$.

Some authors⁵ would like to identify PV as the thermodynamic counterpart of grand canonical partition function : $PV = k_B T \ln \mathcal{Q}$. Let us first derive this relation. To this end, let me tell you of a beautiful formula proposed by Euler, in the context of homogeneous function.

6.3.1 Euler and his Theorem

U is a homogeneous function of S , V and N . U is an extensive property; so are S , V and N . Extensivity means that U is a first order homogeneous function of S , V , and N . Therefore $U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$ where λ is a constant⁶. Euler's trick consists of differentiating both sides of the above equation with respect to λ . We get,

$$\frac{\partial U}{\partial(\lambda S)} \frac{\partial(\lambda S)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda V)} \frac{\partial(\lambda V)}{\partial \lambda} + \frac{\partial U}{\partial(\lambda N)} \frac{\partial(\lambda N)}{\partial \lambda} = U(S, V, N) \quad (6.29)$$

$$S \frac{\partial U}{\partial(\lambda S)} + V \frac{\partial U}{\partial(\lambda V)} + N \frac{\partial U}{\partial(\lambda N)} = U(S, V, N) \quad (6.30)$$

The above is true for any value of λ . In particular it is true for $\lambda = 1$. Substitute in the above $\lambda = 1$ and get,

$$S \frac{\partial U}{\partial S} + V \frac{\partial U}{\partial V} + N \frac{\partial U}{\partial N} = U(S, V, N) \quad (6.31)$$

$$TS - PV + \mu N = U \quad (6.32)$$

6.3.2 \mathcal{Q} : Connection to Thermodynamics

We proceed as follows. From Euler relation : $U = TS - PV + \mu N$, we have $-PV = U - TS - \mu N$. The RHS of this equation is grand potential. Hence,

$$\begin{aligned} -PV &= \mathcal{G}(T, V, \mu) = -k_B T \ln \mathcal{Q}(T, V, \mu) \\ PV &= k_B T \ln \mathcal{Q}(T, V, \mu) \end{aligned} \quad (6.33)$$

6.3.3 Gibbs-Duhem Relation

Now that we are on the Euler's formula, let me digress a little bit and see if the equations we have derived, can be used to establish a relation amongst the intensive properties T , P and μ of the system.

Derivation from $U(S, V, N)$

⁵ Donald McQuairrie, *Statistical Mechanics*, Harper and Row (1976)

⁶ do not confuse λ here with fugacity introduced earlier. Unfortunately I have used the same symbol. You should understand the meaning of λ in the context it is used.

We proceed as follows.

$$U = TS - PV + \mu N, \quad (6.34)$$

$$dU = TdS - PdV + \mu dN + SdT - VdP + Nd\mu \quad (6.35)$$

From the first law of thermodynamics, we have $dU = TdS - PdV + \mu dN$. Hence, $Nd\mu + SdT - VdP = 0$. It follows then,

$$d\mu = -\frac{S}{N} dT + \frac{V}{N} dP = -sdT + vdP \quad (6.36)$$

where s is the specific entropy - entropy per particle and v is specific volume - volume per particle.

6.3.4 Average number of particles in an open system, $\langle N \rangle$

We start with, $\mathcal{Q}(T, V, \lambda) = \sum_{N=0}^{\infty} \lambda^N Q_N(T, V)$. Take the partial derivative of \mathcal{Q} with respect to λ and get,

$$\begin{aligned} \left(\frac{\partial \mathcal{Q}}{\partial \lambda} \right)_{T,V} &= \sum_{N=0}^{\infty} N \lambda^{N-1} Q_N(T, V) = \frac{1}{\lambda} \sum_{N=0}^{\infty} N \lambda^N Q_N(T, V) \\ &= \frac{\mathcal{Q}}{\lambda} \left[\frac{1}{\mathcal{Q}} \sum_{N=0}^{\infty} N \lambda^N Q_N(T, V) \right] \\ &= \frac{\mathcal{Q}}{\lambda} \langle N \rangle \end{aligned} \quad (6.37)$$

Thus the average number of particles in an open system can be formally expressed as,

$$\langle N \rangle = \lambda \frac{1}{\mathcal{Q}} \frac{\partial \mathcal{Q}}{\partial \lambda} = \lambda \frac{\partial \ln \mathcal{Q}}{\partial \lambda} \quad (6.38)$$

6.3.5 Probability $P(N)$, that there are N particles in an open system

We start with

$$\begin{aligned} \mathcal{Q}(T, V, \lambda) &= \sum_{N=0}^{\infty} \lambda^N Q_N(T, V) = \sum_{N=0}^{\infty} \lambda^N \frac{Q_1^N}{N!} \\ &= \exp(\lambda Q_1) \end{aligned} \quad (6.39)$$

The average of N can be formally expressed as,

$$\langle N \rangle = \frac{1}{\mathcal{Q}} \sum_{N=0}^{\infty} N \frac{(\lambda Q_1)^N}{N!} = \sum_{N=0}^{\infty} \frac{\lambda^N Q_1^N}{\mathcal{Q} N!} \quad (6.40)$$

We have already shown $\mathcal{Q} = \exp(\lambda Q_1)$. Therefore,

$$\langle N \rangle = \sum_{N=0}^{\infty} N \frac{(\lambda Q_1)^N \exp(-\lambda Q_1)}{N!} \quad (6.41)$$

We have earlier shown that $\langle N \rangle = \lambda Q_1 = \zeta$ say. Then,

$$\langle N \rangle = \sum_{N=1}^{\infty} N \frac{\zeta^N \exp(-\zeta)}{N!} = \sum_{N=1}^{\infty} N P(N) \quad (6.42)$$

$P(N)$ thus is a Poisson distribution : $P(N) = \frac{\zeta^N}{N!} \exp(-\zeta)$. For Poisson distribution, the mean equals variance. Therefore

$$\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = \langle N \rangle = \zeta = \lambda Q_1. \quad (6.43)$$

6.3.6 Number Fluctuations

In an open system, the energy E and the number of molecules N are random variables. Energy fluctuates when the system goes from micro state to another. The number of molecules fluctuates from one micro state to the other. Let us now derive an expression for the variance of N :

$$\sigma^2 = \langle N^2 \rangle - \langle N \rangle^2.$$

To this end, we start with

$$\mathcal{Q}(T, V, \mu) = \sum_c \exp \left[-\beta \{E(c) - \mu N(c)\} \right] \quad (6.44)$$

In the above

c denotes a micro state of the open system

$E(c)$ denotes the energy of the open system when in micro state c

$N(c)$ denotes the number of particles of the open when in micro state c

Let us now take the partial derivative of all the terms in the above equation, with respect to the variable μ , keeping the temperature and volume constant. We have,

$$\left(\frac{\partial \mathcal{Q}}{\partial \mu} \right)_{T,V} = \sum_c \beta N(c) \exp \left[-\beta \{E(c) - \mu N(c)\} \right] = \beta \langle N \rangle \mathcal{Q}(T, V, \mu) \quad (6.45)$$

$$\left(\frac{\partial^2 \mathcal{Q}}{\partial \mu^2} \right)_{T,V} = \beta \left[\langle N \rangle \left(\frac{\partial \mathcal{Q}}{\partial \mu} \right)_{T,V} + \mathcal{Q} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \right] \quad (6.46)$$

The left hand side of the above equation equals $\beta^2 \langle N^2 \rangle \mathcal{Q}$.

Substituting this in the above, we get,

7

$$\begin{aligned} \left(\frac{\partial \mathcal{Q}}{\partial \mu} \right)_{T,V} &= \sum_c \beta N(c) \exp \left[-\beta \{E(c) - \mu N(c)\} \right] \\ \left(\frac{\partial^2 \mathcal{Q}}{\partial \mu^2} \right)_{T,V} &= \sum_c \beta^2 [N(c)]^2 \exp \left[-\beta \{E(c) - \mu N(c)\} \right] \\ &= \beta^2 \langle N^2 \rangle \mathcal{Q}. \end{aligned}$$

$$\beta^2 \langle N^2 \rangle \mathcal{Q} = \beta^2 \langle N \rangle^2 \mathcal{Q} + \beta \mathcal{Q} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \quad (6.47)$$

$$\sigma^2 = \langle N^2 \rangle - \langle N \rangle^2 = k_B T \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \quad (6.48)$$

Since $\langle N \rangle = \lambda Q_1$, we have,

$$\frac{\partial \langle N \rangle}{\partial \mu} = Q_1 \frac{d\lambda}{d\mu} = \beta \lambda Q_1 \quad (6.49)$$

We have shown

$$\sigma_N^2 = k_B T \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \quad (6.50)$$

Substituting in the above $\frac{\partial \langle N \rangle}{\partial \mu} = \lambda \beta Q_1$, we get,

$$\sigma_N^2 = k_B T Q_1 \beta \lambda \quad (6.51)$$

$$= \lambda Q_1 = \langle N \rangle \quad (6.52)$$

consistent with what we have shown earlier : *the distribution of N is Poissonian with mean=variance= λQ_1*

In what follows, we shall derive an expression for the fluctuations of N in terms of isothermal compressibility - a property measurable experimentally.

6.3.7 Number Fluctuations and Isothermal Compressibility

Let us express the number fluctuations in terms of experimentally measurable properties⁸ of the open system. Let us define

$$v = \frac{V}{\langle N \rangle}.$$

It is called specific volume. It is the volume per particle. We have,

⁸ We shall show that,

$$\left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \frac{\langle N \rangle^2}{V} k_T \quad (6.53)$$

where k_T denotes isothermal compressibility - an experimentally measurable property. Isothermal compressibility is defined as

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (6.54)$$

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = \left(\frac{\partial(V/v)}{\partial\mu}\right)_{T,V} \quad (6.55)$$

$$= -\frac{V}{v^2} \left(\frac{\partial v}{\partial\mu}\right)_{T,V} \quad (6.56)$$

$$= -\frac{\langle N\rangle^2}{V} \left(\frac{\partial v}{\partial\mu}\right)_{T,V} \quad (6.57)$$

In the above we can express,

$$\left(\frac{\partial v}{\partial\mu}\right)_{T,V} = \left(\frac{\partial v}{\partial P}\right)_{T,V} \left(\frac{\partial P}{\partial\mu}\right)_{T,V} \quad (6.58)$$

Employing Gibbs-Duhem relation, we find ⁹,

$$\left(\frac{\partial P}{\partial\mu}\right)_T = \frac{\langle N\rangle}{V} \quad (6.60)$$

Therefore,

$$\left(\frac{\partial v}{\partial\mu}\right)_{T,V} = \frac{\langle N\rangle}{V} \left(\frac{\partial v}{\partial P}\right)_{T,V} = \frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_{T,V} = -k_T \quad (6.61)$$

Finally we get,

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = \frac{\langle N\rangle^2}{V} k_T \quad (6.62)$$

$$\sigma^2 = k_B T \left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} \quad (6.63)$$

$$= k_B T \frac{\langle N\rangle^2}{V} k_T \quad (6.64)$$

$$\frac{\sigma^2}{\langle N\rangle^2} = \frac{k_B T}{V} k_T \quad (6.65)$$

⁹ Gibbs - Duhem relation reads as $\langle N\rangle d\mu = VdP - SdT$. At constant temperature, we have,
 $\langle N\rangle d\mu = VdP$,

$$\left(\frac{\partial P}{\partial\mu}\right)_T = \frac{\langle N\rangle}{V} \quad (6.59)$$

Thus the fluctuations in the number of molecules of an open system is directly proportional to the isothermal compressibility. Hence we expect isothermal compressibility to be positive ¹⁰.

The number fluctuations are small in the thermodynamic limit; they are of the order of inverse of the square-root of the number of particles in the system.

Thus equilibrium fluctuations are related to an appropriate susceptibility which measures the response of the system to a small external perturbation. When heated, the system responds by raising its temperature. Energy absorbed by heat divided by the increase in temperature is called the heat capacity. The volume does not change during this process. We saw that the equilibrium energy fluctuations are proportional heat capacity.

Thus, the susceptibility is heat capacity for energy fluctuations; it is isothermal compressibility for the number fluctuations. These are special cases of a more general principle called *Fluctuation-Dissipation theorem* enunciated by Albert Einstein in the context of Brownian motion.

However, close to first order phase transition, isothermal compressibility diverges. The fluctuations in the number of particles become large; they increase to the order of the system size.

6.3.8 Alternate Derivation of the Relation :

$$\sigma_N^2 / \langle N \rangle^2 = k_B T k_T / V$$

I had, earlier, derived a relation is between the number fluctuation and isothermal compressibility. I had followed closely Pathria ¹¹. Here is an alternate derivation.

Start with a fluctuation-dissipation relation ¹² derived earlier,

$$\sigma^2 = k_B T \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T} \quad (6.66)$$

We consider the reciprocal,

$$\left(\frac{\partial \mu}{\partial \langle N \rangle} \right)_{V,T} \quad (6.67)$$

We observe that μ is a function¹³ of T and P . We are keeping T a constant. Hence μ can change only when P changes.

Gibbs-Duhem relation tells us,

$$\langle N \rangle d\mu = V dP - S dT. \quad (6.68)$$

When T is a constant, we have $dT = 0$. This gives us

¹⁰ The relative fluctuations of energy in a canonical ensemble is proportional to heat capacity at constant volume. Hence we expect heat capacity to be positive.

¹¹ R. K. Pathria, *Statistical Mechanics*, Second Edition, Butterworth and Henemann (1996).

¹² relating number fluctuations to response to small changes in the chemical potential.

¹³ Gibbs and Duhem told us that the three intensive properties T , P , and μ are not all independent. Only two of them are independent. The third is automatically fixed by the other two.

$$d\mu = \frac{V}{\langle N \rangle} dP \quad (6.69)$$

$$\left(\frac{\partial \mu}{\partial \langle N \rangle} \right)_{T,V} = \frac{V}{\langle N \rangle} \left(\frac{\partial P}{\partial \langle N \rangle} \right)_{T,V} \quad (6.70)$$

$$\left(\frac{\partial \mu}{\partial P} \right)_{T,V} = \frac{V}{\langle N \rangle} \quad (6.71)$$

Let us now define $\rho = \frac{\langle N \rangle}{V}$, which denotes the particle density : number of particles per unit volume. We have,

$$\left(\frac{\partial P}{\partial \langle N \rangle} \right)_{V,T} = \left(\frac{\partial P}{\partial (\rho V)} \right)_{V,T} = \frac{1}{V} \left(\frac{\partial P}{\partial \rho} \right)_{V,T} \quad (6.72)$$

The density can be changed either by changing $\langle N \rangle$ and/or V . Here we change ρ infinitesimally, keeping V constant. As a result the pressure changes infinitesimally. Let me repeat : both these changes happen at constant V and T .

As far as P is concerned, it does not care whether ρ has changed by change of $\langle N \rangle$ or of V . Hence it is legitimate to write

$$\left(\frac{\partial P}{\partial \rho} \right)_{V,T} = \left(\frac{\partial P}{\partial (\langle N \rangle / V)} \right)_{\langle N \rangle, T} \quad (6.73)$$

$$= -\frac{V^2}{\langle N \rangle} \left(\frac{\partial P}{\partial V} \right)_{\langle N \rangle, T} \quad (6.74)$$

Thus we get,

$$\begin{aligned} \left(\frac{\partial \mu}{\partial \langle N \rangle} \right)_{V,T} &= \frac{V}{\langle N \rangle} \left(\frac{\partial P}{\partial \langle N \rangle} \right)_{V,T} \\ &= \frac{1}{\langle N \rangle} \left(\frac{\partial P}{\partial \rho} \right)_{V,T} \\ &= -\frac{V^2}{\langle N \rangle^2} \left(\frac{\partial P}{\partial V} \right)_{\langle N \rangle, T} \end{aligned} \quad (6.75)$$

Take a reciprocal of the above and get,

$$\left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T} = -\frac{\langle N \rangle^2}{V^2} \left(\frac{\partial V}{\partial P} \right)_{\langle N \rangle, T} \quad (6.76)$$

Then we get,

$$\sigma_N^2 = k_B T \left[-\frac{\langle N \rangle^2}{V^2} \right] \left(\frac{\partial V}{\partial P} \right)_{T, \langle N \rangle} = k_B T \frac{\langle N \rangle^2}{V} k_T$$

$$\frac{\sigma_N^2}{\langle N \rangle^2} = \frac{k_B T}{V} k_T \quad (6.77)$$

6.4 Energy Fluctuations

We start with the grand canonical partition function and its partial derivatives, the first and second, with respect to the variable β :

$$\begin{aligned} Q &= \sum_i \lambda^{N_i} \exp(-\beta E_i) \\ \left(\frac{\partial Q}{\partial \beta} \right)_{\lambda, V} &= - \sum_i \lambda^{N_i} E_i \exp(-\beta E_i) \\ \left(\frac{\partial^2 Q}{\partial \beta^2} \right)_{\lambda, V} &= \sum_i \lambda^{N_i} E_i^2 \exp(-\beta E_i) \end{aligned}$$

The first and second moment of energy are given by,

$$\langle E \rangle = -\frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right)_{\lambda, V}$$

$$\langle E^2 \rangle = \frac{1}{Q} \left(\frac{\partial^2 Q}{\partial \beta^2} \right)_{\lambda, V}$$

To derive an expression for the fluctuations of energy in a grand canonical ensemble, we proceed as follows.

$$\begin{aligned} \left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_{\lambda, V} &= - \left(\frac{\partial}{\partial \beta} \left[\frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right)_{\lambda, V} \right] \right)_{\lambda, V} \\ &= -\frac{1}{Q} \left(\frac{\partial^2 Q}{\partial \beta^2} \right)_{\lambda, V} + \left[\frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right)_{\lambda, V} \right]^2 \\ &= -(\langle E^2 \rangle - \langle E \rangle^2) \\ &= -\sigma_{E:\text{OPEN}}^2 \end{aligned}$$

We proceed in the same fashion and obtain a similar expression for the fluctuations of energy in a canonical ensemble¹⁴ $\left(\frac{\partial \langle E \rangle}{\partial \beta} \right)_{N, V} = -\sigma_{E:\text{CLOSED}}^2$. Note for an open

system, the partial derivative of energy with respect to β is taken at constant λ and V . For a closed system, the partial derivative of energy with respect to β is taken at constant N and V . What is the relation between $\sigma_{E:\text{OPEN}}^2$ and $\sigma_{E:\text{CLOSED}}^2$?

The key to answering to this question is in the following entities : • $U(T, V, N)$ with N constant and

• $U(T, V, \lambda) = U(T, V, N(T, V, \lambda))$ with N depending on T , V , and λ and with λ kept constant instead of N .

The central relation¹⁵ is,

$$\begin{aligned} {}^{14} Q &= \sum_i \exp(-\beta E_i); \quad \frac{\partial Q}{\partial \beta} = - \sum_i E_i \exp(-\beta E_i); \quad \frac{\partial^2 Q}{\partial \beta^2} = \sum_i E_i^2 \exp(-\beta E_i); \\ \langle E \rangle &= -\frac{1}{Q} \frac{\partial Q}{\partial \beta}; \quad \frac{\partial \langle E \rangle}{\partial \beta} = -\frac{1}{Q} \frac{\partial^2 Q}{\partial \beta^2} + \left(\frac{1}{Q} \frac{\partial Q}{\partial \beta} \right)^2 = -\sigma_{E:\text{CLOSED}}^2 \end{aligned}$$

¹⁵ Equation (6.78) above can be derived from first principles. Formally we start with $U(T, V, \lambda) \equiv U(T, V, N(T, V, \lambda))$. We have,

$$\left(\frac{\partial U}{\partial T}\right)_{\lambda,V} = \left(\frac{\partial U}{\partial T}\right)_{N,V} + \left(\frac{\partial U}{\partial N}\right)_{T,V} \times \left(\frac{\partial N}{\partial T}\right)_{\lambda,V}. \quad (6.78)$$

$$\left(\frac{\partial U}{\partial T}\right)_{\lambda,V} = \lim_{\Delta T \rightarrow 0} \frac{U(T + \Delta T, V, N(T + \Delta T, V, \lambda)) - U(T, V, N(T, V, \lambda))}{\Delta T}$$

In the above we express

$$N(T + \Delta T, V, \lambda) = N(T, V, \lambda) + \Delta T \left(\frac{\partial N}{\partial T}\right)_{\lambda,V} = N + (\Delta N)_{\lambda,V},$$

where we have used the short-hand notation $(\Delta N)_{\lambda,V} = \Delta T \left(\frac{\partial N}{\partial T}\right)_{\lambda,V}$. Therefore

$$\left(\frac{\partial U}{\partial T}\right)_{\lambda,V} = \lim_{\Delta T \rightarrow 0} \frac{U(T + \Delta T, V, N + (\Delta N)_{\lambda,V}) - U(T, V, N)}{\Delta T}$$

We can write

$$\begin{aligned} U(T + \Delta T, V, N + (\Delta N)_{\lambda,V}) &= U(T, V, N) + \Delta T \left(\frac{\partial U}{\partial T}\right)_{V,N} \\ &\quad + (\Delta N)_{\lambda,V} \left(\frac{\partial U}{\partial N}\right)_{T,V} \end{aligned}$$

Therefore,

$$\begin{aligned} \left(\frac{\partial U}{\partial T}\right)_{\lambda,V} &= \left(\frac{\partial U}{\partial T}\right)_{V,N} + \frac{(\Delta N)_{\lambda,V}}{\Delta T} \times \left(\frac{\partial U}{\partial N}\right)_{T,V} \\ &= \left(\frac{\partial U}{\partial T}\right)_{V,N} + \left(\frac{\partial N}{\partial T}\right)_{\lambda,V} \times \left(\frac{\partial U}{\partial N}\right)_{T,V} \end{aligned}$$

The last term in Eq. (6.78) above involving the partial derivative of N with respect to T can be evaluated, see box below.

