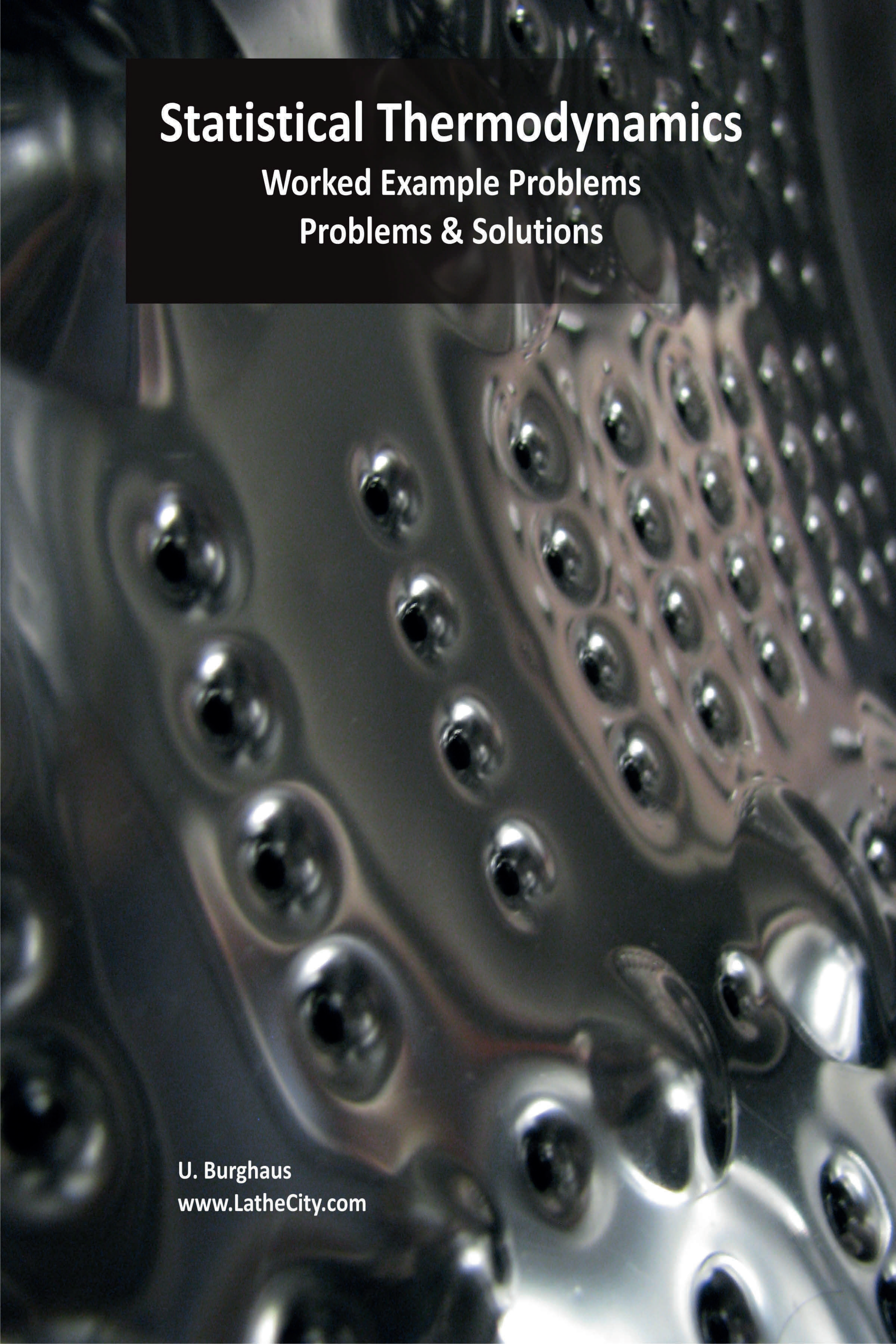


Statistical Thermodynamics

Worked Example Problems

Problems & Solutions

U. Burghaus
www.LatheCity.com

Problems in Statistical Thermodynamics
Worked Example Problems
Problems & Solutions
Uwe Burghaus

ISBN-10: 0991153049
ISBN-13: 978-0-9911530-4-6

sales@LatheCity.com www.LatheCity.com

Preface - in a nut shell …

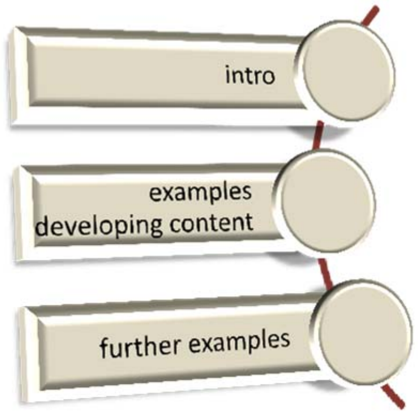
Who may read this book?

This book is primarily written for **(physical) chemistry graduate students**. However, students of physics, engineering, materials science, and biosciences may also find the book relevant to their studies, such as exam preparations, homework, or self-study (see the specific notes given below). In addition, some undergraduate courses do also include statistical thermodynamics. In the US all the college classes are numbered, i.e., I am covering PCHEM 760 for which I have used this textbook. I do not expect deep mathematical background knowledge.

Writing style

I struggled quite a while about what writing style would be the best. As you can already read here, I do use a more or less informal and personal style that appears to me to be the best in a respectful "learning environment" with adults. I got feedback: that's OK. This book is written for students.

How to read this book?



Every subchapter of this book starts with a (very) short introduction section, providing content which is more or less close to a traditional textbook format. However, what follows are examples **(problems/questions and (!) answers)** which will route you through the standard topics of stat thermo (statistical thermo-dynamics). These examples are designed and placed in order to develop the content. Afterwards, more examples ("further problems") may follow. For these "further problems" help is provided, but in some cases no complete solution is given. Work on these "further problems" exercises truly on your own.

The text starts with a primer about math and thermodynamics targeting the needs of stat thermo.

You should be able to read this book as you would read a traditional textbook. However, I recommend getting a standard stat thermo book and read this text perhaps in parallel. (A literature list is given at the end of this book.) This text will be ideal as an exam preparation. In addition, **complete derivations are included** which are often missing in traditional outlines.

Detailed **PowerPoints** on the included CD are also added! Furthermore, the CD includes homework sheets and exams. The solutions for these are only on the instructor CD.

In contrast to traditional stat thermo books, all the derivations are included step-by step and in very detail, keeping the math prerequisites small. You should be able to make it through this book even if you are not a math guru, but start with the math primer even if you may know some of this already. When you have digested this text, it should be much easier reading a traditional and advanced stat thermo book or to survive your graduate stat thermo class. Therefore, perhaps start reading this text the summer before you actually take your stat thermo class. (I am optimistic -☺.)

Bang for your bucks - what to expect from this book?

This book may **not** include all the homework assignments you could not solve by yourself – there are infinite possible stat thermo homework problems. That's also not the point. However, **1)** included are step-by-step outlines of the most important stat thermo topics which are usually included in graduate level classes, i.e., you will now be able to understand these derivations; **2)** standard type problems are discussed as training examples; **3)** example homework and exam sheets are included, again as training exercises. Learning by doing - learning by practicing. The book includes **~600 problems** most of these with complete solutions.

(Sarcastic?) note for physics students

Note this is a statistical thermodynamics book and not a statistical mechanics book. These topics are quite different. This book targets mostly **(physical) chemistry graduate students**. However, being a physicist by training myself, I have to write that it may be a good idea if physicists also would know what thermodynamics is, right? Not just quantum. The chemist's version of thermodynamics (or stat thermo) is usually more applied and more practical which, however, results, in a way, in a deeper understanding. Chemists don't just move around equations. If you read this book, you may, as a physics student, actually "understand" thermodynamics - ☺. I hope that's not offensive – I am a physicist myself. I did start to understand thermodynamics much more deeply myself when teaching it to chemistry students, using perhaps more applied textbooks. Some colleagues also say: "you have to learn thermodynamics three times before really getting it." Another thought: physics students learn a lot about solid state physics. That is a quite tough topic, and I am wondering how to understand lattice vibrations, dispersion curves and whatnot without a pretty solid background in "simple" gas-phase stat thermo, which is mostly described in this book. By the way, I also did add solid state stat thermo.

Materials science students

Materials science is obviously a wide field covering liquids, solids, polymers, ceramics, crystals, amorphous systems, nano-materials, etc. and even biological materials. However, similar to the simple particle-in-a-box problem in quantum, gas-phase stat thermo is simply the basics to all other problems that may benefit from stat thermo. Therefore, this outline will be helpful for materials scientists. In addition, I do include an introduction into solid state stat thermo.

Engineering students

I have seen that even engineering students have to take stat thermo classes, go for it. (I took engineering classes myself.) This text is among the most didactic/pedagogical stat thermo texts currently on the book market, at least in my opinion. However, this is the 1st edition of a rather short book: an example (and solutions) book – it's not a complete and traditional stat thermo textbook. Interdisciplinary research and materials science are booming, meaning that all of us have to look more and more over the edges of our own soup bowls. Go for it if you are an engineering student and perhaps more on the materials science end of the spectrum.

Biology/Biochemistry students

I don't think that many colleges have the requirement for biochemistry students to take a stat thermo class. This may be somewhat of an over-kill; too far out of the discipline. I have seen and used, however, Pchem books for non-chemistry majors that did include a little stat thermo. (I also regularly teach BIOC465.) In that kind of class, there is, however, simply not enough time to develop any significant stat thermo. If you are a biochemist, perhaps try [D/S] (I included a reference list at the end). If you are on the theory side of the biochemistry spectrum (biophysics, bioinorganic chemistry), then, go for it, and read this book.

