Thermodynamics: Course Outline

A. M. Steane, September 27, 2022

Thermodynamics concerns energy, entropy, and the behaviour of almost all physical systems one way or another. It treats in the first instance large systems in thermal equilibrium, or moving slowly from one equilibrium state to another, and then more general methods are developed. It expounds extremely wide-ranging ideas in physics, and is employed in a vast range of applications throughout science.

Thermodynamic concepts, along with quantum theory, underpin the subject of statistical mechanics (or statistical thermal physics). I would recommend to get a good grounding in thermodynamics before embarking on the statistical methods. For example it is good if a student is already familiar with the Helmholtz function, natural variables, and $T^{-1} = \frac{\partial S}{\partial U}$ before they encounter the Boltzmann distribution and the partition function.

Textbooks. There are many; here I list a few:

Thermodynamics, a complete undergraduate course, A. M. Steane, (OUP 2017). This is thorough and precisely matches my approach.

Equilibrium Thermodynamics, C. J. Adkins (3rd edition, CUP 1997). At a similar level, more succinct.

Concepts in Thermal Physics, S. J. Blundell and K. M. Blundell (2nd edition, OUP 2009).

This presents both thermodynamic and statistical reasoning.

The lectures on thermodynamics will be broadly shaped into four parts, leading to four problem sets, with an optional fifth set:

1. basic concepts (state, equilibrium, response function, temperature, function of state, reciprocity theorem, introduction to fundamental relation, empirical temperature and equation of state)

(chapter 2,3,4,5,6 of Steane¹)

2. first and second laws (work and internal energy; heat engine, Carnot theorem, Clausius theorem, entropy)

(chapter 7,8,9,11 of Steane)

3. thermodynamic potentials and methods (natural variables, Maxwell equations, chemical potential, fundamental relation, magnetism, surface tension)

(chapter 12, 13, 14)

4. non-ideal gas, flow process; stability and free energy; thermal radiation; first order phase change

(chapter 15, 16, 17, 18, 19, 20, 22)

5. (optional) the third law, metastable phases; nucleation in phase change; the greenhouse effect

¹A. M. Steane, *Thermodynamics, a complete undergraduate course*, OUP 2017.

Problem sets are best employed after rather than before the relevant lectures, therefore the first set is designed to require less new learning than the others.

The centrally-provided lecture notes consist in my book, plus lecture slides and an occasional summary sheet. The book is available in libraries and I think OUP provides free access for Oxford students to an electronic version.

1 Lecture sequence

Dividing the subject into 13 lectures, we have

- 1 concepts and terminology, some maths, overview
- 2 zeroth law, equation of state, first law, work, heat capacity
- 3 adiabatic expansion, compressibility, examples
- 4 heat engines, Carnot theorem, Clausius theorem, entropy
- 5 what is entropy? examples and calculations, Gibbs paradox, Szilard engine
- 6 chemical potential, Euler relation, thermodynamic potentials, Maxwell relations, natural variables
- 7 heat capacities and equation of state, rods, surface tension, paramagnetism, adiabatic demagnetization
- 8 non-ideal gas, corresponding states, Joule-Kelvin process
- 9 stability and free energy; relation to phase change
- 10 thermal radiation; spectral energy density, Kirchoff's law, pressure
- 11 Wien's laws; introducing first order phase change, Clausius-Clapeyron
- 12 metastable phases, nucleation
- 13 some further ideas

There follows a list of corrections to my thermodynamics book. Please be assured that a lot of care was taken to avoid slip-ups before publication! Long as the list may seem, I believe it is not bad compared to the average for first editions of books of this length.

Errata in Steane, 'Thermodynamics' (2017)

p.19 table 3.2 the last "electric dipole" should be "magnetic dipole"

p.19 text asserts that the ratio of two extensive properties is intensive. This is only true for things like mass and volume whose extensivity has the same number of physical dimensions. But (for example) the ratio of a volume and an area is a length, all extensive.

p.36 update defn of Avagadro's number. (In SI it is now exact and the mass of a mole of $^{12}\mathrm{C}$ is not)

p.40 The surface in the figure has been flipped $x \leftrightarrow y$. To correct, swap x and y axis labels including tick labels.

p.40 after (5.1) it should say the range of x is 0.5 to 1.5 (not 1 to 2)

p.41 after eqn (5.3) the second sentence should say "along a line of constant x"

p.58 eq (6.10) two subscripts are wrong, one on p, one on V in last two parts.

p.61 3rd full paragraph it should say "the gas heats" (not cools)

p.86 eqn (7.42) P on the right should be lower case

p.99 defn of mass unit (in SI) has now changed

p.101 triple point of water is at 273.16 not 273.15 kelvin.

p.139 end of example 10.1 use a not r in the formula

p.201 1st para "Since like charges attract" should be "Since unlike charges attract"

p.214 after (14.105) it should say 'question 14.8' not 'question 14.9'

p.288 top equation should have $_{\perp}$ after ∇

p.297 Ex. (20.3) 2nd answer should be 22 not 21 degrees C.

p.297 Ex. (20.4) is wrong. Replace the first sentence by:

Show that the angle subtended by a sphere of radius r at distance R from its centre is $\sin^{-1}(r/R)$. Show also that for isotropic radiation the flux in the direction at angle θ to the normal of a given small fixed area of surface is proportional to $\cos \theta$ (whether for the emitted or the incident flux).

p.301 Eqn (21.7) has a sign error and should read $e^{-E_a/k_{\rm B}T}$.

p.304 after the equations for x and y it should be y_i not y_1

p.306 Eqn (21.27) should read $\Delta \mathcal{A} \equiv \sum_{i} (\mu_i - \mu_i^{\ominus}) \nu_i$

p.306 Eqn (21.28) has a sign error and should read $\Delta A = -\Delta G = -\Delta H + T\Delta S$.

p.309, 310 The numbering of the exercises should read 21 not 12.

p.324 Footnote 4, $T_{\rm b}$ should be $T_{\rm m}$ in the equation.

p.329 Exercise 22.3 the data should say 18,000 feet, not 18 km.

p.365 box after (25.21) it should say "holds for some value of p, q", (not all values)

p.365 box in item (ii) it should be " $\lambda = B^{-1/q}$ " (not p in the exponent)

p.393 fig 27.2 should have the arrow going the other way and the caption should then read "from cell 2 to cell 1".

p.394 penultimate line of (27.33) the first integration sign and the $dx_{i\neq j}$ should be deleted.

minor issues

p.105 font of d in (8.16) and (8.17)

p.134 ex. (9.10) "is mode" should be "is made"

p.160 end of 1st paragraph insert 'one' so that it reads "from one place to another" p.255 in last paragraph "joint of entropy" should be "joint entropy"