Start with $N(T, V, \mu(T, \lambda))$, where $\mu = k_B T \ln \lambda$. We have,

$$\left(\frac{\partial N}{\partial T}\right)_{\lambda, V} = \left(\frac{\partial N}{\partial T}\right)_{\mu, V} + \left(\frac{\partial N}{\partial \mu}\right)_{T, V} \times \left(\frac{\partial \mu}{\partial T}\right)_{\lambda, V} \quad (6.79)$$

The first term on the right hand side of Eq. (6.79) above can be evaluated, see the box below.

Consider $N(T, V, \mu)$. At constant V we can write,

$$dN = \left(\frac{\partial N}{\partial T}\right)_{\mu} dT + \left(\frac{\partial N}{\partial \mu}\right)_{T} d\mu$$

$dN = 0$ implies,

$$\left(\frac{\partial N}{\partial T}\right)_{\mu} dT = - \left(\frac{\partial N}{\partial \mu}\right)_{T} d\mu$$

$$\left(\frac{\partial N}{\partial T}\right)_{\mu} = - \left(\frac{\partial N}{\partial \mu}\right)_{T} \times \left(\frac{\partial \mu}{\partial T}\right)_{N}$$

Therefore Eq.(6.79) can be written as,

$$\begin{aligned} \left(\frac{\partial N}{\partial T}\right)_{\lambda, V} &= - \left(\frac{\partial N}{\partial \mu}\right)_{T, V} \times \left(\frac{\partial \mu}{\partial T}\right)_{N, V} + \left(\frac{\partial N}{\partial \mu}\right)_{T, V} \times \left(\frac{\partial \mu}{\partial T}\right)_{\lambda, V} \\ &= \left(\frac{\partial N}{\partial \mu}\right)_{T, V} \left[\left(\frac{\partial \mu}{\partial T}\right)_{\lambda, V} - \left(\frac{\partial \mu}{\partial T}\right)_{N, V} \right] \\ &= \left(\frac{\partial N}{\partial \mu}\right)_{T, V} \left[\frac{\mu}{T} - \left(\frac{\partial \mu}{\partial T}\right)_{N, V} \right] \end{aligned} \quad (6.80)$$

In the last step we have made use of the relation : $\left(\frac{\partial \mu}{\partial T}\right)_{\lambda, V} = \frac{\mu}{T}$, see box below.

$$\lambda = \exp(\beta\mu); \quad \mu = k_B T \ln \lambda; \quad \left(\frac{\partial \mu}{\partial T}\right)_{\lambda} = k_B \ln \lambda = \mu/T$$

Consider the term within square brackets on the right hand side of Eq. (6.80); we can show that

$$\left[\frac{\mu}{T} - \left(\frac{\partial \mu}{\partial T} \right)_{N,V} \right] = \frac{1}{T} \left(\frac{\partial U}{\partial N} \right)_{T,V},$$

see box below.

At constant volume we have $dU = TdS + \mu dN$. Therefore,

$$\begin{aligned} \left(\frac{\partial U}{\partial N} \right)_{T,V} &= \mu + T \left(\frac{\partial S}{\partial N} \right)_{T,V} = T \left[\frac{\mu}{T} + \left(\frac{\partial S}{\partial N} \right)_{T,V} \right] \\ &= T \left[\frac{\mu}{T} - \left(\frac{\partial \mu}{\partial T} \right)_{N,V} \right] \end{aligned}$$

In the above, the last step follows from one of Maxwell's relations, see box below.

Maxwell's Relation

$$F = U - TS$$

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

$$= \mu dN - SdT \quad (\text{at constant } V)$$

We have

$$\left(\frac{\partial F}{\partial N} \right)_T = \mu ; \quad \left(\frac{\partial F}{\partial T} \right)_N = -S$$

$$\frac{\partial^2 F}{\partial T \partial N} = \left(\frac{\partial \mu}{\partial T} \right)_N ; \quad \frac{\partial^2 F}{\partial N \partial T} = - \left(\frac{\partial S}{\partial N} \right)_T$$

$$\frac{\partial^2 F}{\partial T \partial N} = \frac{\partial^2 F}{\partial N \partial T} \Rightarrow \left(\frac{\partial \mu}{\partial T} \right)_N = - \left(\frac{\partial S}{\partial N} \right)_T$$

Therefore Eq. (6.80) can be written as, $\left(\frac{\partial N}{\partial T} \right)_{\lambda,V} = \left(\frac{\partial N}{\partial \mu} \right)_{T,V} \frac{1}{T} \left(\frac{\partial U}{\partial N} \right)_{T,V}$.

Now we can go back to Eq. (6.78) and write it as

$$\left(\frac{\partial U}{\partial T} \right)_{\lambda,V} = \left(\frac{\partial U}{\partial T} \right)_{N,V} + \frac{1}{T} \left(\frac{\partial U}{\partial N} \right)_{T,V}^2 \left(\frac{\partial N}{\partial \mu} \right)_{T,V} \quad (6.81)$$

Make use of the relation¹⁶,

$$\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \frac{\sigma_N^2}{k_B T}$$

and re-write Eq. (6.81) as

$$\begin{aligned} \left(\frac{\partial U}{\partial T}\right)_{\lambda,V} &= \left(\frac{\partial U}{\partial T}\right)_{N,V} + \frac{1}{k_B T^2} \sigma_N^2 \left(\frac{\partial U}{\partial N}\right)_{T,V}^2 \\ k_B T^2 \left(\frac{\partial U}{\partial T}\right)_{\lambda,V} &= k_B T^2 \left(\frac{\partial U}{\partial T}\right)_{N,V} + \sigma_N^2 \left(\frac{\partial U}{\partial N}\right)_{T,V}^2 \\ \sigma_{E:\text{OPEN}}^2 &= k_B T^2 C_V + \left(\frac{\partial \langle E \rangle}{\partial \langle N \rangle}\right)_{T,V}^2 \sigma_N^2 \end{aligned} \quad (6.82)$$

Thus the energy fluctuations in an open system has an extra component given by the second term in the above, arising due to fluctuations in the number of particles.

16

$$\mathcal{Q} = \sum_i \exp[-\beta(E - \mu N)]$$

$$\frac{\partial \mathcal{Q}}{\partial \mu} = \beta \sum_i N \exp[-\beta(E - \mu N)]; \quad \frac{\partial^2 \mathcal{Q}}{\partial \mu^2} = \beta^2 \sum_i N^2 \exp[-\beta(E - \mu N)]$$

$$\frac{1}{\mathcal{Q}} \frac{\partial \mathcal{Q}}{\partial \mu} = \beta \langle N \rangle; \quad \frac{1}{\mathcal{Q}} \frac{\partial^2 \mathcal{Q}}{\partial \mu^2} = \beta^2 \langle N^2 \rangle$$

$$\beta \frac{\partial \langle N \rangle}{\partial \mu} = \frac{\partial}{\partial \mu} \left[\frac{1}{\mathcal{Q}} \frac{\partial \mathcal{Q}}{\partial \mu} \right] = \frac{1}{\mathcal{Q}} \frac{\partial^2 \mathcal{Q}}{\partial \mu^2} - \left[\frac{1}{\mathcal{Q}} \frac{\partial \mathcal{Q}}{\partial \mu} \right]^2 = \beta^2 (\langle N^2 \rangle - \langle N \rangle^2)$$

$$\frac{\partial \langle N \rangle}{\partial \mu} = \frac{1}{k_B T} \sigma_N^2$$

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7. Quantum Statistics

7.1 Occupation Number Representation

Let $\{1, 2, \dots\}$ label the single-particle quantum states of a system. Let $\{\epsilon_i : i = 1, 2, \dots\}$ denote the corresponding energies. Notice that there can be several quantum states with the same energy.

We have N non-interacting quantum particles occupying the single particle quantum states. A micro state of the macroscopic system of N (quantum) particles in a volume V is uniquely specified by a string of numbers $\{n_1, n_2, \dots\}$, where n_i is the number of particles in the single-particle quantum state i . Thus, a string of occupation numbers uniquely describes a micro state of a quantum system¹. Note that such a string should obey the constraint : $n_1 + n_2 + \dots = N$. The energy of a micro state is $n_1\epsilon_1 + n_2\epsilon_2 + \dots$. The canonical partition function can now be written as

$$Q(T, V, N) = \sum_{\{n_1, n_2, \dots\}}^* \exp[-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)] \quad (7.1)$$

where the sum runs over all possible micro states *i.e.* all possible strings of occupation numbers obeying the constraint $\sum_i n_i = N$. To remind us of this constraint I have put a star as a superscript to the summation sign.

7.2 Open System and $\mathcal{Q}(T, V, \mu)$

The presence of the constraint renders evaluation of the sum a difficult task. A way out is to transform the variable N in favour of λ , called the fugacity; λ is related to the chemical potential μ ; the relation is $\lambda = \exp(\beta\mu)$. The transform defines the **grand canonical** partition function², see below.

¹ for classical particles, the same string of occupation numbers represent a collection of $N! / \prod_i n_i!$ micro states.

² we have already seen that a partition function is a transform. We start with density of states $\widehat{\Omega}(E)$ and transform the variable E in favour of $\beta = 1/[k_B T]$ to get canonical partition function:

$$Q(\beta, V, N) = \int_0^\infty dE \widehat{\Omega}(E, V, N) \exp(-\beta E(V, N)).$$

We can consider the grand canonical partition function as a transform of the canonical partition function with the variable N transformed to fugacity λ (or chemical potential $\mu = k_B T \ln(\lambda)$.)

$$Q(\beta, V, \lambda) = \sum_{N=0}^{\infty} \lambda^N Q(\beta, V, N) \quad (7.2)$$

This provides a description of an open system with its natural variable : temperature, volume and chemical potential. The system can exchange energy as well as matter with the environment. Thus energy E , and the number of particles N , of the system would be fluctuating around the means $\langle E \rangle$ and $\langle N \rangle$ respectively, where the angular bracket denotes averaging over a grand canonical ensemble of the open system.

Thus we have,

$$\begin{aligned} Q(T, V, \mu) &= \sum_{N=0}^{\infty} \lambda^N \sum_{\{n_1, n_2, \dots\}}^* \exp[-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)] \\ &= \sum_{N=0}^{\infty} \sum_{\{n_1, n_2, \dots\}}^* \lambda^{n_1 + n_2 + \dots} \exp[-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)] \\ &= \sum_{N=0}^{\infty} \sum_{\{n_1, n_2, \dots\}}^* \exp[-\beta(\epsilon_1 - \mu)n_1 - \beta(\epsilon_2 - \mu)n_2 + \dots] \\ &= \sum_{N=0}^{\infty} \sum_{\{n_1, n_2, \dots\}}^* [\exp\{-\beta(\epsilon_1 - \mu)\}]^{n_1} \times \\ &\quad [\exp\{-\beta(\epsilon_2 - \mu)\}]^{n_2} \times \dots \\ &= \sum_{N=0}^{\infty} \sum_{\{n_1, n_2, \dots\}}^* x_1^{n_1} \times x_2^{n_2} \times \dots \end{aligned} \quad (7.3)$$

where a short hand notation : $x_i = \lambda \exp(-\beta \epsilon_i) = \exp[-\beta(\epsilon_i - \mu)]$ is introduced while writing the last line. We have a restricted sum over strings of occupation numbers. The restriction is that the occupation numbers constituting a string should add to N . We then take a sum over N from 0 to ∞ , which removes the restriction. To appreciate this, see Donald A McQuairrie, *Statistical Mechanics*, Harper and Row(1976)p.77;Problem:4-6. I have worked out this problem below.

Consider evaluating the sum, $I_1 = \sum_{N=0}^{\infty} \sum_{\{n_1, n_2\}}^* x_1^{n_1} x_2^{n_2}$, where $n_i = 0, 1, 2$ for $i = 1, 2$, and $\star \Rightarrow n_1 + n_2 = N$. Write down all the terms in this sum explicitly and show it is equivalent to $\prod_{i=1}^2 \sum_{n=0}^2 x_i^n$.

Let n_1 and n_2 denote two integers. Each of them can take values 0, 1, or 2. Consider first the restricted sum :

$$I_1 = \sum_{N=0}^{\infty} \sum_{\{n_1, n_2\}}^* x_1^{n_1} x_2^{n_2} \quad (7.4)$$

where the star over the summation sign reminds us of the restriction $n_1 + n_2 = N$. Thus we get Table (1).

N	n_1	n_2	$x_1^{n_1} x_2^{n_2}$
0	0	0	1
1	1 0	0 1	x_1 x_2
2	2 0 1	0 2 1	x_1^2 x_2^2 $x_1 x_2$
3	3 2 1 0	0 1 2 3	- $x_1^2 x_2$ $x_1 x_2^2$ -
	- 2 -	- 2 -	- $x_1^2 x_2^2$ -
5	-	-	-

Table 1. Terms in the restricted sum

From the table, we can write down I_1 as,

$$I_1 = 1 + x_1 + x_2 + x_1^2 + x_2^2 + x_1 x_2 + x_1^2 x_2 + x_1 x_2^2 + x_1^2 x_2^2 \quad (7.5)$$

Now consider the product over the unrestricted sums,

$$I_2 = \prod_{i=1}^2 \sum_{n=0}^{\infty} x_i^n \quad (7.6)$$

$$\begin{aligned} &= \prod_{i=1}^2 (1 + x_i + x_i^2 + \dots) \\ &= (1 + x_1 + x_1^2) \times (1 + x_2 + x_2^2) \\ &= 1 + x_2 + x_2^2 + x_1 + x_1 x_2 + x_1 x_2^2 + x_1^2 + x_1^2 x_2 + x_1^2 x_2^2 = I_1 \end{aligned} \quad (7.7)$$

In fact we need not have restricted n_1 and n_2 to the values 0, 1, and 2. We could have allowed them to run from zero and infinity, see below.=

$$\begin{aligned}
\sum_{N=0}^{\infty} \sum_{\{n_1, n_2\}}^* x_1^{n_1} x_2^{n_2} &= \sum_{N=0}^{\infty} \sum_{n=0}^N x_1^n x_2^{N-n} \\
&= \sum_{N=0}^{\infty} x_2^N \sum_{n=0}^N \left(\frac{x_1}{x_2}\right)^n \\
&= \sum_{N=0}^{\infty} x_2^N \frac{1 - (x_1/x_2)^{N+1}}{1 - (x_1/x_2)} \\
&= \sum_{N=0}^{\infty} \frac{x_2^{N+1} - x_1^{N+1}}{x_2 - x_1} \\
&= \frac{1}{x_2 - x_1} \left[\frac{x_2}{1 - x_2} - \frac{x_1}{1 - x_1} \right] \\
&= \frac{1}{x_2 - x_1} \left[\frac{x_2(1 - x_1) - x_1(1 - x_2)}{(1 - x_1)(1 - x_2)} \right] \\
&= \left(\frac{1}{1 - x_1}\right) \left(\frac{1}{1 - x_2}\right)
\end{aligned} \tag{7.8}$$

Q E D

We can now write the grand canonical partition function of N quantum particles occupying single-particle quantum states determined by volume V .

$$\begin{aligned}
\mathcal{Q}(T, V, \mu) &= \prod_i \sum_{n=0}^{\text{all}} x_i^n = \prod_i \sum_{n=0}^{\text{all}} [\lambda \exp(-\beta \epsilon_i)]^n \\
&= \prod_i \sum_{n=0}^{\text{all}} [\exp\{-\beta(\epsilon_i - \mu)\}]^n
\end{aligned} \tag{7.9}$$

7.3 Fermi-Dirac Statistics

We have $n = 0, 1$. This is a consequence of Pauli's exclusion principle: No single quantum state can have more than one fermion.

$$\mathcal{Q}_{\mathcal{FD}}(T, V, \mu) = \prod_i [1 + \exp\{-\beta(\epsilon_i - \mu)\}] \tag{7.10}$$

7.4 Bose-Einstein Statistics

We have $n = 0, 1, \dots, \infty$. Let $\exp[-\beta(\epsilon_i - \mu)] < 1 \forall i$. This condition is met if $\epsilon_i > \mu \forall i$. Then we have

$$\mathcal{Q}_{BE} = \prod_i \frac{1}{1 - \exp[-\beta(\epsilon_i - \mu)]} \quad (\epsilon_i > \mu \forall i) \tag{7.11}$$

7.5 Classical Distinguishable Particles

If the particles are classical and distinguishable, then the string $\{n_1, n_2, \dots\}$ will not uniquely specify a micro state. The string will have a set of classical micro states associated with it. The number of micro states associated with the string is given by,

$$\widehat{\Omega}(n_1, n_2, \dots) = \frac{N!}{n_1!n_2!\dots} \quad (7.12)$$

We then have

$$\begin{aligned} \mathcal{Q}_{CS}(T, V, \mu) &= \sum_{N=0}^{\infty} \lambda^N \sum_{\{n_1, n_2, \dots\}}^* \frac{N!}{n_1!n_2!\dots} [\exp(-\beta\epsilon_1)]^{n_1} \times \\ &\quad [\exp(-\beta\epsilon_2)]^{n_2} \times \dots \\ &= \sum_{N=0}^{\infty} \lambda^N \left[\sum_i \exp(-\beta\epsilon_i) \right]^N = \sum_{N=0}^{\infty} \lambda^N [Q_1(T, V)]^N \end{aligned} \quad (7.13)$$

where $Q_1(T, V)$ is the single-particle partition function.

We have already seen that the partition function for classical distinguishable non-interacting point particles leads to an entropy which is not extensive. This is called Gibbs' paradox. To take care of this, Boltzmann asked us to divide the number of micro states by $N!$, saying that the particles are indistinguishable.

The non-extensivity of entropy indicates a deep flaw in classical formulation of statistical mechanics. *Classical particles do not simply exist in nature.* We have only quantum particles : Bosons and Fermions. It is quantum mechanics that would set the things right eventually. But quantum mechanics had not arrived yet, in the times of Boltzmann.

Boltzmann corrected the (non-extensive entropy) flaw by introducing a strange notion of indistinguishability of particles. Genius he was, Boltzmann was almost on the mark. Division by $N!$ arises naturally in quantum mechanical formulation, because of the symmetry of the wave function.

Accordingly in the derivation of grand canonical partition function, we shall divide the classical degeneracy by $N!$, as recommended by Boltzmann, see below, and call the resulting statistics as Maxwell-Boltzmann statistics.