Why does this book not come in a traditional format?

First of all, this book may be available in a traditional format at some point. However, stat thermo is a specialty topics graduate school class with usually close to zero enrollments. Thus, it's a commercially not too promising endeavor. Frankly, if I offer this also as a standard textbook will depend on sales. Secondly, I believe that an example book leads to a more efficient learning experience; otherwise I would have not embarked on this endeavor. Last but not least, the concept of my micro business is to offer only products which are not easily available elsewhere – that concept so far works well. I have not seen too many stat thermo example books on the book market; traditional textbooks certainly exist by the dozen.

My own background

I am a physical chemist, a surface chemist, and a faculty member at North Dakota State University (NDSU), starting there in 2003. I got most of my own education in Physics in Germany and was born in West-Berlin. After many years of postdoc positions (Italy, US, Italy, Germany …) and a habilitation in Germany (German tenure), I found a position at the Chemistry department at NDSU. More you can find here www.uweburghaus.us. I have written several books, (most about practical engineering topics), and I sell those books in the meanwhile by myself, i.e., I own a part time small business. Details are here: www.LatheCity.com.

Introduction

For instructors

Authors (your colleagues) write books driven by passion, or, as an editor once told me “when you feel the urge..then write this review ..”. However, books are also a commercial enterprise; most of us have nine month salaries. Students purchase books recommended by the instructor. Therefore, selling a book requires to catch the teacher rather than the students; sadly enough, at least in the US, that’s true. Big publishers do this by massive advertisements and free copies mailed to instructors (I have a stack in my office). Does that make the book really good? (I haven’t even had the time to read any of those on my stack.) As you can imagine, a small publisher simply doesn’t have these resources. Therefore, I am afraid, as an instructor you would also need to pay for this textbook. This book will have to sell solely because of its quality. As an **instructor**, if you like, send us an e-mail note when you purchase the book and we add **additional materials** to the CD which are not included on the standard student CD such as additional homework assignments, example syllabus, more exams, solutions to homework and exams, etc. If this is requested after purchasing the book you would need to cover shipping costs.

Here is the “urge”: when I started to prepare my first stat thermo lecture, I encountered that a number of sections of most books I found were close to impossible to read. I am an experimentalist and I was rusty on stat thermo, but that observation holds true for sure for most students. There are a few more didactic texts out there, but these do not completely cover the graduate curriculum. I write this in 2014 and sure, I may have overlooked a pearl. The main issue are **missing derivations** and **missing worked examples**. Therefore, I started to write this textbook basically in preparing my class. Stat thermo is, of course, not a new topic, i.e., you will find similar examples and derivations (probably dating back to Boltzmann himself) anywhere. The difference is the presentation style and that I do not expect a deep math background of your students, which is a safe assumption even in grad school. I realize that this book may be used to complement traditional outlines rather than as a stand-alone book. However, as an instructor **it will save you time** with finding examples, making homework, PowerPoints, preparing the class, and making exams.

That the results are already included here (I provide a free-problems-only version at www.LatheCity.com as well as unsolved exercises are included) do usually not impact exams very much unless you offer open book exams. Also, homework can always be modified a little. (PC word files and PDF files are on the CD.) In addition, students have to find the question or a similar one in this book among many examples, i.e., they naturally start to study problems. That was our (?) goal to begin with. (By the way, as we all recognized, every student has in the meanwhile a copy of the “teacher” solutions book of Atkins, or whatever undergrad book you may use.) This text will, however, help your students and will save yourself a lot of time.

Together with this book, I do also offer **PowerPoints** for instructors or for self-studying students. The PowerPoints on the instructor CD include typed derivations, which alone will already save you a lot of time. Why do instructors use a book? Instructors use books mainly to save time in the class preparation and presentation. Am I correct here? **You will save time with this text.**

For instructors (& students) - classroom observations

Over-explaining things and providing every derivation in detail; is that a good idea? Well, perhaps not for every student, but what is the alternative? Realistically? Assume, a student gets stuck in a stat thermo chapter - and they will.

A good student will spend hours and hours going through complex derivations by him-/her-self. Really? Do you believe that? Even in grad school, they have to take a few classes per semester at the same time, research, TA-ing undergrads, etc. - all of that at the same time. That training, *if actually done*, makes the student better. Yes, I would believe that, but do they realistically spend that kind of time on every class? You provide all the gaps in class. Well, perhaps, but why do you then recommend a textbook that only the very best students may read? Just between us – you also will get stuck in traditional stat thermo books … spending hours and hours …

A better but “lazy” student will jump over the section or derivation he/she could not understand and may just memorize the result. Fine, perhaps. Good enough, perhaps. But, the beauty is often in the details, which he/she will never grasp. Also, students considering themselves as “better students” are often not really that good. “I can do this if I have to … I just skip over this now…” They usually wake up after the first midterm.

A weak student will likely be completely frustrated and lost since that student barely understands the concepts and has no clue how to fill-in the gaps of derivations. Thus, not understanding the equations and concepts is the result and the class was useless for that student. That student may survive the exams, somehow, but…he/she will likely hate Pchem afterwards once more. Do we want that to happen?

Explaining things properly and in detail is in my opinion better than an old style textbook which provides a kind of summary, but leaves the “obvious” details to the reader/student.

Balancing the presentation… The PowerPoints which come together with that book include **“in-class homework”** Aehhhhhhhh?

What nonsense is that? I am not a teaching theoretician, but perhaps have a look at [C & EN News], the ACS membership journal, [June 2, 2014 issue, page 31]. They call it **“active learning”,** the latest teaching buzz word, meaning in plain English, things you have done by yourself stick much better to your brain. Well, one doesn’t need to be an educational expert to realize that. However, quantitatively, according to research, statistical analysis of tests they did run: “10% minimum classroom time needed to devote to active learning to see an effect” and “36% drop in student failure rates” due to active learning. They usually look at undergraduate classes, but I guess also for a graduate class it may be a good idea to try this out. Therefore, you see the “in-class homework” in the PowerPoints. (The results can be found in this book.) In addition, the PowerPoints include “self-study” slides and some problems in the notes section of the PowerPoints. Even if most students realistically won’t work on this, it does show what the expectations are. There is also another concept, “assessment based learning”, which all teachers embrace. (In plain English, students work only if they get a good grade for it. That holds true for most graduate students, too.) If they want to pass the exams, it may be a good idea to practice solving problems. Offering bonus homework points for the “in-class homework/ independent study” may be a motivation.

Try by yourself

Literature (for example):

[Wie] Carl E. Wieman, “Large-scale comparison of science teaching methods sends clear message”, PNAS 2014 (111) 8319–8320.

[C & EN] Chemical and Engineering News, ACS membership journal, June 2, 2014 issue, page 31.

PowerPoints included – self-study class

A CD with PowerPoints comes with that book. Please note that the copyright note also applies to these PowerPoints and all documents on the CD. The PowerPoints include a complete class for self-studying and/or over-worked instructors. I did indeed use these PowerPoints in my own classes, i.e., these presentations are student tested. However, consider the PowerPoints as summaries. In most cases these are not complete PowerPoint classes. I do usually use a combination of white-board and PowerPoints for my classes. Assisting instructors, derivations are given as separate pdf files which are linked to the slides. That is, PDF files replace the white board. That will save instructors class preparation time too. Use those typed PDF files if you need to speed up in class, or use the white board to slow down the presentation. The student PowerPoints include the problem numbers instead of PDF files, i.e., all derivations are given as problems in this book.

Voice recordings for self-studying students are not available, yet. However, the PowerPoints include detailed text sections as notes. I don't sell the PowerPoints separately, mostly for formal reasons: separate ISBN numbers would be required, separate copyright registration, etc. And, one does need the printed book anyway. Please note that e-mailing the PowerPoints to your students would violate copyrights, sorry.

Where to find this book and PowerPoints?

Look around at Amazon, eBay, or go to factory direct www.LatheCity.com. Constructive comments from anyone are welcome. Write to sales@lathecity.com if you find typos, mistakes, or want to chat. A problems only version of this book is available for free at www.LatheCity.com We provide a free CD with additional materials to instructors. Write to sales@lathecity.com and provide some proof that you are an instructor and not a student.

Instructor CD

As an **instructor**, if you like, send us an e-mail note when you purchase the book and we add **additional materials** to the CD which are not included on the standard student CD such as additional homework assignments, example syllabus, more exams, solutions to homework and exams, solutions to in-class homework, instructor PowerPoint versions with embedded PDF files of derivations, etc. If this is requested after purchasing the book you would need to cover shipping costs. We don’t provide free prints or instructor CDs without a book purchase.

Conflicts of …

All classes of all instructors are student tested. However, this text and the PowerPoints were written at my home office during my free time without utilizing any university resources, besides that I also taught a stat thermo class at a college. Actually, I do strictly not recommend my own books in my classes, avoiding any conflict of interest issues. Most of my colleagues don’t even know that I am writing books and have a part-time small business (=hobby).

Disclaimer

Trademarks are property of their respective owners. Copyrights on photos are property of their respective owners. Copyright exceptions are detailed on the acknowledgement page at the end of this book. Any legal action brought against Uwe Burghaus/LatheCity shall be tried in the State of North Dakota in Fargo, USA. In no event shall LatheCity’s liability exceed the purchase price paid for our products. We do not warrant that information provided is free of mistakes. Web addresses are given without any warranty or guarantee, web sites may be infected by a computer virus and/or may not provide the best service. Neither the author nor publisher shall be liable for damage arising herefrom.

List of content

I.-III. **Introduction**	Math, thermo, quantum	
IV.-VIII. **Basics**	Ensembles	Canonical, grand canonical, microcanonical, fluctuations, laws, postulates
	Statistics	Boltzmann, partition functions, Bose-Einstein, Fermi-Dirac
X. & XIII. **Applications**	Gas-phase	Monoatomic, diatomic, polyatomic, Maxwell-Boltzmann, Equilibrium, Dynamics
	Solid state	Einstein, Debye models
	Liquids	
XI. **Quantum statistics**	Electron gas, photon gas, Bose-Einstein condensation	

List of content

Introduction to stat thermo

Basics

Applications

Quantum statistics

Misc.

PowerPoints on included CD - list of classes

Instructors-US/Canada. Most graduate classes in the US are usually and officially so-called 4- credit classes (4x50 min/week). However, often these are effectively thought as 3-credit classes. Now, a term has usually 15 weeks, i.e., 15x3 = 45 classes, minus exams and holidays (subtract 5-10 classes for that). The PowerPoints include so far ~36 classes, i.e., about enough to cover a typical stat thermo graduate class (in the US). Most of the PowerPoints (one per class) are fairly packed and may be broken up into two classes, depending on teaching style. I sometimes also did run graduate classes as double-classes, i.e., we meet only twice a week (2x50 min + 1x~50 min) using the longer class for more interactive presentations ("in-class homework"). For example, one may ask students to present examples by themselves (for e.g. homework credit), provide regularly a review class (with examples), or offer questions/answers classes, etc. In summary, the PowerPoints are sufficient to cover a typical stat thermo class in chemistry. Over time, I may add some more special topics or further training sections. If you think that the PowerPoints are destructive to your students, then order a class set of books without CDs. In addition, we can customize the CD content to some extent.

Instructors-Europe. For example, in Germany all classes are usually double-lectures, commonly 2x(2x45) min, i.e., the class content is similar to the US, the format is a little different. Thus, the same PowerPoints should work. However, "graduate classes" do not really exist, i.e., at least at my time, all required classes had to be finished before actually starting to work on a Dr. thesis, which was purely a research degree. Thus, "undergraduates" may take this class in Europe. I am not certain about other European countries; Italy and east Europe appear to use a format similar to the German system. UK is probably closer to US style. In summary, I believe that the structure I have chosen here will work fine mostly everywhere and the PowerPoints can certainly be modified, which will still safe instructors a lot of time. Certainly we offer and ship our products internationally as US law permits.

Self-studying students. If you self-study stat thermo then each PowerPoint covers one class and that's what I would recommend to digest in one sitting. In this text, the references to classes refer to these PowerPoint classes. One PowerPoint usually covers about one (shorter) chapter in a traditional stat thermo textbook. Some more extensive topics are broken up in more than one class (part A, B, …). **Run the PowerPoint, read the notes section, work on the in-class problems, and work on the "further examples section" in this textbook. The PowerPoint will route you through the book, i.e., follow/read the "links attached".** I encourage you, however, to read more than on textbook in parallel. No textbook or PowerPoint can replace a real class. (Although on-line classes are booming in the US, voice recordings are not yet available. Sorry.) As a grad student you approach real live, correct? Thus, use more than one source of information.

PowerPoints, for stat thermo? Really? Yes, it works also for stat thermo and here they are:

Part I. Introduction (5 classes)

- **1)** Intro, what is stat thermo, syllabus, textbooks selection
- **2)** Review of thermodynamics (Primer)
- **3A)** Review of math for stat thermo
- **3B)** Review of math for stat thermos – part II
- **4)** Review of quantum mechanics

■ *Basics*

Part II. Ensembles (7 classes)

- **5A)** Canonical ensemble, most likely distribution, Boltzmann equation
- **5B)** Canonical ensemble and thermodynamics
- **6A)** Grand canonical ensemble
- **6B)** Properties of the grand canonical ensemble
- **7)** Microcanonical ensemble
- **8)** Fluctuations
- **9)** Equivalence of ensembles

Part III. Thermodynamic laws (2 classes)

- **10)** Stat thermo version of the 2nd law
- **11)** The 3rd law of stat thermo

Part IV. Classification of statistical ensembles (4 classes)

- **12a)** Boltzmann (classical) statistics
- **12b)** Properties of the Boltzmann statistics
- **12c)** Practicing Boltzmann – examples

13) Basics of Fermi-Dirac and Bose-Einstein statistics (quantum statistics)

■ *Applications*

Part V. Applications (13 classes)

- **14A)** Monoatomic gas
- **14B)** Stat thermo properties of the monoatomic gas
- **15)** Einstein model, monoatomic crystals, heat capacity of solids
- **16)** Debye model, monoatomic crystals, heat capacity of solids
- **17)** Maxwell-Boltzmann speed distribution
- **18A)** Diatomic ideal gas (translations, vibrations)
- **18B)** Diatomic ideal gas (rotations)
- **18C)** Diatomic ideal gas (thermodynamics functions, symmetries)
- **19)** Polyatomic gas
- **20)** Chemical equilibrium
- **21)** Two level systems (practicing project)
- **22A)** Dynamics – potential energy surfaces
- **22B)** Dynamics – transition state theory

■ *Quantum statistics*

Part VI. Quantum statistics (3 classes)

- **23A)** FD gas (electron gas)
- **23B)** Phonon gas (Blackbody radiation)
- **23C)** Bose-Einstein condensation

■ *Misc.*

Part VII. Special topics (1 class)

- **24)** How are liquids described in stat thermo?

> *Yes, using PowerPoints of somebody else is like handwritten notes from a colleague. But, not quite. The PowerPoints you get for free here will save you a lot of time. (Did you get a classroom with large enough white boards for a stat thermo class? Use PowerPoints.)*

Explanation of symbols and abbreviations

One of the challenges in stat thermo is to understand what the symbols actually denote. Different textbooks use different symbols. Given here are symbols used in the following and those which may be used in other textbooks.

p:	In stat thermo a small p is often used for the pressure (not the momentum)
P:	Thermodynamic pressure (capital P)
V:	Volume
T:	Temperature
S:	Entropy
S_t:	Total entropy
U:	Internal energy, in stat thermo typically assigned to the symbol E rather than U
E:	Energy or internal energy
$\overline{E} = \langle E \rangle$:	Averaged energy
ε:	Energy (of a single particle, “molecular” energies)
E_t:	Total energy
H:	Enthalpy
G:	Gibbs energy
μ:	Chemical potential
A:	“Arbeits”function (German), Helmholtz (free) energy, sometimes F in English textbooks
F:	Gibbs (free) energy, in some books F is apparently the Helmholtz energy
N:	Particle number, also used as an index for grand canonical ensemble ([Hill] uses something that looks like Π as the particle number.)
n:	Also (n) is usually a short hand notation for a distribution. (n)n_j or (n)n_0,n_1,n_3,…n_j. The n_j are the number of species which have energy E_j. Therefore these n are also the degeneracy of states or sometimes called occupation number. The n describe how the available energy states E_j are populated. Therefore, this is a distribution.
n^*:	Most likely configuration, n can also just denote the number of moles
a_j:	In some books used to denote a distribution, see n

Ω:	Total degeneracy of states associated with a distribution. Statistically this is the weight of the distribution. Also often denoted as w.
P_j:	Probability that the molecule is in energy state E_j
j,i:	Running index, usually the number of subsystems of the ensemble rather than the particle number
Q:	Partition function, sum over states, German: Zustandssumme, that symbol is usually for a canonical ensemble, large Q macroscopic system, small q single molecule
q:	molecular partition function such as q_{trans} or q_{rot} for translations or rotations, can also be the heat
q_m:	molar molecular partition function, $q_m = q/n$, n number of moles
Z:	Partition function, sum over states, German: Zustandssumme
Ξ :	Partition function, sum over states, German: Zustandssumme, usually for a grand canonical ensemble
w:	Total degeneracy of states associated with a distribution. Statistically this is the weight of the distribution. Also often denoted as Ω.
q_{rev}:	Heat calculated for a reversible pathway. That's done when calculating the entropy since the entropy is a state function, but heat is not.
k:	Boltzmann constant, k = 1.3806488×10^{-23} J/K = 8.6173324×10^{-5} eV/K
λ :	$\lambda = e^{\beta\mu}$, see quantum statistics and/or grand canonical ensemble, can also be a wavelength
β :	$\beta = \frac{1}{kT}$
n!:	Factorial, 3!=1*2*3; 0!=1
$\sum$:	Summation $\sum_{j=1}^{3} a_j = a_1 + a_2 + a_3$
$\prod$:	Product $\prod_{j=1}^{3} a_j = a_1 * a_2 * a_3$; in [Hill] a similar symbol is used for the total number of systems of an ensemble (great idea?)
∂ :	(partial) derivative
d:	total derivative
Δ:	delta, difference $\Delta = x_1 - x_2$
≈, ~:	Approximately equal

O(): To the order of, for example, $O(N^2)$ the term is of the order of the square of the particle number, also called “big O-notation”

ΔH_f : Heat of fusion (solid→liquid) as constant temperature

ΔH_V : Heat of vaporization (liquid→gas) as constant temperature

T_b: Boiling point

T_f: Freezing point

$\widehat{H}_1; f_1; E_r$: denotes the Hamilton operator, the eigenfunction, and the energy eigenvalue, the index r may denote a particle number or a set of coordinates (x, y, z)

m_s: spin orientation quantum number

n, l, m_l: principal quantum number, angular momentum quantum number, and angular momentum orientation (magnetic) quantum number; unfortunately similar symbols are also used for other parameters

$\phi(\varepsilon)$: density of states as a function of energy (see problem 110)

L: Avogadro constant, R = Lk; nL = N; nR = Nk

B: Boltzmann statistics, same as MB

BE: Bose-Einstein statistics

FD: Fermi-Dirac statistics

LT: Legendre transformation

MB: Maxwell-Boltzmann statistics

QS: Quantum statistics

Quantum: Quantum mechanics

Stat thermo: Statistical thermodynamics (kind of lab slang, I guess)

Reference chart of common symbols

I encourage you to work with more than one textbook, in particular regarding stat thermo and when self-studying the subject. (I do have a few Biochem books, as a physicist - ☺). The problem that then arises: different texts use different symbols for the same thing which, in the beginning, can be very confusing. Topping this of, some books doesn't have a list with explanations of the symbols used – simply sloppy writing style for my taste. (Why should we make it easy for the reader to read the book … never mind.) Therefore, here is a reference chart. Note that some of the "symbols" indeed require a rather complex discussion which depends on the exact application.