7.6 Maxwell-Boltzmann Statistics

Formally we have,

$$\begin{aligned} \mathcal{Q}_{MB} &= \sum_{N=0}^{\infty} \lambda^N \sum_{\{n_1, n_2, \dots\}}^* \frac{1}{n_1!n_2!\dots} \exp[-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)] \\ &= \sum_{N=0}^{\infty} \sum_{\{n_1, n_2, \dots\}}^* \frac{[\lambda \exp(-\beta\epsilon_1)]^{n_1}}{n_1!} \times \frac{[\lambda \exp(-\beta\epsilon_2)]^{n_2}}{n_2!} \times \dots \end{aligned}$$

$$\begin{aligned}
&= \sum_{N=0}^{\infty} \sum_{\{n_1, n_2, \dots\}}^* \frac{[\exp(-\beta(\epsilon_1 - \mu))]^{n_1}}{n_1!} \times \frac{[\exp(-\beta(\epsilon_2 - \mu))]^{n_2}}{n_2!} \times \dots \\
&= \sum_{N=0}^{\infty} \sum_{\{n_1, n_2, \dots\}}^* \frac{x_1^{n_1}}{n_1!} \frac{x_2^{n_2}}{n_2!} \dots \\
&= \left(\sum_{n=0}^{\infty} \frac{x_1^n}{n!} \right) \left(\sum_{n=0}^{\infty} \frac{x_2^n}{n!} \right) \dots \\
&= \exp(x_1) \exp(x_2) \dots \\
&= \prod_i \exp(x_i) = \prod_i \exp[\lambda \exp(-\beta\epsilon_i)] \\
&= \prod_i \exp[\exp\{-\beta(\epsilon_i - \mu)\}] \tag{7.14}
\end{aligned}$$

We can also express the grand canonical partition function for classical indistinguishable ideal gas as,

$$\begin{aligned}
Q_{MB} &= \exp(x_1) \exp(x_2) \dots = \exp \left[\sum_i x_i \right] \\
&= \exp \left[\sum_i \exp[-\beta(\epsilon_i - \mu)] \right] \\
&= \exp[\lambda \sum_i \exp(-\beta\epsilon_i)] \\
&= \exp[\lambda Q_1(T, V)] \tag{7.15}
\end{aligned}$$

7.6.1 $Q_{MB}(T, V, N) \rightarrow \mathcal{Q}_{MB}(T, V, \mu)$

We could have obtained the above in a simple manner, by recognising that

$$Q_{MB}(T, V, N) = \frac{[Q_{MB}(T, V, N=1)]^N}{N!} \tag{7.16}$$

Then we have,

$$\begin{aligned}
\mathcal{Q}(T, V, \lambda) &= \sum_{N=0}^{\infty} \lambda^N \frac{[Q_{MB}(T, V, N=1)]^N}{N!} \\
&= \exp[\lambda Q_{MB}(T, V, N=1)] \tag{7.17}
\end{aligned}$$

7.6.2 $\mathcal{Q}_{MB}(T, V, \mu) \rightarrow \mathcal{Q}_{MB}(T, V, N)$

We start with $\mathcal{Q}_{MB}(T, V, \mu) = \exp[\lambda \mathcal{Q}_{MB}(T, V, N = 1)]$. Taylor expanding the exponential,

$$\mathcal{Q}_{MB}(T, V, \mu) = \sum_{N=0}^{\infty} \lambda^N \frac{\mathcal{Q}_{MB}^N(T, V, N = 1)}{N!} \quad (7.18)$$

The coefficient of λ^N is the canonical partition function³ and hence is given by

$$\mathcal{Q}_{MB}(T, V, N) = \frac{\mathcal{Q}_{MB}(T, V, N = 1)^N}{N!}$$

7.7 Thermodynamics of an open system

We can write the grand canonical partition function for the MB, BE, and FD statistics as

$$\mathcal{Q} = \prod_i \begin{cases} \exp[\exp\{-\beta(\epsilon_i - \mu)\}] & \text{Maxwell - Boltzmann} \\ \frac{1}{1 - \exp[-\beta(\epsilon_i - \mu)]} & \text{BoseEinstein} \\ 1 + \exp\{-\beta(\epsilon_i - \mu)\} & \text{Fermi - Dirac} \end{cases} \quad (7.19)$$

The connection to thermodynamics is established by the expression for grand potential denoted by the symbol $\mathcal{G}(T, V, \mu)$. We have,

$$\mathcal{G}(T, V, \mu) = -k_B T \ln \mathcal{Q}(T, V, \mu) \quad (7.20)$$

Recall from thermodynamics that the \mathcal{G} is obtained as a Legendre transform of $U(S, V, N) : S \rightarrow T; N \rightarrow \mu; \text{ and } U \rightarrow \mathcal{G}$.

$$\mathcal{G}(T, V, \mu) = U - TS - \mu N \quad (7.21)$$

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, N} ; \mu = \left(\frac{\partial U}{\partial N} \right)_{S, V} \quad (7.22)$$

From the above, we get, $d\mathcal{G} = -PdV - SdT - Nd\mu$ It follows,

$$P = - \left(\frac{\partial \mathcal{G}}{\partial V} \right)_{T, \mu} ; S = - \left(\frac{\partial \mathcal{G}}{\partial T} \right)_{V, \mu} ; N = - \left(\frac{\partial \mathcal{G}}{\partial \mu} \right)_{T, \mu} \quad (7.23)$$

If we have an open system of particles obeying Maxwell-Boltzmann, Bose-Einstein, or Fermi-Dirac statistics at temperature T and chemical potential μ , in a volume V , then the above formulae help us calculate the pressure, entropy and average

³ Recall that

$$\mathcal{Q}_{MB}(T, V, \lambda) = \sum_{N=0}^{\infty} \lambda^N \mathcal{Q}_{MB}(T, V, N)$$

number of particles in the system. In fact, in the last section on grand canonical ensemble, we have derived formal expressions for the mean and fluctuations of the number of particles in an open system; we have related the fluctuations to isothermal compressibility - an experimentally measurable property.

The grand potential for the three statistics is given by,

$$\mathcal{G}(T, V, \mu) = -k_B T \ln \mathcal{Q}$$

$$= \begin{cases} -k_B T \sum_i \exp[-\beta(\epsilon_i - \mu)] & \text{Maxwell - Boltzmann} \\ k_B T \sum_i \ln[1 - \exp\{-\beta(\epsilon_i - \mu)\}] & \text{Bose - Einstein} \\ -k_B T \sum_i \ln[1 + \exp\{-\beta(\epsilon_i - \mu)\}] & \text{Fermi - Dirac} \end{cases} \quad (7.24)$$

7.8 Average number of particles, $\langle N \rangle$

7.8.1 Maxwell-Boltzmann Statistics

$$\mathcal{Q}(T, V, \mu) = \prod_i \exp[\exp\{-\beta(\epsilon_i - \mu)\}] \quad (7.25)$$

$$\begin{aligned} \mathcal{G}(T, V, \mu) &= -k_B T \ln \mathcal{Q} \\ &= -k_B T \sum_i \exp[-\beta(\epsilon_i - \mu)] \end{aligned} \quad (7.26)$$

$$\left(\frac{\partial \mathcal{G}}{\partial \mu}\right)_{T, V} = -\sum_i \exp[-\beta(\epsilon_i - \mu)] \quad (7.27)$$

$$\begin{aligned} \langle N \rangle &= -\left(\frac{\partial \mathcal{G}}{\partial \mu}\right)_{T, V} = \sum_i \exp[-\beta(\epsilon_i - \mu)] \\ &= \lambda \sum_i \exp(-\beta \epsilon_i) = \lambda Q_1(T, V, \mu) \end{aligned} \quad (7.28)$$

In the above Q_1 is the single-particle canonical partition function. The above result on $\langle N \rangle$ is consistent with formal result from grand canonical formalism :

The grand canonical partition function is formally given by the transform of canonical partition function. The thermodynamic variable N is transformed to fugacity λ (or to chemical potential $\mu = k_B T \ln \lambda$). Thus we have,

$$\begin{aligned} \mathcal{Q}(T, V, \mu) &= \sum_{N=0}^{\infty} \lambda^N Q(T, V, N) \\ &= \sum_{N=0}^{\infty} \lambda^N \frac{Q_1^N}{N!} \\ &= \sum_{N=0}^{\infty} \exp(\beta \mu N) \frac{Q_1^N}{N!} \\ &= \exp(\lambda Q_1) \end{aligned} \quad (7.29)$$

The grand potential is given by

$$\begin{aligned}
\mathcal{G}(T, V, \mu) &= -k_B T \ln \mathcal{Q}(T, V, \mu) \\
&= -k_B T \lambda Q_1 \\
&= -k_B T \exp(\mu/k_B T) Q_1
\end{aligned} \tag{7.30}$$

The average number of particles in the system is then given by,

$$\langle N \rangle = - \left(\frac{\partial \mathcal{G}}{\partial \mu} \right)_{T, V} = \lambda Q_1(T, V) \tag{7.31}$$

7.8.2 Bose-Einstein Statistics

$$\mathcal{Q}(T, V, \mu) = \prod_i \frac{1}{1 - \exp[-\beta(\epsilon_i - \mu)]} \tag{7.32}$$

$$\ln \mathcal{Q} = - \sum_i \ln [1 - \exp\{-\beta(\epsilon_i - \mu)\}] \tag{7.33}$$

$$\langle N \rangle = - \left(\frac{\partial \mathcal{G}}{\partial \mu} \right)_{T, V} = \sum_i \frac{\exp[-\beta(\epsilon_i - \mu)]}{1 - \exp[-\beta(\epsilon_i - \mu)]} \tag{7.34}$$

7.8.3 Fermi-Dirac Statistics

$$\mathcal{Q} = \prod_i [1 + \exp[-\beta(\epsilon_i - \mu)]] \tag{7.35}$$

$$\mathcal{G} = -k_B T \ln \mathcal{Q} = -k_B T \sum_i \ln [1 + \exp\{-\beta(\epsilon_i - \mu)\}] \tag{7.36}$$

$$\langle N \rangle = - \left(\frac{\partial \mathcal{G}}{\partial \mu} \right)_{T, V} = \sum_i \frac{\exp[-\beta(\epsilon_i - \mu)]}{1 + \exp[-\beta(\epsilon_i - \mu)]} \tag{7.37}$$

7.8.4 Study of a System with fixed N Employing Grand Canonical Formalism

In my next lecture, I shall derive an expression for the mean of occupation number, n_k , of a single particle quantum state. Then we can express $\langle N \rangle = \sum_k \langle n_k \rangle$. These results on $\langle N \rangle$ shall be the same as the one derived in the last three subsections.

Grand canonical formalism is not the best suited for studying ideal gas - classical or quantum. Recall, we introduced an adhoc and awkward - indistinguishability-factor of $N!$, suggested by Boltzmann, to restore the extensivity of entropy while studying closed system. In an open system the number of particles fluctuate and the issue of non-extensivity becomes more awkward.

We shall adopt the following strategy. We shall employ grand canonical formalism, but with a fixed N . The price we have to pay is that in such an approach, the chemical potential is no longer an independent property. It becomes a function of temperature. Let me explain.

Let us say we keep μ fixed and change the temperature⁴. The mean number of particles in the system changes when temperature changes. To restore the value of $\langle N \rangle$ to the fixed value N , we change the chemical potential. In what follows, we shall investigate the behaviour of particles under Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac statistics employing grand canonical formalism but with a fixed N ; This implies μ is not any more an independent property; it is a function of T .

I must say there is nothing unphysical about this strategy. We are studying a physical system enclosed by a non-permeable wall - a wall that does not permit particle exchange. The chemical potential μ , is a well defined property of the system. It is just that μ is not any more under our control⁵. The system automatically selects the value of μ depending on the temperature.

7.9 Fermi-Dirac, Maxwell-Boltzmann and Bose-Einstein Statistics are the same at High Temperature and/or Low Densities

I shall show below that three statistics are the same at high temperatures and / or low densities by an easy method, an easier method and perhaps the easiest method.

7.9.1 Easy Method : $\rho\Lambda^3 \rightarrow 0$

For ease of notation let

$$\eta_i = \frac{\epsilon_i - \mu}{k_B T} \quad (7.38)$$

and write the grand canonical partition function under Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac statistics as

$$Q = \prod_i \begin{cases} \exp[\exp(-\eta_i)] & \text{Maxwell - Boltzmann} \\ \frac{1}{1 - \exp(-\eta_i)} & \text{Bose - Einstein} \\ 1 + \exp(-\eta_i) & \text{Fermi - Dirac} \end{cases} \quad (7.39)$$

Let us make an estimate of η_i at high temperatures and low densities.

We had shown earlier that the canonical partition function for an ideal gas can be written as, see notes,

$$Q(T, V, N) = \frac{V^N}{N!} \frac{1}{\Lambda^{3N}} \quad (7.40)$$

⁴ This is permitted in grand canonical formalism since T and μ are independent properties of the open system. T is determined by the heat bath and μ is determined by the particle bath or reservoir.

⁵ μ is not determined by us externally by adjusting the particle bath.

where the thermal wave length is given by

$$\Lambda = \frac{h}{\sqrt{2\pi mk_B T}} \quad (7.41)$$

The free energy is given by

$$F(T, V, N) = -k_B T \ln Q(T, V, N) \quad (7.42)$$

$$= -k_B T [-3N \ln \Lambda + N \ln V - N \ln N + N] \quad (7.43)$$

When you take the partial derivative of the free energy with respect to N keeping temperature and volume constant, you get the chemical potential⁶. Therefore,

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T, V} = k_B T [3 \ln \Lambda - \ln V + 1 + \ln N - 1] \quad (7.48)$$

$$= k_B T [\ln \Lambda^3 + \ln(N/V)] \quad (7.49)$$

$$= k_B T \ln(\rho \Lambda^3) \quad (7.50)$$

$$\frac{\mu}{k_B T} = \ln(\rho \Lambda^3) \quad (7.51)$$

where $\rho = N/V$ is the number density, *i.e.* number of particles per unit volume. Thus we get,

$$\eta_i = \frac{\epsilon_i}{k_B T} - \ln(\rho \Lambda^3) \quad (7.52)$$

We have earlier shown that classical limit obtains when $\rho \Lambda^3 \rightarrow 0$. Thus in this limit, $\eta_i \rightarrow \infty$ or $\exp(-\eta_i) \rightarrow 0$. Let $x_i = \exp(-\eta_i)$. Let us express the grand canonical partition function for the three statistics in terms of the small parameter x_i .

$$Q = \prod_i \begin{cases} \exp(x_i) & \text{Maxwell - Boltzmann} \\ \frac{1}{1 - x_i} & \text{Bose - Einstein} \\ 1 + x_i & \text{Fermi - Dirac} \end{cases} \quad (7.53)$$

⁶ In thermodynamics we have

$$F = U - TS \quad (7.44)$$

$$dF = dU - TdS - SdT \quad (7.45)$$

From the first law of thermodynamics we have $dU = TdS - PdV + \mu dN$. Substituting this in the expression for dF above we get,

$$dF = -PdV + \mu dN - SdT \quad (7.46)$$

Therefore,

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T, V} \quad (7.47)$$

In the limit $x_i \rightarrow 0$ we have $\exp(\pm x_i) = 1 \pm x_i$ and $(1 - x_i)^{-1} = 1 + x_i$. Therefore in the limit $x_i \rightarrow 0$, we have

$$\mathcal{Q} = \prod_i \begin{cases} \exp(x_i) & x_i \rightarrow 0 \quad 1 + x_i \text{ Maxwell - Boltzmann} \\ \frac{1}{1 - x_i} & x_i \rightarrow 0 \quad 1 + x_i \text{ Bose - Einstein} \\ 1 + x_i & = 1 + x_i \text{ Fermi - Dirac} \end{cases} \quad (7.54)$$

For all the three statistics, the grand canonical partition function take the same expression. Bosons, Fermions and classical indistinguishable particles behave the same way when $\rho\Lambda^3 \rightarrow 0$.

When do we get $\rho\Lambda^3 \rightarrow 0$?

Note that Λ is inversely proportional to square-root of the temperature.

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

Hence $\Lambda \rightarrow 0$, when $T \rightarrow \infty$. For a fixed temperature (Λ is constant), $\rho\Lambda^3 \rightarrow 0$ when $\rho \rightarrow 0$. For a fixed ρ , when $T \rightarrow \infty$ (the same as $\Lambda \rightarrow 0$), then $\rho\Lambda^3 \rightarrow 0$.

- Classical behaviour obtains at **low densities** and/or **high temperatures**.
- Quantum effects manifest only at low temperatures and/or high densities.

7.9.2 Easier Method : $\lambda \rightarrow 0$

Another simple way to show that the three statistics are identical in the limit of high temperatures and low densities is to recognise (see below) that $\rho\Lambda^3 \rightarrow 0$ implies $\lambda \rightarrow 0$. Here $\lambda = \exp(\beta\mu)$, is the fugacity. Let us show this first.

We have shown that

$$\frac{\mu}{k_B T} = \ln(\rho\Lambda^3) \quad (7.55)$$

Therefore the fugacity is given by

$$\lambda = \exp\left(\frac{\mu}{k_B T}\right) = \exp(\ln[\rho\Lambda^3]) = \rho\Lambda^3 \quad (7.56)$$

Thus $\rho\Lambda^3 \rightarrow 0$ implies $\lambda \rightarrow 0$.

In the limit $\lambda \rightarrow 0$ we have, for Maxwell-Boltzmann statistics,

$$\mathcal{Q}_{MB} = \prod_i \exp[\lambda \exp(-\beta\epsilon_i)] \quad (7.57)$$

$$\stackrel{\lambda \rightarrow 0}{\sim} \prod_i (1 + \lambda \exp(-\beta\epsilon_i)) \quad (7.58)$$

In the limit $\lambda \rightarrow 0$, for Bose-Einstein statistics, we have,

$$\mathcal{Q}_{BE} = \prod_i \frac{1}{1 - \lambda \exp(-\beta \epsilon_i)} \quad (7.59)$$

$$\underset{\lambda \rightarrow 0}{\sim} \prod_i [1 + \lambda \exp(-\beta \epsilon_i)] \quad (7.60)$$

For Fermi-Dirac statistics, we have exactly,

$$\mathcal{Q}_{FD} = \prod_i [1 + \lambda \exp(-\beta \epsilon_i)] \quad (7.61)$$

Thus in the limit of high temperatures and low densities Maxwell Boltzmann statistics and Bose Einstein statistics go over to Fermi - Dirac statistics.

7.9.3 Easiest Method $\hat{\Omega}(n_1, n_2, \dots) = 1$

We could have shown easily that in the limit of high temperature and low density, the three statistics are identical by considering the degeneracy factor

$$\hat{\Omega} = \begin{cases} 1 & \text{Bose - Einstein and Fermi - Dirac statistics} \\ \frac{1}{n_1! n_2! \dots} & \text{Maxwell - Boltzmann statistics} \end{cases} \quad (7.62)$$

When the temperature is high the number of quantum states that become available for occupation is very large; When the density is low the number of particles in the system is low. Thus we have a very few number of particles occupying a very large number of quantum states. In other words the number of quantum states is very large compared to the number of particles.

Hence the number of micro states with $n_i = 0$ or $1 \forall i$ are overwhelmingly large compared to the those with $n_i \geq 2$. In any case, in Fermi-Dirac statistics n_i is always 0 or 1.

In other words, when particles are a few in number (number density is low) and the accessible quantum levels are large in number (temperature is high), then micro states with two or more particles in one or more quantum states are very rare. In other words bunching of particles is very rare at low densities and high temperatures. Almost always every quantum state is either unoccupied or occupied by one particle. Very rarely will you find two or more particles in a single quantum state. Hence the degeneracy factor is unity at high temperatures and/or low densities. Hence all the three statistics are identical in the limit of high temperatures and/or low densities.

7.10 Mean Occupation Number

Let us consider the single particle quantum state k with energy ϵ_k . Let n_k be the number of particles occupying the state k . n_k is called the occupation number. It is a random variable. Here we shall calculate the statistics of the random variable n_k .

Let $\langle n_k \rangle$ denote the average occupation number; the averaging is done over a grand canonical ensemble of micro states. Formally we have for Bosons and Fermions,

$$\langle n_k \rangle = \frac{\left[\prod_{i \neq k} \sum_{n=0}^{\text{all}} x_i^n \right] \sum_{n=0}^{\text{all}} n x_k^n}{\left[\prod_{i \neq k} \sum_{n=0}^{\text{all}} x_i^n \right] \sum_{n=0}^{\text{all}} x_k^n} = \frac{\sum_{n=0}^{\text{all}} n x_k^n}{\sum_{n=0}^{\text{all}} x_k^n} \quad (7.63)$$

7.10.1 Ideal Fermions

For Fermions, $n = 0, 1$. Hence

$$\langle n_k \rangle_{FD} = \frac{x_k}{1 + x_k} = \frac{1}{x_k^{-1} + 1} = \frac{1}{\exp[\beta(\epsilon_k - \mu)] + 1} \quad (7.64)$$

7.10.2 Ideal Bosons

For Bosons $n = 0, 1, 2, \dots, \infty$. In other words, a single particle quantum state can hold any number of particles. In fact, we shall see later, that at low enough temperature all the particles would condense into the lowest energy state, *i.e.* the ground state. We call this Bose-Einstein condensation.