$\bar{E}, <E>$	Averaged energy
U, E, ε	(Internal) energy, ε may describe "molecular energies" such as translation, rotations, etc. whereas E usually is the total energy or a "macroscopic energy", or the total energy consistent with a configuration
A, F	Helmholtz (free) energy, "Arbeits"function (German)
n, a, n_i, a_i	Distribution, degeneracy of states, also (n) is usually a short hand notation for a distribution. $(n)n_j$ or $(n)n_0,n_1,n_3,\ldots n_j$. The n_j are the number of species which have energy E_j (or ε_j). Therefore these n are also the degeneracy of states or sometimes called occupation number. The n describe how the available energy states E_j are populated. Therefore, this is a distribution.
Ω, w	Total degeneracy of states associated with a distribution. Statistically this is the weight of the distribution.
Z, Q, q, Ξ	Partition function, sum over states, different symbols are used for different ensembles, large symbols can refer to the total or macroscopic partition function. Z is used for historic reasons (German: Zustandssumme)
$\sum_{N,j} whatever_j =$ $\sum_j whatever_j(N)$ $= \sum_N \sum_j whatever_{j,N}$	Usually more or less the same thing, see grand canonical ensemble
N, Π	Total particle number.

Mathematical formulas

formula	example
n!=1*2*3…*n	3!=1*2*3; 0!=1;
$\sum_{j=1}^{3} a_j = a_1 + a_2 + a_3$ $\sum_{j=1}^{N} f(i) = f(1) + f(2) + \ldots + f(n)$ $\sum_{j=1}^{N} c = Nc\ ; \sum_{i=m}^{n} i = n + i - m$ $\sum_{i=1}^{N} 1 = N + 1 - 1 = N$	Yes, I hope you know that. C and N are constant, i and j are running indicees
$\prod_{j=1}^{3} a_j = a_1 * a_2 * a_3$	
$\lim_{x \to \infty} [1 + \frac{a}{x}]^x = e^a$	
$\sum_{j=0}^{\infty} x^j = (1 - x)^{-1}$	See PowerPoint class 15, 18 (example problem e.g. 323)
$\overline{(x - \overline{x})^2} = x^2 - \overline{x}^2$	Used to calculate fluctuations, see problem 75
$\sum_{i=1}^{m} \sum_{j=1}^{n} x_i x_j = (\sum_{i=1}^{m} x_i)(\sum_{j=1}^{n} y_i)$	See problem 27
$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}$	Taylor expansion of exponential function, see problem 73
$\frac{\partial g(f(x))}{\partial x} = f'(x) g'(x)$	That chain rule is used very often and can be tricky to apply, see e.g. problems 10, 15, 69
$e^{(\sum_j n_j)} = \prod_{j}^{N} e^{n_j}\ ;$ $\sum_{s}^{t} \ln f(n) = \ln \prod_{s}^{t} f(n)$	See FD and BE statistics, see e.g. problem 29, 140

formula	example
ln(1+x)~x for small x	$\ln(\Xi) = \pm\sum_k \ln(1+\lambda e^{-\beta\varepsilon_k}) \to \lambda q$, problem 332
$\lim_{x\to-\infty} e^x = 0$; $\lim_{x\to 0+} \ln(x) = -\infty$	See problem 340, 388
$\lim_{x\to 0\pm} 1/x = \pm\infty$;	
$\int_0^\infty e^{-\alpha x^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$	Gaussian integral, appears e.g. in treatment of the ideal gas, see problem 356, proof can be found e.g. here http://en.wikipedia.org/wiki/Gauss_Integral
$\ln(x!) \approx x\ln(x) - x$	Stirling's formula

For special integrals see also:
http://en.wikipedia.org/wiki/List_of_integrals_of_exponential_functions
http://en.wikipedia.org/wiki/Debye_function

Boltzmann constant	k = 1.3806488×10^{-23} J/K = 8.6173324×10^{-5} eV/K
Planck's constant	h = 6.62606957×10^{-34} Js = $4.135667516\times10^{-15}$ eV/s
Speed of light	c = 2.99×10^{8} m/s hc = 1.98644568×10^{-25} J·m
Avogadro number	$N_A = 6.022\text{x}10^{23}$

Probability theory formulas

$N*(N-1)*(N-2)...2*1=N!$	Number of permutations of N distinguishable species. The 1st species is selected from N species. The 2nd from (N-1) species, etc.
$\frac{N!}{\prod_{i=1}^{B} n_i}$	Number of permutations of N distinguishable species placed in n_i boxes (i = 1..B). See Boltzmann law, class 5A. For indistinguishable objects, divide by N! (see class 12B, corrected Boltzmann statistics).
$\frac{g_i!}{(g_i-N)!N!}$	Number of permutations of N indistinguishable species placed in g_i numbered boxes with no more than one species per box ($g_i = 0$ or $g_i = 1$, see Pauli principle). See Fermi-Dirac statistics, class 13 and class 3b. (For distinguishable species remove 1/N! correction.)
$\frac{(g_i+N-1)!}{(g_i-1)!N!}$	Same as above, but without a restriction on the number of species per box ($g_i = 0, 1, \ldots$). See Bose-Einstein statistics, class 13 and class 3b.

Plausibility explanations/derivations and more equations can be found e.g. in [May]. [E/R] includes a pedagogical outline about probability theory tailored towards pchem/stat thermo applications.

Thermodynamics formulas

$$H = U + PV$$

$$A = U - TS$$

$$G = H - TS = U + PV - TS$$

Total derivatives

$$dU = TdS - PdV$$

$$dH = TdS - PdV + PdV + VdP = TdS + VdP$$

$$dA = TdS - PdV - TdS - SdT = -SdT - PdV$$

$$dG = TdS + VdP - TdS - SdT = -SdT + VdP$$

Partial derivatives

$$(\frac{\partial G}{\partial T})_P = -S; (\frac{\partial G}{\partial P})_T = V \qquad (\frac{\partial U}{\partial S})_V = T; (\frac{\partial U}{\partial V})_S = -P$$

$$(\frac{\partial A}{\partial T})_V = -S; (\frac{\partial A}{\partial V})_T = -P \qquad (\frac{\partial H}{\partial S})_P = T; (\frac{\partial H}{\partial P})_S = V$$

Maxwell relationships

$$(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V = \frac{\beta}{\kappa} \qquad -(\frac{\partial T}{\partial P})_S = (\frac{\partial V}{\partial S})_P$$

$$-(\frac{\partial S}{\partial P})_T = (\frac{\partial V}{\partial T})_P = V\beta \qquad (\frac{\partial T}{\partial V})_S = -(\frac{\partial P}{\partial S})_V$$

Here β and κ are materials constants

Other useful equations

SdT – Vdp + Ndμ = 0 (Gibbs-Duhem)

Sign definition in thermodynamics:	
Work done by the system on the surroundings	**-**
Work done on the system by the surroundings	**+**
Heat adsorbed by the system from the surroundings	**+**
Heat adsorbed by the surroundings from the system	**-**

Stat thermo formulas

Stat thermo postulates *(class 1, problem 126)*

> The time average of a mechanical variable in a thermodynamics system equals the ensemble average in the limit of infinite number of systems of the ensemble that replicate the thermodynamic system.

And

> The systems of the ensemble are distributed uniformly over the allowed quantum states consistent with N, V, and E.

Stat thermo laws *(class 10, problems 230-252)*

1st $E_t = \sum_j n_j E_j$ (usually not stated as such)

2nd $\Delta S = S_f - S_i = k \ln \frac{\Omega_i}{\Omega_f} > 0$

3rd $\lim_{T \to 0K} [\ln(\Omega)] = \ln(\Omega_0) = 0$

Constrains

	Grand canonical ensemble	**Canonical ensemble**
Energy conservation	$\sum_{j,N} n_j(N) E_j(N,V) = E_t$	$\sum_j n_j E_j = E_t$
Particle # conservation	$\sum_{j,N} n_j(N) N = N_t$	N_t
Sub-system conservation	$\sum_{j,N} n_j(N) = \Pi$	$\sum_j n_j = \Pi$
Lagrange multipliers	α, β, γ	α, β

Boltzmann law *(class 5A, problems 130-153)*

$$\frac{n_i}{n_j} = e^{-(E_i - E_j)/kT}; \quad \Omega_t(n) = \frac{N!}{\prod_j n_j!}; \; P_j = \frac{\bar{n}_j}{\Pi} = \frac{\sum_j \Omega(n) n_j(n)}{\sum_j \Omega(n)}$$

Boltzmann distribution *(class 5B, problems 130-153)*

$n_j^* = \Pi e^{-\alpha-\beta E_j}$ (most like population numbers);

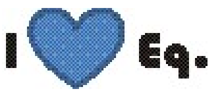
$e^{-\alpha} = \sum_j e^{-\beta E_j} ; \beta = \frac{1}{kT}$