We carry out the summation⁷, in the numerator and and the denominator of the expression for $\langle n_k \rangle$, see above, analytically and get,

$$\langle n_k \rangle_{BE} = \frac{x_k}{(1 - x_k)^2} (1 - x_k) = \frac{x_k}{1 - x_k} = \frac{1}{x_k^{-1} - 1} = \frac{1}{\exp[\beta(\epsilon_k - \mu)] - 1} \quad (7.68)$$

7.10.3 Classical Indistinguishable Ideal Particles

$$\langle n_k \rangle_{MB} = \frac{\left(\prod_{i \neq k} \sum_{n=0}^{\infty} \frac{x_i^n}{n!} \right) \left(\sum_{n=0}^{\infty} n \frac{x_k^n}{n!} \right)}{\left(\prod_{i \neq k} \sum_{n=0}^{\infty} \frac{x_i^n}{n!} \right) \left(\sum_{n=0}^{\infty} \frac{x_k^n}{n!} \right)} = \frac{\sum_{n=0}^{\infty} n \frac{x_k^n}{n!}}{\sum_{n=0}^{\infty} \frac{x_k^n}{n!}} \quad (7.69)$$

⁷ Consider

$$S(x) = 1 + x + x^2 + \dots = \frac{1}{1 - x} \quad (7.65)$$

$$\frac{dS}{dx} = 1 + 2x + 3x^2 + 4x^3 + \dots = \frac{1}{(1 - x)^2} \quad (7.66)$$

$$x \frac{dS}{dx} = x + 2x^2 + 3x^3 + \dots = \frac{x}{(1 - x)^2} \quad (7.67)$$

In the above the summation in the numerator and the denominator are evaluated analytically as follows. We start with the definition,

$$\sum_{n=0}^{\infty} \frac{x^n}{n!} = \exp(x) \quad (7.70)$$

Differentiate both sides of the above equation with respect to x . You get

$$\exp(x) = \sum_{n=0}^{\infty} \frac{nx^{n-1}}{n!} = \frac{1}{x} \sum_{n=0}^{\infty} \frac{nx^n}{n!} = \sum_{n=0}^{\infty} \frac{nx^n}{n!} \quad (7.71)$$

Therefore,

$$\langle n_k \rangle_{MB} = \frac{x_k \exp(x_k)}{\exp(x_k)} = x_k = \exp[-\beta(\epsilon_k - \mu)] = \frac{1}{\exp[\beta(\epsilon_k - \mu)]} \quad (7.72)$$

7.11 Mean Occupation : Some Remarks

We can write for all the three statistics,

$$\langle n_k \rangle = \frac{1}{\exp[\beta(\epsilon_k - \mu)] + a} \text{ where } a = \begin{cases} +1 & \text{Fermi - Dirac} \\ 0 & \text{Maxwell - Boltzmann} \\ -1 & \text{Bose - Einstein} \end{cases} \quad (7.73)$$

Variation of $\langle n_k \rangle$ with energy is shown in the figure, see next page. Note that the x axis is $\frac{\epsilon_k - \mu}{k_B T}$ and the y axis is $\langle n_k \rangle$.

7.11.1 Fermi-Dirac Statistics

We see that for Fermi-Dirac statistics the occupation number never exceeds unity. When $\epsilon_k - \mu$ is negative and $|\epsilon_k - \mu|$ is large the value of $\langle n_k \rangle$ tends to unity. For $\epsilon = \mu$ and $T \neq 0$, we have $\langle n_k \rangle = 1/2$.

It is also clear that at high temperature the chemical potential of a Fermion must be negative, because its behaviour coincides with that of Bosons⁸ and classical indistinguishable particles⁹.

7.11.2 Bose-Einstein Statistics

For Bosons we must have

$$\epsilon_k > \mu \quad \forall k.$$

In particular the lowest value of energy, say ϵ_0 corresponding to the ground state of the macroscopic system, must be greater than μ . Let us take $\epsilon_0 = 0$ without loss of generality. Hence for Bosons μ must be negative. Also μ is a function of

⁸ for Bosons the chemical potential is negative at all temperature, and zero at zero temperature and at temperatures less than a critical temperature called Bose-Einstein condensation temperature.

⁹ for classical indistinguishable particles the chemical potential is negative at high temperature, positive at low temperatures and zero at zero temperature.

temperature. As we lower T the chemical potential increases and at $T = T_{BEC}$, μ becomes zero. T_{BEC} is called the Bose-Einstein condensation temperature. At this temperature the occupancy of the ground state becomes infinitely high. This leads to the phenomenon of Bose-Einstein Condensation .

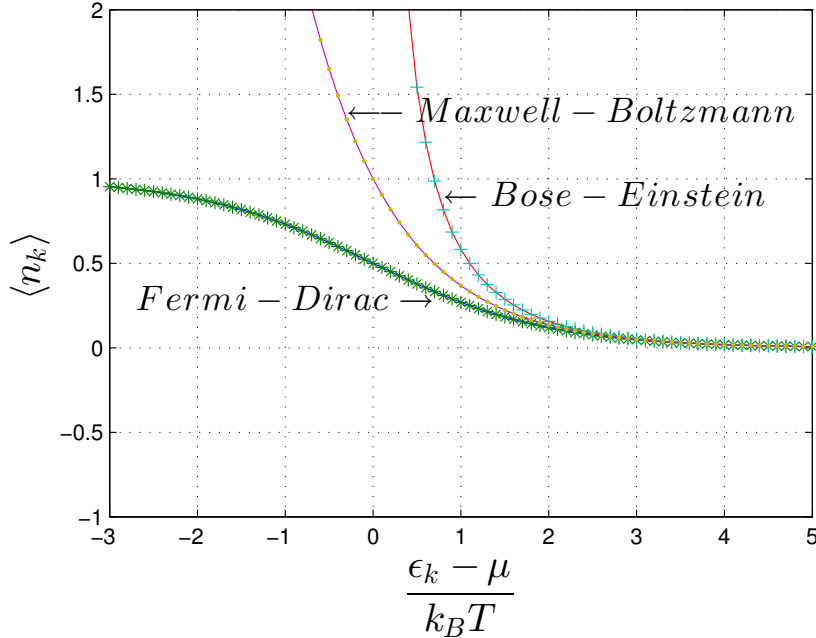


Fig. 7.1. Average occupation number of a quantum state under Bose-Einstein, Fermi-Dirac, and Maxwell-Boltzmann statistics

7.11.3 Maxwell-Boltzmann Statistics

For the indistinguishable classical particles $\langle n_k \rangle$ takes the familiar exponential decay form,

$$\langle n_k \rangle = \exp[-\beta(\epsilon_k - \mu)].$$

7.11.4 At High T and/or Low ρ all Statistics give the same $\langle n_k \rangle$

When

$$\frac{\epsilon_k - \mu}{k_B T} \rightarrow \infty,$$

all the three statistics coincide. We have already seen that at high temperatures classical behaviour obtains. Then, the only way

$$\frac{\epsilon_k - \mu}{k_B T}$$

can become large at high temperature (note in the expression T is in the denominator) is when μ is negative and its magnitude also should increase with increase of temperature.

Thus for all the three statistics, at high temperature, the chemical potential μ is negative and its magnitude must be large.

But then we know

$$\frac{\mu}{k_B T} = \ln(\rho \Lambda^3).$$

This means that $\rho \Lambda^3 \ll 1$ for classical behaviour to emerge¹⁰. This is in complete agreement with our earlier surmise that classical behaviour obtains at low ρ and/or high T . Hence all the approaches are consistent with each other and all the issues fall in place.

7.12 Occupation Number : Distribution and Variance

In the last lecture, I introduced a random variable n_k , which denotes the number of particles in the quantum state k of energy ϵ_k . We call n_k a random variable because it takes values that are, in general, different for different micro states. For Bose-Einstein and Fermi-Dirac statistics, a string of occupation numbers specifies completely a micro state. We found that for Bosons and Fermions, the average value of n_k can be expressed as,

$$\langle n_k \rangle = \frac{\sum_{n=0}^{\text{all}} n x_k^n}{\sum_{n=0}^{\text{all}} x_k^n} \quad (7.74)$$

where, $x_k = \exp[-\beta(\epsilon_k - \mu)]$.

Formally

$$\langle n_k \rangle = \sum_{n=0}^{\text{all}} n P(n) \quad (7.75)$$

In the above $P(n) \equiv P(n_k = n)$ is the probability that the random variable n_k takes a value n . Comparing the above with the first equation, we find

$$P(n) \equiv P(n_k = n) = \frac{1}{\sum_{m=0}^{\text{all}} x_k^m} x_k^n \quad (7.76)$$

where the denominator ensures that the total probability is normalized to unity.

Here, I shall work out explicitly $P(n)$ for Fermi-Dirac, Bose-Einstein, and Maxwell-Boltzmann statistics. We shall calculate the variance of the random variable n_k ; we shall derive the relative fluctuations : the standard deviation divided by the mean, for the three statistics.

¹⁰ Note that $\ln(x) = 0$ for $x = 1$ and is negative for $x < 1$. As x goes from 1 to 0, the quantity $\ln(x)$ goes from 0 to $-\infty$.

7.12.1 Fermi-Dirac Statistics and Binomial Distribution

In Fermi-Dirac statistics the random variable n_k can take only two values : $n = 0$ and $n = 1$. Thus,

$$P(n) = \begin{cases} \frac{1}{1+x_k} & \text{for } n = 0 \\ \frac{x_k}{1+x_k} & \text{for } n = 1 \end{cases} \quad (7.77)$$

We have

$$\langle n_k \rangle = \sum_{n=0}^1 nP(n) = \frac{x_k}{1+x_k},$$

consistent with the result obtained earlier.

For convenience of notation let us denote the mean of the random variable n_k by the symbol ζ . We have,

$$\zeta = \langle n_k \rangle = \frac{x_k}{1+x_k}.$$

We thus have,

$$P(n) = \begin{cases} 1 - \zeta & \text{for } n = 0 \\ \zeta & \text{for } n = 1 \end{cases} \quad (7.78)$$

Thus Fermi-Dirac statistics defines a *quantum coin* with ζ and $1 - \zeta$ as the probabilities of "Heads" ($n = 0$) and "Tails" ($n = 1$) respectively.

Formally,

$$\langle n_k \rangle = \sum_{n=0}^1 nP(n) = \zeta \quad (7.79)$$

$$\langle n_k^2 \rangle = \sum_{n=0}^1 n^2 P(n) = \zeta \quad (7.80)$$

$$\sigma^2 = \langle n_k^2 \rangle - \langle n_k \rangle^2 = \zeta(1 - \zeta) \quad (7.81)$$

The relative fluctuations of the random variable n_k is defined as the standard deviation σ divided by the mean ζ . Let us denote the relative fluctuation by the symbol η . For Fermi-Dirac statistics we have,

$$\eta_{FD} = \frac{\sigma}{\zeta} = \sqrt{\frac{1}{\zeta} - 1} \quad (7.82)$$

7.12.2 Bose-Einstein Statistics and Geometric Distribution

For Bosons,

$$P(n_k = n) = P(n) = x_k^n (1 - x_k) \quad (7.83)$$

from which it follows,

$$\zeta = \sum_{n=0}^{\infty} nP(n) = \frac{x_k}{1-x_k} \quad (7.84)$$

consistent with the result obtained earlier. Inverting the above, we get,

$$x_k = \frac{\zeta}{1+\zeta} \quad (7.85)$$

Then the probability distribution of the random variable n_k can be written in a convenient form

$$P(n) = \frac{\zeta^n}{(1+\zeta)^{n+1}} \quad (7.86)$$

The distribution is geometric, with a constant common ratio $\zeta/(\zeta+1)$. We have come across geometric distribution earlier¹¹.

Calculation of variance is best done by first deriving an expression for the moment generating function given by,

$$\tilde{P}(z) = \sum_{n=0}^{\infty} z^n P(n) \quad (7.87)$$

$$= \frac{1}{1+\zeta} \sum_{n=0}^{\infty} z^n \left(\frac{\zeta}{1+\zeta} \right)^n \quad (7.88)$$

$$= \frac{1}{1+\zeta} \frac{1}{\left(1 - \frac{\zeta z}{1+\zeta}\right)} \quad (7.89)$$

$$= \frac{1}{1+\zeta(1-z)} \quad (7.90)$$

Let us now differentiate $\tilde{P}(z)$ with respect to z and in the resulting expression set $z = 1$. We shall get $\langle n_k \rangle$, see below.

$$\frac{\partial \tilde{P}}{\partial z} = \frac{\zeta}{(1+\zeta(1-z))^2} \quad (7.91)$$

$$\left. \frac{\partial \tilde{P}}{\partial z} \right|_{z=1} = \zeta \quad (7.92)$$

Differentiating twice with respect to z and setting $z = 1$ in the resulting expression shall yield the factorial moment $\langle n_k(n_k - 1) \rangle$, see below.

¹¹ Let me recollect : The simplest problem in which geometric distribution arises is in coin tossing. Take a p -coin. Toss the coin until "H" appears. The number of tosses is a random variable with a geometric distribution $P(n) = q^{n-1}p$. We can write this distribution in terms of $\zeta = \langle n \rangle = 1/p$ and get $P(n) = (\zeta - 1)^{n-1}/\zeta^n$.

$$\frac{\partial^2 P}{\partial z^2} = \frac{2\zeta^2}{[1 + \zeta(1-z)]^3} \quad (7.93)$$

$$\left. \frac{\partial^2 P}{\partial z^2} \right|_{z=1} = \langle n_k(n_k - 1) \rangle = 2\zeta^2 \quad (7.94)$$

$$\langle n_k^2 \rangle = 2\zeta^2 + \zeta \quad (7.95)$$

$$\sigma^2 = \langle n_k^2 \rangle - \langle n_k \rangle^2 = \zeta^2 + \zeta \quad (7.96)$$

$$\eta_{BE} = \frac{\sigma}{\zeta} = \sqrt{\frac{1}{\zeta} + 1} \quad (7.97)$$

For doing the problem, You will need the following tricks.

$$\begin{aligned} S(x) &= \sum_{n=0}^{\infty} x^n = 1 + x + x^2 + x^3 + \dots \\ &= \frac{1}{1-x} \end{aligned} \quad (7.98)$$

$$\begin{aligned} \frac{dS}{dx} &= \sum_{n=1}^{\infty} nx^{n-1} = 1 + 2x + 3x^2 + 4x^3 + \dots \\ &= \frac{1}{(1-x)^2} \end{aligned} \quad (7.99)$$

$$\begin{aligned} x \frac{dS}{dx} &= \sum_{n=1}^{\infty} nx^n = x + 2x^2 + 3x^3 + 4x^4 + \dots \\ &= \frac{x}{(1-x)^2} \end{aligned} \quad (7.100)$$

$$\begin{aligned} \frac{d}{dx} \left(x \frac{dS}{dx} \right) &= \sum_{n=1}^{\infty} n^2 x^{n-1} = 1 + 2^2 x + 3^2 x^2 + 4^2 x^3 + \dots \\ &= \frac{2x}{(1-x)^3} + \frac{1}{(1-x)^2} \end{aligned} \quad (7.101)$$

$$\begin{aligned} x \frac{d}{dx} \left(x \frac{dS}{dx} \right) &= \sum_{n=1}^{\infty} n^2 x^n = x + 2^2 x^2 + 3^2 x^3 + 4^2 x^4 + \dots \\ &= \frac{2x^2}{(1-x)^3} + \frac{x}{(1-x)^2} \end{aligned} \quad (7.102)$$

You can employ the above trick to derive power series for $\ln(1 \pm x)$, see below.

$$\int \frac{dx}{1-x} = -\ln(1-x) = x + \frac{x^2}{2} + \frac{x^3}{3} + \frac{x^4}{4} \dots \quad (7.103)$$

7.12.3 Maxwell-Boltzmann Statistics and Poisson Distribution

For Maxwell-Boltzmann statistics we have,

$$\langle n_k \rangle = x_k \quad (7.104)$$

$$P(n_k = n) \equiv P(n) = \frac{x_k^n}{n!} \frac{1}{\exp(x_k)} \quad (7.105)$$

$$= \frac{\zeta^n}{n!} \exp(-\zeta) \quad (7.106)$$

The random variable n_k has Poisson distribution. The variance equals the mean. Thus the relative standard deviation is given by

$$\eta_{MB} = \frac{\sigma}{\zeta} = \frac{1}{\sqrt{\zeta}} \quad (7.107)$$

We can now write the relative fluctuations for the three statistics in one single formula as,

$$\eta = \sqrt{\frac{1}{\zeta} - a} \quad \text{with } a = \begin{cases} +1 & \text{Fermi - Dirac Statistics} \\ 0 & \text{Maxwell - Boltzmann Statistics} \\ -1 & \text{Bose - Einstein Statistics} \end{cases} \quad (7.108)$$

Let us look at the ratio,

$$r = \frac{P(n)}{P(n-1)}$$

For the Maxwell-Boltzmann statistics, $r = \zeta/n$. The ratio r is inversely proportional to n . This is the *normal* behaviour; inverse dependence of r on n is what we should expect.

On the other hand, for Bose-Einstein statistics, the ratio is given by

$$r = \frac{P(n)}{P(n-1)} = \frac{\zeta}{\zeta + 1}$$

r is independent of n . This means, a new particle will get into any of the quantum states, with equal probability irrespective of how abundantly or how sparsely that particular quantum state is already populated. An *empty* quantum state has the same probability of acquiring an extra particle as an *abundantly* populated quantum state.

Thus, compared to classical particles obeying Maxwell-Boltzmann statistics, Bosons exhibit a tendency to *bunch* together. By nature, Bosons like to be together. Note that this "bunching-tendency" is not due to interaction between Bosons. We are considering ideal Bosons. This bunching is purely a quantum mechanical effect; it arises due to symmetry property of the wave function.

For Fermions, the situation is quite the opposite. There is what we may call an aversion to bunching; call it anti-bunching if you like. No Fermion would like to have another Fermion in its quantum state.

DRAFT

8. Bose-Einstein Condensation

8.1 Introduction

For bosons we found that the grand canonical partition function is given by,

$$\mathcal{Q}(T, V, \mu) = \prod_i \frac{1}{1 - \exp[-\beta(\epsilon_i - \mu)]} \quad (8.1)$$

The correspondence with thermodynamics is established by the expression for grand potential denoted by the symbol $\mathcal{G}(T, V, \mu)$. We have,

$$\begin{aligned} \mathcal{G}(T, V, \mu) &= -k_B T \ln \mathcal{Q}(T, V, \mu) \\ &= k_B T \sum_i \ln [1 - \exp \{-\beta(\epsilon_i - \mu)\}] \end{aligned} \quad (8.2)$$

Recall, from thermodynamics, that \mathcal{G} is obtained by Legendre transform of $U(S, V, N) : S \rightarrow T; N \rightarrow \mu; \text{ and } U \rightarrow \mathcal{G}$.

$$\mathcal{G}(T, V, \mu) = U - TS - \mu N; \quad T = \left(\frac{\partial U}{\partial S} \right)_{V, N}; \quad \mu = \left(\frac{\partial U}{\partial N} \right)_{S, V} \quad (8.3)$$

From the above, we get,

$$d\mathcal{G} = -PdV - SdT - Nd\mu \quad (8.4)$$

It follows,

$$P = - \left(\frac{\partial \mathcal{G}}{\partial V} \right)_{T, \mu}; \quad S = - \left(\frac{\partial \mathcal{G}}{\partial T} \right)_{V, \mu}; \quad N = - \left(\frac{\partial \mathcal{G}}{\partial \mu} \right)_{T, \mu}.$$

If we have an open system of bosons at temperature T and chemical potential μ , in a volume V , then the above formulae help us calculate the pressure, entropy and number of bosons in the system. In fact we have calculated the fluctuations in the number of particles in the open system and related it to isothermal compressibility - an experimentally measurable property.

8.2 $\langle N \rangle = \sum_k \langle n_k \rangle$

For bosons, we found that the average occupancy of a (single-particle) quantum state k , is given by,

$$\langle n_k \rangle = \frac{\lambda \exp(-\beta \epsilon_k)}{1 - \lambda \exp(-\beta \epsilon_k)} \quad (8.5)$$

where λ is fugacity. We have

$$\lambda = \exp(\beta \mu). \quad (8.6)$$

In the above μ is the chemical potential and equals the energy change due to addition of a single particle under constant entropy and volume :

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V}. \quad (8.7)$$

The average number of particles is given by,

$$\langle N \rangle = \sum_k \langle n_k \rangle = \sum_k \frac{\lambda \exp(-\beta \epsilon_k)}{1 - \lambda \exp(-\beta \epsilon_k)} \quad (8.8)$$

We would like to study Bosonic system with a fixed number of bosons at various temperatures *i.e.* a closed system of bosons described by canonical ensemble. However we would like to employ grand canonical ensemble formalism in our study.

In grand canonical ensemble formalism we can vary T and μ independently by choosing appropriate heat bath and particle bath. If T is changed at a fixed value of μ the average number of particles in the system changes.

However if we want to keep N constant, we lose control over μ . When we change the temperature, the chemical potential should change in such a way that the average number of particles remains at the value chosen by us. In other words in a closed system, μ is a function of temperature.

In what follows we shall study a closed system of ideal bosons employing the grand canonical ensemble formalism in which the chemical potential depends on temperature; the dependence is such that the average number of bosons in the system remains the same at all temperatures

8.3 Summation to Integration

$$\sum_k (\cdot) \rightarrow \int d\epsilon (\cdot) g(\epsilon)$$

Let us now convert the sum over quantum states to an integral over energy. To this end we need an expression for the number of quantum states in infinitesimal interval $d\epsilon$ around ϵ . Let us denote this quantity by $g(\epsilon)d\epsilon$. We call $g(\epsilon)$ the density of (energy) states. Thus we have,

$$N = \int_0^\infty \frac{\lambda \exp(-\beta \epsilon)}{1 - \lambda \exp(-\beta \epsilon)} g(\epsilon) d\epsilon \quad (8.9)$$

We need an expression for the density of states. We have done this exercise earlier. In fact we have carried out classical counting and quantum counting and found both lead to the same result. The density of states is given by,

$$g(\epsilon) = V 2\pi \left(\frac{2m}{h^2} \right)^{3/2} \epsilon^{1/2}. \quad (8.10)$$

We then have,

$$N = V 2\pi \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty \frac{\lambda \exp(-\beta\epsilon)}{1 - \lambda \exp(-\beta\epsilon)} \epsilon^{1/2} d\epsilon. \quad (8.11)$$

We note that $0 \leq \lambda < 1$. This suggests that the integrand in the above can be expanded in powers of λ . To this end we write

$$\frac{1}{1 - \lambda \exp(-\beta\epsilon)} = \sum_{k=0}^{\infty} \lambda^k \exp(-k\beta\epsilon). \quad (8.12)$$

This gives us

$$\frac{\lambda \exp(-\beta\epsilon)}{1 - \lambda \exp(-\beta\epsilon)} = \sum_{k=0}^{\infty} \lambda^{k+1} \exp[-\beta(k+1)\epsilon] = \sum_{k=1}^{\infty} \lambda^k \exp[-\beta k\epsilon]. \quad (8.13)$$

Substituting the above in the integral we get,

$$\begin{aligned} N &= V 2\pi \left(\frac{2m}{h^2}\right)^{3/2} \sum_{k=1}^{\infty} \lambda^k \int_0^\infty \exp(-k\beta\epsilon) \epsilon^{1/2} d\epsilon, \\ &= V 2\pi \left(\frac{2m}{h^2}\right)^{3/2} \sum_{k=1}^{\infty} \lambda^k \int_0^\infty \frac{\exp(-k\beta\epsilon) (k\beta\epsilon)^{1/2} d(k\beta\epsilon)}{\beta^{3/2} k^{3/2}}, \\ &= V 2\pi \left(\frac{2mk_B T}{h^2}\right)^{3/2} \sum_{k=1}^{\infty} \frac{\lambda^k}{k^{3/2}} \int_0^\infty \exp(-x) x^{1/2} dx, \\ &= V 2\pi \left(\frac{2mk_B T}{h^2}\right)^{3/2} \sum_{k=1}^{\infty} \frac{\lambda^k}{k^{3/2}} \Gamma(3/2), \\ &= V 2\pi \left(\frac{2mk_B T}{h^2}\right)^{3/2} \frac{1}{2} \Gamma(1/2) \sum_{k=1}^{\infty} \frac{\lambda^k}{k^{3/2}}, \\ &= V \pi \left(\frac{2mk_B T}{h^2}\right)^{3/2} \sqrt{\pi} \sum_{k=1}^{\infty} \frac{\lambda^k}{k^{3/2}}, \\ &= V \left(\frac{2\pi mk_B T}{h^2}\right)^{3/2} \sum_{k=1}^{\infty} \frac{\lambda^k}{k^{3/2}}. \end{aligned} \quad (8.14)$$

We have earlier defined a thermal wave length denoted by the symbol Λ . This is the de Broglie wave length associated with a particle having thermal energy of the order of $k_B T$. It is also called quantum wavelength. It is given by, see earlier notes,

$$\Lambda = \frac{h}{\sqrt{2\pi mk_B T}}. \quad (8.15)$$

The sum over k , in the expression for N given by Eq. (8.14) is usually denoted by the symbol $g_{3/2}(\lambda)$:

$$g_{3/2}(\lambda) = \sum_{k=1}^{\infty} \frac{\lambda^k}{k^{3/2}} = \lambda + \frac{\lambda^2}{2\sqrt{2}} + \frac{\lambda^3}{3\sqrt{3}} + \dots \quad (8.16)$$

Thus we get $N = \frac{V}{\Lambda^3} g_{3/2}(\lambda)$ We can write it as,

$$\frac{N\Lambda^3}{V} = \rho\Lambda^3 = g_{3/2}(\lambda). \quad (8.17)$$

It is easily verified, see below, that at high temperature we get results consistent with Maxwell Boltzmann statistics :

The fugacity λ is small at high temperature. For small λ we can replace $g_{3/2}(\lambda)$ by λ . We get $N = \lambda V/\Lambda^3$. This result is consistent with Maxwell-Boltzmann statistics, as shown below.

For Maxwell-Boltzmann statistics, $\langle n_k \rangle = \lambda \exp(-\beta\epsilon_k)$. Therefore,

$$\begin{aligned} N &= \sum_k \langle n_k \rangle \\ &= \lambda \sum_k \exp(-\beta\epsilon_k) \\ &= \lambda 2\pi V \left(\frac{2m}{h^2} \right)^{3/2} \int_0^\infty d\epsilon \epsilon^{1/2} \exp(-\beta\epsilon) \\ &= \lambda 2\pi V \left(\frac{2m}{h^2} \right)^{3/2} \int_0^\infty \frac{(\beta\epsilon)^{1/2} \exp(-\beta\epsilon) d(\beta\epsilon)}{\beta^{3/2}} \\ &= \lambda 2\pi V \left(\frac{2mk_B T}{h^2} \right)^{3/2} \Gamma(3/2) \\ &= \lambda 2\pi V \left(\frac{2mk_B T}{h^2} \right)^{3/2} \frac{1}{2} \Gamma(1/2) \\ &= \lambda \pi V \left(\frac{2mk_B T}{h^2} \right)^{3/2} \sqrt{\pi} \\ &= \lambda V \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \\ &= \frac{V}{\Lambda^3} \lambda \end{aligned} \quad (8.18)$$

8.4 Graphical Inversion and Fugacity

Let us consider a system of ideal bosons confined to a volume V at temperature T . To ensure that the number of bosons is at a fixed value N , we must keep the system at a value of fugacity such that the resulting grand canonical ensemble average of N equals the chosen value of N . What is the value of λ that would ensure this ? To answer this question we proceed as follows.

First we plot the so-called Bose function : $g_{3/2}(\lambda)$ versus λ , see Fig. 8.1.

For given values of N , V T we can find the value of fugacity by graphical inversion :

- Draw a line parallel to the x axis at $y = NA^3/V$ and
- read off the value of λ at which the line cuts the curve $g_{3/2}(\lambda)$.

Once we get the fugacity, we can determine all other thermodynamic properties of the open system employing the formalism of grand canonical ensemble.

So far so good.

But then we realise that the above graphical inversion scheme does not permit evaluation of the fugacity of a system with NA^3/V greater than 2.612.

This is absurd.

There must be something wrong with what we have done.

8.5 Treatment of the Singular Behaviour

We realise that when NA^3/V approaches 2.612, the fugacity λ approaches unity; the chemical potential μ approaches zero¹. We have already seen that at $\mu = 0$ the occupancy of the ground state diverges. The singular behaviour of the ground state occupancy was completely lost when we replaced the sum over quantum states by an integral over energy : the weighting function is the density of states, given by, $g(\epsilon) \sim \epsilon^{1/2}$. The density of states vanishes at zero energy. Hence we must take care of the singular behaviour separately.

We have,

$$N = \sum_{k \geq 0} \frac{\lambda \exp(-\beta \epsilon_k)}{1 - \lambda \exp(-\beta \epsilon_k)} = \frac{\lambda}{1 - \lambda} + \sum_{k \geq 1} \frac{\lambda \exp(-\beta \epsilon_k)}{1 - \lambda \exp(-\beta \epsilon_k)}. \quad (8.19)$$

In the above, we have separated the ground state occupancy and the occupancy of all the excited states. Let N_0 denote the ground state occupancy. It is given by the first term,

$$N_0 = \frac{\lambda}{1 - \lambda} \quad (8.20)$$

The occupancy of all the excited states is given by the second term, where the sum is taken only over the indices k representing the excited states. Let N_e denote the occupancy of excited states. It is given by,

$$N_e = \sum_k \frac{\lambda \exp(-\beta \epsilon_k)}{1 - \lambda \exp(-\beta \epsilon_k)} \quad (8.21)$$

In the above, the sum over k can be replaced by an integral over energy. In the integral over energy, we can still keep the lower limit of integration as zero, since the density of states giving weight factors for occupancy of states is zero at zero energy. Accordingly we write

$$N = N_0 + N_e \quad (8.22)$$

$$= \frac{\lambda}{1 - \lambda} + \frac{V}{A^3} g_{3/2}(\lambda) \quad (8.23)$$

We thus have,

¹ The chemical potential approaches the energy of the ground state. With out loss of generality, we can set the ground state at zero energy; *i.e.* $\epsilon_0 = 0$.

$$\frac{N\Lambda^3}{V} = \frac{\Lambda^3}{V} \frac{\lambda}{1-\lambda} + g_{3/2}(\lambda) \quad (8.24)$$

Let us define the number of density - number of particles per unit volume, denoted by the symbol ρ . It is given by

$$\rho = \frac{N}{V} \quad (8.25)$$

The function $\lambda/(1-\lambda)$ diverges at $\lambda = 1$, as you can see from Figure (8.2). Hence the relevant curve for carrying out graphical inversion should be the one that depicts the sum of the singular part (that takes care of the occupancy of the ground state) and the regular part (that takes care of the occupancy of the excited states). For a value of $\Lambda^3/V = .05$ we have plotted both the curves and their sum in Figure (8.3). Thus for any value of $\rho\Lambda^3$ we can now determine the fugacity by graphical inversion.

We carry out such an exercise and obtain the values of λ for various values of $\rho\Lambda^3$ and Fig. (8.4) depicts the results. It is clear from Fig. (8.4) that when $\rho\Lambda^3 > 2.612$, the fugacity λ is close unity.

How close can the fugacity λ get to unity ?

Let us postulate²

$$\lambda = 1 - \frac{a}{N}.$$

where a is a number. To determine a we proceed as follows.

We have,

$$\frac{\lambda}{1-\lambda} = \frac{N}{a} - 1 \quad (8.26)$$

$$\approx \frac{N}{a} \text{ if } N \gg a \quad (8.27)$$

We start with,

$$\rho\Lambda^3 = \frac{\Lambda^3}{V} \frac{\lambda}{1-\lambda} + g_{3/2}(\lambda) \quad (8.28)$$

Substitute $\lambda = 1 - a/N$ in the above and get³,

$$\rho\Lambda^3 = \frac{\rho\Lambda^3}{a} + g_{3/2}(1) \quad (8.29)$$

Thus we get,

$$a = \frac{\rho\Lambda^3}{\rho\Lambda^3 - g_{3/2}(1)} \quad (8.30)$$

² We have reasons to postulate $\lambda = 1 - \frac{a}{N}$. This is related to the mechanism underlying Bose-Einstein condensation; we shall discuss the details later. In fact, following Donald A McQuarrie, *Statistical Mechanics*, Harper and Row (1976)p.173 we can make a postulate $\lambda = 1 - \frac{a}{V}$. This should also lead to the same conclusions.

³ $g_{3/2}(1 - a/N) \approx g_{3/2}(1)$,

Thus λ is less than unity and can be very close to unity; the value of $1 - \lambda$ can be as small as the inverse of the total number of particles in the system. Precisely $1 - \lambda$ can be as small as a/N .

The point $\rho\Lambda^3 = g_{3/2}(1) = 2.612$ is a special point indeed. What is the physical significance of this point? To answer this question, consider the quantity $\rho\Lambda^3$ as a function of temperature with ρ kept at a constant value. The temperature dependence of this quantity is shown below.

$$\rho\Lambda^3 = \rho \left(\frac{h}{\sqrt{2\pi m k_B T}} \right)^3 \quad (8.31)$$

At high temperature for which $\rho\Lambda^3 < g_{3/2}(1) = 2.612$, we can determine the value of λ from the equation $g_{3/2}(\lambda) = \rho\Lambda^3$ by graphical or numerical inversion.

At low temperatures for which $\rho\Lambda^3 > 2.612$, we have $\lambda = 1 - a/N$ where

$$a = \frac{\rho\Lambda^3}{\rho\Lambda^3 - g_{3/2}(1)} \quad (8.32)$$

The quantity $\lambda/(1 - \lambda)$ is the number of particles in the ground state. At temperatures for which $\rho\Lambda^3 > 2.612$, we have,

$$N_0 = \frac{\lambda}{1 - \lambda} \quad (8.33)$$

$$= \frac{N}{a} \quad (8.34)$$

$$\frac{N_0}{N} = \frac{1}{a} \quad (8.35)$$

$$= 1 - \frac{1}{\rho\Lambda^3} g_{3/2}(1) \quad (8.36)$$

We can write the above in a more suggestive form by defining a temperature T_{BEC} by

$$\rho\Lambda_{\text{BEC}}^3 = g_{3/2}(1) \quad (8.37)$$

Therefore,

$$\frac{N_0}{N} = \frac{1}{a} = 1 - \frac{\rho\Lambda_{\text{BEC}}^3}{\rho\Lambda^3} = 1 - \left(\frac{\Lambda_{\text{BEC}}}{\Lambda} \right)^3 = 1 - \left(\frac{\sqrt{T}}{\sqrt{T_{\text{BEC}}}} \right)^3 \quad (8.38)$$

$$= 1 - \left(\frac{T}{T_{\text{BEC}}} \right)^{3/2} \quad \text{for } T < T_{\text{BEC}} \quad (8.39)$$

We have depicted the behaviour of the fractional number of particles in the ground state as a function of temperature in Figure (8.5).

8.6 Bose-Einstein Condensation Temperature

Thus we can define the temperature at which Bose-Einstein condensation takes place as,

$$\frac{N}{V} \left(\frac{h}{\sqrt{2\pi m k_B T}} \right)^3 = 2.612 \quad (8.40)$$

$$k_B T_{BEC} = \frac{h^2}{2\pi m} \left(\frac{N}{2.612 V} \right)^{2/3} \quad (8.41)$$

At $T = T_{BEC}$, Bose-Einstein condensation sets in and the ground state occupancy becomes anomalously larger and larger as temperature decreases further.

8.7 Grand Potential for bosons

The grand potential for bosons is given by

$$\mathcal{G}(T, V, \mu) = -k_B T \ln \mathcal{Q}(T, V, \mu) = k_B T \sum_k \ln[1 - \lambda \exp(-\beta \epsilon_k)] \quad (8.42)$$

Now we shall be careful and separate the singular part and regular part to get,

$$\mathcal{G} = k_B T \ln(1 - \lambda) + k_B T \sum_k \ln[1 - \lambda \exp(-\beta \epsilon_k)] \quad (8.43)$$

In the above, convert the sum over k by an integral over $d\epsilon$ by the prescription below,

$$\sum_k (\cdot) \longrightarrow V 2\pi \left(\frac{2m}{h^2} \right)^{3/2} \int_0^\infty (\cdot) \epsilon^{1/2} d\epsilon, \quad (8.44)$$

We get,

$$\mathcal{G} = k_B T \ln(1 - \lambda) - k_B T V 2\pi \left(\frac{2m}{h^2} \right)^{3/2} \int_0^\infty d\epsilon \ln(1 - \lambda \exp(-\beta \epsilon)) \epsilon^{1/2} \quad (8.45)$$

We have

$$\ln[1 - \lambda \exp(-\beta \epsilon)] = - \sum_{k=1}^{\infty} \lambda^k \exp(-k\beta \epsilon) \quad (8.46)$$

Then we have,

$$\begin{aligned}
\mathcal{G} &= k_B T \ln(1 - \lambda) \\
&\quad - k_B T V 2\pi \left(\frac{2m}{h^2}\right)^{3/2} \sum_{k=1}^{\infty} \lambda^k \int_0^{\infty} d\epsilon \epsilon^{1/2} \exp(-k\beta\epsilon) \\
&= k_B T \ln(1 - \lambda) - \\
&\quad k_B T V 2\pi \left(\frac{2m}{h^2}\right)^{3/2} \sum_{k=1}^{\infty} \lambda^k \int_0^{\infty} \frac{(k\beta\epsilon)^{1/2} \exp(-k\beta\epsilon)}{k^{3/2} \beta^{3/2}} d(k\beta\epsilon) \\
&= k_B T \ln(1 - \lambda) - k_B T V 2\pi \left(\frac{2mk_B T}{h^2}\right)^{3/2} \Gamma(3/2) \sum_{k=1}^{\infty} \frac{\lambda^k}{k^{3/2}} \\
&= k_B T \ln(1 - \lambda) - k_B T V \left(\frac{2\pi mk_B T}{h^2}\right)^{3/2} \sum_{k=1}^{\infty} \frac{\lambda^k}{k^{3/2}} \\
&= k_B T \ln(1 - \lambda) - k_B T \frac{V}{\Lambda^3} g_{3/2}(\lambda) \tag{8.47}
\end{aligned}$$

Thus we have,

$$\mathcal{G}(T, V, \lambda) = k_B T \ln(1 - \lambda) - \frac{V}{\Lambda^3} k_B T g_{3/2}(\lambda) \tag{8.48}$$

8.8 Energy of Bosonic System

In an earlier class, I have derived an expression for the average occupancy of a single-particle-quantum-state; it is given by

$$\langle n_i \rangle = \frac{\lambda \exp(-\beta\epsilon_i)}{1 - \lambda \exp(-\beta\epsilon_i)} \tag{8.49}$$

This immediately suggests that the (average) energy of the system is given by

$$U = \langle E \rangle = \sum_i \langle n_i \rangle \epsilon_i = \sum_i \frac{\epsilon_i \lambda \exp(-\beta\epsilon_i)}{1 - \lambda \exp(-\beta\epsilon_i)} \tag{8.50}$$

We can also derive⁴ the above relation employing Grand canonical formalism.

⁴ An open system is described by a grand canonical partition function. It is formally given by,

$$\mathcal{Q}(\beta, V, \mu) = \sum_i \exp[-\beta(E_i - \mu N_i)] \tag{8.51}$$

In the above E_i is the energy of the open system when in micro state i ; N_i is the number of particles in the open system when in micro state i . Let $\gamma = \beta\mu$.

Let us now go to continuum limit by converting the sum over micro states by an integral over energy and get,

$$U = \frac{3}{2} V k_B T \frac{1}{A^3} g_{5/2}(\lambda) \quad (8.56)$$

8.8.1 $T > T_{\text{BEC}}$

Let us now investigate the energy of the system at $T > T_{\text{BEC}}$. When temperature is high, the number of bosons in the ground state is negligibly small. Hence the total energy of the system is the same as the one given by Eq. (8.56).