(see also canonical ensemble and Boltzmann law)

Partition functions of ensembles *(class 12C, problems 284-304)*

Distinguishable particles $Q = q_a q_b q_c$; $q_a = \sum_j e^{-\varepsilon_j^a / kT}$;

$Q = q_a q_b q_c = q^N$; $q = q_a = q_b = \ldots = \sum_j e^{-\varepsilon_j / kT}$



Indistinguishable particles $Q = \frac{q^N}{N!}$

$Q(N,V,T) = \sum_j e^{-E_j(N,V)/kT}$ (Boltzmann)

$\Xi = \prod_k \sum_{n_k=0}^{n_k^{\max}} (\lambda e^{-\beta\varepsilon_k})^{n_k}$ (General case); $\lambda = e^{\beta\mu}$; $\beta = 1/kT$

$\Xi_{FD} = \prod_k [1 + (\lambda e^{-\beta\varepsilon_k})^1]$ (Fermi-Dirac)

$\Xi_{BE} = \prod_k (1 - \lambda e^{-\beta\varepsilon_k})^{-1}$ (Bose-Einstein)

$\Xi_{\substack{FD \\ BE}} = \prod_k (1 \pm \lambda e^{-\beta\varepsilon_k})^{\pm 1}$ (FD/BE)

Partition functions

Diatomic/polyatomic $q = q_{trans} q_{vib} q_{rot} q_{electronic} q_{nuclear}$ (class 18)

$q_{electronic} = \sum_i \Omega_i e^{-\varepsilon_i / kT}$; $q_{nuclear} = 1$;)

Translations $q_{kinetic} = (\frac{2\pi m}{h^2} kT)^{3/2} V = q_t$ (particle-in-a-box, class 14)

Vibrations $q = \frac{e^{-\Theta/2T}}{1 - e^{-\Theta/T}}$ (harmonic oscillator, Einstein crystal, class 15)

Canonical ensemble $Q(N,V,T)$ *(class 5A/B, problems 130-153)*

Characteristic function dA = -SdT – pdV + μdN

Probability
$$P_j = \frac{\overline{n}_j}{\Pi} = \frac{\sum_j \Omega(n) n_j(n)}{\sum_j \Omega(n)}$$

$$\Omega_t(n) = \frac{\Pi!}{\prod_j n_j!}$$

$$P_j(N,V,T) = \frac{e^{-E_j(N,V)/kT}}{Q(N,V,T)}$$
$$Q(N,V,T) = \sum_j e^{-E_j(N,V)/kT}$$

Helmholtz free energy
$$A = -kT\ln(Q)$$

Entropy
$$S = k\ln(Q) + kT\frac{\partial \ln(Q)}{\partial T}|_{N,V}$$

Pressure
$$p = -\frac{\partial A}{\partial V}|_{T,N} = kT\frac{\partial \ln(Q)}{\partial V}|_{N,T}$$

Chemical potential
$$\mu = \frac{\partial A}{\partial N_i}|_{T,V,N\neq N_i} = -kT\frac{\partial \ln(Q)}{\partial V}|_{V,T}$$

Internal energy
$$U = E = \overline{E} = kT^2\left(\frac{\partial \ln(Q)}{\partial T}\right)_{N,V}$$

Fluctuations
$$\sigma_E^2 = kT^2 C_p\ ;\ \sigma_p^2 = kT\left[\frac{\partial \overline{p}_i}{\partial V} - \frac{\partial p_i}{\partial V}\right]$$

Energy
$$\overline{E} = kT^2\frac{\partial \ln(Q)}{\partial T}$$ (Problem 141a)

Grand Canonical ensemble $\Xi(V,T,\mu)$ *(class 6A/B, problems 154-187)*

Characteristic function $d(pV) = SdT + Nd\mu + pdV$

Partition function

$$\Xi(V,T,\mu) = \sum_{j,N} e^{-E_j(N,V)/kT} e^{-N\mu/kT} = \sum_N [e^{-E_j(N,V)/kT} \sum_j e^{-N\mu/kT}]$$

$$= \sum_N Qe^{-N\mu/kT}$$

Probability

$$P_j = \frac{\overline{n}_j(N)}{\Pi} = \frac{n_j^*(N)}{\Pi} = \frac{e^{-\beta E_j(N,V)}e^{-\gamma N}}{\sum_{i,N'} e^{-\beta E_i(N',V)}e^{-\gamma N'}} = \frac{e^{-\beta E_j(N,V)}e^{-\gamma N}}{\Xi}$$

$$\gamma = -\mu\beta = -\frac{\mu}{kT}$$

Number of possible states $\Omega_t(n) = \dfrac{\sum_{j,N} n_j(N)!}{\prod_{j,N} n_j(N)!}$

Pressure $pV = kT\ln(\Xi)\,;\; p = kT(\dfrac{\partial \ln(\Xi)}{\partial V})\Big|_{\mu,T}$

Entropy

$$S = k\ln(\Xi) + kT\frac{\partial \ln(\Xi)}{\partial T}|_{\mu,T} = -k\sum_j P_j(N)\ln[P_j(N)]$$

Fluctuations $\sigma_N^2 = kT(\dfrac{\partial \overline{N}}{\partial \mu})_{V,T} = \dfrac{\overline{N}^2 kT\kappa}{V}$

Micro Canonical ensemble $\Omega(N,V,E)$ *(class 7, problems 188-204)*

Entropy $dS = \dfrac{1}{T}dE + \dfrac{p}{T}dV - \dfrac{\mu}{T}dN$

Pressure $\dfrac{p}{kT} = \dfrac{\partial \ln(\Omega)}{\partial E}|_{N,E}\,;\, \dfrac{1}{kT} = \dfrac{\partial \ln(\Omega)}{\partial E}|_{N,V}$

Chemical potential $\dfrac{\mu}{kT} = -\dfrac{\partial \ln(\Omega)}{\partial N}|_{V,E}$

Boltzmann equation $S = k\ln(\Omega)$

"Gibbs" ensemble $\Delta(N,T,P)$ *(problems 222, 223, 227, 229)*

Characteristic function G = E – TS + pV; dG = -SdT + Vdp + μdN;
$G = -kT\ln(\Delta)$

Partition function $\Delta = \sum_V \sum_j e^{-E_j/kT - pV/kT}$;

$$\Delta = [\frac{(kT)^{5/2}(2\pi m)^{3/2}}{ph^3}]^N = \mathrm{X}^N$$ (for ideal gas)

Fluctuations $\sigma_H^2 = kT^2 C_p$

Fluctuations (class 8A/B, problems 205-229)

Canonical ensemble energy $\sigma_E^2 = kT^2 C_p$

Grand canonical ensemble energy $\sigma_E^2 = kT(\frac{\partial \overline{N}}{\partial \mu})_{V,T} = \frac{\overline{N}^2 kT\kappa}{V}$

Average of a distribution function

$\overline{g}(x) = \frac{\sum_i \mathrm{g_i} f_i}{\sum_i f_i}$ for example

$$P_j = \frac{\overline{\mathrm{n}}_\mathrm{j}}{N} = \frac{1}{N}\frac{\sum_j w_j n_j}{\sum_j w_j} = \frac{1}{N}\frac{\sum_j w_j(n) n_j(n)}{\sum_j w_j(n)}$$

Pressure $\overline{p} = \sum_i \mathrm{p_i} P_i = \sum_i (\frac{\partial \mathrm{E_j}}{\partial \mathrm{V}}) P_i =_i \frac{\sum_i (\frac{\partial \mathrm{E_j}}{\partial \mathrm{V}}) f_i}{\sum_i f_i} = \frac{\sum_i (\frac{\partial \mathrm{E_j}}{\partial \mathrm{V}}) e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$

with $P_i = \frac{f_i}{\sum_i f_i} = \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$

Energy $\overline{E} = \sum_i E_i P_i = \frac{\sum_i \mathrm{E_i} e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$

Density of states for 3D particle in box

For an electron/photon gas multiply by fator of two for degeneracy of electron spin/polarization of wave.

$$\omega(\varepsilon)d\varepsilon = \frac{\pi}{4}(\frac{8m}{h^2})^{3/2}V\varepsilon^{1/2}d\varepsilon = 2\pi(\frac{2m}{h^2})^{3/2}V\varepsilon^{1/2}d\varepsilon =$$

$$2\pi(\frac{1}{\pi\hbar^2})^3 V(2m)^{3/2}\varepsilon^{1/2}d\varepsilon$$ *(class 4, problems 110-111)*

$$g(\nu)d\nu = \frac{4\pi}{c^3}V\nu^2 d\nu$$

Monoatomic ideal gas (particle-in-box) *(class 14A/B, problems 354-375)*

Partition function $q_{kinetic} = (\frac{2\pi m}{h^2}kT)^{3/2}V$

Thermal de Broglie wavelength $\Lambda = \frac{h}{p} = \frac{h}{(2\pi mkT)^{1/2}}$

Helmholtz energy

$$A(N,V,T) = -kT\ln(Q) = -NkT\ln\{(\frac{2\pi mkT}{h^2})^{3/2}\frac{Ve}{N}\}$$

Gibbs energy

$$G = -kT\ln(Q) + NkT = -kTN\ln(\frac{q}{N}); G_m = -RT\ln(\frac{q_m}{L})$$

Pressure

$$p = NkT(\frac{\partial\ln(q)}{\partial V})_T = NkT\frac{1}{V} = \frac{2}{3}\rho ;(\rho = U/V)$$

Energy $E = NkT^2(\frac{\partial\ln(q)}{\partial T})_V = \frac{3}{2}NkT$

Heat capacity $C_V = (\frac{\partial E}{\partial T})_{V,N} = \frac{3}{2}Nk$

Entropy $S = Nk\{\ln[(\frac{2\pi mkT}{h^2})^{3/2}\frac{Ve^{5/2}}{N}]\}$

Chemical potential $\mu = -kT\ln\{(\frac{2\pi mkT}{h^2})^{3/2}\frac{V}{N}\}$

Diatomic ideal gas *(class 18A-C, problems 426-473)*

Key $X_{total} : X_{translations} ; X_{rotations} ; X_{vibrations} ; X_{electronic}$

Partition function

$$q_{total} = (\frac{2\pi mkT}{h^2})^{3/2} V \frac{8\pi^2 IkT}{\sigma h^2} \frac{e^{-\beta h\nu/2}}{(1-e^{-\beta h\nu})} \omega_{e_1} e^{D_e/kT}$$

Partition function- high temperature limit

$$q_V = e^{-\beta h\nu/2} \sum_{n=0}^{\infty} e^{-\beta h\nu_n/2} \to e^{-\beta h\nu/2} \int_0^{\infty} e^{-\beta h\nu_n/2} = \frac{kT}{h\nu} = \frac{T}{\Theta_v};$$

$$q_{rot} = \frac{T}{\Theta_r} = \frac{8\pi^2 IkT}{h^2}$$

Heat capacity $$C_{total} = \frac{3}{2}nR + nR + nR(\frac{\Theta_v}{T})^2 \frac{e^{\Theta_v/T}}{(e^{\Theta_v/T}-1)^2}$$

Helmholtz energy

$$A_{total} = -NkT\{\ln[\frac{2\pi(m_1+m_2)kT}{h^2}]^{3/2} \frac{Ve}{N} + \ln[\frac{8\pi^2 IkT}{\sigma h^2}] - \frac{h\nu}{2kT}$$

$$-\ln[1-e^{h\nu/kT}] + \frac{D_e}{kT} + \ln[\omega_{e_1}]\}$$

Internal energy

$$E_{total} = NkT\{\frac{3}{2} + \frac{2}{2} + \frac{h\nu}{2kT} + \frac{h\nu/kT}{e^{h\nu/kT}-1} - \frac{D_e}{kT}\}$$

Entropy

$$S_{total} = NkT\{\ln[\frac{2\pi(m_1+m_2)kT}{h^2}]^{3/2} \frac{Ve^{5/2}}{N} + \ln[\frac{8\pi^2 IkTe}{\sigma h^2}]$$

$$+ \frac{h\nu/kT}{e^{h\nu/kT}-1} - \ln[1-e^{h\nu/kT}] + \ln[\omega_{e_1}]\}$$

Pressure $$p = NkT(\frac{\partial \ln(q)}{\partial V})_T = NkT\frac{1}{V}$$

Chemical potential $$F = NkT\{\frac{\mu^0}{kT} + \ln p\}$$

$$\mu^0 = kT\{-\ln[\frac{2\pi(m_1+m_2)kT}{h^2}]^{3/2} kT - \ln[\frac{8\pi^2 IkT}{\sigma h^2}] +$$

$$+\frac{h\nu}{2kT} + \ln[1-e^{h\nu/kT}] - \frac{D_e}{kT} - \ln[\omega_{e_1}]\}$$

Polyatomic ideal gas *(class 19, problems 474-492)*

	Vibrations	**Rotations**	
	$x=3n-5$ (linear) $x=3n-6$ (non-linear)	**linear**	**nonlinear**
Partition function	$q=\prod_{i=1}^{x}\frac{e^{-\Theta_i/2T}}{1-e^{-\Theta_i/T}}$	$q_{rot}=\frac{T}{\sigma\Theta_r}=\frac{8\pi^2 IkT}{\sigma h^2}$	$q_{rot}=\frac{\pi^{1/2}}{\sigma}(\frac{T^3}{\Theta_A\Theta_B\Theta_C})^{1/2}$ $=\frac{\pi^{1/2}}{\sigma}(\frac{8\pi^2 I_A kT}{h^2})^{1/2}(\frac{8\pi^2 I_B kT}{h^2})^{1/2}$ $(\frac{8\pi^2 I_C kT}{h^2})^{1/2}$
Heat capacity	$C_V = Nk\sum_{i=1}^{x}(\frac{\Theta_i}{T})^2\frac{e^{\Theta_i/T}}{(e^{\Theta_i/T}-1)^2}$	$C_{rot}=\frac{\partial E}{\partial T}=Nk$	$C_{rot}=\frac{\partial E}{\partial T}=\frac{3}{2}Nk$
Energy	$E = Nk\sum_{i=1}^{x}(\frac{\Theta_i}{2}+\frac{\Theta_i}{e^{\Theta_i/T}-1})$; $\Theta_i=\frac{h\nu_i}{k}$	$E_{rot}=NkT^2\frac{\partial \ln q_{rot}}{\partial T}$ $=NkT$	$E_{rot}=NkT^2\frac{\partial \ln q_{rot}}{\partial T}$ $=\frac{3}{2}NkT$

An extended list of equations for polyatomic molecules can also be found in [McQ, chapter 8-3].

$q_{electronic}=\sum_i \Omega_i e^{-\varepsilon_i/kT}$; $\Omega_i=1$; $q_{nuclear}=1$;

$q_{kinetic}=(\frac{2\pi(m_1+m_2)}{h^2}kT)^{3/2}V$ are the same equations as for diatomic molecules. The complete partition function would be given by $q=q_{trans}q_{vib}q_{rot}q_{electronic}q_{nuclear}$, for example.

Maxwell-Boltzmann speed distribution *(class 17, problems 420-425)*

$$N(\varepsilon)d\varepsilon = 4\pi N(\frac{m}{2\pi kT})^{3/2} v^2 e^{-\frac{1}{2}mv/kT} dv$$

$$f(V_x) = \sqrt{\frac{m}{2\pi kT}} e^{-mV_x^2/2kT} dV_x;\ f(c) = 4\pi c^2 (\frac{m}{2\pi kT})^{3/2} e^{-mc^2/2kT} dc$$

Classical limit *(problems 416-419)*

Quantum mechanics $n \to \infty; h \to 0; a \to \infty; m \to \infty$

$$E_n \to E; \psi_n \to \psi;\ ZPE \to E_0 = 0$$

Stat thermo $q = \sum e^{-\varepsilon_i/kT} \to \frac{kT}{h\nu}; h \sum_{\substack{quantum \\ states}} e^{-\varepsilon_i/kT} \to \int_{\substack{phase \\ space}} \int e^{-\varepsilon_i/kT}$

Harmonic oscillator (Einstein/Debye model of crystals) *(class 15/16, problems 376-415)*

	Einstein	Debye
Partition function	$Q = e^{-\varphi(0)/2kT} q^{3N}$; $q = \frac{e^{-\Theta/2T}}{1 - e^{-\Theta/T}}$	Density of states $g(\nu)d\nu = \frac{4\pi}{c^3} V\nu^2 d\nu$
Heat capacity	$C_V = 3Nk(\frac{\Theta}{T})^2 \frac{e^{\Theta/T}}{(e^{\Theta/T} - 1)^2}$	$C_V = 3Nk[4D(u) - \frac{3u}{e^u - 1}]$ $D(u) = \frac{3}{u^3} \int_0^u \frac{x^3 du}{e^x - 1}$
	$C_V = \frac{12\pi^4}{5}(\frac{T}{\Theta_D})^3 + \eta R \frac{\pi^2}{2}(\frac{T}{\Theta_F}) \approx T^3 + T$	
$T \to \infty$	$C = 3Nk$	$C = 3Nk$
$T \to 0$	$C = 3Nk(\frac{\Theta}{T})^2 e^{-\Theta/T}$	$C \approx (\frac{T}{\Theta_D})^3$

Chemical equilibrium *(class 20, problems 493-506)*

$$S \xrightarrow[\text{isolated system}]{} \max \Rightarrow A \xrightarrow[\text{V, T, N const}]{} \min \Rightarrow Q \to \max$$

$$\nu_A A + \nu_B B \Leftrightarrow \nu_C C + \nu_D D$$

Equilibrium constant $K(T) = \dfrac{\rho_C^{\nu_C} \rho_D^{\nu_D}}{\rho_A^{\nu_A} \rho_B^{\nu_B}}$;

$$K(P) = \frac{p_C^{\nu_C} p_D^{\nu_D}}{p_A^{\nu_A} p_B^{\nu_B}} = (kT)^{(\nu_C + \nu_D - \nu_A - \nu_B)} K(T)$$

Quantum statistics: Fermi-Dirac gas, electron gas *(class 23A, problems 520-534)*

Fermi function (Fermi distribution) $f_{FD} = f(\varepsilon) = \dfrac{1}{1 + e^{(\varepsilon_k - \mu)/kT}}$

Population numbers $n_i^* = \dfrac{g_i}{e^{\alpha + \beta\varepsilon_i} + 1}$; $\beta = \dfrac{1}{kT}$; $\alpha = -\dfrac{\mu}{kT}$ (g_i degeneracy)

Average number of Fermions (with energy ε_i) $\bar{n}_i = g_i n_i$ or using density of states $dN = \omega(\varepsilon) f(\varepsilon)$

Density of states of a free electron gas $\omega(\varepsilon) d\varepsilon = 2\dfrac{\pi}{4}\left(\dfrac{8m}{h^2}\right)^{3/2} V \varepsilon^{1/2} d\varepsilon$