We can write Eq. (8.56) in a more suggestive form, see below. We have,

$$\begin{aligned} \rho A^3 &= g_{3/2}(\lambda) \\ \frac{N A^3}{V} &= g_{3/2}(\lambda) \\ V &= \frac{N A^3}{g_{3/2}(\lambda)} \end{aligned} \quad (8.57)$$

Substituting the above expression for V in Eq. (8.56) we get

$$U = \frac{3 N k_B T}{2} \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} \quad (8.58)$$

8.8.2 $T \leq T_{\text{BEC}}$

For temperatures less than T_{BEC} , the ground state gets populated anomalously. The bosons in the ground state do not contribute to the energy. For $T \leq T_{\text{BEC}}$, we have $\mu = 0$. This means $\lambda = 1$ ⁵. Substituting $\lambda = 1$ in Eq. (8.56) we get,

$$U = \frac{3}{2} V k_B T \frac{1}{A^3} \zeta(5/2) \quad (8.59)$$

Then we get,

$$\mathcal{Q}(\beta, V, \mu) = \sum_i \exp(-\beta E_i) \exp(+\gamma N_i) \quad (8.52)$$

We differentiate \mathcal{Q} with respect to the variable β , keeping γ constant. (Note that T and μ are independent in an open system described by grand canonical ensemble). We get

$$\frac{\partial \mathcal{Q}}{\partial \beta} = - \sum_i \epsilon_i \exp[-\beta \epsilon_i + \gamma N_i] \quad (8.53)$$

$$-\frac{1}{\mathcal{Q}} \frac{\partial \mathcal{Q}}{\partial \beta} = -\frac{\partial \ln \mathcal{Q}}{\partial \beta} = \langle E \rangle = U \quad (8.54)$$

For bosons, we have,

$$\mathcal{Q} = \prod_i \frac{1}{1 - \lambda \exp(-\beta \epsilon_i)} \ln \mathcal{Q} = - \sum_i \ln[1 - \lambda \exp(-\beta \epsilon_i)] U = \sum_i \frac{\epsilon_i \lambda \exp(-\beta \epsilon_i)}{1 - \lambda \exp(-\beta \epsilon_i)} \quad (8.55)$$

⁵ we have postulated that $\lambda = 1 - \mathcal{O}(1/N)$ for $T \leq T_{\text{BEC}}$.

We also have,

$$V = \frac{N(\Lambda_{\text{BEC}})^3}{\zeta(3/2)} \quad (8.60)$$

Hence for $T < T_{\text{BEC}}$, we have

$$\begin{aligned} U &= \frac{3}{2} N k_B T \frac{(\Lambda_{\text{BEC}})^3}{\Lambda^3} \frac{\zeta(5/2)}{\zeta(3/2)} \\ &= \frac{3}{2} N k_B T \frac{\zeta(5/2)}{\zeta(3/2)} \left(\frac{T}{T_{\text{BEC}}} \right)^{3/2} \end{aligned} \quad (8.61)$$

Thus we have,

$$U = \begin{cases} \left[\frac{3}{2} N k_B T \right] \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} & \text{for } T > T_{\text{BEC}} \\ \left[\frac{3}{2} N k_B T \right] \frac{g_{5/2}(1)}{g_{3/2}(1)} \left(\frac{T}{T_{\text{BEC}}} \right)^{3/2} & \text{for } T < T_{\text{BEC}} \end{cases} \quad (8.62)$$

8.9 Specific Heat Capacity of bosons

8.9.1 $\frac{C_V}{Nk_B}$ for $T > T_{\text{BEC}}$

Let us consider first the case with $T > T_{\text{BEC}}$. We have

$$\frac{U}{Nk_B} = \frac{3}{2} T \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} \quad (8.63)$$

$$\frac{1}{Nk_B} \frac{\partial U}{\partial T} = \frac{C_V}{Nk_B} = \frac{\partial}{\partial T} \left[\frac{3T}{2} \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} \right] \quad (8.64)$$

To work out the derivative in the above, we need the following :

First Relation : $\frac{\partial}{\partial T} [g_{3/2}(\lambda)] = -\frac{3}{2T} g_{3/2}(\lambda).$

Proof :

We start with $\rho\Lambda^3 = g_{3/2}(\lambda)$. Therefore,

$$\frac{\partial}{\partial T}[g_{3/2}(\lambda)] = 3 \rho \Lambda^2 \frac{\partial \Lambda}{\partial T} = 3 \rho \Lambda^3 \frac{\partial}{\partial T} \left(\frac{h}{\sqrt{2\pi m k_B T}} \right) \quad (8.65)$$

$$= -\frac{3}{2} \rho \Lambda^2 \frac{h}{\sqrt{2\pi m k_B}} \frac{1}{T^{3/2}}$$

$$= -\frac{3}{2T} \rho \Lambda^2 \frac{h}{\sqrt{2\pi m k_B T}}$$

$$= -\frac{3}{2T} \rho \Lambda^3 = -\frac{3}{2T} g_{3/2}(\lambda) \quad (8.66)$$

—————**Q.E.D**

Second Relation : $\frac{\partial}{\partial \lambda}[g_{n/2}(\lambda)] = \frac{1}{\lambda} g_{(n/2)-1}(\lambda).$

Proof :

We have by definition, $g_{n/2}(\lambda) = \sum_{k=1}^{\infty} \frac{\lambda^k}{k^{n/2}}$. Therefore,

$$\begin{aligned} \frac{\partial}{\partial \lambda}[g_{n/2}(\lambda)] &= \frac{\partial}{\partial \lambda} \left[\sum_{k=1}^{\infty} \frac{\lambda^k}{k^{n/2}} \right] = \sum_{k=1}^{\infty} \frac{k \lambda^{k-1}}{k^{n/2}} = \frac{1}{\lambda} \sum_{k=1}^{\infty} \frac{\lambda^k}{k^{(n/2)-1}} \\ &= \frac{1}{\lambda} g_{(n/2)-1}(\lambda) \end{aligned} \quad (8.67)$$

— **Q.E.D**

8.9.2 Third Relation : $\frac{1}{\lambda} \frac{d\lambda}{dT} = -\frac{3}{2T} \frac{g_{3/2}(\lambda)}{g_{1/2}(\lambda)}$

Proof :

We proceed as follows :

$$\frac{\partial}{\partial T}[g_{3/2}(\lambda)] = \frac{\partial}{\partial \lambda}[g_{3/2}(\lambda)] \left[\frac{d\lambda}{dT} \right] : -\frac{3}{2T} g_{3/2}(\lambda) = \frac{1}{\lambda} g_{1/2}(\lambda) \frac{d\lambda}{dT} \quad (8.68)$$

From the above we get, $\frac{1}{\lambda} \frac{d\lambda}{dT} = -\frac{3}{2T} \frac{g_{3/2}(\lambda)}{g_{1/2}(\lambda)}$ —**Q.E.D**

We have,

$$\begin{aligned}
\frac{C_V}{Nk_B} &= \frac{\partial}{\partial T} \left[\frac{3T}{2} \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} \right] \\
&= \frac{3}{2} \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} + \frac{3T}{2} \frac{\partial}{\partial T} \left[\frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} \right] \\
&= \frac{3}{2} \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} - \frac{3T}{2} \left[\frac{g_{5/2}(\lambda)}{g_{3/2}^2(\lambda)} \frac{\partial g_{3/2}(\lambda)}{\partial T} - \frac{1}{g_{3/2}(\lambda)} \frac{\partial g_{5/2}(\lambda)}{\partial \lambda} \frac{d\lambda}{dT} \right] \\
&= \frac{3}{2} \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} - \frac{3T}{2} \left[\frac{g_{5/2}(\lambda)}{g_{3/2}^2(\lambda)} \left\{ -\frac{3}{2T} g_{3/2}(\lambda) \right\} - \frac{1}{g_{3/2}(\lambda)} \left\{ \frac{1}{\lambda} g_{3/2}(\lambda) \right\} \frac{d\lambda}{dT} \right] \\
&= \frac{3}{2} \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} - \frac{3T}{2} \left[\frac{g_{5/2}(\lambda)}{g_{3/2}^2(\lambda)} \left\{ -\frac{3}{2T} g_{3/2}(\lambda) \right\} - \frac{1}{\lambda} \frac{d\lambda}{dT} \right] \\
&= \frac{3}{2} \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} - \frac{3T}{2} \left[\frac{g_{5/2}(\lambda)}{g_{3/2}^2(\lambda)} \left\{ -\frac{3}{2T} g_{3/2}(\lambda) \right\} + \frac{3}{2T} \frac{g_{3/2}(\lambda)}{g_{1/2}(\lambda)} \right] \\
&= \frac{3}{2} \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} + \frac{9}{4} \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} - \frac{9}{4} \frac{g_{3/2}(\lambda)}{g_{1/2}(\lambda)} \\
&= \frac{15}{4} \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} - \frac{9}{4} \frac{g_{3/2}(\lambda)}{g_{1/2}(\lambda)} \tag{8.69}
\end{aligned}$$

8.9.3 $\frac{C_V}{Nk_B}$ for $T < T_{\text{BEC}}$

Now, let us consider the case with $T < T_{\text{BEC}}$. We have,

$$\frac{U}{Nk_B} = \frac{3}{2} T \frac{g_{5/2}(1)}{g_{3/2}(1)} \left(\frac{T}{T_{\text{BEC}}} \right)^{3/2} \tag{8.70}$$

$$\frac{1}{Nk_B} C_V = \frac{3}{2} \frac{g_{5/2}(1)}{g_{3/2}(1)} \frac{5}{2} \left(\frac{T}{T_{\text{BEC}}} \right)^{3/2} \tag{8.71}$$

Thus we have,

$$\frac{1}{Nk_B} C_V = \begin{cases} \frac{15}{4} \frac{g_{5/2}(\lambda)}{g_{3/2}(\lambda)} - \frac{9}{4} \frac{g_{3/2}(\lambda)}{g_{1/2}(\lambda)} & \text{for } T > T_{\text{BEC}} \\ \frac{15}{4} \frac{g_{5/2}(1)}{g_{3/2}(1)} \left(\frac{T}{T_{\text{BEC}}} \right)^{3/2} & \text{for } T < T_{\text{BEC}} \end{cases} \tag{8.72}$$

The specific heat is plotted against temperature in Figure (8.6). The cusp in the heat capacity at $T = T_{\text{BEC}}$ is the signature of Bose-Einstein condensation. Asymptotically $T \rightarrow \infty$, the heat capacity tends to the classical value consistent with equi-partition.

8.10 Mechanism of Bose-Einstein Condensation

Let the ground state be of energy $\epsilon_0 \geq 0$. For example consider particle in a three dimensional box of length L . The ground state is

$$(n_x, n_y, n_z) = (1, 1, 1).$$

The ground state energy is

$$\epsilon_{1,1,1} = \epsilon_0 = \frac{3h^2}{8mL^2}.$$

The chemical potential is always less than or equal to ϵ_0 . As temperature decreases, the chemical potential increases and comes closer and closer to the ground state energy $\epsilon_0 \geq 0$. Let us estimate how close μ can get to ϵ_0 . In other words, we want to estimate the smallest possible value of $(\epsilon_0 - \mu)/[k_B T]$. To this end, consider the expression for the average number of bosons in the ground state. Let us denote this by N_0 . It is given by,

$$N_0 = \frac{1}{\exp\left[\frac{\epsilon_0 - \mu}{k_B T}\right] - 1} \quad (8.73)$$

As temperature goes to zero, the chemical potential goes toward the ground state energy. For a non-zero value of T , when $\frac{\epsilon_0 - \mu}{k_B T}$ is small, we can write

$$\exp\left(\frac{\epsilon_0 - \mu}{k_B T}\right) = 1 + \frac{\epsilon_0 - \mu}{k_B T} \quad (8.74)$$

Substituting this in the expression for N_0 , given above, we get,

$$N_0 = \frac{k_B T}{\epsilon_0 - \mu(T)} \quad (8.75)$$

N_0 goes to zero⁶ as $T \rightarrow \infty$. At high temperature, the ground state occupancy is extremely small, as indeed it should.

Therefore we have,

$$\frac{\epsilon_0 - \mu}{k_B T} = \frac{1}{N_0} \quad (8.76)$$

The largest value that N_0 can take is N , *i.e.* when all the particles condense into the ground state. In other words, the smallest value that $1/N_0$ can take is $1/N$. Hence $(\epsilon_0 - \mu)/[k_B T]$ can not be smaller than $1/N$. The smallest possible value it can take is $1/N$ - inverse of the number of particles in the entire system.

$$\frac{\epsilon_0 - \mu}{k_B T} \geq \frac{1}{N} \quad (8.77)$$

Thus, measured in units of $k_B T$, the chemical potential shall always be less than the ground state energy at any non-zero temperature. At best, the quantity $(\epsilon - \mu)$, expressed in units of thermal energy ($k_B T$), can only be of the order of $1/N$.

But, remember. For a physicist, small is zero and large is infinity

⁶ For large T , the numerator is large; but the denominator is also large. Note that $\mu(T)$ is negative and large for large T . In fact the denominator goes to infinity faster than the numerator.

Therefore the chemical potential can never take a value close to any of the excited states, since all of them invariably lie above the ground state. In a sense, *the ground state forbids the chemical potential to come close to any energy level other than the ground state energy.* It sort of guards all the excited states from a close visit of μ . As $T \rightarrow 0$, the number of bosons in the ground state increases.

This precisely is the subtle mechanism underlying Bose-Einstein condensation.

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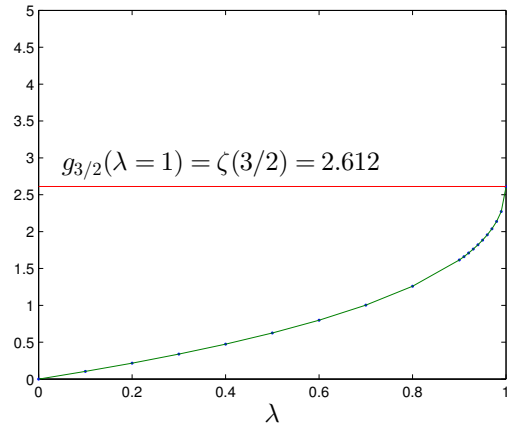


Fig. 8.1. $g_{3/2}(\lambda)$ versus λ . Graphical inversion to determine fugacity

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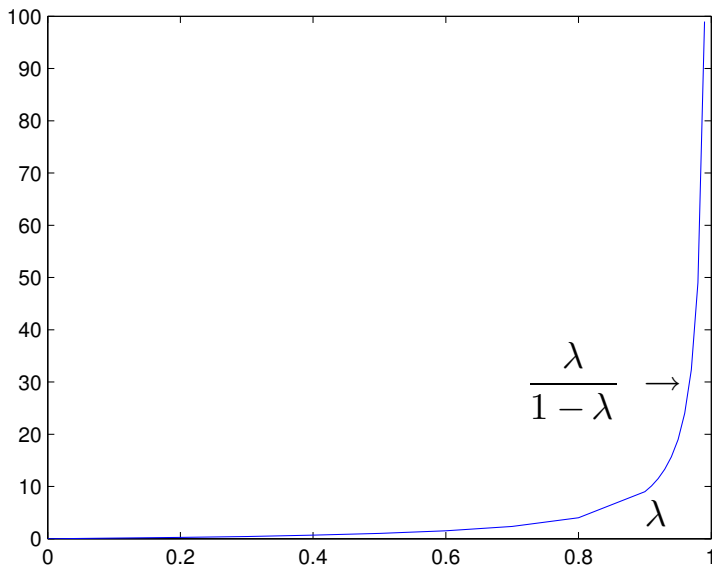


Fig. 8.2. Singular part of N

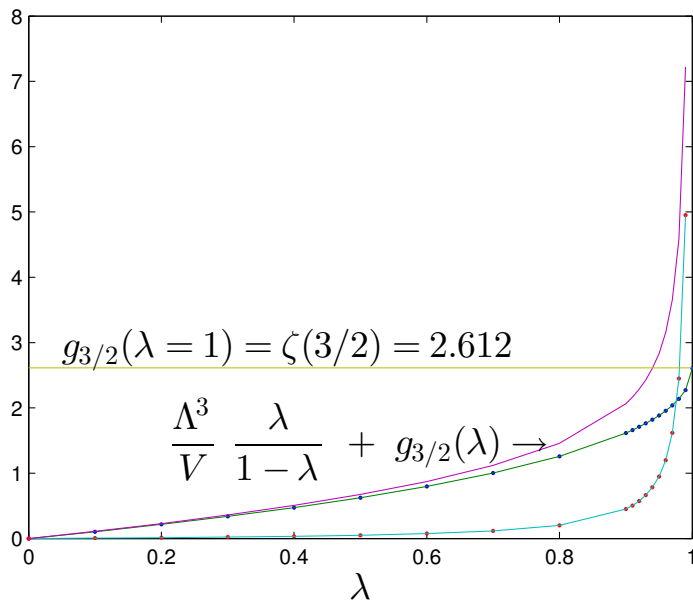


Fig. 8.3. $\rho\Lambda^3$ versus λ . The singular part $[\Lambda^3/V][\lambda/(1-\lambda)]$ (the bottom most curve), the regular part $g_{3/2}(\lambda)$ (the middle curve), and the total ($\rho\Lambda^3$) are plotted. For this plot we have taken Λ^3/V as 0.05

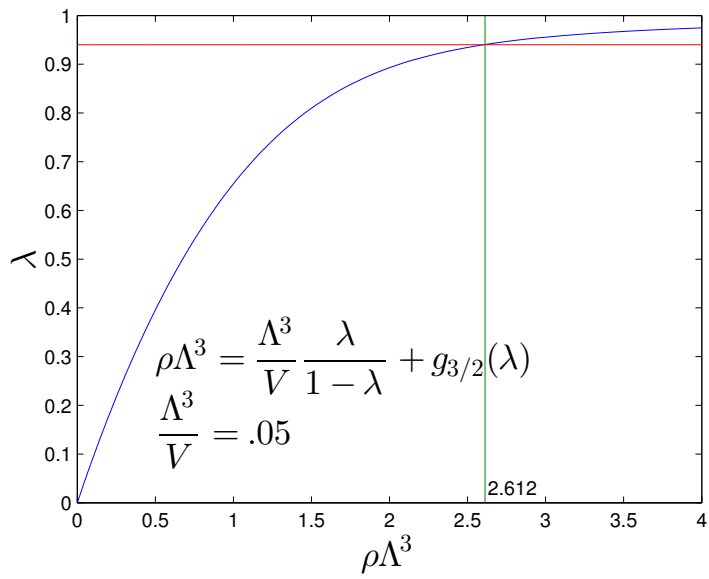


Fig. 8.4. Fugacity λ versus $\rho\Lambda^3$

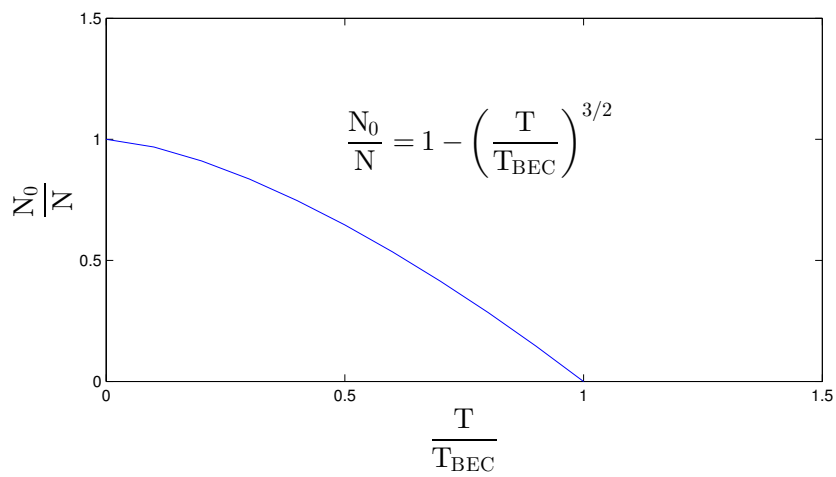


Fig. 8.5. Ground state occupation as a function of temperature

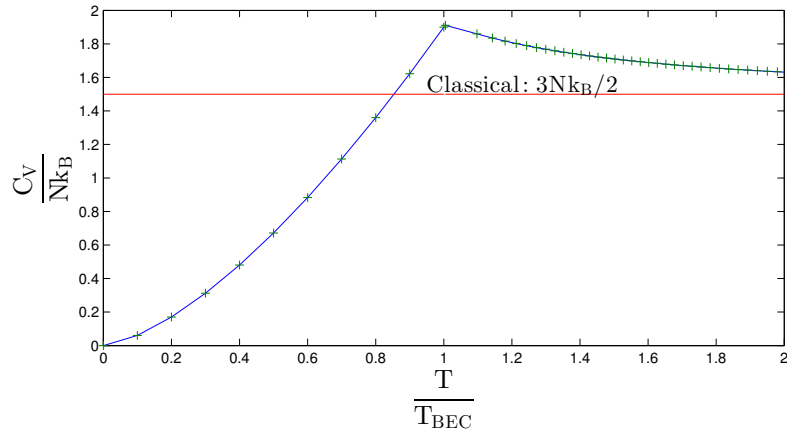


Fig. 8.6. Heat capacity in the neighbourhood of Bose - Einstein condensation temperature

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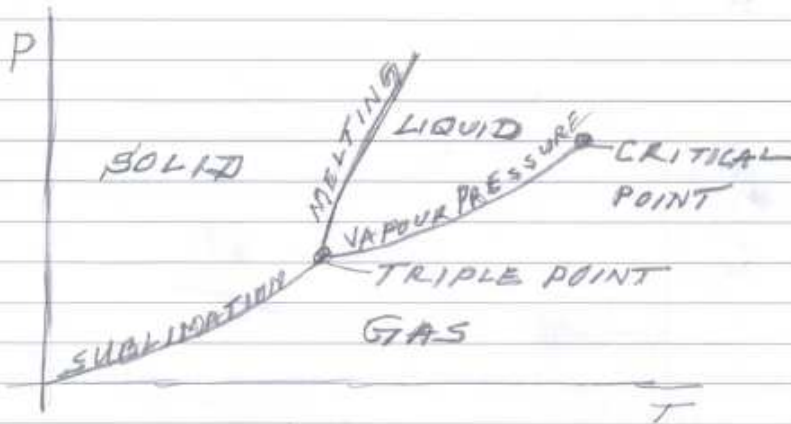
9. Elements of Phase Transition

I shall provide an elementary introduction to phase transition. The topics covered include phase diagram of a normal substance; coexistence curves : (i) sublimation curve, (ii) melting curve, and (iii) vapour pressure curve; triple point; critical point; first order phase transition; latent heat; second order phase transition; critical phenomena; derivation of Gibbs - Duhem relation starting from Gibbs free energy; Clausius-Clapeyron equation; Anomalous expansion of water upon freezing; and an exotic behaviour of Helium-3 at low temperatures.

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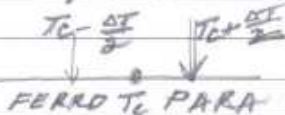
①
 STATISTICAL MECHANICS-2015 I.K.P.N.
 PHASE TRANSITION.

Phase diagram of a NORMAL substance



Astonishing: A sharp line separates two phases.

e.g. an infinitesimal change across T_c can drive the system from one phase to the other.



COEXISTENCE LINES:

- Sublimation line
- Melting line
- Vapour pressure line

(3)

When we cross coexistence line
we get FIRST ORDER
PHASE TRANSITION

AN ABRUPT CHANGE IN A
PROPERTY

The molecules aggregate
differently on either side
of the coexistence line
requiring different amount
of energy.

ONLY when we supply or
remove the required energy
can we cross the line

The energy difference — for the
two types of aggregation —
is called LATENT HEAT.

The three lines meet at
the TRIPLE POINT.

The vapour pressure line
terminates at the
CRITICAL POINT

To the best of our (experimental)
knowledge, the melting line
goes on and on to infinity.
It does not terminate.



THE DISTINCTION BETWEEN
THE LIQUID PHASE AND
GASEOUS PHASE DECREASES AS
YOU MOVE TOWARD THE
CRITICAL POINT.

THE DIFFERENCE DISAPPEARS
AT THE CRITICAL POINT

AT THE CRITICAL POINT
WE HAVE

SECOND ORDER
PHASE TRANSITION.

THE TRANSITION IS CONTINUOUS;
DOES NOT REQUIRE LATENT HEAT

ALL THE RESPONSE FUNCTIONS
DIVERGE AT $T = T_c$.

LARGE FLUCTUATIONS IN
EXTENSIVE PROPERTIES

THE FLUCTUATIONS GROW LARGER AND
LARGER AS YOU APPROACH T_c FROM
ABOVE OR BELOW... WARNING US
OF THE FORTH COMING TRANSITION.

(4)

Absrupt first order transition sends out no such warning signals. It just comes, unexpressed

A bit of thermodynamics:

coexistence lines:

Phase-1 and phase-2
e.g. ice and water
coexist on the line

A molecule residing in the 'solid' phase has no compelling reasons to move to 'liquid' phase and vice versa.

A molecule can live in both phases with equal ease....

$$\Rightarrow \mu_1(T, P) = \mu_2(T, P)$$

On the coexistence line, the two phases are in 'diffusive' equilibrium i.e. number of molecules migrating from phase 1 to 2 is the same as that migrating from phase-2 to 1.

consider a neighbouring point on the same coexistence line

(5)

$$\mu_1(T, P) = \mu_2(T, P)$$

$$\mu_1(T + \Delta T, P + \Delta P) = \mu_2(T + \Delta T, P + \Delta P)$$

DIGRESSIONGibbs free energy: $G(T, P, N)$

Legendre transform:

$$S \rightarrow T$$

$$V \rightarrow P$$

$$U(S, V, N) \rightarrow G(T, P, N)$$

$$G = U - TS + PV \quad \left. \frac{\partial U}{\partial S} \right|_{V, N} = T; \quad \left. \frac{\partial U}{\partial V} \right|_{S, N} = -P$$

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

$$S = - \left. \frac{\partial G}{\partial T} \right|_{P, N} \quad V = \left. \frac{\partial G}{\partial P} \right|_{T, N}$$

$$\mu = \left. \frac{\partial G}{\partial N} \right|_{T, P} \quad G \text{ is FIRST ORDER} \\ \text{HOMOGENOUS IN } N$$

Euler theorem

$$G(T, P, \lambda N) = \lambda G(T, P, N)$$

$$\frac{\partial G}{\partial(\lambda N)} \frac{\partial(\lambda N)}{\partial \lambda} = G(T, P, N)$$

$$N \cdot \frac{\partial G}{\partial N} = G(T, P, N)$$

$$\boxed{\mu N = G}$$

(5)

$$\mu N = G = U - TS + PV$$

$$\mu dN + N d\mu = \mu dN - S dT + V dP$$

$$N d\mu = -S dT + V dP$$

$$d\mu = -\left(\frac{S}{N}\right) dT + \left(\frac{V}{N}\right) dP$$

$$\boxed{d\mu = -s dT + v dP} \quad \begin{array}{l} s = \frac{S}{N} \\ v = \frac{V}{N} \end{array}$$

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -s \quad ; \quad \left(\frac{\partial \mu}{\partial P}\right)_T = v$$

$$\mu_1(T+\Delta T, P+\Delta P) = \mu_2(T+\Delta T, P+\Delta P)$$

$$\mu_1(T, P) + \Delta T \frac{\partial \mu_1}{\partial T} + \Delta P \frac{\partial \mu_1}{\partial P} = \mu_2(T, P) + \Delta T \frac{\partial \mu_2}{\partial T} + \Delta P \frac{\partial \mu_2}{\partial P}$$

$$\Delta T \left[\frac{\partial \mu_1}{\partial T} - \frac{\partial \mu_2}{\partial T} \right] = \Delta P \left[\frac{\partial \mu_2}{\partial P} - \frac{\partial \mu_1}{\partial P} \right]$$

$$\Delta T \left[-s_1 + s_2 \right] = \Delta P \left[v_2 - v_1 \right]$$

$$\frac{\Delta P}{\Delta T} = \frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1}$$

$$\boxed{\frac{dP}{dT} = \frac{s_1 - s_2}{v_1 - v_2}} \quad \begin{array}{l} \text{Clausius-} \\ \text{Clapeyron} \\ \text{equation.} \end{array}$$

The slope of the
coexistence curve is

(7)

$$\frac{dP}{dT} = \frac{S_1 - S_2}{v_1 - v_2}$$

Phase-1 ; solid

Phase-2 ; liquid

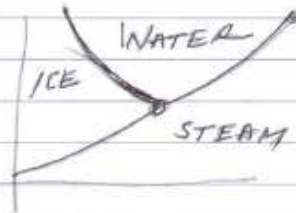
It is obvious $S_1 < S_2$:

Solid is ordered ; liquid is disordered.

If $\frac{dP}{dT}$ is positive then $v_1 < v_2$
 for a given quantity of substance,
 i.e. the liquid phase requires
 more volume than solid phase.
 — True for normal
 substances.

But ICE-WATER : ANOMALOUS

Melting line has
 negative slope!!



$$\frac{dP}{dT} = \frac{S_1 - S_2}{v_1 - v_2}$$

↓
 -ve

$S_1 - S_2$ is -ve.

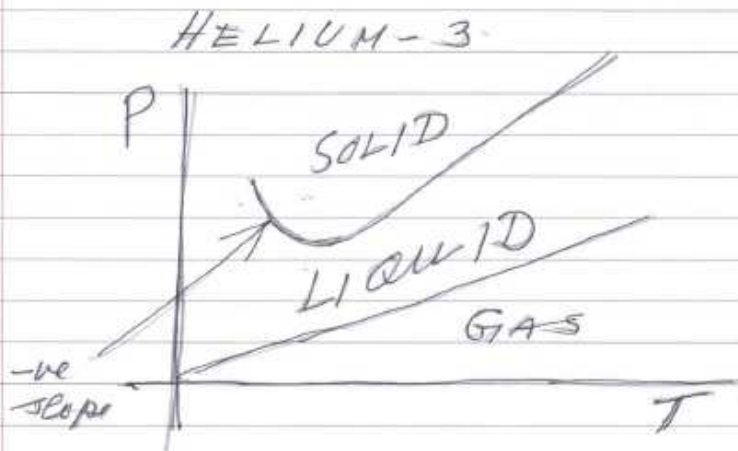
Therefore $v_1 - v_2$ should be +ve.

$$v_{ICE} > v_{Water}$$

When water freezes into ice,
 it expands.

DO NOT KEEP BOTTLE OF BEER
 IN A FREEZER. The bottle
 will break!!

⑧



$$\frac{dP}{dT} = \frac{S_1 - S_2}{v_1 - v_2}$$



-ve $v_1 - v_2$ is negative.

$v_2 > v_1$ like normal substance
liquid requires more volume.

∴ $S_1 - S_2$ must be +ve.

SOLID He^3 has more entropy
than liquid !!

Liquid is MORE ORDERED
THAN SOLID !!

At low temperatures, if you
heat liquid He^3 it becomes
Solid Helium !!

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10. Statistical Mechanics of Harmonic Oscillators

10.1 Classical Harmonic Oscillators

Consider a closed system of $3N$ harmonic oscillators at temperature T . The oscillators do not interact with each other and are distinguishable. Let us derive an expression for the single-oscillator partition function.

The energy of an harmonic oscillator is given by

$$E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 \quad (10.1)$$

where q and p are the position and momentum respectively, of the one dimensional harmonic oscillator. ω is the characteristic frequency of the oscillator and m its mass. A simple pendulum executing small oscillations is a neat example of an harmonic oscillator.

We have,

$$Q_1(T) = \frac{1}{h} \int_{-\infty}^{+\infty} dq \int_{-\infty}^{+\infty} dp \exp \left[-\beta \left(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 \right) \right] \quad (10.2)$$

We can write the above in a convenient way as a product of two Gaussian integrals, one over dq and the other over dp , as

$$Q_1(T) = \frac{1}{h} \int_{-\infty}^{+\infty} dq \exp \left[-\frac{1}{2} \frac{q^2}{\left(\sqrt{\frac{k_B T}{m\omega^2}} \right)^2} \right] \times \int_{-\infty}^{+\infty} dp \exp \left[-\frac{1}{2} \frac{p^2}{(\sqrt{mk_B T})^2} \right] \quad (10.3)$$

Let σ_1 and σ_2 denote the standard deviations of the two zero-mean Gaussian distributions. These are given by,

$$\sigma_1 = \sqrt{\frac{k_B T}{m\omega^2}} \quad (10.4)$$

$$\sigma_2 = \sqrt{mk_B T} \quad (10.5)$$

$$\sigma_1 \sigma_2 = \frac{k_B T}{\omega} \quad (10.6)$$

We have normalization identity for a Gaussian

$$\int_{-\infty}^{+\infty} dx \exp\left[-\frac{1}{2} \frac{x^2}{\sigma^2}\right] = \sigma\sqrt{2\pi} \quad (10.7)$$

Therefore,

$$Q_1(T) = \frac{1}{h}(\sigma_1\sqrt{2\pi})(\sigma_2\sqrt{2\pi}) = \frac{k_B T}{\hbar\omega} \quad (10.8)$$

If all the oscillators are identical *i.e.* they all have the same characteristic frequency of oscillations, then

$$Q_{3N}(T) = \left(\frac{k_B T}{\hbar\omega}\right)^{3N} \quad (10.9)$$

On the other hand if the oscillators have distinct characteristic frequency $\{\omega_i : i = 1, 2, \dots, 3N\}$, then

$$Q_{3N}(T) = \prod_{i=1}^{3N} \frac{k_B T}{\hbar\omega_i} \quad (10.10)$$

where we have considered $3N$ harmonic oscillators with $3N$ characteristic frequencies.

10.1.1 Helmholtz Free Energy

The free energy of a system of $3N$ non-interacting, identical classical harmonic oscillators is given by

$$F(T, V, N) = -3Nk_B T \ln\left(\frac{k_B T}{\hbar\omega}\right) = 3Nk_B T \ln\left(\frac{\hbar\omega}{k_B T}\right) \quad (10.11)$$

If the oscillators have different frequencies then

$$F(T, V, N) = -k_B T \sum_{i=1}^{3N} \ln\left(\frac{k_B T}{\hbar\omega_i}\right) \quad (10.12)$$

If N is large we can define $g(\omega)d\omega$ as the number of harmonic oscillators with frequencies in an interval $d\omega$ around ω . The sum can be replaced by an integral,

$$F(T) = -k_B T \int_0^{\infty} \ln\left(\frac{k_B T}{\hbar\omega}\right) g(\omega) d\omega \quad (10.13)$$

We have the normalization

$$\int_0^{\infty} g(\omega) d\omega = 3N \quad (10.14)$$

Once we know of free energy, we can employ the machinery of thermodynamics and get expressions for all other thermodynamic properties of the system, see below.

10.1.2 Thermodynamic Properties of the Oscillator System

$$F(T, V, N) = U - TS \quad (10.15)$$

$$\begin{aligned} dF &= dU - TdS - SdT \\ &= -SdT - PdV + \mu dN \end{aligned} \quad (10.16)$$

Thus for a system of identical, non-interacting classical harmonic oscillators

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T, N} = 0 \quad \text{why?} \quad (10.17)$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T, V} = k_B T \ln \left(\frac{\hbar \omega}{k_B T} \right) \quad (10.18)$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V, N} = N k_B \left[\ln \left(\frac{k_B T}{\hbar \omega} \right) + 1 \right] \quad (10.19)$$

We also have,

$$U = - \left(\frac{\partial \ln Q}{\partial \beta} \right)_{V, N} = 3N k_B T, \quad (10.20)$$

consistent with equipartition theorem which says each quadratic term in the Hamiltonian carries $k_B T/2$ of energy. The Hamiltonian of a single harmonic oscillator has two quadratic terms - one in position q and the other in momentum p .

We also find that the results are consistent with the Dulong and Petit's law which says that the heat capacity at constant volume is independent of temperature:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3N k_B = 3nR \quad (10.21)$$

$$\frac{C_V}{n} = 3R \approx 6 \text{ calories (mole)}^{-1} \text{ (kelvin)}^{-1} \quad (10.22)$$

More importantly, the heat capacity is the same for all the materials; it depends only on the number of molecules or the number of moles of the substance and not on what the substance is. The heat capacity per mole is approximately 6 calories per Kelvin.

10.1.3 Quantum Harmonic Oscillator

Now let us consider quantum harmonic oscillators. The energy eigenvalues of a single one dimensional harmonic oscillator is given by

$$\epsilon_n = \left(n + \frac{1}{2} \right) \hbar \omega : n = 0, 1, 2, \dots \quad (10.23)$$

The canonical partition function for a single (quantum) harmonic oscillator is then,

$$\begin{aligned}
Q_1(\beta) &= \exp(-\beta\hbar\omega/2) \sum_{n=0}^{\infty} [\exp(-\beta\hbar\omega)]^n \\
&= \frac{\exp(-\beta\hbar\omega/2)}{1 - \exp(-\beta\hbar\omega)} \tag{10.24}
\end{aligned}$$

The partition function of a collection of $3N$ non-interacting quantum harmonic oscillators is then given by

$$Q_N(T) = \frac{\exp(-3N\beta\hbar\omega/2)}{[1 - \exp(-\beta\hbar\omega)]^{3N}} \tag{10.25}$$

If the harmonic oscillators are all of different frequencies, the partition function is given by

$$Q(T) = \prod_{i=1}^{3N} \frac{\exp(-\beta\hbar\omega_i/2)}{1 - \exp(-\beta\hbar\omega_i)} \tag{10.26}$$

The free energy is given by,

$$\begin{aligned}
F(T, V, N) &= -k_B T \ln Q_{3N}(T) \\
&= 3N \left[\frac{1}{2} \hbar\omega + k_B T \ln \{1 - \exp(-\beta\hbar\omega)\} \right] \tag{10.27}
\end{aligned}$$

For $3N$ independent harmonic oscillators with different frequencies we have

$$F = \sum_{i=1}^{3N} \left[\frac{\hbar\omega_i}{2} + k_B T \ln \{1 - \exp(-\beta\hbar\omega_i)\} \right] \tag{10.28}$$

$$= \int_0^{\infty} d\omega \left[\frac{\hbar\omega}{2} + k_B T \ln \{1 - \exp(-\beta\hbar\omega)\} \right] g(\omega) \tag{10.29}$$

$$\int_0^{\infty} d\omega g(\omega) = 3N \tag{10.30}$$

We can obtain the thermodynamic properties of the system from the free energy. We get,

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \frac{1}{2} \hbar\omega + k_B T \ln [1 - \exp(-\beta\hbar\omega)] \tag{10.31}$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = 0 \tag{10.32}$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} = 3N k_B \left[\frac{\beta\hbar\omega}{\exp(\beta\hbar\omega) - 1} - \ln \{1 - \exp(-\beta\hbar\omega)\} \right] \tag{10.33}$$

$$U = - \frac{\partial \ln Q}{\partial \beta} = 3N \left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp(\beta\hbar\omega) - 1} \right] \tag{10.34}$$

The expression for U tells that the equipartition theorem is the first victim of quantum mechanics : *Quantum harmonic oscillators do not obey equipartition theorem.* The average energy per oscillator is higher than the classical value of $k_B T$. Only for $T \rightarrow \infty$, we have $k_B T \gg \hbar\omega$, the "quantum" results coincide with the "classical" results. Let $x = \frac{\hbar\omega}{k_B T}$. Then Eq. (10.34) can be written as

$$\frac{U}{3Nk_B T} = \frac{x}{2} + \frac{x}{\exp(x) - 1} \quad (10.35)$$

We have plotted U measured in units of $3Nk_B T$ as a function of oscillator energy $\hbar\omega$ measured in units of $k_B T$. It is seen that when $x \rightarrow 0$ ($T \rightarrow \infty$), this quantity tends to unity, see also below, implying that classical result of equipartition of energy obtains at high temperature. Quantum effects start showing up only at low temperatures.

In the limit $x \rightarrow 0$ ($T \rightarrow \infty$), we have,

$$\frac{U}{3Nk_B T} \underset{x \rightarrow 0}{\sim} \frac{x}{2} + \frac{x}{x + \frac{x^2}{2} + \frac{x^3}{6} + \mathcal{O}(x^4)} \quad (10.36)$$

$$= \frac{x}{2} + \frac{1}{1 + \frac{x}{2} + \frac{x^2}{6} + \mathcal{O}(x^3)} \quad (10.37)$$

$$= \frac{x}{2} + 1 - \frac{x}{2} - \frac{x^2}{6} + \frac{x^2}{4} + \mathcal{O}(x^3) \quad (10.38)$$

$$= 1 - \frac{x^2}{6} + \frac{x^2}{4} + \mathcal{O}(x^3) \quad (10.39)$$

$$= 1 + \frac{x^2}{12} + \mathcal{O}(x^3) \quad (10.40)$$

$$= 1 \quad (10.41)$$

The heat capacity at constant volume is given by

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N} \quad (10.42)$$

$$= \frac{3N}{k_B} \left(\frac{\hbar\omega}{T} \right)^2 \frac{\exp[\beta\hbar\omega]}{(\exp[\beta\hbar\omega] - 1)^2} \quad (10.43)$$

The second victim of quantum mechanics is the law of Dulong and Petit. The heat capacity depends on temperature and on the oscillator frequency. The heat capacity per mole will change from substance to substance because of its dependence on the oscillator frequency. Only in the limit of $T \rightarrow \infty$ (the same as $\beta \rightarrow 0$), do we get the classical results.

The temperature dependence of heat capacity is an important "quantum" outcome. We find that the heat capacity goes to zero exponentially as $T \rightarrow 0$. However experiments suggest that the fall is algebraic and not exponential. The heat capacity is found to go to zero as T^3 . This is called T^3 law.

10.1.4 Specific Heat of a Crystalline Solid

In the above we studied the behaviour of a collection of independent identical harmonic oscillators in a canonical ensemble. We shall see below how such a study

is helpful toward understanding of the behaviour of specific heat of crystalline solid as a function of temperature.