; $N = \displaystyle\int_0^\infty \omega(\varepsilon) f_{FD} d\varepsilon$

Fermi energy, chemical potential (T = 0K) $\mu_0 = \left(\dfrac{3N}{8\pi V}\right)^{2/3} \dfrac{h^2}{2m}$;

$$\mu_0 = \varepsilon_F = kT_F ; \qquad \mu(T) \approx \mu_0 [1 - \frac{\pi^2}{12}\left(\frac{kT}{\mu}\right)^2 \pm \ldots]$$

Internal energy

$$U = \int_0^\infty \varepsilon N(\varepsilon) d\varepsilon z = \frac{3}{5} N \varepsilon_F [1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2 - \frac{\pi^4}{16}\left(\frac{T}{T_F}\right)^4 + \ldots]$$

Heat capacity $C = \dfrac{dU}{dT} = \dfrac{1}{2}\pi^2 Nk \dfrac{T}{T_F} \pm \ldots$;

$$C_{total} = C_{electrons} + C_{bulk} \approx T + T^3$$

Helmholtz energy $A = U - TS = nkT_F[\frac{3}{5} - \frac{\pi^2}{4}(\frac{T}{T_F})^2 + ...]$

Pressure $p = -\frac{\partial A}{\partial V} = \frac{2}{3}\overline{E} = \frac{2}{3}\frac{U}{V}$

Entropy $S = \int \frac{C}{T}dT = \frac{\pi^2}{2}Nk[(\frac{T}{T_F}) - \frac{\pi^2}{10}(\frac{T}{T_F})^3 + ...]$

Quantum statistics: Bose-Einstein gas, photon gas *(class 23B, problems 535-555)*

BE distribution for photons $f_{Ph} = \frac{1}{e^{h\nu/kT} - 1}$

Population numbers $n_i = \frac{g_i}{e^{\alpha + \beta\varepsilon_i} - 1}$; $\beta = \frac{1}{kT}$; $\alpha = -\frac{\mu}{kT}$ (g_i degeneracy)

Average number of Fermions (with energy ε_i) $\overline{n}_i = g_i n_i$ or using density of states $dN = \omega(\varepsilon) f(\varepsilon)$

Density of states of a free electron gas $\omega(\nu)d\nu = 2\frac{4\pi\mathrm{V}}{\mathrm{c}^3}\nu^2 d\nu$

Chemical potential $\mu = 0$

Internal energy $u(\nu)d\nu = \frac{8\pi\mathrm{hV}}{\mathrm{c}^3}[\frac{\nu^3}{e^{h\nu/kT} - 1}]d\nu$;

$u(\lambda)d\lambda = 8\pi\mathrm{hVc}\frac{1}{e^{hc/\lambda kT} - 1}d\lambda$ (Blackbody equation)

Total energy $\rho = \Diamond T^4$ (Stefan Boltzmann law); $T\lambda_{\max} = \mathrm{constan}$ (Wien's displacement law)

Heading capacity $C_{Photons} = 4\Diamond VT^3$; $\Diamond = \frac{8}{15}\pi^5\frac{1}{h^2}\frac{1}{c^3}k^4$

Helmholtz energy $A = -\frac{1}{3}\Diamond VT^3$

Pressure $P = \frac{1}{3}\Diamond T^4 = \frac{1}{3}\rho$ (energy density $\delta = \frac{U}{V}$)

Entropy $S_{Photons} = \frac{4}{3}\Diamond VT^3$

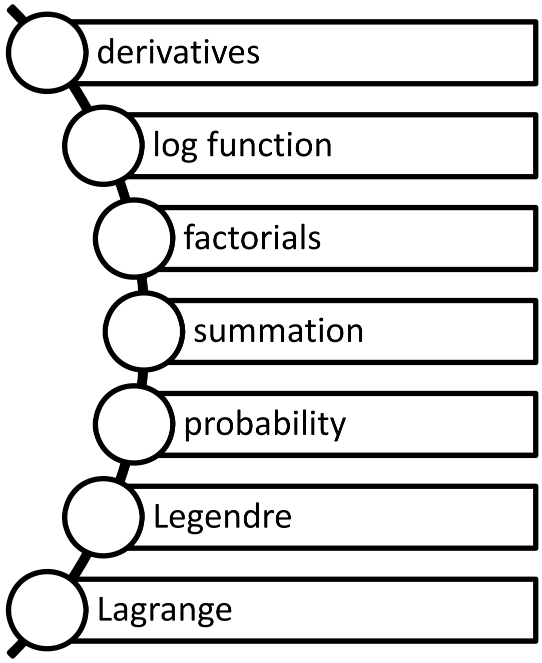
Quantum statistics: Bose-Einstein condensation

(class 23C, problems 556-569)

Ground state/excited state population $\frac{N_0}{N} = 1 - \frac{N_{ext}}{N} = 1 - (\frac{T}{T_B})^{3/2}$

Condensation temperature $T_{BEC} = (\frac{N_{ext}}{2.612V})^{2/3} \frac{h^2}{2\pi mk}$

I. Mathematical problems________*class 3A/B*



The following problems are often encountered as part of derivations in statistical thermodynamics (stat thermo). The steps in-between are often missing in traditional textbooks, but can be a major challenge for beginning graduate students. Help is given here. Go through these math problems before you start with stat thermo chapters, would be my suggestion. Some problems are very simple. Too simple? So what? In that case, do these fast or skip them. However, for most students I know, that section was helpful. And, not all problems are that simple.

This math section is separates in problems related to

- differentials,
- logarithm-functions,
- factorials,
- summations,
- probability theory,
- Legendre transformations,
- and Lagrange's method.

Some problems, of course, require a combination of skills. For example, quite common in stat thermo are complicated derivatives of summations including the ln-function.

Here are some math rules for differentials which I consider first in this chapter:

Class summary …

By the way, on the CD that accompanies this book are several summary PowerPoints, including one that summarizes only concepts. Have a look, since the following section is not complete.

613. List and discuss the most important concepts of stat thermo.
HELP See summary PowerPoints.

614. How were the different statistics developed?
SOLUTION Some outlines focus on the partition functions (see [McQ]). Thus, one can write a general partition function that includes FD, BE and B statistics, see problem 325. Form here all other thermodynamic functions can be calculated. An equivalent approach is using probability theory and the weight of the distribution (see e.g. [May],[Band]) to calculate the most probable distribution, see problem 338. From the most probable distribution, probabilities and partition functions follow.

615. Write a ¼ - 1 page summary about what you learned in this class.
SOLUTION Looking at the content page gives one a good idea how this class is structured and how stat thermo may be structured. We started by developing the so-called ensemble stat thermo. Accordingly, a thermodynamics system is described as a collection (called ensemble) of smaller subsystems. Usually at least three types of ensembles are distinguished depending on what parameters are allowed to vary. Probably the most important one is the grand canonical ensemble. Here, m, V, T are constant, but the particle number is a parameter or variable. Using that ensemble approach, various equations can be set up which allow for calculating thermodynamic parameters from the partition function of the model system. Basically everything follows from that partition function. Partition functions allow to calculate macroscopic parameters from molecular parameters which is the main goal of stat thermo. A partition function measures or describes the available states of a system. These states can be populated based on different rules leading to classical Boltzmann stat thermo or quantum stat thermo. The number of species that can populate the same state is unrestricted in Bose-Einstein stat thermo, but restricted according to the Pauli principle in Fermi-Dirac statistics. Different applications such as gaseous species, solid state systems, or liquids are just described by different partition functions.

Further reading and references

I always encourage my students to read more than one textbook (per class) and start trusting in themselves: Does it make sense what the author is writing? Is this a typo? Don't trust blindly in a textbook. Think by yourself, etc. Unfortunately, it's for most students an unrealistic suggestion since the curriculum is over-filled already, but there is also a spring break, summer, etc. for reading books.

I did not develop any stat thermo myself, I don't do directly research in this area myself. Thus, I did read stat thermo books starting to learn that theory myself, including the following:

[McQ] Donald A. McQuarrie, Statistical Thermodynamics, ISBN 1-891389-15-7, 2000, 640 pages, $60, hard cover (first published apparently in 1976)

This appears to be the Chemist's bible of stat thermo, most instructors apparently "use" this book. However, at least the first chapters are, in my opinion, basically unreadable, at least for (experimental) graduate students. (The intro appears to claim that it is written for graduate students, two semester class.) Mentioning this to my colleagues, it usually turns out that they recommend this book, but have written an own lecture draft over the years. I encountered often somewhat sweaty eyes and a proud look on the face: "yes, I made it and survived/read this book myself, … but mostly I use my own lecture draft for my class." Not sure if the proud look is related to the first or 2nd part of this statement. Well, interesting concept. And, you know in the meanwhile, German's like sarcasm. This book reminds me more to a Primer rather than a textbook, but it is very comprehensive. Derivations are (mostly) missing ("see problem xyz").

[Hill] Terrell L. Hill, An introduction to statistical thermodynamics, ISBN 0-486-65242-4, 1960, 508 pages, $20, paperback

The beginning is quite similar to [McQ.], but some sections are a little more didactic, i.e., not "all" derivations are skipped. I mostly used initially this textbook for my own studies since I could not find a better one at that point of time. It is hard to read (a number of sections are basically unreadable), however. Also here the later (more applied) chapters are better and include even occasionally examples! Despite the similarity to [McQ], interestingly, it's apparently older than [McQ].

→Many chapters in [McQ, 2000] and [Hill, 1960] are nearly identical, in my opinion. Subchapters in either one are sometimes clearer than in the other (*vice versa*). Therefore, reading (at least) these two standard books in parallel was efficient to me. Usually, I did brows over each chapter first,

to see where this is going. Then went back and did try to fill in the missing derivations. Perhaps the same strategy works for you & now you have some help with this "problem & results" booklet. The first edition of [McQ] dates apparently back to the 1970th.