A crystal is a collection of say N atoms organized in a regular lattice. Let $\{x_1, x_2, \dots, x_{3N}\}$ specify the $3N$ positions of these atoms. For example we can consider a periodic array of atoms arranged at regular intervals along the three mutually perpendicular directions, constituting a three dimensional cubic structure. We can think of other structures like face-centred cubic (FCC), body centred cubic (BCC) lattices.

An atom vibrates around its lattice location say $(\bar{x}_i, \bar{x}_{i+1}, \bar{x}_{i+2})$. It does not make large excursions away from its lattice location. We must bear in mind that the atoms are not independently bound to their lattice position. They are mutually bound¹.

Consider a total of N atoms organized in a three dimensional lattice. Each atom executes *small* oscillations about its mean position. In the process of oscillations each atom pulls and pushes its neighbours; these neighbours in turn pull and push their neighbours and so on. The disturbance propagates in the crystal. We can set up equations of motion for the three coordinates of each of the atoms. We shall have $3N$ coupled equations. Consider the Hamiltonian of a solid of N atoms with position coordinates are $\{x_1, x_2, \dots, x_{3N}\}$. When the system of atoms is in its lowest energy, the coordinates are $x_{1,0}, x_{2,0}, \dots, x_{3N,0}$. Let $V(x_1, x_2, \dots, x_{3N})$ denote the potential energy. We express the potential energy under harmonic approximation, as

$$\begin{aligned}
 V(x_1, x_2, \dots, x_{3N}) &= V(x_{1,0}, x_{2,0}, \dots, x_{3N,0}) + \\
 &\sum_{i=1}^{3N} \left(\frac{\partial V}{\partial x_i} \right)_{x_{1,0}, x_{2,0}, \dots, x_{3N,0}} (x_i - x_{i,0}) + \\
 &\sum_{i=1}^{3N} \sum_{j=1}^{3N} \frac{1}{2} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_{x_{1,0}, x_{2,0}, \dots, x_{3N,0}} (x_i - x_{i,0})(x_j - x_{j,0}) \quad (10.44)
 \end{aligned}$$

The first term gives the minimum energy of the solid when all its atoms are in their equilibrium positions. We can denote this energy by V_0 .

The second set of terms involving the first order partial derivatives of the potential are all identically zero by definition : V has a minimum at $\{x_i = x_{i,0} \forall i = 1, 3N\}$

¹ To appreciate the above statement, consider a class room wherein the chairs are already arranged with constant spacing along the length and breadth of the class room. The students occupy these chairs and form a regular structure. This corresponds to a situation wherein each student is bound independently to his chair.

Now consider a situation wherein the students are mutually bound to each other. Let us say that the students interact with each other in the following way : Each is required to keep an arm's length from his four neighbours. If the distance between two neighbouring students is less, they are pushed outward; if more, they are pulled inward. Such mutual interactions lead to the student organizing themselves in a two dimensional regular array

I shall leave it to you to visualize how such mutual nearest neighbour interactions can give rise to three dimensional arrays.

The third set of terms involving second order partial derivatives describe harmonic vibrations. We neglect the terms involving higher order derivatives and this is justified if only small oscillations are present in the crystalline .

Thus under harmonic approximations we can write the Hamiltonian as,

$$H = V_0 + \sum_{i=1}^{3N} \frac{1}{2} \left(\frac{d\xi_i}{dt} \right)^2 + \sum_{i=1}^{3N} \sum_{j=1}^{3N} \alpha_{i,j} \xi_i \xi_j \quad (10.45)$$

where

$$\xi = x_i - \bar{x}_i \quad (10.46)$$

$$\alpha_{i,j} = \frac{1}{2} \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_{\bar{x}_1, \bar{x}_2, \dots, \bar{x}_{3N}} \quad (10.47)$$

We shall now introduce a linear transformation from the coordinates $\{\xi_i : i = 1, 3N\}$ to the normal coordinates $\{q_i : i = 1, 3N\}$. We choose the linear transformation matrix such that the Hamiltonian does not contain any cross terms in the q coordinates.

$$H = V_0 + \sum_{i=1}^{3N} \frac{1}{2} m (\dot{q}^2 + \omega_i^2 q_i^2) \quad (10.48)$$

where $\{\omega_i : i = 1, 3N\}$ are the characteristic frequencies of the normal modes of the system. These frequencies are determined by the nature of the potential energy function $V(x_1, x_2, \dots, x_{3N})$. Thus the energy of the solid can be considered as arising out of a set of $3N$ one dimensional, non interacting, harmonic oscillators whose characteristic frequencies are determined by the nature of the atoms of the crystalline solid, the nature of their mutual interaction, the nature of the lattice structure *etc.*.

Thus we can describe the system in terms of independent harmonic oscillators by defining a normal coordinate system, in which the equations of motion are decoupled. If there are N atoms in the crystals there are $3N$ degrees of freedom. Three of the degrees of freedom are associated with the translation of the whole crystal; and three with rotation. Thus, there are strictly $3N - 6$ normal mode oscillations. If N is of the order of 10^{25} or so, it doesn't matter if the number of normal modes is $3N - 6$ and not $3N$.

We can write the canonical partition function as

$$Q = \prod_{i=1}^{3N} \frac{\exp(-\beta \hbar \omega_i / 2)}{1 - \exp(-\beta \hbar \omega_i)} \quad (10.49)$$

There are $3N$ normal frequencies. We can imagine them to be continuously distributed. Let $g(\omega)d\omega$ denote the number of normal frequencies between ω and $\omega + d\omega$. The function $g(\omega)$ obeys the normalization

$$\int_0^\infty g(\omega)d\omega = 3N \quad (10.50)$$

We have,

$$-\ln Q = \sum_{i=1}^{3N} \left[\frac{\beta \hbar \omega_i}{2} + \ln \{1 - \exp(-\beta \hbar \omega_i)\} \right] \quad (10.51)$$

$$= \int_0^{\infty} \left[\frac{\beta \hbar \omega}{2} + \ln \{1 - \exp(-\beta \hbar \omega)\} \right] g(\omega) d\omega \quad (10.52)$$

The problem reduces to finding the function $g(\omega)$. Once we know $g(\omega)$, we can calculate the thermodynamic properties of the crystal. In particular we can calculate the internal energy U and heat capacity, see below.

$$\begin{aligned} U &= \int_0^{\infty} \left[\frac{\hbar \omega}{2} + \frac{\hbar \omega \exp(-\beta \hbar \omega)}{1 - \exp(-\beta \hbar \omega)} \right] g(\omega) d\omega \\ &= \int_0^{\infty} \left[\frac{\hbar \omega}{2} + \frac{\hbar \omega}{\exp(\beta \hbar \omega) - 1} \right] g(\omega) d\omega \end{aligned} \quad (10.53)$$

$$C_V = k_B \int_0^{\infty} \frac{(\beta \hbar \omega)^2 \exp(\beta \hbar \omega)}{[\exp(\beta \hbar \omega) - 1]^2} g(\omega) d\omega \quad (10.54)$$

The problem of determining the function $g(\omega)$ is a non-trivial task. It is precisely here that the difficulties lie. However, there are two well known approximations to $g(\omega)$. One of them is due to Einstein and the other due to Debye.

10.1.5 Einstein Theory of Specific Heat of Crystals

Einstein assumed all the $3N$ harmonic oscillators to have the same frequency. In other words,

$$g(\omega) = 3N \delta(\omega - \omega_E) \quad (10.55)$$

where ω_E is the Einstein frequency or the frequency of the Einstein oscillator. The Einstein formula for the heat capacity is then given by

$$C_V = 3Nk_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{\exp(\hbar \omega_E / [k_B T])}{(\exp(\hbar \omega_E / [k_B T]) - 1)^2} \quad (10.56)$$

Let us define

$$\Theta_E = \frac{\hbar \omega_E}{k_B} \quad (10.57)$$

and call Θ_E as Einstein temperature. Verify that this quantity has the unit of temperature. In terms of Einstein temperature we have,

$$C_V = 3Nk_B \left(\frac{\Theta_E}{T} \right)^2 \frac{\exp(\Theta_E / T)}{[\exp(\Theta_E / T) - 1]^2} \quad (10.58)$$

- Show that in the limit of $T \rightarrow \infty$, the heat capacity of the Einstein solid tends to the value $3Nk_B = 3R = 6 \text{ cal (mole)}^{-1}K^{-1}$ predicted by Dulong and Petit.
- Show that in the low temperature limit,

$$C_V \underset{T \rightarrow 0}{\sim} 3Nk_B \left(\frac{\Theta_E}{T} \right)^2 \exp(-\Theta_E/T) \quad (10.59)$$

Experiments suggest T^3 decay of C_V with temperature. In the next class I shall discuss Debye's theory of heat capacity. We will find that Debye's theory gives the T^3 law.

10.1.6 Debye Theory of Specific Heat

Debye assumed a continuous spectrum of frequencies, cut off at an upper limit ω_D . Let us call it Debye frequency. Debye assumed based on an earlier work of Rayleigh, that $g(\omega) = \alpha\omega^2$, where the proportionality constant depends on the speed of propagation of the normal mode, its nature², its degeneracy³. From the normalization condition,

$$\alpha \int_0^{\omega_D} \omega^2 d\omega = 3N \quad (10.60)$$

we get, $\alpha = 9N/\omega_D^3$. Thus we have

$$g(\omega) = \begin{cases} \frac{9N}{\omega_D^3} \omega^2 & \text{for } \omega \leq \omega_D \\ 0 & \text{for } \omega > \omega_D \end{cases} \quad (10.61)$$

Let us now calculate C_V under Debye's theory. We start with

$$C_V(T) = k_B \int_0^{\infty} \frac{(\beta\hbar\omega)^2 \exp(\beta\hbar\omega)}{[\exp(\beta\hbar\omega) - 1]^2} g(\omega) d\omega \quad (10.62)$$

Let

$$x = \beta\hbar\omega \quad (10.63)$$

$$\Theta_D = \frac{\hbar\omega_D}{k_B} \quad (10.64)$$

Θ_D is called the Debye temperature. Then we have,

$$C_V = (3Nk_B) \times 3 \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^4 \exp(x)}{[\exp(x) - 1]^2} dx \quad (10.65)$$

² transverse or longitudinal

³ transverse mode is doubly degenerate and longitudinal mode is non-degenerate, etc..

Let us consider the integral in the above expression and write,

$$I = \int_0^{\Theta_D/T} \frac{x^4 \exp(x)}{(\exp(x) - 1)^2} dx \quad (10.66)$$

Integrating by parts⁴ we get,

$$I = \frac{1}{\exp(\Theta_D/T) - 1} \left(\frac{\Theta_D}{T} \right)^4 + 4 \int_0^{\Theta_D/T} \frac{x^3}{\exp(x) - 1} dx \quad (10.67)$$

The expression for heat capacity is then,

$$C_V = (3Nk_B) \left[-3 \left(\frac{\Theta_D}{T} \right) \frac{1}{\exp(\Theta_D/T) - 1} + 12 \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3}{\exp(x) - 1} dx \right] \quad (10.68)$$

Let us now consider the behaviour C_V in the limit of $T \rightarrow \infty$. we have $T \gg \Theta_D$. We can set $\exp(\Theta_D/T) \approx 1 + (\Theta_D/T)$; also in the integral we can set $\exp(x) = 1 + x$. Then we get,

$$C_V = 3Nk_B \left[-3 + 12 \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} x^2 dx \right] \quad (10.69)$$

$$= 3Nk_B(-3 + 4) \quad (10.70)$$

$$= 3Nk_B \quad (10.71)$$

In the low temperature limit we have $T \ll \Theta_D$. We start with,

$$C_V = 3Nk_B \left[-3 \left(\frac{\Theta_D}{T} \right) \frac{1}{\exp(\Theta_D/T) - 1} + 12 \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{x^3}{\exp(x) - 1} dx \right] \quad (10.72)$$

In the limit $T \rightarrow 0$, the first term inside the square bracket goes to zero like $\exp(-\Theta_D/T)$. The upper limit of the integral in the second term inside the square bracket can be set to ∞ . From standard integral tables⁵, we have,

$$\int_0^{\infty} \frac{x^3}{\exp(x) - 1} dx = \frac{\pi^4}{15} \quad (10.73)$$

Thus we have in the low temperature limit,

$$C_V \underset{T \rightarrow 0}{\sim} \frac{12\pi^4}{5} Nk_B \left(\frac{T}{\Theta_D} \right)^3 \quad (10.74)$$

⁴ Take $u(x) = x^4$ and $dv(x) = \exp(x)dx/[\exp(x) - 1]^2$

⁵ The integral equals $\Gamma(4)\zeta(4)$, where $\Gamma(\cdot)$ is the gamma function and $\zeta(\cdot)$ is the Riemann zeta function. $\Gamma(4) = 3! = 6$ and $\zeta(4) = \pi^4/90$. See *e.g.* G B Arfken and H J Weber, *Mathematical Methods for Physicists*, Fourth Edition, Academic Press, INC, Prism Books PVT LTD (1995).

10.1.7 Riemann Zeta Function

In an earlier class, we came across an integral,

$$\int_0^\infty \frac{x^3}{\exp(x) - 1} dx \tag{10.75}$$

The value of the integral is $\pi^4/15$.

This is a particular case of a more general result based on Riemann zeta function,

$$\int_0^\infty \frac{x^p}{\exp(x) - 1} dx = \Gamma(p + 1)\zeta(p + 1) \tag{10.76}$$

where $\Gamma(\cdot)$ is the usual gamma function defined as

$$\Gamma(z) = \int_0^\infty x^{z-1} \exp(-x) dx \text{ for } \text{Real}(z) > 0, \tag{10.77}$$

and $\zeta(\cdot)$ is the Riemann zeta function, see below. Note $\zeta(2) = \pi^2/6$ and $\zeta(4) = \pi^4/90$, etc..

Riemann zeta function is defined as

$$\zeta(p) = \sum_{n=1}^\infty n^{-p} \tag{10.78}$$

Take $f(x) = x^{-p}$ and then

$$\int_1^\infty x^{-p} dx = \begin{cases} \left. \frac{x^{-p+1}}{-p+1} \right|_1^\infty & \text{for } p \neq 1 \\ \left. \ln x \right|_1^\infty & \text{for } p = 1 \end{cases} \tag{10.79}$$

The integral and hence the series is divergent for $p \leq 1$ and convergent for $p > 1$.

10.1.8 Bernoulli Numbers

Bernoulli numbers B_n are defined by the series

$$\frac{x}{\exp(x) - 1} = \sum_{n=0}^\infty \frac{x^n}{n!} B_n \tag{10.80}$$

which converges for $|x| < 2\pi$.

By differentiating the power series repeatedly and then setting $x = 0$, we obtain

$$B_n = \left[\frac{d^n}{dx^n} \left(\frac{x}{\exp(x) - 1} \right) \right]_{x=0}. \tag{10.81}$$

- Show that $B_0 = 1$; $B_1 = -1/2$; $B_2 = 1/6$; $B_4 = -1/30$;
 $B_6 = 1/42$; $B_{2n+1} = 0 \forall n \geq 1$.

Euler showed that,

$$B_{2n} = (-1)^{n-1} \frac{2(2n)!}{(2\pi)^{2n}} \sum_{p=1}^{\infty} p^{-2n}, \quad n = 1, 2, 3, \dots \quad (10.82)$$

$$= (-1)^{n-1} \frac{2(2n)!}{(2\pi)^{2n}} \zeta(2n), \quad n = 1, 2, 3, \dots \quad (10.83)$$

- Employing the above relation between Bernoulli numbers and Riemann zeta function, show that

$$\zeta(2) = \frac{\pi^2}{6} \quad \zeta(4) = \frac{\pi^4}{90} \quad (10.84)$$

$$\zeta(6) = \frac{\pi^6}{945} \quad \zeta(8) = \frac{\pi^8}{9450} \quad (10.85)$$

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Index

- adiabatic process 82
Avijit Lahiri 10
- Balescu, R 9, 64
Bernoulli numbers 167
Bernoulli, Daniel 41
Binomial distribution 27, 31, 32, 122
Boltzmann entropy 44, 88
Boltzmann, Ludwig Eduard 3, 4, 13,
14, 18, 60, 68, 88, 109, 113
Boltzmann-Gibbs-Shannon entropy 4,
80
Bose-Einstein condensation 118–120,
132, 133, 139–141, 145
Bose-Einstein statistics 111, 113, 114,
116, 117, 119, 122, 125
Bosons 109, 116, 118, 119
bosons 90, 127, 128, 134, 136, 141
- Callen, H B 9, 11
canonical ensemble 44, 63, 66, 71, 79,
80, 89, 90, 97, 128
canonical partition function 64–66,
68–70, 84, 89–91, 105, 163
Carlo Rovelli 5
Carnot, Sadi 3
Central Limit Theorem 38
Chandler, D 9
characteristic function 34, 37, 38
chemical potential 56, 71, 90, 97, 105,
111–115, 119, 120, 127, 128, 131, 140,
141
Chowdhury, Debashish 9
Clausius 3, 79
closed system 63–66, 71, 72, 77, 79, 80,
157
cumulant 35, 38
cumulant generating function 35
- Debye frequency 165
Debye temperature 165
Debye's theory of specific heat 165
- delta function 46, 48
density of states 52, 66, 69, 90, 105,
128
determinism 6
Dittman, R. H. 12
Dugdale, J. S. 12
Dulong and Petit's law 161
- Einstein temperature 164
Einstein's theory of specific heat 164
Einstein, Albert 3, 97
ensemble 18, 19, 22
entropy 90
Entropy : Statistical 4
Entropy : Thermodynamics 4
equi-partition theorem 84, 139
ergodicity 16, 87, 89
Euler theorem 92
event 16
- factorial moment 28, 123
Feller, Willam 33
Fermi, Enrico 12
Fermi-Dirac statistics 108, 111, 113,
114, 116, 117, 119, 122
Fermions 109, 116, 118
fermions 90
Finn, C. B. P. 12
first law of thermodynamics 88, 115
Fourier transform 34, 38
fugacity 89, 90, 105, 128, 130–132
- Gabriel, Weinreich 12
Gaussian distribution 33, 34, 38
geometric distribution 122, 123
Gibbs ensemble 27
Gibbs ensemble 18, 22, 24
Gibbs, J. W. 3, 10, 22
Gibbs-Duhem relation 92, 96, 97
Glazer, M. 11
Goodstein, David 9
grand canonical partition function 114

- grand canonical ensemble 71, 80, 87, 90, 128, 131
- grand canonical partition function 89, 90, 92, 99, 105, 108, 109, 115, 116, 127, 135
- grand potential 90–92, 111, 112, 127
- harmonic oscillators 157–159, 163
- Helmholtz 3
- Helmholtz free energy 66, 68, 90, 91, 158
- Huang, Kerson 10
- ideal gas 83
- ideal gas law 41, 43
- isolated system 64, 69–71, 78, 80
- isothermal compressibility 95, 97, 112, 127
- Kelvin 3
- Kittel, C. 11
- Kondepudi, Dilip 12
- Krömer, K. 11
- Lagrange method 73, 77
- Lee, Joon Chang 10
- Legendre transform 79, 90, 111, 127
- Maxwell’s demon 8
- Maxwell’s ensemble 27
- Maxwell, James Clerk 3, 18
- Maxwell-Boltzmann statistics 33, 109, 111, 112, 114, 116, 117, 124, 125, 130
- McQuairrie, Donald A. 9, 77, 90, 92, 106
- method of most probable distribution 70
- micro canonical ensemble 45, 66, 69, 80, 90
- microcanonical ensemble 89
- moment generating function 29, 30, 38, 123
- moments 35
- Newton 3
- open system 8, 71, 80, 87, 88, 91, 94, 95, 111, 114, 127, 131, 135
- Palash, B. Pal 9
- Pathria, R. K. 9, 97
- Pauli’s exclusion principle 108
- Planck, Max 12
- Poisson distribution 32, 33, 38, 94, 125
- Prigogine, Ilya 12
- probability density function 17, 34
- quantum statistics 105
- random variable 17, 29, 122, 123
- Rief, F. 9
- Riemann zeta function 166, 167
- sample space 15, 19
- Schröder, Daniel V. 11
- Schrodinger 3
- Second law of thermodynamics 3, 7, 8
- Sethna, James P. 11
- Shantini, R. 12
- Stauffer, Dietrich 9
- Stirling Formula 23
- thermal wave length 129
- theta function 46, 48
- time-reversal invariance 6
- Van Ness, H. C. 9, 11
- Wark, J. 11
- Zamansky, M. W. 12