[Sch] E. Schrödinger, Statistical thermodynamics, ISBN 0-486-66101-6, 1946, 94 pages, $4, paperback

Often cited. Recommended reading for the most ambiguous graduate students. It's cheap and looks nice on the book rack, right? Actually, I found a few interesting details which are spelled out more clearly by Schrödinger then by other authors.

[Mac] Andrew Maczek, Statistical thermodynamics, Oxford Chemistry Primers, ISBN 0-19-855911-9, 1998, 92 pages, paperback

Actually this primer is easier to read than e.g. [McQ]. Get one of these after you finished your stat thermo class, would be my suggestion. Unfortunately, it does not include quantum statistics and stops with the diatomic gas model. Some subchapters are quite didactic and nice.

[E/R] Thomas Engel, Philip Reid, Thermodynamics, ISBN 0-321-61503-4, 2006, 600 pages, hard cover

This is an undergraduate level thermodynamics books. However, chapters 12- 15 (approx. 80 pages) are an introduction to stat thermo. This is probably the most didactic text I have found so far, reminds one a little on Atkins. Recommended reading. Unfortunately, as common, these types of undergrad books simply don't cover the content of a graduate class. What is in here is basically, chapter one in [Hill] or [McQ] plus a few applications (diatomic gas). If you have the time, read this book before you take your first stat thermo class. It will help you not to get lost already in the first week. By the way, Atkins (another Chemist's bible) does not really include any stat thermo, as far as I can tell. [E/R] have written a couple of books which are available as one two semester book (thermo and quantum) or two separate one semester books. Paperback prints are also available.

[Lim] Yung-Kuo Lim (Ed.), Problems and solutions on thermodynamics and statistical mechanics, major American universities PhD qualifying questions and solution, compiled by the physics coaching class university of science and technology china, ISBN 981-02-0055-2, 1990, 400 pages, $20, paperback

Hurrah, this is an example book, yeah. Unfortunately, it includes mostly stat mechanics problems and only a dozen or two about stat thermo. Most of the problems are quite tuff. "A training book for American universities". That must be old Berkeley exams or

Acknowledgement

Many thanks to the students of the Spring 2015 class which did act as "Guinea Pigs" for the first draft of this book. A number of typos in text and equations were eliminated as well as the fluctuations chapter modified. Specifically acknowledged are Mindika Tilan Nayakasinghe, Nilushni Sivapragasam, and Brendan Gifford.

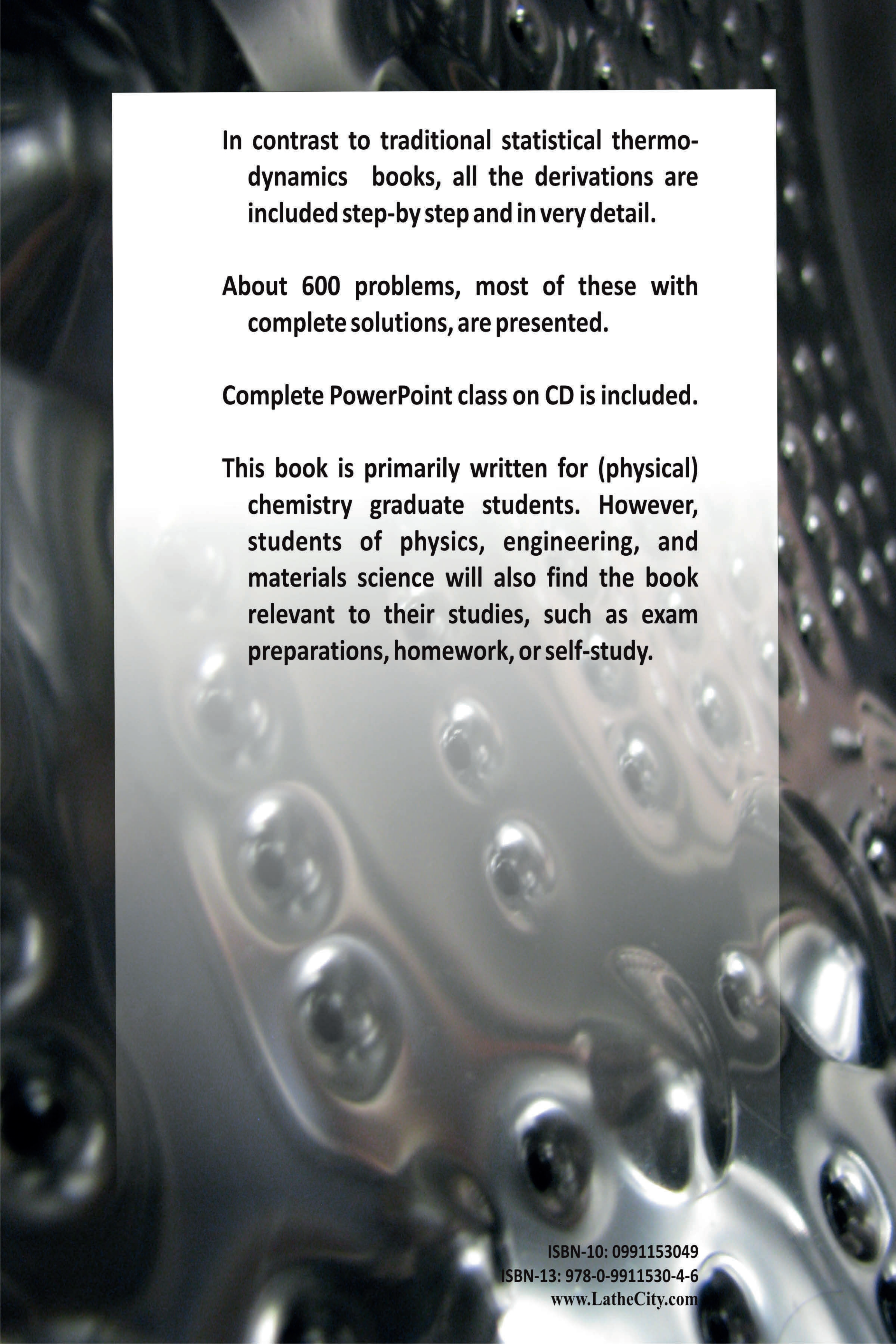
Figure acknowledgement

The following statement is required by US copyright law. All images were made by the author (i.e. © Copyright 2014, 2015 by U. Burghaus) except the following which are herewith **excluded** from copyright of the author: photo of Fermi (National Archives and Records Administration, 1943-1949) and Dirac (1933, http://nobelprize.org/ nobel_prizes/ physics/laureates/ 1933/ dirac.html) are freely Licensed through Wikimedia Commons (http:// commons.wikimedia.org/wiki/Main_Page); photo of Boltzmann (1902, original source Universität Wien), Einstein (1921, http://web.archive.org/web/20071026151415/http://www.anzenbergergallery.com/en/article/134.html), and Bose (1925) are public domain; Oppenheimer (http://en.wikipedia. org/wiki/Robert_Oppenheimer) and Born (http://en. wikipedia.org/wiki/ Max_born) photos are from Wikipedia and these are public domain; Lenard Johns, his photo is Copyright by Computer Laboratory, University of Cambridge, reproduced by permission; photo of James Clerk Maxwell is public domain, as a work from sometime before 1890 is in the public domain, original source Engraving of James Clerk Maxwell by G. J. Stodart from a photograph by Fergus of Greenack, G. J. Stodart - Frontpiece in James Maxwell, The Scientific Papers of James Clerk Maxwell, Ed: W. D. Niven, New York, Dover, 1890, downloaded from http://en.wikipedia.org/wiki/James_Clerk_Maxwell in 2014; painting of Lagrange is public domain, from http://en.wikipedia.org/ wiki/Lagrange. Walter H. Schottky http://en.wikipedia.org/wiki/ Walter_ H._Schottky; and Michael Polanyi, public domain, original author is unknown, found in Manchester archives - https://www.flickr.com/photos/ manchesterarchiveplus/5213045000/, download from http://en.wikipedia. org/wiki/ Michael_Polanyi in 2014; Eugene Wigner, public domain photo Nobel foundation - http://nobelprize.org/nobel_prizes/ physics/laureates/1963/ wigner-bio.html download from http://en.wikipedia.org/wiki/ Eugene_ Wigner; photo of John Cromwell Mather is public domain (http://en. wikipedia.org/wiki/John_C._Mather#mediaviewer/File:John-C Mather.jpg); Max Planck image is in public domain http://en.wikipedia.org/ wiki/Max_ Planck; Erwin Schrödinger (public domain, http://en. wikipedia.org/wiki/ Erwin_Schr%C3%B6 dinger#mediaviewer/File: Erwin_Schr %C3%B6 dinger. jpg); Josiah Willard Gibbs, public domain (http://en.wikipedia. org/wiki/ Josiah_Willard_Gibbs)

That information is provided to the best of my knowledge. Most images were obtained in 2014. Owner of the copyright of these above listed images/photos are their respective owners.

How to contact us

Any meaningful comment is well-come, write to sales@LatheCity.com rather than to my university e-mail account. We will ignore harassment, nonsense, and/or spam. Also, we cannot solve your homework problems for you, sorry. Other books and original publications should be available through your library system.



In contrast to traditional statistical thermodynamics books, all the derivations are included step-by step and in very detail.

About 600 problems, most of these with complete solutions, are presented.

Complete PowerPoint class on CD is included.

This book is primarily written for (physical) chemistry graduate students. However, students of physics, engineering, and materials science will also find the book relevant to their studies, such as exam preparations, homework, or self-study.

ISBN-10: 0991153049
ISBN-13: 978-0-9911530-4-6
www.LatheCity.com